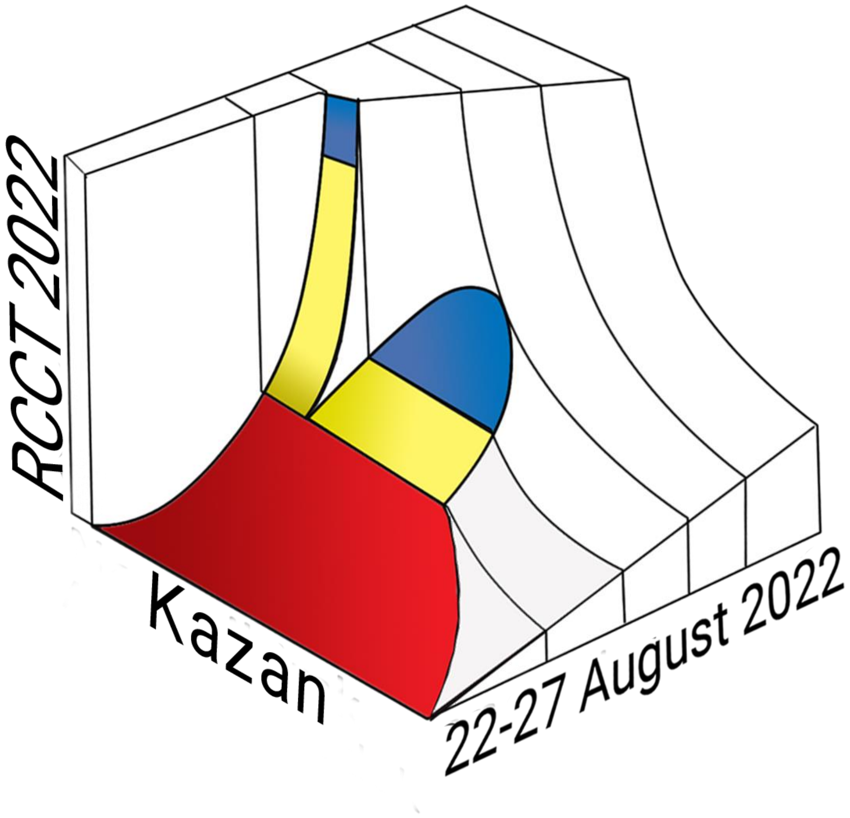
# XXIII International Conference on Chemical Thermodynamics in Russia

**August 22-27, 2022**
**Kazan, Russia**



**RCCT – 2022**

# BOOK OF ABSTRACTS

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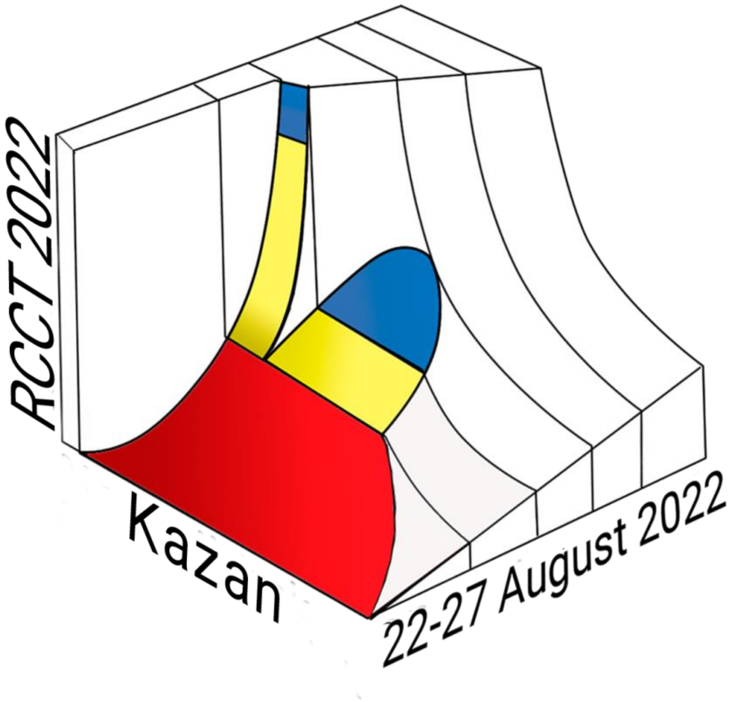

## RCCT – 2022

# BOOK OF ABSTRACTS

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**Kurnakov Institute of General and Inorganic Chemistry of Russian Academy of Sciences**

**Kazan Scientific Center of Russian Academy of Sciences**

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# PREFACE

**XXIII International Conference on Chemical Thermodynamics in Russia, RCCT-2022 August 22-26, 2022, Kazan, Russia: Abstracts.** – Kazan, 2022. - 361 p.

This book contains the scientific program and the abstracts of presentations at the XXIII International Conference on Chemical Thermodynamics in Russia (RCCT-2022). The conferences on Chemical Thermodynamics are among the largest held in Russia since 1961. RCCT is an important scientific event not only for Russian but also for the international research community, being among the largest conferences on Chemical Thermodynamics. The conference traditionally covers all aspects of chemical thermodynamics from fundamentals to applications, including multidisciplinary approaches and related fields of science.

Until 1977 a conference of this series was called “All-Union Conference on Calorimetry" and later, until 1992, "All-Union Conference on Calorimetry and Chemical Thermodynamics". Today the RCCT International Conferences are organized every two years by large Russian scientific centers that have included Moscow (2005, 2013), Saint Petersburg (2002, 2019), Ivanovo (2007), Kazan (2009), Samara (2011), Nizhny Novgorod (2015) and Novosibirsk (2017).

This year the conference brings together more than 250 scientists from 32 cities and 15 countries; many of them are young researches, including undergraduate and graduate students. Two junior poster awards have been established by the organizers for the best poster presentations: the RCCT-2022 junior poster award “Excellence in Chemical Thermodynamics” and “Lev G. Berg award”, a special award is dedicated to the founder of theory of Differential Thermal Analysis, the first president of the International Confederation for Thermal Analysis (ICTA), professor Lev G. Berg.

The scientific program of RCCT2019 includes plenary and keynote lectures, 4 parallel sessions of oral presentations and 3 poster sessions. These contributions reflect the latest trends in Chemical Thermodynamics, including the development and application of theory, new experimental techniques and computer simulation for various systems. It is our pleasure to thank all the participants of RCCT-2022 and to welcome you in Kazan.

On behalf of the organizers,

Boris N. Solomonov, RCCT-2022 Vice-chair

# CONFERENCE TIMETABLE

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| 9.00-20.00 | **Check in. Registration** |
| Monday, **22.08.2022** | |
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| 10.00-10.40 | Shchekin A.K., EFFECTS OF CONFINEMENT FOR SMALL AGGREGATES (p. 25) |
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| 16.25-16.40 | Makarov E.G. (p. 137)<br>Novel tetra-azide and triazole derivatives of thia- and calix[4]arene with free phenolic hydroxyls | 16.25-16.40 | Vorozhtsov V.A. (p. 141)<br>Mass spectrometric study and modeling of the thermodynamic properties of the $Al_2O_3$-$SiO_2$-$ZrO_2$ system | | | | |

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|---|---|
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| 9.20-9.40 | Sineva S.I. HIGH-TEMPERATURE PHASE EQUILIBRIA IN THE Fe-Sn-S SYSTEM (p. 151) |
| 9.40-10.00 | Lőrinczy D.M. APPLICATION OF DSC FOR STUDYING THE DOSE DEPENDENT EFFECT OF CYCLOPHOSPHAMIDE TREATMENT ON ACTIN (p. 152) |
| 10.00-10.20 | Meier R. GROUP CONTRIBUTION REVISITED: THE ENTHALPY OF FORMATION OF ORGANIC COMPOUNDS WITH “CHEMICAL ACCURACY” (p. 153) |
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| 12.00-12.40 | Tovbin Yu.K. EQUILIBRIUM DROPS: A DIFFERENCE BETWEEN THERMODYNAMICS BY CLAUSIUS AND GIBBS IN TASKS OF THE PHASE EQUILIBRIUM (p. 39) |
| 12.40 | Closing ceremony |
| **Saturday**, **27.08.2022** |  |
| 10.00-13.00 | Training seminar on Fast Scanning Calorimetry |

# ABSTRACTS

# PLENARY LECTURES

# HIGH TEMPERATURE MASS SPECTROMETRIC STUDY OF THE MULTICOMPONENT SYSTEMS BASED ON RARE EARTH OXIDES AND HAFNIA

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The rare earth oxides (REO) and hafnia are considered as the base of the promising materials for various high temperature technologies, including aircraft engineering and nuclear industry [1]. For instance, multicomponent systems containing REO, $ZrO_2$, and $HfO_2$ can be used for development of modern thermal barrier coatings for gas turbine engine blades, which is of special interest in the aerospace sector since the ceramics based on stabilized $ZrO_2$, which is traditionally used for this purpose, is reaching the limits of its thermal stability [2]. However, application of these materials at high temperatures may be limited because of the selective vaporization of the components and phase transformations in the condensed phase. This emphasizes the importance of examining vaporization processes and thermodynamic properties of the ceramics based on the REO and $HfO_2$, which was carried out for the first time in the present study by the Knudsen effusion mass spectrometric (KEMS) method using as the example the ceramics based on the $La_2O_3$-$Sm_2O_3$-$Y_2O_3$-$HfO_2$ and $La_2O_3$-$Sm_2O_3$-$ZrO_2$-$HfO_2$ systems, including the $La_2O_3$-$Sm_2O_3$ system.

It was shown that, at the temperatures below 2500 K, the composition of the gaseous phase over the samples in the $La_2O_3$-$Sm_2O_3$-$Y_2O_3$-$HfO_2$ and $La_2O_3$-$Sm_2O_3$-$ZrO_2$-$HfO_2$ systems corresponded to the vapor species over the pure lanthanoid oxides, namely, LaO, SmO, Sm, and O. The partial pressures of the vapor species, the vaporization rates of the samples, and the lanthanoid oxide activities were determined by KEMS at the temperature 2330 K in the quaternary systems under consideration as well as in the $La_2O_3$-$Sm_2O_3$ system at the temperature 2323 K. The obtained values of the component activities indicated negative deviations from the ideality in the systems under study.

In the $La_2O_3$-$Sm_2O_3$ system, the concentration dependence of the $La_2O_3$ activities was approximated by the Redlich-Kister [3] and Wilson [4] polynomials to obtain the excess Gibbs energy values and the $Sm_2O_3$ activities in the concentration range 0-57 mol. % $La_2O_3$. Application of the Wilson method [4] also allowed evaluation of the excess entropies and enthalpies of formation from the oxides in the binary system under consideration at the temperature 2323 K.

The lanthanoid oxide activities determined for the first time by KEMS in the samples of the $La_2O_3$-$Sm_2O_3$-$Y_2O_3$-$HfO_2$ and $La_2O_3$-$Sm_2O_3$-$ZrO_2$-$HfO_2$ systems were compared with the results of calculation of the corresponding values based on the data in the binary systems using the semi-empirical Kohler [5], Redlich-Kister [3], and Wilson [4] methods, as well as the generalized lattice theory of associated solutions [6]. It was found that the best agreement of the calculated data with the experimental values of lanthanoid oxide activities was observed when the thermodynamic properties in the quaternary systems under study were obtained using the semi-empirical Wilson method.

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# TOWARDS SCREENING OF POLYMORHISM AT SUPERCRITICAL PARAMETERS OF STATE

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Supercritical fluid technologies (SCF) are increasingly used for the synthesis and directed modification of materials and composites. Such functionalized materials are required for a wide range of applications in medicine (e.g., implants and tissue engineering matrices), pharmacy (e.g., increased bioavailability of dosage forms, sustained-release and controlled release), optics (e.g., in the development of composites with polymers quantum dots needs for optoelectronics or composites of polymers with carbon nanotubes for the needs of the photonics), catalysis (composites of nanoparticles of metal catalysts with highly porous polymers) and many other areas of science and practice.

In these processes, the crucial role played by such unique properties of supercritical fluids (SCF) as customizable density of the medium; high rates of heat and mass transfer and, at the same time, high solvent power; ultra-low surface tension. One of the most promising SCF technologies for pharmacy is formation of crystalline particles of drugs. The main advantages of their use include the following:

- Obtaining micronized forms of the target substance with the ability to control the particle size of the obtained crystals in a wide range.
- High degree of purity of the target product obtained using either rapid expansion of supercritical solution (RESS) or using the method based on the effect of anti-solvent (SAS). In this case, there are practically no residual traces of solvent in the final product.
- The ability to control the polymorphism of the obtained target product by changing the thermodynamic parameters of the supercritical fluid system from which crystallization is performed and, as a result, the possibility of obtaining a sample with the required polymorphic purity.

The screening of polymorphism is usually fully empirical procedure. The new methodology for conformational type of polymorphism introduces in this report. Such methodology consist on screening of conformers distributions as function of states parameters and allow to predict polymorphs formation. In order to perform polymorph predicted procedure, the combination of experimental (IR and NMR spectroscopies) and computational (Quantum chemistry calculations, molecular dynamics simulations, density functional theory) approaches have been applied.

# EFFECTS OF CONFINEMENT FOR SMALL AGGREGATES IN NUCLEATION AND MICELLIZATION

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Recently, a number of works have appeared devoted to the consideration of confinement effects in the thermodynamics of small systems [1-4]. Speaking about the effects of confinement in the thermodynamic and kinetic theory of aggregation, we will keep in mind the peculiarities of the description of aggregation in metastable systems with finite sizes in comparison to aggregation in bulk phases. Nucleation of droplets in pores, nucleation of bubbles in microdroplets, deliquescence and efflorescence at condensation on soluble particles, as well as the existence of stable aggregates with different sizes in molecular dynamics simulations of nucleation and micelle formation in simulation cells provide examples of systems where the confinement effects lead to new thermodynamic and kinetic regularities. Let us note that studies of confinement effects have a rich history. The fact that new phase nuclei in a confined system may be in unstable and stable equilibrium, and a stable nucleus is larger than an unstable one, was first noted by Konobeevskii [5]. A general thermodynamic study of the stability of a new phase nucleus at nucleation in confined systems under different conditions was carried out by Rusanov [7]. Schmelzer et al. [8] performed a systematic study of the related problems for bubble, droplet, and crystal formation, including a kinetic description of the Ostwald ripening in closed systems, and found that only one nucleus at nucleation in a closed metastable system of finite size can reach a stable state. Kožíšek and Demo [9] numerically studied the effect of depletion of the metastable phase on nonstationary nucleation in a closed system and found that, at high supersaturations, the kinetics is affected by the choice of the initial size distribution of subcritical clusters. In this communication, the role of the confinement effects in micellization will be considered in detail and compared with the case of nucleation of droplets and bubbles. We will obtain an explicit expression for additional contribution to the work of aggregation at homogeneous nucleation and at the formation of direct and reverse micelles in a system with a finite number of monomers under isothermal and nonisothermal conditions and study the consequences of its presence. The problem has an analytical solution [2], which makes it possible to show that in the case of confined nucleation there is a range of supersaturations of the system in which formation of nuclei is impossible, and with an increase in supersaturation, along with a maximum, the aggregation work has an additional minimum. In the case of confined micellization, the maximum and minimum of the aggregation work existing near and above the critical micelle concentration (cmc), noticeably shift, as does the cmc value itself. A new analytical expression will be presented for the nonequilibrium size distribution of micelles between the maximum and minimum of the aggregation work as the final equilibrium of the confined micellar system is approached [10].

**Acknowledgements** This work was supported by the RFBR, project no. № 20-03-00641a.

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# ORGANICS MATTER: COMMON FEATURES IN ENERGETICS OF POLYMER DERIVED CERAMICS, METAL ORGANIC FRAMEWORKS, AND OTHER HYBRID MATERIALS

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Hybrid materials are solids containing both organic and inorganic constituents bound together in crystalline or amorphous structures, often showing distinct ordering and/or phase separation on the nanoscale. Relatively strongly bound examples include simple salts of organic cations, hybrid perovskites where organic cations substitute for large inorganic ones, polymer derived ceramics and their precursors, and metal organic frameworks (MOFs), in which inorganic nodes are connected by organic linkers. More weakly bound examples include intergrowths of organic and inorganic films or fibers, where the interactions occur mainly at interfaces. Advanced solution calorimetry measures their formation energetics. The organic ion, linker, or layer plays a dominant role in energetics because of its ability to change its geometric configuration, affecting both vibrational and electronic structures, and giving rise to interplay between enthalpy and entropy effects.

# ESTIMATIONS OF THE LIQUID AND SOLID HEAT CAPACITY OF LARGE MOLECULES BY GROUP ADDITIVITY

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Group additivity is very useful technique for estimating heat capacities of organic substances. This contribution examines two concerns regarding the use of the technique developed in this laboratory. The first of these concerns examines whether large polycyclic hydrocarbons exhibit the same heat capacity behavior that large polycyclic aromatic hydrocarbons do relative to their parent compounds. The second addresses the observation that group values for liquids have had a tendency to overestimate the heat capacities of large organic liquids; similar use of group values for solids do not appear to do so. A protocol is described for the estimation of both liquid and solid heat capacities at $T$ = 298.15 K of large molecules by combining group additivity with retrosynthetic and synthetic analysis. This protocol can adjust for the overestimation observed with large liquid compounds and can also take advantage of currently available experimental data of related substances.

# THERMODYNAMIC STUDY OF FORMAMIDINIUM LEAD IODIDE ($CH_5N_2PbI_3$) FROM 5 TO 357 K

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In the present study the molar heat capacity of solid formamidinium lead iodide (CH5N2PbI3) has been measured over the temperature range from 5 to 357 K using a precise automated adiabatic calorimeter. In the above temperature interval, three distinct phase transitions have been found in the range from 49 to 56 K, from 110 to 178 K, and from 264 to 277 K. The standard thermodynamic functions of the studied perovskite, namely, the values of the heat capacity $C^\circ_p(T)$, the enthalpy $[H^\circ(T) - H^\circ(0)]$, the entropy $S^\circ(T)$ and the $[G^\circ(T)-H^\circ(0)]$, have been calculated for the temperature range from 0 to 345 K based on the experimental data. The results have been discussed and compared with those available in the literature measured by nonclassical or less precise methods [1,2].

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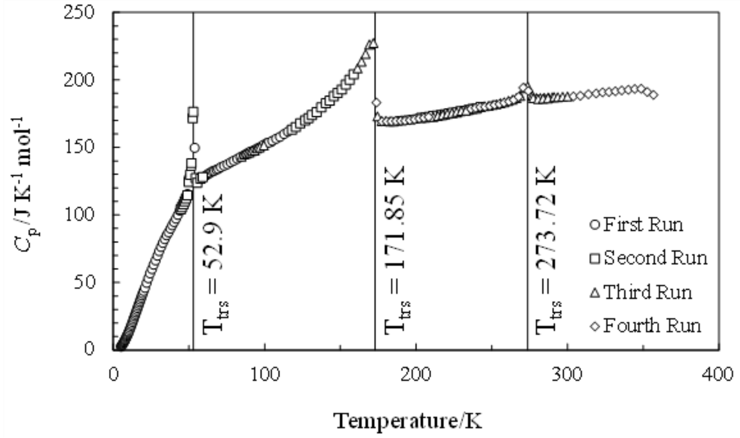

**Figure 1.** Molar heat capacities of formamidinium lead iodide (FAPI) in the range from 5 to 357 K.

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# GIBBS–HELMHOLTZ EQUATION: PRACTICAL APPLICATIONS IN THERMOCHEMISTRY

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The thermodynamic feasibility of a chemical process is determined by the sign of the Gibbs reaction energy. The Gibbs-Helmholtz equation applied to thermochemistry is clearly represented by the enthalpic and entropic contributions to the Gibbs energy. The thermochemical methods useful to derive these contributions from experiment and theory are collected and analyzed. The concept of the in-silico" based Gibbs-Helmholtz equation was proposed. The application of the "in-silico" procedure to modern areas of chemistry such as hydrogen storage and ionic liquids was demonstrated.

Various areas of application will be presented in which the Gibbs-Helmholtz equation can help to optimize chemical-engineering problems. This includes the synthesis of the platform chemicals, the utilization of the renewable sources (glycerol, lignin, etc.), and hydrogen storage. A useful combination of quantum chemistry with experimental methods has been developed and applied to the determination of liquid-phase equilibrium constants, which are essential for chemical technology.

In the context of hydrogen storage, Gibbs energies have proven important to calculate the equilibrium temperatures specific to the reversibility of hydrogenation of liquid organic hydrogen carriers. Thereby, nitrogen-containing heterocycles, furfuryl alcohol and diphenyl ether derivatives were screened using the equilibrium temperature for the selection of the most promising LOHC systems.

The combination of combustion experiments with diamonds and graphite with high-precision calorimetry and quantum-chemistry has disproved the superior stability of diamonds at extremely low temperatures, which theorists suspected. Thereby, the textbook paradigm was re-enforced that graphite is the most stable modification of carbon at atmospheric pressure at all temperatures below 400 K, even very close to absolute zero.

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# THERMODYNAMIC PROPERTIES OF MIXED OXIDES FOR THERMAL BARRIER COATINGS: RE ZIRCONATES, HAFNATES, TANTALATES

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The increase in the efficiency of modern aircraft engines and turbine-type power plants is inhibited due to the impossibility of increasing the temperature in the hot zones due to the achievement of limits of temperature and phase stability of materials used in the design of parts of these devices - superalloys and ceramic coatings. At one time, the application of a thermal barrier coating (TBCs) designed of zirconium dioxide stabilized with yttrium oxide (7-8YSZ) made it possible to achieve significant progress. However, the upper temperature limit of the YSZ coatings is 1150-1200°C. Additionally, zirconium dioxide is characterized by high oxygen-ion conductivity, which leads to oxidation of internal metal parts. Moreover, engines have reached temperatures at which ingested debris (CMAS) forms silicate melts that chemically and mechanically attack TBCs, leading to premature failure. Protective coating on turbine blades made of superalloy, experiencing maximum exposure to temperature and ingested debris, have a few-layer coating of TGO, bond coat and mixed oxide.

All above mentioned tendencies lead to the design of new materials for TBC. The candidates for these coatings are mixed oxides – RE zirconates ($RE_2Zr_2O_7$), hafnates ($RE_2Hf_2O_7$) and tantalates ($RETaO_4$ and $RE_3TaO_7$). All these substances have the high melting temperature and oxygen mobility lower than in YSZ.

Mixed oxides were synthesized by reverse co-precipitation with the following step-wise annealing at final temperature 1400°C. Specimens were identified by X-ray diffraction, SEM and ICP-MS analysis.

Thermal behavior of compounds was studied by DTA/TG in the range 300-1800 K to determine the possible anomalies related with the phase transitions.

The measurement of the heat capacity of these compounds by relaxation (PPMS-9 Quantum Design), adiabatic (BKT-3) and differential scanning calorimetry (Netzsch STA 449 F1 Jupiter) in the temperature range of 2-1300 K allowed us to determine reliable thermodynamic values and, using our and literature data on the enthalpy of formation, to evaluate thermodynamic stability in the studied temperature range by Gibbs energy values. Schottky heat capacity anomalies associated with the splitting of *f*-electron levels under the effect of a crystal field are determined and their contributions to entropy are calculated. Differences in $C_p$ values and the course of curves are due to lanthanide compression and the presence of Schottky anomaly.

The study by differential scanning calorimetry showed the absence of weight loss and phase transformations in the region up to 1800 K. Extrapolation of the $C_p(T)$ dependence to the high temperature region using the Mayer-Kelly equation allowed us to estimate the stability of complex oxides in an interval inaccessible to experimental study.

The study of high-temperature oxides by powder X-ray diffraction in the range of 298-1273 K made it possible to determine the change in the parameters and volumes of the unit cell of the crystal lattice, as well as to estimate the coefficients of thermal expansion. Changes in the volumes $V(T)$ of the unit cell of mixed oxides studied are close to linear.

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# METAL-ORGANIC COMPOUNDS FOR GAS-PHASE DEPOSITION: HOW DO WE TINKER WITH THERMODYNAMIC AND THERMOCHEMICAL DATA POOL?

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Volatile metal-organic compounds are involved as precursors for producing functional film materials by gas-phase deposition. To optimize the technological deposition conditions, knowledge about the vapor pressure and thermodynamics of sublimation or vaporization of the precursor used is indispensable. Obviously, the experimental conditions for the volatilization of complexes with various metals and ligands vary significantly. Moreover, as a rule, thermodynamic data for the same precursor, obtained by different methods and in different labs, also differ considerably in vapor pressures, melting temperatures, as well as the interrelated enthalpies of sublimation, vaporization, and fusion. As a result, we are faced with a data pool (see fig.1) which cannot be compared, rationalized, or favored, and deposition experiments are inevitably carried out under empirically determined conditions.

In focus of this contribution, there is a general algorithm for diagnosing data on the thermodynamics of solid-gas, liquid-gas, and solid-liquid phase transitions for metal β-diketonates which are the most-known precursors. It is based on "structure-property" correlations and the group additivity principles [1,2]. The approach has been developed and tested for a number of metal tris-β-diketonates [3].

**Acknowledgements** The financial support of the work was provided by the Russian Science Foundation and the Government of the Novosibirsk Region (project no. 22-23-20182)

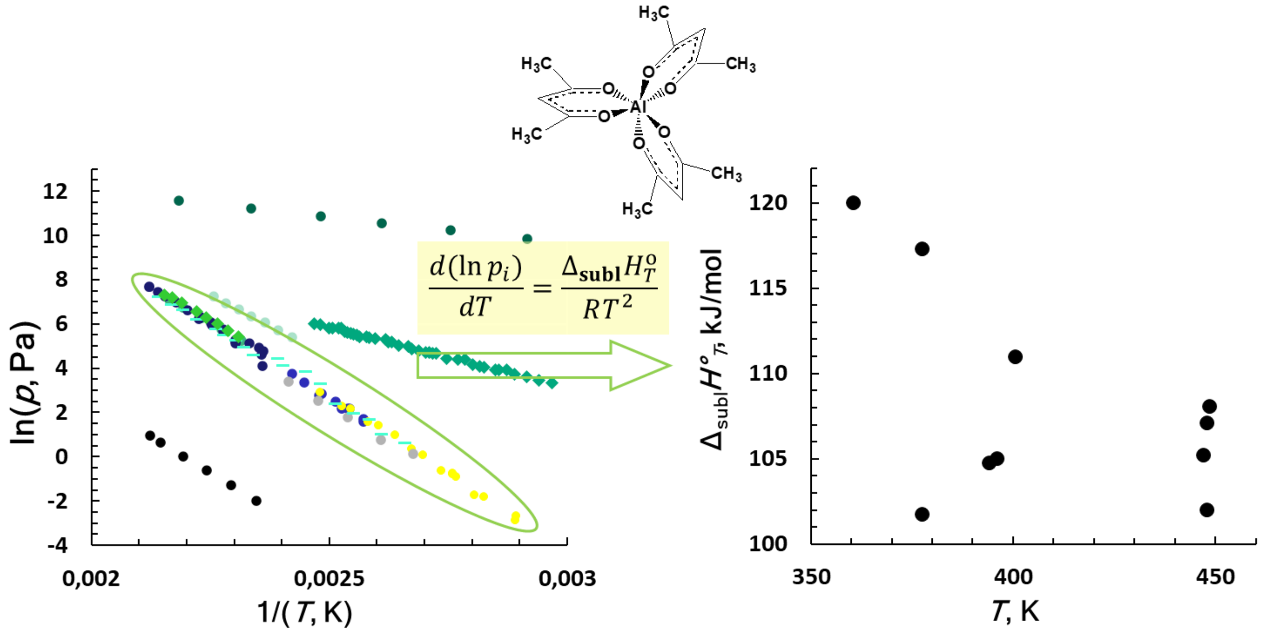

**Figure 1.** An example of the scatter of sublimation enthalpy values approximated with the Clausius-Clapeyron equation from the closest data on aluminum acetylacetonate vapor pressures.

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# THE DISSOLUTION THERMODYNAMICS AS THE KEY TO UNDERSTANDING VARIOUS PHYSICOCHEMICAL PROCESSES

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The present contribution reports the author's research in the field of the thermodynamics of dissolution and solvation of organic nonelectrolytes.

The study of the thermodynamics of dissolution of alkanes in various solvents enabled to create a method for evaluating the contribution of the solvation into the thermodynamic parameters of solvent-solvent and solvent-solute interactions. The devised solvent-solvent interaction parameter was used as a solvent property when describing the influence of the medium on various physicochemical processes. This made possible to create an alternative to the electrostatic model of the medium effect on the conformational equilibria, the frequency shifts of valence oscillations in the IR spectrum, and many other phenomena.

The study of the thermodynamics of dissolution of alkanes in the associated solvents made possible to create a method for evaluating the contribution of the solvophobic effect into the enthalpy and Gibbs energy of solvation. The nature of the solvophobic effect in the framework of such a model is discussed.

The study of the thermodynamics of dissolution and solvation of geometric isomers in various media allowed establishing that neither the dipole moments of the solute molecule, nor the dipole moments of the individual bonds in the molecule, nor the higher-order multipoles or the dielectric permittivity of the solvent, affect the thermodynamic functions of dissolution and solvation. This enables the formulation of the additivity principle for the thermodynamics of the solvation of nonelectrolytes.

For solvent-solute systems with hydrogen bonding the general schemes for determining the thermodynamic parameters of hydrogen bonding based on the dissolution thermodynamics data have been developed.

The schemes for calculation of the solvation enthalpy have been developed based on the detailed “structure-property” analysis of the nonelectrolyte solvation enthalpy data. The combination of the experimental enthalpies of dissolution and the calculated enthalpies of solvation makes possible to create a method for calculating the enthalpies of evaporation and sublimation at 298K.

A comparative analysis of the enthalpy of dissolution at 298K and the fusion enthalpy at the melting temperature allowed us to create a way to adjust the enthalpy of melting to 298K.

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# FAST SCANNING CALORIMETRY: NEW OPPORTUNITIES FOR CHEMICAL THERMODYNAMICS

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Fast Scanning Calorimetry (FSC) is new calorimetric technique which allows for controlled heating and cooling with scanning rate of up to $10^6$ K/s [1]. The extremely fast heating and cooling rates provide new opportunities in several areas of chemical thermodynamics.

First, the application of fast heating enables study of the fusion process of thermally labile compounds that decompose upon heating using the conventional differential scanning calorimetry [2]. By extension this provides an opportunity to study fusion of the metastable polymorphs [3].

Second, rapid cooling allows supercooling for even relatively fast crystallizing compounds, and then the heat capacity of the supercooled melt can be measured. These data can be used to evaluate the temperature dependence of the phase transitions involving liquid state [4].

Third, a small sample size and relatively large surface area allows studying of the evaporation and sublimation of the low volatile compounds using a variation of the thermogravimetric technique [5].

Finally, fast scanning calorimetry allows to realize temperature programs to study kinetics of the processes like polymer nucleation and crystallization or protein folding [6,7]. Careful interpretation of the results of such studies in terms of thermodynamic models provides deeper understanding of the driving forces for these processes.

Further development of the applications of FSC, which still is a relatively young experimental technique, may open even more exciting opportunities in the field of chemical thermodynamics.

**Acknowledgements** This work has been supported by the Kazan Federal University Strategic Academic Leadership Program (‘PRIORITY-2030’)

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# THERMOCHEMISTRY OF NATURAL GAS STORAGE

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The International Energy Agency (IEA) predicted a 30% increase in global natural gas demand by 2040 under current policies [1]. Thus, an urgent question arises about efficient storage and transportation of natural gas, including associated petroleum gas. Today, the storage and transportation of natural gas in the form of gas hydrates is a promising alternative to the existing technologies due to some of the inherent advantages [2]. To implement this technology, it is necessary to control the kinetics of hydrates formation and decomposition by adding proper GHPs [3]. Surfactants have been reported as the most efficient gas hydrate promoters for gas storage and transportation; however, high toxicity and huge foaming are two severe challenges for gas storage strategy based on promoting the gas hydrates formation using surfactants.

The present study used castor oil as an eco-friendly resource to develop novel biosurfactants for methane storage. The transmission and scanning electron microscopies, dynamic light scattering, and interfacial tension measurements revealed the surfactant properties of sulfonated castor oil (SCO). In addition, a high-pressure autoclave and a micro differential scanning calorimeter tests unveiled SCO as an effective kinetic hydrate promoter. The results showed that SCO significantly enhanced the rate of methane hydrate formation. A maximum of 76±2% water-to-hydrate conversion was observed in 0.1 wt % SCO solution under stirring conditions. Pure water, 0.1 wt % SCO, and 0.1 wt % sodium dodecyl sulfate (SDS) solutions allowed 50% conversion to be achieved for 329±50, 39±20, and 27±4 min, respectively. This made the castor oil-based reagent as effective as the well-known kinetic hydrate promoter (SDS). Furthermore, the SCO solution's foam ratio and stability were 8.25 and 2.75 times lower than SDS. Besides, SCO showed a more favorable safety profile for humans and the environment as its cytotoxicity was 1.5 times lower than SDS.

It was also decided to compare the synergistic effect of two surfactants - SCO and SDS - in a porous medium under static conditions. In the case of methane hydrate, when promoters are added to the system at a concentration of 0.5 wt%, the conversion of water to hydrate increases with increasing water saturation, in contrast to the system with pure water. Apparently, this is due to the fact that promoters enhance the growth of hydrate in the gas phase and on the cell walls due to capillary inflow of water. This effect is not observed for gas mixture hydrates, which reveals the difference in the promotion of hydrates of different types (sI, sII). Kinetic calculations using the Avrami equation showed that both reagents increase the rate of hydrate formation, but for SCO this can be achieved at lower values of supercooling. It can be concluded that sulfonated castor oil is a promising reagent for solving the problem of slow hydrate formation during gas storage and transportation.

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# MEAN-FIELD THEORY OF MACROSCOPIC FORCES IN INHOMOGENEOUS IONIC FLUIDS

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Ionic fluids (plasma, electrolyte solutions, molten salts, and room temperature ionic liquids) have recently attracted a lot of researchers' and chemical engineers' attention. This was mostly caused by the use of ionic fluids in various applications, including lipid and ion-exchange membranes, biomacromolecules, colloids, batteries, fuel cells, supercapacitors, *etc*. In all these examples, ionic fluids, which either interact with the charged surface of the membrane, macromolecule, colloid, or electrode surface or are confined in charged nanopores, are strongly inhomogeneous. Due to the inhomogeneity of the ionic fluid, the local electrical neutrality is violated, so that its description requires numerical solution of one or another self-consistent field equation for the electrostatic potential with appropriate boundary conditions: the classical Poisson-Boltzmann (PB) equation or its generalizations. The latter are known in the literature as modified PB equations.

In this talk, I will present a field-theoretical approach based on the thermodynamic perturbation theory and within it derive a grand thermodynamic potential of the inhomogeneous ionic fluid as a functional of electrostatic potential for an arbitrary reference fluid system. I will obtain a modified PB equation as the Euler-Lagrange equation for the obtained functional. Applying Noether's theorem to this functional, I will derive a general mean-field expression for the stress tensor consistent with the respective modified PB equation. I will derive a general expression for the macroscopic force acting on the dielectric or conductive body immersed in an ionic fluid. In particular, I will derive a general mean-field expression for the disjoining pressure of an ionic fluid in a slit pore. I will apply the developed formalism to describe three ionic fluid models of practical importance: nonpolarizable models (including the well-known PB and Poisson-Fermi equations), polarizable models (ions carry nonzero permanent dipole or static polarizability), and models of ion-dipole mixtures (including the well-known Poisson-Boltzmann-Langevin equation). For these models, I will obtain modified PB equations and respective stress tensors, which could be valuable for different applications, where it is necessary to estimate the macroscopic forces acting on the dielectric or conductive bodies (electrodes, colloids, membranes, *etc*.) together with the local electrostatic potential (field) and ionic concentrations.

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# APPLICATION OF THE THIRD LAW OF THERMODYNAMICS TO THE STUDY OF PHASE DIAGRAMS

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The third law of thermodynamics states that when the temperature tends to absolute zero, the entropy of the system also tends to zero, i.e. the system goes into a completely ordered state [1]. The decomposition of solid solutions into components or stoichiometric compounds in a quasi-equilibrium process is inevitable.

The formation of ordered phases leads to a sharp restriction of the concentration region of homogeneity of the disordered phase (Hume-Roseri rule). In this case, the area of homogeneity becomes strongly temperature-dependent.

The time to reach equilibrium increases exponentially with a decrease in temperature. For each system, there are temperatures below which it is impossible to achieve equilibrium.

The use of the third principle of thermodynamics allows extrapolation of experimental data and completion of phase diagrams to the absolute zero of the equilibrium temperature [2,3] (Fig.1a).

Acceleration of equilibrium can be achieved by various methods, including using fluxes [4], (Fig.1b).

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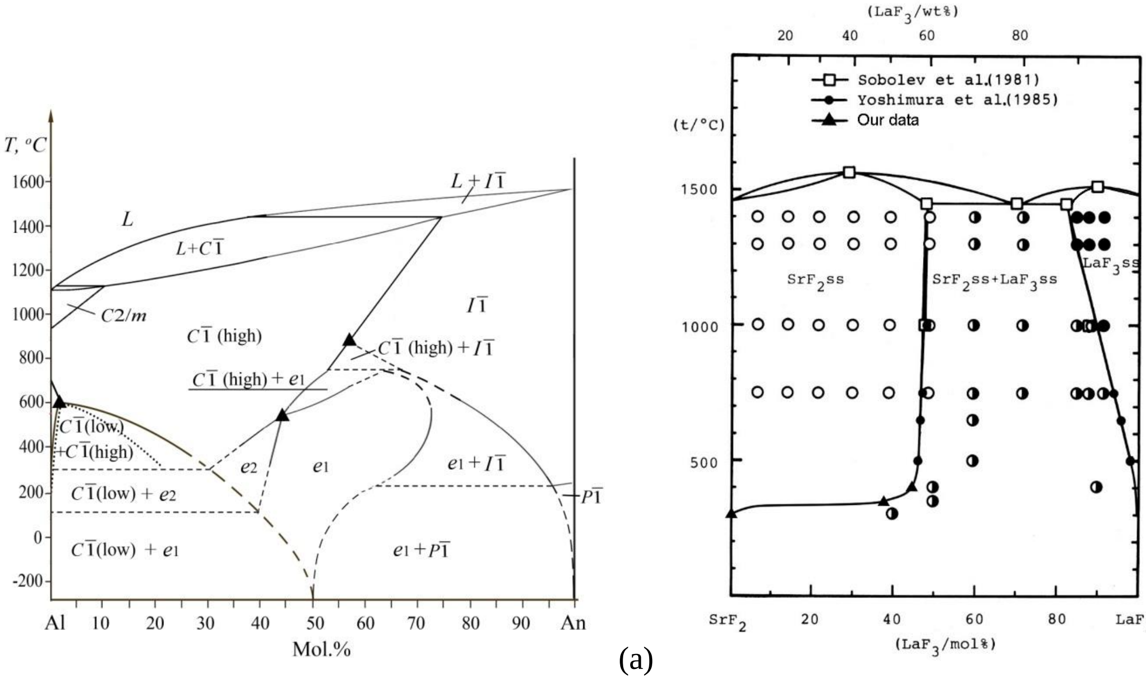

(a) (b)

**Figure 1.** Phase diagrams of the systems: a – albit-anortite, b - SrF$_2$+-LaF$_3$ [4].

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# LIMITS OF STABILITY OF METASTABLE PHASES AND METASTABLE PHASE EQUILIBRIA IN SIMPLE ONE-COMPONENT SYSTEM

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The boundaries of significant instability of superheated and supercooled liquid, superheated crystal and supersaturated vapor were investigated in Lennard-Jones particle systems using molecular dynamic simulation. Shortwave static and dynamic instability of supercooled liquid, stability criteria of isotropic and anisotropic solid were considered. The absence of a longwave instability boundary (spinodal) in the supercooled fluid was demonstrated.

In the phase diagram of a one-component system, there are two characteristic points: triple, where three phases coexist with each other, and critical, where the liquid–gas phase equilibrium ends and the coexisting phases become identical. The triple point is not special unlike the critical point.

Metastable extensions of all lines of phase equilibria beyond the triple point were determined. Two coexisting phases are metastable with respect to the third phase on these extensions. It is shown that the liquid–crystal and crystal–gas phase equilibria line also has finite critical points. These points are located in metastable regions and, due to the different symmetry of the coexisting phases, there is no phase identity here. The endpoint of the melting line is the point where its metastable extension meets the spinodal of the stretched (superheated) liquid. The metastable extension of the sublimation line ends on the spinodal of the superheated crystal (Fig. 1).

The properties of the critical endpoints of the melting and sublimation lines were investigated. It is discussed how the existence of endpoints of liquid–crystal and crystal–gas affects nucleation processes.

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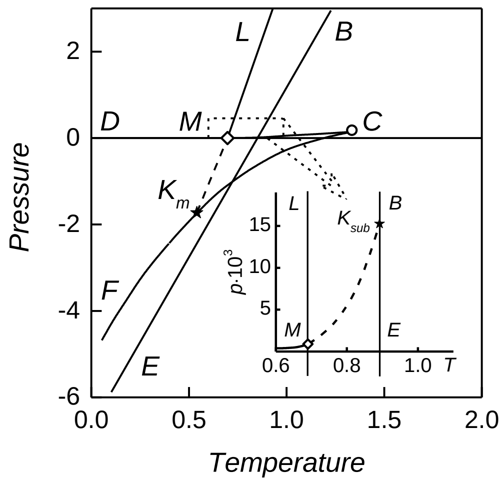

**Figure 1.** Melting line *LM*, sublimation line *DM* and their metastable extension (dash lines $MK_m$ и $MK_{sub}$, respectively); spinodal of liquid *CF*, and crystal *BE*; triple point *M* and critical point *C*; critical endpoint of melting line $K_m$ and sublimation $K_{sub}$ (in units of parameters of Lennard-Jones potential).

# APPLICABILITY OF POPULAR FUNCTIONALS IN CALCULATIONS OF THE ENERGY, THERMODYNAMIC AND SPECTROSCOPIC PROPERTIES OF SUBSTANCES

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Theoretical study of compounds requires preliminary calibration of models and methods. At this modeling stage, the reliability of models and their statistical errors are determined. In quantum chemistry, the final error consists of the errors of the all model elements, namely: the physical description, the calculation method, the basis sets, the grids used and mathematical algorithms. All this makes it difficult to choose the optimal combination of "method/basis" for calculating the substance properties [1, 2].

Calibration of the most popular functionals was done using the ADF program [3] at evaluating the enthalpy of formation and vibrational frequencies, as well as the contribution of internal rotation. Methods B1LYP, B1PW91, B3LYP, BHandH, BHandHLYP, BLYP, BP, CAMY-B3LYP, HTBS, KMLYP, LCY-BLYP, LCY-BP86, LCY-PBE, LDA, M06, M06-2X, M06-HF, M06L, mPBE, mPW, MPW1K, MPW1PW, O3LYP, OLYP, OPBE, OPBE0, PBE, PBE0, PBEsol, PW91, revPBE, revTPSS, RPBE, TPSS, TPSSH, X3LYP and HF were used to calculate $E_{total}$ and enthalpy of formation with the Sleter Cartesian basis set QZ4P (at the variation limit). The application of the QZ4P basis set and the program settings [1, 2] are chosen so that these errors can be attributed to the internal structure of the functionals. A large number of Slater functions in the QZ4P basis set does not imply its use in conventional calculations of polyatomic molecules, therefore, the dependence of $E_{total}$ on the type (size) of the basis set with QZ4P, aug-TZ2P and TZ2P has been studied. It is shown that the optimal combinations for DFT/TZ2P are DFT = M06, M06L, CAMY-B3LYP, TPSS.

Determining of the physicochemical properties with "chemical" accuracy requires taking into account the anharmonicity of vibrations and conformational transformations in non-rigid compounds. At the moment, the greatest difficulty in solving the problem of internal rotation is the search for the cross section of the potential energy surface (PES), the substitution of which in the Schrodinger torsion equation would allow obtaining calculated spectra close to experimental ones. To assess the accuracy of the PES the functionals were selected: BLYP, BP86, GAM, HTBS, KT1, KT2, mPBE, mPW, N12, OLYP, OPBE, PBE, PBEsol, PW91, revPBE, RPBE, HF, B1LYP, B1PW91, B3LYP, BHandH, BHandHLYP, KMLYP, MPW1K, MPW1PW, O3LYP, PBE0, X3LYP, LDA, M06L, MN15L, MVS, revTPSS, SCAN, TPSS, M06-2X, M06-HF, M06, MN15, TPSSH, CAM-B3LYP, CAMY-B3LYP, HSE03, HSE06, LCY-BLYP, LCY-BP86, LCY-PBE, M11, MN12-SX, N12-SX, WB97, WB97X, WB97X, LCY-PBE, MPW1K, M11, B1PW91, N12-SX, BLYP, HSE06, PBE0, SCAN, M06-2X, TPSSH, MPW1PW, HSE03. Near the variation limit with QZ4P basis set the best results were shown by BHandH, WB97, LCY-BP86, WB97X, LCY-PBE, MPW1K, M11, B1PW91, N12-SX, BLYP, HSE06, PBE0, SCAN, M06-2X, TPSSH, MPW1PW, HSE03.

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# EQUILIBRIUM DROPS: A DIFFERENCE BETWEEN THERMODYNAMICS BY CLAUSIUS AND GIBBS IN TASKS OF THE PHASE EQUILIBRIUM

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Liquid equilibrium drops in the saturated vapor were discovered by methods of statistical thermodynamics [1]. The concept of the «equilibrium» means that there is a strict equilibrium between the drop and surrounding vapor including three partial equilibria: mechanical, thermal and chemical. The latter conditions for the phase equilibrium have been derived by Gibbs for macroscopical phases [2]. That is, in these equilibrium drops at isothermal conditions ($T=const$) there are realized equalities for internal pressure of vapor and liquid $P_\alpha = P_\beta$, and also equality of chemical potentials $\mu_\alpha = \mu_\beta$, here $\alpha$ and $\beta$ are symbols of the coexisting phases. The equilibrium drops could not be realized in classical thermodynamics [2]. In another words, a discovery of the equilibrium drops indicates a basic error in classical thermodynamics for the surface phenomena and small systems as well as in all the statistical theories of the curved interface derived on the basis of the classical thermodynamics.

It has been found out later that the above error is linked with improper usage of experimental data on characteristic relaxation times of momentum transfer $\tau_P$, mass transfer $\tau_\mu$, and heat energy transfer $\tau_T$. In the general case, the following relationships are hold: $\tau_P << \tau_T << \tau_\mu$, however nowadays, the classical and statistical thermodynamics of curved interfaces uses assumption $\tau_P >> \tau_T$ .

The relationship between the second law of thermodynamics in R. Clausius' treatment [3] and J. W. Gibbs' thermodynamics [2] is discussed. The second law of thermodynamics in R. Clausius treatment is formulated more generally than Gibbs' thermodynamics, which considers only strictly equilibrium values of thermodynamic functions. Gibbs' approach generalizes the statistical mechanical theory of equilibrium for thermodynamic variables, except for the difference between the periods of relaxation of all thermodynamic parameters. For small systems, this approach consists of replacing the real physical nature of systems with the stratification of coexisting phases using a model with an interface of mobile phases in contact with a foreign (nonequilibrium) body. For solids, this results in confusion of concepts of the complete phase equilibrium of a system and the mechanical equilibrium of a deformed solid. These two problems are revealed using the molecular kinetic theory of condensed phases, ensuring a self-consistent description of three aggregate states and their interfaces [1,4].

The correct accounting for $\tau_P << \tau_T$ has clarified various results for classical thermodynamics and statistical thermodynamics, including a general definition of a surface tension for any curved interfaces, and a conception about self-consistent for kinetic models, i.e. an equality of direct and reverse reaction rates must give the same equilibrium constants as those constructed in the framework of equilibrium distribution [1,4]. The list of the discrepancies following from the Gibbs's thermodynamics is given. Possibilities of correct calculations of the surface tension by different methods of statistical thermodynamics are discussed.

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# KEYNOTE LECTURES

# PARTITIONING OF N-OCTANOL IN MIXED MICELLAR SOLUTIONS OF TRITON WITH 1-METHYL-3-OCTYLIMIDAZOLIUM CHLORIDE: EXPERIMENT AND MODEL PREDICTIONS

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Micelle-mediated separation is an attractive noninvasive technique, particularly for the biocomponents having fragile molecules. The design of the separation processes requires knowledge of the equilibrium distribution of species between the solution and the multicomponent micellar aggregates. Measurement of this distribution and its modeling are both quite challenging. The properties of the aggregates, including their shape and polydispersity typically respond to the variation of the solution composition, and partitioning of a component between the aggregates and their environment depends, in turn, on the aggregate characteristics.

A molecular-thermodynamic model has been proposed recently [1,2] that describes aggregation equilibrium and partitioning of components for mixtures of nonionic and ionic surfactants and an organic additive. We continue this work here, performing experimental studies of aqueous mixtures of Triton TX-114 and 1-methyl-3-octylimidazolium chloride (surface active ionic liquid) with/without added n-octanol (model biocomponent). Experimental data on n-octanol partition coefficients (head-space chromatography) and 2D NOESY NMR spectra are reported. For varying composition of the system, the calculated distribution of n-octanol between the polydisperse aggregates and aqueous environment is compared with experimental data. The results are discussed in light of predicted structural details of the aggregates (the number of hydrogen bonds in corona and hydration numbers, etc.).

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# FLUOROSUBSTITUTED METAL PHTHALOCYANINES: PHYSICOCHEMICAL PROPERTIES AND THIN FILMS

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Being stable organic semiconductors, MPcs are used in energy conversion devices (photovoltaic and solar cells), transistors, optical devices, and as active layers of chemical sensors [1]. In order to use phthalocyanines in these electronic devices they should be deposited as thin films with controllable thickness, orientation, and ordering. Thin films of unsubstituted and fluorinated phthalocyanines can be obtained by physical vapor deposition (PVD) or Organic Molecular Beam Deposition (OMBD) due to their volatility in vacuum. One of the quantitative characteristics of volatility is the pressure of saturated vapor of the compound at a certain temperature. Measurements of temperature dependence of vapor pressure can be useful both in improvement of the operating conditions of phthalocyanines sublimation to purify them from various volatile admixtures and in optimization of the regimes of thin film and crystal growth [2].

In this work, we study the influence of fluorosubstitution on the crystal structure of phthalocyanines of cobalt, iron, copper, and vanadyl and analyze the correlations between the structure and volatility of these complexes. The single crystal structures of $MPcF_4$ (M= Co, Fe, Cu, VO) were refined; their vapour pressure was determined as a function of temperature by the Knudsen effusion method and the standard thermodynamic parameters $\Delta H_T$ and $\Delta S^o_T$ of the sublimation process were determined. These characteristics were compared with those of unsubstituted MPc and hexadecafluorosubstituted derivatives. Hirshfeld surface analysis was used as a powerful tool for the visualization and to offer better insight into intermolecular contacts in these molecular structures.

The structural features of metal phthalocyanine thin films and their application as active layers of chemiresistive gas sensors are also discussed.

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# EXTERNAL FIELDS METHOD IN MOLECULAR SIMULATION AND THERMODYNAMICS OF 2D CRYSTALS

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We present a general methodology for determining thermodynamic characteristics of orientationally ordered rigid crystals. The proposed approach is based on the kinetic Monte Carlo simulation of the gas-crystal system under two external fields imposed on the elongated simulation cell. The first one is the external potential imposed on the gas phase, while the other, the so-called damping field, reduces the intermolecular potential at the crystal edges and switches it off in the gas phase. As a result, we obtain the equilibrium system of the crystal and the ideal gas having the same chemical potential at a given temperature. Therefore, one can determine the chemical potential of the crystal using its analytical expression for the ideal gas phase. The damping field creates the pressure change between the coexisting phases that is similar to thermophoresis phenomenon due to the temperature gradient. Generally, the effect of the damping field is equivalent to the temperature increase in the same system, but in our case it does not make the system non-equilibrium as it maintains at constant temperature. The excess pressure in the crystal produced by this effect can be compensated by the negative external potential in the gas phase. Such technique was applied to thermodynamic analysis of the trimesic acid monolayer explicitly accounting for hydrogen bonds, the dispersion and electrostatic potentials. This system is an example of the wide class of self-assembled organic molecular layers which are applied in organic electronics, sensors and catalysis. We have considered equations of state, the chemical potential, Helmholtz free energies and entropies of three polymorphous structures: honeycomb, flower-like and hexagonally close-packed structure in a wide range of temperatures and pressures as well as conditions of polymorphous transitions. The calculated free energy and entropy excellently obey the Gibbs-Duhem equation, which confirms thermodynamic consistency of our approach. We have also considered thermodynamic properties of the gas phase of the 2D trimesic acid at high temperatures and found that the critical temperature is less than the temperature of disassembly of crystalline phases. So, the disassembly occurs as a sublimation rather melting. The approach does not have any limitations and therefore has a clear prospective in thermodynamic analysis of rigid crystals of any density.

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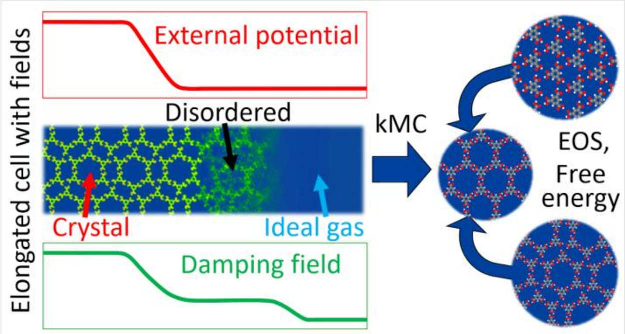

**Figure 1.** Scheme of the methodology applied in the study.

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# EXPERIMENTAL CALORIMETRY FOR STUDY OF MATERIALS BASED ON ORGANIC, ORGANOELEMENT AND POLYMERIC COMPOUNDS

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This work is devoted to the fundamental problem, namely the application and development of methods of chemical thermodynamics and experimental calorimetry in study of materials and compositions based on organic, organoelement and polymeric compounds. Among these perspective compounds, the most thoroughly investigated representatives are fullerides and fullerene complexes with organoelement ligands, fullerene-containing polymers, carbosilane and liquid crystalline dendrimers with different nature of the surface layer. The discussion and conclusions are based on the results of complex precision calorimetric determination of the temperature dependences of heat capacities and characteristics of the revealed phase transitions in a wide temperature range.

In the present work, the temperature dependences of heat capacities of the above compounds in different states (amorphous, crystalline, partially crystalline, liquid crystalline) were determined in the temperature interval from 6 to 870 K by precision adiabatic vacuum calorimetry (BCT-3 with discrete heating, Termis, Moscow region, Russian Federation) and differential scanning calorimetry (DSC 204 F1 *Phoenix*, Netzsch–Gerätebau, Selb, Germany). As a result, the revealed phase, physical and relaxation transformations were detected and discussed. The analysis of the obtained complex of standard thermodynamic and thermochemical characteristics of the investigated objects, the qualitative and quantitative dependences "thermodynamic property – composition", as well as the most general trends of changes in thermodynamic properties of compounds on their structures and physical states is given in detail. The established dependences can be successfully used for the prediction of methods of synthesis of the advanced materials with the required characteristics.

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# INSIGHTS ON GLASS DYNAMICS FROM AGING FAR BELOW THE GLASS TRANSITION

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The non-equilibrium nature of the glasses results in their slow evolution towards equilibrium, a phenomenon known as physical aging. A wealth of activity has been traditionally conducted close to the glass transition temperature, $T_g$, where aging exhibits monotonous behavior and its kinetics is assisted by the main $\alpha$ relaxation. In this contribution, I will show how extending the temperature range of aging to temperatures further below $T_g$, may convey insights of utmost importance on the molecular mechanisms involved in the kinetics of glass equilibration and their temperature dependence. Specifically, I will show that, in a wide variety of glass formers, aging persists even when conducted far below $T_g$ where the $\alpha$ relaxation is expected to diverge to astronomical time scale. The role fast mechanisms of equilibration assisting aging and the possible change of behavior of the $\alpha$ relaxation are discussed.

# NOVEL APPROACHES FOR CHARACTERIZING NANOHETEROGENEITY IN IONIC LIQUIDS

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Segregated polar and apolar domains forming in the liquid phase of some ionic liquids have a complicated interpenetrating structure. Visual analysis of molecular dynamics trajectories does not always allow to identify the existence of domains and cannot be used to estimate their size. We discuss possible methods to characterize domain structure from momentary configurations of ionic liquids. Some of them have been used previously and other are suggested for the first time. Several ammonium-based protic ionic liquids with different propensity to domain segregation (strong, weak, or no segregation as witnessed from experimental studies [1, 2]) are considered. Molecular dynamics simulations of these liquids are performed using models based on the OPLS-AA force field with scaled ion charges.

Results show that, in addition to well-known peaks of the structure factor at low $q$ values and features of the radial distribution function, there are several other ways to recognize domain segregation and determine the domain length scale. Domain-forming ionic liquids show peaks of Ripley's functions, peaks and large-period oscillations of finite-volume radial distribution function integral or difference of such integrals for polar and apolar atoms, and peaks of local atom density variance. These peaks disappear with increasing temperature due to disruption of segregated domains. All the studied liquids show stronger polar than apolar aggregation, i.e. apolar fragments are more homogeneously distributed in space. At the same time, both polar and apolar fragments form continuous percolation structures, which in the strict sense leads to the existence of a single polar and a single apolar domain in the whole volume of liquid.

The nanostructure of ionic liquids directly affects their solvation properties. The solubility of apolar species is governed by the probability of cavity formation, which is significantly higher in domain-forming ionic liquids. These cavities are shown to form predominantly in apolar domains.

The suggested approaches can be applied to various nanostructured liquids including both ionic and molecular solvents and mixtures, as well as other systems with mesoscale ordering.

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# EXPERIMENTAL AND THEORETICAL INVESTIGATION AND CRITICAL ASSESSMENT OF THERMODYNAMIC DATA FOR PURE IN, CU AND SOME BINARY SYSTEMS FROM 0K

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Thermodynamic data for crystalline indium and copper were assessed using extended Einstein model from 0K. The liquid phase was described using two state models. During assessment careful analysis of the experimental data was carried out. It appeared that although indium and copper are frequently used as reference material for determination of thermodynamic properties there is lack of experimental data for the heat capacity of indium and a pretty large descripancy in the experimental data for pure copper. For these reason and accurate analysis of experimental data was needed as well as additional experimental investigations were carried out.

In order to full fill the need for a precise evaluation of $S^o298$ we needed to use an additional technique of multiple Einstein functions, which allows the experimental heat capacity and enthalpy data for the solid phase to be approximated accurately from 0K up to the melting point.

It had been shown previously that the application of the new models for pure elements sometimes requires the use of two Einstein temperatures (e.g. for Sn, Ge ,Si C, In) to describe the thermodynamic properties of the phases. In the present work we discuss methods to define the Einstein temperature for metastable phases of elements, which has been described using multiple Einstein temperatures, and the variation of these Einstein temperatures with composition to account for the composition dependence of the excess entropy. This approach is demonstrated here for some binary systems, which shows solid solution regions.

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# LIQUID PHASE SPLITTING AND CRITICAL STATES IN QUATERNARY SYSTEMS WITH CHEMICAL REACTIONS: NEW EXPERIMENTAL DATA

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In this paper, we briefly present the review of experimental data on solubility, liquid-liquid equilibrium (LLE), chemical equilibrium (CE) and critical states of LLE in the systems with chemical interaction which have been obtained in our research group in recent years. These data relate to quaternary systems with reactions of esterification and hydrolysis of carboxylic acid esters. The new data sets were obtained for the following systems: formic acid + ethanol + ethyl formate + water; acetic acid + ethanol + ethyl acetate + water; acetic acid + n-propanol + n-propyl acetate + water; acetic acid + n-butyl alcohol + n-butyl acetate + water; propionic acid + ethanol + ethyl propionate + water; propionic acid + n-propanol + n-propyl propionate + water; propionic acid + n-butanol + n-butyl propionate + water. Some of the references on few recent papers are listed below [1-4]. In all systems, the presence of water as a component leads to limited mutual solubility. These results include the data both for quaternary mixtures and for binary and ternary subsystems. The compositions of critical states of LLE were also determined.

The study of solubility was carried out by "cloud-point technique" method with some modifications (as a rule, at polythermal conditions). In the LLE investigations we used gas chromatography (GC) and nuclear magnetic resonance (NMR) methods for analytical determination of phase compositions. Experimental LLE data were correlated using NRTL model and compared with the values calculated by UNIFAC model.

In this presentation, we will discuss some general features of the topology of phase diagrams of multicomponent systems with chemical reactions and limited solubility. For example, for industrial applications, the fact of establishing CE in a homogeneous area or in the region of reaction mixture splitting is of interest. The answer to this question is given by the data on the relative disposition of the binodal surface and the CE surface in the composition tetrahedron. A special case is the discussion of relatively new singularities such as manifolds of critical states. The location of these manifolds in the concentration space is also of particular interest: conducting processes in the supercritical region guarantees the absence of splitting, for instance, during a reaction. In the case of the systems with ester synthesis reaction at polythermal conditions this manifold is a surface in composition tetrahedron with a curve corresponding to chemically equilibrium critical states. The polythermal critical surfaces could be constructed on the basis of the data on the position of critical curves in a tetrahedron of composition at different temperatures. Some illustration of critical surfaces and critical curves for chemically equilibrium states will be presented.

We believe that these new data will be useful not only for the development of thermodynamic databases, but also for the industrial design of the synthesis of esters.

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# POLYMER AND METAL POWDERS FOR ADDITIVE MANUFACTURING GUIDED BY DIFFERENTIAL FAST SCANNING CALORIMETRY

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Due to difficulties in the solidification process, like material flow, crack formation and porosity for metals and polymers, additive manufacturing is still limited to a restricted set of materials. To improve the solidification process during additive manufacturing, and thus enable the manufacturing of high-strength and functional products, the powder materials must be designed and deep understanding of the melting/solidification processes must be developed. Differential Fast Scanning Calorimetry (DFSC) method allows in-situ characterisation of phase transformations at process-relevant heating and cooling rates of powder-sized samples. Thus, it allows fundamental guidance for powder modification and provides valuable information for modelling.

An industrial aluminium alloys AA7075, AA2024, AA6061, modified with different nanoparticles, showed strong correlation between the crystallization undercooling and cracking of laser powder manufactured parts. Modification of polyamides and polyethylene for Additive manufacturing was studied by DFSC.

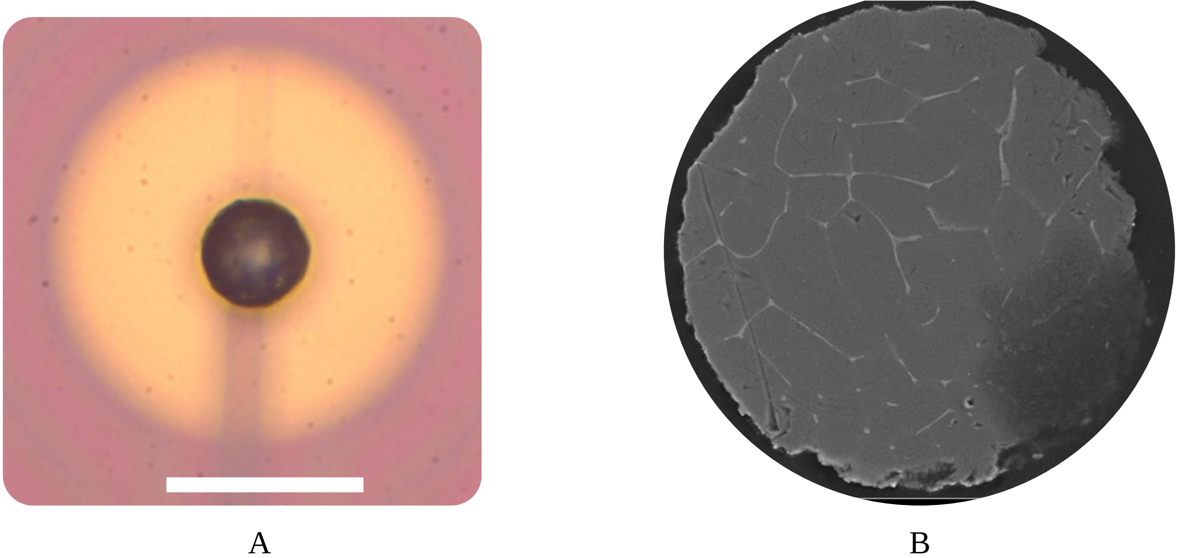

***Figure 1.*** Additive manufacturing AA7075 powder particle, modified with TiC nanoparticles on the Fast Scanning Calorimetric chip sensor – A. It’s cross-section in SEM after solidification at 10,000 K/s – B.

# PROTEINS, POLYELECTROLYTES AND COPOLYMERS FOR PULMONARY SURFACTANTS

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Pulmonary surfactant (PS) is a complex mixture of different lipids and proteins. In spite of low concentrations of proteins in PS (less than 10%), they are indispensable components. It is generally accepted that hydrophobic proteins SP-B and SP-C control the redistribution of lipids between the surface and subsurface layers at surface compression and expansion.

In this work, the dynamic surface properties of PS solutions were investigated by the methods of dilational surface rheology. A new approach to the analysis of nonlinear rheological properties was developed with the aim of estimation of the dilational surface elasticity in the region of extremely low surface tensions corresponding to physiological conditions. It was shown that the proteins in a lipid monolayer decrease its dynamic leading to a looser packing of the lipids. This effect was confirmed by ellipsometry and infrared reflection adsorption spectroscopy. Moreover, the action of SP-B and SP-C proteins resulted in a decrease of the main relaxation time of surface stresses in the region of high surface pressures due to the acceleration of component respreading under permanent surface deformations [1, 2]. Then, different synthetic polyelectrolyte and copolymers were used as analogs of SP-B and SP-C proteins. It was shown that only at optimal ratio of electrostatic and hydrophobic interactions between lipids and macromolecules one can achieve properties required for PS.

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# THE DEPENDENCE OF THERMODYNAMIC PROPERTIES OF POLYPHENYLENES ON THEIR STRUCTURE

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Polyphenylenes are polymers which comprise the related phenylene groups in the main chain and their sequence can be interrupted by bridging atoms or groups of atoms. Currently, there are polyphenylenes of linear and three-dimensional structures, which formation is determined by the methods of their synthesis. The properties of polyphenylenes depend on the molecular masses and structure of the macromolecule, for example, on the presence of substituents in aromatic rings, non-phenylene units and branched structure or isomerism of phenylene groups. Previously, the mainly chain (linear) polymers were subject of research. The linear polyphenylenes are non-melting and insoluble solids in organic solvents, having high level of radiation resistance and improved dielectric properties.

In the last years, polymers related to polymer macromolecules (superbranched polymers and dendrimers) have been synthesized. It has a great potential for obtaining of functional nanoscale materials with unique electronic, optical, magnetic and chemical properties to necessary for the development of new technologies and biomedicine [1, 2].

However, the thermodynamic properties of linear polyphenylenes containing only phenylene groups, namely, the heat capacity $C_p°(T)$, enthalpy $H°(T) - H°(0)$, entropy $S°(T)$ and Gibbs energy were studied in the 70s of the last century. The present investigation summarizes the thermodynamic data of twenty known linear, superbranched and dendritic polyphenylenes obtained by precision adiabatic vacuum and differential scanning calorimetry in the range from 5−(350 − 600) K. The experimental data were used to calculate standard thermodynamic functions of polyphenylenes over the range from $T \rightarrow 0$ to 350 K for different states and the standard enthropies of formation at 298.15 K. In the above intervals, the thermodynamic characteristics of glass transition and glassy state were detected for all investigates samples. The thermodynamic characteristics of the revealed phase and physical transformations known linear, superbranched and dendritic polyphenylenes were evaluated and analyzed. The most general dependencies of thermodynamic characteristics of polyphenylenes on their structure, in some cases, composition have been experimentally established. It allows revealing and predicting practically important compounds properties of linear and three-dimensional structures of this group. The obtained thermodynamic properties can be used in the development of industrial technologies for their synthesis and following application.

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# SOLVOPHOBIC AND SOLVOPHILIC EFFECTS IN UREA AND TETRAMETHYLUREA SOLUTIONS

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Hydrophobic hydration and hydrophobic interaction play the major role in various chemical phenomena such as formation of nanoscale micelles and bilayer membranes, molecular recognition, *etc*. There is only little evidence that similar but more weakly pronounced effects take place in highly ordered *via* H-bonds non-aqueous solvents such as ethanolamines or glycols [1,2]. However, the important information for comparative analysis is scarce. Here, we focus on solvation and the solute-solute interaction in solutions of hydrophobic tetramethylurea (TMU) and hydrophilic urea (U) in three solvents forming a three-dimensional H-bond network, *viz.* water, ethylene glycol (EG) and formamide (FA) in a wide temperature range. We compare standard enthalpies and heat capacities of solution and transfer to highlight common features and fundamental differences in U and TMU solvation in aqueous and non-aqueous media. The enthalpic, free energy, entropic *etc*. virial parameters of the solute–solute pair interaction in a liquid phase are computed both in water and non-aqueous solvents in terms of the excess function concept. Special attention is paid to the analysis of the second virial coefficient and its temperature changes (see the Figure). Our comparative analysis highlights several unique features of the TMU-TMU pair interaction in non-aqueous media which are very similar to those observed in water. We show that the solvophobic interaction between TMU molecules in EG and, especially, in FA does exist and leads to TMU aggregation both in aqueous and non-aqueous media.

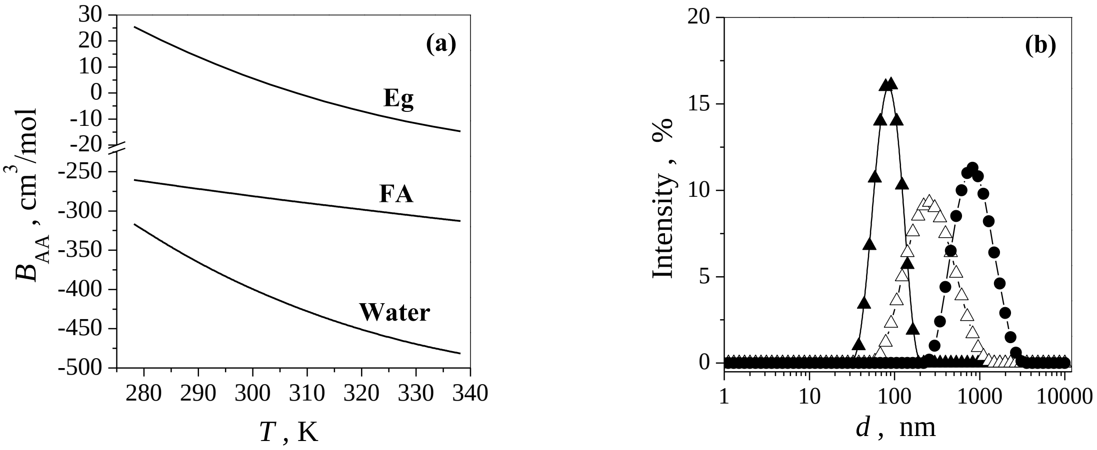

**Figure.** (a) Temperature dependence of the second virial coefficients, $B_{AA}$ of the TMU–TMU pair interaction in water, FA and Eg; (b) dynamic light scattering in TMU solutions in water (▲), FA (●) and Eg (△) at $X_{TMU}$ = 0.068 TMU mole fraction.

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# GELATIN AS A STABILIZER FOR EMULSIONS: MOLECULAR MODIFICATION

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Gelatin, a degradation product of the fibrillar protein collagen, is one of the biopolymers that is widely used in industry. Gelatin has surfactant properties and is used to stabilize emulsion systems. One way to enhance the stabilizing properties is the molecular modification of gelatin by complexation with polysaccharides. The polysaccharide-gelatin polyelectrolyte complexes that are formed during biopolymer interaction are considered to be the basis for the creation of new emulsion materials in biotechnology, medicine, pharmaceuticals, the food industry. The creation of materials is based on the self-organization principles of the complexes in the bulk of the aqueous phase. The driving force behind the formation of non-covalent complexes is the intermolecular interactions that take place between gelatin and polysaccharides, including electrostatic interactions, hydrogen bonds, and hydrophobic interactions. The combined use of proteins and polysaccharides in the composition of the complexes contributes to the mutual enhancement of their physicochemical properties: their stabilizing ability and resistance to changes in external factors (pH, the presence of salts, changes in temperature). The influence of complex formation with polysaccharides of various nature on the physicochemical properties (stability, dispersion, rheological properties) of gelatin emulsions is shown.

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# PROTEIN MICROGEL LAYERS AT THE LIQUID-GAS INTERFACE

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The protein supermolecular particles, amyloid fibrils and microgels, have found numerous applications in various areas of industry and in medecine [1]. Although some applications are connected with the stabilization of foams and emulsions, any information on surface properties of the dispersions of protein aggregates is scarce. The main difficulty consists in a strong influence of the impurities, which are produced by hydrolysis in the course of the aggregate formation. Although purification of the protein microgel dispersion by manifold centrifugation does not give a possibility to get rid entirely of the impurities, it allows observations of the distinctions between the properties of spread and adsorbed layers of protein nano- and microparticles on the one hand, and the properties of the layers of protein molecules on the other hand [2]. The spread layers of purified microgel display the much higher surface elasticity than the elasticity of spread layers of native proteins. An important distinction between the properties of the layers of microgel and the layers of native proteins consists in different mechanisms of the layer collapse. While the surface pressure isotherms of native BLG layers are smooth up to the surface pressure of approximately 63 mN/m, the compression of the BLG microgel layers leads to noticeable random fluctuations of the surface pressure indicating the formation of three-dimensional bunches of particles in the layer. The deformation of protein particles at surface compression proves to be less significant than in the case of poly(N-isopropylacrylamide) microgel indicating the absence of a thick and soft corona in the former case.

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# HOMODESMOTIC METHOD FOR STUDYING THE MOLECULAR ENERGETICS OF ORGANIC COMPOUNDS

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A modern study of a wide variety of chemical problems is unthinkable without quantitative information about the thermodynamic characteristics of the compounds involved in the process under study. A weighty and reliable alternative to sophisticated and resource–intensive experimental methods for determining energy parameters – enthalpies of formation $\Delta_f H°$, bond dissociation energies *BDE* etc. - are theoretical methods using various ideas (principle of additivity, comparative approach) and an arsenal of techniques of modern computational chemistry, primarily quantum chemistry. The submitted report provides a brief analysis of existing methods of theoretical thermochemistry, special attention is paid to the main ideas and methodology of the homodesmotic variant of the comparative determination of thermochemical quantities of organic compounds.

The development of the homodesmotic method for studying the molecular energetics of organic compounds is proposed in the form of the concept of a complete set of homodesmotic reactions (HDR). The implementation of the concept is used the graph-theoretic method of analyzing the structure of the compound under study. The advantage of the concept of a complete set of HDRs over the conventional approach consists in (1) increasing the reliability of the theoretical estimate of the thermochemical quantity, (2) controlling the reproducibility of a result and the possibility of reasonable accounting for unreliable reference data, (3) simple algorithmization and programming of the routine selection of HDRs of a complete set, (4) analysis of non-valent and secondary energy effects, (5) an extremely successful combination and complementarity with the computational methods of quantum chemistry. It should be noted that, although the methods of quantum chemistry are very appropriate in the author's technique, the homodesmotic method can in principle be used without quantum chemical calculations at all.

The report contains extensive factual material obtained by the author using the homodesmotic method over the past 10 years, when studying the molecular energetics of molecular and radical structures, non-valent effects. The main results are reported in the papers [1-9]. The possibility of using the method to evaluate the energy-derived characteristics of organic compounds is also shown.

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# VORONOI-DELAUNAY METHOD. APPLICATIONS TO SOLUTIONS

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General geometric theorems establishing spatial relations between atoms and voids between them were proved by mathematicians G.F. Voronoi and B.N. Delaunay at the beginning of the last century. Currently, it presents a powerful scientific tool for investigation of computer models of various molecular systems, both biological and solutions. Modern MD modeling allows to create reliable models that can be confidently used to study the structural and dynamic properties of solutions. Such models reproduce well the existing experimental data. However, their main value is that they can be used to explore what cannot be extracted from the experiment. Important information can be obtained using the Voronoi-Delaunay method.

By calculating the volumes of the Voronoi regions of atoms, it is possible to determine the real volumes that relate to different components of the solution. This *geometrical* partial volume differs from the known *thermodynamic* partial volume. Establishing the relationship between them helps to give a structural interpretation of the behavior of the observed volumetric properties of solutions [1]. It opens up addition opportunities to study the formation of associates in solutions with increasing concentration. Calculation of the volumes related to different components of the ionic liquid (anions, head cations and alkyl substituents) makes it possible to single out more and less dense regions in the ionic liquid. On the other hand, the empty Delaunay sphere (interstitial sphere) represents the real void between the atoms of the system. Spheres with large radii indicate the presence of large voids. Using them, it was shown that gas molecules dissolved in an ionic liquid bring an additional empty volume, which is localized exclusively in their nearest environment [2].

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# THERMODYNAMICS OF MOLECULAR RECOGNITION AND POLYMORPHISM

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Genuine molecular recognition is a desired property of supramolecular and biological receptors. Normally, their selectivity is very moderate once the substrates have a number of competing isomorphic compounds. To boost selectivity of molecular interactions, their cooperativity in receptor matrix is needed, which can be reached in guest inclusion by crystalline supramolecular hosts with phase transition and guest-induced polymorphism [1]. In several cases, an absolute selectivity was observed with formation of a metastable polymorph after inclusion and release of only one guest compound by calixarene [2, 3]. This is a kind of smart property, where the host crystal packing remembers selectively a previously included guest [1].

The problem with search of polymorphs that can be induced by inclusion and release of some specific guest compounds is vast amount of target material and related extensive experimental work needed for polymorph screening. In this screening, the most amount of the studied material is consumed by such a commonly used method as DSC needed to determine the phase transition parameters. To ease these requirements, the fast scanning (chip-based) calorimetry (FSC) was used in the present work [4, 5]. For this method, simultaneously formed microcrystals of different polymorphs with a mass of dozens nanogram may be chosen from the same crystalline powder using optical microscope and then studied by FSC with a heating rate above 1000 K/s. This approach makes polymorph screening much more efficient especially for expensive and less stable substances, as well as for compounds synthesized in very small amount.

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# STRUCTURAL FACTOR CONTROLLING SELF-ASSEMBLY BEHAVIOR AND FUNCTIONAL ACTIVITY OF SURFACTANT SYSTEMS

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Self-assembling systems based on amphiphilic compounds (surfactants, macrocycles, polymers) play important role in both fundamental researches and practical applications. Therefore, of significant importance is the establishment of the relationship between the structure of amphiphiles and their properties. In our work, the systematic design of cationic surfactants has been carried out beginning with classical homological series of trimethyl ammonium (TMA-n) surfactants as reference surfactants, towards series of triallylammonium (TAA-n), imidazolium (Im-n), morpholinium (Mph-n), triphenyphosphonium (TPP-n), diazabicyclo[2.2.2]octane, piperidinium (Pip-n), pyrrolidinium (Pyr-n) amphiphilic derivatives, mono- and dicationic, with some of them functionalized with hydroxy- or hydrxyalkyl fragment. For these homological series, quantitative characteristics of aggregation were evaluated, such as critical micelle concentration (cmc), free energy of adsorption and micellization, hydrodynamic radius, zeta-potential, counterion binding, etc. It was demonstrated that most significant changes occurred upon the transition from TMA- to TPP-series, as well as upon the transition from mono- to dicationic analogs. Along with aggregation properties functional activity is studied and analyzed in terms of structural specificity of surfactants. In this context, solubilization capacity, antimicrobial activity, binding with DNA, modification of nanocarriers were investigated. Cationic surfactants are documented to show obvious structure-activity correlation which can be used to control the wide spectrum of practical potentiality of the surfactant based systems.

**Acknowledgment:** This work was financially supported by Russian Science Foundation (project № 19-73-30012).

# THE USE OF THE THERMODYNAMIC APPROACH FOR ADVANCED OXIDE CERAMICS DEVELOPMENT

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Ceria and zirconia-based ceramics are important materials for high- and intermediate-temperature electrochemical applications. However, the shift to an advanced ceramics manufacturing having temperature and phase stability, and sufficient conductivity requires the development of the complex approaches for oxide precursors and ceramics investigation. The use of thermodynamic approach offers a great possibility to track the thermal evolution of the system, investigate high-temperature stability of oxide ceramics, the temperature dependencies of their electrical and transport properties.

The present work offers the state-of-art in a field of manufacturing of the advanced ceramics with desired properties. The analysis of thermal prehistories of binary and ternary zirconia and ceria based systems via simultaneous thermal analysis (STA) is discussed. The application of Knudsen effusion mass spectrometry technique equipped with a tungsten twin effusion cell for thermodynamic stability investigation of $ZrO_2$ based and $CeO_2$ based solid solutions is highlighted. The STA and Knudsen effusion mass spectrometry techniques are demonstrated to be an efficient tool for choosing the optimal conditions of precursors synthesis as well as ceramics compositions with the highest thermodynamic stability are discussed.

**Acknowledgements** The financial support of the work was provided by the Council on grants of the President of the Russian Federation, grant number 75-15-2021-370. XPS, DSC data were obtained Centres for Thermogravimetric and Calorimetric Research, studies in surface science at SPBU Research park.

# ORAL PRESENTATIONS

# MOLECULAR DYNAMICS STUDY OF VISCOSITY AND EXCESS ENTROPY OF HYDROCARBONS

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Rosenfeld and Dzugutov have conjectured universal relations between the scaled transport coefficients of simple liquids and the excess entropy or pairwise entropy, respectively [1, 2]. These conjectures have been shown to hold for various types of liquids. In atomistic simulations, the scaling with respect to the pairwise entropy is more convenient to study, as the pairwise entropy can be computed easily for atomic liquids from the pair correlation function. However, there is a problem of pair entropy definition for molecular substances.

In this work, we propose a new method of estimation of the pair contribution to the excess entropy for hydrocarbon liquids. We present the results on viscosity-excess entropy and viscosity-pair entropy Rosenfeld scaling for n-pentane and n-dodecane with the OPLS-AA/CM1A force field [3] and 1,1-diphenylethane with OPLS-AA/CM1A and COMPASS [4] force fields, and compare the results with the available experimental and correlation data. We show that our method accounts for 75-90% of excess entropy changes in molecular liquid, comparable to the pair entropy contribution in atomic liquids.

The comparison of the viscosity-excess entropy curves shows correspondence between the OPLS-AA and COMPASS results (Fig. 1), however the OPLS-AA force field overestimates the viscosity-density dependence. We can thus assume that the systematic errors in transport coefficients with the OPLS-AA force filed are due to the lower entropy in this model, compared to the real substances.

**Acknowledgements** The study was done within the framework of the HSE University Basic Research Program.

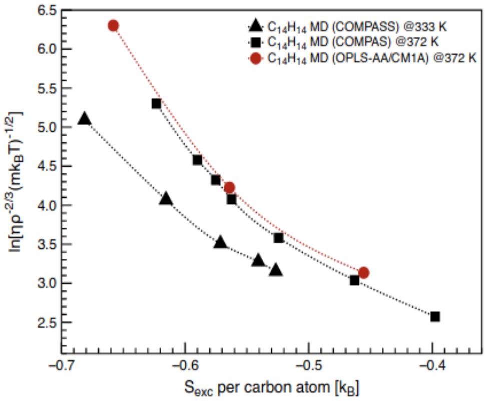

**Figure 1.** The dependence of the scaled viscosity on the estimated total excess entropy for 1,1-diphenylethane.

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# CRYSTAL NUCLEATION IN AMORPHOUS SYSTEMS: UNIVERSAL SCALING RELATIONS

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One of the most popular scenarios for the crystallization of supercooled liquid is the process of crystal nucleation and the subsequent growth of crystalline nuclei. Depending on how supercooling was initially achieved and under what conditions the subsequent crystallization of a supercooled liquid (or an amorphous solid) occurs, it is possible to obtain a material whose structure, and, consequently, the physical and mechanical properties can be very diverse. In this regard, understanding the initial stage of crystallization as a phase transition seems to be very necessary and important.

Crystal nucleation in atomistic/molecular systems occurs, as a rule, on nanometer spatial scales; the critical size of a crystalline nucleus under certain conditions can be only a few tens of particles. As a result, wide opportunities in research in this area are opening up for methods of molecular dynamics simulations. The results obtained using both classical and quantum mechanical molecular dynamics simulations not only complement the data of traditional experiments on microscopy, diffraction, spectroscopy, etc., but also allow one to reveal completely new patterns in the processes of crystal nucleation.

In this work, we will show that the temperature dependences of the rate characteristics of crystal nucleation processes are described by universal scaling relations [1–6].

**Acknowledgements** The computational part of this study is supported by the Theoretical Physics and Mathematics Advancement Foundation “Basis” (Project No. 20-1-2-38-1).

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# NATIONAL CHALLENGES IN MATERIAL INFORMATICS

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Material informatics is a globally accepted trend in material science. Databases and machine learning has become a universally acknowledged tool in creating and exploring new materials and engineering different goods. In this paper we explore key spheres of interest for material scientists in Russia and globally, using information from research papers and patents published in the last 10 years. We acknowledge a growing demand for a closer interaction between business and science in creating collaborations and mutually beneficial research projects. To facilitate communication we propose to start a material.business project to support communication and to attract investments for teams working on the frontiers of material informatics.

# NON-EQUILIBRIUM THERMODYNAMICS OF ENCELADUS ICE SHIELD: HOW LATTICE-BOLTZMANN MODELING HELPS US ESTABLISH WHAT'S INSIDE

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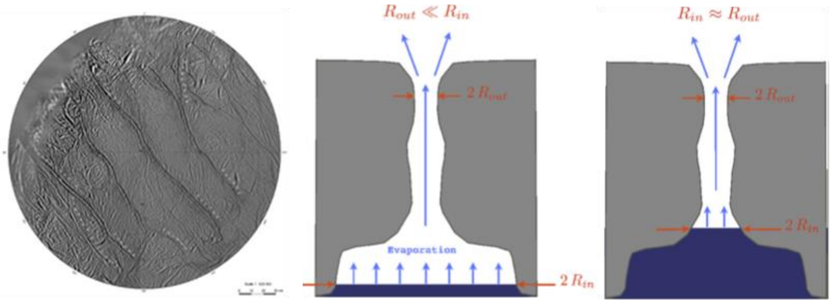
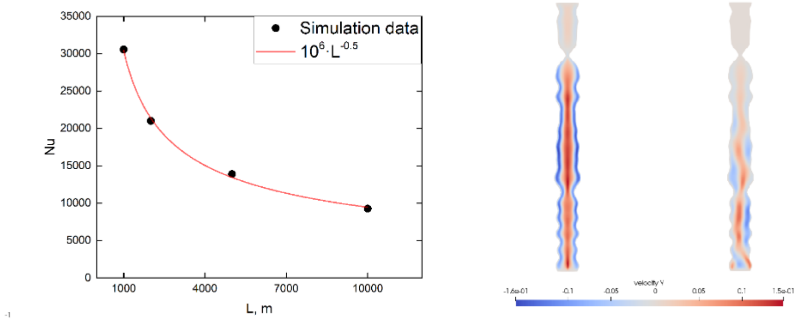
Enceladus is an ice satellite of Saturn, discovered by the Cassini mission and has a unique natural phenomenon – "tiger strips", geyser cracks at the south pole with a total length of about 500 km. Due to the data on the chemical composition and the presence of water, this phenomenon has significant astrobiological potential. Such a phenomenon attractive vigorous experimental and theoretical research efforts, with the latter aimed at the construction of geophysical model of Enceladus core and ice shell using the limited experimental data available. Heat and mass transfer from the subglacial ocean depths to the satellite surface is very complicated due to high salinity of the water, tidal forces, complex structure of the porous core and geothermal activity, etc.

In this work, the convective heat and mass transport in water confined to vertical slit-shaped channels with aspect ratio up to $10^4$ that reproduce the conditions of Enceladus tiger stripes are explored with Lattice-Boltzmann method. The steady heat flux in the planar slip channels is shown to decay proportionally to inverse square root of the channel height, which is an important qualitative relationship. Undulations on the walls reduce the heat flux if no-slip boundary conditions are imposed, but may even intensity the flux if the friction is reduced and substantial slip of between water and the ice walls is allowed. In all systems the total heat flux from hot reservoir at the bottom to vacuum at the top was substantially lower than that the flux estimated from experimental observations of Enceladus.

The results of this work allow analysis of hypotheses on the conditions of the hot water ocean below the ice shield and the shape of the channels, in particularly suggesting that the channels are far from slit-like and perhaps the cracks are much wider (cavern-like) down below the stripes visible on the Enceladus surface.



Left: Enceladus tiger stripes (planetary.org) Center & right: contrasting views of gas evapo rating from a subsurface liquid flowing through a cylindrical conduit to vacuum. A large evaporating surface (center panel) might be required to avoid implausibly large temperature gradients in the liquid (right panel) [1,2].



Left: Nusself number of simulated convection flow in channels of different lengths (straight walls). Points - simulation data. Line - approximation.
Right: Fields of velocity component (same as gravity direction) at different simulation times.

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# HOMODESMOTIC METHOD FOR DETERMINING THE ENTHALPY OF FORMATION OF FREE ALKYL RADICALS

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Free radicals are intermediates of many important chemical processes, and the study of their thermochemical characteristics is an urgent task of modern physical organic chemistry. This work is devoted to the development of a protocol for calculating the standard enthalpies of formation ($\Delta_f H°$) of free alkyl radicals; primary, secondary, tertiary $C_5$-$C_9$ hydrocarbon radicals of normal and branched structure were selected as the test set. The method being developed is based on the author's concept of a complete set of homodesmotic reactions (HDR), described in [1]. HDR is a formal thermochemical equation, which is based on the preservation of a number of balances: material, bond, group, isogyric, and the balance of non-valence interactions. If these balances are preserved, the thermal effect ($\Delta_r H°$) of a correctly designed HDR should be close to or equal to zero. If reliable data on $\Delta_f H°$ of the reference structures participating in the HDR are available, it becomes possible to calculate $\Delta_f H°$ of the analyzed compound. The smallest structure available for analysis using the described technique should contain 5 carbon atoms for free alkyl radicals in the main chain, which is necessary to account for the influence of the electron of the radical center on neighboring carbon atoms. The complete sets of HDRs containing from 1 to 22 independent HDRs were constructed for 107 compounds of the test set. The *pri*- and *sec*-propyl radicals and ethane were chosen as the minimal reference structures (*tert*-butyl – for tertiary alkyls), the remaining structures correspond to the decomposition of the molecular graph of the analyzed compound.

To prove the constructed HDRs are of acceptable quality (thermoneutral HDR) the thermal effects $\Delta_r H°$ of the latter were calculated in the M062X/cc-pVTZ approximation using the Gaussian-09, Revision C1 software package. It should be noted that as a result of the search for the most stable conformations of radical structures, a previously unknown effect of stabilization of the radical center in the skewed *gauche* conformation of the hydrocarbon chain was revealed. It is shown that the constructed HDRs are practically “ideal”, the calculated values of $\Delta_r H°$ do not exceed 1.7 kJ/mol. Using $\Delta_f H°$ of reference structures, $\Delta_f H°$ of the studied compounds were calculated, on the basis of which the bond dissociation energies (*BDE*) C-$CH_3$ and C-H in the corresponding alkanes radicals were calculated. The data obtained made it possible to analyze the change in bond strengths in alkanes depending on their structure. The largest range of the bond dissociation energies is found for tertiary alkyl radicals (371–400 kJ/mol), which is associated with greater possibilities for stabilizing the radical center. The presentation will discuss the subtle effects of radical structure on *BDE*.

Thus, the protocol for the determination of $\Delta_f H°$ of free alkyl radicals is developed. The use of the concept of complete set of HDRs makes it possible to determine $\Delta_f H°$ of *pri*-, *sec*-, and *tert*-alkyl radicals with a high degree of accuracy, the array of $\Delta_f H°$ for alkyl radicals is increased by more than six times.. The calculated results show good agreement with known experimental data.

**Acknowledgements** The reported study was funded by RFBR according to the research project № 20-33-90194.

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# SELECTIVITY OF GAS SEPARATION MEMBRANES: AN APPROXIMATE PREDICTIVE MODEL

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Polymeric membranes are used to separate nitrogen from air, carbon dioxide from natural gas, $C_{2+}$ hydrocarbons from natural gas, for separation of olefins and paraffins. For most of the polymers studied, permeability measurements were performed in single gas conditions. However, experimental data accumulated over the years show that measurements of permeabilities of pure gases cannot serve as a reliable basis for characterizing membranes in mixed-gas conditions. The so-called ideal selectivity $\alpha_{12}$, calculated by the ratio of the permeabilities for pure gases 1 and 2 can differ rather significantly from the actual, mixed-gas selectivity $\alpha_{12}^{mix}$ [1-3].

An approximate model based on linear irreversible thermodynamics to predict the mixed-gas selectivity of non-porous and microporous polymeric membranes was developed [4]. Under certain simplifying assumptions, analytical expressions for permeability and selectivity of polymeric membranes in mixed-gas conditions were derived. Input parameters for the model are pure-gas selectivity and the solubility coefficients.

For the actual selectivity of a binary gas mixture separation we obtained following expression

$$\alpha_{12}^{mix} = \frac{1}{2x_1}\left(g + \sqrt{g^2 + 4x_1x_2\alpha_{12}}\right)$$

$$g \equiv \frac{1-e^{-B}}{B}\left(\alpha_D - 1\right)\left(x_1\alpha_S + x_2\right) + x_1\alpha_S - x_2\alpha_D\,,$$

where $\alpha_{12}$ is the ideal selectivity, $\alpha_S$ is the ideal solubility selectivity, $\alpha_D = \alpha_{12}/\alpha_S$ is the ideal diffusivity selectivity, $x_i$ is the molar fraction of component *i* in feed gas mixture, *B* is the membrane Peclét number. It was found that the coupling between penetrant fluxes causes the membrane selectivity to deviate from pure gas selectivity. For diffusion-selective membranes, there is a reduction in selectivity, while for sorption-selective membranes there is an enhancement in selectivity with respect to pure gas selectivity. In the absence of flux coupling ( $B = 0$ ) the $\alpha_{12}^{mix}$ is equal to the ideal selectivity. In the limit of large Peclét numbers, the mixed-gas selectivity $\alpha_{12}^{mix}$ tends to the value of the ideal solubility selectivity. As estimates have shown, the Peclét number is less or of the order of unity in hydrocarbon separation by glassy polymers. A rough quantitative agreement of the model predictions with the experimental data was obtained.

The presentation also discusses the effect of temperature on the selectivity of polymeric membranes and a generalization of the developed thermodynamic model for the multicomponent gas separation.

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# STUDY OF THE BITUMEN PHASE COMPOSITION BY CALORIMETRIC METHOD

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The method of calorimetry is widely used for the analysis of bitumen. Bitumen DSC curves show the effects of devitrification, cold crystallization and a wide endothermic melting effect in the temperature range from -30 to 70 $^{o}$C.

The use of the temperature modulation DSC (MDSC) gives additional possibilities for studying the processes of formation of the bitumen phase composition. MDSC provides greater sensitivity than conventional DSC. The technique makes it possible to separate the relaxation thermokinetic glass transition processes from the thermodynamic phase processes of melting and crystallization [1]. At studying of bitumen and their fractions by the MDSC method it was shown that the bitumen phase structure strongly depends on temperature and time conditions. In the heating cycle on the non-reversing heat flow curves of bitumen there are exothermal effect (− 42 to − 14 °C) from cold crystallization of low molecular weight saturated hydrocarbons, endothermal effect (− 10 to 70 °C) of melting a ordered phase of high molecular weight saturated hydrocarbons. On the reversing heat flow curves there are low temperature (>-16 $^{o}$C) devitrification of low molecular weight saturated and aromatic hydrocarbons and high temperature 70 to 90 °C) devitrification of asphaltenes (fig. 1a).

There is a strong correlation ($R^2$=0.98) between the enthalpy of endothermal effect from − 10 to 70 °C formed by high molecular weight saturated hydrocarbons and the degree of penetration. Also it was shown that the high value of enthalpy of endothermal effect from − 10 to 70 °C indicates the formation of a gel structure in bitumen. These facts allow us to conclude that the steric hardening of bitumen is associated with the formation of ordered structures by high molecular weight saturated hydrocarbons.

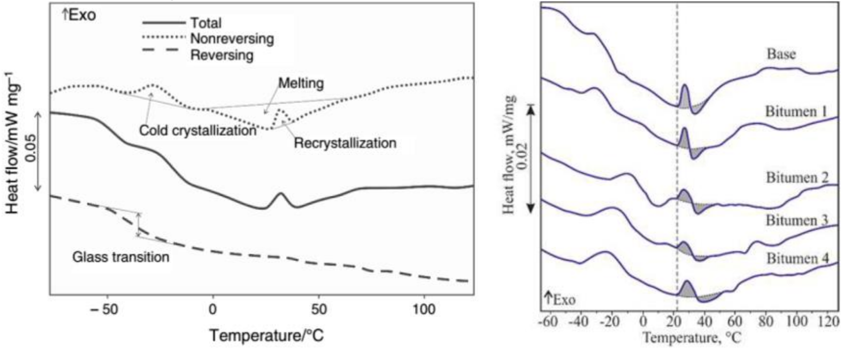

**Figure 1.** The bitumen’s heat flow curves

The next stage of the study was a detailed examination of endothermal and cold crystallization effects. It was proposed that the broad endothermic effect was the three overlapping thermal events: a broad endothermic background and a double pair of "recrystallization exotherm-dissolution endotherm" (fig. 1b). The onset of the recrystallization exotherm and the intensity of both phenomena depend on the annealing temperature and time. It was shown that the annealing time and temperature, and the cooling rate affect the value of the cold crystallization exotherm enthalpy through a change in the amount of the substance involved in the process. Correct interpretation of thermal effects can provide a more accurate determination of bitumen’s phase composition.

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# PARTICULARITIES OF STRUCTURE AND THERMODYNAMIC PROPERTIES OF LAYERED PEROVSKITE PHOTOCATALYSTS

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Layered oxide materials are intensively investigated due to wide range of physical and chemical properties (conductivity, magnetism, catalytic and photocatalytic activity). Last years layered oxides attract attention as high efficient photocatalysts in reactions of hydrogen production and using as precursors for the preparations of nanosheets and nanocomposites. These two important areas of layered oxides application are fully results from particularity of their structure [1,2].

Thermodynamic properties of these materials continue to be rather scarce even such kind of information is an essential for the understanding of many phenomena and for the practical using.

Herein it will be considered the influence of peculiarities of layered type of structure on heat capacity, thermodynamic properties, photocatalytic activity, stability and ability for the exfoliation to nanosheets for two classes of perovskite-like layered oxides belonging to Ruddlesden-Popper and Dion-Jacobson phases with different thickness of perovskite layers and different cationic content in perovskite blocks and interlayered space.

The overview on low-temperature heat capacity and standard thermodynamic properties of cation-ordered layered perovskite-like titanates $NaLnTiO_4$ and $A_2Ln_2Ti_3O_{10}$ (A=H, Na, K; Ln=La, Nd, Gd) it will be present. The nature of alkali and rare-earth elements and type of structure will take into account to reveal the influence on the heat capacity of layered oxides [3-7].

It will be shown the opportunity to predict the thermodynamic properties by the application of the additivity principle of heat capacity for layered compounds built of fragments of various structural types.

It will be considered from thermodynamic point of view the high photocatalytic activity of layered oxides and their organic-inorganic derivatives in water and water-organic media.

The explication of the layered structure splitting for sheets of several nanometers thickness it will be done from data of thermodynamic properties.

Phase transitions and its influence on photocatalytic properties will be also in scope of presentation.

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# NANOTHERMODYNAMICS: DIFFICULTIES, ADVANCES AND PROSPECTS

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*Dedicated to the 90th anniversary of Prof. A.I. Rusanov*

To date, several approaches to nanothermodynamics can be distinguished, of which the following three seem to be the main ones: 1) experimental and theoretical study of the size dependences of the thermodynamic characteristics of nanoparticles, for example, the melting temperature and enthalpy without considering the size dependences of the surface characteristics; 2) extension of the Gibbs method of surface excesses to small objects; 3) Hill's method. The main difficulty in applying the subdivision potential introduced by T. Hill is connected, in our opinion, with the fact that this quantity does not behave as intensive even from a formal point of view. However, Hill's idea that characteristics of small objects should be rather referred not to a single small object, but to an ensemble of nanoparticles, is quite reasonable in relation to any approach to nanothermodynamics. The main difficulty associated with applying the Gibbs method to nanoparticles is due to the impossibility (in the general case) of a clear separation of the bulk phase and surface layer in a real small object, and, consequently, the impossibility of implementing the usual approach to introducing a geometric separating surface. However, A.I. Rusanov back in the 6 proposed to attribute the Gibbs excesses not to the bulk phase of the nanoparticle itself, but to the mother phase, i.e. the phase from which a small object is obtained by dispersion. In [1], one of the authors introduced a more general concept of the comparison phase, which will be more adequate if a relevant mother phase does not exist. Along with the development of nanothermodynamics, there has been a tendency to deny the applicability of thermodynamics to nanosystems. In particular, some authors believe that nanoparticles should be characterized by huge fluctuations in properties. In [2], we showed that for metal nanoparticles, fluctuations are noticeable, but not very large.

To demonstrate the applicability of the Gibbs method even to small metal nanoclusters with a size of about 1 nm, we estimated the surface energy of icosahedral metal nanoparticles of various sizes as well as the edge and vertex energies. The results of the estimates are compared with the results for other linear and point interfaces, including the estimates by A.I. Rusanov. The estimates were carried out within the framework of the local coordination approximation proposed earlier [3].

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# PHOTOCATALYTIC ACTIVITY OF LAYERED PEROVSKITE-LIKE OXIDE $H_2La_2Ti_3O_{10}$ INTERCALATED WITH *n*-OCTYLAMINE

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Perovskite-like layered oxides are compounds with a specific structure composed of alternating blocks with perovskite structure (layers) and blocks with a different structure (interlayer). In such structures the interlayer cations typically can be replaced by other cations (ion-exchange reactions) and also introduction of guest molecules into the interlayer space (intercalation) is possible. Perovskite-like layered oxides are known as efficient and promising photocatalysts for hydrogen production from water or organic compounds. Our recent studies showed, that the intercalation of organic amines into the interlayer space of some layered oxides leads to a dramatic increase in photocatalytic activity [1,2]. In this work we use the platinized *n*-$OcNH_2$-intercalated layered titanate $H_2La_2Ti_3O_{10}$ as a photocatalyst and investigate the dependence of hydrogen production rate on the methanol content in the water-methanol mixture under UV-light.

Initially the titanate was obtained in its alkaline form $K_2La_2Ti_3O_{10}$ by conventional solid-state synthesis. The protonated form $H_2La_2Ti_3O_{10}$ was obtained from $K_2La_2Ti_3O_{10}$ by treatment with hydrochloric acid. Then the two-step intercalation was accomplished: at the first step methylamine was introduced into the interlayered space and then it was substituted by *n*-octylamine. Platinum nanoparticles were loaded on the obtained sample by irradiating its suspension in 1% methanol aqueous solution containing $H_2PtCl_6$ with UV-light.

Photocatalytic activity was measured by irradiating the suspensions of obtained sample in water-methanol mixture with alcohol content varying from 0 to 90 mol.% with UV-light in a special designed reaction cell attached to a gas circulation system. The amount of evolved hydrogen was determined every 5 min by gas chromatography. The final dependence of the reaction rate on the alcohol content is shown on Fig. 1. It can be satisfactorily approximated by a Langmuir – Hinshelwood type equation and reaches saturation at ca. 10 mol.%.

Additionally, we discussed the meaning and applicability of the term «reaction order» concerning our system. A theoretical study was carried out to link the reaction order with the partial molar reaction rates in a concentrated solution. Finally, we applied the derived equations to our experimental data and calculated a 3D-surface that displays the dependence between reaction orders with respect to water and methanol and the composition of the solution.

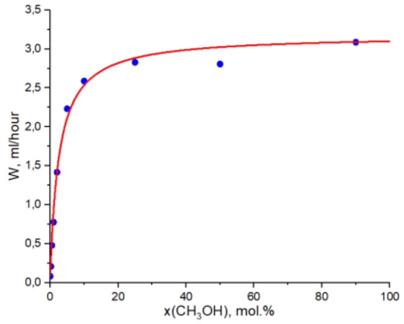

**Figure 1.** Dependence between hydrogen evolution rate and methanol content.

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This work was supported by the Russian Science Foundation (project №19-13-00184). Authors are grateful to Saint Petersburg State University Research Park: Center for X-ray Diffraction Studies, Center for Thermal Analysis and Calorimetry, Center for Chemical Analysis and Materials Research.

# SELF-ASSEMBLY, SORPTION AND THERMAL PROPERTIES OF SHORT-CHAIN OLIGOPEPTIDES

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Short-chain oligopeptides which are capable to self-assembly in solutions and in solid phase are attractive building blocks for the design of new nanostructured materials with complex, hierarchical architectures. Such materials can have specific properties, such as piezoelectric activity, specific electrochemical behavior, high optical nonlinearity and nanoscale wettability, as well as magnetic susceptibility and luminescence. Some short-chain oligopeptides can form porous crystals with hydrophobic or hydrophilic layers or channels. As a result, such crystals exhibit zeolite-like properties, and can selectively bind some gases or separate mixtures of gases. At the same time, it should be noted that the properties of oligopeptides have not been sufficiently studied to date.

The present work is the first reported comprehensive study of sorption properties, self-assembly in solid state and thermal behavior of some short-chain oligopeptides.

The unusual sorption properties of $_L$-leucyl-$_L$-leucine toward organic vapors was observed, which exhibited an increase in the sorption volume of the dipeptide phase with increasing sorbate molecular size. The way for control of the self-assembly of $_L$-leucyl-$_L$-leucine with formation of different micro- and nanostructures using solvents or vapors with different physicochemical properties was proposed.

The ability of $_L$-leucyl-$_L$-leucyl-$_L$-leucine crystals to remember the included benzene was demonstrated. The memory effect appears as a sequential endo- and exothermic effects on the DSC curve after benzene leaves the clathrates. The heat effects of these processes depend on the benzene content in the mixture used to saturate the tripeptide. Therefore, the values of transitions enthalpy can be used for a quantitative determination of benzene in the analyzed sample.

A new insight into the role of water in the formation of organogels with dipeptide *cyclo*(leucyl-leucyl) and crystals of glycyl-glycine has been demonstrated. In the presence of excess water, *cyclo*(leucyl-leucyl) is capable of forming organogels with linear and cyclic alkanes. In case of amorphous film of glycyl-glycine water molecules initiate the transition of dipeptide molecules to the zwitterionic form and stabilize it without formation of clathrates.

The thermal properties of few dipeptides were studied. The critical temperatures of their cyclization in the solid state and kinetic parameters of these reactions were determined. A correlation between the structure of the oligopeptide and the temperature of the solid-state reaction was found. The effect of temperature on the morphology of dipeptide film and result of chemical reaction was visualized using atomic-force microscopy.

The results obtained are essential for improving the technologies for producing organic nanostructures based on oligopeptides on solving problems of biomedicine, ecology, energy, etc.

**Acknowledgements** The financial support of subsidy allocated to Kazan Federal University for the state assignment in the sphere of scientific activities from the Ministry of Science and Higher Education of the Russian Federation No. 0671-2020-0061.

# ROLE OF AN INTRAMOLECULAR HYDROGEN BOND IN LIDOCAINE CONFORMER DISTRIBUTION AND POLYMORPH STABILITY

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In this work, we investigated the conformational equilibria of molecules in a saturated lidocaine (LDCN) solution in $scCO_2$ under heating conditions in the temperature range of 35–80ºC along three isochores corresponding to the $scCO_2$ density of 1.1, 1.3 and 1.5 of its critical value. The quantum-chemical calculation results showed that out of 68 LDCN molecule conformers, only conformers with an intramolecular hydrogen bond are realized within the studied range of parameters of state. This bond forms between the amide group proton and the diethyl-substituted amino group nitrogen.

Based on the IR spectroscopy data, we showed that with an increase in the fluid phase temperature and density, the LDCN solubility in $scCO_2$ increases significantly, reaching the concentration about $10^{-1}$ mol·L$^{-1}$. However, despite a significant increase in the equilibrium concentration of LDCN in $scCO_2$, no intermolecular hydrogen bonds are formed between its molecules. As a consequence, in the phase diagram region studied, its molecules exist the monomeric form in the solution. Moreover, regardless of the $scCO_2$ phase density, the heating does not destroy the intramolecular hydrogen bond in the LDCN molecule. Nevertheless, it changes the conformational equilibrium of the LDCN molecules in the $scCO_2$ phase. Such changes are related to the variation in the internal LDCN molecule geometry, in which, according to the quantum chemical calculations, conformers can differ in the mutual orientation of the two ethyl groups in the structure of the $CH_2{-}N{<}(C_2H_5)_2$ flexible fragment. These conformers can be divided into two groups according to their energy and vibrational parameters of the amide group C=O fragment.

Based on the analysis of the data obtained in the IR spectroscopy study, it was found that with an increase in the $scCO_2$ phase density, the temperature effect on the conformational equilibrium decreases. Thus, at the highest density of the fluid phase studied, the ratio of conformations remains constant in the considered temperature range. Finally, we showed that the conformational changes in LDCN molecules in the $scCO_2$ phase that occur with a temperature increase are completely reversible, i.e. the LDCN molecules return to their original conformational state when the system is cooled to the initial temperature. Such behavior is directly related to the presence of an intramolecular hydrogen bond in the lidocaine molecule structure, which remains stable in the phase diagram region studied and, consequently, prevents the conformational transition of the LDCN molecule. This fact allowed us to assume that, regardless of the SCF solution parameters of state in the considered phase diagram region, LDCN crystallization from this solution will lead to the formation of the same stable polymorph. This assumption was confirmed based on the XRPD analysis of micronized forms of LDCN obtained from its solution in $scCO_2$ by various methods: via crystallization from the SCF solution by slow cooling and subsequent depressurization. We also found that the degree of crystallinity of the micronized form of LDCN obtained from its solution in $scCO_2$ decreases compared to the initial LDCN form.

The IR spectroscopy experiment was performed using the molecular fluid spectroscopy facility (http://www.ckp-rf.ru/usu/503933/) of G.A. Krestov Institute of Solution Chemistry of the Russian Academy of Sciences.

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# THE ROLE OF WATER IN GUEST INCLUSION BY NATIVE CYCLODEXTRINS

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The selection of appropriate cyclodextrin (CD) is one of the main problems in their practical application. The problem with this choice is that the applied inclusion compounds (clathrates) are often prepared in a solid phase using solid CDs. This technique has its advantages: large yields, shorter process time, less water or other competing solvent, lower costs for solvent removal. In addition, CD based are used in a solid form for many applications. But systematic comparison of the receptor properties of different cyclodextrins with the same set of guests has been carried out only using data on complex formation in aqueous solutions, what is insufficient for characterizing formation of CD solid clathrates. For this characterization, thermodynamic parameters for the inclusion of various guests by solid cyclodextrins are required to be obtained. Also, in most industrial cases CD clathrates are prepared from solid hydrated CDs, with additional water to make technological pastes and slurries. In this case, water acts both as activating agent for guest inclusion and competing guest. For various CDs, the ratio of these roles has significant differences as show our studies of hydration Gibbs energies. The highest affinity of αCD to water can be the main reason why it is not used so often as of βCD.[1] This problem can be solved using hydration level/history control.[2] Also, for all native CDs, water-like organic guests can show better results being applied instead of water.[3] Analysis of the role of water and inclusion thermodynamics allowed to find the recommendation for better preparation method for each native CD.

**Acknowledgements** The work was supported by Russian Science Foundation grant №22-23-00367, https://rscf.ru/project/22-23-00367.

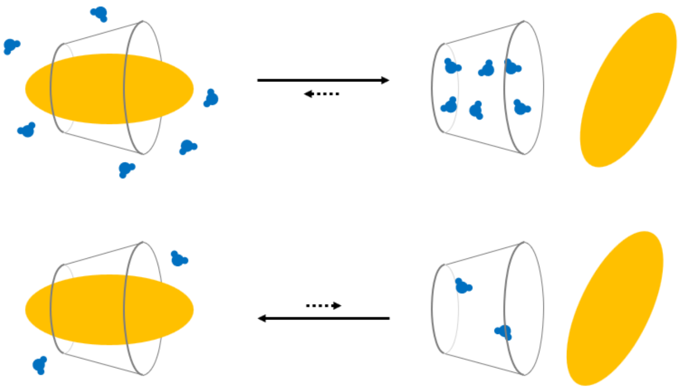

**Figure 1.** Competing and activating roles of water for guest inclusion by cyclodextrin.

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# THERMODYNAMIC PROPERTIES OF AN ORGANIC SINGLE CRYSTAL SCINTILLATOR: 9-PHENYLCARBAZOLE

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The thermochemical study of relevant heteropolycylic compounds, presenting oxygen, nitrogen and sulphur as heteroatoms, has been developed in our Research Group by the last years, with the main purpose of establish correlations between structurally related compounds, to understand the effect of the molecular structural characteristics on the energetic parameters of those compounds [1].

Carbazole derivatives is one of the classes of compounds within the scope of our research. These compounds have interesting optical and electronic properties such as photoconductivity and photorefractivity. In the field of electroluminescence, carbazole derivatives are often used as the materials for hole-transporting and light-emitting layers because of their high charge mobility and thermal stability and show blue electroluminescence due to the large bandgap of the improved planar biphenyl unit by the bridging nitrogen atom [2].

The carbazole derivative proposed in this communication, on which the thermodynamic studies have developed, is the 9-phenylcarbazole. This compound is considered is one of the brightest organic single crystal scintillators in existence and is a very promising organic neutron detector for a multitude of applications including homeland security, nuclear non-proliferation, nuclear physics, and non-destructive testing [3].

The enthalpy of formation in the crystalline phase of 9-phenylcarbazole, at $T$ = 298.15 K, was derived from bomb combustion calorimetry, and its enthalpies of sublimation and fusion were derived from the Knudsen effusion method and differential scanning calorimetry, respectively. The gas-phase enthalpy of formation, at $T$ = 298.15 K, of 9-phenylcarbazole was derived from the experimental studies developed. This parameter was also obtained through computational work performed using the composite G3MP2//B3LYP approach and a set of selected working reactions. The experimental and computational enthalpies of formation will be discussed and compared with related heteropolycyclic compounds.

**Acknowledgments:** This work was supported by the Fundacão para a Ciência e Tecnologia (FCT) to CIQUP, Faculty of Science, University of Porto (Project UIDB/00081/2020), IMS-Institute of Molecular Sciences (LA/P/0056/2020)). VLSF is financed by national funds through the FCT-I.P., in the framework of the execution of the program contract provided in paragraphs 4, 5 and 6 of art. 23 of Law no. 57/2016 of 29 August, as amended by Law no. 57/2017 of 19 July.

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# TEMPERATURE DEPENDENCE OF PHASE TRANSITION ENTHALPIES OF ORGANIC NON-ELECTROLYTES

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In spite of a long history of research, experimental investigations into the thermodynamics of phase transitions (vaporization, fusion, and sublimation) remain among the most difficult branches of Physical Chemistry. In this report the problems of classical experimental and empirical calculation methods for determining the enthalpies of phase transitions are briefly described. Attention was primarily paid to the fact that, depending on the object of choice and technique, the phase transition enthalpies are measured under completely different conditions, thus obstructing critical analysis and development of quantitative structure-property relationships [1].

A new way to study the phase transition enthalpies as functions of temperature was developed. This way is based upon solution calorimetry procedure and the revealed regularities in the solution and solvation enthalpies of organic non-electrolytes. First, the approaches for determining the enthalpies of vaporization, sublimation and melting at a standard temperature of 298.15 K are described [2-3]. Second, methods for adjusting the enthalpies of phase transitions from 298.15 K to an arbitrary temperature were developed [4-5].

The developed approaches compete with modern experimental techniques in terms of accuracy.

**Acknowledgements** The financial support of Russian Science Foundation (Grant No. 21-73-00006) is acknowledged.

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# SCANDIUM(III) β-DIKETONATES AS MOCVD PRECURSORS: THERMODYNAMIC AND “STRUCTURE-PROPERTY” RELATIONSHIPS

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Volatile metal compounds with organic ligands are widely used as precursors for producing a variety of functional films and coatings by the MOCVD method. The first stage of this process is the steam formation of the precursor(s), therefore it is necessary to have reliable knowledge on their vapor pressures as well as the thermodynamic characteristics of sublimation or vaporization (enthalpy and entropy) to select the precise deposition conditions. The volatilization conditions of such substances vary greatly in relation to the combination of the central atom and the ligand environment. Prediction of vapor pressures and thermodynamic characteristics of precursors would enable the selection of suitable substances beforehand and help to prevent unnecessary gas-phase deposition experiments. Furthermore, such a prediction thermodynamic model can also be used to monitor the quality of both as-received and already existing thermodynamic data.
At this stage of the work, there was developed a diagnostic model by means of the "structure-property" relationship. We focused our attention to the scandium(III) β-diketonate complexes. In a row of compounds, substituents in ligands were varied which allowed us to examine influence of such changes on the thermodynamic properties - the enthalpy of vaporization in our case. In order to compare the thermodynamic data among themselves and to further reveal the "structure-property" relationships it is essential to relate the values of these characteristics to a unified temperature, which was accomplished using methodology developed by us. With the help of the diagnostic model, we have obtained mutually consistent data on the enthalpies and entropies of vaporization, sublimation, and melting of scandium(III) β-diketonates at 298.15 K. From these values, equations for the temperature dependence of the saturated vapor pressure over the solid and liquid complexes were obtained. With their help, it is possible to calculate vapor pressures over broad temperature ranges, which makes it possible to carry out deposition experiments under precise conditions.

**Acknowledgements** The financial support of the work was provided by the Russian Science Foundation and the Government of the Novosibirsk Region (project no. 22-23-20182).

# EXPERIMENTAL AND THEOERTICAL THERMODYNAMIC STUDY OF 1-BENZYL-4-PHENYL-1*H*-1,2,3-TRIAZOLE AND 1,3-BIS(1-METHYL-1*H*-TETRAZOL-5-YL)PROPANE IN GASEOUS AND CONDENSED AGGREGATE STATES

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The results of experimental and theoretical thermodynamic study of 1-benzyl-4-phenyl-1*H*-1,2,3-triazole (BnPhT) and 1,3-bis(1-methyl-1*H*-tetrazol-5-yl)propane (BMTP) in condensed and gaseous aggregate states are represented. Samples of BnPhT and BMTP were synthesized and prepared for calorimetric studies according to the methods described in [1] and [2] respectively. The chromatographic purity of the substances was >99.99 and 99.93 wt. % respectively.

The heat capacities of the substances in condensed state at saturation pressure in the range of (80 to 370) K (Figure 1, 2) were determined in TAU-10 vacuum adiabatic calorimeter [3]. It has been established that BMTP has a complex thermal behavior sue to the presence of a solid-phase transition crII–crI. Based on the smoothed heat capacity values, the standard thermodynamic functions of BnPhT and BMTP in the condensed state were calculated in the range of (80 to $T_{\text{fus}}$) K. The thermodynamic fusion parameters of the substances under study were determined using the DSC in the temperature range of (300 to 420) K.

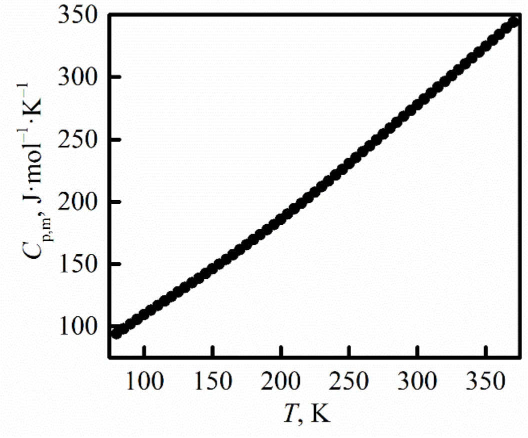

Figure 1. Heat capacity temperature dependence of the BnPhT in the condensed state in the range of (80 to 370) K

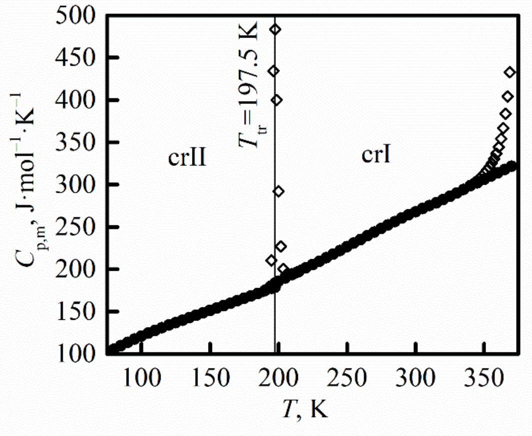

Figure 2. Heat capacity temperature dependence of the BMTP in the condensed state in the range of (80 to 370) K

The standard enthalpies of combustion of crystalline BnPhT and BMTP were determined in a combustion calorimeter B-08-MA [4] and were equal to be –(8080.0 ± 2.9) and –(4884.3 ± 2.5) kJ·mol$^{-1}$ respectively. To calculate standard thermodynamic functions of the studied substances in the ideal gas statistical thermodynamics and quantum chemical approaches were used. To calculate the sublimation enthalpies of the compounds, a model based on molecular descriptors and fingerprints was proposed.

**Acknowledgements** This work was supported by State Program of Scientific Investigations «Chemical processes, reagents and technologies, bioregulators and bioorganic chemistry» (project No 2.1.1)

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# RELATIONS BETWEEN STRUCTURE AND THERMAL BEHAVIOR OF MOCVD PRECURSORS: IRIDIUM (I) COMPLEXES WITH CYCLOOCTADIENE-1,5 AND BETA-DIKETONATE DERIVATIVES

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Nowadays the production of Ir-based coatings by Metal-Organic Chemical Vapor Deposition (MOCVD) gains interest for catalytic, microelectonic and medical application. However, the limit is the paucity of the volatile iridium compounds (precursors) that can be used in MOCVD. To design the effective precursors for this purpose, it is necessary to establish the "structure-thermal property" relations. The complexes of Ir(I) with cyclooctadiene-1,5 (cod) and β-diketonate derivatives $R_1C(X_1)CHC(X_2)R_2$ consist the promising and available class of MOCVD precursors.

Therefore, the aim of this work was to reveal the effect of the ligand modification on the volatility and stability of the complexes formed. The β-diketonates ($X_1 = X_2 = O$) were varied to explore the influence of terminal substituent such as $R_1 = R_2 =$ Me (*acac*), $^t$Bu (*thd*), $CF_3$ (*hfac*); $R_1 = CF_3$, $R_2 =$ Me (*tfac*); $^t$Bu (*ptac*), Ph (*btfac*). β-Iminoketonate ligands L ($X_1 = NR_3$, $X_2 = O$) were involved to evaluate the donor group influence: $R_3 =$ H, $R_1 = R_2 =$ Me (*i-acac*); $R_3 =$ Me, $R_1$ = Me, $R_2$ = Me (*Mei-acac*), $R_2 = CF_3$ (*Mei-tfac*), $R_3 = NMe_2$, $R_1$ = Me, $R_2$ = Me (*dmha*), $R_2 = CF_3$ (*dhmt*).

The synthesized complexes were characterized carefully. The structures were determined by single crystal X-ray diffraction. The first "screening" of thermal properties was carried out by TG-DTA. The key result was the increase of $R_3$ substituent leads to the decrease in thermal stability in condensed phase. Then, the DSC was applied to determine the temperature and thermodynamic parameters of melting. Here, the complex with L = *acac* is more fusible than L = *i-acac* due to N-H…O bonds in the latter structure, while an increase of $R_3$ leads to a decrease in the melting point.

The temperature dependencies of the saturated vapor pressure over the solid complexes were measured by flow (transition) method. According to obtained data, thermodynamic parameters of sublimation were calculated and quantitative volatility row was established: L = *hfac* > *tfac* > *ptac* > *acac*> *thd* > *i-acac* > *Mei-acac*> *btfac*.

To shed light on "structure-thermal property" relations, the crystallographic analysis of intermolecular interactions as well as the calculation of the crystal lattice energy via DFT-GGA approximations (PBE functional) was carried out. Thus, the highest volatility of [Ir(cod)(hfac)] was associated with shortened "antibonding" (F…F) contacts. The lowest volatility of [Ir(cod)(btfac)] related with the high number of "bonding" interactions per molecules that clearly formed the dimeric species the crystals. In general, the calculated crystal lattice energies are correlates well with the sublimation enthalpies taking into account the temperature differences.

**Acknowledgements** The financial support in the synthesis and investigation of complexes with β-diketonate ligands was funded by the RSF (research project No. 20-15-00222).

# THERMAL PERTURBATIONS AT CRYSTAL NUCLEATION IN GLASSES AND POLYMERS

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Glass forming materials and polymers play an important role in the development of new advanced materials. Controlled crystallization used to create artificial microstructures has many applications. In this communication, we consider local thermal perturbations in supercooled glass-forming liquids during the nucleation and decay of nuclei of a crystalline phase. An important property of glass-forming liquids is the relaxation of the heat capacity of such liquids with a change in their temperature. The effect of dynamic heat capacity is significant for fast local thermal perturbations. The nonequilibrium thermal response of glass-forming materials to fast local thermal perturbations is described using an integral equation with dynamic heat capacity. It is shown that local thermal perturbations associated with the formation of nuclei of the crystalline phase significantly affect the rate of nucleation in supercooled glass-forming liquids. The obtained knowledge can be useful for the technology of nanostructured materials.

# CRYSTALLIZATION KINETICS AND GLASS-FORMING ABILITY OF DRUGS FROM FAST SCANNING CALORIMETRY DATA

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The use of the amorphous drugs is a modern approach for the enhancement of bioavailability. The high cooling rate needed to obtain the metastable amorphous state often makes impossible its investigation using conventional laboratory methods such as DSC, X-ray powder diffractometry. One of the ways to overcome this problem may be the application of Fast Scanning Calorimetry. This method allows direct determination of the critical cooling rate of the melt and kinetic parameters of the crystallization. In the present work, the amorphous states of various drugs were create using Fast Scanning Calorimetry. Critical cooling rates and glass transition temperatures were determined. The kinetic parameters of cold crystallization were determined using both model-based and model-free approaches. The results were compared with the data from isothermal crystallization experiments. It is shown that the Nakamura crystallization model can be used to describe the crystallization process and to predict the long-time stability of the amorphous forms of the drugs. The approaches presented may find applications in predicting the storage time and choosing the optimal storage conditions of the amorphous drugs prone to crystallization.

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# THE STABILITY OF POLY-L-LACTIDE NUCLEI ACCORDING TO THE CLASSICAL NUCLEATION THEORY AND FAST SCANNING CALORIMETRY

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Poly-L-lactide (PLLA) is an important biodegradable and biocompatible thermoplastic material which is used in various industries. PLLA is a relatively slow crystallizing polymer unlike other thermoplastics (e.g., polyamide-6,6). This present problems for the practical applications but permits detailed investigation of its nucleation behavior.

The study of the kinetic characteristics of the PLLA nucleation process at temperatures close to the glass transition temperature can be performed using the fast scanning calorimetry (FSC) method. Due to the low addenda heat capacity and the small size of the calorimetric sensor chip, heating and cooling rates up to $10^6$ K/s can be achieved by FSC.

The temperature program for studying of nuclei stability was based on the Tammann's nuclei development method, in which transition rate from the nucleation stage to the growth stage was varied. Using the described temperature program, the dependences of the melting enthalpy of the crystalline phase on the duration of the nucleation stage and the transition rate from the nucleation stage to the growth stage were obtained.

From the obtained dependences the critical heating rate was determined. Above the critical rate, the nuclei formed at the nucleation stage can no longer be stabilized during the transition from the nucleation stage to the growth stage. For PLLA, this critical speed is 1000 K/s.

After that, an attempt to estimate the size distribution of nuclei formed at the nucleation stage and to compare the obtained data with the theoretical predictions of CNT was made. To perform this, between the nucleation and cooling stages the sample was rapidly heated to temperatures from 130 °C to 180 °C and immediately cooled. These experiments were performed with varying conditions of the nucleation stage. The obtained dependences of the melting enthalpy of the crystalline phase on the intermediate heating temperature are in qualitative agreement with the predictions of CNT [1].

The obtained dependences also allow to calculate the linear growth rate of nuclei, which is about $10^{-4}$ nm/s for temperatures close to the glass transition temperature. The estimated nuclei growth rate is about five orders of magnitude lower than the linear crystal growth rate.

Summarizing, Tammann's method provides the possibility not only to study nucleation kinetics but also to gain information about the development of the cluster-size distribution and nuclei stability.

**Acknowledgements** The financial support from the Ministry of Education and Science of the Russian Federation, grant 14. Y26.31.0019.

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# FSC STUDY OF CRYSTALLIZATION KINETICS OF CROSS-LINKED POLY(BUTYLENE TEREPHTHALATE)

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The emergence of new applications of cross-linked polymers causes a growing interest in their study. Changes in the structure of polymers due to cross-linking should affect the packing of macromolecules and the rate of crystallization, but there is still almost no experimental data on the influence of the cross-linking density on the kinetics of crystallization.

The development of fast scanning calorimetry (FSC) method has made it possible to suppress not only the process of crystal growth, but also nucleation of polymers, and to study these processes using isothermal or non-isothermal temperature regime. Previously, we used the FSC method to study the influence of the cross-linking density on the rate of crystallization and nucleation of cross-linked polycaprolactone (PCL) [1–2]. We have reported that an increase in the number of cross-links leads to a monotonic decrease in the critical crystallization cooling rate and an increase in the crystallization and nucleation half-times.

In the present work, we synthesized copolymers of terephthalic acid and 1,4-butanediol cross-linked with glycerol. The molar ratio of 1,4-butanediol and glycerol in the initial reaction mixture varied from 19:1 to 4:1, the polyester without glycerol was also prepared as a control sample. The 1H NMR method was used to determine the content of the glycerol cross-links in the obtained samples. The molar fraction of glycerol in the samples ranged from 2 to 7%.

From the FSC analysis of the crystallization kinetics, we found that crystallization slows down with an increase in the spatial cross-link density. Samples with more than 5 molar % of glycerol do not show a melting peak during heating. The results suggest that a slowdown of crystallization with increasing crosslink density is a general trend for different polymers.

**Acknowledgements** This work was supported by the Russian Federation President Grant MD-1444.2021.1.3.

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# QSPR MODELS FOR PHASE TRANSITION AND DECOMPOSITION TEMPERATURE OF IONIC LIQUIDS

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The working temperature range of Ionic Liquids (IL) is determined by their liquid state range, where the IL's melting point/glass transition and decomposition temperatures define the lower and upper limits of the range, respectively. Computational prediction of the structure of new ILs with required properties, e.g. which can exist in a liquid state at room temperature and are stable up to high temperatures, is a much less time-consuming and less expensive approach than stepwise synthesis and experimental examination of all presupposed ILs. Therefore, in the present work the quantitative structure–property relationship (QSPR) models were developed to predict the glass transition temperature ($T_g$), melting point ($T_m$), and decomposition temperatures ($T_d$) of ILs. We showed that a use of component validation protocol provided a better agreement of statistical parameters for the training and test sets. The performance of various modeling algorithms and descriptor sets was discussed and compared and advantages of descriptor-less as well as multi-task modeling were shown. An explanation of the models using statistical analysis of functional groups and Molecular Matched Pairs were provided for the mixtures for the first time. The experimental data and models, which are the first publicly available models for prediction of transition and decomposition temperatures of ILs, are publicly available online at http://ochem.eu/article/140250.

**Acknowledgements** The financial support of the Ministry of Science and Higher Education of the Russian Federation (No. 075-15-2021-579)

# PREDICTING THERMODYNAMIC PROPERTIES OF IONIC LIQUIDS AT HIGH PRESSURES BASED ON THE REFERENCE DATA AT AMBIENT PRESSURE

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Herewith we report a self-consistent group of methods for predicting thermodynamic properties of ionic liquids at elevated pressure as isothermal equations of state with initial conditions determined by the respective properties found experimentally only at ambient pressure. The key idea is in the consideration of reduced thermodynamic fluctuations (i.e. ratios of the thermodynamic fluctuation of an actual ionic liquids to the same quantity for a hypothetic medium under the same volume-pressure-temperature conditions), which are shown as functions of the density only irrespectively to the thermodynamic path. In particular, the scaling $(M/RT)(\rho\kappa_T)^{-1}{\sim}\exp(k_\rho\rho)$ and $(M/RT)u^2{\sim}\rho^{k_u}$ fulfils for the inverse reduced density fluctuations and pressure fluctuations respectively (here $\rho$, $\kappa_T$, $u$, $M$, $R$ are the density, the isothermal compressibility (can be expressed at ambient pressure via the density, the speed of sound, and the isobaric heat capacity), the speed of sound, the molar mass, and the gas constant, respectively).

The approach based on the density fluctuations leads to so-called Fluctuation Theory-based Equation of State (FT-EoS), which already demonstrated its predictive capacity for the dataset of 80 different ionic liquids with an overall relative absolute average deviation close to 0.14% [1] and obtained a strict mathematical support from the theory of thermodynamic linear analysis as well as the predictive approach to the speed of sound based on the pressure fluctuations [2]. Newly evaluated testing of the speed of sound's predictions based on the whole dataset given by the NIST's database ILThermo indicated the relative average absolute deviation is close to 0.85 %.

Finally, due to the interplay of the thermal conductivity with density and the speed of sound within the frame of the Bridgman-Osida-Horroks-McLaughlin theory, it is possible to use the developed approach for predicting also the pressure-dependent change of this transport property when the data at ambient pressures are available and reach accuracy comparable with the uncertainty of direct measurements, see a particular example in Fig. 1.

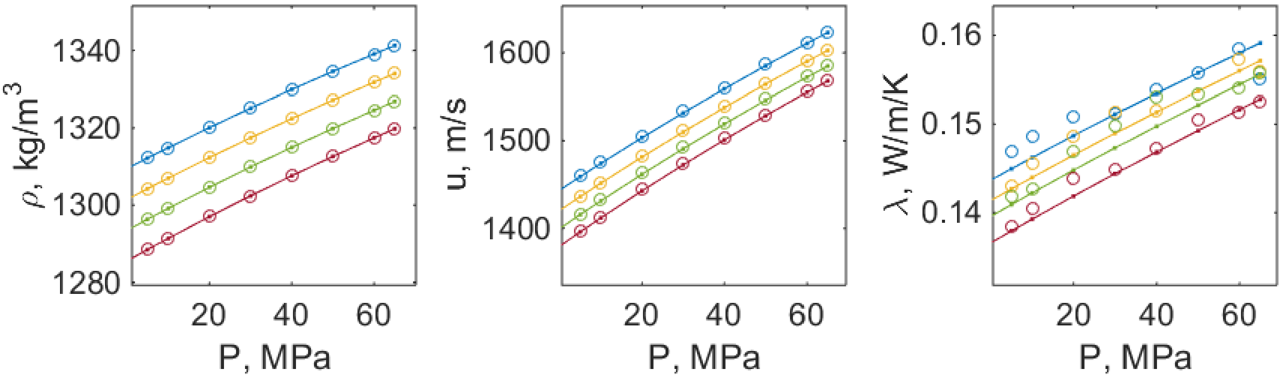

**Figure 1.** An example of the predicted (lines) and experimental (circles) densities, speeds of sound and thermal conductivities of [bmim][TfO] for the temperature interval (283.15 – 343.15) K.

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# POLYMERIZED IONIC LIQUIDS FOR THE ENHANCED BIOEXTRACTION

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Aqueous biphasic systems (ABSs) containing water-miscible ionic liquids (ILs) and kosmotropic inorganic salt are known as an effective media for liquid-liquid extraction of a wide range of biomaterials [1, 2]. The ABSs containing ILs of various structures have been extensively studied [1, 2]. Polymerized ILs (polyILs) are considered as new promising agents for the enhanced bioextraction [3, 4].

In this work, we discuss phase behavior and partitioning of L-tryptophan and vanillin (as model biocomponents) in ABSs based on polyILs that consist of poly(diallyldimethylammonium) or poly(1-butyl-3-vinylimidazolium) cations and halide or amino acid anions (glycinate, leucinate, lysinate) (Figure 1). These data are compared with the behavior of ABSs containing 1-alkyl-3-methylimidazolium ILs with the same counterions.

Aqueous and aqueous-salt solutions of polyILs have been studied experimentally (TGA/DSC, viscosity measurements, static and dynamic light scattering). By means of Molecular Dynamics simulation, we have obtained the data on conformation and local structure of polyIL chains, diffusion and binding of counterions. Both the experimental and MD results allow us to discuss the specificity of counterions (in particular, the effect of the anion concentration on the chain conformation).

Finally, we conclude by discussing the structural design of ILs for the enhanced phase splitting ability and for highly efficient liquid-liquid extraction performance.

**Acknowledgements** The financial support of RSF (project No. 20-13-00038). Scientific research was performed at the Research park of St. Petersburg State University (Center for Magnetic Resonance, Center for Chemical Analysis and Materials Research, Center for Thermogravimetric and Calorimetric Research, Computing Center).

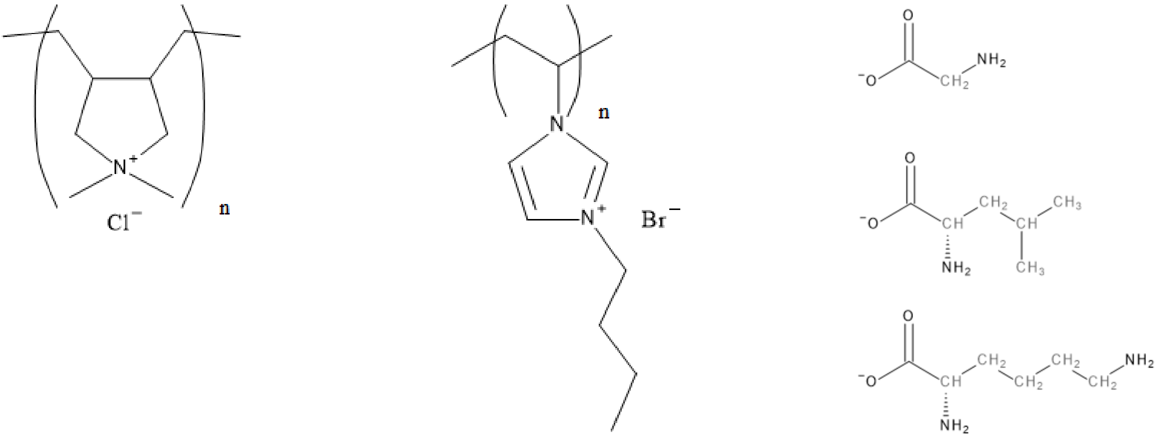

**Figure 1.** Chemical structures of polyILs and amino acid anions.

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# THERMODYNAMIC FUNCTIONS OF FORMATION OF 1-ETHYL- AND 1-BUTHYL-3-METHYLIMIDAZOLIUM CLORIDES

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Often, when developing new industrial technologies, evaluative, empirically selected conditions are used, without considering to the modern methods of chemical engineering. This approach incurs additional economically and environmentally baseless costs of resources and energy. Chemical thermodynamics methods make it possible to determine the optimal conditions of technological processes that allow achieving maximum yield of the product with the lowest energy and resource costs. Ionic liquids are a promising material for introduction into chemical industry. It is necessary to know the thermodynamic properties of ionic liquids to construct technological processes involving them. The objects of this work are two commercially demanded ionic liquids: 1-ethyl-3-methylimidazolium (EmimCl) and 1-butyl-3-methylimidazolium chlorides (BmimCl). The aim of the present work is the determination of the complete set of standard formation functions of EmimCl and BmimCl in the crystal, liquid, and gaseous state: $\Delta_f H^0_{298.15}$, $\Delta_f S^0_{298.15}$, $\Delta_f G^0_{298.15}$. For this purpose, a comprehensive thermodynamic study of two ionic liquids EmimCl and BmimCl were carried out by experimental and calculation methods. Isobaric heat capacity of crystal and liquid EmimCl was determined by low-temperature vacuum adiabatic calorimetry in the temperature range from 8 to 375 K. Experimental heat capacity curve of crystal EmimCl and literature data of BmimCl [1] were fitted by linear combination of Einstein's functions and were integrated; as a result, the following thermodynamic functions for EmimCl and BmimCl were calculated: standard entropy $S^0_m(T)$, heat content $H^0_m(T)– H^0_m(0)$ and Gibbs energy $G^0_m(T)– H^0_m(0)$ in the temperature range from 0 K to the melting point of the corresponding substance. Melting parameters of these substances were measured by DSC and adiabatic calorimetry. Standard enthalpies of dissolution of crystal EmimCl and BmimCl in water at 298.15 K were measured by isothermal solution calorimetry. Based on these data, standard enthalpies, entropies and Gibbs energies of formation were calculated for crystal and liquid phases of EmimCl and BmimCl at 298.15 K. Standard enthalpies of EmimCl and BmimCl formation in the gaseous state at 298.15 K were defined *via* quantum chemistry methods. Vapor pressure of EmimCl and BmimCl were obtained by the Knudsen Effusion Mass-Spectrometry method. With the help of these data standard entropies and Gibbs energies of EmimCl and BmimCl formation in the gaseous state at 298.15 K were received. The analysis and comparison of the obtained thermodynamic characteristics with the literature data was carried out [2].

**Acknowledgements** Investigation was performed in framework of Program "Chemical Thermodynamics"(AAAA-A16-116061750195-2) and by financial support of Russian Science Foundation (Grant no.20-73-00211).

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# LIQIUD-LIQUID EQULIBRIUM AND PARTITIONING OF BIOCOMPONENT IN AQUEOUS MIXTURES OF IONIC LIQUID OF DIFFERENT STRUCTURE AND KOSMOTROPIC SALT

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Aqueous biphasic systems (ABSs) based on ionic liquid (IL) and kosmotropic salt are considered as promising for the liquid-liquid extraction of biomolecules [1]. By chemical modification of ILs' ions it is possible to influence intermolecular interactions and, as a result, obtain ABSs with the required properties. Among the modified ILs amino acid ILs (AAILs) attract special attention because of their low toxicity [2] and likely biocompatibility. Another example of modified ILs is polymerized ILs (PILs), which have recently been considered as new promising candidates for the enhanced bioextraction [3].

The main aim of this work is to investigate the effect of chemical structure of ILs on liquid-liquid equilibrium (LLE) in ABSs and on the partitioning of model solute (L-tryptophan) between liquid phases. The range of objects under study includes: conventional halide ILs based on 1-alkyl-3-methylimidazolium cation; AAILs synthesized by exchanging halide anions for amino acid anions; PILs based on cations of poly-(diallyldimethylammonium) or poly-(1-butyl-3-vinylimidazolium) with halide or amino acid counterions.

As a result, new systematic data on the phase behavior and partition coefficients of L-tryptophan in ABSs with the studied ILs/AAILs/PILs were obtained [4,5]. The results were discussed in terms of hydrophobic interaction, chaotropic-kosmotropic interaction, salting-out and hydrogen-bonding.

The experimental work was supplemented by molecular thermodynamic modeling of LLE and partitioning behavior in some IL/AAIL-based ABSs with the aid of ePC-SAFT EOS. Two versions of the model (original [6] and advanced [7]) were applied and modeling results of both were compared with experimental data. Moreover, for the proper estimation of model parameters we complemented the existing experimental data on osmotic coefficients for a series of halide ILs solutions using the isopiestic method in the concentration range up to 10 mol/kg. The advanced version of ePC-SAFT gives satisfactory agreement with the experimental results. We show that ePC-SAFT is an efficient tool predicting phase behavior and partitioning of target solutes in IL-based ABSs. Taking into account the ever-increasing number of new modified ILs, prediction of such properties becomes very important.

We believe that the results of our work will help to find the ABS with the desired extraction properties and the data obtained will be useful for the development of alternative methods of extraction in the field of "green chemistry".

**Acknowledgements** We thank RSF (project No. 20-13-00038) for financial support. Scientific research was performed at the Research park of St. Petersburg State University (Center for Magnetic Resonance, Center for Chemical Analysis and Materials Research, Center for Thermogravimetric and Calorimetric Research).

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# EMPTY VOLUME IN IONIC LIQUIDS AND ITS CONNECTION WITH THE SOLUBILITY OF GASES

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The connection between the empty volume and the dissolution of gases in ionic liquids (ILs) is widely discussed in the literature. According to known theoretical concepts, the dissolution process can be divided into two hypothetical steps: the formation of a cavity for the solute molecule, and the placement of the solute in this cavity, determining the solute-solvent interactions. There are some works showing that the formation of a cavity makes a significant contribution to the solubility of gases in ILs and can even prevail over the energy of the interactions between dissolved molecules and ions of ILs. In this work, we study intermolecular voids for $CO_2$, $O_2$, $N_2$, and $CH_4$ mixtures in the $[C_nMIM][NTf_2]$ ILs using molecular dynamics simulation and quantitative analysis of voids by the Voronoi-Delaunay method. We have shown that the dissolved gas molecule locally loosens the IL, causing the formation of the additional voids larger than the average voids in the solution. At the same time, the $CO_2$ molecule forms a significantly smaller amount of the additional empty volume than $O_2$, $N_2$, and $CH_4$. This correlates with their solubility: $CO_2$ dissolves noticeably better than other gases. In addition, we studied the distributions of dissolved gas molecules near different components of ILs, i.e. the anions, the imidazole rings of the cations, and the alkyl substituents of the cations. It has been shown that $CO_2$ molecules are predominantly located near the anions, while all other studied gases are located near the alkyl substituents of the cations. It is discussed that $CO_2$ adds less empty volume to the IL, since it is located mainly in denser regions, while the other gases are located in looser regions near the alkyl substituents. The smaller additional empty volume in the $CO_2$ mixtures and its high solubility allow us to to suppose that the dissolution of $CO_2$ has lower energy of a cavity formation.

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# HEAT CAPACITY IN THE INTERVAL 80 – 370 K AND PARAMETERS OF PHASE TRANSITIONS OF BARIUM DOPPED STRONTIUM FERROMOLYBDATE

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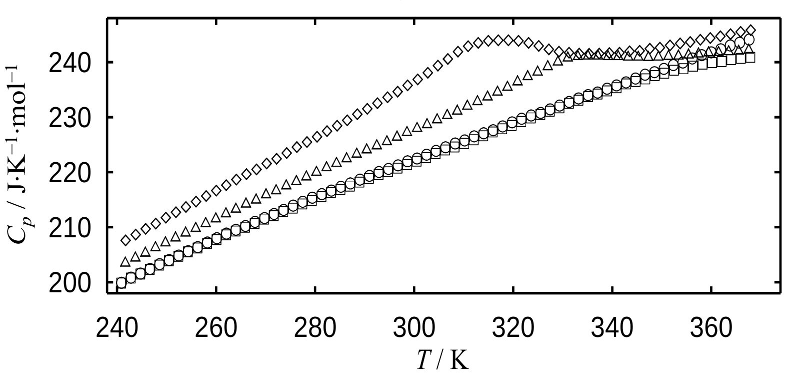
Polycrystalline samples of $Sr_{2-x}Ba_xFeMoO_{6-\delta}$ ($x = 0.8$ (I), $x = 1.0$ (II), $x = 1.4$ (III) and $x = 1.8$ (IV)) were obtained by solid-phase synthesis from initial «puriss. spec.» reagents $SrCO_3$, $BaCO_3$, $Fe_2O_3$, and $MoO_3$. Grinding and mixing of the stechiometric mixture of initial reagents were carried out in a vibrating mill in ethanol for 3 hours. The resulting mixtures were dried at a temperature of 350 K, pressed into pellets 10 mm in diameter and 4–5 mm thick, and annealed in a polythermal regime at temperatures (300–1470) K in an argon flow and a heating rate about 2 K $min^{-1}$, followed by quenching at room temperature. According to the data of X-ray phase analysis, it was established that the obtained samples had a single-phase composition.

The heat capacities of the $Sr_{2-x}Ba_xFeMoO_{6-\delta}$ samples were measured in an automatic vacuum adiabatic calorimeter TAU-10 (Termis, Moscow, Russia) between (80 and 370) K. The relative expanded uncertainty in the heat capacity measurements did not exceed ±0.4 %. The contribution of the heat capacity of the sample to the total heat capacity of the system was at least 25 %.

For II, III, and IV samples at $T > 240$ K, reproducible anomalies due to the transition of oxides from the ferromagnetic to the paramagnetic state (second-order phase transitions) were found. It was determined that with a decrease in the barium content in the sample, these anomalies become less pronounced, and the heat capacity curves in the transition region become flatter (Fig. 1). The heat capacity of the sample I was monotonic increase with increasing temperature. The thermodynamic parameters of phase transitions (Curie temperatures, excess enthalpies and entropies) were determined for II, III, and IV samples.The excess heat capacities in the transition region were found as differences between the experimental values of the heat capacity and the regular components of the heat capacity of the samples. It was found that the Curie temperatures for samples II, III, and IV, determined from the maximum excess heat capacity in the phase transition region and from the temperature dependences of the magnetization, agree within 2 K. The excess enthalpies and entropies of phase transitions were found by temperature integrating the excess heat capacity and the reduced excess heat capacity, respectively. It has been established that the Curie temperatures decrease, while the excess enthalpies and entropies of transitions increase with increasing barium content ($x$) in the samples.

**Acknowledgements** This work was supported by State Program of Scientific Investigations «Materials Science, New Materials and Technologies» (Project no. 1.1, 2021-2025)



○– I, □– II, Δ– III, ◊ – IV

**Figure 1.** The temperature dependences of the heat capacity of $Sr_{2-x}Ba_xFeMoO_{6-\delta}$

# CALCULATION OF TEMPERATURE DEPENDENCES OF HEAT CAPACITY OF ALKALINE BORATES

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Alkaline and alkaline earth borates are currently widely used in various industries, including materials for nonlinear optics and LED technologies [1, 2]. The production of new materials often requires expensive and complex experiments. Theoretical methods, in turn, make it possible to solve a number of technological problems before carrying on experiments. One of these methods is physicochemical modeling using the "Selector-C" software package [3]. To create a physicochemical model of a borate system, a thermodynamic database of stable and metastable components existing in the system is needed. Fundamental handbooks [4, 5] contain data only for a limited number of alkali borates: $MBO_2$, $M_2B_4O_7$, $M_2B_6O_{10}$, $M_2B_8O_{13}$, where M = Li, Na, K. The purpose of this work was determination of the temperature dependences of the heat capacity for alkaline borates of the $xM_2O$-$yB_2O_3$ system, where x, y = 1, 2, 3, 4, 5 using regression analysis.

The values of the heat capacity for each compound of the $xM_2O$-$yB_2O_3$ system at different temperatures were obtained by regression analysis taking into account the data on borates presented in the reference books ($MBO_2$, $M_2B_4O_7$, $M_2B_6O_{10}$, $M_2B_8O_{13}$). The coefficients of the heat capacity equations were estimated by the Shomate method.

The approach we use gives good results, the deviation of the calculated and reference values of the heat capacity for metaborates does not exceed 1-2%, for the other compounds, on average 5-8%. The largest deviations are observed at room temperature and decrease with temperature.

As a result, the heat capacity coefficients for alkali borates of the composition $xM_2O$-$yB_2O_3$ were obtained, where x, y = 1, 2, 3, 4, 5; M = Li, Na, K. In the future, these results will be used to create a physicochemical model of the borate system.

**Acknowledgements** The financial support of work was provided by the Russian Science Foundation (RSF project no. 22-17-20005).

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# COMPLEX THERMAL ANALYSIS OF OXIDE MATERIALS SYNTHESIS PROCESSES VIA COMBUSTION REACTIONS TAKING INTO ACCOUNT CHARGE GENERATION

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During the study of synthesis processes of oxide materials via the combustion reactions of organic-nitrate precursors, the phenomenon of high-density charge generation was discovered [1]. The obtained charged nanoparticles of complex oxides (*CO*) are mutually repelled from each other, this leads to the emergence of only point contacts between them and the appearance of excess surface energy. Thermal analysis of *CO* synthesis processes was added by very significant parameter characterizing the intensity of charge generation [1]: measurement of the precursor-earth potential difference reaching hundreds of volts. By changing the composition of the initial precursors for synthesis, it is possible to control the generation of charges and, accordingly, the sintering temperature of the obtained *CO* up to several hundred degrees. This is provided by the level of excess energy that dissipates as heat during sintering of materials. This aspect is very important when obtaining oxide composites containing layers of different compositions which can be sintered in a single process cycle by adjusting the shrinkage temperature of the combined preforms.

Charges in precursors, as the analysis of the ongoing processes showed, arise due to the removal of ionized molecular groups into the environment, among which may be molecules of water (carry away an electron), nitric oxide (positively charged) [2], etc. The generation of charges is greatly facilitated by the lability of the oxidation state of metal ions included in *CO*. Complex thermal analysis, taking into account the composition of the released gaseous products and the generation of charges, made it possible to establish a number of parameters that determine the intensity of charge generation and their sign. Among such parameters is the composition of the gas medium where combustion is carried out. For example, an inert or reducing medium generally reduces the lability of metal ions with respect to the change in oxidation state [2]. The removal of charged molecular particles is strongly influenced by the external electromagnetic field, which also allows the regulation of charge generation processes. Recently, a number of studies have been carried out to study the influence of this factor on the generation of charges and the formation of target properties of *CO*, in particular, lanthanum manganites, strontium hexaferrite, etc. The studied properties of such *CO* include hysteresis characteristics, the magnetoresistive and magnetocaloric effect.

Quite interesting effects were additionally discovered during research. So, when synthesizing strontium hexaferrite (*SH)* (including doped with lanthanum and cobalt) from precursors containing glycine, iron-glycine complexes appear in aqueous solutions, as indicated by the results of spectrophotometric analysis. Such complexes form large layered heterogeneous crystalline forms, where twinning is also observed. During the combustion of these precursors, long branched fibers are formed, including intermediate synthesis products, in particular magnetite. The study of the driving forces of their formation is of great interest: whether magnetic interaction of precursor particles and their orientation in space is possible due to the directivity of the long crystallographic axis of the original crystals. When *SH* is obtained from amorphized precursors containing polyvinyl alcohol, this phenomenon is not observed. At the same time, the process of "cold" combustion with the synthesis of intermediate phases at RT, which can be facilitated by the high catalytic properties of iron ions, was observed [3].

**Acknowledgements** The study was carried out a grant from the Russian Science Foundation No. 22-23-00718.

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# THERMODYNAMIC PROPERTIES OF THE $Na_2O$-BaO-$B_2O_3$ SYSTEM

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The $Na_2O$–BaO–$B_2O_3$ ternary system is of great importance for growing crystals of low-temperature modification of barium metaborate (β-$BaB_2O_4$). This modification of barium metaborate combines excellent non-linear optical characteristics, good mechanical properties and very low hygroscopicity. The synthesis of this compound can be carried out from a multicomponent melts of the $Na_2O$-BaO-$B_2O_3$ system at a restricted temperatures range. The vaporization processes and of the $Na_2O$-BaO-$B_2O_3$ melts were investigated in the temperature range of 1290-1750 K by the Knudsen effusion mass spectrometry technique. Using data on the component activities of $NaBO_2$, $B_2O_3$ and $BaB_2O_4$ in melts at the temperature 1330 K thermodynamic properties of $Na_2O$-BaO–$B_2O_3$ system, which are represented as the Gibbs energies, the excess Gibbs energies were calculated as a function of the melt composition.

Barium carbonate, sodium carbonate and boric acid with purissimum grade (the content of main substance not less than 99 %) were taken as reagents. The mixtures of the initial substances in the needed proportions were grinded in a jasper mortar during two hours. The synthesis of the glasses was performed in platinum crucibles in silite furnace at temperatures of 1000–1200 $^0$C in the air atmosphere. The temperatures of the synthesis were selected in the dependences of sample compositions.

The studied glasses of $Na_2O$-BaO-$B_2O_3$ system may be divided for three groups by their evaporation character. The samples of first group may be presented as another ternary system $NaBO_2$ – $BaB_2O_4$ - $B_2O_3$. The partial pressures of sodium borate and boron oxide do not differ much at the same temperature. This fact allows to obtain the values of activities of $NaBO_2$ and $B_2O_3$ by experimental method of differential KEMS. According to the phase diagram, all samples of second group are in homogeneous melt at temperature 1330 K. Hence, the activity of barium borate may be calculated by the Gibbs-Duhem equation. In the third group, the mole fraction of boron oxide is equal 50 %. These samples may be presented as the binary system $NaBO_2$ – $BaB_2O_4$. Partial pressures of the sodium and barium borates are differ much at the same temperature. The sodium borate $NaBO_2$ is selectively evaporates at temperature range 1250-1400 K and barium borate accumulates in the condensed phase. $BaB_2O_4$ begin to evaporate from the temperature 1600 K. The big difference in partial pressures of sodium and barium borates gives possibility to obtain pure barium borate by selective evaporation of sodium borate from the binary system $NaBO_2$ – $BaB_2O_4$. The activity of $NaBO_2$ in the pseudobinary system $NaBO_2$-$BaB_2O_4$ is equal unity. This is consistent with the data of ref. [1], according to which a mixture of barium borates (β-$BaB_2O_4$) and sodium ($NaBO_2$) is formed in this section.

The values of activities of all three components in the $NaBO_2$–$BaB_2O_4$-$B_2O_3$ ternary system are characterized by the negative deviation from ideal case. The deviation extent is increasing with decreasing concentration of the respective component in the glass.

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# THERMODYNAMIC BEHAVIOUR OF PALLADIUM IN LICL–KCL–CSCL EUTECTIC MELT

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A sludge of intermetallides of radioactive noble metals (RNM) with actinides is formed in the anode region during the electrofining of metallic spent nuclear fuel (SNF) or metallized ceramic SNF. In the future, it is necessary to isolate actinides to reduce the radiotoxicity of this waste with high heat generation, as well as the isolation of valuable components - for example, palladium. It should be noted that SNF as a raw material is a richer product compared to ores, which are currently the main primary source of platinum metals [1].

To extract palladium from the sludge of spent fuel processing, it is necessary to study its thermodynamic behaviour in the working melt. In the present study ternary LiCl–KCl–CsCl eutectic mixture was used due to low melting temperature (263 ˚C).

The temperature dependence of the conditional standard potential, the Gibbs energy change, the enthalpy and entropy of palladium chloride formation and the activity coefficient were determined in molten LiCl-KCl-CsCl eutectic by the method of square wave voltammetry.

The obtained thermodynamic data can be used in the development of the operation of palladium separation in the form of anode sludge during SNF electrorefining and the operation of its production in the form of high-purity metal from anode sludge.

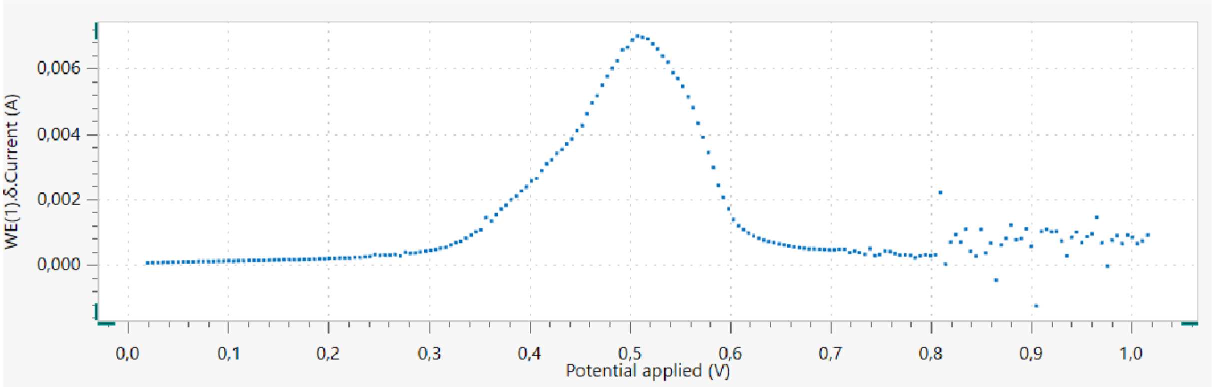

**Figure 1.** Example of a square wave voltammogram recorded in LiCl–KCl–CsCl – $PdCl_2$ melt (0,485 wt. % Pd) at 400 ˚C.

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# THERMODYNAMIC MODELLING OF SYSTEMS CONTAINING LIQUID CRYSTALS

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Liquid crystals (LC) are widely used in many applications including display technologies. The type of intermolecular interactions is important both for the solvent choice for the final purification of mesogens and for the component selection (LC, dichroic dyes, low viscosity additives) for LC mixtures.

4-n-Alkyloxybenzoic acids $C_nH_{2n+1}$-O-$C_6H_4$-COOH (where $C_6H_4$ is p-phenylene, n = 6, 9, 10, 16), 4-n-alkyloxy-4'-cyanobiphenyls $C_nH_{2n+1}$-O-$C_6H_4$-$C_6H_4$-CN (n = 4 – 7), *p*-butyloxyphenyl *p*'-n-alkyloxybenzoates (n = 6 – 10) and *p*-n-alkyloxybenzyliden-*p*'-toluidenes (n = 4, 6, 9, 10) are used as mesogens. Complete T-x-diagrams of LC – non-mesogen systems and solubility curves in solvents of different classes (n-alkanes, cycloalkanes, aromatic and chlorine-organic compounds, ethers, esters, alcohols, acetone, dioxane, nitriles) are obtained by the thermal analysis (DTA, polarizing microscopy, solubility and visual polythermal analysis) methods. Phase diagrams have two invariant equilibria at least. Melting of crystalline mixtures in systems occurs by the eutectic reaction. A boundary nematic (smectic) solution is formed by the metatectic reaction.

Excess thermodynamic functions for SLE equilibria are estimated. The Hildebrand and Hansen solubility parameter are proposed for the description of LC – solvent systems. A scheme of Stefanis group contributions is proposed [1] for calculating the Hansen solubility parameters ($\delta_d$, $\delta_p$, $\delta_h$ are components responsible for the dispersion, polar interaction and hydrogen bonds). The Hildebrand and Hansen solubility parameters, vaporization enthalpy and molar volumes for LC are calculated by the group contributions method. The data for solvents are taken from [2].

Concepts of the "reduced radius" (Ra) and the Teas solubility triangle [2] are used for the demixing (LLE) prediction and solubility correlation.

$$R_a^2 = 4.(\delta_{d(1)} - \delta_{d(2)})^2 + (\delta_{p(1)} - \delta_{p(2)})^2 + (\delta_{h(1)} - \delta_{h(2)})^2$$

With the difference increasing in the types of intermolecular interaction, and the solubility parameters of the components, Ra increases and, accordingly, the solubility of mesogens ($x_1$) decreases.

Method based on the solubility parameters gives a possibility to predict LLE equilibria and solubilities of mesogens in the selected solvents.

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# PHASE STABILITY AND THERMODYNAMIC MODELLING OF ALLOYS BASED ON THE CO-CR-MN SYSTEM

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High entropy alloys (HEAs), consisting of five or more principal elements, exhibit more attractive mechanical and structural properties compared with conventional alloys. The widely studied Co-Cr-Fe-Mn-Ni HEA, named Cantor alloy, shows a face-centered cubic (FCC) crystal structure, and displays a good ductility. However, the Cr-rich σ phase is reported to precipitate during the long-term low-temperature annealing, and the appearance of this phase is thought to be deleterious to its mechanical properties. There was only one source found studying phase equilibria in Co-Cr-Mn subsystem of Cantor alloy (Fig. 1 a, b) [1], therefore it was chosen as aim for current work.

Alloys of Co-Cr-Mn system were arc melted and homogenized for 300 hours at ~1050 and 1150 °C. The resulting microstructures were characterized by a combination of scanning electron microscopy, X-ray diffraction and differential scanning calorimetry. Also drop solution calorimetry experiments of sigma-phase samples were performed. The obtained experimental data is essential for the establishment of the database of Co-Cr-Fe-Mn-Ni system.

Based on equilibrium data obtained, a thermodynamics description of the ternary Co-Cr-Mn phase diagram has been developed using the CALPHAD method. The thermodynamic assessment will be shown and compared to experimental data from the current work and the literature. **Acknowledgements** The authors gratefully acknowledge the financial support of the Russian Science Foundation, project № 18-73-10219P

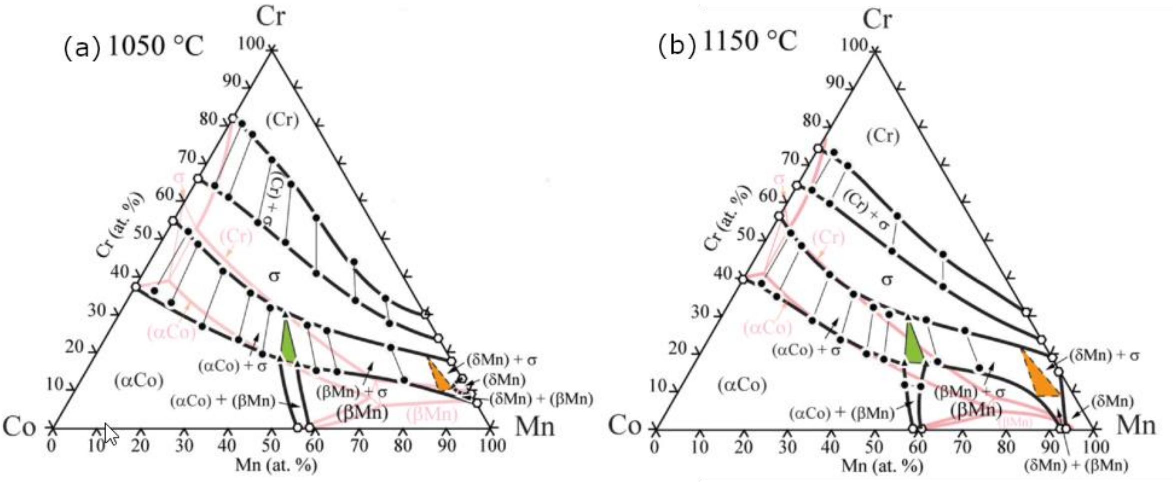

**Figure 1.** Isothermal sections of Co-Cr-Mn system [1]

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# PHASE DIAGRAM FOR THE IN – SE SYSTEM ACCORDING TO THE DATA OF THE THERMAL, STRUCTURAL AND VAPOR-PRESSURE INVESTIGATIONS

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High-temperature highly symmetrical phases in A(III) – B(VI) systems are the promising candidates for new materials with outstanding thermoelectric, radiation-resistant, catalytic and other properties, which are due to a high concentration of the so-called intrinsic vacancies. Some of these vacancies can be replaced by atoms of various impurities, which stabilize the phase and additionally allow one to vary its properties. The well-known basis for the synthesis of crystalline samples is data on the phase diagram of the system. However, for the phase diagrams of the A(III) – B(VI) systems, there are significant discrepancies in the literature data. For the system under study in this work – for the In-Se system – these mismatches apply even to the general form of the *T-x* diagram.

The study of the *T-x*-diagram for the In – Se system was carried out using the differential thermal analysis, as well as a new static version of the thermal method – chromato-thermographic analysis (ChTA). The obtained data were supplemented by the results of optical-vapor-pressure studies using auxiliary components - indium chlorides and bromides. An analysis of the equilibrium of indium selenides using the halides vapors makes it possible to obtain the significant thermodynamic information on the In – Se system and plot the lines of monovariant equilibria on the $p_{\mathrm{In}} - T$ diagram for the coexistence of the vapor with two solid phases In addition, the noticeable solubility of indium halides in the indium-selenium melts, which we discovered, made it possible to refine the position of some horizontal lines, as well as the liquidus line on the *T-x*-diagram.

As a result of investigation, the T-x diagram for the In - Se system was obtained. The phase relations in this system and the structures of some indium selenides are discussed taking into account the data of the performed X-ray studies. In particular, the polymorphic transformations of indium sesquiselenides have been studied. It was found that one of the high-temperature modifications of $In_2Se_3$ turned out to be a highly symmetrical phase ($P6_3mmc$).

It was concluded that there is a noticeable difference between the phase diagram for the In - Se system and the diagrams of other A(III) – B(VI)-systems, which is expressed primarily in a larger number of phases for the indium-selenium system and in a greater tendency for this the system to the appearance of metastable states.

**Acknowledgements** The work was supported by the Russian Foundation for Basic Research, project No. 20-33-90238 (graduate students).

# PHASE TRANSITIONS, CRITICAL AND SUPERCRITICAL PHENOMENA IN TERNARY MIXTURE OF WATER +1-PROPANOL+*N*-HEXANE

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The *PVTx* properties of the two ternary 0.6628water+0.1987propanol-1+0.1385*n*-hexane and 0.3333water+0.3333propanol-1+0.3333*n*-hexane mixtures were measured. The measurements were made along 29 liquid and vapor isochores between (7.0 and 656.7) kg·m$^{-3}$ for each mixture and over the temperature range from (373 to 673) K at pressures up to 60 MPa. Temperatures and pressures (*P-T* phase diagram, dew-bubble point curve) at the liquid-gas phase transition point for each fixed density were measured using break point technique. The critical property data for the ternary mixtures were obtained from the measured *PVT* data in the critical region. The excess molar volumes of the ternary mixture were calculated using the measured molar volumes of the mixture and the reference molar volumes of the pure components in the supercritical region. The pressure dependence of $V_{\mathrm{m}}^{\mathrm{E}}$ along the near – and supercritical isotherms from (543 to 573) K exhibits maximum at pressures between (6.46 and 8.73) MPa. The maximum shifts to high- pressure range with increasing the temperature. All the derived excess molar volumes in the experimental temperature range are positive. The present study showed that at temperatures and pressures close to the critical point of mixture and one of the components (pure propanol -1) the behavior of $V_{\mathrm{m}}^{\mathrm{E}}$ considerable (anomaly) changes. The measured data at low densities and pressures (vapor phase) were used to calculated the second and third virial coefficients of the mixtures at high temperatures, which are directly related with the intermolecular potential function, $\phi_{ij}(r,\sigma_{ij},\varepsilon_{ij})$ for like and unlike molecules of the mixtures. The measured *PVT* data along the selected near- and supercritical isotherms depicted in Fig. 1.

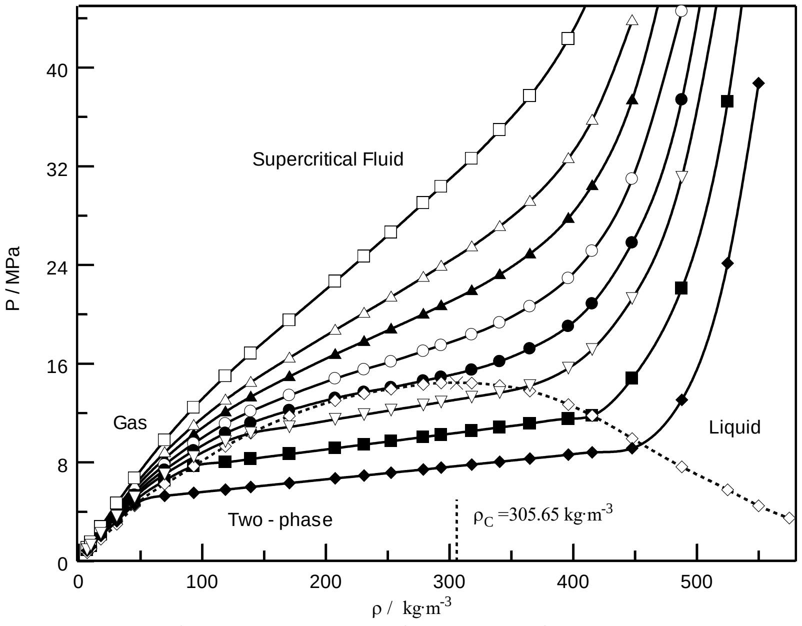

**Figure 1.** Measured values of pressure as a function of density along the selected near- and supercritical isotherms for ternary 0.6628 water+0.1987propanol-1+ 0.1385 *n*-hexane mixture.

# MODELING OF DSC CURVES OF POLYSTYRENE DURING GLASS TRANSITION: FROM CONVENTIONAL TO FAST COOLING RATES

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Development of a complete theory of glass transition is one of the general challenges for the modern physics [1,2], thus the analysis of related problems is always required. Experimental study and theoretical description of glass transition is very important due to modern technological applications of glasses and also their frequent occurrences in our everyday life.

Polymers, being good glass formers, allow thorough studying glass transition effects. The applicability of various theoretical models can be made. In this work experimental and theoretical investigations of glass transition of atactic polystyrene in a broad range of cooling rates were performed [3]. The cooling rates, $q_c$, covered the range from the very slow to ultra-fast speeds ($5\cdot10^{-6}$-$10^{6}$ K/s). The corresponding heating rates were 0.5, $5\cdot10^{3}$ and $5\cdot10^{4}$ K/s.

Capability of commonly employed theoretical techniques for $C_p$ modeling to describe all the obtained data was considered during last several years. For the slow cooling rates, it was shown that the conventional approaches (e.g., Tool-Narayanaswamy-Moynihan model) with a single set of parameters do not fit the experimental data well [2-3]. In this report we review and analyze the results of these investigations and discuss their applications to fast and ultra-fast cooling rates. Finally, we obtained non-temperature-dependent linearity and non-exponentiality parameters. Some applications of relaxation laws with cross-over behavior, and models operating with configurational entropy instead of fictive temperature as the structural parameter are discussed. The master-curve type behavior of normalized heat capacity curves is analyzed within all reached modeling frameworks.

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# NEW APPROACH FOR VAPOR PRESSURE DETERMINATION BY MEANS OF FAST SCANNING CALORIMETRY

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Nowadays, one of the most important problems of physical chemistry is reliable determination of the vapor pressure in a wide temperature range. This parameter is very important for modeling of the pollutants transport processes in the atmosphere. However, commonly employed methods for the vapor pressure determination of the low-volitile compounds usually require a sufficiently high signal. Thus, the temperatures at which the experiments can be performed are undesirably close to the onset of decomposition. To overcome these difficulties was suggested an application of the fast scanning calorimetry method for high-speed thermogravimetry [1]. Due to nanogram-scale in the FSC approach is the significantly enlarged surface-to-volume ratio compared to conventional tensimetric methods. For this reason, in many cases, the decomposition has a minor influence on the measurements.

The main equation in the FSC approach has the following form [1]:

$$p_{\text{sat}} = \frac{dm}{dt}\cdot\frac{RT_{\text{vap}}}{A_{\text{vap}}M_{\text{A}}\beta_{\text{c}}} \qquad (1)$$

where $p_{\text{sat}}$ is the saturation vapor pressure of the sample at temperature $T_{\text{vap}}$ in Pa; $dm/dt$ is the mass-loss rate in $\text{g}\cdot\text{s}^{-1}$; $A_{\text{vap}}$ is the vaporization/sublimation interface area in $\text{m}^2$; $M_{\text{A}}$ is the molecular mass of the sample in $\text{g}\cdot\text{mol}^{-1}$; $R$ is the universal gas constant, 8.314462 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and $\beta_{\text{c}}$ is the mass-transfer coefficient in $\text{m}\cdot\text{s}^{-1}$.

The Temperature, the mass-loss rate, and the vaporization/sublimation surface area can be determined experimentally. To measure the mass-loss rate was used the temperature program shown in Figure 1. To obtain the vaporization/sublimation surface area was used an optical microscope. To determine the mass-transfer coefficient in this work were developed special calculation procedures.

The reliability of the procedures was checked by comparison of the vapor pressures measured in this work with the well-founded literature values for some polyaromatic and long-chain compounds. After successful validation, these procedures were used for the vapor pressure determination of the low-volatile compounds for which literature data were inconsistent.

**Acknowledgements** The financial support of Ministry of Science and Higher Education of the Russian Federation (MSHE RF), No. 0671-2020-0061.

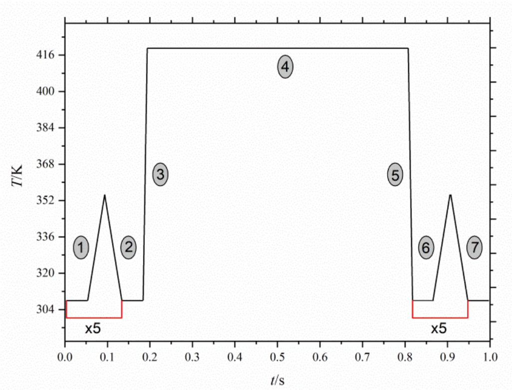

**Figure 1.** Temperature program for mass-loss rate determonation.

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# VAPORIZATION ENTHALPY OF ORGANIC NON-ELECTROLYTES IN A WIDE TEMPERATURE RANGE: PENCIL AND PAPER *vs* EXPERIMENTAL MEASUREMENTS

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Vaporization enthalpy plays a key role in vapor-liquid equilibrium, heat balances and thermochemical cycles. Being a measure of intermolecular interactions, vaporization enthalpy is widely used as parameter in number of theoretical models. The growing number of organic compounds needed to be studied attract interest to procedures of quick estimation of the vaporization enthalpy. However, the majority of approaches available nowadays ignore or poorly account the temperature dependence of the vaporization enthalpy given by Kirchhoff's law of Thermochemistry:

$$\Delta_{\mathrm{l}}^{\mathrm{g}}H(T_2) = \Delta_{\mathrm{l}}^{\mathrm{g}}H(T_1) + \int_{T_1}^{T_2} \Delta_{\mathrm{l}}^{\mathrm{g}}c_{\mathrm{p,m}}dT$$

Since 1993, an empirical approach proposed by Chickos and coworker is used for estimation of $\Delta_{\mathrm{l}}^{\mathrm{g}}c_{\mathrm{p,m}}$ and Kirchhoff's integral [1]:

$$-\Delta_{\mathrm{l}}^{\mathrm{g}}c_{\mathrm{p,m}} / (\mathrm{J \cdot mol^{-1} \cdot K^{-1}}) = 10.58 + 0.26 \cdot c_{\mathrm{p,m}}(\mathrm{l},\ 298.15\ \mathrm{K}) / (\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$$

The quality of this approach strongly depends on molecular size and temperature range, being insufficiently low for large molecules or in a wide temperature range. As an alternative, we proposed another empirical correlation, based on relationships between change of the heat capacity and vaporization enthalpies, and analyzed its dependence on the molecular structure [2-4]:

$$-\Delta_{\mathrm{l}}^{\mathrm{g}}c_{\mathrm{p,m}} / (\mathrm{J \cdot mol^{-1} \cdot K^{-1}}) = a + b \cdot \Delta_{\mathrm{l}}^{\mathrm{g}}H(298.15\,\mathrm{K}) / (\mathrm{kJ \cdot mol^{-1}})$$

Proposed approach combined with the previously developed group additive schemes for estimation of $\Delta_{\mathrm{l}}^{\mathrm{g}}H(298.15\mathrm{K})$ was used to calculate more than 1500 vaporization enthalpies of more than 700 organic non-electrolytes of different structure in a wide temperature range. Calculated values were found to be in a good agreement with the experimental ones. The quality of proposed approach was significantly higher the predictions according to widely used Chickos *et al.* scheme and some other group additive schemes for estimation of $\Delta_{\mathrm{l}}^{\mathrm{g}}H(T)$ [2-4].

Additionally, vaporization enthalpies of more than 10 low-volatile organic compounds of different structure at elevated temperatures were measured and compared with the results of prediction. Agreement within the typical experimental error was observed for all cases.

Proposed approach can be used for accurate estimation of the vaporization enthalpy at the temperature of interest or for quick examination of the quality of questionable experimental data.

**Acknowledgements** This work was supported by the Russian Science Foundation (Project No. 21-73-00006).

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# THERMAL AND SUPRAMOLECULAR PROPERTIES OF OLIGOPEPTIDES

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Currently, oligopeptides are being actively studied because various nanostructures with biocompatibility and low toxicity can be obtained on their basis. Such structures exhibit biological activity and may have a wide range of biomedical applications. A popular way to obtain nanostructures based on oligopeptides is the heat treatment. However, during the oligopeptides heating the chemical reactions can occur with the formation of other compounds with different properties. Therefore, for the correct application of heat treatment in such systems, the information on the critical temperatures above which the processes of self-organization of oligopeptides turn into chemical reactions is needed. In addition to oligopeptide nanostructures the crystals based on oligopeptides are of interest, because they may be used to store volatile anesthetics and gases or to separate gas mixtures. Such crystals can exhibit supramolecular properties such as recognition of organic compounds and memory of the previously bonded guest.

In the present work, we studied the thermal properties of dipeptides glycyl-glycine, $_{\text{L}}$-isoleucyl-$_{\text{L}}$-alanine, $_{\text{L}}$-leucyl-$_{\text{L}}$-phenylalanine, and $_{\text{L}}$-phenylalanyl-$_{\text{L}}$-leucine in the solid phase, as well as clathrates of tripeptide based on leucine using simultaneous thermal analysis.

The temperatures of the onset of cyclization of dipeptides in the solid phase were determined. The kinetic parameters of these reactions, including the activation energy, the Arrhenius factor, and the reaction order were calculated.

It was found that an increase in the size of the amino acid residues in the dipeptide molecules leads to the decrease in the temperature of cyclization.

The formation of clathrates of the tripeptide $_{\text{L}}$-leucyl-$_{\text{L}}$-leucyl-$_{\text{L}}$-leucine with organic compounds was studied by the method of static headspace gas chromatographic analysis. The thermal stability of tripeptide clathrates was studied by simultaneous thermal analysis.

The ability of leucine-based tripeptide crystals to remember the previously bonded guests was found. The memory effect appears as a sequential endo- and exothermic effects on the DSC curve corresponding to the polymorphic transitions of oligopeptide after the guest leaves the clathrates.

The results obtained can be useful for the development of methods for the preparation of nanomaterials based on oligopeptides, and also for the methods for preparation of 2,5-diketopiperazine derivatives, and for the molecular recognition of vapors of organic compounds.

**Acknowledgements** This work has been supported by the Kazan Federal University Strategic Academic Leadership Program (‘PRIORITY-2030’)

# CONTROL OF HYDROGEN BONDING IN PHOTOACTIVE ORANGE CAROTENOID PROTEIN BY NONCANONICAL SUBSTITUTIONS OF TYROSINE-201

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In orange carotenoid protein (OCP) Tyrosine-201 (together with tryptophan 288) is a key residue involved in the formation of the hydrogen bond with the ketocarotenoid and thereby prevents spontaneous activation of the protein-carotenoid complex. To elucidate the strength, geometry and chemistry of this interaction, we used orthogonal translation and systematically substituted Tyr-201 with specific halogen analogues. In particular, we have exchanged the aromatic side chain of Tyr-201 with analogues that have chlorine, bromine or iodine atoms at the meta-position of the aromatic ring. These subtle changes should not cause major perturbations of the protein structure but should have strong effects on hydrogen bonding abilities of neighboring -OH group. We first assessed these interactions using quantum chemistry and molecular dynamics methods, and then experimentally verified the predicted differences in hydrogen bond strength. We have shown that the strength of the interactions of the ketocarotenoid with Tyr-201 decreases with increasing substituent proton affinity. This leads to increase of the importance of hydrogen bonding with Trp-288 accompanied by characteristic changes in the optical properties of the chromophore and the photocycle of the whole protein-chromophore complex. Such genetically encoded chemical modification of individual atoms and their systematic *in situ* variation in complex protein structures provides an excellent basis for turning the orange carotenoid protein into a practical tool for optogenetics and other practical applications.

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# STUDY OF THE COCRYSTALLIZATION EFFECT ON THE CARBAMAZEPINE THERMAL STABILITY

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Crystal engineering of multicomponent crystals of drugs is a relatively young branch of science. Therefore, it is necessary to develop clear criteria and methods to quickly and efficiently detect the formation of cocrystals, salts and its polymorphic forms. In the existing world standards context, it is important to ensure maximum efficiency and environmental friendliness of the process - the main conceptual principles of "green technology" that are relevant at the moment [1]. The sublimation method, as a method for obtaining new crystalline forms of medicinal compounds, has several advantages: simplicity of impurities separation, ease tuned, fast, and allows obtaining diffraction quality single crystals [2, 3].

The aim of the work was to evaluate the applicability of the cosublimation (sublimation of a physical mixture of a two-component system) and resublimation (sublimation of a pre-prepared cocrystal) methods to obtain multicomponent crystals of carbamazepine. The cosublimation and resublimation experiments were carried by vacuum sublimation and transpiration methods. The obtained samples were studied by powder X-ray diffraction, differential scanning calorimetry, thermomicroscopy, and mass spectrometric analysis. The samples for resublimation were obtained by liquid-assisted grinding on a Pulverisette planetary micromill.

Cosublimation and resublimation of a two-component mixture were carried out at temperatures below the melting point of the low-temperature component. As a result of the experiment, it was found that the cosublimation of carbamazepine with 4-hydroxybenzamide at temperatures exceeding 110 °C leads to the degradation of carbamazepine to iminostilbene. Upon resublimation of the [carbamazepine+4-hydroxybenzamide] (1:1) cocrystal, the process of thermal degradation of carbamazepine to iminostilbene begins at temperatures exceeding 150°C. In order to interpret the results of the sublimation experiment, a phase diagram of the (carbamazepine + 4-hydroxybenzamide) system was constructed. It was found that the carbamazepine thermal degradation process for cosublimation starts at temperatures corresponding to the eutectic melting of the physical mixture of carbamazepine and 4-hydroxybenzamide, and for resublimation, at the eutectic melting temperature of the cocrystal [carbamazepine + 4-hydroxybenzamide] (1:1) and 4-hydroxybenzamide.

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# INFLUENCE OF THE STRUCTURE OF ESTERS OF NATURAL HYDROXYCARBOXYLIC ACIDS ON THERMODYNAMIC AND THERMOPHYSICAL PROPERTY

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The industrial production of lactic acid is mainly based on renewable sources since it is estimated that about 90% is produced microbiologically. Glycolic and malic acid are another attractive potential molecules-platform obtained from biorefinery processes. In the fermentation process hydroxy acid is produced as an aqueous solution. The costs associated with separation and purification account for more than 50% of the total costs. The reactive distillation process with alcohol and followed hydrolysis of esters allows reducing the cost of products. The great interest the reactive distillation optimization require knowledge of thermodynamical and thermophysical properties such as vaporization enthalpy, vapor pressure, viscosity and density of glycolic, lactic and malic acid esters.

This work presents a collection of experimental vaporization enthalpy, densities and viscosities for the esters of glycolic, lactic and malic acid and alcohols $C_1$-$C_8$. The aim was to provide practical information on the relationship property-structure.

The vaporization enthalpies of alkyl glycolates, alkyl lactates and dialkyl malates obtained in our previous works were used to estimate the contribution of the hydroxyl group and hydrogen bond in the liquid phase. The contribution of the hydroxyl group and the overall hydrogen bond in esters of hydroxycarboxylic acids in the pure liquid phase can be found with help of experimental vaporization enthalpies and a conception of homomorph compounds. We used three homologous series alkyl acetates, alkyl propionates and dialkyl succinates for alkyl glycolates, alkyl lactates, and dialkyl malates. Vaporization enthalpies of alkyl acetates and alkyl propionates were taken from NIST Chemistry WebBook.

The contribution of the hydroxyl group and the hydrogen bonds for alkyl lactates (14.4-12.6 kJ/mol) and dialkyl malates (13.4-8.3 kJ/mol) is less than of the alkyl glycolates (19.9-16.9 kJ/mol). The decrease in the contribution of the hydroxyl group and HB to the enthalpy of vaporization can be explained by the presence of substituents near the hydroxyl group in molecules alkyl lactate and dialkyl malate. For alkyl glycolates, these contributions have the close value except for pentyl and octyl glycolate. But for dialkyl malates, this contribution decreases with increasing the number of C-atoms in a linear alcohol residue in the molecule of esters except for dibutyl matate. Unfortunately, there is no enough information for alkyl lactates for clear conclusions.

Inter- and intramolecular interaction of esters in the liquid phase should influence thermophysical properties such as densities and viscosities. Density and viscosity in a temperature range of 293.15–363.15 K for esters of glycolic, lactic and malic acid were obtained by pycnometer and Pinkevitch capillary viscometer.

The density decreases as the alkyl chain increase for each ester homologous series especially for the first member. The maximum density changes are found for methyl and ethyl esters. The high densities of methyl and ethyl esters indicate it is an efficiently packed compound into intermolecular hydrogen bonding. The kinematic viscosity increases as the alkyl chain increase for each homologous series except for methyl lactates and dimethyl malate. The kinematic viscosity for dimethyl malate increase is exceptionally strong as compared with other esters especially at the low temperature due to increase the strength of intramolecular interaction. The competition between inter- and intra-molecular interactions doesn’t significantly affect the kinematic and dynamic viscosity of alkyl glycolates and alkyl lactates.

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# THERMOCHEMICAL AND STRUCTURAL PROPERTIES OF THE NEW SULPHUR-CONTAINING COMPOUNDS WITH RELEVANCE ON ATMOSPHERIC CHEMISTRY

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We have computationally studied the thermochemical and structural properties of a variety of sulphur-containing organic compounds with relevance on atmospheric chemical processes, such as the oxidation of dimethyl-sulfide, the most abundant biological source of sulphur to the marine atmosphere [1], or the products coming from $SO_3$, which is a critical intermediate for the sulphur cycle in the atmosphere [2]. A reliable estimation of the standard molar enthalpies of formation, $\Delta_f H_m^o$(g), and the bond dissociation enthalpies, *BDE,* in the gas phase at 298.15 K has been performed, by means of atomization [3] and isodesmic reactions methods using G*n* (*n* = 3, 4) [4,5], M05-2X (DFT) and other levels of theory.

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# ALKYL-SUBSTITUTED BIPHENYLS AS POTENTIAL CANDIDATES FOR LIQUID ORGANIC HYDROGEN CARRIERS

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Despite the growing use of renewable energy sources, fossil fuels remain dominant. The difficulty of extraction, gradual depletion, and the environmental problems that accompany this are forcing scientists to look for an acceptable alternative. Hydrogen may become such an alternative in the near future due to its high relevance in the context of the transition to renewable energy sources. Hydrogen is a highly efficient and unique energy carrier that can be used both stationary and mobile. However, having a large number of significant advantages in the use of hydrogen, its transportation and storage remains a problem. A potential solution to this problem can be the use of liquid organic hydrogen carriers (LOHC), which allow hydrogen to be accumulated inside an aromatic molecule as a result of catalytic hydrogenation reactions and released in dehydrogenation processes in reversible cycles [1]. Aromatic compounds may be good candidates for such purposes. The best-known representatives of LOHC today are N-ethylcarbazole [2] and benzyltoluenes [3]. Strict requirements are imposed on LOHC, firstly, they must have low melting points, sufficient thermal stability, secondly, favorable thermodynamics and dehydrogenation kinetics, and thirdly, high availability of starting components. However, there are not so many suitable aromatic compounds that could fully meet these requirements. Alkyl-substituted biphenyls can be considered as potential LOHC candidates. Modern development and optimization of industrial technologies requires a significant and reliable amount of thermodynamic data. These data are necessary for the development of efficient thermal management in the synthesis of LOHC on an industrial scale. In this work, we compare and evaluate a set of our own experimental and literature data on the standard molar thermodynamic properties of the formation and phase transitions of substituted alkyl biphenyls. High-level quantum chemical methods (G3MP2 and G4) were used both to test the experimental values of the enthalpies of isomerization reactions and to estimate the enthalpies of hydrogenation/dehydrogenation reactions of alkyl-substituted biphenyls. The enthalpies of reversible reactions of hydrogenation/dehydrogenation of alkyl biphenyls obtained during the study were calculated and compared with other liquid organic hydrogen carriers. The results obtained show that the studied compounds can be considered as potential LOHC.

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# STUDY OF THE THERMODYNAMIC PROPERTIES OF ORGANOSILICON DENDRIMERS AND THEIR CORRESPONDING NANOGELS WITH DIFFERENT NATURE TERMINAL GROUPS

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Hyperbranched polymers are a special type of dendritic macromolecules with a very high branching density and a tree-like structure. Recently, hyperbranched polymers have received much attention due to their unique physical and chemical properties as well as their promising applications in various fields, from biomedicine to nanocatalysis. Many different types of hyperbranched polymers are known and investigated. Among them, organosilicon dendrimers and nanogels are the most promising and intensively studied compounds. They are characterized by thermodynamic stability, biocompatibility, low characteristic viscosity and high flexibility compared with linear polymers.

This work is a continuation of studies of thermodynamic properties of carbosilane dendrimers [1-3]. The aim of this work was to study the standard thermodynamic properties of carbosilane dendrimers first and third generations with phenyldioxalane terminal groups; siloxane dendrimers from the first to the fourth generations with trimethylsilyl terminal groups; polymethylsilsesquioxane nanogels with blocking trimethylsilyl groups in a wide temperature range by precise adiabatic calorimetry and differential scanning calorimetry, in addition, study of the dependence of their thermodynamic properties on the chemical nature and structure.

The temperature dependences of the heat capacities of the studied compounds were determined for the first time.

For all samples, the glass transition and the low-temperature structural anomaly were detected, and the thermodynamic characteristics of these transformations were calculated and analyzed. The standard thermodynamic functions, namely, the heat capacity Cp°(T), the enthalpy [H°(T)−H°(0)], the entropy [S°(T)−S°(0)], and the Gibbs energy [G°(T)−H°(0)] were determined for different physical states of the investigated samples. As a result, the physicochemical discussion and comparison of thermodynamic properties of organosilicon dendrimers, nanogels and previously studied hyperbranched polymers were done. The purpose of the analysis was to identify the dependences of these properties on number of generation and nature of the outer layer of macromolecules.

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# RESEARCH OF THE SYSTEMS AMINO-ALCOL – WATER

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The water-monoethanolamine (MEA) and water-3-aminopropanol (3AP) systems were studied.
Research methods: differential scanning calorimetry, heat capacity measurement, IR spectroscopy and quantum chemical calculations, dynamic light scattering.
Main results: phase diagrams of the studied systems were built; the found low-temperature liquid phases were explained by the presence of mixed spatial networks of hydrogen bonds in the systems as a consequence of a rather strong amino alcohol-water interaction leading to the formation of $MEA_n \cdot H_2O_m$ and $3AP_n \cdot H_2O_m$ associates in the liquid phase and compounds in the solid phase. When studying the temperature dependence of the heat capacity of pure MEA, a solid-phase transition was registered in the region of 200-220K.
The studied systems are widely used in cryobiology for long-term storage of living cells and organs due to the presence of low-temperature liquid phases, the difficulty of crystallization, and the ease of vitrification at very low temperatures, which is explained by the presence of spatial mixed networks of H-bonds in these systems.

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# THERMODYNAMIC MODELS OR AQUEOUS, ORGANIC AND ELECTROLYTE SOLUTIONS

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Most modern industrial processes include one or more of the following stages: crystallization, extraction, distillation, chemical transformations. To select the optimal conditions of the process, information is needed on the thermodynamic models that are used for engineering calculations in various process simulation software. Thermodynamic models are usually subject to several requirements, which include the following: 1) the ability to describe different types of experimental data, 2) predictive ability, 3) the use of the least number of variable parameters, 4) the simplicity of mathematical expressions. Most thermodynamic models satisfy only some of these requirements. An alternative to the existing models can be a Generalized Local Composition Model (GLCM) [1]:

$$\frac{G^{ex}}{RT\sum_i n_i} = \sum_i x_i \ln\frac{\phi_i}{x_i} + \frac{z}{2}\sum_i q_i x_i \ln\frac{\theta_i}{\phi_i} - \sum_i q_i x_i \ln\left(\sum_j \theta_j \tau_{ji}\right) + \sum_i x_i \ln\left(\sum_j x_j \rho_{ji}\right)$$

$$\theta_i = \frac{x_i \times q_i}{\sum_j x_j \times q_j}, \phi_i = \frac{x_i \times r_i}{\sum_j x_j \times r_j}, \tau_{ij} = \rho_{ij} \times exp\left(-\frac{a_{ij}}{T}\right),$$

where $x_i$ – mole fraction of the $i$-th component; $q_i$ and $r_i$ – structural parameters; $z$ – coordination number set equal to 10; $a_{ij}$ and $\rho_{ij}$ – temperature dependent parameters of binary interactions. For a binary system at a given temperature, the number of adjustable parameters in GLCM can reach four. For a similar case, UNIQUAC and Wilson models each have 2 adjustable parameters, while NRTL model has 3 parameters. A larger number of parameters compared to similar models leads to the fact that the Generalized Local Composition Model is more flexible. And in the case of highly non-ideal solutions, GLCM makes it possible to describe together various kinds of experimental data (phase equilibria, thermodynamic and thermochemical properties of the solution) with a higher accuracy. If there is no need to use all four parameters of the model, it is possible to use a simplified version of the model with a smaller set of parameters.

GLCM may be modified to take into account the presence of charged species in the solution [2]. The suggested electrolyte version of the Generalized Local Composition Model (eGLCM) contains three contributions to the excess Gibbs energy: a long-range electrostatic interaction term represented by the modified Pitzer-Debye-Hückel equation, which takes into account concentration dependence of the solution dielectric permittivity, the contribution of the short-range interaction between all the species, represented by the GLCM, and the middle-range interaction term responsible for interactions involving charged species that are not explained by the long–range term.

The proposed model allows solving many problems of applied thermodynamics. A flexible GLCM model describes various kinds of experimental data (LLE, VLE, SLE, activities of components, heats of mixing, etc.) using a single set of parameters in such rather complex systems as water-alcohol solutions, immiscible water-organic solutions with extremely low mutual solubility, mixed-solvent electrolyte solutions.

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# DEPENDENCE OF FORMAL ELECTRODE POTENTIAL ON IONIC STRENGTH

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The precision of calibration of the electrode pair (or combined electrode as it is in our case) influences the accuracy of experimental pH determination. The ionic strength effect on the formal electrode potential might be significant. At the same time, the influence of ionic strength on the Nernst's slope is expected to be negligible because none of the constants or variables involved (RT/nF) are dependent on I value. There is a limited number of papers devoted to the study of ionic medium effects on the standard electrode potential [1, 2]. The results of our calibration experiments at different ionic strength values (Fig.1) are in general agreement with the reported data.

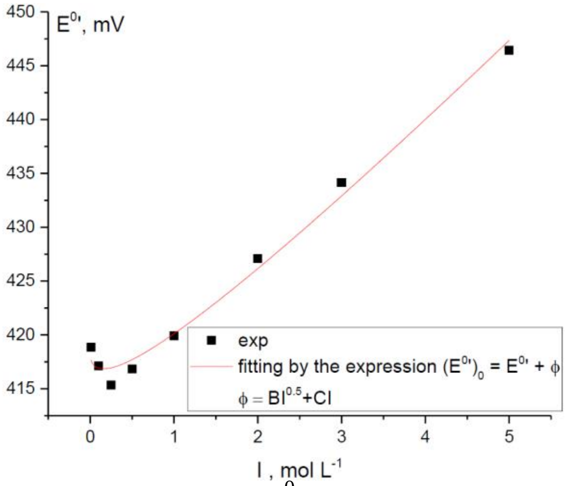

**Figure 1 .** Fitting of the dependence of E$^0$ on ionic strength by non-linear function

Nernst's slope dependence on the indifferent electrolyte concentration is negligible, while the formal electrode potential follows the J-like trend [1] with the increase in the I value (Fig. 1), which can be described by the following equation [1]:

$$(E^{0'})_0 = E^{0'} + \phi = E^{0'} + BI^{0.5} + CI \qquad (1);$$

where $(E^{0\,'})_0$ is a limiting value of the formal electrode potential at zero ionic strength; $E^{0\,'}$ is the formal electrode potential at the specific ionic strength; $\varphi$ is an empiric function with empiric coefficients $B$ and $C$. According to our data (Fig. 1), $(E^{0\,'})_0$ = 418.30±1.17 mV, $B$ = -7.23±2.53; $C$ = 9.05 ± 1.06.

Despite the similar J-like trend observed in the paper [1] and current contribution, the values of $(E^{0\,'})_0$ and $B$, $C$ coefficient determined by us differ significantly from those reported. The probable reason is the differences in the electrode construction and materials used for electrodes manufacturing. However, it should be noted that in the range of the ionic strength values of 0.10-1.0 mol L$^{-1}$ the influence of I on E$^{0}$' is negligible. The same was observed earlier [1].

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# AMMONIUM – PHOSPHONIUM – ISOTHIURONIUM AMPHIPHILES: CMC, SOLUBILIZING CAPABILITY AND CATALYTIC EFFECT

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Surfactants can be considered universal building blocks for the nanocontainer formation. Furthermore, amphiphiles can act both as a basis of nanocontainers (micelles, microemulsions, vesicles, etc.) and as modifiers of nanocontainer properties (polymer-colloidal complexes, hybrid liposomes, organic-inorganic carriers, etc.). The surfactant head group is a key element determining the amphiphile properties. The chemical nature of the charged atom, the presence of cyclic fragments and additional centers for the formation of non-covalent interactions are just some of the main characteristics of the head group.

Our main scientific interest is in cationic surfactants due to their high potential in biomedical application. The purpose of this work is to study the homologous series of cationic surfactants in the line ammonium – phosphonium – isothiuronium amphiphiles. The main focus is on the study of aggregation, solubilization and catalytic properties of surfactants in individual aqueous solutions, as well as in the presence of polymers, nonionic amphiphiles, and hydrotropic additives.

An analysis of the surface tension isotherms made it possible to estimate the thermodynamic parameters at the water-air interface. The solubilization capacity of micellar nanocontainers toward the model hydrophobic substrate Orange OT and non-steroidal anti-inflammatory drugs was studied. Phosphonium surfactants were tested as catalysts for nucleophilic substitution reactions in phosphorus acid esters in individual solution and in mixed compositions with polymers and nonionic surfactants. The processing of kinetic dependences according to the pseudophase model of micellar catalysis made it possible to obtain the values of the binding constant of the substrate and nucleophile with aggregates, the rate constant in the micellar pseudophase, and the acceleration of reaction. At the final stage, the studied surfactants were used to modify the surface of liposomes in order to impart a positive charge and enhance their penetration through biological barriers, including the cell membrane, the blood-brain barrier, and the skin. The high efficiency of modified liposomes was proved by a complex of *in vitro, ex vivo* and *in vivo* experiments.

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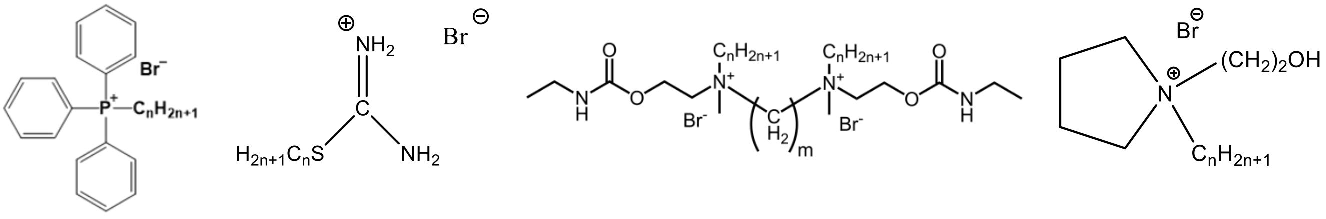

**Figure 1.** Chemical structures of compounds under study.

# NEW MACROCYCLIC AMPHIPHILES FOR SENSING AND GREEN MICELLAR&METAL/PHOTOCATALYSIS

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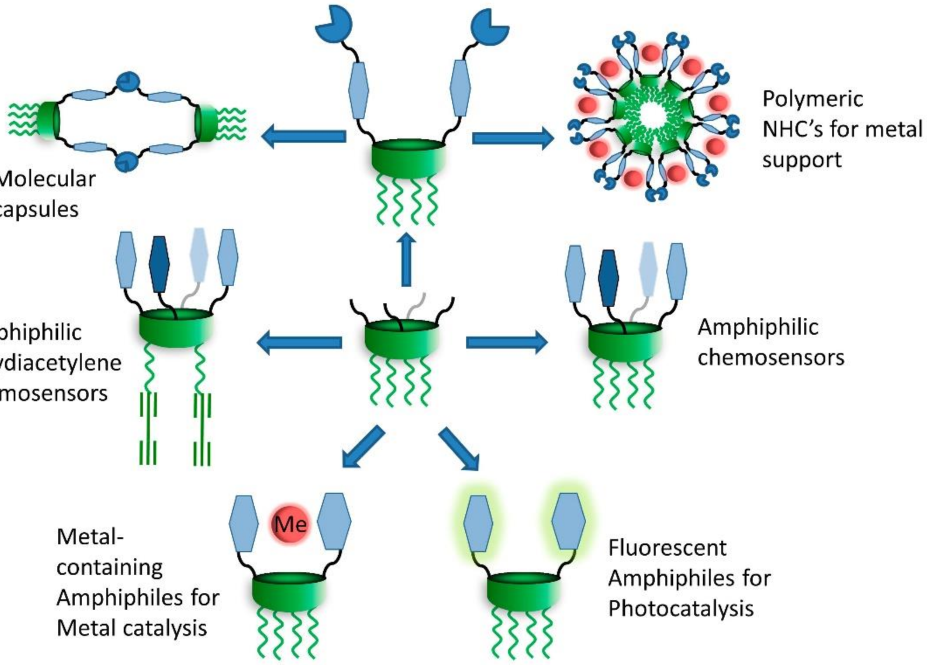
The formation of the nanoscale objects by the self-assembly of small molecules is an attractive strategy that brings with it the challenge of controlling the size and structure of the assemblies through interactions on the molecular scale. Design of new amphiphilic synthetic receptors with high affinity to specific guests attracts a great attention since its can be used in molecular recognition, drug delivery, catalysis, cell mimics, gene transfer and many other applications.

Herein we present synthesis of novel triazolyl p-tert-butyl(thia)calix[4]arene derivatives containing alkyl or dyinoic fragments at the lower rim synthesized using stepwise selective functionalization using Cu-catalyzed azide-alkyne cycloaddition. Obtained macrocycles were successfully used for recognition of biologically relevant molecules in water solutions giving signal through dye displasement or colorimetric response of polydiacetylene backbone.



Besides molecular recognition calixarene amphiphiles with imidazolium fragments are of great demand since they can be excellent precursors for metal – N-heterocyclic carbene complexes. The use of macrocycles with NHC chelate ligands opens great prospects for the production of new amphiphilic metal complex compounds combining both micellar and metal-centered catalysts. Empowerment of amphiphilic macrocycles with triple bonds and azide groups gives opportunity to form polymeric NHC carriers by sequential supramolecular self-assembly followed by cross-linking of macrocycles using CuAAC reaction as well as molecular capsules for sensing/metal chelating/catalysis. Introduction of the dye fragments into the amphiphilic core opens great prospects to use such systems for the photocatalytic organic transformations in aqueous media.

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# AGGREGATION OF CARBAMATE GEMINI SURFACTANTS AND THEIR POTENTIAL AS LIPOSOME MODIFIERS

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With a wide application range, surfactants are lately often used as liposome modifiers, that provide targeting, stability, impart membrane-penetrating properties. Nanoparticle zeta potential reflects their surface charge, which plays an important role when the liposomes are applied *in vitro* or *in vivo*. Cellular uptake, targeting, stability can be affected by adjusting the zeta potential of nanoparticles.

In this work, series of cationic carbamate gemini surfactants (fig. 1) were synthesized and analyzed from the aggregation standpoint. Tensiometry, conductometry, fluorimetry and spectrophotometry were used to derive aggregation thresholds, aggregation thermodynamic parameters, micellar polarity, solubilization capacity and other practically important surfactant properties.

Additionally, the carbamate gemini surfactants were used to modify phosphatidylcholine- and cholesterol-based liposomes. The addition of cationic surfactants to the lipid bilayer affects liposome zeta potential. Different surfactant molar ratios and tail lengths were screened to evaluate the dependence of surface charge using electrophoretic light scattering technique. Environmental conditions such as pH and ionic strength also affect the zeta potential. A comparison of the effects produced by cationic gemini surfactants and conventional cationic lipid dioleoyl-3-trimethylammonium propane (DOTAP) on liposome zeta potential in controlled pH and ionic strength conditions was carried out. Release profiles of a model dye rhodamine B were characterized using kinetic models.

**Acknowledgment:** This work was financially supported by Russian Science Foundation (project № 19-73-30012).

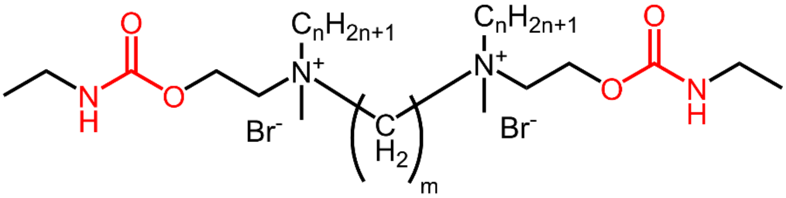

**Figure 1.** General structure of the carbamate gemini surfactants N,N’-dialkyl-N,N’-bis(2-(Ethylcarbamoyloxy)ethyl)-N,N’-dimethylalkane-1,n-diammonium bromides, n-s-n(Et).

# AMPHIPHILIC NHC PRECURSORS BASED ON IMIDAZOLE-4,5-DICARBOXYLIC ACID: SYNTHESIS AND AGGREGATION IN AQUEOUS MEDIA

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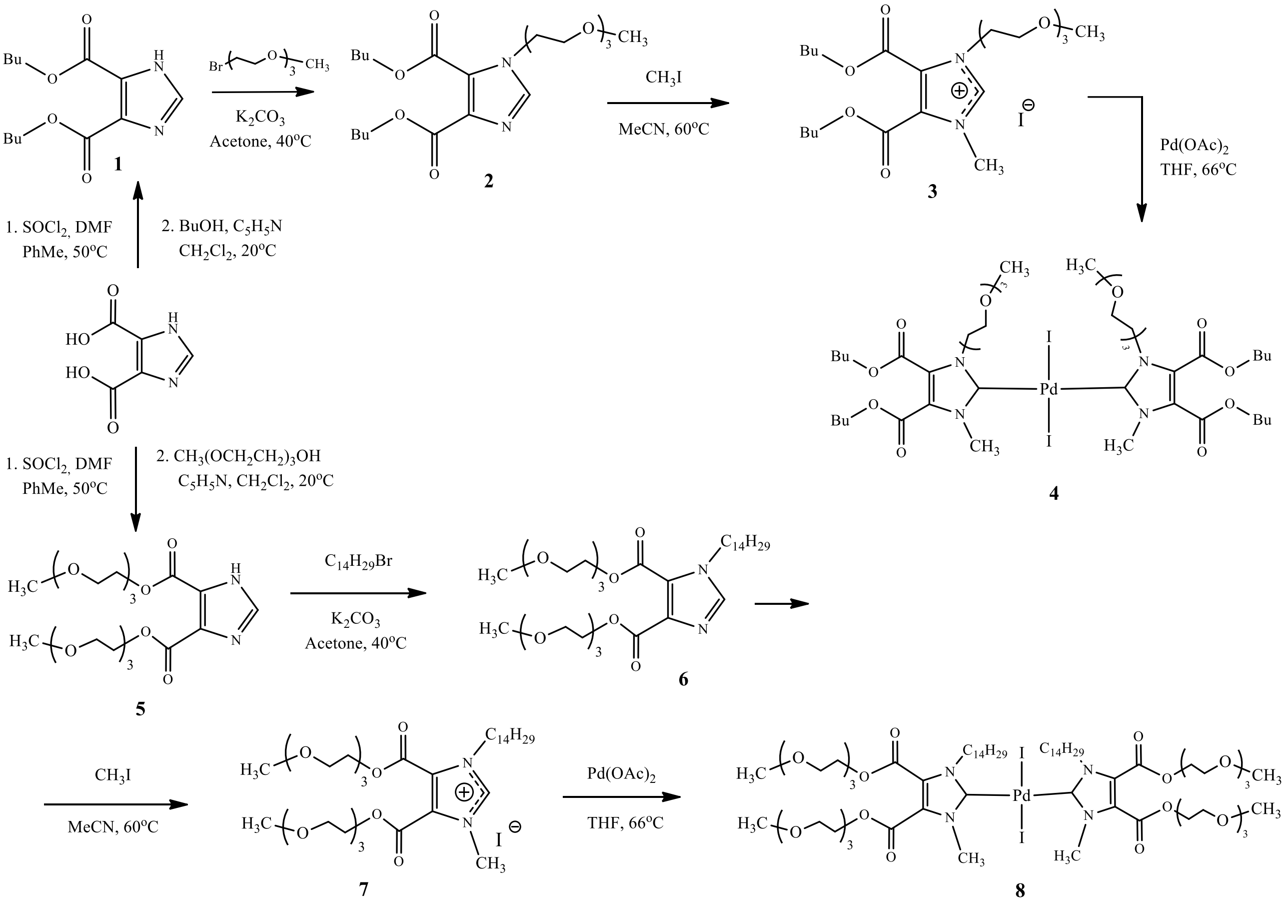
There is a growing interest to amphiphilic catalysts of cross-coupling reactions. Such catalysts allow carrying out cross-coupling reactions in water by forming emulsions. The structure of imidazole-4,5-dicarboxylic acid allows to obtain an amphiphilic catalyst bearing hydrophobic alkyl and hydrophilic triethyleneglycol substituents. The space separation of the hydrophilic and lipophilic area of the molecule is achieved with the help of the structural features of imidazole-4,5-dicarboxylic acid derivatives and the possibility to modify the carboxylic groups and imidazole nitrogen atoms seperately. Beside their hydrofilicity, triethyleneglycol groups also possess phase-transpher properties, wich can help to transfer the molecules of water-insoluble reagents into aqueous media.

Simple synthetic procedures allow to introduce triethyleneglycol substituents either nearby the carbene centre or at a distance from it. This possibility allows the NHC complexes **4** and **6** to form aggregates with different structure.

**Acknowledgment** The work was supported by a grant from the Russian Science Foundation № 22-13-00304



# SIMULATION OF SURFACTANT ADSORPTION AT LIQUID-LIQUID INTERFACE: WHAT WE MAY EXPECT FROM HARD AND SOFT-CORE MODELS?

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The performance of a surfactant in a particular technology is determined by the $c$-Γ-γ relationship, that is, the interdependence between the bulk concentration $c$, adsorption Γ and the interfacial tension γ. The presentation addresses a well-known discontent between experimental measurements that yields γ($c$) (typically at higher $c$, Γ unknown) and simulations that allow the calculations of γ(Γ) ($c$ is difficult to determine). We attempt to create a consistent picture of surfactant behavior by interpreting the simulation and experimental results with the Redlich-Peterson model, which is thermodynamically consistent and flexible. First, we study alkyl ether carboxylate surfactants ($C_nH_{2n+1}O(CH_2CH_2O)_mCH_2COO^-Na^+$) at decane – water interface, --experimentally with the spinning drop method and with atomistic molecular dynamics simulations. The simulations showed only semiquantitative agreement with the experiments: surfactants interfacial concentrations corresponding to a particular value of tension are systematically higher than the values derived from the experiments. Simulations of surfactants with different lengths of the alkyl tail $n$ and EO segments $m$ revealed general tendencies related to the surfactants interactions in the layer. The ethylene oxide segment elongation decreases the monolayer density and increases the effective elasticity at $m$<8, have almost no influence at $m$>8, which we explain by the interplay of electrostatic and steric interactions between the heads.

Next, we employ dissipative particle dynamics with soft-core forcefield tested against experimental data on micellization of surfactants in water. Three nonionic surfactants are considered: $C_{12}(EO)_6$), Triton X100, and two alkyl glucoside surfactants ($C_{10}G_1$ and $C_{12}G_1$). The head-head interactions are of different origins for different surfactant groups. The densities of the adsorbed monolayer at CMC mostly agree with the experimental data, and a reasonable agreement was obtained for the interfacial tension at CMC. At the same time, we found significant discrepancies between the simulated and experimental adsorption isotherms. We explain them by the oversimplified forcefield: when the parameters are fitted to the free energies of bulk solutions, they may not correctly reproduce the interfacial free energies.

**Acknowledgements** We thank Min Sci.& High.Ed. for financial support (grant 075-10-2020-119)

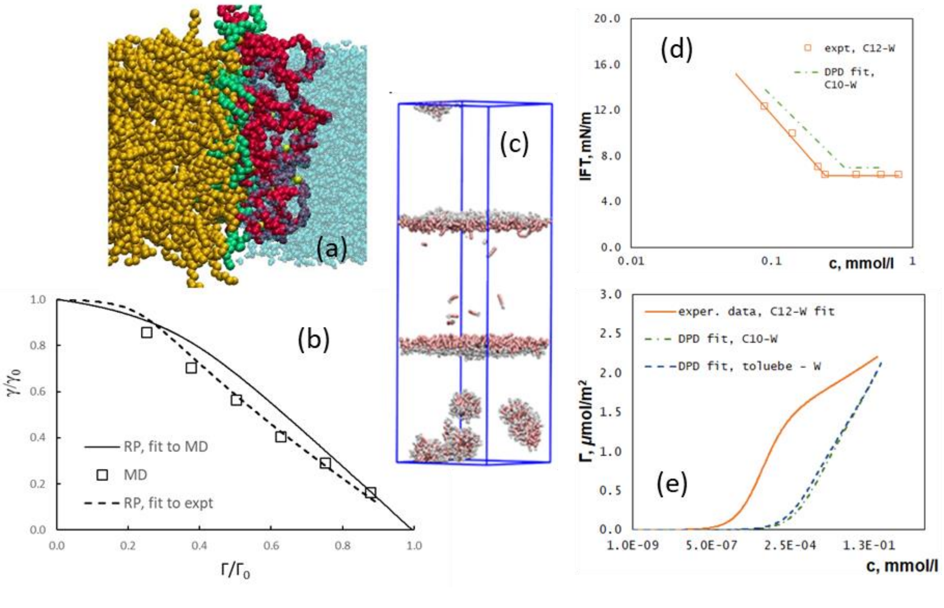

Fig.1. (a) $C_{11}E_{11}A$ surfactant at C10-H2O interface (b) experimental vs simulated γ(Γ) for that system (note the scaling!) (c) DPD simulation of $C_{12}G_1$ surfactant at C10-$H_2O$ interface (d,e) adsorption isotherms for the same system obtained from fit of RP equation to the experimental and DPD data γ($c$) and Γ($c$)

# HYDRATION EFFECT ON ENCAPSULATION OF INDOMETACIN BY SOLID CYCLODEXTRINS

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Water plays an important role in the successful preparation of cyclodextrin (CD) inclusion complexes with drugs, what is required to increase their bioavailability. The ratio of activating and competing roles of water affects the efficiency of guest inclusion in solid systems with different CDs. For example, the competing role of water is dominant for guest inclusion by α-CD [1, 2], what can be a reason for the smaller scale of its practical application compared to β-CD. Hydration activates the encapsulation of hydrophobic guests by β-CD [3], and optimization of the hydration level is required for guests with medium hydrophobicity, since excess or lack of water limits their inclusion [3].

In this work, we studied the effect of hydration on the inclusion properties of γ-CD for volatile organic guests and a solid model compound – indomethacin, using static headspace gas chromatography, TG/DSC/MS analysis, X-ray powder diffractometry and IR spectrometry. The obtained data were compared with similar results of previous studies for α-CD and β-CD [1-3]. The ratio of competing and activating roles of water was determined depending on the size of the native CD macrocycle and the molecular structure of a guest.

Inclusion of the model drug indomethacin by native CDs made it possible to evaluate the hydration effect on preparation of inclusion compounds by the ball milling method. The efficiency of indomethacin encapsulation by γ-CD and β-CD under these conditions significantly depends on their hydration. The obtained results may be useful in the development of technological processes for the encapsulation of drugs.

**Acknowledgements:** The reported study was funded by RFBR, project number 20-31-70001.

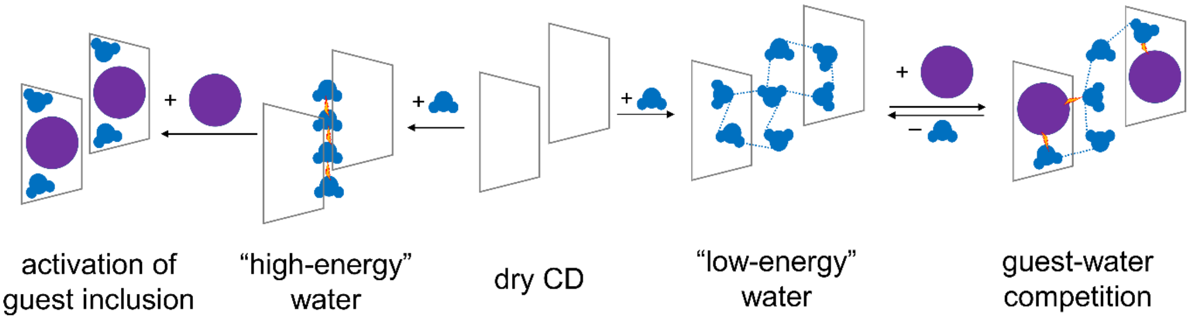

**Figure 1.** Activating and competing roles of water in guest encapsulation

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# FORMATION OF MIXED DNA/POLYELECTROLYTE LAYERS AT THE WATER–AIR INTERFACE

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In spite of the growing interest to the formation of ordered 2D nanostructures from double-stranded DNA at various interfaces, underlying intermolecular interactions still require elucidation. It has recently been revealed that a 2D network of threadlike or fibrous aggregates is formed at the solution-air interface of mixtures of DNA and hydrophobic cationic polyelectrolytes. The absence of toroidal DNA/polyelectrolyte aggregates, which are commonly found in the solution bulk, at the solution-air interface led us to assume that the formation of threadlike aggregates is localized at the interface. Spreading hydrophobic polyelectrolyte at the surface of buffer solution and injecting DNA into the bulk allows one to test this assumption as well as obtain additional information regarding the formation mechanism of fibrous DNA/polyelectolyte aggregates at the interface.

In the present work we investigate the penetration of DNA into the spread monolayer of hydrophobic cationic polyelectrolyte - poly(N,N-diallyl-N-hexyl-Nmethylammonium) chloride (PDAHMAC). A suite of techniques – rheology, microscopy, ellipsometry, and spectroscopy – are applied to gain insight into the main steps of the adsorption layer formation, accompanied by non-monotonic kinetics of various surface properties. The change in surface properties after the addition of DNA is preceded by a long induction period only if the initial surface pressure of the PDAHMAC monolayer corresponds to a quasiplateau region of the PDAHMAC monolayer compression isotherm. A decrease in the initial surface pressure leads to a disappearance of the induction period. This observation can be accounted for by the steric hindrances, which hamper the interaction between DNA and PDAHMAC when the monolayer is compressed. However, the micromorphology of mixed DNA/PDAHMAC film does not depend noticeably on the initial surface pressure of the PDAHMAC film. The obtained results provide a new perspective on the nanostructure formation involving nucleic acids building blocks, which is important in the design of gene delivery vehicles and electronic devices.

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# THE IMPACT OF THROMBINE ON DYNAMIC SURFACE PROPERTIES OF FIBRINOGEN SOLUTIONS

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The interaction of fibrinogen and thrombin plays a key role in blood clotting process. The formation fibrin clot is a subject of numerous studies [1,2]. However, the formation of fibrin film on air-water interface attracts less attention [3], despite the fact that it prevents blood bleeding and wound infection [4]. The dynamic surface elasticity and dynamic surface tension was measured by the oscillation ring method as function of surface age and components' concentration. The dynamic surface tension proved to be almost insensitive to the changes of surface layer structure. It remains close to the results for pure fibrinogen. Unlike surface tension kinetic dependencies of the dynamic surface elasticity show a significant difference from pure protein solutions. With the increase of the ferment concentration and at protein concentrations higher than $1*10^{-7}$ the dependences first become nonmonotonic and then demonstrate significant increase of the dynamic surface elasticity. It could be assumed that different surface elasticity values correspond to different steps of adsorption and fibrinogen-fibrin transition. First, the fibrinogen reaches the interface – the dynamic surface elasticity increases up to the values for pure protein solutions (about 55 mN/m). Then the interaction of fibrinogen with thrombin leads to the unfolding of fibrinogen – elasticity drops to 25 mN/m due to the displacement of some segments of unfolded molecule to the distal region of the surface layer. Thirdly, the fibrin monomers arrange into long threadlike aggregates and dynamic surface elasticity increases. With the increase of ferment concentration, the number of surface aggregates and their morphology change. At relatively low concentrations of thrombin (25-100 UN/l) the surface elasticity increases up to 80 mN/m. When the thrombin concentration approaches 300 UN/l the dynamic surface elasticity become two times higher than for pure protein solutions. Such behavior is consistent with the previous results for dispersions of fibril aggregates of globular proteins.

Ellipsometry, atomic force microscopy (AFM) and Brewster angle microscopy were applied to the system under study in order to simplify interpretation of the dynamic surface elasticity data. The kinetic dependences of the ellipsomeric angle $\Delta$, which is proportional to the adsorption value, show that addition of thrombin leads to a slight increase of $\Delta$. However, the dependences for mixed solutions are close to each other regardless the ferment concentration. The images obtained by Brewster angle microscopy show that the extended fibrin film is not formed until the thrombin concentration reaches 100 UN/l. The presence of fibrin film become evident after applying a mechanical disturbance. One can see the light regions corresponding to film and the dark regions corresponding to water. More detailed information on the film morphology can be obtained by AFM. The obtained results support the assumptions made from the analysis of the kinetic dependences of the dynamic surface elasticity. One can see the step-by-step transition from individual long and relatively rare fibril aggregates to wide branching ribbons and finally to a continuous film.

**Acknowledgements** The work was financially supported by the Grants of the President of RF (MK-2176.2021.1.3)

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# INFLUENCE OF ORGANIC SOLVENTS ON THERMAL STABILITY AND DENATURATION MECHANISM OF LYSOZYME

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Aqueous-organic solvents have several advantages in comparison with water as media for enzyme-catalyzed reactions. However, it is necessary to keep the enzyme in the native state during the reaction. Therefore, it is important to know how the nature and concentration of the cosolvent affects the stability of proteins.

In the work, we have studied the thermal stability of hen egg-white lysozyme in the mixtures of water with common organic solvents (acetone, acetonitrile, dimethyl formamide, dimethyl sulfoxide, 1,4-dioxane, tetrahydrofuran, methanol, isopropanol, tert-butanol) using capillary differential scanning calorimetry (DSC). The protein concentration in the experiments was 1 mg/ml, the scan rate varied in the range 0.5 – 2 K/min. Additionally, the circular dichroism (CD) signal of lysozyme at 290 nm was followed in the temperature range 10-90 °C at the heating rate 0.5 K/min.

In all the studied systems, addition of the organic cosolvent leads to a decrease in the denaturation temperature of lysozyme. For the mixtures with the same mole fraction of cosolvent, the denaturation temperature decreases in the following order: dimethylsulfoxide (weakest denaturant) > methanol > acetonitrile, dimethylformamide > acetone > isopropanol, 1,4-dioxane > tert-butanol > tetrahydrofuran (strongest denaturant). This series correlates with the effect of the organic solvent on solvation process of non-polar solutes.

In the presence of organic cosolvents, the temperature of disruption of the tertiary structure of lysozyme determined from the near-UV CD experiments is lower than its temperature of denaturation in DSC experiments. It can be suggested that increasing concentration of the organic cosolvent favors formation of a partially unfolded state with disrupted tertiary structure and mostly preserved secondary structure. In addition, denaturation of lysozyme in mixtures of water with various solvents is preceded by a state with an increased fraction of α-helices.

# FILMS OF LYSOZYME FIBRILLAR AGGREGATES ON THE WATER SURFACE

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In aqueous lysozyme solutions the formation of aggregates of various shapes and sizes in particular amyloid fibrils is possible with a change in pH and temperature. Despite the significant surface activity of lysozyme fibrils and their use to stabilize foams and emulsions in various industries, information about the properties of adsorbed and spread films of lysozyme fibrillar aggregates on the water surface is extremely limited.

In this study, the methods of surface rheology are applied to adsorbed and spread films of fibrillar lysozyme aggregates on the water surface at different ionic strength and pH of the subphase to estimate the mechanism of formation of these films. Atomic force microscopy and Brewster angle microscopy were used to determine the films morphology. It is shown that the properties of lysozyme fibrillar films differ markedly from the properties of native protein films. After spreading a concentrated solution of lysozyme fibrils onto the water surface, it was possible to obtain higher values of surface pressure and dynamic surface elasticity compared to the values for native protein films. Differences in the surface properties of adsorption films of fibrils and native protein are less significant. Based on the data obtained, a model of the film of lysozyme fibrillar aggregates on the water surface is proposed.

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# HELMHOLTZ ENERGY: IS IT ENERGY OR NOT?

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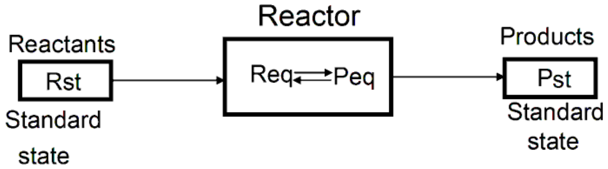
**Properties of the Helmholtz function.** It is generally accepted that the Helmholtz energy is energy, and the work in a reversible isothermal process is done at the expense of the Helmholtz energy. The expression for the Helmholtz energy follows easily from the first law $A = U - TS$. It can be generally accepted that A is the part of the internal energy of the system responsible for doing work:
$U = A + TS$. A perplexed question immediately arises - how can $U$ be divided into two nonequivalent parts. In the case of reversible isothermal process $w = \Delta U - T\Delta S = \Delta(U - TS) = \Delta A$. This implies that the work is equal to the change in the Helmholtz energy (no doubts), but that the work done is due to the Helmholtz energy needs additional proof, although at first glance it seems that the work was really done at the expense of Helmholtz's energy. If $A$ is an energy, then the term $TS$ must also be an energy. Due to P. Atkins the member $TS$ must be a carrier of thermal energy, but it's not true.
Consider, for example, helium atoms. The atoms in helium gas has only the energy of thermal (kinetic) motion, but, for example, at heating $\Delta U \neq T\Delta S$
**Helmholtz energy cannot produce work.** Let us consider the process of reversible isothermal transformation of reactants into products under the conditions of a chemical reaction.



**Stage 1**. In the isothermal and reversible process, we transfer the reactants from the standard state to the state in which they are in equilibrium with the products in the reactor but without introducing reactants into the reactor. In this case, work is done equal to the change in the Helmholtz energy. $W_1$(R) = $\Delta A$ (Req) - $\Delta A$(Rst), but what is real source of energy for work production? The reaction has not yet taken place since the reactants were not introduced into the reactor. This source of energy can only be the internal energy of the surroundings, which is transferred to the system through heat to perform work for reactants transportation.
**Stage 2**. Introduction of reactants into the reactor. The work is zero due to the equality of the chemical potentials of the reactants outside and inside the reactor. $W_2 = 0$
**Stage 3**. Chemical reaction in reactor. The work is zero due to the equilibrium. $W_3 = 0$
**Stage 4**. Transfer of products from the reactor to the standard state. The work is done by the heat of the surroundings, but not by the Helmholtz energy. $W_4$(R) = $\Delta A$ (Pst) - $\Delta A$(Peq).
Hence: w = $w_1 + w_4$ = $\Delta A$(products) – $\Delta A$( reactants) = $\Delta U$ (surroundings).Thus, work is not done at the expense of the Helmholtz function, and this once again proves that the Helmholtz function is not energy. The Helmholtz energy only allows the calculation of the transferred energy. CONCLUSION: (1) Helmholtz energy is not energy; (2) Helmholtz energy does not produce work; (3) the Helmholtz energy serves only for calculations of the transferred energy; (4) the work of chemical systems is produced only by heat of the surroundings; (5) reaction energy does not use for work production and in the form of heat is transferred to the ssurroundings; (6) reversible work is produced from the heat of the surroundings, and the heat of reaction can be used to heat other devices. Therefore, we can obtain double energy due to two different sources of energy: heat of reaction and heat of the surroundings; (7) the Helmholtz energy is better called the Helmholtz function.

# EVALUATION OF THE BINDING PROPERTIES OF DRUGS TO ALBUMIN FROM DSC THERMOGRAMS

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Thermodynamic protein-ligand binding constants can be determined by different experimental techniques including spectroscopic, calorimetric, chromatographic, electrochemical. All experimental methods have numerous limitations and in many cases provide unreliable results. Differential scanning calorimetry (DSC) is a common method for studying thermal stability of proteins and other biomacromolecules. Its main advantage is a good reproducibility of protein denaturation profiles and the denaturation peak maximum temperature. DSC is also used often to identify ligand binding from denaturation peak shift, but the attempts to extract the binding constant values from DSC data are limited to a few works.

In the present work, the DSC technique is used to study binding of nine drug molecules with different affinity to bovine serum albumin (BSA). The denaturation curves in the presence the various amounts of these ligands were obtained. Strong BSA binders significantly change in denaturation temperature and enthalpy. The magnitude of changes can be related to the binding affinity at the temperature of denaturation. We fitted the temperature of the peak maximum and the peak area to a two-state model of denaturation and determined the first and second sequential protein-ligand binding constants as well as the number of drug molecules binding to BSA at high excess of ligand.

The obtained values are shown to be in agreement with the data from previous studies using different experimental methods. The results show the potential of the DSC method as a tool to obtain the reliable values of protein-ligand binding constants including the second binding constant.

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# STEP-SCAN DIFFERENTIAL SCANNING CALORIMETRY FOR INVESTIGATION OF PROTEIN DENATURATION

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Differential scanning calorimetry with temperature modulation (TMDSC) is a development of the DSC technique in which the scanning rate is set by some periodic function. TMDSC allows the evaluation of reversible and irreversible contributions of the total heatflow independently.

The temperature profile of the step-scan method consists of repeating segments consisting of short heating or cooling, followed by isotherms. At each new step the system is taken out of equilibrium then settles into a new equilibrium state during the isotherm.

There are few literature examples of TMDSC application for protein denaturation studies [1, 2], whereas step-scan method was used only once in protein research [3]. Thus the present work was aimed at analysis of theoretical denaturation curves in step-scan regime, getting the experimental curves of lysozyme denaturation in water, DMSO-water, and glycerol mixtures with capillary DSC device and fast scanning calorimeter. Complex heat capacity and its real and imaginary contributions were calculated for lysozyme denaturation process. Negative temperature coefficient of the excess heat capacity was detected. The ability of TMDSC technique to improve the resolution and the baseline quality of the calorimetric curves was demonstrated.

**Acknowledgements** The financial support of RFBR №20-34-90140.

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# MONOETHANOLAMINE HYDRATION AS SEEN BY DIELECTRIC RELAXATION SPECTROSCOPY AND QUANTUM CHEMICAL CALCULATIONS

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Due to the well-developed infrastructure and relatively low mining cost gas and other fossil fuels sustain the leading position on the power sources market. As a consequence, it is anticipated that the annual anthropogenic emission of greenhouse gases into the atmosphere will constantly increase. Although in the past decades carbon capture, utilization, and storage technologies have been intensively developed, the conventional technology of wet absorption by amines and their aqueous solutions is still widely used for capturing $CO_2$.

In the present work, we studied dielectric properties of one of the most widely used $CO_2$ absorbants, monoethanolamine (MEA), and its mixtures with water covering an entire miscibility range and frequencies from 50 MHz to 89 GHz at $T$ = 298.15 K. When evaluating the present data we noticed (see Figure 1a) that for MEA/water their excess static permittivities, $\varepsilon_s^{\mathrm{E}}$, and excess molar volumes, $V_{\mathrm{m}}^{\mathrm{E}}$, have the same shape. This observation suggests that for the static permittivity of these mixtures packing effects largely dominate, whereas persistent dipole-dipole correlations appear to be negligible. Indeed, the dielectric spectra can be best fit as a superposition of the relaxations arising from reorientations of MEA-associated dipoles, slow water molecules surrounding the solute and bulk (rather unperturbed) water, see Figure 1b. The spectra treatment reveals that although a MEA molecule rather strongly interacts with ~4 $H_2O$ (slowed-down) molecules their rotation is only partly synchronized. This conclusion is also supported by the detailed analysis of the solute amplitudes and relaxation times and by thermodynamics of the step-by-step MEA hydration obtained with a help of quantum chemical calculations.

**Acknowledgements** The present research was funded by the Russian ScienceFoundation (project no. 22-23-00913).

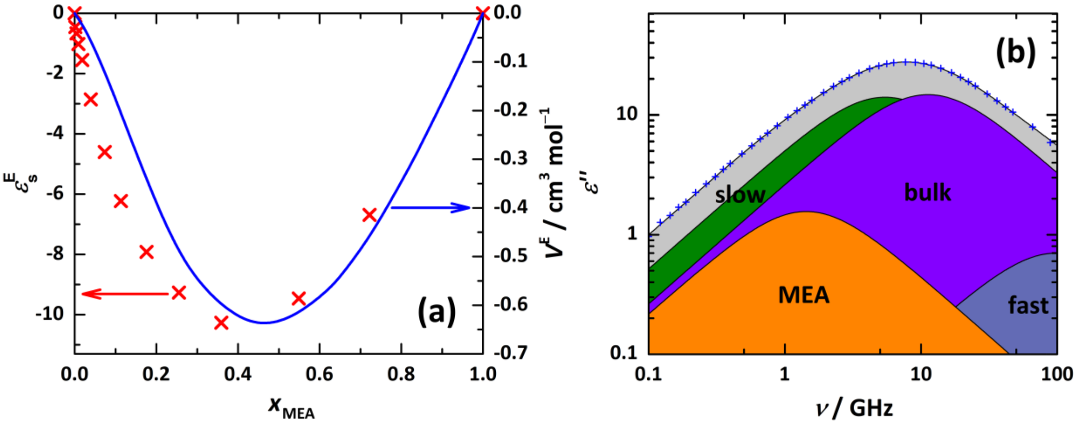

**Figure 1.** (a) Excess molar volume ($V_{\mathrm{m}}^{\mathrm{E}}$, blue line) and excess static permittivity ($\varepsilon_s^{\mathrm{E}}$, red crosses) as a function of MEA mole fraction, $x_{\mathrm{MEA}}$, at $T$ = 298.15 K. Arrows address the data to appropriate axes. (b) Dielectric spectra decomposition obtained with the 4 Debye model for the solution of 30% MEA in water ($c_{\mathrm{MEA}}$ = 5.000 M).

# COMPARISON OF DIFFERENT COMPUTATIONAL TECHNIQUES FOR EVALUATION OF QUERCITIN CONFORMERS

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In computational chemistry, forcefields (FF) are aimed to calculate the energies and geometries of chemical systems without the direct treatment of electrons, using so called “ball and springs” concept. Ab-initio (or quantum mechanical (QM)) methods solve approximate forms of the electronic Schrodinger wave equation for a chemical system, considering the electrons as individual wave particles. Semi-empirical (SE) methods contain simplifications of most resource costly steps in QM methods, preserving (as supposed) QM accuracy together with MM speed.[1] All methods are of extreme importance for different fields of chemistry, including drug design, where calculations of geometries and energies is a key step for “in-silico” process.[2] Wrong identification of conformers and their energies may result in false elucidation or wrong acceptance of potential drug candidates. Thus, comparison and error margins identification of different computational methods is highly recommended at least on some chemical molecules.

In this work we choose the product of the quercetin glycosylation as a model system for comparison of different computational techniques. Several FF, SE, and QM (DFT) methods were chosen to compare them within method as well as across different computational concepts.

Quercetin is a natural flavanol which contains five -OH groups which may interact with another five -OH groups of glucose, resulting in 25 combinations of the reaction product. Considering possible alpha and beta anomer products, this results in constructing 50 chemical systems, each of which contains at least several conformers. Two hundred conformers were generated for every possible product, further reduced to one – most preferable from thermodynamic point of view. Energies of every conformer were calculated using several FF methods and two SE (PM6-D3H4 and PM7) methods. DFT calculations were performed over most stable conformers evaluated by other methods to confirm stability rate of possible reaction products.

This work shows cons and pros of different methods and shed light on future development of computational techniques for evaluation of molecular conformers geometries and energies.

**Acknowledgements:** Financial support of RSF 21-13-00046 grant is acknowledged as well as computational resources of NSU (http://nusc.nsu.ru/) and SSCC (http://www.sscc.icmmg.nsc.ru/).

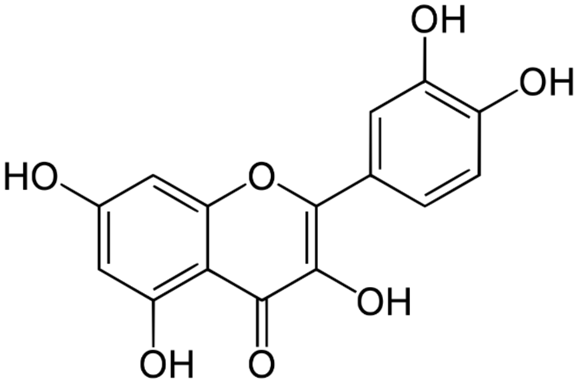

**Figure 1.** Structural formula of quercetin.

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# A NEW APPROACH TO THE CALCULATION OF SOLVATION EFFECTS IN BIOMOLECULAR SOLUTIONS IN THE FRAMEWORK OF THE CLASSICAL DENSITY FUNCTIONAL THEORY

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In the pharmaceutics an estimation of the binding affinity of a ligand (pharmaceutical drug) to a target protein plays a key role for virtual screening since this affinity reflects stability of the formed complex. This is important since a ligand with a higher protein affinity is known to provide a therapeutic effect at a lower concentration. One of the grand challenges for computational chemistry is to estimate the binding affinity (binding constant) of a ligand (L) to a protein (P), i.e., the P–L binding free energy (BFE). To date, there is a large set of non-empirical methodologies for estimating BFE such as virtual screening, end-point approaches, alchemical and pathway methods, etc. If one moves from virtual screening to pathway approaches in this set, an accuracy of BFE calculation increases but their costs also increase. Therefore, despite the abundance of computational methods, the fast and simultaneously inexpensive prediction of P−L BFE with high accuracy (1-2 kcal/mol) remains as one of the grand challenges of computational chemistry.

When calculating the P−L BFE, it is necessary to take into account the free energy of solvation/desolvation (FES) which can make a significant contribution to the BFE. The calculation accuracy of FES directly determines the calculation accuracy of BFE. Computer simulations using the techniques mentioned above are applied for calculating the required solvation term in the binding energy of the PL complex but have the same problem to calculate the BFE quickly and accurately.

In this contribution we present two new ideas on how to increase the efficiency and accuracy of SFE calculations by the statistical mechanics methods in the framework of theory of liquids such as 3D-reference interaction site model (3D-RISM) and renormalized site density functional theory (RSDFT) approaches. The first is realized by calculating the parameters of complex formation of biomolecules in a limited region of their hydration shell to increase the speed of calculations. The second is based on new parameterization of the solvation (hydration) free energy functional to improve the accuracy of calculations. The development of a new approach provides new opportunities for in silico studies of the solvation effects in solutions.

**Acknowledgements** This work was supported by the Russian Science Foundation (project No. 22-23-00184, https://rscf.ru/en/project/22-23-00184/).

# QUANTUM CHEMICAL STUDY OF THE INTERATOMIC INTERACTION OF DIATOMIC ARGIDES

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Argon is often used as a buffer gas for the inductively coupled plasma mass spectrometry (ICP-MS). However, given the high density of argon in the ICP-MS experiments, it can interact with the other plasma components forming argides. Even a small fraction of argide can significantly affect the mass spectra obtained due to its signal overlapping with the ones coming from the studied substances [1].

To quantify the prevalence of argides in plasma, thermodynamic data are needed. In this report we focus on diatomic argon compounds. The calculation of the thermodynamic functions is based typically on molecular constants obtained experimentally. In the case of argides due to low dissociation energy the experimental data is hard to obtain, therefore ab initio calculations become an alternative.

The calculation technique based on the interatomic potentials obtained from the quantum chemistry methods is presented in [2,3]. Here we report on the results for quantum chemistry calculations of $ArN^+$ and ArN interatomic potentials for the low-lying electronic states (figure 1). The MRCI (multireference configuration interaction) method has been employed including spin–orbit interaction. Using the interatomic potentials, the Shrödinger equation has been solved numerically to get the rovibronic partition function. Finally, the thermodynamic properties have been obtained for the ArN and ArN+ species in the gas phase. Computational errors are estimated.

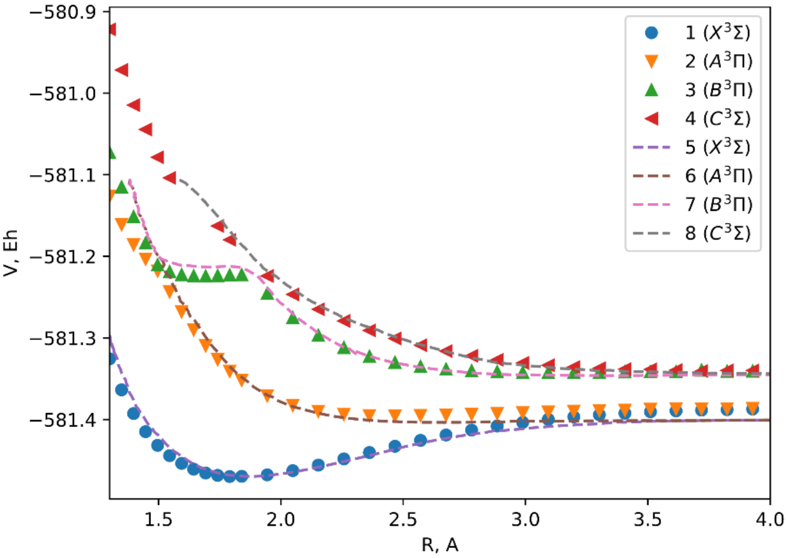

**Figure 1.** Low-lying triplet electronic states of $ArN^+$.

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# PRESSURE-TEMPERATURE PHASE DIAGRAMS NEAR THE TRIPLE POINT OF FOUR BENZALDEHYDES

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This work presents a thermodynamic study of the phase transition equilibria of four benzaldehydes. The vapor pressures of both crystalline and liquid phases (including supercooled liquid) of syringaldehyde, 3,4,5-trimethoxybenzaldehyde, 4-(dimethylamino)benzaldehyde and of the liquid phase of veratraldehyde were determined using a diaphragm manometer static method [1]. Besides, the sublimation vapor pressures of the compounds were also measured using a Knudsen mass-loss effusion method [2]. The standard molar enthalpies, entropies and Gibbs energies of sublimation and of vaporization of the four benzaldehydes were derived from the experimental results and the phase diagrams representation of the ($p$,$T$) results, in the neighborhood of the triple points, were built. The thermal analysis of the compounds studied was also performed using differential scanning calorimetry. The enthalpy of the O−H⋯O intermolecular hydrogen bonds formed in the crystals of syringaldehyde was determined and new contributions of the formyl group to the values of sublimation properties of benzaldehydes are proposed.

**Acknowledgements** This work was supported by the Fundacão para a Ciência e Tecnologia (FCT) (funded by national funds through the FCT/MCTES (PIDDAC)) to CIQUP, Faculty of Sciences, University of Porto (Project UIDB/00081/2020) and IMS-Institute of Molecular Sciences (LA/P/0056/2020)). A.R.R.P.A. is financed by national funds through the FCT-I.P., in the framework of the execution of the program contract provided in paragraphs 4, 5 and 6 of art. 23 of Law no. 57/2016 of 29 August, as amended by Law no. 57/2017 of 19 July. B.D.A.P. also thanks FCT for the award of a PhD research grant (UIDP/00081/2020_RG2).

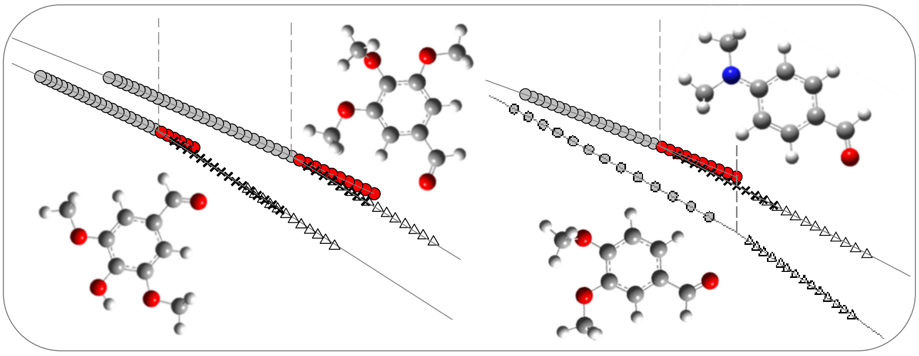

**Figure 1.** Phase diagrams representation of the ($p$,$T$) results, in the neighborhood of the triple points of syringaldehyde, veratraldehyde, 3,4,5-trimethoxybenzaldehyde and 4-(dimethylamino)benzaldehyde.

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# HEAT EFFECTS OF PHASE AND CHEMICAL PROCESSES IN A MULTICOMPONENT SYSTEM WITH CHEMICAL INTERACTION

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The study of thermochemical behavior of reacting systems in the chemical equilibrium is an important task from both basic and applied point of view. Correct thermochemical data in the case of simultaneous phase and chemical processes are of particular importance for chemical technology and fundamental problems of thermodynamics: the problems of separating the thermal effects of mixing and chemical reactions are non-trivial. A fairly limited number of modern studies are devoted to these complex problems, although experimental information on the thermochemical characteristics of multicomponent systems with chemical interaction is necessary not only for the development of appropriate databases, but also for understanding the nature of the processes.

In work detailed experimental data on excess enthalpies in binary systems acetic acid - ethyl alcohol, ethyl alcohol - water, acetic acid - ethyl acetate, acetic acid - water at 313.15 K were obtained [1]. Data on the heats of mixing in the quaternary system acetic acid - ethanol - ethyl acetate - water 313.15 K were obtained (Fig. 1). Data on the chemical equilibrium in the system with the reaction of ethyl acetate synthesis at 313.15 K [2] were obtained (Fig. 2). There were obtained data on the heat of reaction for the synthesis of ethyl acetate at 313.15 K using the developed technique that allows to take into account the totality of thermal effects accompanying the mixing and synthesis process.

**Acknowledgements** Authors are grateful for the financial support of the Russian Science Foundation (grant 21-13-00038).

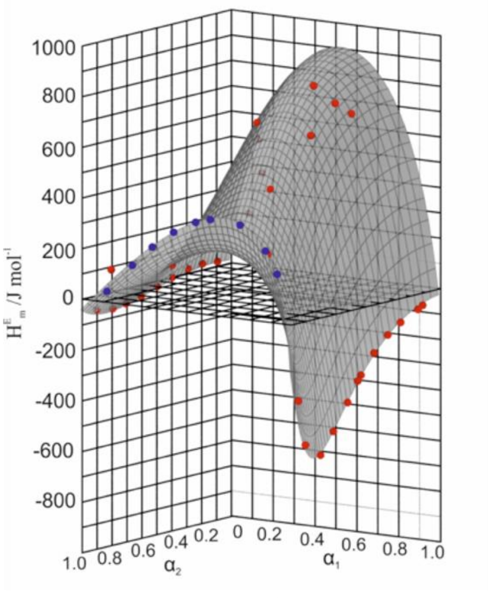

**Figure 1.** Dependence of the excess enthalpy of the quaternary system on the chemical equilibrium compositions represented in the transformed α-variables.

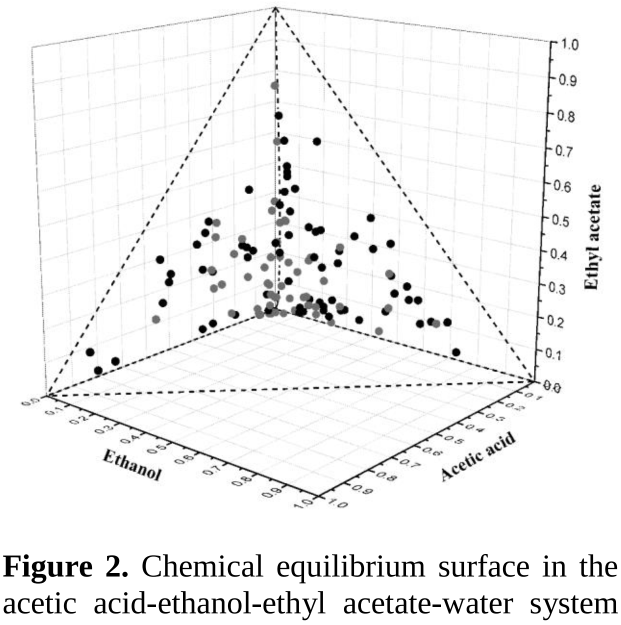

**Figure 2.** Chemical equilibrium surface in the acetic acid-ethanol-ethyl acetate-water system at 323.15 K: composition points determined by gas chromatography ● and NMR ●

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# EXPERIMENTAL STUDY AND CALPHAD MODELING OF THE AG-IN-PD TERNARY

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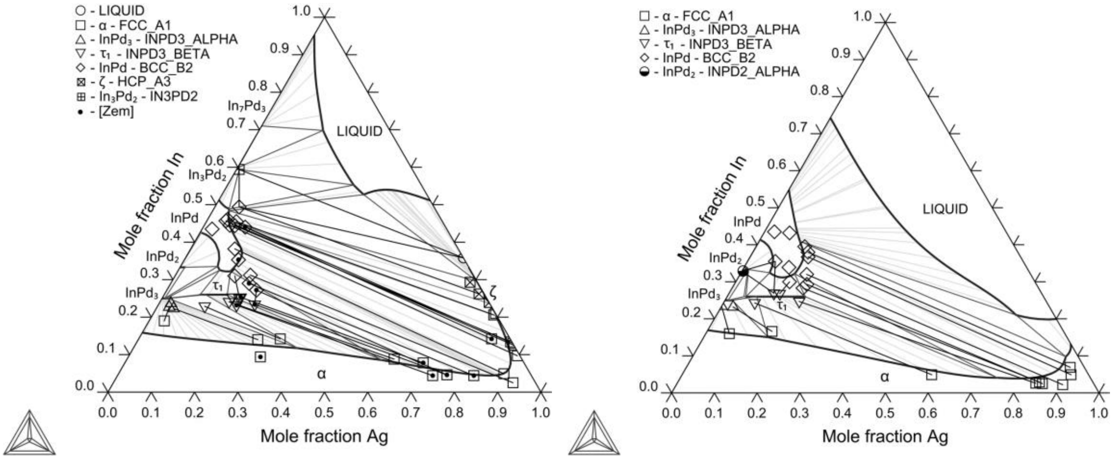
Palladium-based alloys are widely used in various industries: chemical, electrical, automotive, hydrogen energy and medicine. The most usual components of palladium alloys are coinage metals, as well as non-transitional low-melting elements like indium or tin [1].

The aims of this work were experimental investigation and thermodynamic modeling of phase equilibria in the Ag-In-Pd ternary.

Experimental study of phase equilibria was performed by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) and X-ray diffraction (XRD). Several samples were studied also by DTA/DSC. The solubilities of the third components in binary phases has been established. The ternary compound $\tau_1$ exists at about 25 at. % In from 4 to approx. 17.5 at. % Ag. Tetragonal crystal structure with $Al_3Ti$ prototype has been proposed for that phase.

New thermodynamic calculation of the Ag–In–Pd system was performed basing on both published and obtained in this work experimental results. For the Ag-In, Ag-Pd, and In-Pd binaries published thermodynamic descriptions [2-4] were accepted. Good agreement with the experimental data was achieved for both phase equilibria and thermodynamic properties of the phases. The correctness of the obtained description is additionally confirmed by the good convergence of the calculation results with the DSC/DTA results. Calculated isothermal sections of the Ag–In–Pd system at 500 and 800°C in comparison with the experimental data obtained in this study are presented on Fig. 1.

**Acknowledgements** This study was supported by the Russian Science Foundation, project number 22-23-00565, https://rscf.ru/en/project/22-23-00565/



(a) (b)

**Figure 1.** Calculated isothermal sections of the Ag–In–Pd system at 500°C (a) and 800°C (b) in comparison with the experimental data obtained in this study.

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# THERMODYNAMIC FEATURES OF ENANTIOMER ADSORPTION ON THE SURFACES WITH SUPRAMOLECULAR CHIRALITY

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Chirality is the geometric property of an object not to coincide with its mirror image. The chirality of all living things remains one of the mysteries of Nature. When looking for the source of the first chiral shift that gave rise to the biopolymerization of L-amino acids and D-sugars during the prebiotic Earth, it is necessary to consider not only molecular chirality, but also its other forms. Of interest is supramolecular chirality, since many natural crystals (eg quartz) are enantiomorphic with supramolecular chirality. Therefore, an important topic is the study of the processes of adsorption of enantiomers and chiral recognition on surfaces with supramolecular chirality. In this paper, we study the patterns of change in isosteric heats of adsorption $q_{st}$ and differential entropies of adsorption $\Delta S_{dif}$ with surface coverage $\theta$ for enantiomorphic crystals of hippuric acid and phloroglucinol.

Enantiopure crystals were obtained under Viedma ripening conditions according to literature procedures. The adsorption isotherms of limonene and α-pinenes vapors were measured on the obtained samples under gas chromatography conditions at various temperatures. Differences in adsorption isotherms were tested for statistical significance using a t-test. The dependence of lnp on 1/T was used to calculate the isosteric heats of adsorption, which were further used to calculate the differential entropies of adsorption.

Dependency analysis $q_{st}$ vs. $\theta$ shows the difference in the mechanisms of adsorption of enantiomers on crystals of hippuric acid and phloroglucinol. Thus, the regularities of the isosteric heat of limonene adsorption variation on hippuric acid and phloroglucinol were dramatically different. For hippuric acid, qst increased with increasing amounts of adsorbed limonene, while for phloroglucinol, qst was almost unchanged. In both cases, the heat of adsorption was below the heat of liquefaction of limonene, at the average measurement temperature. It can be concluded that the interactions between the limonene molecules were stronger than between limonene and the crystal surface. This is also confirmed by the shape of the adsorption isotherms.

It was shown, that during the limonene and α-pinene adsorption on hippuric acid, the molecules were adsorbed quite close to each other, even at low coverages. With a further increase in molecule concentration on the surface, the interaction force between the surface and the enantiomer becomes sufficient to allow the formation of the enantiomer layer. In the case of phloroglucinol, the adsorption energy of the limonene enantiomers was too low to allow the formation of an ordered layer sufficient for satisfactory chiral recognition. It can be assumed that qst was even lower on bromotriphenylmethane crystals and as a result there was no chiral discrimination. Since the chiral recognition of α-pinene enantiomers on hippuric acid was at the limit of experimental error, it could be assumed that at slightly lower $q_{st}$ values at infinite dilution, the isotherms will coincide under any conditions. In that case, the limit of chiral recognition would correspond to $q_{st} \approx 1/3L$.

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# SEPARATION OF AZEOTROPIC MIXTURES: NOVEL APPROACHES OF USING CHOLINE CHLORIDE BASED DEEP EUTECTIC SOLVENTS

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Deep eutectic solvents (DES) which are intensively investigated in recent time present especial interest for scientists. They are considered as the way for ‘green chemistry’ future with minimized affection of chemical-based pollutants. DESs can be useful for solving different issues: for instance, some DESs show promise to be $CO_2$ capture with high carbon dioxide solubilities, low vapor pressures and high thermal stabilities [1]. Otherwise, DESs possess several key characteristics that demonstrate great potential to facilitate new biocatalytic pathways [2]. Furthermore, DESs can be used as extractants for separation different mixtures like biodiesel, aromatic hydrocarbons, gas and biologically active compounds [3]. Particularly, DESs are considered as new generation solvents for separation azeotropic mixtures e.g., for purification ester from alcohol in esterification reaction. This way opens the perspectives in using DES for ester-based second-generation biofuels and all-new fuel additives for gasoline.

This work is a continuation of the investigation of liquid-liquid equilibria (LLE) of DES formed by choline chloride and dibasic carboxylic acids/glycerol/urea in alcohol-ester systems [4-6]. Herein, we consider the ability to separate mixtures of alcohols with its acetate esters (ethyl acetate, *n*-propyl acetate, *n*-butyl acetate) using choline chloride – 1,2-ethanediol and choline chloride – 1,2-propanediol deep eutectic solvents. Tie-lines were obtained at temperatures 293.15 K and 313.15 K and atmospheric pressure. The compositions of coexisting organic and DES phases are determined by 1H NMR-spectroscopy. The extraction performance was characterized with distribution coefficients and values of selectivity for used alcohols. NRTL model was applied to correlate LLE in these systems.

**Acknowledgements** The financial support of the Russian Science Foundation (grant 20-73-10007) is gratefully acknowledged. The authors thank the Resource Centers of Saint Petersburg State University "Magnetic Resonance Research Centre" for the help in analytical investigations.

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# INVESTIGATION OF THE EFFICIENCY OF THE ETHANOL – ETHYL FORMATE SYSTEM SEPARATION BY VARIOUS DESSs BASED ON CHOLINE CHLORIDE

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The development of green chemistry is extremely relevant. it is aimed at reducing the negative impact of chemical production on the environment. Particularly, a lot of attention is paid to the search for new, environmentally friendly solvents. Deep eutectic solvents (DESs) are considered one of the most promising environmentally friendly and economically viable alternatives to traditional volatile organic solvents and ionic liquids [1–2]. DES is a liquid at ambient temperature system consisting of a hydrogen bond donor (HBD) and acceptor (HBA), which have a higher melting point than the DES they form.

The efficient use of environmentally friendly solvents has an important impact in optimizing synthesis and purification processes in various types of chemical technology, in particular in the production of esters. The data on phase behavior of systems involving reagents and synthesis products, as well as substances involved in the purification process, are needed to optimize the processes for the production of esters.

In the current work, the liquid-liquid equilibria (LLE) in heterogeneous systems ethanol – ethyl formate – DES was studied at 20 and 40 °C and atmospheric pressure. The investigation was carried out with various DESs based on choline chloride (ChCl) and some HBAs: glycerol (Gl), urea (Ur), glutaric acid (Glu) and ethylene glycol (EG).

For the investigation ethanol – ethyl formate – DES equilibrium systems with different ratios of components were prepared. Samples of each phase from these systems were analyzed by $^1$H NMR spectroscopy. Phase diagrams based on obtained LLE data were constructed. Distribution coefficients and selectivity values were calculated. Dependences of selectivity on ethanol mass fraction are presented at Fig. 1. Comparison with the separation efficiency of other ethanol – ester systems by the same DESs were analyzed. Correlation of experimental LLE data by NRTL equation was carried out. Calculated data showed a good agreement with experiment.

**Acknowledgements.** This research was carried out with financial support of Russian Science Foundation (grant 20-73-10007) in study of LLE at 40 °C and with financial support of the Council for Grants of the President of the Russian Federation (grant MK-3520.2022.1.3.) in study of LLE at 20 °C. Analytical part of the research was performed at Magnetic Resonance Research Centre of Saint Petersburg State University.

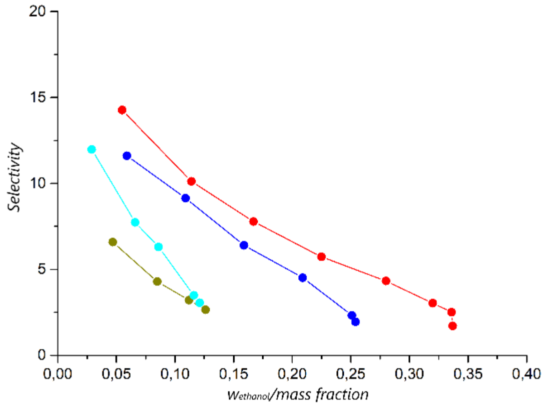

**Figure 1.** Dependence of selectivity on ethanol mass fraction at 313.15 K for the systems ethanol – ethyl formate – DES (ChCl/Gl (●), ChCl/Ur (●), ChCl/Glu (●), ChCl/EG (●).

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# STIMULI-RESPONSIVE NANOCARRIERS FOR SUBSTRATE BINDING AND RELEASE

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The creation of nanocarriers for controlled binding and release of substrates is one of the fastest growing areas of science [1]. Nanocarriers are needed in medicine for imaging and targeted delivery of drugs, in agriculture to improve the efficiency and reduce the toxicity of pesticides, in industry to create new types of catalytic systems [2].

Recently, we have developed a new approach to the creation of nanocarriers [3]. The approach is based on the self-assembly followed by dynamic polymerization of amphiphilic derivatives of resorcinarenes – macrocyclic compounds analogues of calixarenes. The bowl-shaped form of resorcinarenes is hydrophobic and soluble only in organic solvents but introduction of hydrophilic moieties on the upper rim gives it amphiphilic properties, due to which resorcinarenes can act as emulsifiers. In a microemulsion media, they assembly at the oil/water interface so that hydrophilic moieties of resorcinarenes are faced to water while the tails of the lower rim are directed into the oil dispersed phase (Figure 1). Cross-linking of the tails with reversible covalent bonds results in the formation of stimuli-responsive polymer nanoparticles that can be applied for stimuli-controlled release of substrates.

Nanocarriers based on resorcinarenes have several advantages over conventional carriers such as liposomes, micelles and so on. Resorcinarenes are most often nontoxic and are synthesized with the use nonpoisonous reagents. A polymeric spherical network formed during the polymerization, holds the substrates stronger than linear polymeric or supramolecular nonpolymeric carriers. Decomposition of the nanocarriers leads to the formation of small pieces – resorcinarene derivatives which should greatly facilitate their excretion from the body. Previously, using this approach, we have obtained nanocarriers for controlled binding of substrates and their application in targeted drug delivery and for creation new catalytic systems. The research results will be shown in the presentation.

**Acknowledgements** This work was funded by the government assignment for FRC Kazan Scientific Center of RAS and subsidy allocated to Kazan Federal University for the state assignment in the sphere of scientific activities (N 0671-2020-0063).

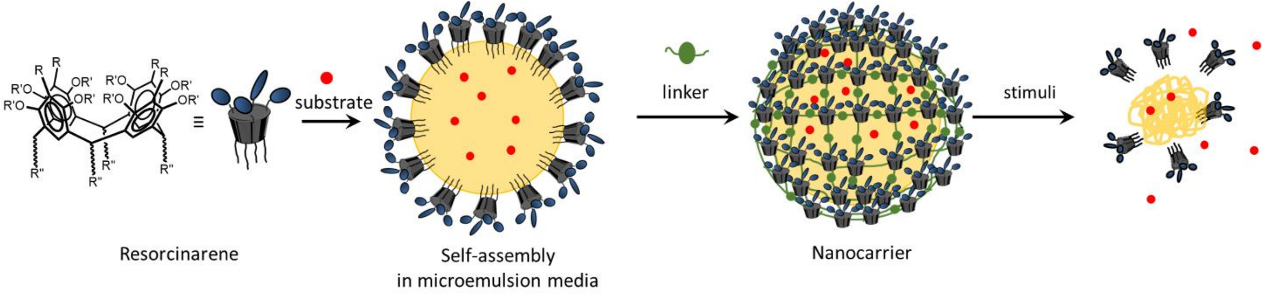

**Figure 1.** Nanocarrier development strategy by microemulsion polymerization of resorcinarene derivatives for stimuli-responsive substrate delivery.

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# MODELLING MICELLES IN POLAR AND NON-POLAR SOLVENTS: FROM SINGLE AGGREGATE TO AGGREGATES SIZE DISTRIBUTION

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Micellar solutions contain surfactant aggregates with different aggregation numbers [1] but it is quite difficult to observe the size distribution of the aggregates in laboratory experiments, e.g., using dynamic light scattering and nuclear magnetic resonance methods. In this respect, molecular dynamics modeling methods can be of great use, since they allow one to study transport and structural properties of a single aggregate with arbitrary aggregation number [2] and of a set of aggregates. This communication presents the results of complex all-atom molecular dynamics modeling of aqueous solutions of an ionic surfactant (sodium dodecyl sulfate, SDS) [3,4], also in the presence of decane molecules solubilized in SDS micelles [5], and of the solutions of a nonionic surfactant $C_{12}E_4$ in polar (water) and non-polar (heptane) solvents. In the case of SDS, both salt-free micellar solutions and solutions with the additions of sodium chloride and calcium chloride were considered. When constructing the models of the considered molecular systems, the all-atom force fields CHARMM36 and CGenFF v. 4.4 were used. Molecular dynamics simulations were carried out using the MDynaMix and Gromacs 2020.1 software packages.

During the simulations, spontaneous formation of one or several aggregates in the simulation box took place. By analyzing the molecular dynamics trajectories, we calculated the diffusion coefficients and the average radii of the formed aggregates which enabled us to estimate the viscosities of the simulated micellar solutions using the Stokes-Einstein formula [4,5]. At certain concentrations of $CaCl_2$, the formation of “islands” consisting of negatively charged head groups of SDS and positively charged $Ca^{2+}$ ions was observed in the crowns of the aggregates which in its turn led to the formation of stable dumbbell-shaped micelles [5].

We also studied the direct and inverse micelles of the nonionic surfactant $C_{12}E_4$ formed, respectively, in water at $T = 298$ K and in heptane at $T = 223$ K. For a system made of 100 $C_{12}E_4$ molecules and 4000 heptane molecules and simulated at a temperature $T = 283$ K the 1 μs long molecular dynamics trajectory was obtained which made it possible to obtain a distribution of aggregates over the aggregation numbers. The distribution included not only the inverse micelles but also surfactant monomers, dimers, trimers, etc, as it should be in real micellar solutions [1]. Such distributions, in principle, can be used to estimate the work of aggregation of a micelle [6]. The local maximum of the obtained distribution was located at $n$=87 close to the distribution’s right end. This fact can be related to the effect of the small size of the simulation cell [7].

**Acknowledgements** This work has been supported by the grant from the Russian Foundation for Basic Research (RFBR 20-03-00641_A).

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# REDUCTIVE CLEAVAGE OF C-O BONDS IN *P-TERT*-BUTYLCALIX[4]ARENE DERIVATIVES IN THE PRESENCE OF HYDRAZINE

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Calix[4]arenes are a class of macrocycles that pay great attention due to their possibility of functionalizing both the upper and lower rims and obtaining various macrocycles derivatives [1]. As is known, 1,3-diynes are used for the synthesis of π-conjugated acetylene polymers. Due to the formation of a conjugated chain and the ability to change side substituents, polydiacetylenes have different chromatic properties [2]. The conjugation of diacetylenes with calix[4]arene makes it possible to synthesize precursors for various compounds.

Heterocycles play a significant role in medical chemistry because their fragments can be found in many biomolecules. Various heterocyclic compounds are formed as a result of the reaction of nucleophiles with diacetylenic derivatives. The modification of calix[4]arenes with nitrogen-containing heterocyclic groups makes it possible to obtain macrocyclic clusters of known therapeutic drugs, as well as promising ligands for metal complex catalysis [3].

In the present work, we have discussed the functionalization of calix[4]arenes with diacetylene derivatives and features of their reactivity with hydrazine.

This work was supported by Russian Scientific Foundation № 21-73-10062

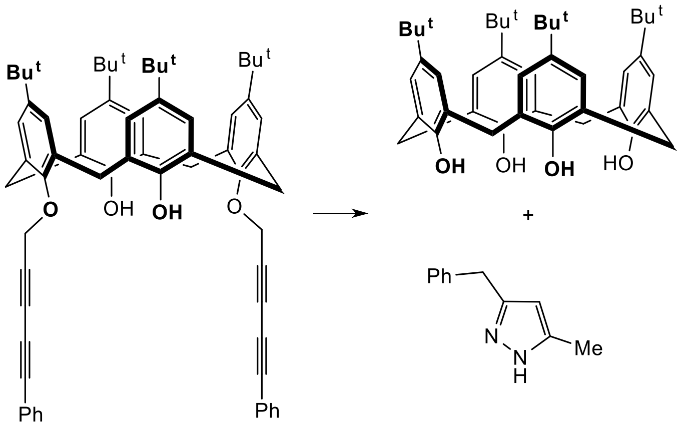

**Figure 1.** Hydrazine reductive cleavage of C—O bonds in O-substituted derivative of 4-tert-butylcalix[4]arene

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# NOVEL TETRA-AZIDE AND TRIAZOLE DERIVATIVES OF THIA- AND CALIX[4]ARENE WITH FREE PHENOLIC HYDROXYLS

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Calix[4]arenes are cyclic macromolecules consisting of four phenolic fragments linked together by methylene groups (or thiol groups in the case of thiacalix[4]arenes). The introduction of azide fragments into the structure of calix[4]arenes makes it possible to use these macrocycles as reagents in “click reactions” to obtain a wide range of water-soluble compounds under mild conditions. In addition, the presence of hydroxyl groups on the lower rim of the macrocycle opens up the possibility of obtaining functional materials based on them through metal binding, covalent crosslinking, or ionic interactions.

As a result of this work, a procedure for obtaining a universal synthetic platform based on thia- and calix[4]arene derivatives was developed. This strategy consists in consecutive azo coupling (or nitration for thiacalixarene derivatives), reduction and diazotization reactions (Fig. 1). According to the X-ray diffraction of calixarene **4**, there is a ring hydrogen bond in the structure, and two molecules, located in opposite directions, are packed in the crystal cell. Close contacts between them, most likely having the nature of π-π stacking. The obtained tetraazide derivatives with free hydroxyl groups, were used to obtain triazoles with phenyl, hydroxymethyl and polyamine fragments.

This work was supported by Russian Scientific Foundation № 22-13-00304.

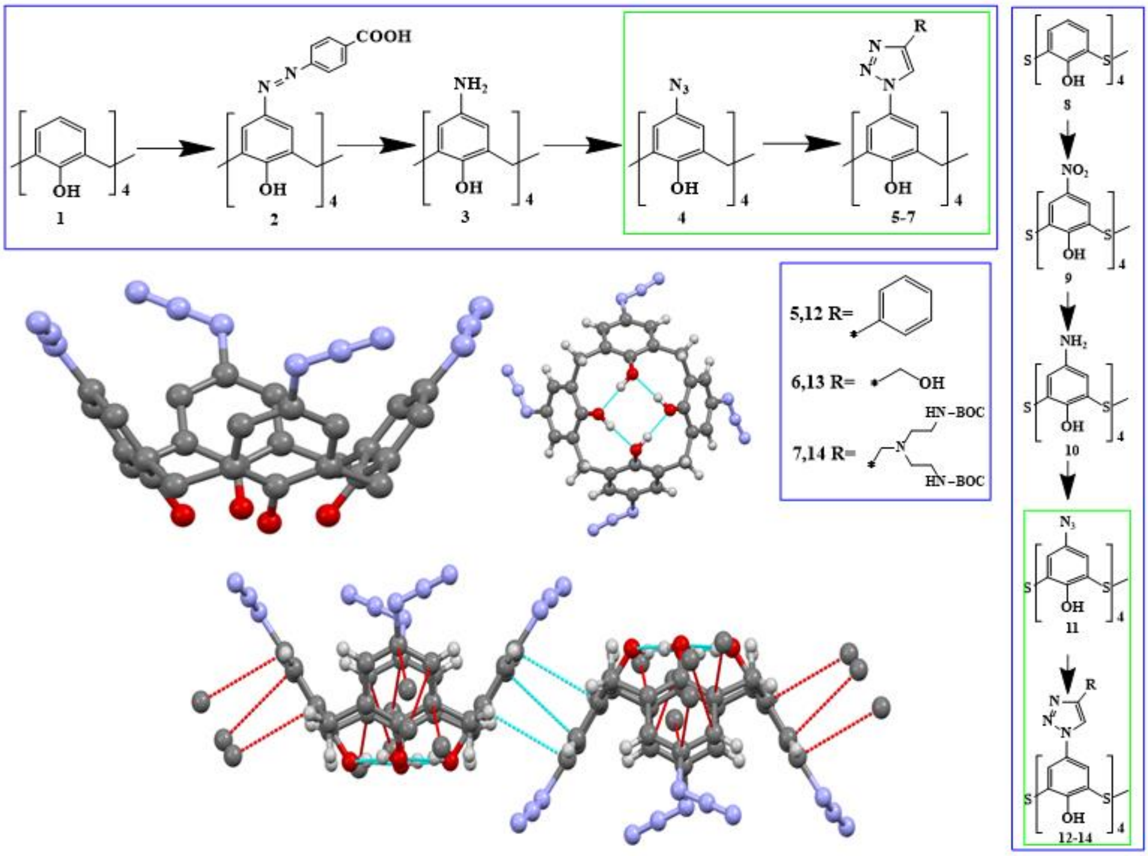

**Figure 1.** Synthetic strategy for obtaining target compounds and X-ray diffraction of calixarene **4**

# THERMODYNAMIC CHARACTERISTICS OF CESIUM DIMOLYBDATE AND LITHIUM MONOMOLYBDATE DOPING BY 10% CESIUM

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Compounds on the basis of alkali metal molybdates, in particular, single crystals of cesium and lithium molybdates, are promising materials for optoelectronics, high energy physics, etc. [1–2]. It was shown in paper [1] that cesium dimolybdate ($Cs_2Mo_2O_7$) had higher luminescence light yield than lithium molybdate. In this regard, cesium dimolybdate can be considered as promising material to search rare events.

In this paper, crystals of cesium dimolybdate and lithium molybdate doped by 10% cesium ($Li_{1.8}Cs_{0.2}MoO_4$) were grown by low-temperature-gradient Czochralski technique. $Cs_2Mo_2O_7$ crystal was grown from its own melt. Deeply purified $MoO_3$ and $Cs_2CO_3$ (SP 19-2, TU 6-09-4759-79, 99.99%) were used as precursors. $Li_{1.8}Cs_{0.2}MoO_4$ crystal was grown from initial components: $Li_2CO_3$ (SP 20-2, TU 6-09-4757-84, Novosibirsk Rare Metals Plant), deeply purified $MoO_3$ and $Cs_2MoO_4$ (TU 6-09-04-80-82). Crystals were identified by X-ray powder diffraction.

To determine thermodynamic characteristics, solution calorimetry at 298.15 K and differential scanning calorimetry were used [2–3]. The dissolution enthalpies of $Cs_2Mo_2O_7$, $MoO_3$ were measured by solution calorimetry in 0.4 M KOH. Based on measured experimental and literature data, the standard formation enthalpy, lattice enthalpy, and stabilization energy were calculated. It was shown that standard formation enthalpy and lattice enthalpy were increasing in series $Cs_2MoO_4$-$Cs_2Mo_2O_7$.

The heat capacity of $Li_{1.8}Cs_{0.2}MoO_4$ crystal was measured by DSC calorimetry in the temperature range of 319-710 K. It was shown that there were no phase transitions in this temperature range. The heat capacity is well described by cubic polynomial.

**Acknowledgements** This work was supported by Russian Science Foundation (project No. 19-19-0095, continuation)

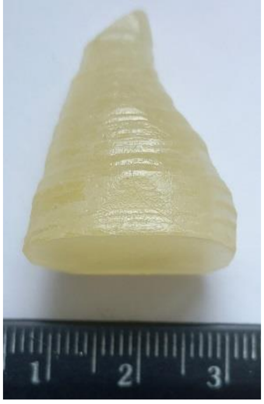

**Figure 1.** Kristal of $Cs_2Mo_2O_7$.

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# INORGANIC-ORGANIC DERIVATIVES OF LAYERED PEROVSKITE-LIKE OXIDES THERMAL STABILITY AND PHOTOCATALYTIC ACTIVITY

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Protonated layered perovskite-like oxides are solid crystalline substances in which two-dimensional perovskite blocks alternate with interlayer spaces populated by protons. Being solid acids, they are able to react with some organic compounds giving inorganic-organic derivatives, i.e. substances consisting of chemically bonded inorganic and organic parts in which the former serves as a spatial frame. Their formation may occur in two ways: either as intercalation of organic bases following an acid-base mechanism, or as grafting, that is a process similar to well-known esterification in organic chemistry. Inorganic-organic derivatives may demonstrate many times greater photocatalytic activity as compared with initial titanates that makes them promising materials for hydrogen production from various aqueous media.

The present work is devoted to investigation of thermal stability and photocatalytic activity of amine and alkoxy derivatives of protonated titanates and niobates. Characterization of the samples is performed using X-ray diffraction, thermogravimetry, simultaneous thermal analysis coupled with mass spectrometry, elemental CHN-analysis, Raman, diffuse reflectance and nuclear magnetic resonance spectroscopy as well as scanning electronic microscopy. Photocatalytic activity of derivatives is studied in the reaction of hydrogen generation from an aqueous solution of methanol.

It is shown that many of inorganic-organic derivatives obtained are thermally stable materials (Figure 1) achieving extremely high apparent quantum efficiency of hydrogen evolution of 30-40% in the spectral range 220-340 nm.

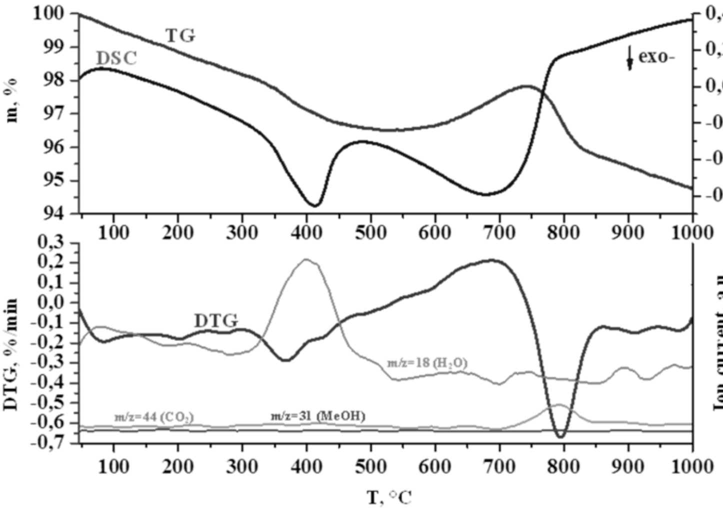

**Figure 1.** Simultaneous thermal analysis of the methoxy derivative of $H_2Nd_2Ti_3O_{10}$

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# STUDY OF $Al_2O_3$ - $ZrO_2$ -$Yb_2O_3$ PRECURSORS BY THE DIFFERENTIAL SCANNING CALORIMETRY

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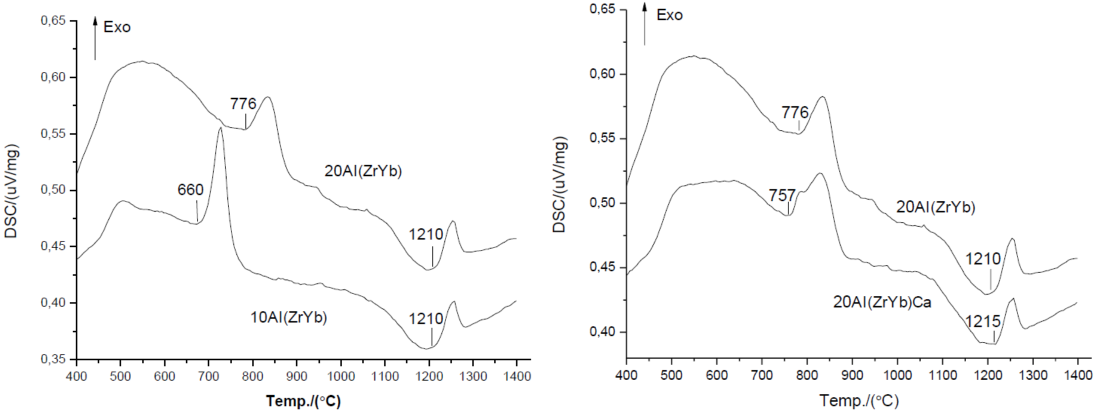
Ceramic materials based on aluminum and zirconium oxides, due to chemical stability, high mechanical strength, resistance to brittle fracture, and biological inertness, are widely used both in engineering and in medicine. Currently, intensive research has been conducted to develop ceramic composites based on them, which have improved performance, especially important to medical applications: high service life without the need of revision surgery.

The aim of this work was to study the thermochemical reactions occurring at the modification of $Al_2O_3$ - $ZrO_2$ - $Yb_2O_3$ nanosystems by cations of alkaline earth elements introducing at the stage of obtaining hydrogels, and the development of engineering materials. Synthesis of precursors was performed by the hydrolysis sol gel method using 1 M solution of crystalline salts.

The study of the thermodynamic properties of the xerogel system in the temperature range of 25-1450°C using both – the differential scanning calorimetry (DSC) and the X-ray diffraction (XRD) analyses are presented.



a) b)

**Figure1.** DSC of samples a) 10Al(ZrYb), 20Al(ZrYb) b) 20Al(ZrYb), 20Al(ZrYb)Ca

It was found that with the increasing of the $Al_2O_3$ content in the investigated $Al_2O_3$-$ZrO_2$-$Yb_2O_3$ systems, the crystallization temperature of solid solutions based on $ZrO_2$ is shifting towards higher temperatures. This indicates the including of Al cations into the structure and the formation of a complex solid solution. This fact is illustrated in figure 1-a by comparing the thermograms of xerogels containing 10 and 20 mol.% $Al_2O_3$.

This statement is confirmed by calculations of the parameters of elementary cells of complex solid solutions of $Al_nZr_{1-n}O_2$. It is established that the modification of systems with cations of alkaline-earth elements changes the configurations and size of thermoeffect (was estimated according to the enthalpy). Probably, the change in the first thermal effect corresponding to the crystallization of solid solutions based on $ZrO_2$ (figure 1-b) is caused by the including of modifying cations into its structure.

The change in the value of the second thermal effect associated with the crystallization of a stable form of aluminum oxide is probably determined by the simultaneous formation of a second aluminum-containing phase, the presence of which is confirmed by X-ray diffraction analysis.

In the heat–treated samples at the temperature of 1400°C, the following phases are identified – a solid solution based on $ZrO_2$ with tetragonal structure, $\alpha$–$Al_2O_3$ and the corresponding hexaaluminates.

# MASS SPECTROMETRIC STUDY AND MODELING OF THE THERMODYNAMIC PROPERTIES OF THE $Al_2O_3$-$SiO_2$-$ZrO_2$ SYSTEM

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The knowledge of the vaporization behavior and thermodynamic properties of the $Al_2O_3$-$SiO_2$-$ZrO_2$ system is essential for better understanding of high-temperature performance of materials based on this system and methods of their synthesis. The vapor phase over the samples and the thermodynamic activities of components were investigated with the MS-1301 mass spectrometer for high-temperature Knudsen effusion studies. The samples were vaporized from tungsten effusion twin-cells heated by electron bombardment. The molecular species identified in the vapor over the $Al_2O_3$-$SiO_2$-$ZrO_2$ system were the same as those detected over the binary $SiO_2$-$ZrO_2$ system in our earlier study [1]. Due to a much higher volatility of $SiO_2$ compared to other oxides the partial pressure measurements were carried out at the temperature as low as 1920 K and therefore only SiO, O, $WO_2$, $WO_3$, and traces of $SiO_2$ species could be observed in the vapor.

From the relation between the $SiO^+$, $WO_2^+$ и $WO_3^+$ ion currents measured in mass spectra of the vapor over the samples and over pure oxides, $SiO_2$ activities for 14 compositions in the $Al_2O_3$-$SiO_2$-$ZrO_2$ system were determined. The obtained the component activity data were used for the thermodynamic modeling of the $Al_2O_3$-$SiO_2$-$ZrO_2$ system on the basis of the generalized lattice theory of associated solutions. Optimized concentration dependences of $Al_2O_3$, $SiO_2$, and $ZrO_2$ activities and the excess Gibbs energy were obtained. In Fig.1 $\Delta G^E$ are shown in comparison with the results obtained in [1] from the data for the limiting binary systems. Both sets of curves indicate strong negative deviations from the ideal behavior.

**Acknowledgements** The financial support of Russian Foundation for Basic Research, grant No 20-53-05013, is gratefully acknowledged.

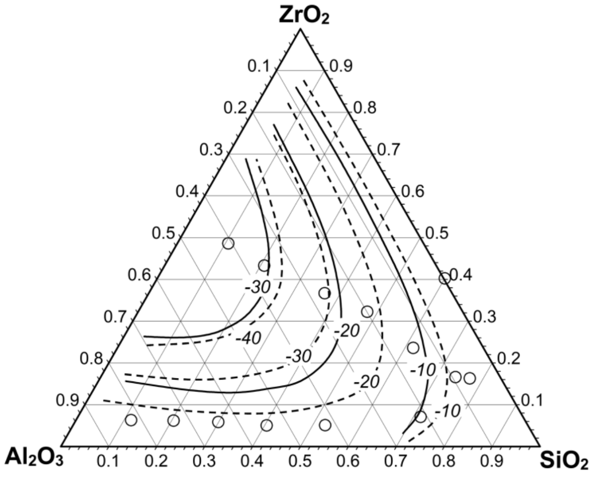

**Figure 1.** Excess Gibbs energy in the $Al_2$-$SiO_2$-$ZrO_2$ system at $T$=2500 K calculated from the $SiO_2$ activity in the ternary system, solid lines, and in the $SiO_2$-$ZrO_2$ and $Al_2$-$ZrO_2$ systems, dashed lines.

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# AN EXPERIMENTAL INSIGHT ON THE THERMOCHEMISTRY OF NAPHTHALENE DIOLS

Maria D. M. C. Ribeiro da Silva, Vera L. S. Freitas, Joaquim M. I. Mendes, Paulo, M. S. Sousa

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The lack of reliable thermochemical data for polycyclic aromatic hydrocarbons and their derivatives lead us, for the last decades, to the development a systematic study of thermodynamic properties of several classes of those compounds with the main purpose of the establishment of relations between their energetic and structural properties, as well as understanding their reactivity.

The present study reports the thermochemical and thermophysical characterization of two naphthalene diols derivatives, 1,7-dihydroxynaphthalene and 2,7-dihydroxynaphthalene (Figure 1), yielding new experimental thermodynamic data for the two compounds.

The work involves the determination of combustion energies by static bomb calorimetry, the determination of phase transition enthalpies using differential scanning calorimetry and high temperature Calvet microcalorimetry, as well as the measurement of vapor pressures at different temperatures by the Knudsen effusion method.

The values obtained for the standard ($p^{o}$ = 0.1 MPa) molar enthalpies of formation of the two compounds in the crystalline phase, at $T$ = 298.15 K, as the corresponding enthalpies of fusion and sublimation, at $T$ = 298.15 K, are presented. The enthalpies of formation of the two compounds in the gaseous phase, at $T$ = 298.15 K, were also derived and discussed in terms of the energetic-structural relationships.

1,7-dihydroxylnaphthalene 2,7-dihydroxylnaphthalene

**Figure 1.** Molecular formulae of the two naphthalene diols derivatives.

**Acknowledgments** This work was supported by the Fundacão para a Ciência e Tecnologia (FCT) to CIQUP, Faculty of Science, University of Porto (Project UIDB/00081/2020), IMS-Institute of Molecular Sciences (LA/P/0056/2020)).

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# NEW RELATIONSHIP BETWEEN ENTHALPIES OF VAPORIZATION AND SOLUTION FOR MOLECULAR AND IONIC LIQUIDS

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The enthalpy of vaporization is an important parameter for studying the energy of intermolecular interactions, solubility, determining the volatility of pollutants [1]. Experimental determination of the enthalpy of vaporization can be complicated by such properties of the compounds under study as: high reactivity, difficulty in obtaining high-purity compounds, etc. For these cases, empirical calculation methods are developed based on the "structure-property" relationship that makes it possible to calculate the vaporization enthalpy using the structural parameters without significant material and financial resources. In recent decades, many different additive calculation procedures have been proposed. In this paper, we will show the limitations of scheme for calculation of the enthalpy of vaporization. One such limitation is the different contributions of methylene groups to the enthalpy of vaporization of various homologous series. On the other hand, with a similar analysis, it can be seen that the contribution of the methylene group to the enthalpy of solvation for different homologous series is the same. Thus, the use of the enthalpy of solvation to create an additive scheme is methodologically correct. In this work, the causes of these phenomena are investigated and regularities are found that explain the observed differences not only for molecular, but also for ionic liquids. These regularities made it possible to propose a method for determining the enthalpies of vaporization of molecular and ionic liquids at 298.15 K. In addition, these regularities made it possible to predict the heats of solution of alkanes in molecular and ionic liquids. Comparison of the enthalpies of vaporization and solution obtained in the present work with the literature data showed the high accuracy of the proposed approach.

**Acknowledgements** This paper has been supported by the Kazan Federal University Strategic Academic Leadership Program ('PRIORITY-2030')

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# HEAT CAPACITY AND THERMODYNAMIC FUNCTIONS OF CRYSTALLINE COPPER(II) DIPIVALOYLMETHANATE FROM 0 TO 430 K

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Copper(II) dipivaloylmethanate (or Cu(dpm)$_2$) belongs to the class of metal beta-diketonates that crystallize in the lattice of molecular type. Copper beta-diketonates are used as precursors in the manufacture of functional coatings (superconducting materials, integrated circuit interconnections, etc.) by chemical vapor deposition. This work presents the results of experimental determination of the heat capacity of Cu(dpm)$_2$ by adiabatic and scanning calorimetry methods. These results were obtained for the first time.

A sample of copper(II) dipivaloylmethanate was prepared and purified as described in [1]. Purity of the final compound is not lower than 99.8 %. The sample at room temperature is a dark-blue crystalline powder. The X-ray phase analysis of the polycrystalline sample was performed at room temperature with a Shimadzu XRD-7000 X-ray diffractometer. The experimental diffractogram fully matches the theoretical one calculated from the data [2] for monocrystalline Cu(dpm)$_2$.

The heat capacity of the sample was measured in the range from 5.44 to 309.32 K in a vacuum adiabatic calorimeter (laboratory-made) described earlier [3]. The standard platinum resistance thermometer was applied to measure the temperature of the sample. The standard uncertainty for the temperature was $u(T) = 0.01$ K. Previously [3], the heat capacity of a standard sample of benzoic acid (NIST SRM 39j) was measured in the range of 13.83 to 302.07 K to verify the accuracy of the calorimeter. It is shown that the relative deviations of the measured heat capacity of benzoic acid from the reference [3] were less than 0.9% at $T/\mathrm{K} \leq 20$ and less than 0.23% at $T/\mathrm{K} > 20$.

For the experimental study of the heat capacity in the range of 300 – 430 K, a NETZSCH DSC 204 F1 Phoenix differential scanning calorimeter was used. In accordance with the calibration results and measurements of standard substances (synthetic sapphire and benzoic acid), the experimental uncertainty is not more than 2.0% in heat capacity and 0.5 K in temperature.

No thermal anomalies were detected in the functional behavior of heat capacity; therefore, Cu(dpm)$_2$ does not undergo any phase transformation in the temperature range under examination. Based on the obtained data, the smoothed values of heat capacity, entropy, enthalpy, and reduced Gibbs energy were calculated in the temperature range from 0 K to 430 K.

An analysis of the obtained results in comparison with the literature data for other dipivaloylmethanates was performed. It was found that the phonon component is the main one in the heat capacity of these complexes. The calculation of intermolecular and intramolecular heat capacity components was carried out for the compounds under consideration. Analysis of the results showed that the intramolecular component of the heat capacity is a multiple of the number of ligands and within the isoligand group makes approximately the same and dominant (>90%) contribution to the total heat capacity of each complex. The intermolecular contribution to the heat capacity correlates with the mass of the molecules and reaches, in the limit, ≈6R.

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# THE REARRANGEMENT ENERGY OF FRAMEWORK RADICALS

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Энергии перестройки каркасных радикалов определены на основе энтальпий образования каркасных соединений и их радикалов. По модели Н.Н. Семенова [1] процесс мономолекулярного радикального распада молекулы состоит из отделения радикальных фрагментов молекул ($R_1$ и $R_2$) и превращения их в радикалы ($R_1^\bullet$ и $R_2^\bullet$). Уравнения химической физики, связывающие термодинамические характеристики соединений: энергии диссоциации связей D, энтальпию образования вещества $\Delta_f H^o(R_1R_2)_{(g)}$, энтальпии образования радикалов $\Delta_f H^o R^\bullet$, средние термохимические энергии связей $E_i$, энтальпии атомизации соединения $\Delta_{at}H$, энтальпии образования атомов $\Delta_f H_{at}$ и ε (энергии перестройки фрагментов молекул в радикалы) имеют вид:

$$D(R_1 - R_2) = \Delta_f H^o R_1^\bullet + \Delta_f H^o R_2^\bullet - \Delta_f H^o(R_1R_2)_{(g)} = E(R_1 - R_2) + \varepsilon_{R1} + \varepsilon_{R2}; \qquad (1)$$

$$\Delta_{at}H = \Sigma\Delta_f H_{at} - \Delta_f H^o(R_1R_2)_{(g)} = \Sigma E_i = \Sigma E_{R1} + \Sigma E_{R2} + D(R_1 - R_2) - \varepsilon_{R1} - \varepsilon_{R2};$$

Постоянство величин $\Sigma E_R$ и $\varepsilon_R$, равенство 0 для ε атомов и $D \equiv E$ для двухатомных молекул позволяет существенно расширить количество радикалов, для которых возможно рассчитывать $\varepsilon_R$ и $\Sigma E_R$.

Используя данные по энтальпиям образования соединений, их радикалов [2], энергии С – С и С – Н связей из [3] и уравнения (1), рассчитаны энергии перестройки $\varepsilon_R$ ряда каркасных радикалов (кДж·моль$^{-1}$): норборнила-1 (бицикло[2,2,1]гепт-1- ила), $C_7H_{11}^\bullet$, 6.1; бициклооктан-1-ила, $C_8H_{13}^\bullet$, 6.1; тетралин-1-ила (1,2,3,4-тетрагидронафталин-1-ила), $C_{10}H_{11}^\bullet$, - 8.2; кубан-1-ила, 78.9; транс-октагидронафталин-1-ила, $C_{10}H_{17}^\bullet$, - 6.5; адамантан-1-ила, $C_{10}H_{15}^\bullet$, - 6.5; адамантан-2-ила, $C_{10}H_{15}^\bullet$, 2.2. Из величин энергий перестройки радикалов каркасных структур можно заключить, что образование радикалов при углеродах атомах

$C_2$ и $C_3$ несколько снижает энергетику радикалов относительно углеводородных радикалов. Энергии перестройки радикалов каркасных соединений находятся в пределах погрешности энтальпий образования радикалов. Для кубана энергия напряжения составляет 574.1 кДж·моль$^{-1}$. Появление радикальной частицы $C_3^\bullet$ в кубан-1-иле дополнительно напрягает каркас кубана около 80 кДж·моль$^{-1}$.

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# THERMODYNAMIC PERTURBATION THEORY FOR MOLTEN ALKALI HALIDES

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Despite the relative simplicity of interionic interactions in alkali metal halide melts, a quantitative statistical-thermodynamic theory has not yet been developed. We present a variant of thermodynamic perturbation theory (TPT), which uses the model of charged hard spheres as a reference system and allows taking into account weaker terms due to the polarizability of ions [1]:

$$F_{liq} = F_{chs} + F_{pol} \equiv F_{chs} + \frac{1}{4\pi^2} \cdot \sum_{i,j} \sqrt{x_i x_j} \int_0^\infty \varphi_{ij}^1(k) \cdot \left(S_{ij}^0(k) - \delta_{ij}\right) \cdot k^2 \mathrm{d}k + \frac{\rho}{2} \cdot \sum_{i,j} x_i x_j \, \varphi_{ij}^1(0) \,,$$

where $F_{chs}$ is the free energy of the charged hard spheres, $S_{ij}^0(k)$ is the partial structure factor of the reference system, $\varphi_{ij}^1(k)$ is the Fourier transform of the perturbation due to the induction interaction.

Estimations and analysis of the extra contribution to the thermodynamic characteristics of alkali halide melts were carried out [2]. The perturbation due to the induced dipoles is confirmed to be negative for all alkali halides, while the reduced value of the extra term lies in the range from a few to 10% for free energy. The absolute values of the ion-induced dipole term are greater in those melts where the Coulomb interaction is also greater. Generally, the proposed model is quantitatively successful when describing the enthalpy and its temperature dependence without fitting parameters.

All experimental data on the heat capacities of molten alkali halides near their melting points have been analyzed depending on the cation-anion composition [3]. The isochoric heat capacities of all 20 liquid alkali halides were calculated using this variant of the thermodynamic perturbation theory. Trends in the change in heat capacity over both the ratio of ionic radii and polarizabilities are described. On this basis, the recommended values of heat capacities were selected from the variety of experimental data. It is shown that the reduced isochoric heat capacity ($C_V/k_B$) should increase with the mismatch in the cation and anion radii, as an even function with a minimum. Charge-induced dipole interactions lead to breaking of the specific Coulomb symmetry, contributing to a more significant increase in heat capacity in salts containing the smallest cations, as well as the largest and most polarizable anions.

Several variants of the equation of state for molten alkali halides are considered using the thermodynamic perturbation theory. The main attention is focused on taking into account charge-induced dipole term to pressure as well. The value of the extra induction contribution to the pressure is about 5–10 percent from the Coulomb one and, thus, leads to a better agreement between the calculated and experimental data. It was shown that the equation of state through the energy gives the better results as compared to the experimental data on molten alkali halides near their melting point. Trends in density change with the ionic radii and the polarizabilities were analyzed.

The proposed TPT model was also applied to calculate phase equilibria between ionic crystals and melts [4]. On this basis, the melting points of all 20 alkali halides were calculated, and the dependence of melting temperatures was analyzed as the cation-anion composition changed. A decrease in melting temperatures with increasing differences in the cation and anion sizes was shown. Herewith, the discrepancy between the calculated and experimental data for all salts does not exceed 10 percent.

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# CONFORMATIONAL PREFERENCES OF FENAMATES IN SUPERCRITICAL STATE PARAMETERS OF THE SOLVENT BASED ON NOESY DATA

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Polymorph screening is an integral part of drug compound design and improvement. Of special interest in such studies is not only packing polymorphism, but also conformational polymorphism. For example, non-steroidal anti-inflammatory drugs (NSAIDs) belonging to the fenamate group, which were widely used in the past, have several polymorphic forms, depending on the molecule conformation. Identification of the major conformation is an essential step in understanding crystal nucleation from solutions and supercritical fluids. This work presents the results of conformational screening for a group of fenamates (mefenamic, flufenamic and tolfenamic acids) based on Nuclear Overhauser Effect Spectroscopy (NOESY) data. It also reports the results of determination of the internuclear distances within the isolated spin pair model (ISPA) and evaluation of the major conformations of fenamate molecules in DMSO-d6 and a mixed solvent based on $scCO_2$ and DMSO-d6 with phase separation.

An essential part of the realized procedure is recording 1D ($^1$H, $^{13}$C) NMR and 2D ($^1$H-$^{13}$C HSQC, $^1$H-$^{13}$C HMBC, $^1$H-$^1$H NOESY) NMR spectra and assigning the resonance signals to the respective protons in the fenamate molecule structure. The conformer proportions are calculated based on the Nuclear Overhauser Effect Spectroscopy data and quantum-chemical calculations in the framework of DFT (density functional theory). It is established that the major conformation in all the cases considered is the one realized in one of the fenamate polymorphic forms. However, in supercritical state parameters, the percentage (proportion) of the major conformers becomes smaller. The results obtained show the potential effectiveness of the NMR spectroscopy method in selecting conditions for polymorphic form nucleation using supercritical fluid technologies. The NMR spectroscopy experiment was performed using the molecular fluid spectroscopy facility (http://www.ckp-rf.ru/usu/503933/) of G.A. Krestov Institute of Solution Chemistry of the Russian Academy of Sciences (ISC RAS) (Russia).

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# MOLECULAR SIMULATION OF THE PERVAPORATION PROCESS

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The abstract should be formatted using the template provided and must be submitted online. This is the abstract sample. Text of your abstract should be submitted in Microsoft Word (2007 or later version) format. Abstracts will be included in the Conference materials.

Membrane separation processes are widely used in industry. Molecular simulation methods make it possible to study the influence of the chemical composition and structure of the membrane on the technological parameters of the separation process. In this work, two approaches were used for simulation. The first is the equilibrium method of molecular dynamics. Using this method, the diffusion coefficients of the components in the membrane and adsorption isotherms were calculated. The second is non-equilibrium method a modification of the DCV GCMD method [1] for studying the pervaporation process. This method makes it possible to calculate the fluxes of the components, the distribution of the densities of the components in the membrane and the near-boundary region (the region of concentration polarization).

In simulated systems membranes represent as a atoms rigidly fixed at the nodes of the crystal lattice. The mixture to be separated on membranes consisted of two types of atoms. The only difference in the intermolecular interaction was that one of the types was twice as strongly attracted to the membrane atoms. For this system, the diffusion coefficients in the membrane were calculated depending on the composition and density.

Studies of systems with different composition and thickness of the membrane were carried out using the nonequilibrium method. Comparison of the results of the non-equilibrium and equilibrium methods showed that the concentrations at the membrane boundary coincide in both cases. Thus, even on the molecular scale, local equilibrium conditions are established at the boundaries.

Concentration distributions were calculated using a mathematical model for describing transport across the membrane. A good agreement with the results of non-equilibrium simulation was obtained.

One of the limitations of molecular simulation methods is the small number of atoms in the simulated systems. Current computational possibility allows to simulate membrane thicknesses of about 10 nm. The thickness of the active layer of industrial membranes is more than ten times greater. In this work, it was shown that a combination of mathematical modeling using the results of equilibrium and non-equilibrium molecular simulation allows solving this problem.

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# VOLUMETRIC PROPERTIES OF AQUEOUS ALCOHOL SOLUTIONS: A VORONOI ANALYSIS

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Volumetric properties such as partial molar volume are of major interest in solution thermodynamics. They are often used to study the structure of solutions. One should remember, however, that volumetric properties are the properties of the whole solution even if they are formally ascribed to one of the components. It could be quite interesting to measure individual volumes of components in the solution. It is even more tempting to connect such volumes with observed solution volumetric properties. That is impossible in an experiment, but one can do it working with molecular dynamics models.

Recently we have suggested a concept of Voronoi molar volume of a component [1, 2]. It is the mean value of volume ascribed to component molecules in solution. One can calculate it from a molecular dynamics trajectory using the Voronoi tessellation. Voronoi molar volume can be also considered as a solution volumetric property. We obtain equations expressing the mostly used volumetric properties (excess molar volume, apparent molar volume, and partial molar volume) via Voronoi volumes of components. Our equations contain explicit contributions of solvent and solute and it is thus possible to examine the features on volumetric characteristics curves.

We have applied our method with aqueous solutions of small monoatomic alcohols: methanol, ethanol, 1- and 2-propanol. It was found that the Voronoi molar volume of both solvent and solute is decreasing and a slope of such decrease is lowering when concentration is rising. We ascribe such behavior to an association of alcohol molecules. Solution excess molar volume, apparent, and partial molar volumes of the components are calculated. The reason for minima occurring on these curves is connected with the finishing of the water Voronoi volume change.

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# ENERGY STORAGE MATERIALS AND SENSORS

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Energy and environment protection research have attracted significant attention. Studies of economic, highly efficient, and safe hydrogen storage materials (HSMs) are of great importance in fuel cell-based vehicles. Hydrogen sensors for real-time monitoring are necessary for dehydrogenation and hydrogenation. It is of great significance and research value to explore the hydrogen sensor with a rapid, safe, and reliable response to ensure human life and property safety. On the other hand, the application of phase change materials (PCMs) for solar thermal-energy storage has received considerable attention in recent years due to their high storage density. In recent years, our research effort has been focused in developing HSMs and PCMs based on micro/nano-technology, etc. The promising nanomaterials for HSMs such as $MH_x$: M= Mg, La, Ni, etc., alanate, borohydride, and MOF were conducted in our lab. Several microencapsulated PCMs and composite PCMs with good performance have been synthesized through *in-situ* assembly, and their applications in thermal regulation of gypsum boards are presented. Furthermore, gas sensors with fast response and selective detection with good reproducibility and short recovery time have been fabricated. In this presentation, I will summarize materials for hydrogen/heat energy storage and sensors and some of the recent results in my group.

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# HIGH-TEMPERATURE PHASE EQUILIBRIA IN THE Fe-Sn-S SYSTEM

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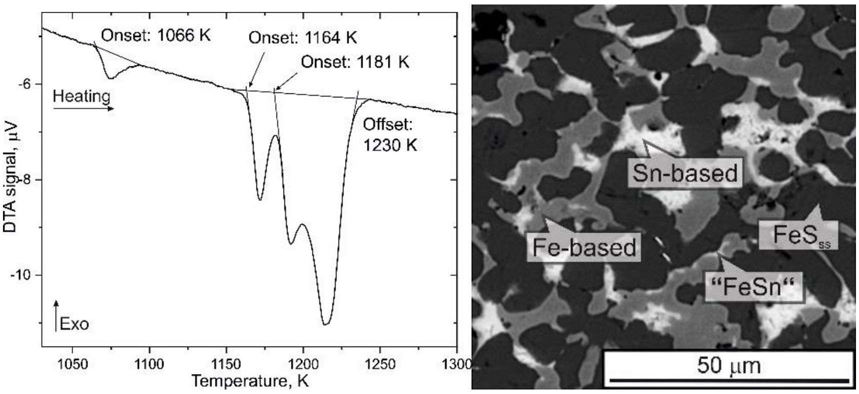
Phase equilibria in the Fe-Sn-S system have been studied experimentally at high temperatures. Selected compositions of the system have been prepared from metals and sulphide mixtures in prefixed laboratory conditions. Experimental samples have been examined by methods of differential scanning calorimetry and scanning electron microscopy coupled with an energy dispersive spectroscopy. A vertical FeS-SnS section has been plotted and compared with available literature data. Liquidus and solidus projections of the ternary Fe-Sn-S system have been studied based on obtained results. Compositions and temperatures of some invariant points on liquidus projection were defined experimentally for the first time. A miscibility gap in the liquid phase has been studied. Boundaries of the miscibility gap as well as tie-lines on the liquidus projection have been determined. Figure 1 illustrates typical structure (a) and DSC heating curve (b) from one of the experimental samples located on “liquid+(Fe,Sn)S+α(FeSn)” monovariant line of the Fe-Sn-S system.



(a) (b)

**Figure 1.** BSE-image (a) and DSC-curve of the (wt.%) 56Fe-24Sn-20S experimental sample

# APPLICATION OF DSC FOR STUDYING THE DOSE DEPENDENT EFFECT OF CYCLOPHOSPHAMIDE TREATMENT ON ACTIN

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The application of DSC in medical science was an important experience in the last decades to earn information about thermal transitions which are linked to the structural changes of proteins. Thus, we carried out DSC scans to investigate the direct effect of cyclophosphamide (CP) on the structural thermodynamics of actin. The actin is the essential unit protein of cytoskeleton and muscle sarcomeres. The continuous management of filaments is the key machinery of eukaryotic cytoskeletal plasticity which based on the different complexes with divalent cations ($Ca^{2+}$ or $Mg^{2+}$) and nucleotides (ATP, ADP). Any structural modification of nucleotide binding sites in G actin can bind ATP or ADP under different cation conditions and can initialize the remodeling of the cleft and change the stiffness of two main domains. It has been demonstrated that run of DSC curves, melting temperature ($\boldsymbol{T_{ms}}$) together with the enthalpy change ($\boldsymbol{\Delta H_{cal}}$) exhibit clear CP effect on binding clefts. In case of $Ca^{2+}$ G-actin it is manifested in a well separated second high denaturation temperature, because of the CP binding into the cleft. This way the nucleotide binding cleft with subdomain 1 and 3 seems less flexible, indicating clear sensitivity to CP treatment. In F-actin samples the main peak represents the thermal denaturation of subdomain 1 and 3, and the increased calorimetric enthalpy administrating $Ca^{2+}$ as well as CP refers to a more rigid structure. These alterations can be the molecular background in the malfunction of muscle in case of polyneuropathy after CP treatment. The other interesting point of our study is the evolutionary importance of physical links between the domains to understand the multidomain development of protein functions. We have analyzed the thermal stability modifier act of interdomain links in proteins, monitored by DSC, with the concept of that how did the nucleotide binding cleft between the two main domains of actin affect the activation energy of them if it was blocked by CP binding. We have investigated the importance of interdomain linkers on the thermodynamic properties of actin. $Ca^{2+}$ and $Mg^{2+}$ bound G-actin can be stabilized by CP binding or by polymerization. CP treatment of $Ca^{2+}$ F-actin lacks the structural integrity of a more flexible polymer and shows same stability as CP bound monomers. However, $Mg^{2+}$ F-actin did not show any kinetic response to the CP treatment. We can assume that the CP binding blocks the interdomain linkers of actin which originally reduced the stability of domains thus resulted a more reactive and variable structure with the thermodynamic advantage in the development of multidomain proteins. Of interest, even a single dose of CP modifies the whole structural dynamics of each subdomain in actin monomers.

# GROUP CONTRIBUTION REVISITED: THE ENTHALPY OF FORMATION OF ORGANIC COMPOUNDS WITH “CHEMICAL ACCURACY”

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Group contribution (GC) methods to predict thermochemical properties are of eminent importance to process design. However, for the experimental scientist for whom such predictions are of relevance, the accuracies are often far from sufficient for reliable application [1]. Compared to previous works, we present an improved group contribution parametrization for the heat of formation of organic molecules exhibiting chemical accuracy, i.e., a maximum 1 kcal/mol (4.2 kJ/mol) difference between the experiment and model, while, at the same time, minimizing the number of parameters [2,3]. The latter is extremely important as too many parameters lead to overfitting and, therewith, to more or less serious incorrect predictions for molecules that were not within the data set used for parametrization. It was found to be important to explicitly account for common chemical knowledge, e.g., geminal effects or ring strain, which avoids pure numerical fitting of parameters but takes account known physico-chemical effects leading to proper chemistry and more reliable predictability. The group-related parameters were determined step-wise: first, alkanes only, and then only one additional group in the next class of molecules. This ensures unique and optimal parameter values for each chemical group.

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# COMPUTERIZED MEASURING DEVICES IN ADIABATIC CALORIMETRY

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Использование мощных вычислительных средств компьютера непосредственно в процессе поддержания адиабатического режима и измерений температуры позволяет существенно усовершенствовать классический метод адиабатического калориметра. Компьютер управляет блоком, включающим в себя периферийные микропроцессоры, аналоговые выходные каналы управления нагревателями и высокоточные каналы измерения температуры. Такая интегрированная компьютерно-измерительная система позволяет использовать более сложные алгоритмы, чем классический метод ступенчатого нагрева. Выполняемые компьютером вместе с микропроцессорами измерительного блока вычисления используют математическую модель калориметрической ячейки и адиабатизирующих экранов, а также априорную информацию о свойствах образца. Эти алгоритмы учитывают конструкцию экранов, измеряемые статические и динамические градиенты на них, выравнивание температуры в контейнере и образце – все это позволяет существенно повысить точность измерений теплоемкости. Высокоточный измерительный блок с разрешением порядка 20 нВ значительно снижает требования к адиабатике, что позволяет реализовать точные калориметрические измерения даже в безвакуумных системах.

Реализованные в программном обеспечении и выполняемые в реальном времени методы нелинейной регрессии позволяют аппроксимировать нелинейные тренды при длительном выравнивании температуры в образце.

Конечным результатом наших разработок, проводимых в последние тридцать лет, явился ряд базовых криостатов для теплофизических измерений и компьютерно-измерительная система АКСАМИТ-11, которые представлены в отдельном стендовом докладе.

# POSTER PRESENTATIONS

# DEPENDENCE OF THE STANDARD THERMODYNAMIC PROPERTIES OF POLYOXIMES ON THE COMPOSITION

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The increased interest in the synthesis and study of polymers containing oxime groups in macromolecules is explained by the possibility of using them for various technological and analytical purposes. Despite the numerous prospects for the polyoximes use, a comprehensive study of their thermodynamic properties was not practically carried out. The aim of this work was to study the influence of the poly(1-hydroxyimino)trimethylene (further in the text – ethane) fragments percentage on the thermodynamic properties of polyoximes. Four samples of polyoximes with different contents of ethane fragments were studied: 100%, 86.7%, 85.4%, 76.6%. All of them were synthesized at the Institute of Problems of Chemical Physics of the Russian Academy of Sciences and characterized by NMR and IR spectroscopy, elemental analysis and gel permeation chromatography.

Heat capacity in the range of 6 to 500 K was studied for the first time by precise adiabatic vacuum calorimetry and differential scanning calorimetry. The combustion energies of the samples were determined by using a static-bomb combustion calorimeter with an isothermal cover. According to the obtained data the standard thermodynamic functions of polyoximes from $T \to 0$ to (410-430) K and their thermochemical characteristics of the formation at $T = 298.15$ K were calculated. All the obtained characteristics were compared with each other.

It was found the linear dependences of the isotherms of the heat capacity, enthalpy and entropy of heating on the ethane fragments content. For example, Figure 1 shows the dependences of the heat capacity on the composition at three temperatures.

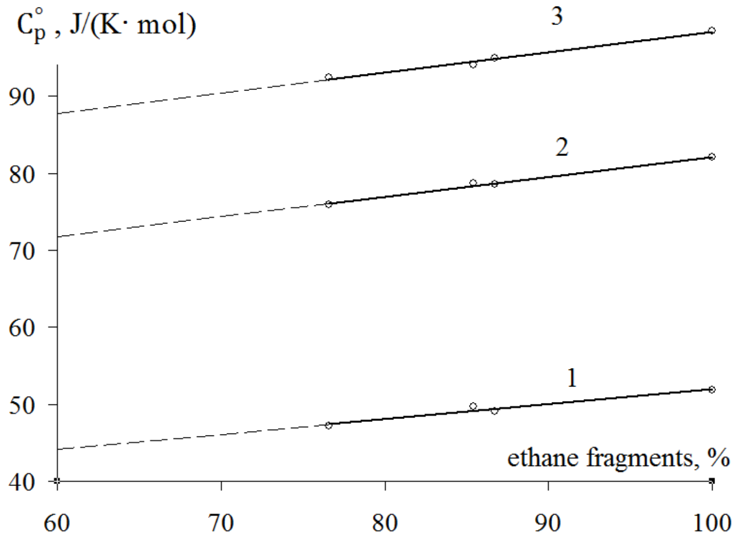

**Figure 1.** Isotherms of the heat capacity dependence on the molar fraction of ethane fragments: at 150 K (1), 250 K (2) and 298.15 K (3).

The obtained dependences allow us to predict the properties of new unstudied compounds of this class of polymers.

# THERMODYNAMIC PROPERTIES OF PHASE TRANSITION OF 2-METHYLQUINOLINE, 2-CHLOROQUINOLINE AND 2-PHENYLQUINOLINE

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Quinoline derivatives are extremely useful in medicine. Therefore, thermodynamic properties of them are essential to know their quality and stability. The medicine may expose to phase transition during setting under struggle environments or transportation conditions. Consequently, thermodynamic characters of phase transition for 2-methylquinoline (Quinaldine), 2-chloroquinoline and 2-phenylquinoline were investigated. The sublimation/vaporization enthalpy of the compounds were determined by using solution calorimetry-additivity scheme approach. Solution calorimetry was used to measure solution enthalpies of the compounds in benzene solvent at 298.15 K. Solvation enthalpy of the compounds were calculated by additivity scheme method. In addition, transpiration method was applied to determine vapor pressures over 2-Chloroquinoline for first time. Sublimation/vaporization enthalpy, entropy, and free energy for 2-methylquinoline, 2-chloroquinoline and 2-phenylquinoline were determined from crystalline/liquid to gas phase. In the present study, the thermochemical characteristics values were exhibited smaller uncertainties than those of literature values. Moreover, in this work was illustrated that thermodynamical investigated to 2-position of quinoline compound when substituted by methyl, chloro and phenyl groups.

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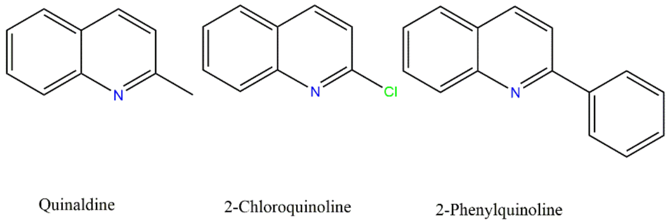

**Figure 1.** Chemical structure of the quinolines.

# KINETIC AND THERMODYNAMIC CONTROLS OF ZINK CYAMELURATE CRYSTAL FORMATIONS

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The dynamic combinatorial library (DCL) of cyamelurates consists of 17 tautomers of cyameluric acid and their ions, as well as metal aquacomplexes. That leads to a variety of compounds in the $Zn(NO_3)_2$ – $K_3(C_6N_7O_3)$ – $H_2O$ system. All compounds are obtained with impurity amorphous and crystalline phases, which complicates their study. In this work, metastable phases of zinc, nickel and iron cyamelurates were obtained and their crystal structures were determined for the first time. Kinetic control of chemical reactions allowed us to isolate two zinc cyamelurate metastable phases. The metastable compound $K_2Zn(C_6N_7O_3H)_2\cdot 8H_2O$ is formed immediately after mixing the precursor solutions, and after two hours it is converted to another metastable compound $Zn(C_6N_7O_3H)\cdot 5H_2O$. Due to hydrate isomerization, after 12 hours in the mother liquor the latter transforms into a thermodynamically stable compound of the same composition. The features of the synthesis and crystalline structure of zinc cyamelurates can be interpreted from the standpoint of the non-classical nucleation theory. The crystal structures of the synthesized compounds $K_2Zn(C_6N_7O_3H)_2\cdot 8H_2O$, $Zn(C_6N_7O_3H)\cdot 5H_2O$ and $Zn(C_6N_7O_3H_2)_2\cdot 8H_2O$ allowed us to conclude that decomposition of supersaturated zinc solution lead to formation of double electric micelles. They can be considered as nanoreactors playing an important role in crystal nucleation.

The features of synthesis and crystal structure of zinc cyamelurates, indicating a nonclassical nucleation, allowed us to propose the stages of crystal formation. Colloidal particles with an electric double layer, formed due to the concentration decay, play an important role in crystal nucleation. Inside such particles, the precursors transform into building blocks, which generate crystal nuclei through self-assembly process. The chemical composition of the crystal nucleus depends on the composition of the colloidal particle. Isolation of metastable phases by means of kinetic control has demonstrated its significance in obtaining crystalline substances, which make it possible to draw a conclusion regarding the process of crystal nucleation, provided that the object of study is successfully selected.

**Acknowledgements.** This work was supported by Russian Foundation for Basic Research (grant 20-08-00097) and by M.V.Lomonosov Moscow State University Program of Development.

# THERMODYNAMIC MODELING OF LAYERED STRUCTURES BASED ON GRAPHITE OXIDE

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The subject of the study was graphite oxides (GO) synthesized by the Hammers (H-GO) and Brodie (B-GO) method. The increased interest in GO is explained by its properties: mechanical strength, hydrophility and the ability to dissolve in polar solvents. Aqueous colloidal solutions are a convenient medium for producing composites based on graphene oxide. In addition, GO posessis the ability to selectively sorb liquids. Sorption is a reproducible characteristic of the GO sample and is accompanied by swelling (an increase in interplane distances), i.e. the sorbed liquid is mainly located in the interplane space of the GO.

It is proposed to consider structures of graphite oxides B-GO and H-GO swollen in polar solvents as thermodynamic phases. The structures of the H-GO are solid solutions, the more ordered structures of the B-GO being solvates with narrow areas of homogeneity. The suggested approach made it possible for the first time to construct diagrams of the state of binary systems graphite oxide / polar solvent for systems B-GO / normal alcohol in a series from methanol to nonanol. When moving along this row, the type of the status diagram changes twice. Explained are changes in the properties of swollen structures with changes in temperature, pressure and composition. Several types of phase transitions were recorded and interpreted as incongruent melting of solvates. Transitions between different heterogeneous regions of the state diagram were experimentally observed.

The behavior of the systems observed in our experiments was described using diagrams of three types. In the diagram of the first type there are two solvates (I and II). This diagram describes the systems B-GO / methanol and ethanol. Systems B-GO / butanol, pentanol, hexanol, heptanol are described by a diagram of the second type. Solvates I, II and III are present here. Finally, five solvates I-V are shown in diagrams of the state of B-GO / octanol and nonanol. The designation of solvates in different systems with the same Roman numeral indicates the same internal structure of the solvate. A layered model of the structure of swollen B-GO structures was proposed (parallel layers of polar liquid between the planes of graphite oxide). For example, structure III contains three "layers" of polar liquid between adjacent planes of graphite oxide. The "layer" is characterized by the amount of sorption. The appearance of a new "layer" of liquid increases the interplane distance by a certain amount.

It is shown that solvates I, III, V are stable, and solvates with an even number of layers are less stable. II melts incongruently when heated and solvate IV is detected only in a narrow temperature range in 1-octanol and 1-nonanol systems.

Phase diagrams summarize our experimental data obtained by DSC method, isopiestic and isothermal TG (boundaries of phase regions). The phases were identified by XRD method in equilibrium and nonequilibrium experiments.

For the first time, the existence of two types of similar phase transitions, differing in temperature and enthalpy of transformation, was noted. In the first case, a liquid layer in contact with the graphene plane is incongruently melted (a typical example is $CH_3OH$), in the other, a layer located in the center of the sorbed liquid mass ($C_8H_{17}OH$ and $C_9H_{19}OH$). In the second case, the transition temperature is close to the melting temperature of the sorbed liquid (+5-10 degrees), in the first case, the difference can be up to +110 degrees.

**Acknowledgements** The work is supported by RFBR grant No. 19-08-00498.

# THERMODYNAMIC CALCULATION OF BOUNDARIES OF SOLID SOLUTIONS IN SYSTEMS PBTE–$Bi_2Te_3$–$Sb_2Te_3$ AND PbTe–SnTe–$Bi_2Te_3$

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Bismuth, tin, and lead tellurides are thermoelectric materials with low thermal conductivity, as well aspromising materials for creating topological insulators [1,2]. This paper presents isothermal sections of the phase diagrams of systems PbTe–$Bi_2Te_3$–$Sb_2Te_3$ and PbTe–SnTe–$Bi_2Te_3$, with the indication of the boundaries of solid solutions, determined based on methods of physicochemical analysis using thermodynamic calculations.

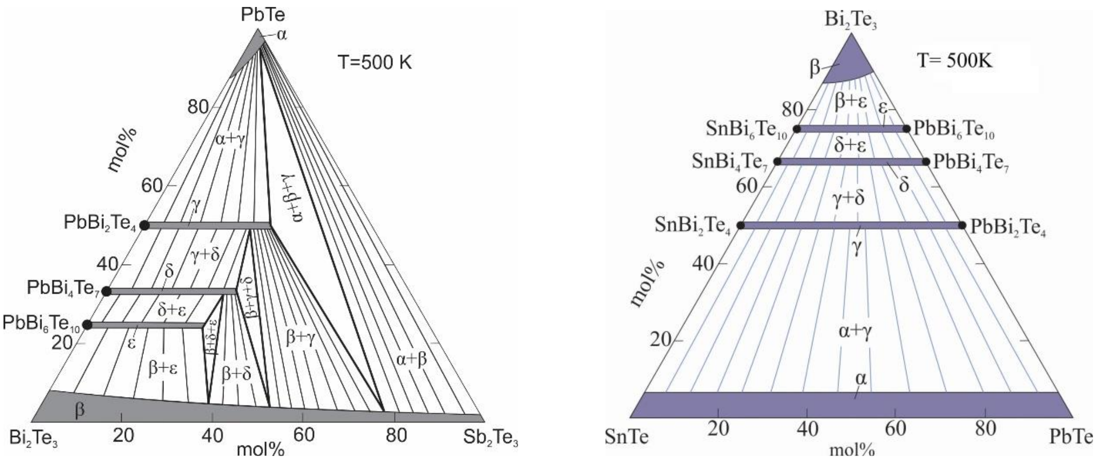

**Figure.** Isothermal sections of the PbTe–$Bi_2Te_3$–$Sb_2Te_3$ and PbTe–SnTe–$Bi_2Te_3$ system

To determine the compositions of liquid and solid solutions in equilibrium, the following equations were used [3]

$$x_i^l = \frac{1-\exp(F_1(T))}{\exp(F_2(T))-\exp(F_1(T))}\ ; \qquad x_i^s = x_i^l \cdot \exp(F_2(T))$$

$$F_i(T) = (\Delta S_i^o - \Delta H_i^o/T)/R + \Delta\bar{G}_i^{exs,l/s}/RT$$

Here *l* and *s* represent of liquid and solid solutions that are in equilibrium; $x_i^l$ and $x_i^s$ are molar fractions of components for liquid and solid solutions; $\Delta\bar{G}_i^{exs,i/s} = \left(\Delta\bar{G}_i^{exs,l} - \Delta\bar{G}_i^{exs,s}\right)$ - difference between excess Gibbs free energies of the components of liquid and solid solutions . $\Delta S_i^o$ and $\Delta H_i^o$ are formation enthalpy and entropy of solid solutions basen of initial compounds.

## Acknowledgement

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# ACCELERATION OF METHANE HYDRATE NUCLEATION BY CRYSTALS OF HYDRATED SODIUM DODECYL SULFATE

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One of the current trends in the study of gas hydrates is currently the study of substances that accelerate the formation of gas hydrates from water and gas under static conditions [1-3]. These properties are possessed by surface-active substances (surfactants), in particular sodium dodecyl sulfate (SDS), which is the most actively studied substance in this capacity [3-6]. Under static conditions, the formation of hydrate, as a rule, occurs at the gas-water interface, while the resulting hydrate film blocks mass transfer and practically stops the process of hydrate formation. The degree of water to hydrate conversion is usually a few percent. In the presence of a surfactant dissolved in water, the hydrate is formed in the form of a loose mass saturated with water, which is squeezed out onto the walls of the reactor. In this case, 80-90% of the water turns into a hydrate. In addition, studies have shown that hydrate nucleation occurs faster in SDS solutions than in pure water [6, 7].

The features of methane hydrate nucleation from a 0.1 wt % SDS solution were studied in a high-pressure optical cell. In a number of experiments (~12 hours at 10°C and atmospheric pressure), transparent crystals appeared on the surface of the solution - one of the low-water SDS hydrates, most likely a dihydrate. These crystals serve as powerful accelerators of methane hydrate nucleation.

At a steady state methane pressure of 3.1 MPa and a temperature of 0°C, nucleation of the hydrate in 0.1 wt % SDS solution occurred within 2 - 4 min. Crystals of hydrated SDS do not have a significant effect on the features of the process of further growth of methane hydrate - the growth of the hydrate occurs in the form of a loose mass extruded onto the walls of the reactor.

It has been shown that hydrated crystals of this substance precipitated from dilute solutions of sodium dodecyl sulfate accelerate the nucleation of methane gas hydrate. The results obtained add significant details to the available information on the mechanisms of hydrate formation in SDS solutions and can form the basis for the development of a new class of kinetic promoters of hydrate formation.

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# SOME FEATURES OF THE PROCESS OF HYDRATE FORMATION ON AQUEOUS FOAM STABILIZED BY SURFACTANTS

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This work presents experimental studies of methane hydrate formation from aqueous foam stabilized by surfactants. The experiments were carried out in a high-pressure optical chamber using photo and video recording.

Multicomponent foaming solution was used in this work. The solution contained two types of surfactants: 1.0 wt% of sodium dodecyl sulfate (96.33%, Galaxy, India) and 1.0 wt% of nonionic surfactant OP-10 (LLC Sintez OKA, Russia). The solution was stabilized with carbomer and glycerin. When choosing the components of the solution, preference was given to components with a minimal thermodynamic inhibitory effect on hydrate formation. Hydrate formation began at a temperature of 0.5°C and a pressure of 13 MPa.

It is shown that at the interface of the foam-solution are formed a polycrystalline conical conglomerates (hydrate needles) at the moment, when the front of hydrate formation reaches this boundary. It is noted that these formations have an elongated shape and are oriented along the normal to the surface of the hydrate growth front. Upon melting, the needles retain a transparent hydrate framework, but lose their tightness. As a result, gas is displaced by liquid from their inner volume into foam cells from which these formations have grown. The secondary formation of hydrate needles has been studied.

**Acknowledgements** The financial support of the Russian Science Foundation № 22-19-00092.

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# THERMODYNAMICS OF SORPTION OF SODIUM OLEATE ONTO COPPER-MOLYBDENUM ORE

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In mining and metallurgical complexes, the innovativeness and capacity to produce are not a future requirement but the present realities that have determined the industry development trends for many years. Modern enrichment technologies of ore from new deposits should ensure products from medium and low-quality raw materials caused by highly dispersed mineral inclusions of rock and ore bodies. In Kazakhstan, ore materials, including Py-Cu-Mo, Cu, Cu-Pb, and Fe-Mn ores, are scattered over a significant area and come from a very considerable depth. In this regard, new ways of intensifying the enrichment processes should consider an integrated approach involving the physical chemistry of minerals in terms of complexing and sorption abilities and the effective usage of selective reagents for a particular mineral. This research presents an experimental study of pulp chemistry and surface chemistry underlying the enrichment of Cu-Mo ore, which involves sorption processes. Material characterization methods used include X-ray fluorescence and FTIR spectroscopies, EDS analysis, etc. The thermodynamics and kinetics of adsorption have been estimated to find the selectivity of sodium oleate toward Cu-Mo ore under the optimal conditions. The entropy-enthalpy compensation effect in desorption has been found [1]. An observed exponential increase in differential sorption energy works only in a narrow interval in the degree of surface filling corresponded to dehydrated areas. Thus, the energy density values for the main minerals in Cu-Mo ore have been calculated [2]. As is detected, the entropy contribution to Gibbs energy likely compensated by enthalpy decreases when the proton-accepting ability of metal oxides from Cu to Mo ($i_{\mathrm{Cu(II)\text{-}O}}$ = 32%, $i_{\mathrm{Mo(IV)\text{-}O}}$ =43%) enhances. Also, the ionic metal-chalcogen (oxygen) bond's contribution to the binding strength of the organic reactant is established.

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# ELECTROFLOTATION IN WASTEWATER TREATMENT FROM CHROMIUM (VI) IONS: THERMODYNAMIC ANALYSIS

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It is known that the primary type of galvanic production waste is wastewaters containing high amounts of heavy metal ions, especially chromium (VI) ions [1]. Purifying such effluents presents significant challenges due to the impossibility of recovering free metals from sludge with complex compositions. One alternative way to solve such a problem is to use a closed water supply system including electroflotation. This method can decrease the content of heavy metals in wastewaters lower than maximum allowable concentrations by fine hydrogen and oxygen bubble generated from water electrolysis. The current research presents the electroflotation purification of wastewater model solutions containing Cr(VI) ions. The basic conditions of electroflotation are current of 4 A and voltage of 140 V. Process duration in min and pH are 15-120 and 8-12, respectively. The rate constants for the electroflotation depending on temperature and pH of the reaction medium have been determined from residual concentration-time dependence for Cr(VI) ions after the treatment to estimate the changes in entropy and enthalpy of activation (table).

Table - The effect of pH on Cr(VI) extraction by electroflotation

| | pH | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|
| | | $\Delta S^{\#}$, J·mole$^{-1}$·K$^{-1}$ | | | | |
| T, K | 298 | -826.89 | -277.61 | -824.53 | -822.02 | -40.25 |
| | 303 | -826.91 | -277.63 | -824.55 | -822.04 | -40.26 |
| | | $\Delta H^{\#}$, kJ·mole$^{-1}$ | | | | |
| T, K | 298 | -144.68 | 22.32 | -144.68 | -144.68 | 93.70 |
| | 303 | -144.76 | 22.24 | -144.76 | -144.76 | 93.62 |

According to the authors [1], a negative value of entropy of activation is typical for reactions in which an intermediate formed on the electrode surface is more ordered and compact than ions in solution. Considering thermodynamics, the mobility of active particles due to electrostatic forces has played a leading role in the electroreduction of Cr(VI) ions at pH 8, 10 and 11. Alternatively, in an alkaline environment with pH 9 and 12, water molecules are most likely to be involved in forming an activated intermediate. The changes in enthalpy of activation also confirm this mechanism. To sum up, it is found that electroflotation proceeds most intensively under a temperature of 303 K and pH 8, 10 and 11 with a purification degree up to 98%.

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# MOLECULAR SIMULATION OF THE PERVAPORATION PROCESS

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Physico-chemical properties far exceed some of the initial information, representation for modeling and design of chemical industry processes. One approach for calculating transport properties is to use excess entropy. The use of excess entropy is widely replaced as a scaling factor in global isomorphism theory. Thus, the relationship between excess entropy and transport factors was demonstrated on a variety of pure substances: hydrocarbons, model Lennard-Jones fluid, and others.

In this work, the excess entropy approach was used to calculate the transport properties of pure substances with a dipole molecules and nonideal mixtures using the Lennard-Jones fluid as an example.

To determine the transport properties (diffusion coefficients, viscosity and thermal conductivity) of pure substances, it is necessary to divide the phase diagram into 3 regions: one region for gases and the supercritical state and two for the liquid phase. In each of these areas, it is proposed to determine by its own equations, while each of the areas is connected by values on the border of these areas. In the gas and supercritical regions, the Chapman–Enskog equation gives a good description. The Stockmayer potential was used to calculate the collision integral and intermolecular interaction. Entropy was calculated using the equations of state. In the regions of the liquid phase, the connection of transport properties was carried out through an exponential dependence on the difference in entropy at the desired point and at the boundary of the region. In each of the regions for the liquid phase, one tuning parameter was used, which was found from the experimental data. Calculations have shown that the proposed method good agreement in a wide range of states.

Also, the excess entropy was used for the diffusion coefficients of the mixture of properties of the Lennard-Jones mixture. The system under study consisted of two types of components. Between molecules of the same type were identical. The difference in intermolecular interaction was in cross interactions. Calculations were made of the thermodynamic properties and diffusion coefficients of such a mixture at various densities and compositions. The diffusion coefficient in a mixture was associated with the diffusion of a pure component through the difference in the entropy of the mixture and the pure component. The calculations showed qualitative and quantitative agreement with the results of numerical experiments.

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# CALVE CALORIMETRY AND P-C ISOTHERMS: COMPARATIVE ANALYSIS OF THERMODYNAMIC DATA

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The discovery of large number of intermetallic compounds (IMC) with the general formula AB, AB2, AB3, AB5, etc. that had the property of reversibly absorbing and desorbing hydrogen at normal conditions made by scientists in the 1970s allowed us to think about replacing traditional hydrocarbon fuel with hydrogen today. The multicomponent alloys on the base of Zr-Ti-Mn-V with hexagonal Laves phase structure C14 are the one of IMCs family. Varying stoichiometry of IMCs and alloying of new elements it is possible to obtain new compound with preset properties. The purpose of this work was to show how a slight change in the composition of the IMC can affect the hydrogen-sorption properties of the compound. The initial IMCs Ti0.9Zr0.1MnYVX (x=0.1, 0.5, 0.6, 0.7, y=1.2, 1.3, 1.4) were prepared as described in [1] by melting stoichiometric mixture of starting components: Ti (99.99%), Zr (99.99%), electrolytic manganese (99.9%) and vanadium (99>9%). X-ray powder diffraction analysis of the initial IMCs and their hydrides were performed with Huber G 670 Image Plate Guinier camera (Cu Kα radiation). According to XRD data initial compounds were single-phase IMCs with the hexagonal Laves phase structure C14 (space group P63/mmc). When the initial compounds were hydrogenated, their crystal structure did not change, but only the lattice parameters increased in about 23%. The reaction of hydrogen interaction with Ti0.9Zr0.1MnYVX was studied by Calvet calorimetry at 60, 80 and 100°C and hydrogen pressure up to 50 atm. An application of this method to the study of thermodynamic properties of the IMC-H2 system allowed us to obtain simultaneously two functional dependences: the change of the equilibrium pressure of hydrogen and the partial molar enthalpy of the reaction of hydrogen with IMCs on the hydrogen content in the IMCs. In addition on the base of van't Hoff equation we calculated thermodynamic parameters of hydrogen interaction with IMCs (ΔHdes.) =f(C) и ΔSdes.=f(C)) too and compared the results obtained during calorimetric measurements with the results calculated from P-C measurements. The results obtained by the calorimetric method show that the values of the enthalpy of the hydrogen reaction with the IMC change with the temperature of the process under the study, as well as with the concentration of hydrogen in the IMC. It has been shown that at in the Ti0.9Zr0.1MnYVX -H2 systems there are two regions with constant reaction enthalpies, that is, two hydride phases are formed - Ti0.9Zr0.1MnYVXH2 and Ti0.9Zr0.1MnYVXH~3, and the enthalpy of formation of the tri-hydride is higher than that of the di-hydride. It should be marked that the increase of hydrogen concentration in the metallic matrix results in the increase of the partial enthalpy values of hydrogen interaction with IMC in absolute magnitude. This phenomenon, as we assume, is possible due to the presence of some distortion in the metal sub-lattice caused by the further absorption of hydrogen by the hydride phase which is explained by the nature of the change in the enthalpy of the reaction. We calculated the values of max storage capacity and working capacity (1-10atm) for investigated IMCs from P-C-T measurements. Ti0.9Zr0.1Mn1.2V0.1 has the best max storage capacity (1.97wt%) at 53 atm and 60°C. However, the best working capacity (1-10atm, 60°C) is 1.34 wt% for Ti0.9Zr0.1Mn1.4V0.5.

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# CALORIMETRIC STUDY OF HYDROGEN INTERACTION WITH $DY_2FE_{17}$

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At the first time the Dy2Fe17-H2 system was studied by the Calvet-calorimetric method. Earlier this system was studied by means DSC method.

The initial sample of Dy2Fe17 was prepared by arc melting of the stoichiometric mixture composed of its metals 2-17: 25.5 wt.% Dy and 74.5 wt. % Fe (a purity grade is higher than 99.9%) under a pure argon atmosphere (1.5 atm). Further the $Dy_2Fe_{17}$ sample was subjected to homogenizing annealing in a vacuum resistance furnace at a temperature of 1150°C for 24 hours. X-ray phase analysis of the initial $Dy_2Fe_{17}$ alloy and $Dy_2Fe_{17}H_{4.0}$ hydride was performed on a Rigaku Ultima IV diffractometer (Co Kα radiation and a graphite monochromator. Powder X-ray analysis of the initial sample $Dy_2Fe_{17}$ showed that it was single-phase material with the hexagonal structure $Th_2Ni_{17}$-type (space group $P6_3/mmc$), the refined unit lattice parameters: a=8,3794(8)Å, c=8,3372(3)Å, c/a=0,995. X-ray phase analysis of the hydride showed that during the hydrogenation the initial compound structure did not change, and the anisotropic expansion of the crystal lattice occurred (a=8,5512Å, c=8,3461Å, c/a=0,976).

The study of hydrogen interaction with $Dy_2Fe_{17}$ was carried out by the calorimetric method and plotting P-C isotherms using the calorimeter of Tean-Calvet type DAK-12, connected with a Sievert's-type volumetric apparatus. The apparatus scheme, the procedure of experiment carrying out and the treatment of obtained results were described elsewhere [1]. The calorimetric investigation of the $Dy_2Fe_{17} – H_2$ system has been carried out in the temperature range from 200 to 300°C and the hydrogen pressure up to 50 atm. The absorption and desorption processes were studied and as results we obtained the P=f(C), ΔH= f(C) and ΔS= f(C) dependences (C= H/ $Dy_2Fe_{17}$, P-equilibrium hydrogen pressure, ΔH- enthalpy, ΔS- entropy). In the P – C - T isotherms there is no plateau as it was shown in the work [2]. However, in the plot of the ΔH= f(C) for $Dy_2Fe_{17}$ for hydrogen absorption and desorption we can select two regions where enthalpy values retain constant: $0.1<C<1.3$ and $1.8<C<2.6$. Further increase of C leads to sharp reduction of the enthalpy values in magnitude. It is known [3] that in the hexagonal structure of $Th_2Ni_{17}$-type the hydrogen atoms occupy two different sites: three octahedral interstices [2R-6Fe] 9e and two tetrahedral interstices 18 g [2R-2Fe]. In the work [4] authors on the base different physical experiments showed that the octahedral site was thermodynamically more stable than the tetrahedral one. The hydrogen atoms at first begin to fill the octahedral interstices 9e and then tetrahedral one 18g. Comparing our data obtained for the hydrogen absorption with the data from work [4] we can suppose that two regions with constant enthalpy values on the curve of ΔH= f(C) correspond to filling firstly the octahedral interstices 9e and then the tetrahedral one. Analyzing the obtained data on the enthalpy of hydrogen absorption by $Dy_2Fe_{17}$ compound, we can assume that the introduction of hydrogen into octahedral interstices 9e occurs with different energies.

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# TESTING CARNAHAN–STARLING AND RUSANOV EQUATIONS OF STATE FOR HARD SPHERES IN DENSITY FUNCTIONAL CALCULATIONS OF PROFILES AND SURFACE TENSION OF DROPLETS AND BUBBLES

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We have compared the Rusanov equations of state [1] for hard spheres with the widely-used Carnahan–Starling equation [2] and tested them against the virial expansion with extrapolated 18 coefficients [3]. We have studied both the properties of a homogeneous system of hard spheres (comparing the dependences of the pressure, the chemical potential and the free-energy density on the packing fraction — the dimensionless number density of hard spheres) and a model problem with inhomogeneous density distribution — calculation of density profiles and surface tension of droplets/bubbles formed in a bulk gas/liquid phase.

The full and a narrower ranges of the packing fraction of hard spheres have been considered. It is shown that in general the 6th-order Rusanov equations agree better with the virial expansion over the full range of the packing fraction, but this is due to the high-density region. In the low- and medium-density regions, the Carnahan–Starling equation shows slightly better agreement with the 18-coefficient virial expansion. A different value of the fitting parameter in the Rusanov equation (optimized for the narrower packing fraction range) substantially improves the agreement of the Rusanov equation with the virial expansion within this range.

Using the dependences of the chemical potential and the free-energy density on the local packing fraction for the considered equations of state, within an integral density functional theory, we have calculated the molecular density profiles in radially nonuniform spherical small droplets and bubbles of an argon-like substance and plotted the surface tension of small droplets and bubbles vs the curvature of their equimolecular surface. The choice of the equation of state is shown to affect the values of quantities characterizing the two-phase equilibrium, e.g., of the chemical potential or the surface tension at a flat interface, and can shift the droplet or bubble size [4].

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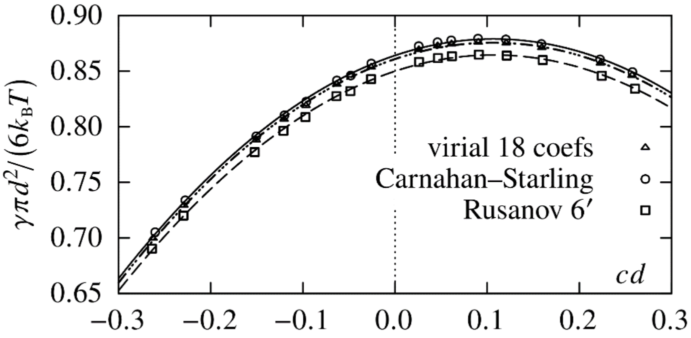

**Figure 1.** Dimensionless surface tension vs bubble/droplet curvature ± $d/R$ (with $d$ the hard-sphere diameter) from integral density functional calculations with different equations of state.

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# THERMODYNAMIC STUDY OF THE $Cu_2Si(Ge)S_3$ AND $Cu_8$ $Si(Ge)S_6$ COMPOUNDS BY EMF AND DSC METHODS

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Complex copper chalcogenides are of interest as functional materials with variable valuable properties [1]. In particular, copper compounds of types $Cu_2B^{IV}X_3$ (where $B^{IV}$-Si, Ge, Sn; X-S, Se, Te) and $Cu_8B^{IV}X_6$ (known as argyrodite family compounds) are attracting more and more attention as promising candidates for environmentally friendly and low-cost thermoelectric materials [2, 3]. Furthermore, some of $Cu_2B^{IV}X_3$ compounds and high-temperature phases of $Cu_8B^{IV}X_6$ have high ionic conductivity via $Cu^+$ cations and can be used in design of ion-selective electrodes, solid electrolytes, etc. [4].

The aim of this work is thermodynamic study of the $Cu_2Si(Ge)S_3$ and both modifications of $Cu_8Si(Ge)S_6$ compounds. All four compounds were synthesized from high-purity elements (at least 99.999 wt% purity) from Evochem Advanced Materials GMBH in evacuated to $\sim 10^{-2}$ Pa and sealed quartz ampoules. Synthesis was carried out in a two-zone furnace.

The investigations were carried out by EMF method with a solid Cu+-conducting electrolyte, as well as by means of DSC using differential scanning calorimeter 404 F1 Pegasus system from NETZSCH. For EMF measurements, reversible concentration chains

$$(-)\ Cu \mid Cu_4RbCl_3I_2 \mid Cu \text{ in alloy } (+),$$

were assembled, in which the superionic conductor $Cu_4RbCl_3I_2$ served as an electrolyte, and equilibrium crystalline alloys of the systems Cu-Si(Ge)-S system served as right-hand electrodes. Right electrode compositions were selected based on the phase diagram.

EMF measurements were done in the temperature range of 290–390 K with the accuracy of ±0.1 mV using the high-resistance Keithley 2100 6 1/2 digital multimeter.

For the $Cu_8Si(Ge)S_6$ compounds EMF measurements were first carried out in the temperature range of existence of the low-temperature modification, and then in the range of existence of the high-temperature one.

From the EMF measurements, the partial molar functions of copper in alloys were calculated.

Based on constructed solid state phase equilibria diagrams, the potential-forming reactions for ternary compounds were found, from which standard thermodynamic functions of formation and standard entropies of $Cu_2Si(Ge)S_3$ and both modifications of $Cu_8Si(Ge)S_6$ compounds were calculated.

The heats of polymorph transitions were calculated using respective thermodynamic functions of both modifications of compounds while $Cu_8Si(Ge)S_6$ entropies of polymorph transitions using the formula $\Delta S_{p.t.} = \Delta H_{p.t} / T_{p.t.}$

Thermodynamic functions of polymorph transformations of the $Cu_8SiS_6$ and $Cu_8GeS_6$ compounds also were determined by DSC which is considered one of the most advanced and highly sensitive methods of phase analysis. Obtained by both methods dates were in agreement within experimental error.

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# ESTIMATION OF VAPORIZATION AND SUBLIMATION ENTHALPIES OF TERPENES AND TERPENOIDS AT 298.15 K

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Terpenes and terpenoids are classes of bioorganic substances found in natural oils, flowers, trees, fruits and other biological objects. They are widely used in parfume, medical, veterinary and chemical industrials. Thermochemical properties, which are used in synthesis and purification processes, of these compounds poorly presented in literature. This is due to the fact that classical convection methods are difficultly apply for these substances.

In this work the vaporization and sublimation enthalpies of 7 terpenes and 5 terpenoids were estimated by solution calorimetry method. Is was shown, that solution calorimetry method can be useful tool to estimate phase transition enthalpies at 298.15K when classical convection methods are hardly applicable.

By this method vaporization/sublimation enthalpies ($\Delta_{\text{vap/sub}}H$) can be found from solution ($\Delta_{\text{soln}}H^{\text{A}_i/\text{S}}$) and solvation ($\Delta_{\text{solv}}H^{\text{A}_i/\text{S}}$) enthalpies in the same solvent (S):

$$\Delta_{\text{vap/sub}}H^{\text{A}_i} = \Delta_{\text{soln}}H^{\text{A}_i/\text{S}} - \Delta_{\text{solv}}H^{\text{A}_i/\text{S}} \tag{1}$$

Solution enthalpy in equation (1) can be measured by solution calorimetry or found from excess enthalpies of mixing. Solvation enthalpy in this method can be calculated from linear dependence of solvation enthalpy and molar refraction [1] or by using additive schemes [2-3]. In this work, to determine solvation enthalpies of terpenes and terpenoids was used additive scheme proposed in work [3]. By this scheme, solvation enthalpy of any aliphatic compound in *n*-heptane can be determined from group contributions of fragments of molecule:

$$\Delta_{\text{solv}}H^{\text{A}_i/n\text{-heptane}} = \sum_{j=1}^{g} n_{ij} \cdot h_j \qquad (2),$$

where $n_{ij}$ – number of structural parameter ($h_j$).

In work [3] it was found that vaporization enthalpy of any hydrocarbon can be found from solvation enthalpy in *n*-heptane by the following equation:

$$\Delta_{\text{vap}}H^{\text{A}_i} = -\Delta_{\text{solv}}H^{\text{A}_i/n\text{-heptane}} \tag{3}$$

The vaporization enthalpies of 7 terpenes were determined from Eqs. (2) and (3). To determine vaporization enthalpies of terpenoids were measured solution enthalpies in *n*-heptane. Estimated by solution calorimetry method vaporization enthalpies of terpenes and terpenoids were compared by literature data. In was shown that vaporization enthalpies of terpenes estimated from Eqs. (2) and (3) in good agreements with experimental values. Vaporization and sublimation enthalpies of terpenoids determined from solution calorimetry and calculated solvation enthalpy for bisabolol, cedrol and linalool in agreements with literature data. At the same moment sublimation enthalpies of menthol and verbenol estimated by the proposed approach do not agree with literature values.

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# THERMODYNAMIC CHARACTERISTICS OF DYES SORPTION ON COAL SORBENTS FROM TEXTILE PRODUCTIONS WASTEWATER AFTER THEIR CHEMICAL TREATMENT WITH A COAGULANT ON THE BASIS OF DICYANDIAMIDE

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Pollution of the environment, in particular water resources, is a real factor that significantly affects the quality of human life. Inefficient wastewater treatment, especially in the textile industry, is a major problem. Inorganic and polymeric coagulants are widely used to purify industrial waters from dyes. However, a significant part of the reagents used does not allow achieving a high degree of purification and, above all, decolorization of the effluent. Therefore, work aimed at the development of new polymeric coagulants that effectively clean wastewater and meet the criteria for environmental and biological safety are relevant.

In this paper, we studied the process features of the deposition of direct and active dyes (4 samples of a different spectrum of colors were used) applied in the textile industry of enterprises in the Ivanovo region.

The thermodynamic and kinetic characteristics of the dyes sorption by carbon sorbents at the final stage of the purification process after treatment of the effluent with a coagulant based on dicyandiamide were determined.

When performing the work, static and kinetic research methods were used with the involvement of chemical (gravimetry, titration) and physicochemical (potentiometry, spectrophotometry, IR spectroscopy) methods of analysis. The results were processed using the methods of mathematical modeling and multivariate statistical analysis.

A mechanism for the process of dye sorption on the sorbents surface is proposed. Dye sorption isotherms are obtained, which have an S-shaped character. By processing the latter within the linear coordinates of the theory of volume filling of micropores, the adsorption characteristics are calculated.

The dyes sorption kinetics was studied depending on the medium pH and the added coagulant amounts. The kinetic curves of sorption of all dyes by the carbon sorbent are of the same type, have a curved shape, and are characterized by the maximum relative rate of the process at the initial moment of time, which then monotonically increases. The contribution of diffusion processes to the sorption kinetics of the studied dyes has been established. The constants of the process of internal and external diffusion are determined.

The obtained thermodynamic characteristics determine the spontaneity of sorption, but the process as a whole is quite complex.

The prospects of using a coagulant based on dicyandiamide for effective purification and decolorization of wastewater from textile industries are shown.

# THERMODYNAMIC PARAMETERS OF POSITIVE AND NEGATIVE IONS IN THE GAS AND LIQUID PHASES AND THEIR CHANGE DURING SOLVATION

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The aim of the work is to create a database of standard values of thermodynamic parameters of positive and negative ions in aqueous solutions [1,2].

There are no standard values for ions in aqueous solutions prior to our work.

Based on the data obtained, the thermodynamic parameters of solvation of monatomic positive ions were calculated with accuracy ± 1 kJ/mol.

Currently, we have two systems for the thermodynamic parameters of various substances: standard, which $\Delta_f H(\mathrm{A}^{\mathrm{o}}_{\mathrm{st}}) = 0$ kJ/mol $\Delta_f G(\mathrm{A}^{\mathrm{o}}_{\mathrm{st}}) = 0$ kJ/mol, and conventional in which . $\Delta_f H^{\mathrm{o}}_{\mathrm{conv}}(\mathrm{H}^+_{\mathrm{aq}}) = 0$ kJ/mol $\Delta_f G^{\mathrm{o}}_{\mathrm{conv}}(\mathrm{H}^+_{\mathrm{aq}}) = 0$ kJ/mol $S^{\mathrm{o}}_{\mathrm{conv}}(\mathrm{H}^+_{\mathrm{aq}}) = 0$ J/(mol·K)

The equations [1] were used for calculations

$$\Delta_f H^{\mathrm{o}}_{\mathrm{standard}}(\mathrm{A}^{n+}_{\mathrm{aq}}) = \Delta_f H^{\mathrm{o}}_{\mathrm{conv}}(\mathrm{A}^{n+}_{\mathrm{aq}}) + n\cdot\Delta_f H^{\mathrm{o}}(\mathrm{H}^+_{\mathrm{aq}}) = \Delta_f H^{\mathrm{o}}_{\mathrm{conv}}(\mathrm{A}^{n+}_{\mathrm{aq}}) + n\ 386.25,\ \text{kJ/mol},$$

$$\Delta_f G^{\mathrm{o}}_{\mathrm{standard}}(\mathrm{A}^{n+}_{\mathrm{aq}}) = \Delta_f G^{\mathrm{o}}_{\mathrm{conv}}(\mathrm{A}^{n+}_{\mathrm{aq}}) + n\cdot\Delta_f G^{\mathrm{o}}(\mathrm{H}^+_{\mathrm{aq}}) = \Delta_f G^{\mathrm{o}}_{\mathrm{conv}}(\mathrm{A}^{n+}_{\mathrm{aq}}) + n\cdot 412.5,\ \text{kJ/mol},$$

$$S^{\mathrm{o}}_{\mathrm{standard}}(\mathrm{A}^{n+}_{\mathrm{aq}}) = S^{\mathrm{o}}_{\mathrm{conv}}(\mathrm{A}^{n+}_{\mathrm{aq}}) + n\cdot S^{\mathrm{o}}(\mathrm{H}^+_{\mathrm{aq}}) = S^{\mathrm{o}}_{\mathrm{conv}}(\mathrm{A}^{n+}_{\mathrm{aq}}) - n\cdot 43.54,\ \text{J/(mol·K)}.$$

In this work, the values of thermodynamic parameters in the process of solvation ( $\Delta\Phi^{\mathrm{o}}_{\mathrm{solvation}}$ ) are calculated based on the standard values of parameters in the liquid and gas phases. The solvation parameters were calculated using the equations

$$\Delta\Phi^{\mathrm{o}}_{\mathrm{solvation}}(\mathrm{A}^{n+}) = \Delta\Phi^{\mathrm{o}}_{\mathrm{standard}}(\mathrm{A}^{n+}_{\mathrm{aq}}) - \Delta\Phi^{\mathrm{o}}_{\mathrm{standard}}(\mathrm{A}^{n+}_{\mathrm{gas}})$$

My data base contains two tables, which contain data on the standard parameters of positive ions (172 ions) and negative (75 ions).

Thus, our work allows us to consider the question of determining the standard thermodynamic parameters of ions in aqueous solutions and their solvation energies close to the final solution.

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# THIRD GENERATION CALPHAD ASSESSMENT OF DATA FOR PURE SI AND GE AND THE BINARY SI-GE SYSTEM

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New thermodynamic descriptions of data for pure elements should cover the most recent experimental data, be based on physical models and provide reliable data over a large temperature range: from 0 K to temperatures well above the melting point. An extended Einstein model [1] for the crystalline phases and a two-state liquid model [2], used as a basis for third-generation CALPHAD assessments, have been applied to the critical assessment of data for a number of pure elements and some compounds. These models have been shown to be very effective.

The present work is devoted to an evaluation and application of the third-generation CALPHAD models to the description of the thermodynamic properties of pure silicon and germanium, and the binary system Si-Ge. The pure crystalline phases were evaluated with the extended Einstein model [1]. Additionally the values for the standard entropies were reassessed using a Planck-Einstein model [3]. For the first time we included descriptions of the properties of pure Si and Ge in the amorphous forms from 0 K. The reliability of new descriptions of the data for the pure elements was tested in an assessment of data for the binary Si-Ge system.

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# PHASE TRANSITIONS AND CRITICAL PROPERTIES OF $C_3H_7OH$+$C_8H_{18}$ SYSTEM

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By using free ballast volume piezometer [1] and the compressibility method along the isochores the values of $p,\rho$ and $p,\rho,T$- relations of 1-propanol and n-octane binary mixtures ($x$=0.2, 0.5, 0.8 mole fractions of n-octane) are obtained including two phase (liquid⇄gas), one phase (liquid, gaseous), critical and supercritical regions.

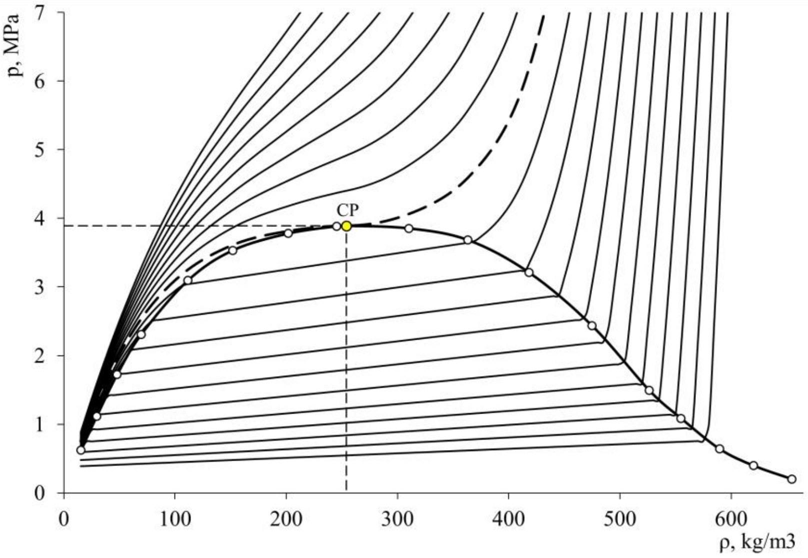

**Fig**. Phase diagram of 1-propanol–n-octane binary mixture of 0.5 mole fraction

Using our own experimental data on $p,\rho$ and $p,\rho,T$- relations of 1-propanol and n-octane binary mixtures and isochoric P-T break point technique the values of the phase transition parameters $p_s,\rho_s,T_s$ (lg⇄l and lg⇄lg l-liquid, g–gas) were determined.

Using grapho-analytical method combining with the scaling behavior the critical parameters ($p_c,\rho_c,T_c$) depending on composition of mixture are evaluated.

Dependence of compressibility factor $Z=pV_m/RT=p/RT\rho_m$ on density, temperature and composition of mixture at one phase (liquid, gaseous) along the phase coexistence curve is described by polynomial equation of state –expansion of compressibility factor $Z$ into series in powers of reduced density $\omega=\rho/\rho_c$; temperature $\tau=T/T_c$ and composition [2].

$$Z = p/RT\rho_m = 1 + \sum_{i=1}^{m}\sum_{j=0}^{n}\sum_{k=0}^{s} a_{ijk}\omega^i \cdot x^k/\tau^j,$$

$$\text{or } p = RT\rho_m\left[1 + \sum_{i=1}^{m}\sum_{j=0}^{n}\sum_{k=0}^{s} a_{ijk}\omega^i \cdot x^k/\tau^j\right].$$

Average relative deviation of calculated values of pressure is 1.5 %. Thermodynamic parameters of 1-propanol and n-octane binary mixtures are calculated.

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# VAPORIZATION AND THERMODYNAMIC PROPERTIES OF THE SrO-$Al_2O_3$ SYSTEM STUDIED BY KNUDSEN EFFUSION MASS SPECTROMETRY

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The strontium aluminates may be used as refractory construction materials that may be used up to 2000 $^0$C or as the materials for immobilization of long-lived radioactive waste. The SrO-$Al_2O_3$ system is the part of the more complicated oxide systems that use for the creation of the new radio-transparent materials. The exploitation of such materials at high temperatures demands the knowledge about of thermal stability of the compounds and solid solutions that formed in the SrO-$Al_2O_3$ system.

Synthesis of the samples in the SrO-$Al_2O_3$ system was carried out by ceramic method at the temperature 1250 $^0$C. The solid $SrCO_3$ and $Al_2O_3$ of “pro analysis” (less than 1% of impurities) quality were used for the synthesis. Characterization of the samples was accomplished with the use of XRD. The temperature dependences of partial pressures of vapor species over $4SrO{\cdot}Al_2O_3$, $3SrO{\cdot}Al_2O_3$, $SrO{\cdot}Al_2O_3$, $SrO{\cdot}2Al_2O_3$ and $SrO{\cdot}6Al_2O_3$ in a wide range of temperatures were determined by Knudsen effusion mass spectrometry (KEMS) method on mass spectrometer MS-1301. The samples were vaporized from twin tungsten Knudsen effusion cell heated by electron impact. The molecular beam was ionized by electron ionization with energy of the ionizing electrons equal to 30 eV. The temperature was measured by optical pyrometer EOP-66 with ±10 K accuracy in temperature range 1500-2000 K. The sample was placed in one cell of twin cell. The strontium carbonate was placed inside the reference cell because $SrCO_3$ is completely decompose at the temperature range 1000-1200 K which much lower than vaporization temperature of strontium oxide.

According to the phase diagram of the SrO-$Al_2O_3$ system and taking into account big difference between volatilities of strontium and aluminum oxides the evaporation these compounds may be written as follows reactions (1)-(23):

$$Sr_4Al_2O_7\ (s) = Sr_3Al_2O_6\ (s) + Sr\ (g) + O\ (g) \quad (1)$$

$$Sr_3Al_2O_6\ (s) = SrAl_2O_4\ (s) + 2\ Sr\ (g) + 2\ O\ (g) \quad (2)$$

$$2\ SrAl_2O_4\ (s) = SrAl_4O_7\ (s) + Sr\ (g) + O\ (g) \quad (3)$$

$$3\ SrAl_4O_7\ (s) = SrAl_{12}O_{19}\ (s) + 2\ Sr\ (g) + 2\ O\ (g) \quad (4)$$

$$SrAl_{12}O_{19}\ (s) = 6\ Al_2O_3\ (s) + Sr\ (g) + O\ (g) \quad (5)$$

The obtained values of partial pressures of Sr above the samples under study allow to determine the activities of SrO in condensed phase. The activity values of the $Al_2O_3$ in the SrO-$Al_2O_3$ system were calculated by the method proposed in work [1]. The thermodynamic properties of the SrO-$Al_2O_3$ system at high temperatures are characterized by negative deviation from ideality.

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# ESTIMATION OF THE TEMPERATURE DEPENDENCE OF THE SUBLIMATION ENTHALPIES OF AROMATIC COMPOUNDS

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The sublimation process is the transition from a bound crystalline state to a free gaseous state. The enthalpy of sublimation characterizes intermolecular interactions in crystal lattice and its energy.

In spite of fundamental and practical importance, obtaining reliable sublimation enthalpies is not a trivial task [1]. Among other difficulties, depending on the available equipment and compound studied, the measurements are carried out at different temperatures. It is known that enthalpies of sublimation significantly depend on temperature. Therefore, an important step to check the agreement between experimental sublimation enthalpy values is to find its functional dependence on temperature.

In this study we have reviewed and critically analyzed the values of enthalpies of sublimation of aromatic compounds. Based on previous studies of aromatic compounds, we proposed a method that enables to determine the temperature dependence of the enthalpy of sublimation using enthalpy of fusion at the melting temperature, the enthalpy of solution of the crystal at 298.15 K, and the molecular structure [2, 3].

As a result, we analyzed 180 compounds in the temperature range from 258 to 456 K. By comparing the sublimation enthalpies calculated by our method with the literature values, after their critical analysis and the exclusion of obvious dropouts, the standard deviation was 1.4 $\text{kJ}\cdot\text{mol}^{-1}$. We also compared the calculated values with those derived from the Kirchhoff equation using experimentally measured crystal and gas heat capacities for 17 compounds. The standard deviation from this was 2.3 $\text{kJ}\cdot\text{mol}^{-1}$.

We also tested the predictive capability of the Chickos scheme, widely used for temperature adjustment of the enthalpies of sublimation of organic non-electrolytes.

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# EFFECT OF COMPLEX FORMATION ON VOLUME PROPERTIES OF URACIL IN BUFFER SOLUTIONS WITH GLYCYL-L-TYROSINE AT VARIOUS TEMPERATURES

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DNA-protein recognition plays a central role in gene expression and regulation. Despite increasing data on DNA-protein complexes, the molecular mechanism of DNA-protein recognition is not well understood yet. Besides, the increasing interest in the physicochemical studies of nucleic acid bases and their derivatives is due mainly to their biological and pharmaceutical importance. The investigations of the nature and the forces that stabilize nucleic acid structures and their complexes with other molecules are not only of fundamental significance but may also find practical applications. Understanding the interactions between the components of nucleic acids and proteins molecules, in particular the nucleobases and peptides, is especially important because these interactions facilitate key biological functions ranging from protein synthesis to DNA repair. Uracil contains consecutive hydrogen bond donor and acceptor groups. Aromatic peptides possess a hydrophobic rings and hydrophilic groups of amino acid residues. Specific interaction between the active groups of the peptides and nucleic acid bases can be used for the selective recognition of nucleic acid base sequences by proteins.

The investigations of the interactions of model compounds of protein and nucleobases under conditions of various temperatures and pH have been rather scarce reported. The aim of this work was to study the effect of complexation on volume characteristics of uracil (Ura) in aqueous phosphate buffer solution (saline) containing glycyl-L-tyrosine (Gly-Tyr) at various temperatures. The density ($\rho$) of solution was measured using a digital precision vibrating densimeter (model DMA-5000 M, Anton Paar, Austria). The concentration of peptide was fixed at (0.0125±0.0002) $\mathrm{mol\cdot kg^{-1}}$. The concentration of uracil was varied within the range (0.0070 – 0.0301) $\mathrm{mol\cdot kg^{-1}}$. The combined standard uncertainty of the measured density was estimated to be $\pm 7\times 10^{-2}$ $\mathrm{kg\cdot m^{-3}}$. The measurements were carried out at temperatures of (288.15, 298.15, 303.15, 308.15 and 313.15) K.

The apparent molar volumes (${}^{\varphi}V_{\mathrm{Ura}}$) and partial molar volumes at infinite dilution (${}^{\varphi}V^{o}_{\mathrm{Ura}}$) of uracil in buffer solutions of glycyl-L-tyrosine have been calculated from experimental values of density. The higher positive $\mathrm{V}^{o}_{\varphi,\mathrm{Ura}}$ values for Ura in 0.0125 $\mathrm{mol\cdot kg^{-1}}$ Gly-Tyr buffer compared to the aqueous buffer solution at each temperature suggest that the interactions between Gly-Tyr zwitterions and Ura molecules are predominant. The $(\partial^{\varphi}V^{o}/\partial T)_{\mathrm{p}}$ and $(\partial^{2\varphi}V^{o}/\partial T^{2})_{\mathrm{p}}$ parameters were determined for Ura in aqueous buffer solution and for Ura in aqueous Gly-Tyr buffer solution. The interaction of Gly-Tyr with Ura is accompanied by complex formation, that as the function ${}^{\varphi}V_{\mathrm{Ura}}=\mathrm{f}(m_{\mathrm{Ura}})$ has a maximum corresponding to the stoichiometry of the complex. No the stoichiometry of complexes was found to depend on temperature. The trend in $(\partial^{\varphi}V^{o}/\partial T)_{\mathrm{p}}$ and $(\partial^{2\varphi}V^{o}/\partial T^{2})_{\mathrm{p}}$ values for Ura in aqueous amino acid buffer solutions at various temperatures suggest uracil to be a structure promoter in aqueous 0.0125 $\mathrm{mol\cdot kg^{-1}}$ Gly-Tyr buffer solutions. The molecular complexes between Gly-Tyr and Ura molecules can be formed due to zwitterion-hydrophilic interactions, hydrophobic forces and hydrogen bonding.

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# THERMODYNAMICS OF INTERACTION BETWEEN SOME PEPTIDES AND NUCLEIC ACID BASES: URACIL AND CYTOSINE

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Interactions between proteins and RNA underlie the effects of viruses on a living organism. Elucidating the fine molecular mechanisms of inhibition of these processes requires the study of factors that provide the stability of the formed complexes of proteins with nucleic acids. In the aqueous medium, the resulting complexes can be stabilized due to intermolecular interactions of various types, including: electrostatic, charge transfer, hydrogen binding, acid-base, stacking, and hydrophobic effects. Therefore, this is relevant to study the mechanism and forces motivating the interaction between heterocyclic nucleic acid base molecules as RNA fragments and peptides as protein fragments.

The purpose of the work is to study the patterns of interaction of nucleic acid bases with amino acids and peptides, depending on their structure. Thermodynamic parameters of interaction have been obtained from calorimetric results. The constants, $\lg K_r$, and enthalpies of complex formation, $\Delta_r H^m$, were determined by processing the calorimetric data using the Heat program. The subjects of the study are peptides such as: glycyl-L-glutamic acid and α-L-alanyl-L-tyrosine as donors and acceptors of hydrogen bonds; as well as α-L-alanyl-L-α-L-alanine, which can only be a donor of H-bonds. Peptides and nucleic bases contain groups capable of acid dissociation and protonation in aqueous solution. Therefore, all experimental measurements will be performed in buffered saline at a constant index of pH=7.4. This makes it possible to stabilize ionic forms of peptides and nucleic bases in an aqueous solution.

It was found that the peptides GlyGlu, AlaTyr, which are donors and acceptors of H-bonds, form moderately stable molecular complexes with uracil and cytosine, $\lg K_r$ values range from 1.5 to 2.5. The complex formation is accompanied by a slight exothermic effect. In contrast, the formation of complexes with the H-bond donor Ala-Ala peptide is an endothermic process. Based on a comparison of the data, the possible involvement of various reaction sites of peptide and nucleic base molecules in the interaction between them is discussed.

**Acknowledgements.**
The financial support of the Russian Science Foundation, grant No. 22-23-01118.

# THE PHENOMENON OF PARTIAL ISOBARIC COMPRESSIBILITY ("NEGATIVE EXPANSIBILITY") OF UREA AS A SOLUTE IN *TERT*-BUTANOL AND METHANOL MEDIA: A CONPARATIVE ANALYSIS

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The phenomenon of decreasing the standard, $V_2^{\rm o}$ (partial, $\bar{V}_2^{\infty}$, or apparent, $V_{\emptyset,2}^{\infty}$, at infinite dilution), molar volume of a solute (2) with increasing temperature was the first disclosed when studying the solutions of urea (U) in methanol (MeOH) [1,2]. By now, such an atypical temperature-dependent volume effect established experimentally for a few systems including water (W) solutions in MeOH and *tert*-butanol (*t*-BuOH) [3]. Despite the continuing interest in this phenomenon (named *partial isobaric compressibil*ity or PIC), no information is available on its structural nature. Since MeOH is the only solvating medium in which the PIC phenomenon occurs when both W and U are dissolved, one would be expected a similar effect for U in *t*-BuOH, too. Hence, the main goal of this report is the analysis of data derived densimetrically to study the PIC phenomenon induced by U as a solute in *t*-BuOH and MeOH. The results of our experiments are shown in Figure 1, from which it follows that the $E_{p,2}^{\rm o} = (\partial V_2^{\rm o}/\partial T)_p$/(cm$^3$·mol$^{-1}$·K$^{-1}$) value is *ca.* -0.151 and -0.030 (in average) for U in *t*-BuOH and MeOH, respectively. Like the case of W-containing alcohols [3], a physical prerequisite for PIC of U may be the lack of intermediate alkyl moieties in MeOH and *t*-BuOH molecules, a fact accounting for a stronger effect of terminal methyl groups on the donor/acceptor ability of hydroxy-group, as well as the formation of an openwork structure with voids in *t*-BuOH. Obviously, here the configuration of molecular packing of the solvation complex formed is more stable to temperature changes than the structural organization of the neat alcohol. Herewith the $v_{22}$–$T$ functions in Figure 2 show that the U– *t*-BuOH interaction, unlike the U – MeOH one, is not dominated by H-bonding.

**Acknowledgements.** The partial financial support of RFBR 20-415-37002_reg has been provided.

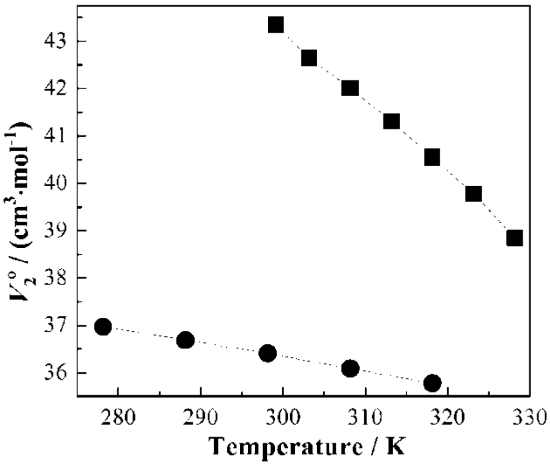

**Figure 1.** Standard molar volumes of urea (2) in MeOH (●) [2] and *t*-BuOH (■) as a function of temperature.

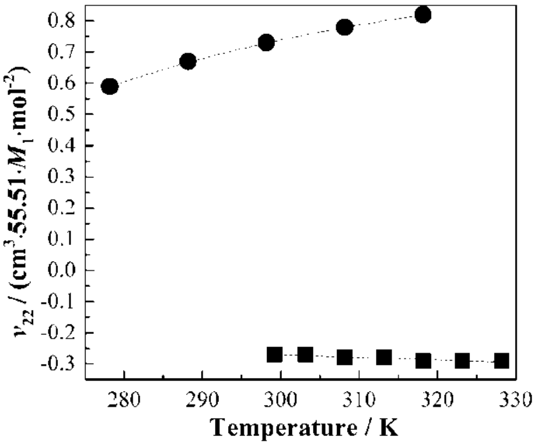

**Figure 2**. Volume-related parameters of pairwise U–U-interaction in MeOH (●) [2] and *t*-BuOH (■) as a function of temperature.

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# СРАВНИТЕЛЬНАЯ ХАРАКТЕРИСТИКА ЭНТАЛЬПИЙНЫХ ПАРАМЕТРОВ МЕЖМОЛЕКУЛЯРНОГО ВЗАИМОДЕЙСТВИЯ МОЧЕВИНЫ И ТЕТРАМЕТИЛМОЧЕВИНЫ В ВОДЕ, ЭТИЛЕНГЛИКОЛЕ И ФОРМАМИДЕ ПРИ T = 288 – 328 K

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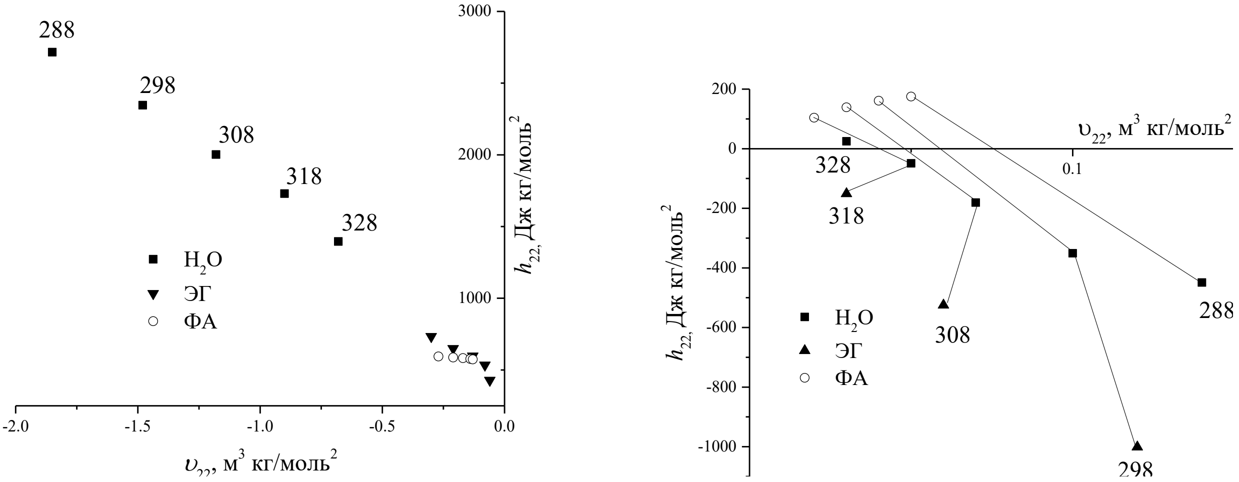
С целью изучения проявлений сольвофильных и сольвофобных эффектов в растворителях с пространственной сеткой водородных связей (вода, этиленгликоль, формамид) из калориметрических данных рассчитаны энтальпийные гомотактические коэффициенты парных ($h_{22}$) и тройных ($h_{222}$) взаимодействий между сольватированными молекулами мочевины (М) или тетраметилмочевины (ТММ) в интервале температур 288.18 – 328.15 К. Для анализа межмолекулярных взаимодействий в рассматриваемых растворах наряду с энергетическим фактором следует принимать во внимание и особенности структурной упаковки. Для этого использованы корреляции между $h_{22}$ и объемными параметрами парного 2–2-взаимодействия ($v_{22}$) между сольватированными молекулами М или ТММ в растворителях рассматриваемого здесь ряда.



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Корреляция между энтальпийными и объемными коэффициентами парного 2–2-взаимодействия в растворах ТММ (а) и М (б) в воде, этиленгликоле и формамиде при различных температурах

Видно, что для гидрофобной ТММ (рис. а) наблюдается общая корреляция между энтальпийными и объемными коэффициентами парного 2–2-взаимодействия, указывающая на качественную аналогию межмолекулярных взаимодействий и структурных образований в изученных системах. Для растворов М в исследованных растворителях (рис. б) полученный массив данных распадается на различные корреляции $h_{22} = f(v_{22})$, как в зависимости от природы растворителя, так и от температуры (б). Это указывает на то, что межмолекулярные взаимодействия мочевины с изученными растворителями имеют существенные различия. В докладе обсуждаются возможные причины изменения параметров взаимодействия в зависимости от температуры и свойств растворителей и растворенных веществ.

# ANALYSIS OF VARIOUS ISO-MANIFOLDS IN MULTICOMPONENT SYSTEMS WITH BIAZEOTROPIC CONSTITUENTS

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The complexity of the liquid-vapor phase equilibrium diagrams of biazeotropic systems gives rise to the problem of separation of such mixtures. Therefore, it is necessary to carry out a detailed study of their phase behavior in the presence of additional substances, for example extractive agents (EA).

Earlier, the authors [1] proposed an approach to selecting an effective EA for the separation of binary biazeotropic mixtures via extractive distillation. This approach is based on the analysis of the mutual course in the concentration triangle of the derivative system (the base separated mixture with an EA) of iso-lines that characterize certain properties of the separated binary mixture.

The purpose of this study is to analyze the mutual position of various iso-manifolds to assess the possibility of separating multicomponent mixtures formed by carboxylic acids and their butyl esters by sulfolane. Iso-manifolds include manifolds of equal to 1 relative volatility ($\alpha$), that reflect the evolution of pseudoazeotropes in sections with a constant concentration of the extractive agent [2]; pseudoideal manifolds, along which the activity coefficients of the components of the base (separated) mixture are equal to each other [3]; isothermal-isobaric manifolds generated by Bancroft points in binary azeotropic constituents.

To assess the effectiveness of sulfolane, we analyzed iso-manifolds in derived diagrams of four- and five component systems formed by the components of the base mixture of butylpropionate (BP) – propionic acid (PA) – butylbutyrate (BB) – butyric acid (BA) and EA. In the concentration simplex (tetrahedron, pentatope), these iso-manifolds are hypersurfaces. This fact increases the dimension of the problem and significantly complicates the analysis of the mutual position of these iso-manifolds. In this regard, the analysis was carried out using scans of the concentration tetrahedron and pentatope.

Our study of derivative diagrams of four component systems [4] combined in a single pentatope scan allowed us to determine the favorable ratio of the separated mixture and the EA for an effective separation process.

Thus, based on the analysis of the phase behavior of the studied mixtures in the presence of sulfolane, it is possible to implement extractive distillation of the BP-PA-BB-BA mixture at a concentration of sulfolane above 80 % mol, which corresponds to the ratio of the amounts of EA and the base mixture as 4:1. This conclusion was verified and confirmed by mathematical modeling of different extractive distillation modes of the base mixture of equimolar composition.

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# EFFICIENT REMOVAL IONS CR (VI) ON WASTEWATER BY ANION EXCHANGE MATERIAL BASED ON PVC

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Present work, we studied the process of obtaining anion exchanger by chemical modification of plasticized polyvinylchloride with Urea. To study the structure morphology of the PPE-2 anion exchanger different characterization techniques such as XRD, FTIR, and SEM were applied. Moreover, the synthesized anion exchanger PPE-2 was used as effective removal for hexavalent chromium ions in aqueous media. Among the toxic metal ions, chromium is one of the widely used elements in industrial processes, such as metal finishing, textile dyeing, coating, pigments, batteries, leather tanning, etc. [1, 2]. Therefore, the wastewater of such an enterprise contains huge amounts of chromium ions. That why The World Health Organization (WHO) has recommended that the maximum permissible concentration of total chromium in drinking water be less than 0.05 mg/L [2]. Corresponding adsorption kinetics best fit the pseudo-second order model that followed a Freundlich isotherm. In the case of hexavalent chromium ions, the maximum adsorption capacity of PPE-2 was 227,8 mg/g. Thermodynamic data revealed spontaneous endothermic processes and was a chemisorption reaction. In addition, results show that the anion exchanger (PPE-2) has 98% for removing hexavalent chromium ions containing from wastewater.

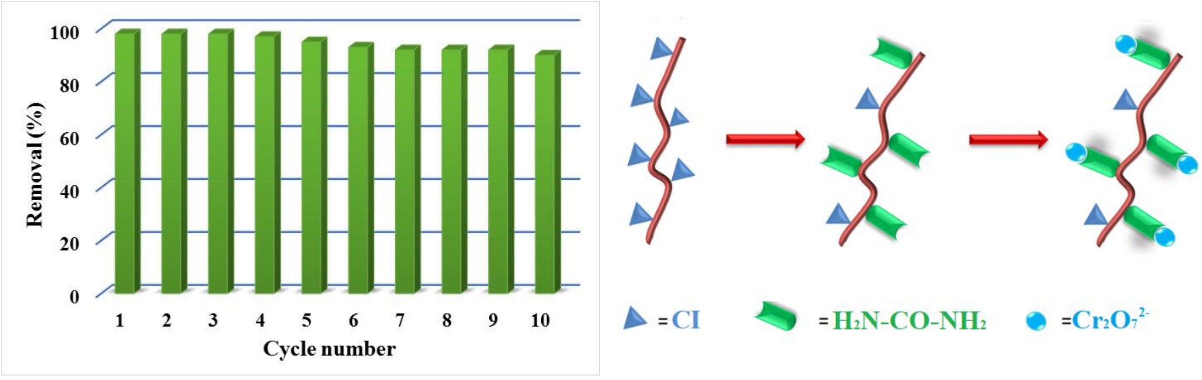

**Figure 1.** Sorption cycles of Cr (VI) ions by anion exchanger.

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# ON COALESCENCE TIME OF FREE DROPLETS IN VAPOR: MOLECULAR DYNAMICS APPROACH

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Droplet coalescence is a phenomena important in many natural and industrial processes, such as cloud formation, emulsion coagulation, inkjet printing, filtration, etc. Droplet coalescence dynamics has attracted considerable attention in recent years due to advances in industrial applications. Several continuous theories mostly focusing on the evolution of the meniscus shape have been developed in the literature. Experimental studies are mostly focused on droplet collision.

The present work explores the dynamics of droplet coalescence by means of molecular dynamics simulations. In each computer experiment, two single-component nanodroplets are suspended in saturated vapor. The droplet sizes vary from several hundred to several thousand Lennard-Jones particles at three different temperatures. Once the droplets make contact, the resulting larger droplet relaxes into a spherical equilibrium shape. Through trajectory analysis, the experimental scaling of growth rate of the liquid bridge [2] forming between the combining droplets is confirmed. Coalescence time is approximated by fitting the exponential "relaxation" part of the gyration radius plot inferred by the trajectories. The approximated relaxation time of the coalesced droplet is found to be proportional to the sizes of the parent droplets and almost independent of the temperature. Increase in temperature leads to increase in variance of coalescence time and the size of the final droplet, but does not change the overall coalescence dynamics.

**Acknowledgements** The Authors acknowledge the use of Zhores [1] for obtaining the results presented in the proceedings.

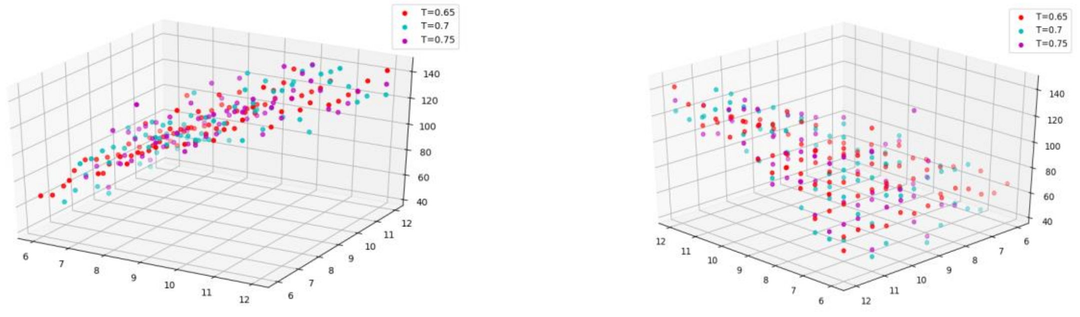

**Figure 1.** Coalescence time plotted as a function of initial droplet radii, $r_l < r_r$. Different colors represent different system temperatures.

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# LIDOCAINE CONFORMATIONAL PREFERENCES UNDER ISOTHERMAL CONDITIONS

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Obtaining new polymorphic forms of biologically active substances is one of the promising methods of drug design and modification. As early as in the 1970-s, scientists distinguished between two main types of polymorph formation: by changing the molecule packing in the crystal and by using different molecule conformations in unit cells of polymorph crystals (conformational polymorphism) [1]. It is conformational polymorphism that is characteristic of some biologically active substances used in pharmaceutics (ibuprofen, some fenamates, carbamazepine, etc.) [2-4] and their modernization is quite an urgent problem. Currently, one of the promising methods of finding new polymorphs is based on supercritical fluid technologies employing supercritical carbon dioxide as the solvent (SAS, RESS, GAS, PGSS et.al.). It is possible to change the proportions of conformers of small molecules of drug compounds in a supercritical fluid solution by changing parameters of state (pressure and temperature). Subsequent extraction will help obtain the required polymorph with the major molecule conformation in a saturated fluid solution, as it was shown by studying carbamazepine in [5].

In this work, Nuclear Overhauser Effect Spectroscopy (NOESY) was used to conduct a comprehensive study of the lidocaine molecule conformational behavior under isothermal conditions (35°C). The experiment revealed the proportions of the conformers of the compound under study depending on pressure (10 MPa – 30 MPa) at a step of 1 MPa. The major conformation in the low-pressure range of 10-20 MPa was the one with an N-H…N intramolecular hydrogen bond, whereas at the pressure of 22 MPa, the lidocaine molecule conformers in the scCO2 solution were found to be equiprobable, with the contribution of ≈50%:50%. A further pressure increase led to an inversion of the conformational states up to the conformer ratio of ≈5%:95% (35°C and 30 MPa). This study showed that Nuclear Overhauser Effect Spectroscopy as an NMR spectroscopic method is a powerful tool for selecting thermodynamic state parameters for implementation of a variety of processes, such as conformational transitions in solutions and fluids. The NMR spectroscopy experiment was performed using the molecular fluid spectroscopy facility (http://www.ckp-rf.ru/usu/503933/) of G.A. Krestov Institute of Solution Chemistry of the Russian Academy of Sciences (ISC RAS) (Russia).

**Acknowledgements** The work was funded by the Russian Science Foundation (grant No. 22-13-00257).

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# PHASE EQUILIBRIA IN ME($CH_3SO_3$)$_2$-$H_2O$ (ME=CO, NI, MN) SYSTEMS

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Recovery of heavy elements from industrial wastes (e.g., spent lithium ion batteries or nickel alloys) becomes crucial both from environmental and economic points of view. Such processes often include leaching with an acid, e.g. methanesulfonic acid, which is regarded as a green-chemistry reagent [1]. Using thermodynamic modeling, one can optimize recycling processes. The base for a thermodynamic model are binary parameters, as well as stability parameters of phases which exist in binary systems, as well as in multicomponent systems. The aim of the work is to continue research started with $Me(CH_3SO_3)_2$-$H_2O$ (Me=Cu, Zn)[2, 3] concerning vapor-liquid (VLE) and solid-liquid equilibria (SLE) in 3d-metal methanesulfonate - water systems.

SLE in the $Me(CH_3SO_3)_2$-$H_2O$ (Me=Co, Ni, Mn) systems were studied by isothermal solubility and DSC. TG and XRD were used to reveal solid phases in equilibria with the solution. Water vapor pressure was determined by static method at 288.15 K, 298.15 and 308.15 K in the $Me(CH_3SO_3)_2$-$H_2O$ (Me=Co, Ni, Mn) systems. Although in two systems (Me=Ni, Mn) there were low-temperature stable hydrates which are isostructural to $Zn(CH_3SO_3)_2 \cdot 12H_2O$ [2] , in the third the low-temperature hydrate was quite different, $Co(CH_3SO_3)_2 \cdot 9H_2O$. Following hydrates were revealed as well during the study: $Co(CH_3SO_3)_2 \cdot 6H_2O$, $Co(CH_3SO_3)_2 \cdot 4H_2O$, $Ni(CH_3SO_3)_2 \cdot 6H_2O$, and $Mn(CH_3SO_3)_2 \cdot 2H_2O$.

Based on VLE and SLE (ice melting curve), parameters of the Pitzer-Simonson-Clegg (PSC) model were obtained. Due to rather low solubility, a suitable description was obtained using only $\alpha^0$, $\alpha^1$, $\beta^0$, $\beta^1$, whereas U, V, W were fixed as 0. Similar results were reported earlier for $Cu(CH_3SO_3)_2$-$H_2O$ [3]. Stability parameters of all the hydrates were estimated from binary solubilities using only 2 parameters. Binary phase diagram fragments were calculated with the resulted parameters using the PSC model.

**Acknowledgements** The financial support of RSCF 21-73-00039

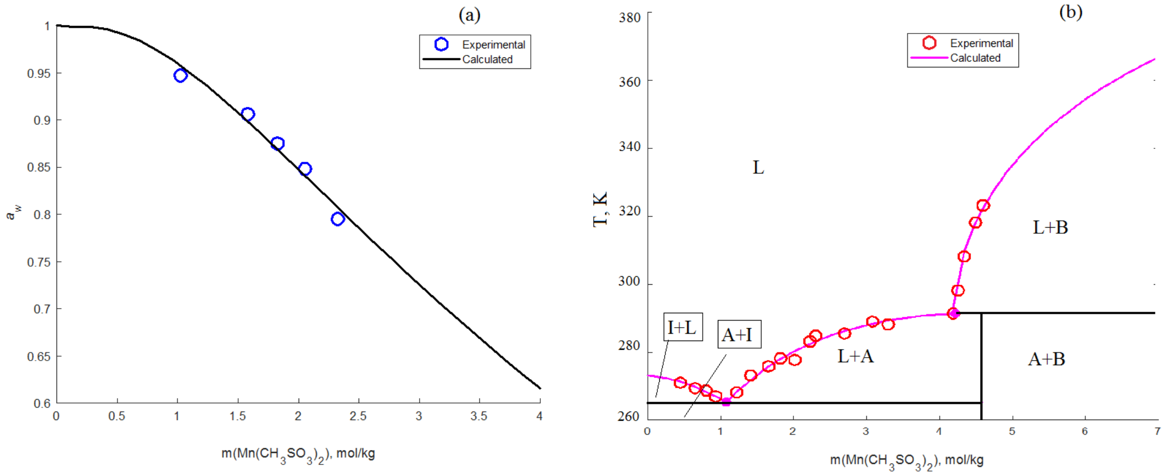

**Figure 1.** (a) Water activity at 298.15 K in $Mn(CH_3SO_3)_2$-$H_2O$ (b) SLE in $Mn(CH_3SO_3)_2$-$H_2O$. L-liquid, I-ice, A- $Mn(CH_3SO_3)_2 \cdot 12H_2O$, B- $Mn(CH_3SO_3)_2 \cdot 2H_2O$

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# LOW-TEMPERATURE THERMODYNAMIC AND MAGNETIC PROPERTIES OF COPPER BIS-HEPTAFLUORODIMETHYLOCTANEDIONATE

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Copper bis-heptafluorodimethyloctanedionate ($Cu(C_{10}H_{10}F_7O_2)_2$ or $Cu(fod)_2$) is a promising precursor for the production of films of various functional purposes by the CVD method [1]. Comprehensive studies of the physicochemical properties are necessary to determine and develop the applied potential of this complex. This report presents the results of studies of the thermodynamic and magnetic properties of $Cu(fod)_2$ at low temperatures.

The sample of $Cu(fod)_2$ was prepared and purified by Sigma-Aldrich. The sample under study was defined in detail by infrared spectroscopy, DTA/TG and elemental analysis. The purity of the final compound was better than 99.9%.

The heat capacity of the sample was measured in the range from 6 K to 300 K in a vacuum adiabatic calorimeter (laboratory-made) described earlier [2]. The experimental values of heat capacity were used to compute integral thermodynamic functions (entropy, enthalpy, and reduced Gibbs energy) in the range of 0 to 300 K. An anomaly of heat capacity has been discovered with a maximum at $T_c \approx 225$ K, which points to the phase transformation of the $Cu(fod)_2$ complex. In the neighbourhood of the heat capacity anomaly measurements with short temperature rise were made in order to determine the detailed shape of the heat capacity curve. Anomalous contributions to entropy and enthalpy have been revealed.

The static magnetic susceptibility of investigated compound $\chi(T)$ has been measured by SQUID magnetometer (Quantum Design MPMS-XL) in the range 2–300 K to determine the nature of the anomaly. No magnetic susceptibility anomalies were found in the studied temperature range; the magnetic susceptibility is well described by the Curie-Weiss law over the entire temperature range. In other words, the observed phase transition cannot be of magnetic nature.

A thermogram (the time dependence of calorimeter temperature while heating in adiabatic conditions with a constant power) was taken in the region of the anomaly, which does not indicate any signs of a first-order phase transition, and suggests that we are observing a second-order phase transition. The entropy $\Delta S_{an}$ of the transition coincides within good accuracy with the value $R\ln 2$. This $\Delta S_{an}$ of phase transition is the evidence of a possible transformation of two equally probable states (low-temperature phase) into a single state (high-temperature phase) or about phase transition of type order-disorder. For detailed analysis of the nature of the observed phase transition, one needs to conduct special research.

**Acknowledgements** The research was supported by the Ministry of Science and Higher Education of the Russian Federation (project number 121031700314-5).

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# HEAT CAPACITY AND THERMODYNAMIC FUNCTIONS OF YTTERBIUM TITANATE AT TEMPERATURES FROM 80 TO 320 K

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The physicochemical properties of rare-earth titanates are extensively researched generally at temperatures below 10 K, where their structural features manifest themselves most distinctively. At the same time, the thermodynamic functions in the range from liquid helium temperature to room temperature have not been investigated yet for many of them. This study presents the results of measuring the heat capacity of ytterbium titanate $Yb_2Ti_2O_7$ by adiabatic calorimetry and determining its thermodynamic properties.

A sample of ytterbium titanate was obtained by high-temperature solid-phase synthesis from ytterbium oxide $Yb_2O_3$ of chemically pure grade and titanium oxide $TiO_2$ of special purity grade. The synthesis was performed in several stages in an inert argon atmosphere at the temperature of final annealing of 1400°C and the time of 48 hours. After each stage, the product was carefully ground in an agate mortar and the sample phase composition was monitored.

The matching of the synthesized sample crystal structure to $Yb_2Ti_2O_7$ compound was confirmed by X-ray powder diffraction using the PDF-2 database. The sample pycnometric density is 7.29 g/cm$^3$, that is consistent with the known data.

Heat capacity measurements were carried out on a low-temperature adiabatic calorimeter [1] in liquid nitrogen. The sample weight was 3.57 g, the measurement step varied from 2 to 3 K. The measurements resulted in several series with good reproducibility. The scatter of experimental points from the smoothed curve in the range of 80–320 K did not exceed ±0.3%.

To estimate a low-temperature contribution to the heat capacity of the compound, we used data from [2], where a ytterbium titanate sample was measured in the range from 0.4 to 30 K. The interval between 30 and 80 K was extrapolated using a combination of the Debye and Einstein functions. Based on the data obtained, the thermodynamic functions of $Yb_2Ti_2O_7$ were calculated at temperatures up to 320 K, and the measurement and extrapolation uncertainties were determined.

The standard thermodynamic functions of ytterbium titanate are as follows: $C_{p,298}$=224.5±1.5 J/(mol·K), $S°_{298}$=251.6±4.4 J/(mol·K), $H°_{298}-H°_0$=37.83±0.26 kJ/(mol·K).

**Acknowledgements** The research is funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan (Grant No. AP09259070).

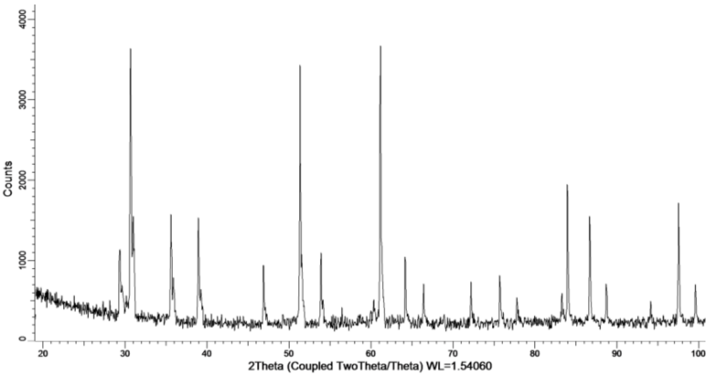

**Figure 1.** X-ray diffraction pattern of the synthesized sample $Yb_2Ti_2O_7$.

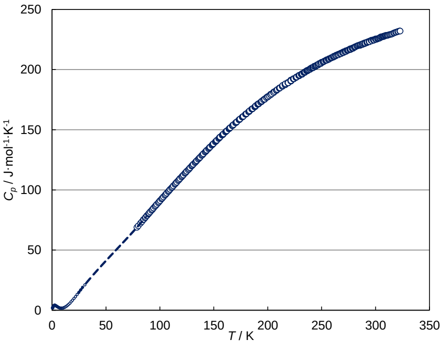

**Figure 2.** Molar heat capacity of $Yb_2Ti_2O_7$.

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# THE THERMODYNAMIC PROPERTIES OF 4-METHYLDIOXOLAN-1,3 IN THE CONDENSED STATE

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The thermodynamic properties of 4-methyldioxolan-1,3 (I) in glassy, crystalline and liquid states were studied by low-temperature adiabatic calorimetry. The commercial sample of I with an initial purity of 96 mas. % was dehydrated over metallic sodium and purified by multiple fractional distillation. The purity of the sample was more than 99.8 mas. % according to GLC.

The heat capacities of I were measured in a automatic vacuum adiabatic calorimeter TAU-10 (Termis, Moscow, Russia) [1] between (80 to 370) K. An iron-rhodium resistance thermometer with $R_0 = 50\ \Omega$, calibrated for ITS-90 by VNIIFTRI (Mendeleyevo, Moscow Region, Russia), was used for temperature measurements with the standard uncertainty of 0.01 K. The relative expanded uncertainty in the heat capacity measurements did not exceed ±0.4 %. The contribution of the heat capacity of the sample to the total heat capacity of the system was at least 40 %.

It was found that when liquid cooled from $T = 290$ K with a rate of $(0.03 - 0.01)\ \mathrm{K \cdot s^{-1}}$ is supercooled with the subsequent formation of a glassy phase. In case of measuring the heat capacity in the heating mode the devitrification of the sample was occurred in the range (95 to 108) K. Spontaneous crystallization of the supercooled liquid began at $T = 115$ K. It was found that as a result of abnormally slow crystallization, a metastable crystalline phase was formed within about 2 days. During the measurement of its heat capacity in the range (146 to 174) K, a spontaneous exothermic transition into the stable crystal occurred. In further studies, in order to obtain a stable crystalline phase, the sample after the start of crystallization was slowly heated to $T = 174$ K and kept at this temperature for (10 to 20) h until the temperature drift of the calorimeter was constant. The glass transition temperature and the heat capacity jump during the devitrification were equal to

$$T_\mathrm{g} = (106.37 \pm 0.02)\ \mathrm{K} \text{ and } \Delta_\mathrm{gl}^\mathrm{l} C_p = (72.44 \pm 0.65)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}.$$

The temperature of fusion of the absolutely pure compound I $T_\mathrm{fus} = (176.49 \pm 0.02)$ K and the purity of the studied sample $x = (99.06 \pm 0.05)$ mol. % were determined by fractional melting experiments. A significant discrepancy in the values of the mass and molar fraction of the main substance in the studied sample is most likely due to the water presence of about 0.1 mas. % in it (taking into account the nature of the substance). Based on the principle of additivity, such a water content leads to an increase in the specific heat capacity of the liquid sample by about 0.1 % compared to absolutely pure (dry) I, which is 4 times less than the stated measurement uncertainty and therefore may not be taken into account when calculating the thermodynamic functions. Influence of impurity water on the heat capacity of the sample in the crystalline and glassy state is even less. The enthalpy and entropy of fusion were found from the results of three series of measurements:

$$\Delta_\mathrm{cr}^\mathrm{l} H_\mathrm{m}^\circ = (8527 \pm 10)\ \mathrm{J \cdot mol^{-1}} \text{ and } \Delta_\mathrm{cr}^\mathrm{l} S_\mathrm{m}^\circ = (48.31 \pm 0.06)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}.$$

The standard thermodynamic functions (entropy, reduced enthalpy and Gibbs energy) in the condensed state were calculated based on the smoothed values of the heat capacity and fusion parameters.

**Acknowledgements** The work was carried out according to task GB 41-14 «Study of thermodynamic properties of heterocyclic compounds to optimize the processes of their production and processing» (2021-2025).

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# POLY-NHC-AGGREGATES BASED ON BIS-IMIDAZOLIUM DERIVATIVES OF CALIXARENES WITH OXYETHYLAZIDE/PROPARGYL FRAGMENTS

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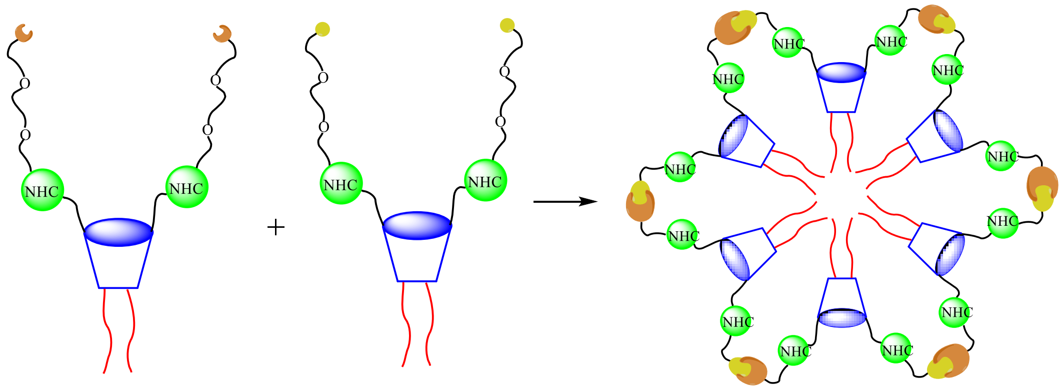
The discovery and study of N-heterocyclic carbenes has caused a violent revolution in modern organic chemistry in the last 30 years. NHC, having a high σ-donating and low π-acceptor character, are excellent ligands for transition metal coordination compounds. Such complexes show excellent catalytic activity in cross-coupling reactions, hydrogenation, olefin metathesis, etc. [1, 2].

The synthesis and study of poly-N-heterocyclic carbenes has recently become a priority. Such compounds provide a variety of organometallic compounds with different geometric structures. Their case is polymeric NHC, which are formed by copolymerization of NHC monomers containing the corresponding functional groups [3]. Such systems provide high catalytic activity, as well as the possibility of their re-extraction and use. Calix[4]arenas have proven to be unique platforms for the creation of such polymer aggregates. The presence of imidazolium derivatives with azide and alkynyl fragments on the upper rim of macrocycles makes it possible to obtain micellar-like nanoparticles by click chemistry, which can be used in organocatalysis, metal complex catalysis, sorption, etc.

In this work, based on amphiphilic imidazolium calix[4]arenes with hydroxyethylazide/alkynyl fragments, a polymeric NHC carrier was obtained by primary self-organization of macrocycles followed by their covalent crosslinking under the conditions of an azide-alkyne cycloaddition reaction in the presence of copper iodide (scheme 1). It has been shown that a system of polymer aggregate and palladium acetate leads to an increase in conversion and selectivity in a model Suzuki cross-coupling reaction.



**Scheme 1.** Synthesis of poly-NHC-aggregate

The work was supported by the Russian Science Foundation grant 22-13-00304.

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# THERMOPHYSICAL PROPERTIES OF CHITOSAN MODIFIED BY ALKYL FRAGMENTS INTRODUCTION AND ENZYMATIC IMPACT

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The usage of chitosan for biomedical applications is promising due to the biocompatibility and biodegradability of this polymer. However, low strength characteristics lead to the need for its modification to obtain fiber- and film-forming materials, which determines the need to study the thermophysical properties of modified chitosan.

The purpose of this work is to investigate the thermophysical properties of chitosan modified by the introduction of alkyl fragments and enzymatic impact.

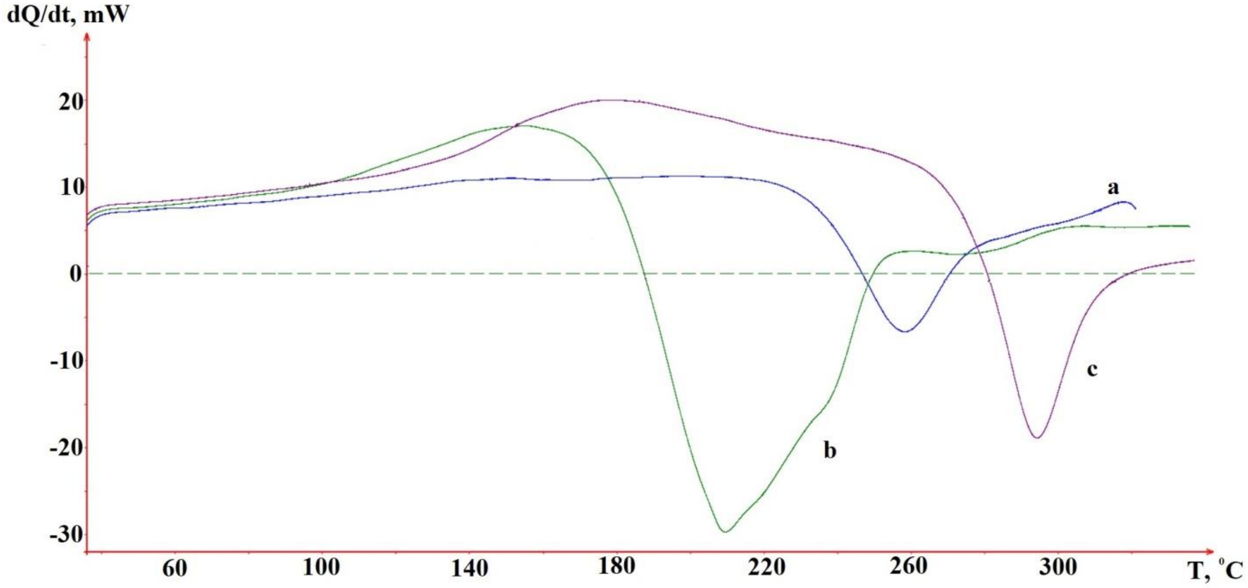

**Figure 1.** DSC: a – chitosan, b – chitosan affected by enzyme, c – chitosan with alkyl fragments.

There are no clear transitions up to the decomposition temperature on the DSC curves of the initial chitosan ($M_w$ 4•10$^5$). The modified samples have a glass transition temperature of 130° C – enzymatic treatment, 150 ° C – alkylated chitosan.

Along with this, the introduction of an alkyl fragment increases the destruction temperature up to 295 °C, while a decrease in the molecular weight during enzymatic treatment ($M_w$ 0.2•10$^5$) reduces the destruction temperature down to 210 ° C.

The observed effects can be explained by a change in the structure of chitosan. According to X-ray phase analysis, the modified samples are characterized by an amorphous structure, whereas the original sample contains up to 40% of crystal structures.

Film samples based on modified chitosan were obtained. An increase in the physico-mechanical properties of samples is observed when alkyl substituents are introduced into the structure of polysaccharide units.

# INVESTIGATION OF THE CRYSTAL STRUCTURE AND SATURATED VAPOR PRESSURE OF TETRAFLUOROSUBSTITUTED METAL PHTHALOCYANINES $MPcF_4$-np (M = Zn, VO)

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Among organic semiconductors, metal phthalocyanines attract the interest of researchers due to a set of unique properties, such as chemical and thermal stability, the ability to sublimate in a vacuum without decomposition, combined with unique electrical properties. To create semiconductor layers in electronics, it is necessary to strictly observe the conditions of deposition, thickness, orientation, and ordering of phthalocyanine films. Due to the ability to sublimate in vacuum without decomposition, phthalocyanines films can be obtained by physical vapor deposition (PVD) or organic molecular beam deposition (OMBD). The measurement of temperature dependences of saturated vapor pressure is the main characteristic of the volatility of complexes. The saturation vapor pressure value can be used to improve the quality of sublimation to purify them, as well as to optimize the deposition processes for creating layers in organic electronics. In addition, the thermodynamic parameters of sublimation can be used to evaluate intermolecular interactions in the solid phase.

To date, data on the saturated vapor pressure for unsubstituted $H_2Pc$ and a number of complexes with metals, MPcs (M = Ni, Zn, VO, TiO, Pb, Cu), have been published [1–5]. Thermodynamic parameters of sublimation for some tetrafluorosubstituted phthalocyanines with fluorine substituents in the peripheral positions ($MPcF_4$-p, Fig. 1, a) have also been studied [6].

In this work, we studied tetrafluorosubstituted metal phthalocyanines with fluorine substituents in the non-peripheral positions ($MPcF_4$-np, M = Zn, VO) (Fig. 1, b) and compared the obtained values. Saturated vapor pressure was measured by the Knudsen effusion method. For these compounds, standard thermodynamic parameters $\Delta H_T$ and $\Delta S_T^0$ of sublimation processes were calculated. The crystal structures of the studied compounds were also determined by X-ray diffraction, thin films were obtained by PVD, and the phase composition of the films was also studied.

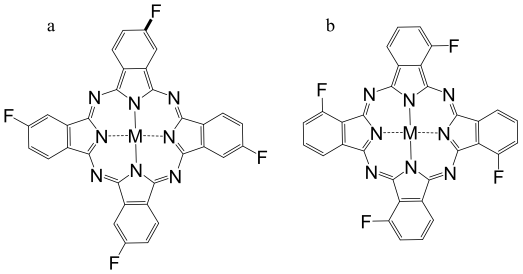

**Figure 1.** The structure of tetrafluorosubstituted metal phthalocyanines $MPcF_4$ in (a) peripheral and (b) in non-peripheral position of the fluorine atom.

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# ESTIMATION OF SOME PHYSICOCHEMICAL PROPERTIES OF FUNCTIONAL HAEMOSTATIC POLYMER MATERIALS BASED ON CARBOXYMETHYL CELLULOSE AND COLLAGEN

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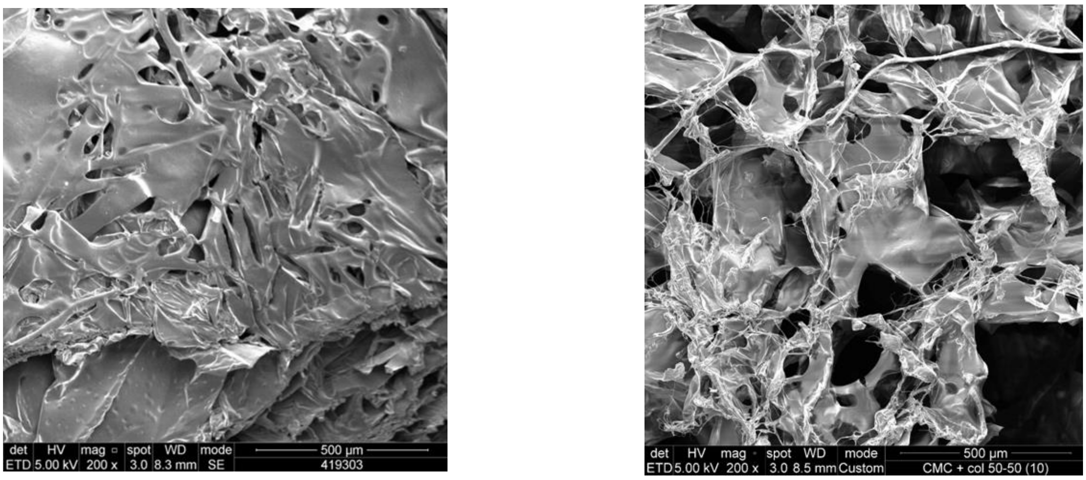
Studying hemostatic materials belongs to the research focuses of modern material chemistry due to their property to prevent bleeding that is urgent in clinical practice [1]. Among the most prospective materials for hemostatic implants, one can note composite materials based on collagen and cellulose derivatives. The premises of their advantages are determined by the specificity of collagen's molecular structure and the content of positively charged amino groups that can lead to the activation of the haemostasis system by increasing platelet adhesion to the damaged vessel wall. This process would be supported by its operation in a complex with a stable polysaccharide gel.

In this work, we consider the synthesis and investigation of physicochemical properties of functional polymer materials produced on the base of marine clams and Na-carboxymethyl cellulose (CMC). Their target usage as absorbent sponges determines the principal parameters, which were explored by methods of chemical and thermodynamic analysis supplied with the scanning electron microscopy (see, e.g., Fig. 1): water absorption, swelling, and the respective open and total porosity.

The set of explored compounds includes pure collagen and CMC salt-based as well as a spectrum of their mixtures.



(a) (b)

Figure 1. Scanning electron microscopy images revealing morphology of sponges based on carboxymethyl cellulose (a) and the carboxymethyl cellulose–collagen composite material (b).

It is revealed that introducing collagen into the composition increases the structure's porosity and decreases spontaneous dissolution, which is a typical characteristic of CMC-based implants. This feature provides an opportunity to control the range of biodegradation of such a functional material and argues in favour of the application of the composite material formed by the optimized mixture of these two polymers as an applicative hemostatic implant with high-efficient adsorption properties.

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# MODELING OF THE PHASE EQUILIBRIA IN THE Zr-C-O SYSTEM

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The Zr-C-O system is considered as a promising base for oxycarbide ultra high temperature ceramics that can be used in mechanical engineering, aerospace sector, and nuclear industry. For instance, zirconium oxycarbide is extensively studied for application as fuel cladding due to its low neutron absorption cross-section, high thermal and chemical stability, as well as capacity for fission product trapping [1, 2]. However, development of the synthetic routes and identification of the correct exploitation conditions of the materials based on the Zr-C-O system at high temperatures are at present hindered substantially because of the contradictions in the phase equilibria data available in this system. The present study is devoted to calculation of the phase diagram of the Zr-C-O system and comparison of the obtained phase equilibria information with the data found earlier [3].

Modeling of the phase equilibria in the Zr-C-O system was carried out using the NUCLEA database and GEMINI2 Gibbs energy minimizer [4]. Four polythermal sections and four isothermal sections of the phase diagram at the temperatures 2120 K, 2500 K (Figure 1), 3000 K, and 4097.36 K were calculated in the system under study. In this ternary system, the phases of the pure components (metallic Zr, graphite, and $O_2$) were found in addition to intermediate phases of the binary systems, namely, zirconium dioxide possessing three polymorphic modifications (monoclinic, tetragonal, and cubic) and the solid solution based on zirconium carbide $ZrC_{1-x}$, where $x \geq 0.02$, with the cubic fluorite structure. It should be mentioned that, in the solid solution based on $ZrC_{1-x}$, dissolution of up to 15 mol. % of O was observed to form oxycarbide solid solution $ZrC_xO_y$ designated in Figure 1 as FCC_B1.

**Acknowledgements** The reported study was funded by RFBR and ROSATOM according to the research project № 20-21-00056.

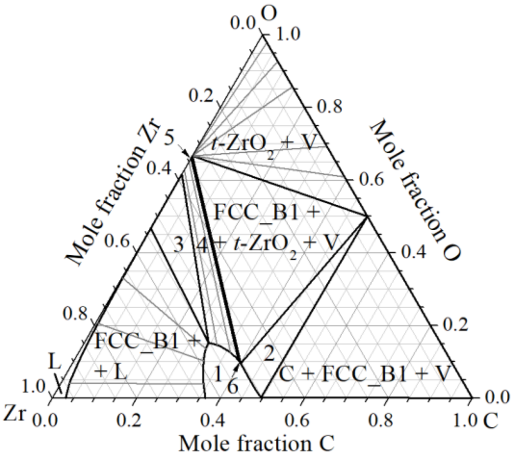

**Figure 1.** Isothermal section of the phase diagram of the Zr-C-O system at the temperature 2500 K calculated using the NUCLEA database: 1 – FCC_B1, 2 – FCC_B1 + V, 3 – FCC_B1 + L + *F*-$ZrO_{2-x}$, 4 – FCC_B1 + *F*-$ZrO_{2-x}$, 5 – FCC_B1 + *F*-$ZrO_{2-x}$ + *t*-$ZrO_2$, 6 – FCC_B1 + *t*-$ZrO_2$.

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# LIQUID ORGANIC HYDROGEN CARRIERS: CHEMICAL EQUILIBRIUM OF HYDROGENATION/DEHYDROGENATION REACTIONS

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The transition to hydrogen energy requires reliable and safe storage of hydrogen. In this study, we studied the storage of hydrogen using liquid organic water carriers (LOHC) (Figure 1).

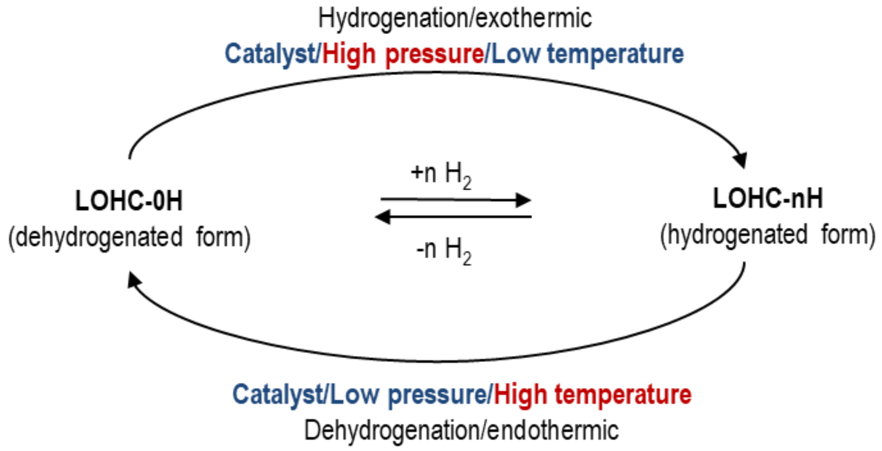

**Figure 1.** Hydrogenation-dehydrogenation cycle of liquid organic hydrogen carriers

LOHC technology is based on the process of reversible hydrogenation of unsaturated organic compounds. Hydrogenation and dehydrogenation reactions can be carried out under thermodynamic control conditions. In this case, the composition of the reaction mass will be determined by the thermodynamics of the reactions. Thus, the study of the chemical equilibrium of hydrogenation-dehydrogenation makes it possible to determine the conditions of hydrogenation and dehydrogenation of organic compounds.

In this work, the chemical equilibrium of aromatic hydrocarbons and N-containing compounds was studied. The chemical equilibrium was carried out in a heated autoclave over a Pt and Pd catalysts with varying reaction conditions: temperature (548-623 K), pressure (20-90 bar), hydrogen/LOHC ratio (0-28 mol/mol). The substances were dissolved in n-heptane in the amount of 2% wt. The fully hydrogenated product was then used as reactant in the dehydrogenation reaction. For each system, the achievement of an equilibrium state was proved by the invariance of the composition of the equilibrium mass over time by varying the type and amount of the catalyst, as well as by achieving an equilibrium state on the part of the reagent and the product. Analysis of the reaction mixture was done with GC; identification of the components was performed by GCMS method.

The results of the study of chemical equilibrium were additionally verified by comparing the data with combustion calorimetry and quantum chemical calculations.

**Acknowledgements** The financial support of the Ministry of Science and Higher Education of the Russian Federation (theme No. AAAA-A12-1111100072-9) part of the state task of the Samara State Technical University (creation of new youth laboratories).

# USING FAST SCANNING CALORIMETRY TO REDUCE MELTING POINT OF SUBSTANCES WITH ENANTIOTROPIC POLYMORPHIC TRANSITION

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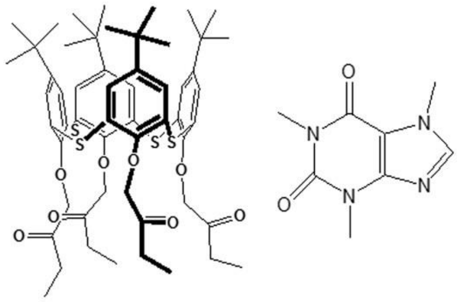
Reduction of the melting point is important for the preparation of bioavailable amorphous dosage forms, films for EUV lithography and organic light-emitting diodes by melt-quenching. Such reduction is required when the sample degrades near the equilibrium melting temperature [1]. To solve this problem, a sufficiently fast heating is necessary, which gives for the sample no time to decompose at fusion or decreases its melting point. The latter can be performed if the substance undergoes a polymorphic transition during heating [1].

In this work, we studied the possibility of decreasing the melting point of substances with endothermic (enantiotropic) polymorphic transition. For this, ultrafast heating is used with the rate up to 50000 K/s. Calixarene (**1**) and caffeine (**2**), Fig. 1, were chosen as the compounds with enantiotropic polymorphic transition. The kinetics of their polymorphic transition was studied using the conventional differential scanning calorimetry (DSC). Based on the data obtained, suitable kinetic models were found to predict the heating rate required to inhibit the solid state polymorphic transition and reduce melting points of **1** and **2**. The calculation results were experimentally confirmed by fast scanning calorimetry (FSC). For calixarene (**1**), which can't sublimate upon heating, the melting point can be reduced by 50 °C.

**Acknowledgements** This study was supported by Federal Academic Leadership Program Priority-2030 in Kazan Federal University, and subsidy allocated to Kazan Federal University for the state assignment in the sphere of scientific activities No. 0671-2020-0061



**1** **2**

**Figure 1.** Structures of research objects.

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# HEAT CAPACITY ANOMALIES NOT ATTRIBUTED TO PHASE TRANSITIONS

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Sometimes, the $C_p(T)$ curve of compounds in which there are no phase transitions may have an unusual shape. This behavior of the heat capacity can be explained by two factors: (1) hindered rotation of the structure fragments and (2) population of electronic levels caused by their splitting at the effect of a crystal field (Schottky anomaly).

## 1) Hindered rotation

The hindered rotation is realized when the amplitude of the vibrational oscillations reaches values at which a transition to another potential well is possible. The conditions for the transition from oscillation to hindered are: a small moment of inertia and relative "non-rigidity" of the crystal lattice. The rotation barrier of spinning top in a simplified form can be estimated by the equation:

$V_0 = (h\nu + 5h^2/8\pi^2 I)^2/(2h^2/\pi^2 I)$, where $I$ is the moment of inertia.

The examples of such group are $BH_4^-$, $NH_4^-$, $CH_3^+$, etc.

The shape of $C_{rot}(T)$ curves depending on the size of the rotation barrier is shown in Fig.1. Fig. 2 presents the $C_p(T)$ of cesium borohydride measured by adiabatic calorimetry [1] and DSC [2].

## 2) Schottky anomaly

One of the most characteristic examples of the Schottky anomaly is the splitting of the $f$ electronic levels of lanthanides and actinides under the action of the crystal field. This leads to the appearance of a bell-shaped anomaly on the $C_p(T)$ curve, which contributes throughout the entire temperature range of the existence of the compound.

$$C_x/R = \{\Sigma_i g_i(\varepsilon_i/kT)^2 \exp(-\varepsilon_i/kT)\}/Z - [\{\Sigma_i g_i(\varepsilon_i/kT)\exp(-\varepsilon_i/kT)\}/Z]^2.$$

The shape of anomaly curve depends both on the structure of the electronic shell of the $RE^{3+}$ ions and on the structure of crystal lattice. Heat capacity of diamagnetic lanthanum and lutetium allows calculation the anomalous contribution by the assessment of lattice contribution, $C_{lat}$, of magnetic compounds. Schottky anomalous contributions estimated from measured heat capacity of phosphates of Nd and Eu presented in the Figs.3 and 4 as an examples.

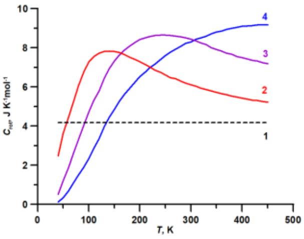

Fig.1. **1** $V_0$=0 kJ, **2** $V_0$=4 kJ, **3** $V_0$=4 kJ, **4** $V_0$=12 kJ

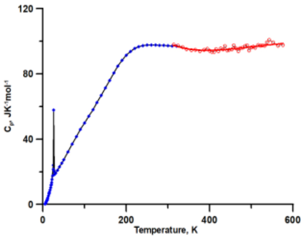

Fig 2. $C_p(T)$ of $CsBH_4$: blue diamonds – adiabatic calorimetry [1], red circles – DSC [2]

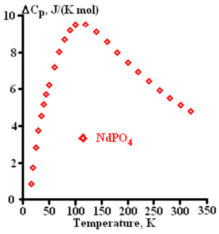

Fig.3. Schottky anomaly of $NdPO_4$ [3]

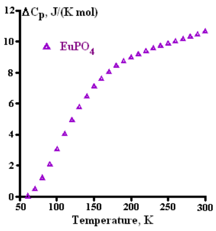

Fig.4. Schottky anomaly of $EuPO_4$ [4]

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# MESOPOROUS SILICA NANOPARTICLES MODIFIED BY IMIDAZOLIUM SURFACTANT FOR INTRAVENOUS DELIVERY OF 2-PAM

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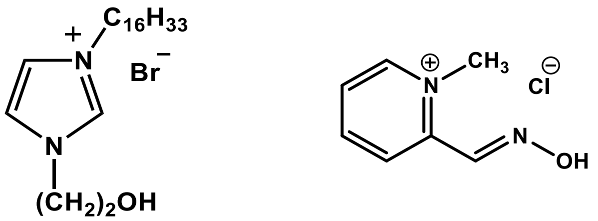
The use of mesoporous silica nanoparticles (MSN) as nanocontainers is one of the promising directions in the field of drug delivery. Such particles are characterized by low toxicity, and the presence of reactive hydroxyl groups on their surface opens up the possibility of modifying them with different chemical fragment [1].

At the first stage of the work, mesoporous silica particles were synthesized and characterized by a set of physicochemical methods. The textural properties of the sample obtained were characterized by the nitrogen (N) adsorption/desorption method. The N sorption isotherm corresponds to type IV (according to the IUPAC classification) with a hysteresis loop H1, reflecting the process of capillary condensation in mesopores. Such a loop is typical for mesoporous structures with cylindrical geometry of pores open on both sides. Surface area of the MSN calculated by multipoint BET method (Brunauer-Emmett-Teller) is 1809 $m^2/g$; the average diameter and total pore volume calculated by BJH method (Barrett-Joyner-Halenda) are 2.71 nm and 1.22 $cm^3/g$, respectively. In a continuation of the work, a technique was developed for the loading of acetylcholinesterase reactivator pralidoxime chloride (2-PAM) into mesoporous particles using cationic imidazolium surfactant with hexadecyl hydrocarbon chain (IA-16(OH), figure 1). Inclusion of the mixed IA-16(OH)-2-PAM system into the MSN leads to surface recharging (from -40 mV to +39 mV) and an increase in $D_h$ of the MSN (from 300 to 340 nm). It was shown that MSN-IA-16 (OH)-2-PAM particles have a smooth surface and an ellipsoid shape that retains after the IA-16(OH)-2-PAM loading, which was confirmed by scanning electron microscopy. The encapsulation efficiency of formulation toward 2-PAM was equal to 25%, which was calculated by spectrophotometry and thermography methods. The appearance of new bands (3082, 2925, 2833, 2737 $cm^{-1}$) in the IR spectra of MSN-IA-16(OH)-2-PAM, which correspond to the bands for IA-16(OH) and 2-PAM, is a confirmation of 2-PAM encapsulation. It has been established that IA-16(OH)-2-PAM contained in the MSN has low hemolytic and agglutination activity. *In vivo* tests on the rats demonstrated that the intravenous administration of nanoformulated 2-PAM at a concentration of 2 mg/mL leads to 15±4.9% reactivation of the brain acetylcholinesterase.

**Acknowledgment:** This work was financially supported by Russian Science Foundation (project № 19-73-30012).



IA-16 (OH)    2-PAM

**Figure 1.** Chemical structures of IA-16(OH) and 2-PAM.

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# THERMODYNAMICS OF COMPLEXATION OF NATIVE AND POLYMERIC β-CYCLODEXTRINS WITH BARICITINIB

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Baricitinib (BCN) is a new generation immunomodulator that was approved in 2017 for the treatment of rheumatoid arthritis. BCN is a selective inhibitor of Janus kinases and exhibits anti-inflammatory, immunomodulatory, and antitumor effects. The use of BCN is limited by its poor aqueous solubility, which results in serious side effects. As it is known, solubility of medicinal compounds can be improved by complex formation with cyclodextrins (CDs) – oligosaccharides capable to form host-guest inclusion complexes. In this connection, complexation of BCN by native and polymeric β-cyclodextrins was studied in the present work.

First of all, solubility of BCN in buffers with a physiological pH value was determined at 17-37 °C and the thermodynamic parameters of the dissolution process were calculated. It was found that the solubility of BCN in the acidic medium (pH=1.6) is higher than in neutral and slightly alkaline media (pH 4-8) due to protonation of the drug compound. Dissolution of BCN in buffer with pH=6.8 is endothermic process and accompanied by higher $\Delta_{\text{soln}}G^0$ compared to the buffer with pH=1.6.

Solubility of BCN in buffer with pH=6.8 was increased in the presence of cyclodextrins under consideration. Solubilizing effect of native and polymeric β-CDs is approximately the same (Fig. 1). Solubility rise is caused by the inclusion complex formation which was confirmed by the $^1$H NMR data. The cross peaks observed in 2D $^1$H ROESY spectra between the inner cyclodextrin proton H-3 and H20, H25 protons of BCN indicate the possible location of the pyrrolo[2,3-d]pyrimidin-fragment inside the macrocyclic cavity.

The thermodynamic parameters of the complex formation of BCN with native and polymeric β-CDs were obtained and analyzed. It has been established that 1:1 complexes formed by β-CD are enthalpy-entropy stabilized, whereas the complexation with polymeric β-CD is characterized by the negative enthalpy and entropy changes. Stability constants of the complexes of BCN with these β-CDs are very close. The revealed difference in the enthalpy and entropy changes is explained in terms of different driving forces responsible for the complex formation.

**Acknowledgements** This work was supported by Russian Science Foundation (grant №21-73-00119).

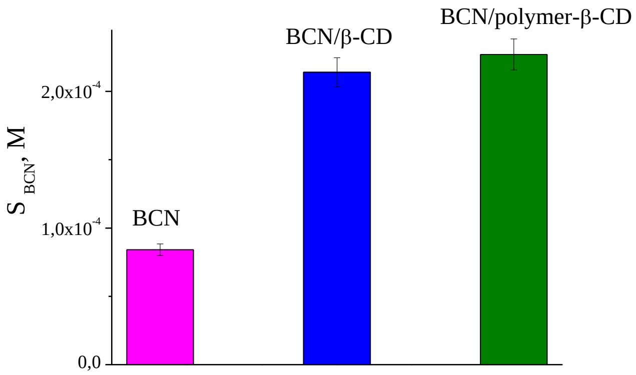

**Figure 1.** Solubility of BCN in the presence of cyclodextrins (c = 0.01 mol/kg) at 25 °C.

# THERMODYNAMIC PARAMETERS OF SOLUBILIZATION OF ANTIRHEUMATIC DRUGS BY PLURONIC F127

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Currently, the main task of the pharmaceutical chemistry is not only the development and synthesis of new medicinal compounds, but also the improvement of existing ones. The main problem concerning the majority of the medicinal compounds is their low solubility in water. To achieve a desired therapeutic effect, such drugs are prescribed in large doses, which lead to the appearance of unwanted side effects. To increase the aqueous solubility of the drugs, the effective solubilizers are proposed and designed. A promising direction in this area is the use of micelle-forming block copolymers – Pluronics. Pluronic micelles are aggregates consisting of a hydrophobic core formed by polypropyleneoxide blocks and a hydrophilic shell consisting of polyethyleneoxide fragments. Presumably, the inclusion of medicinal compounds in the hydrophobic core of the micelle will positively affect their solubility in the aqueous solutions. Pluronic F127 (Fig. 1) can be appropriate solubilizer since it has a large hydrophobic core suitable for the inclusion of bulky drug molecules.

The aim of the present work was to study the thermodynamic features of micellar solubilization of antirheumatic drugs such as methotrexate and sulfasalazine (Fig. 1) by Pluronic F127.

Solubility of methotrexate and sulfasalazine in the presence of variable concentrations of Pluronic F127 in buffer solutions with a physiological pH (1.6 and 6.8) was determined at different temperatures (15-40 $^{o}$C). Phase solubility diagrams were plotted and used for calculation of solubilization capacity (CE) and distribution coefficient ($K_m$)– parameters determining the solubilization efficiency. Thermodynamic parameters such as free energy, enthalpy and entropy of solubilization were determined using the van’t Hoff approach. The obtained CE, $K_m$ and thermodynamic functions of solubilization were discussed in terms of influence of the structure and ionization state of the drugs on the inclusion in the micelles of Pluronic F127.

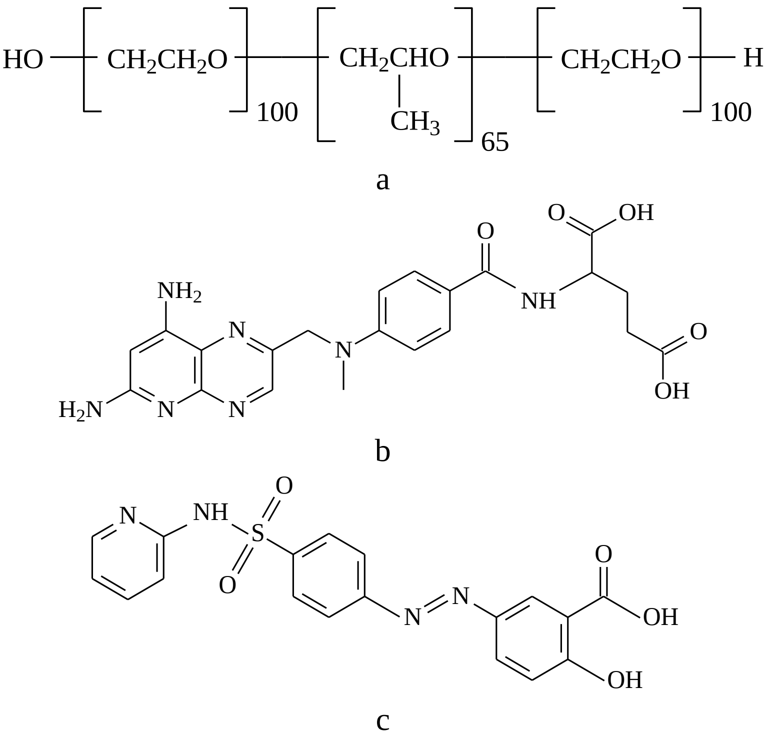

**Figure 1.** Structural formulas of Pluronic F127 (a), methotrexate (b), and sulfasalazine (c).

# NEW EXPERIMENTAL INVESTIGATION OF THE PHASE EQUILIBRIA IN THE Cu-Sm AND Co-Cu-Sm SYSTEMS

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The alloys of the Cu-Sm system are the basis for the development of permanent magnets with high energy density and magnetic fields, stable in various environmental conditions and wide temperature range. It is known from the literature, that alloying of alloys containing Co17Sm2 with copper, promotes the formation of non-magnetic particles $(Cu,Co)_5Sm$ along the grain boundaries of $Co_{17}Sm_2$, which increases the total coercivity[1]. The information about the nature of formation and stability range of both $Cu_5Sm$ and $Cu_4Sm$ phases, as well as the temperatures and character of the other phase equilibria in the Cu-Sm system are rather contradictory. The Co-Cu-Sm system, in its turn, was also studied in a limited temperature range (partial isothermal sections at 800 and 1200°C [2], 850°C [3] and 850°C [4]) and concentrations up to 20%Sm. Isothermal sections described earlier contradict each other in terms of $Cu_6Sm$ и $(Cu,Co)_5Sm$ stability ranges. Such way, the purpose of the current work is the investigation of the phase equilibria in the Cu-Sm and Co-Cu-Sm systems over the entire concentration range.

For the description of phase equilibria during crystallisation there were prepared alloys by arc-melting in argon atmosphere. Alloys were studied by SEM/EPMA, DTA, XRD in the as-cast and annealed states. As a result, for the first time there were determined the solubilities of the third components in binary compounds of the Cu-Sm and Co-Cu-Sm systems near solidus: for CuSm, $Cu_2Sm$ the solubility of cobalt is 17 and 7 at.%, respectively; the solubility limits of copper for $Co_3Sm$, $Co_2Sm$, $Co_7Sm_2$ и $Co_{17}Sm_2$ are 7, 9, 12 и 15% (at.), respectively. There were also found new ternary compounds, $\tau_1$ (Cu-(17-27)at.%Co-50at.%Sm) and $\tau_2$ (Co-(5-10)at/%Cu-67at.%Sm), supposedly with the structural types $PuNi_3$ and $Co_7RE_{12}$. Subsequently, new versions of the Cu-Sm and Co-Cu-Sm diagrams were proposed, which will make it possible to create new alloy compositions with a unique set of properties.

**Acknowledgement:** The study was supported by Russian Science Foundation project № 18-73-10219-П.

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# SYNTHESIS, SELF-ASSOCIATION AND INTERACTION WITH BSA OF CALIXRESORCINE CARBOXYBETAINES AND CARBOXYBETAINE ESTERS

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It is known that the unique properties of zwitter-ionic compounds make them a top of interest in the field of biotechnology and nanomedicine. The high hydrophilicity of zwitter-ionic compounds and the resistance to protein adsorption can be used in the development of drug delivery systems, since the hydrophilicity extends the period of circulation, enhances therapeutic effectiveness and prevents the formation of antibodies to the nanomaterial [1]. On the other hand, amphiphilic calixresorcines can serve as a platform for diverse biomedical applications due to their easy synthesis, distinct receptor properties and self-assembly capabilities [2]. The aim of our work was to introduce zwitter-ionic carboxybetaine fragments into the structure of amphiphilic calixresorcines and to study their self-association and interaction with model protein BSA (Figure 1). Also the hemolytic activity and cytotoxicity of the compounds were studied. The receiving of carboxybetaine calixresorcines includes the synthesis of their carboxybetaine esters derivatives. Thus the properties of carboxybetaine and their esters can be compared. We have obtained tetraundecyl- and tetrapentylcalix[4]resorcines, functionalized by ester and carboxybetaine groups. The compounds were characterized by $^1$H and $^{13}$C NMR, IR spectroscopy and ESI. The self-association of macrocycles was studied by fluorimetry, DLS and FT-PGSE NMR study. It can be concluded that the self-association of carboxybetaine macrocycles are more pronounced than of their carboxybetaine esters. The interaction of macrocycles with BSA was studied by fluorimetry, synchronous fluorimetry and DLS methods. The values of quenching constants, binding constants, number of binding sites, and thermodynamic parameters of BSA-macrocycles interaction were determined. It was shown that the driving forces of interaction are van der Vaals forces and H-bonding. It was found that in comparison with their esters derivatives carboxybetaine calixresorcines interact with BSA more weakly. Also the cytotoxicity of carboxybetaine calixresorcines is lower than of their esters. These results show the potential of carboxybetaine calixresorcines in biomedical application.

**Acknowledgements.** This work was funded by the government assignment for FRC Kazan Scientific Center of RAS and subsidy allocated to Kazan Federal University for the state assignment in the sphere of scientific activities (N 0671-2020-0063). The authors gratefully acknowledge the Assigned Spectral-Analytical Center of FRC Kazan Scientific Center of RAS.

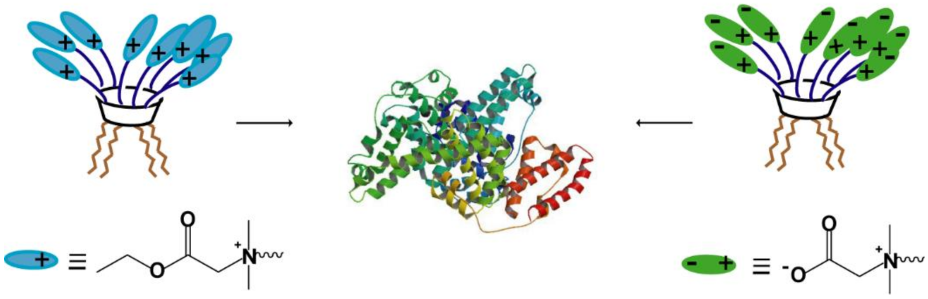

**Figure 1.** The schematic presentation of compounds structures.

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# PHASE EQUILIBRIUM IN THE Sn–P–Ge SYSTEM

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Binary compounds of elements of group IV (Si, Ge, Sn) and group V (P, As) form layered structures in which two-dimensional layers with a covalent bond are connected by weak van der Waals forces [1,2], and with this points of view can be considered promising 2D materials. However, it should be noted that the preparation of crystals of compounds of this class is associated with significant difficulties. In particular, germanium phosphide decomposes according to the peritectic scheme at 998 K, and a pressure of $26 \cdot 10^3$ hPa develops [2]. In [3] an attempt was made to obtain GeP samples from melt solutions in tin, which significantly softened the synthesis conditions. Nevertheless, the resulting alloys contained tin phosphides as an accompanying phase. The study of phase equilibria and the construction of the phase diagram of the Ge–P–Sn ternary system would make it possible to approach the preparation of both bulk and two-dimensional samples of germanium phosphide from a qualitatively different standpoint, as well as to determine the possibility of doping them with tin.

Three polythermal cross sections of the Ge–P–Sn system: $Sn_4P_3$–Ge, $Sn_4P_3$–GeP and $SnP_3$–Ge were studied by differential thermal analysis (DTA) and X-ray phase analysis (XRD). Alloys were obtained by single-temperature synthesis at T=1233 K in thick-walled quartz ampoules evacuated to a residual pressure of $5 \cdot 10^{-4}$ hPa. Then, homogenizing annealing was carried out for 150 h at a temperature of 753 K.

An X-ray diffraction study of $Sn_4P_3$–Ge alloys showed that the samples are a eutectic mixture of two phases: germanium and tin phosphide $Sn_4P_3$. According to DTA data, the eutectic point exists at a temperature of 800 K and a composition of 18 mol.% germanium. The decomposition of $Sn_4P_3$ according to the syntectic scheme leads to the appearance of a three-phase region ($Sn_4P_3$+$L_1$+$L_2$) on the diagram. For the $Sn_4P_3$–GeP polythermal cross section, the $Sn_4P_3$ and GeP phases were detected by X-ray diffraction. It should be noted that the high phosphorus vapor pressure developed during the synthesis led to depletion of the samples in phosphorus; therefore, low-intensity germanium lines were also observed in the X-ray diffraction patterns. For the $SnP_3$–Ge section, alloys with a germanium content of more than 20 mol. % also represented a heterophase mixture of $Sn_4P_3$, GeP and Ge, and at a lower content, in addition to $Sn_4P_3$ and GeP reflections, $SnP_3$ lines were fixed on the diffraction patterns. Thus, the phase subsolidus delimitation of the phase diagram of the Ge–P–Sn ternary system is carried out by the sections $Sn_4P_3$–Ge, $Sn_4P_3$–GeP, and $SnP_3$–GeP.

It has been established that the invariant peritectic equilibrium L+Ge ↔ $Sn_4P_3$+GeP and the eutectic process L ↔ $Sn_4P_3$+GeP+$SnP_3$ are realized in the system. The study of alloys with polythermal cross sections $Sn_4P_3$–GeP and $SnP_3$–Ge by the DTA method made it possible to determine the temperatures of these processes, equal to 795 K and 790 K, respectively.

According to the model of regular solutions, a thermodynamic calculation of the isotherms of the liquidus surface of germanium and germanium phosphide was carried out. The obtained liquidus temperatures agree satisfactorily with the experimental data.

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# MOLECULAR ASSOCIATION AND SELF-DIFFUSION IN CHLOROFORM – ACETONE, DMSO SYSTEMS

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Molecular association affects the physicochemical properties of solutions, in particular, self-diffusion. The self-diffusion coefficient is a characteristic of the particles motion of the mixture components in the state of its thermodynamic equilibrium (self-diffusion). Thus, the dependences of the self-diffusion coefficients on the parameters of mixture state are of interest for developing molecular kinetic theories of solutions by comparing relationships based on them with experimental data [1]. In this work, an experimental ($^1$H PGSE NMR (pulsed gradient spin-echo nuclear magnetic resonance) method) and theoretical (athermal associated solution model [2], molecular dynamics simulation, and quantum-chemical calculations) study of molecular association and self-diffusion in binary systems acetone – chloroform and DMSO – chloroform has been presented. According to the literature data [3, 4], the negative deviation from the ideality of the thermodynamic properties of the binary systems acetone – chloroform and DMSO – chloroform is associated with the formation of heteroassociates. At the same time, unlike acetone, the formation of DMSO self-associates is possible [4, 5]. According to the analysis based on the UNIQUAC associated-solution theory (athermal associated solution model), self-diffusion coefficients in the acetone – chloroform system are described with a sufficient degree of accuracy by model with the formation of only heteroassociates 1:1. A more accurate description of self-diffusion in the DMSO – chloroform system is observed when using model with the formation of heteroassociates 1:1 and DMSO dimers. Analysis of interaction energy of DMSO and acetone with the same species showed that the energy of formation of self-associates (dimers) of acetone is much smaller than the energy of formation of DMSO dimers. This shows why it is important to take into account self-associates of DMSO when one approximates the experimental data of self-diffusion coefficients by model approach, and why it is enough to be limited by the heteroassociates 1:1 for acetone – chloroform mixture.

**Acknowledgements** This research was funded by the Russian Science Foundation, No. 22-23-00685, https://rscf.ru/en/project/22-23-00685/.

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# EFFECT OF MOLECULAR ASSOCIATION ON THE DISSOLVING POWER OF THE BINARY SOLVENT METHANOL – CARBON TETRACHLORIDE

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The effect of molecular association on the thermodynamic and other properties of the binary system methanol – carbon tetrachloride is considered in detail in [1]. According to the presented results, this system can be considered as a multicomponent system consisting of methanol self-associates of various shapes and size. The presence of OH-group in the methanol molecule makes it possible not only to form self-associates, but also methanol – solute heteroassociates. Previously, we have studied the solvation of caffeine in carbon tetrachloride – methanol mixtures by molecular dynamics simulation have determined the main centers of hydrogen bonding and concentration dependence of hydrogen bonds caffeine – methanol for different atoms [2]. In the current work an experimental (isothermal saturation method) and theoretical (ASL (Associated Solution + Lattice,) model, molecular dynamics simulation) study of the caffeine solubility in the binary solvent inert component (carbon tetrachloride) and self-associated component (methanol) has been performed. According to the experimental data, the concentration dependence of the caffeine solubility has a maximum in the region of 0.5 mole fraction of the cosolvent. The maximum is also observed for the concentration dependence of the Gibbs energy of solvation calculated within the framework of molecular dynamics simulation. Within the framework of the ASL model, it was shown that the main contribution to solubility is made by the caffeine – methanol heteroassociation [3].

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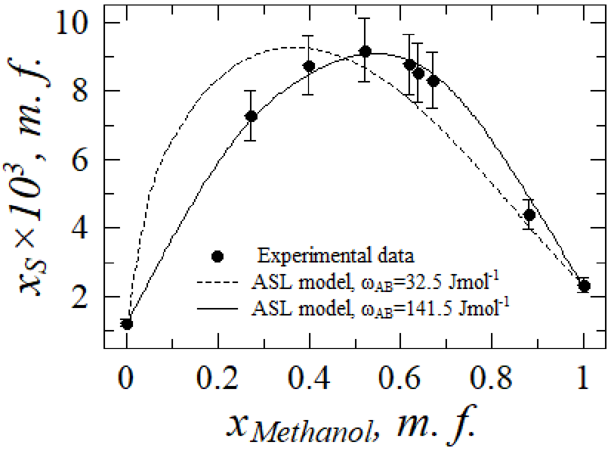

**Figure 1.** Experimental and theoretical concentration dependences of the caffeine solubility, $x_S$ , in the binary solvent methanol – carbon tetrachloride at 298.15 K [3].

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# THERMODYNAMIC PROPERTIES OF CHITOSAN COPOLYMERS

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The synthesis of biodegradable and biocompatible polymer materials is of current importance. These materials are widely used in medicine and they decompose into eco-friendly substances under environmental conditions.

Chitosan is a derivative of natural chitin, which is the second most abundant polysaccharide in nature after cellulose and widely distributed in natural sources, such as crustaceans, insects, algae, and fungi. Chitosan is a nontoxic, biodegradable, biocompatible polymer with antimicrobial activity. It has a great potential for a wide range of uses due to its versatile biological, chemical and physical properties. Nowadays, the application of chitosan and its derivatives includes a variety of fields such as pharmaceutics and biomedicine, wastewater treatment, cosmetics, food packaging, and agriculture. Nevertheless, due to low mechanical strength and relatively poor solubility of chitosan in water or in organic solvents, modification of the polymer is required.

The high activity and complexing ability of chitosan functional groups allow it to be combined with various biologically active substances and synthetic polymers. The most convenient method for combining such properties is the preparation of graft and block copolymers of chitosan, along with mixture compositions based on homopolymers.

The modification of chitosan can provide the development of new class of synthetic composite materials with a wide range of the desired properties. The investigation of the standard thermodynamic properties of copolymers in a wide temperature range by methods of calorimetry allows us to reveal and analyze practically important dependences of thermodynamic properties of copolymers on their composition.

The present investigation is devoted to a comprehensive calorimetric study of the standard thermodynamic and thermophysical properties of chitosan copolymers. In this work, for the first time, the heat capacities of of chitosan–poly(d,l-lactide) and chitosan–poly(2-ethylhexyl acrylate) copolymers were measured in the temperature range from 6 to 350 K by precision adiabatic vacuum calorimetry, and their thermophysical properties were studied in the range from 270 to 560 K by differential scanning calorimetry. The thermal stability of the studied samples was determined by thermogravimetric analysis. In the above intervals, the glass transition was detected for all investigated samples, and their thermodynamic characteristics were determined, analyzed, and compared with those for chitosan, polylactide and poly(2-ethylhexyl acrylate).

The obtained experimental data were used to calculate the standard thermodynamic functions of copolymers, namely the heat capacity $C_p°(T)$, enthalpy $H°(T) - H°(0)$, entropy $S°(T)$ and Gibbs energy for the range from $T \rightarrow 0$ to 350 K for different states and the standard characteristics of their formation at $T = 298.15$ K.

It is concluded that the synthesis of copolymers based on chitosan, poly(d,l-lactide) and poly(2-ethylhexylacrylate) leads to a change in their physicochemical characteristics. The most general qualitative and quantitative dependences of thermodynamic and thermochemical characteristics of copolymers on their composition were experimentally obtained. These dependencies allow us to predict practically important physicochemical properties of copolymers of unknown compositions.

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# THERMOPHYSICAL PROPERTIES OF PHYTOSTEROLS

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In the present research the thermophysical properties of phytosterols were investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC) in the range of 300−800 K. As a result, the areas of their thermal stability were established. The thermodynamic characteristics of melting and crystallization have been determined. The dependence of thermophysical properties on the composition and nature of phytosterols has been concluded.

Phytosterols are a group of steroids alcohols that are natural components of plant cell membranes and contribute to the regulation of the fluidity and permeability of cell membrane [1]. The most common plant phytosterols are β-sitosterol, sitostanol, campesterol and campestanol. Phytosterols are characterized by hypocholesterolemic properties, and have anti-inflammatory, anti-atherogenic, anti-cancer and antioxidant activity. These substances are also used as a starting material for the production of therapeutic steroids. In industry, phytosterols are isolated from vegetable oils or from by-products of wood pulp processing, mainly from tall oil or tall oil pitch [2].

Phytosterol samples were characterized by GLC as their silylated derivatives. The hemihydrate and anhydrous form of phytosterols was confirmed by XRPD and near infrared spectroscopy, as well as Karl Fischer titration.

In this work, commercially available samples from various manufacturers and laboratory samples were studied by TG and DSC methods. A comparative analysis of the thermophysical properties of the studied samples with literature data was carried out. For one of the samples, the heat capacity was studied in the region of 260–570 K. The results can be used in solving problems in the design of plan for processing by-products of pulp and paper mills to obtain phytosterols.

**Acknowledgements** This work was performed with the financial support of the Ministry of Education and Science of the Russian Federation (Contract No. 0729-2020-0039).

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# DYNAMICS OF THERMAL DECOMPOSITION OF THE DOUBLE COMPLEX SALT $[CU(TN)_{2})]_{3}[FE(CN)_{6}]_{2}\cdot 8H_{2}O$

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The properties of copper-iron double complex salt (DCS) are being actively studied at the present time. For example, the products of their thermolysis can be used as catalysts. To use thermolysis products as functional materials, it is important to be able to obtain precisely specified phase composition of these products.

Thermal decomposition of the $[Cu(tn)_{2})]_{3}[Fe(CN)_{6}]_{2}\cdot 8H_{2}O$ was studied by thermogravimetry (TG) under linear heating with temperature ramps of 5, 7 and 20 K/min. Repeated experiments performed for each heating rate confirmed proper reproducibility of data. The experiments revealed complex multistage nature of decomposition reaction accompanied by mass loss.

The model-based kinetics evaluation method was used to create complex formal kinetic model. Estimation of the kinetic parameters for such a model required the application of the nonlinear optimization technique [1]. Since the initial reagent is an individual substance, the hypothesis of the reaction scheme consisting of several consecutive stages was adopted to create the model. TG data showed that the reaction comprises at least six stages; in addition, the position of the mass loss rate (DTG) peaks along the temperature axis suggested that some of the stages are of self-acceleration type. The model structure consistent with the hypothesis is as follows:

$A\rightarrow B1\rightarrow B2\rightarrow B3\rightarrow B4\rightarrow B5\rightarrow B6$

The quality of experimental data description by the model created is shown in Fig. 1 a, b (the last slow stage with small mass loss is shown partially). It should be emphasized that the model has been created based on only two data sets that correspond to slow heating of 5 and 7 K/min, whereas the result of fast heating of 20 K/min was used to validate the model. As shown in Fig. 1, the model predicts the course of the reaction proceeding under significantly different conditions quite well, which confirms the consistency of the model.

The applications of the TSS-ARKS software designed by CISP Ltd [2] were applied, specifically ARKS TA for TG data processing and ARKS FK for model creation and simulations.

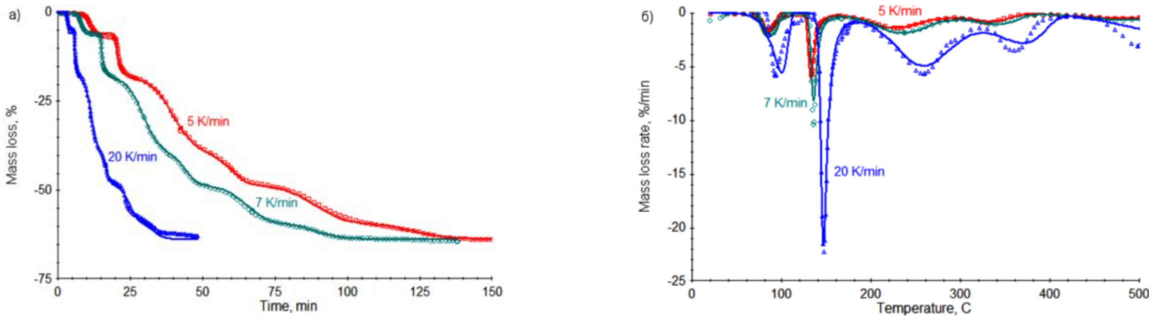

**Figure 1.** Decomposition of the DCS. Correspondence of experimental responses and responses calculated by the kinetic model. a) mass loss curves; b) mass loss rate curves; dotted curves - experimental responses; solid curves - model calculation.

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# MD SIMULATION OF A POLYCATION CHAIN WITH VARYING COUNTERIONS IN SOLUTION AND PREDICTIONS FROM THE STATISTICAL FIELD THEORY

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Simulations and modeling of polyelectrolyte solutions is a field with long history and numerous practical applications. Nevertheless, the development of an analytical model of a polyelectrolyte that takes into account the location of charge within the ionic species remains as yet a challenging task. In the recent years, the field theory techniques have been advanced considerably, making possible to describe solutions that contain ionic particles of complex electrical structure. An important test of theoretical predictions is the comparison with the results of computer simulations using reasonably realistic model potentials.

In the present work, we perform molecular dynamics (MD) simulations of poly(dimethyl diallyl ammonium) salts in water, with halide or amino acid counterions: PDADMAX where X=Cl$^-$, Lys$^-$, Leu$^-$, Gly$^-$. A full-atom model potential (OPLS-AA force field as included in the Gromacs simulation package) is used. We examine the behavior of polycations with different backbone lengths (20, 40, 60, 80, 100, 200, and 400 monomers) in dilute solution at 298 K. For PDADMACl and PDADMALeu systems, we perform simulations in presence of a salt background (0.5M NaCl or 0.5M NaLeu). The simulation results are used for testing a model of polyelectrolyte chains in solution developed with the aid of the variational field theory [1]. The model takes into account the connectivity of the charged monomers along the polyelectrolyte backbone and the hard core interactions between these monomers and the counterions in solution. The charges are located off-center of ions; the many-body Coulomb interactions are treated in the random phase approximation [2].

We compare predictions from the theory with our MD data on the structure and conformation of chains, including the gyration radii and charge-charge correlation functions. Particularly, we discuss effects of the counterion nature and concentration (especially for the amino acid anions as compared with Cl$^-$), and the viability of the model in reflecting these effects.

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# HETEROGENEOUS EQUILIBRIA AND VAPORIZATION BEHAVIOR OF $In_2O_3$ IN THE PRESENCE OF Pt

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Evaluation of the influence of noble metals on the thermodynamic properties of metal oxides obtained in high-temperature studies is a crucial task due to regular use of sample holders and containers made from noble metals for investigations. The problem arises from the ability of a material such as Pt or Ir etc. to dissolve other metals. When the equilibrium vapor of an oxide contains metal species, active dissolution through the gas phase is probable, which can lead to incorrect research results. In this work, vaporization in the In–O–Pt system was studied by Knudsen effusion mass spectrometry (KEMS) using quartz effusion cell. Co-evaporation of weighted $In_2O_3$ and Pt foil was conducted under isothermal conditions (1550 K) till complete vaporization of $In_2O_3$. Then the foil was analyzed by weighting, XRD, and EDS analyses.

The qualitative gas phase composition determined in the KEMS experiment was identical to the vapor composition of pure $In_2O_3$. However, the partial pressures of the vapor species, and hence the quantitative composition of the vapor, reached the values corresponding to pure $In_2O_3$ only at the end of the vaporization experiment. Analysis of the Pt foil showed the formation of the $Pt_3In$ intermetallic compound. These results can be interpreted by means of reaction (1). The initial phase composition of the sample [Pt + $In_2O_3$] corresponded to the equilibrium state of the In–O–Pt system at the oxygen pressure (ambient pressure) sufficient to suppress the sublimation of $In_2O_3$ in accordance with the equilibrium constant of reaction (1).

$$Pt(s) + 5In_2O_3(s) = Pt(In)_x(s) + (4\text{-}x)In(g) + 3In_2O(g) + 6O_2(g) \qquad (1)$$

Under effusion conditions, in the absence of ambient pressure, the system tends to the equilibrium phase composition of the condensed phase [$Pt(In)_x$ + $In_2O_3$] in agreement with reaction (1). This caused a high partial pressure of oxygen at the beginning of the experiment. As the Knudsen method provides for effusion of the vapor from the cell, the observed changing in partial pressures of the vapor species during the experiment corresponded to a quasi-equilibrium process of shifting of the figurative point of the In–O–Pt system towards the less volatile component Pt in the phase diagram. The closeness of the system state to the equilibrium was confirmed by values of the enthalpies of vaporization reactions of $In_2O_3$ obtained from the experiment data by the third-law calculations. These enthalpies were in agreement with ones obtained for pure $In_2O_3$ previously [1]. Nevertheless, the partial pressures of the vapor species over the sample under study were quite different from those corresponding to pure $In_2O_3$. Thus, it can be concluded that Pt is not a suitable cell material for high-temperature investigations of $In_2O_3$ under non-oxidizing conditions. Its use may result in incorrect partial pressures of the vapor species and erroneous vapor composition of pure $In_2O_3$. Moreover, Pt cell/container contaminations can affect results of future experiments. In view of similarity of properties of noble metals, the formation of intermetallic compounds and, consequently, the influence on vaporization processes should be expected when such materials are used for high-temperature investigations of oxides containing metal species in the equilibrium vapor.

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# THERMODYNAMICS OF MIXED-LIGAND COMPLEX FORMATION OF ZINC IONS WITH ORNITHINE AND HISTIDINE

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Systems containing a metal cation and amino acid residues of the basic type (His, Lys, Orn) or with polar side chain groups (Ser, Thr, Cys) have been actively studied for several decades. The main problem in this case is the determination of coordination modes of amino acid residues in the composition of the anionic and zwitterionic forms. Only potentiometric data here do not provide the necessary information, and it is necessary to involve data from other methods, most often spectral ones. Since the study of Zn – His – Orn ternary system was previously carried out mainly using the potentiometric method, it was of interest to clarify the ionic composition of solutions and to reveal the features of ligand coordination in mixed complexes based on a comparative analysis of thermodynamic data.

In this work, mixed-ligand complex formation of zinc with natural L-ornithine and L-histidine was studied. A series of pH-potentiometric titrations of solutions ($ZnSO_4$ + HOrn·HCl + HHis) with a NaOH solution at 25ºC and an ionic strength of 0.5 ($KNO_3$) were carried out at ratios Zn : His : Orn = 1:1:1, 1:1 :2 and 1:2:1. The experimental data of pH-potentiometric measurements were processed using the PHMETR computer program. The agreement between the calculated and experimental curves at the ratio Zn : His : Orn = 1:1:1 was achieved by taking into account the formation of mixed complexes of the types $ZnHOrnHis^+$ and $ZnH_2OrnHis^{2+}$ along with the ZnOrnHis complex. In other cases, the formation of mixed complexes of the types $ZnHnHis_2Orn$ (n=0, 1, 2) and $ZnHnHisOrn_2$ (n= 2, 3) (charges are omitted) was revealed.

The polyvariant character of coordination of the studied amino acids makes the identification of the composition of mixed complexes with anionic and zwitterionic forms of amino acids a rather difficult task, requiring the use of data from different methods. As the composition of mixed complexes was established, the full thermodynamic parameters of the processes of their formation were calculated using calorimetric data. Heat effects were measured on an ampoule mixing calorimeter with an isothermal shell and a thermister temperature sensor. The calorimetric data were processed using the HEAT computer program. NMR data were used to confirm the conclusions regarding the possible structure of ternary complexes. For the system under consideration, $^1H$ and $^{13}C$ NMR spectra were taken. NMR spectra were recorded on Bruker AVANCE III-500 instrument. Cyclohexane was used as external standard.

The obtained thermodynamic characteristics, along with NMR data, made it possible to propose the most probable coordination mode of amino acid residues in mixed complexes. A comparative analysis of the thermodynamic parameters of formation of mixed complexes of zinc and nickel was also carried out.

# THERMODYNAMIC PARAMETERS OF PROTOLYTIC EQUILIBRIA FOR SOME DIPEPTIDES IN AN AQUEOUS SOLUTION

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This work presents results of investigations of acid-base interaction processes in aqueous solutions of L-valyl-L-valine, D,L-valyl-D,L-leucine, D,L-valyl-glycine, D,L-leucyl-glycine, L-leucyl-L-leucine, D,L-alanyl-D,L-leucine, L-alanyl-L-isoleucine, D,L-alanyl-glycine, D,L-alanyl-D,L-serine, D,L-alanyl-D,L-histidine, glycyl-L-histidine, β-alanyl-glycine, glycyl-glycine, glycyl-β-alanine, glycyl-L-alanine, glycyl-D,L-valine, glycyl-D,L-norvaline, glycyl-D,L-leucine, glycyl-D,L-glutamine, glycyl-D,L-serine, glycyl-D,L-threonine, glycyl-L-aspartic acid, glycyl-L-glutamic acid.

Thermodynamic parameters (log K, ΔG, ΔH, ΔS) of protolytic equilibria have been determined at 298.15 K and at ionic strength values from 0.1 to 1.5 M ($KNO_3$). Stepwise dissociation and protonation constants of these dipeptides were determined potentiometrically. The equilibrium concentration of hydrogen ions was determined by measuring the electromotive force of a glass electrode and a silver – silver chloride reference electrode using a P-363/3 potentiometer with a pH-340 pH-meter-millivoltmeter as the null-instrument. The heat effects of the relevant equilibria were measured calorimetrically. The calorimetric measurements were performed in an isothermal jacket ampoule flow-mixing calorimeter equipped with a thermistor sensor and an automatic recorder of the temperature–time curve. The unit was tested against the heat of solution of crystalline potassium chloride in water.

The influence of "background" electrolyte concentration on the thermodynamic parameters for the protolytic equilibria of the dipeptides investigated was under consideration. The data obtained were extrapolated to the zero ionic strength. The corresponding thermodynamic quantity values have been calculated for the standard solution (log K°, ΔG°, ΔH°, ΔS°). The results have been compared with the corresponding data on related compounds (amino acids, complexones, peptides and diamines) investigated in this laboratory earlier [1-12]. Dependences of the reaction thermodynamic quantities on a side substituent hydrophobicity of the C- and N-terminal amino acid residue and on the distance between the carries of positive and negative charges have been discussed. As ancillary part of this study, the spatial, electronic and energy parameters for isolated molecules and ions of some aminocarboxylates have been computed.

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# THERMODYNAMIC PROPERTIES AND PHASE EQUILIBRIA IN THE Na – K – Al – $SO_4$ – $H_2O$ SYSTEM

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Phase Change Materials (PCM) are used for latent heat storage. They change their physical phase and either absorb or release heat. This phase change occurs at a phase transition temperature. We focus on PCM based on inorganic salt mixtures because they have high enthalpy of phase transition, provide an opportunity to change phase transition temperature by varying the composition of mixtures and are inflammable.

The purpose of this work is to build a thermodynamic model of the $Na^+$-$K^+$-$Al^{3+}$-$SO_4^{2-}$-$H_2O$ system containing some compounds which can potentially be used for PCM mixtures. Pitzer-Simonson-Clegg (PSC) model was proposed for describing the Gibbs energy of the liquid.

Physicochemical properties of binary subsystems $Na_2SO_4$ – $H_2O$, $K_2SO_4$ – $H_2O$, $Al_2(SO_4)_3$ – $H_2O$ are presented in literature. As for ternary subsystems physicochemical properties of the subsystem $K^+$-$Na^+$-$SO_4$ are presented in the literature, but for other subsystems $Na^+$-$Al^{3+}$-$SO_4^{2-}$-$H_2O$ and $K^+$-$Al^{3+}$-$SO_4^{2-}$-$H_2O$ only limited data on solid-liquid equilibria are available, thus it is necessary to conduct an additional experimental study of these systems.

Water activity in the $Na^+$-$Al^{3+}$-$SO_4^{2-}$-$H_2O$ system was investigated for six solutions at 15, 25 and 35°C by static total pressure apparatus. Water activity in the $K^+$-$Al^{3+}$-$SO_4^{2-}$-$H_2O$ system was investigated for three solutions at 25 °C by dew point detector AQUALAB 4TE. Also solid-liquid equilibria in the $Na^+$-$Al^{3+}$-$SO_4^{2-}$-$H_2O$ system at 10°C were studied using the method of isothermal solution saturation. Concentration of the solutions was defined by complexometric titration and gravimetric methods.

PSC models of binary subsystems $Na_2SO_4$ – $H_2O$ and $K_2SO_4$ – $H_2O$ presented in literature were reproduced and parameters of PSC model for the $Al^{3+}$-$SO_4^{2-}$-$H_2O$, $Na^+$-$Al^{3+}$-$SO_4^{2-}$-$H_2O$ and $K^+$-$Al^{3+}$-$SO_4^{2-}$-$H_2O$ subsystems were calculated using literature data and obtained experimental data.

The research was funded by RFBR and Moscow city Government according to the project № 21-33-70031.

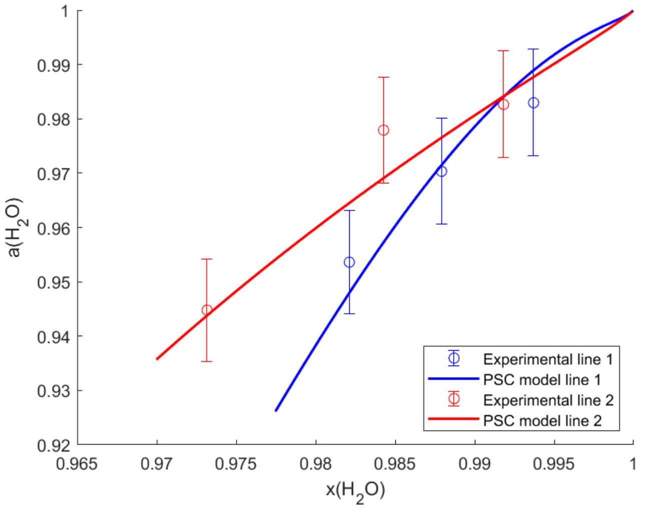

**Figure 1.** Water activity in the $Na^+$-$Al^{3+}$-$SO_4^{2-}$-$H_2O$ system at 25°C, line 1: $n(Na^+)/n(Al^{3+})$ = 0.60, line 2: $n(Na^+)/n(Al^{3+})$ = 5.34

# KINETIC OF THERMAL DESTRUCTION OF N-PROPANOL

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By the method of isothermal pressure increasing at closed system [1] the values of thermal decomposition points (decomposition temperatures) of pure n-propanol and dissolved in water are obtained for different composition of alcohol (x= 0.8, 0.5, 0.2 mol. fraction of n-propanol).

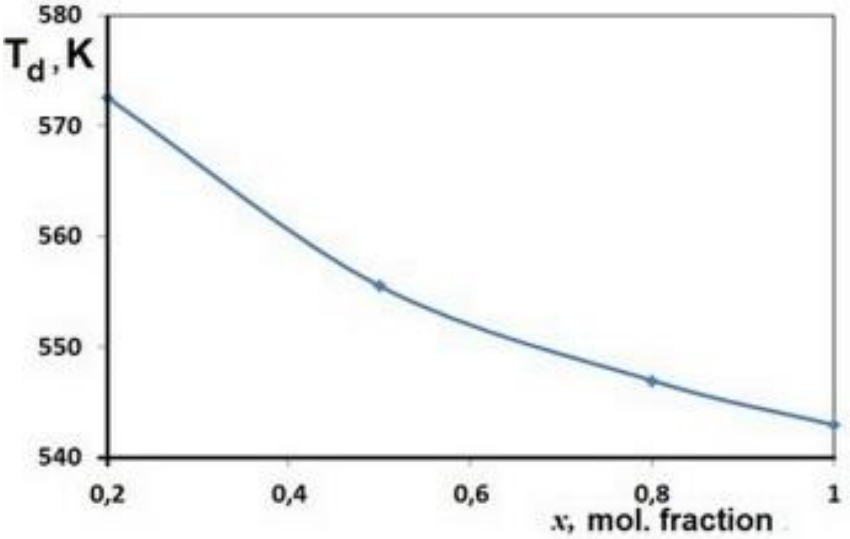

**Figure 1.** Dependence of decomposition points of n-propanol in water solution from composition of alcohol

Using data on pressure increasing of the researched system at constant temperature the rate of thermal destruction of n-propanol in the range of temperatures from 523.15 to 66.315 K was evaluated.

Since the process of thermal decomposition of hydrocarbons and alcohols is a first order reaction [2,3] the rate of destruction of the n-propanol molecules can be described by next formula.

$$dp/d\tau = k \cdot p, \quad k = 1/p \cdot dp/d\tau$$

Where k is a rate constant, p is a pressure of the system and *dp/dτ* is a change pf pressure in time.

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# INVESTIGATING LARGE ANISOTROPIC PLASTICITY OF PYRAZINAMIDE MOLECULAR CRYSTALS USING COMPUTATIONAL METHODS

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Molecular crystals had been usually described as brittle entitiesbefore work published in 2006 by Reddy et., who reported the phenomenon of bending organic crystals.[1,2] Based on the survey of 60 molecular crystals, the 17 of them could be bent, they suggested the qualitive model which state that bending crystals should have layered structure and different strength of intermolecular interactions in two orthogonal interactions. Several experimental and theoretical studies were contributed and more examples were reported in the years ahead, but no qualitive model have been developed so far, despite the connection between the intermolecular interactions and bending behavior certainly exist[3]. Moreover, the number of known plastically bending crystals according to our estimations hardly exceeds several tens whereas the number of structures in crystal databases is significantly more than one million. While layered structures are common among molecular crystals, that rise the question why bending crystals is so rare phenomenon?

In this research we focus on studying of plastic bending properties in organic crystals using an example of pyrazinamide polymorphs with the aid of quantum and molecular mechanic methods in attempt to unveil the nature of the bending phenomenon of molecular crystals. Pyrazinamide system has several polymorphs which contain one bending and one non-bending form[1]. Thermodynamic properties of all phases, including packing energy, stability and conformational energies were calculated using molecular mechanics and DFT (with periodic boundary conditions) methods. Additionally, energies of specific contacts and interactions within and outside of layers were calculated and correlated to the final bending property (Fig.1).

Preliminary data, obtained using computational methods on static model, shed light to the understanding of organic crystal bending on molecular level.

**Acknowledgements:** This research was funded by the Russian Science Foundation, grant number 21-73-00094 (https://rscf.ru/en/project/21-73-00094/)

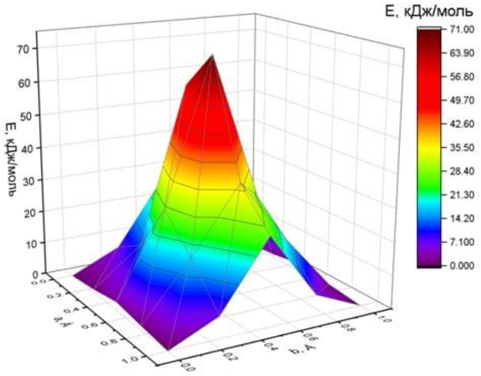

**Figure 1.** Potential energy surface of layers' interactions shifted in different crystallographic directions.

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# OBTAINING OF A PHARMACEUTICALLY ACCEPTABLE UMIFENOVIR SALT USING SUPERCRITICAL ANTISOLVENT PRECIPITATION

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The development and creation of new dosage forms with increased bioavailability is one of the most promising development directions of modern pharmacology. This is due to the fact that their use allows minimizing the frequency of drug intake and at the same time optimizing the concentration of the active pharmaceutical component in the blood plasma. One of the best approaches to overcome the problem of low solubility without modifying the pharmacophore structure of the API is a development of new crystalline forms such as salts or co-crystals. The method of Supercritical AntiSolvent precipitation and its varieties are well suited for carrying out rapid screening of various crystallization conditions, including the search for optimal conditions of obtaining cocrystals and salts for medical purposes. It is a method of producing micro-, submicro-, and nanoparticles, in which a supercritical fluid acts as a precipitant (anti-solvent). In most cases, CO2 is used as such supercritical fluid. The SAS method has one decisive advantage over the conventional solution method for the formation of multicomponent crystals, namely, the purity of the product from contamination by organic solvents, which is of fundamental importance to the pharmaceutical industry. Umifenovir hydrochloride (PubChem CID: 9958103) (ethyl 6-bromo-4-[(dimethylamino)methyl]-5-hydroxy-1-methyl-2-(phenylsulfanylmethyl)indole-3-carboxylate hydrochloride monohydrate), the Arbidol trademark, is an antiviral drug with an immunomodulatory effect for the treatment and prevention of influenza A and B, Zika virus and many other types of respiratory diseases. The main problem arising in the treatment of viral diseases is the need for frequent drugs. Arbidol is practically insoluble in water and therefore has low bioavailability, forcing patients to take the drug at short intervals. One of the ways to solve this problem is to develop a dosage form of arbidol with higher water solubility. One of such approaches is synthesis of arbidol multicomponent crystals with other biologically active compounds.

We describe the technique for the formation of multicomponent crystal consisting of umifenovir and pharmaceutically acceptable salicylic acid. The solubility of the obtained salt and, as a result, bioavailability, is higher than in the initial umifenovir. The thermal and temporal stability of the salt was analyzed and proved using X-ray diffraction, differential scanning calorimetry, and thermogravimetric analysis.

It has been found that the obtained salt is stable at least at the time scale of our study. The solubility and bioavailability of the obtained salt is higher than that of the initial umifenovir. It has been established that when arbidol salts are obtained by the SAS method, no crystalline solvates are formed with the solvent used, in contrast to the conventional solution method for producing multicomponent crystals described in the literature earlier.

**Acknowledgements** This work was supported by the Russian Science Foundation (grant No. 22-13-00257).

# DESIGNING THE AGGREGATION WORK FOR A CYLINDRICAL MICELLE USING MINIMIZATION BY MICELLE SHAPE PARAMETERS

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The key characteristic of the thermodynamic and kinetic description of micellar systems is the minimal work of formation of aggregate with a specified aggregation number $n$ of surfactant molecules (the aggregation work) at a specified surfactant concentration in solution. The aggregation work is related to the equilibrium distribution of aggregates in aggregation numbers at given values of the bulk concentration of surfactant monomers and solution temperature. In the thermodynamics of micelle formation, the equilibrium distribution determines all equilibrium characteristics of the dispersed system, including the degree of micellization, the average aggregation number, and the dispersion of micelle aggregation numbers [1].

Despite the considerable number of works devoted to models of aggregation work for spherical micelles (see, for example, [2,3]), systems with cylindrical micelles remain poorly studied. The piecewise expression for aggregation work for cylindrical micelles used in [4] has an important weak point being just interpolating formula. A more realistic model should give a possibility of different micelle shapes at a fixed aggregation number into consideration.

We proposed here a new appropriate model in which the optimal micellar shape parameters are selected in terms of minimizing the aggregation work with respect to length of the micelle for a fixed aggregation number. The optimal curve of the aggregation work obtained in this way is shown in Figure 1. The main advantage of such a model in comparison to the piecewise model is more accurate description of the aggregation work in the transition zone from spherical to cylindrical aggregates. This is important for the analysis of micellar system relaxation spectrum.

**Acknowledgements** This work was supported by Russian Foundation for Basic Research (№ 20-03-00641a), The Euler International Mathematical Institute (agreement № 075-15-2022-287).

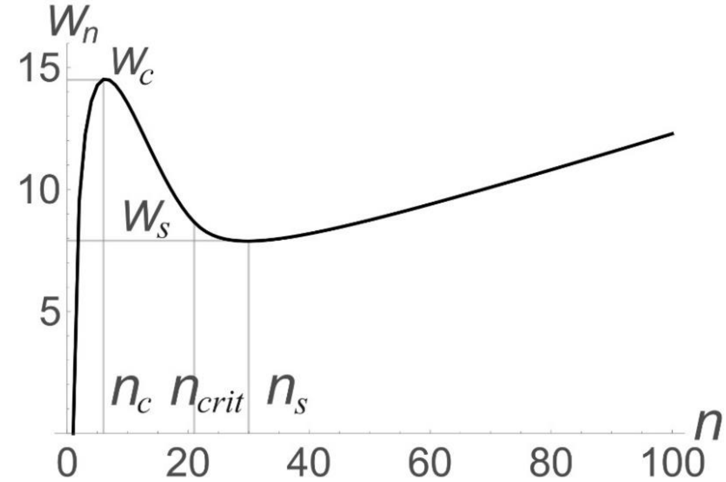

**Figure 1.** Aggregation work $W_n$ of a cylindrical micelle as a function of aggregation number $n$.

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# RADIO BRIGHTNESS CONTRASTS OF AQUEOUS SOLUTIONS OF SALTS IN THE MILLIMETER REGION OF THE SPECTRUM

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The radio-brightness characteristics of aqueous solutions of salts (1:1, 2:1 and 3:1 electrolytes) were studied using a highly sensitive radiometer at a frequency of 61.2 GHz in laboratory conditions. Different radio brightness effects (different signs of changes in radio brightness temperatures) are shown for solutions with weakly hydrating ($K^+$, $Cs^+$, $[PdCl_4]^{2-}$) and more strongly hydrating ($Li^+$, $Na^+$, $Mg^{2+}$, $Mn^{2+}$, $Al^{3+}$) ions (see Figs. 1 and 2).

Experimental characteristics are compared with calculated data from dielectric spectra. The calculated data were obtained using the Fresnel formula, which reflects the relationship of the complex permittivity ($\varepsilon^*(\nu)$) (dielectric properties) with the reflection coefficient ($R(\nu)$) (optical properties). On the example of the salt solutions considered, a good agreement of experimental and calculated radio brightness parameters is shown in the initial concentration range, where hydration changes of water in salt solutions prevail. The emission coefficients ($\chi$) associated only with dipole dielectric losses, i.e. without taking into account the ionic component of the losses, were also calculated. As can be seen from Fig. 3 (on the example of $MgCl_2$ solutions), in this case there is no correspondence between the experimental and calculated values. In the mm region, it is necessary to take into account the spectral contributions of both dipole and ion losses.

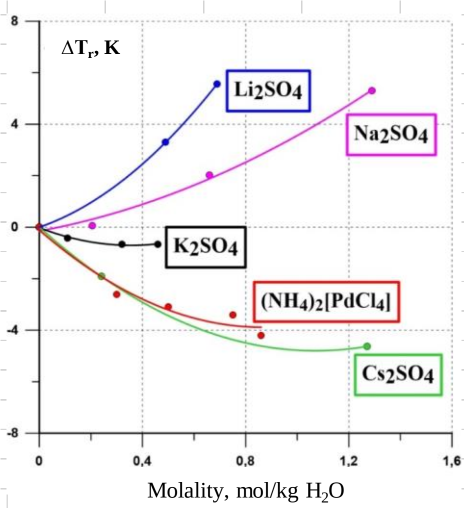

*Fig. 1. Changes in radio brightness temperatures $\Delta T = T_r(solution) - T_r(water)$, K for alkali metal sulfates and $(NH_4)_2[PdCl]_4$*

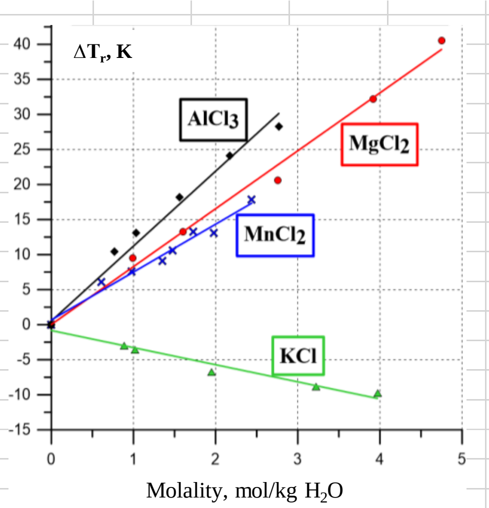

*Fig. 2. Changes in radio brightness temperatures $\Delta T = T_r(solution) - T_r(water)$, K for metal chlorides of different valence*

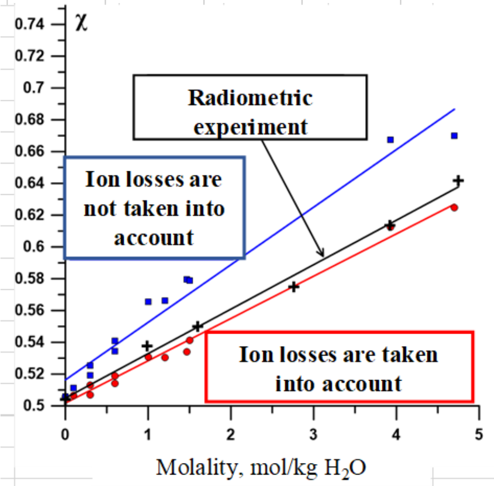

*Fig. 3. Concentration dependences of the radiation coefficient ($\chi$) for $MgCl_2$ solutions with/without ionic losses*

Radiometer signals in the mm region of the spectrum are informative for determining changes in hydration and ion dynamics. Such information can be useful in technological practice and for describing biological objects in which different effects are manifested not in pure water, but in aqueous media, where radio brightness contrasts and associated energy changes can increase.

The work was carried out within the framework of the state task of the IGIC RAS in the field of fundamental scientific research.

# INOCULATION OF ALUMINIUM POWDERS FOR ADDITIVE MANUFACTURING GUIDED BY DIFFERENTIAL FAST SCANNING CALORIMETRY

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Recent advantages in Differential Fast Scanning Calorimetry (DFSC) found their application in additive manufacturing (AM) and Laser Powder Bed Fusion (LBBF) particularly. The size of the DFSC sample – 10-20 microns in diameter – as well as temperature scanning rate range – up to 100,000 K/s – fully covers both rapid laser melting and solidification after it, and thus ideally suits for modelling.

Cold cracking is a serious issue in AM. Extensive modification of traditional materials is required in order to match the conventional production mechanical properties. The DFSC allows to prove the modification efficiency using only a few AM powder particles, and thus reducing the cost of powder production.

It was found that the particle solidification temperature and scatter has strong correlation with the results of LPBF processing of the aluminum alloys. A correlation between AM product microstructure and undercooling in FSC is presented for three variants of AA7075 alloy modification with TiC nanoparticles. The wet chemical deposition was found to provide inconsistent inoculation. Mechanical deposition showed excellent mechanical properties for LPBF and least scattered undercooling in DFSC. The newly designed deposition in the powder volume is presented and discussed. Issues in temperature measurement at different rates are discussed and solutions is provided.

# SELF-ORGANIZING SYSTEM BASED ON THE COMPLEX OF ALKYLATED DERIVATIVE OF 1,4-DIAZABICYCLO[2.2.2]OCTANE WITH PALLADIUM DICHLORIDE IN WATER-DMSO MEDIUM

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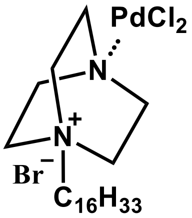
The ability of amphiphilic complexes of transition metals to self-association in aqueous, aqueous-organic, and non-aqueous media determines their practically useful properties, including catalytic and solubilization activity [1, 2]. A new amphiphilic metallocomplex based on 1-hexadecyl-4-aza-1-azoniabicyclo[2.2.2]octane bromide and palladium(II) chloride of 1:1 metal-ligand composition has been synthesized and characterized.



The process of self-association of a metallosurfactant in a water-DMSO medium (50:50%, vol) at 55 °C was studied using tensiometry, conductometry, potentiometry, dynamic and electrophoretic light scattering and spectrophotometry (solubilization of the hydrophobic dye Orange OT). The aggregation parameters of the metallocomplex were determined (the critical aggregation concentration (CAC), the degree of binding of bromide ions with aggregates, the hydrodynamic diameter of particles, the zeta potential of the self-associated system, and its solubilizing ability). The aggregation threshold of the complex in a mixed solvent is low (0.8 mM). Large, presumably, vesicular aggregates with a size of 240 nm are formed in the region of $CAC_1$. The rearrangement of the structure of supramolecular assemblies and their enlargement to 300 nm (and then to 420 nm) occurs at 2.6 mM ($CAC_2$). An increase in the zeta potential in the studied concentration range from +27 to +54 mV indicates an increasing stabilization of the system. The presence of a metallosurfactant favorably affects the solubility of the hydrophobic dye. In the region of the aggregation threshold of the complex, the content of the Orange OT dye in the solution increases by three times. The formation of aggregates of the palladium complex in the water-DMSO medium and their solubilization activity indicate the potential of using the systems under study as nanocontainers for practically useful substrates, including drugs.

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# THERMODYNAMIC PROPERTIES OF 2,2,3,3,4,4,5,5-OCTAFLUOROPENTYL ACRYLATE OVER THE RANGE FROM T → (0 TO 345) K

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Fluorine-containing monomers are used in a variety of coatings applications because of their heat and chemical resistance, weatherability, low refractive index, non-cohesiveness, water and oil repellency, and electric insulating properties. The investigation of the standard thermodynamic properties of 2,2,3,3,4,4,5,5-octafluoropentyl acrylate (OFPA) in a wide temperature range by precision calorimetry allows to determine the thermochemical parameters of polymerization processes at different temperatures as to estimate the ceiling temperature. In the present work the temperature dependence of heat capacity of OFPA in crystalline and liquid states was measured in the temperature range from $T$ = (6 to 345) K by precision adiabatic vacuum calorimetry. The standard thermodynamic quantities of fusion namely temperature, enthalpy and entropy for OFPA as the estimation of sample purity under study were obtained. Using low-temperature heat capacity data the structure topology of monomer was established as a linear–planar. From experimental data the standard thermodynamic functions of OFPA, namely, the heat capacity $C_{\mathrm{p}}^{\mathrm{o}}(T)$, enthalpy $H°(T) – H°(0)$, entropy $S°(T)$ and Gibbs energy $G°(T) – H°(0)$ have been calculated for the range from $T \to 0$ to 345 K for crystalline and liquid states. Using literature data [1] for poly-OFPA and results of present work the thermodynamic characteristics of polymerization processes have been calculated and discussed.

**Acknowledgements** By the support of the federal academic leadership program «Priority 2030» of the Ministry of Science and Higher Education of the Russian Federation.

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# THERMODYNAMIC DESCRIPTION OF HIGH-ENTROPY OXIDE PHASES WITH THE M-TYPE HEXAFERRITE STRUCTURE

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Research aimed at the creation and study of high-entropy ceramics began in 2015 [1] and is currently continuing to develop rapidly. The attention of researchers was initially attracted by simple oxide systems formed by divalent or trivalent metals. Somewhat later, works appeared devoted to the study of high-entropy systems with a more complex crystal structure. In particular, high-entropy oxides with the structure of spinel, fluorite, and perovskite were obtained. Despite the fact that research in this area began relatively recently, a number of reviews devoted to the creation and study of high-entropy ceramics have appeared to date, for example [2-3].

In the course of our work in recent years, new high-entropy oxide phases (HEO) with the M-type hexaferrites structure have been synthesized and studied [4-6]. The possibility of obtaining HEO with the M-type hexaferrites structure (general formula is $AB_{12}O_{19}$) of various compositions has been experimentally proved. The structure and properties of the obtained samples were also studied.

The aim of this work was to determine what approaches can be used for the thermodynamic description of HEO with the M-type hexaferrites structure. Also, the purpose of the work was to compile a database of thermodynamic functions describing individual substances involved in the formation of a high-entropy oxide phase of this kind. The analysis of experimental data on the process and results of the synthesis of HEO with the M-type hexaferrites structure, carried out in the course of the work, made it possible to propose the use of a two-sublattice model. In this model, the first sublattice is formed by atoms of the A type, and the second sublattice by complexes of $B_{12}O_{19}$ atoms. Within each of the sublattices, the deviation from ideality is described by the Redlich–Kister polynomials. It is proposed to consider real or hypothetically existing substances with the formula of the form $AB_{12}O_{19}$ as components of a solid solution, where A is Ba, Sr, Pb, Ca; and B – Fe, Al, In, Ga, Ti, Co, Mn, Ni, Zr, Zn, Cu, Cr. For all these substances, the values of the standard enthalpies of formation, standard entropies, and temperature dependences of the isobaric heat capacity are proposed. These values are partly borrowed from various sources, and for the most part are the result of evaluation by various semi-empirical methods.

The developed model and the proposed values of thermodynamic functions characterizing the individual components of the HEO with the M-type hexaferrite structure made it possible to form a user database within the "FactSage (version 8.0)" software package. The generated database opens up wide opportunities for further work on improving the developed model, optimizing the model parameters and thermodynamic modeling of the solid-phase synthesis of HEO with the M-type hexaferrites structure.

**Acknowledgements** The reported study was funded by RFBR according to the research project № 20-33-90113.

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# INVESTIGATIONS OF THE THERMAL PROPERTIES OF COMPOUNDS TYPES OF EuLnCuSe$_3$ (Ln=La-Lu)

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New compounds the type of EuLnCuSe$_3$ (Ln= La, Ce, Nd, Sm, Gd, Er, Ho) were first synthesized by ampoule method [1]. Compounds of similar types are increasingly attracting scientists which is due to their optical and magnetic properties [1,2]. The study of thermal properties is a very important basis for the practical application of these compounds as semiconductor materials. Previously, the results of thermal analysis were published only for some compounds EuLnCuSe$_3$ (Ln=Lanthanides) [1].

Thermal analysis was carried out on device SETARAM SETSYS Evolution, PtRh-6%–PtRh-30%. Samples weighing of 80-90 mg were put inside of quartz conical ampoule with the volume of 100 mkl, evacuated and sealed. Analysis was carried out in the conditions: heating rate 5°C/min, gas carrier – Ar, purge rate of gas is 50 ml/min. The results of DSC were handled by means of SETSOFT 2000 device.

Five compounds EuLnCuSe$_3$ (Ln=Tb, Dy, Ho, Tm, Lu) were totally studied, on basis of these and early published information [1], diagram of the thermal property changes for the whole range of compounds EuLnCuSe$_3$ (Ln=La-Lu) (pic. d) was constructed. According to the measurement data of thermal analysis of compounds EuLnCuSe$_3$ (Ln=La, Ce, Nd) solid-phase decomposes (рис. a), EuSmCuSe$_3$ melts incongruently, for compounds EuLnCuSe$_3$ (Ln=Gd, Tb, Lu) two-phase transition and incongruent melting are typical. Melting effect of compounds with Tb and Lu was barely noticed, but crystalized effects were distinctly manifested with cooling (pic. b). The compounds EuLnCuSe$_3$ (Ln=Dy, Ho, Er, Tm) manifesting three-phase transformation and melt incongruently (pic. c). Melting temperature of compounds of Dy и Tm were not discovered since maximal running temperature of thermal analysis devise is insufficient.

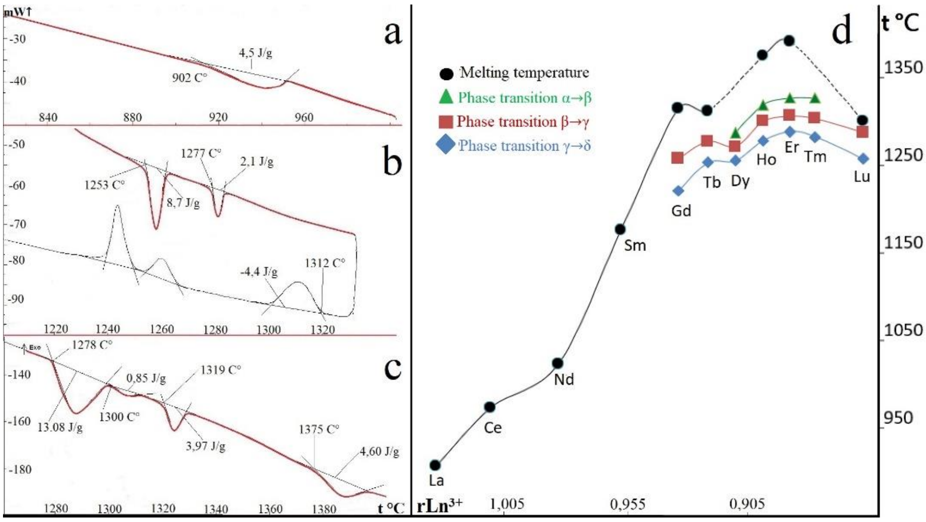

**Figure 1.** Thermograms of compounds EuLaCuSe$_3$ (a), EuTbCuSe$_3$ (b), EuHoCuSe$_3$ (c), changes of the thermal properties of compounds types of EuLnCuSe$_3$ (La-Lu) (d)

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# THERMODYNAMIC STUDY OF WATER EVAPORATION PROCESSES FROM *α*-, *β*- AND *γ*-CYCLODEXTRIN HYDRATES

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Cyclic macromolecules consisting of 6, 7, or 8 glucopyranose units, respectively are $\alpha$-, $\beta$- and $\gamma$-cyclodextrins (CDs). These units form hollow truncated cone cavity with hydrophilic exterior and hydrophobic interior, which can include a wide range of guest molecules, thereby forming various host-guest inclusion complexes. These inclusions may beneficially change of CD physicochemical characteristics such as solubility, thermal stability, volatility, resistance to oxidation, visible and UV light, etc. Because of these properties CDs are widely used in in various fields of chemistry and also in pharmaceutical, food and cosmetic industries. Since the process of complex formation is essentially a replacement reaction of water molecules located in CD cavities by hydrophobic guest molecules water plays an important role in formation of the CDs inclusion complexes. Meanwhile, quantitative data on equilibria between CDs and $H_2O$ are very scarce and contradictory, which makes it difficult to produce high-quality materials.

The purpose of this work is a comprehensive study of the $\alpha$-, $\beta$- and $\gamma$-CD hydrates dehydration processes by DSC and static method with glass membrane-gauge manometers. The measurements have been realized in the wide intervals of temperature ($313 \leq T/\text{K} \leq 506$), pressure ($1 \leq p/\text{Torr} \leq 760$) and composition ($\text{CD}^*x\text{H}_2\text{O}$, $2.6 \leq x \leq 15$). The accuracy of measurements for static setup was 0.5 Torr, 0.5 K and 0.01 formula units in the values of pressure, temperature and solid phase composition, accordingly [1].

As a result of this study thermal stability of investigated compounds was established, thermal effects of solid-phase transitions were measured, temperature dependences of pressure for dehydration processes were obtained (four types of dehydration processes were studied), enthalpies and entropies of dehydration were determined and Gibbs energy change in the process of binding water with CDs was calculated. On the base of information obtained the conclusions about the nature of the interactions between host (CDs) and water guest molecules were drown. The experimental results obtained by 2 independent methods (DSC and static) are in good agreement with each other. The main results on $\alpha$-cyclodextrin hydrates are published in [2-3].

The accumulation of quantitative information about the dehydration processes of $\alpha$-, $\beta$-, $\gamma$-CDs hydrates will allow one to synthesize functional materials with desired properties in the future.

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# IONIC MICELLE MICROENVIRONMENT AS STUDIED BY NUMERICAL SOLUTION OF POISSON EQUATION

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In various experiments micelles manifest themselves as the charged particles of dispersed phase, each composed of a core, formed by surfactant ions with a part of counterions rigidly bound to its surface. Every micelle is surrounded by a diffuse layer containing the rest of counterions. The part of diffuse layer, limited by the slipping plane, moves with the particle during its thermal diffusive motion. This slipping plane determines the micelle hydrodynamic radius $r_\zeta$, which is often considered as the micelle size. The electric potential of slipping plane, called the electrokinetic or ζ-potential of micelle, is an experimentally determined quantity. The goal of the present work is the theoretical and computational study of interconnection between the micelle spherical morphology and its hydrodynamic parameters (hydrodynamic radius and electrokinetic potential). Since there are no equations connecting these parameters, such estimation can be performed only numerically. By numerical solution of the Poisson equation for two most often used approximations, the Poisson-Boltzmann (PB) model and the Jellium-Approximation (JA) one, the electric potential decay from potential of dispersed phase particles was defined. In our calculation model we are proceeding from the fact that the slipping (shear) surface divides solution around micelle into two parts, differing in viscosity. The potential decay curves calculated by us numerically indicate the existence of two regions associated with an uneven decrease in the bulk density of counterions with increase in distance from micellar particle, when very fast potential decay turns into a very slow one. So, the enlarged counterion concentration near micelle can be associated with the increased solution viscosity and the breakpoint of decay can be correlated with the hydrodynamic radius of micelles. However, it is impossible to specify this distance only by the shape of numerically calculated decays. Therefore, we have developed a new approach which allowed us to determine this boundary distance. A new methodological approach to analyze the reaction of micelle potential decay on small variability of CMC value was proposed [1]. It made possible to determine the dimension parameter, which in presence of weak thermal effects approximately corresponds to the micelle hydrodynamic radius, and to calculate micelle electrokinetic potential. The results of theoretical calculations were compared with our previous experimental data on the thickness of the SDS micelle hydrophilic layer obtained by SAXS [2]. A good agreement between the calculated and measured values was obtained, and it was noted that for low concentrations the experimental values are more correctly described by the PB model, but for concentrations greater than 100 mM the JA model is more preferable. It was ground that the slipping plane is located near the outer Stern plane and is separated from it only by a few molecular layers of water. The influence stronger than the thermal one can shift the slipping plane closer to the micelle core. Accordingly, the smallest hydrodynamic micelle size is determined by the outer Stern plane. The results of our work allowed us to conclude that the micelle is not something soft and watery, but according to its specified structure it is a more solid-like particle than was previously assumed. The proposed approach can be extended for investigation other effects of a physicochemical nature, in particular, those observed with addition of external electrolyte or nanoparticles [3].

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# ASSOCIATIVE FORMS OF AMPHIPHILIC BLOCK COPOLYMERS AND THEIR INTERACTION WITH CARBON NANOMATERIAL

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Block copolymers, poloxamers and poloxamines, have attracted research interest due to their original thermoresponsive properties, application for drug delivery, and potential possibility to create stable suspensions of nanoparticles, primarily carbon nanotubes. The addition of carbon nanotubes to the functional materials leads to significant modulation of their association and properties. At low temperatures both poly(ethyleneoxide)-PEO and poly(propyleneoxide)-PPO blocks are hydrophilic; copolymers exist as unimers in the state of non-Gaussian coils. At 20-40°C water begin to work as a selective solvent for various blocks. The PEO blocks swell and dissolve well, while the PPO blocks, on the contrary, tend to limit the contact surface with water, folding into compact helical structures. Copolymers dispersed in water tend to aggregate and form self-associated structures, usually called micelles. We have studied the self-association/micellization properties and dispersibility of MWCNTs in aqueous solutions of amphiphilic block copolymers: the PEO-PPO-PEO poloxamers L64 and F127 and reverse-sequential poloxamine DA157 [1]. The number of NMR approaches was applied, such as self-diffusion measurements and spectral analysis including alterations of chemical shift and resonance line width. The absence of strictly defined critical micelle concentration, when micelles of constant size start forming, was found. The stepwise character of alteration of PPO methyl protons line width indicates the lowing of molecular mobility under the packing of polymers into micelles. NMR experiments allowed estimation of CMC values as 0.2-0.8 mM for F127 and 10-40 mM for L64. The obtained collection of NMR data let us to propose, that solutions of amphiphilic polymers are polydisperse in size of aggregates/micelles. The hypothesis about the two-stage nature of copolymer molecules association/micellization has been proposed. First, unimer hydrophobic blocks connect into cord-like associates/micelles and then these associates join into spherical micelles or liquid crystal domains. The cord-like curved formations with dimensions (10-12)×(2-3) nm for synperonic L64 and diproxamine DA157 and 25×(3-5) nm for Pluronic F127 coexist with unimers in a relatively wide range of temperatures and concentrations. The appearance of asymmetric aggregates at low temperatures (25–30°C) was noted also in [2]. The two-stage nature of F127 association is also confirmed by surface tension measurements. The transmission electron microscopy study of block copolymers revealed a variety of their associative forms. The interaction peculiarities of various associates for different block copolymers with multi-wall carbon nanotubes (MWNTs) from carbon nanomaterial Taunit were considered. For L64 an accumulation of polymer surfactants near MWNTs was observed not only in the form of large spherical associates, but also in the form of random and micellar networks concentrated between nanotubes. Liquid crystallin domains consisting of ordered cord-like micellar associates sizing up to 120 nm, possibly separated by water layers, were observed for F127 copolymer and diproxamin. A mechanism was proposed for interaction of X-shaped diproxamine molecules with carbon surface, which makes it possible to explain the observed NMR effects in presence of MWNTs.

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# APPLICATION OF SOLUTION CALORIMETRY METHOD FOR DETERMINATION OF VAPORIZATION AND SUBLIMATION ENTHALPIES OF CYANATE ESTERS

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Development of new promising monomers with desired properties and the study of their reactivity is one of the pressing problems. Cyanate esters can be used as monomers for thermally initiated polymerization. Such polymers can exhibit unique physical and chemical properties: plasticity, elasticity, highly efficient electrical insulation, impact resistance, high reflectivity and others [1].

It is known that the choice of solvent affects on reaction mechanism, reactivity of reagents, and reaction yield. The interaction of a solute with a solvent is described using the enthalpy of solvation ($\Delta_{\mathrm{solv}}H^{\mathrm{A}_i/\mathrm{S}}$). Experimentally, this parameter can be found from the enthalpies of vaporization/sublimation ($\Delta_{\mathrm{vap/sub}}H^{\mathrm{A}_i}$) and solution ($\Delta_{\mathrm{soln}}H^{\mathrm{A}_i/\mathrm{S}}$):

$$\Delta_{\mathrm{solv}}H^{\mathrm{A}_i/\mathrm{S}} = \Delta_{\mathrm{soln}}H^{\mathrm{A}_i/\mathrm{S}} - \Delta_{\mathrm{vap/sub}}H^{\mathrm{A}_i}$$

(1)

At the same moment, Eq.1 can be useful to obtain vaporization/sublimation enthalpies at 298.15 K from experimental solution enthalpy and calculated solvation enthalpy. It has been shown that the solution calorimetry method (Eq.1) can be useful to estimate phase transition enthalpies thermally unstable and hardly volatile compounds, as well as compounds capable of thermal polymerization [2].

In this work scheme for calculation of solvation enthalpies of cyanate esters in benzene, acetonitrile and tetrahydrofurane was proposed. It was applied for evaluation of vaporization and sublimation enthalpies of cyanatobenzene, 4-cyanato-*p*-terphenyl, 1,4-dicyanatobenzene, 4,4’-dicyanato-biphenyl and 4,4’’-dicyanato-*p*-terphenyl.

The reliability of the developed method of solution calorimetry is confirmed by the good agreement between the enthalpy of sublimation of mono- and di-cyanate esters obtained by solution calorimetry and fast scanning calorimetry.

Vapor pressure and thermodynamics of phase transition of two cyanate esters were measured by using fast scanning calorimetry and transpiration method. Vapor pressure data and enthalpies of vaporization obtained by various methods are in good agreement.

The study showed that enthalpies of phase transitions are in good agreement to each other, which allows us to recommend them for future thermochemical calculations of process with studied cyanate esters

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# PHYSICOCHEMICAL AND $NH_3$ SENSING PROPERTIES OF THIN FILMS OF LIQUID CRYSTALLINE ZINC PHTHALOCYANINES

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Metallophthalocyanines (MPcs) and their derivatives have various interesting properties that are used in such areas as optical storage, electrochromic displays, photovoltaic cells and sensing devices. Thin films of MPc are of particular interest for the active layers of chemical sensors for the detection of hazardous gases (e.g. $NO_2$, $SO_2$ $NH_3$, amines). The physicochemical and sensor properties of MPc films depend both on the molecular structure of phthalocyanines and on the structural features of their thin films, e.g. their ordering and morphology. The introduction of long alkyl substituents in the phthalocyanine ring not only increases the solubility of compounds, but also often leads to the fact that phthalocyanines begin to exhibit liquid crystalline (LC) properties. It is known that heating of the films of LC phthalocyanine at the temperature of the existence of the LC phase leads to the formation of oriented films, which in turn affects their sensor characteristics [1].

In this study, LC properties and sensor performance of thin films of a series LC zinc(II) phthalocyanines (ZnPc) were studied, among them octakis-hexylthio-substituted, tetrakis-hexylthio-substituted, octakis-(tetraoxyethylene)oxy-substituted, octakis-(trioxyethylene)thia-substituted zinc(II) phthalocyanine, tetrakis-(2-(dodecyloxy)-1-[(dodecyloxy)methyl]ethoxy)-substituted derivatives. Liquid crystalline properties of ZnPc derivatives were investigated by polarized optical microscopy, differential scanning calorimetry, and X-ray diffraction analysis. The structural features of ZnPc thin films deposited by a spin-coating technique were studied by the methods of UV-vis spectroscopy and X-ray diffraction. The chemiresistive sensor response toward low concentrations of ammonia (1-5 ppm) was studied. The correlation between liquid crystalline properties of zinc phthalocyanines, their films alignment, and sensing properties were also discussed.

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# CONFORMATIONAL MANIFOLD OF MEFENAMIC ACID IN SC-$CO_2$. COMPUTER SIMULATION

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Many of the drug compounds have a low solubility and as consequence a low bioavailability. One of the way to enhance solubility is using of polymorph with lowest energy of crystalline lattice. The use of supercritical fluids for reaching of such purpose is one of the most perspective methods. The formation of a particular polymorphic modification is determined by a series of characteristics, one of which is the conformational manifold of the compound. Mefenamic acid is a non-steroidal anti-inflammatory drug from the fenamate group, which has analgesic, anti-inflammatory and antipyretic effects and mefenamic acid is used to treat mild to moderate pain.

We studied the conformational manifold of mefenamic acid in this work. Molecular dynamics simulations of mefenamic acid in supercritical $CO_2$ at different values of the state parameters performed in this work. The simulations were carried out using two force fields (GAFF and OPLS). The conformational manifold of mefenamic acid was studied by the metadynamics method. The results of this study are discussed in the report.

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# CONFORMATIONAL MAINFOLD OF LIDOCAINE IN SC-$CO_2$. QUANTUM-CHEMICAL CALCULATIONS AND MOLECULAR DYNAMICS SIMULATIONS

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Polymorphism is crucial characteristics of drug compounds. The ability of compounds to form more than one crystalline structure leads to a diversity of physical properties like solubility, bioactivity for different polymorphs that is quite important for pharmacy. Therefore, it is necessary to understand the mechanisms of manifestation of polymorphism. One of the factors of polymorphism is the conformational mainfold of the drug compound molecule.

Lidocaine is a local anesthetic and hearty depressant. Quantum-chemical calculations of the conformers of the lidocaine molecule were carried out in this work. The calculations were performed by the DFT method with the APFD functional, including the dispersion correction and the 6-311++G(2d,2p) basis. There are several bonds in the molecule around which rotation can occur, leading to different conformers. A large number of possible conformers have been found, but not all of them can be realized due to the presence of large barriers to intramolecular rotation.

Also, within this work, the molecular dynamics simulation of lidocaine in supercritical carbon dioxide in the NPT ensemble was performed in a wide range of state parameters. The method of metadynamics was applied to study the conformational manifold of lidocaine. The results of these studies are discussed in the report.

**Acknowledgements** This work was supported by the Russian Science Foundation (grant No. 22-13-00257).

# THERMODYNAMIC MODELING OF Ni-Cr-Si-B+TiC AND Ni-Cr-Si-B+WC SYSTEMS IN A WIDE TEMPERATURE RANGE

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Nickel-based self-fluxing alloys, namely Ni-Cr-Si-B alloys, are widely used to obtain wear-resistant coatings that are applied to various parts of machines and mechanisms by methods of flame spraying, plasma spraying and surfacing. An additional increase in the operational characteristics of the surface layers is possible due to the introduction of a number of additional strengthening components (carbides, borides, intermetallides, oxides, etc.) into the surfacing materials.

The purpose of this work is thermodynamic modeling of the equilibrium composition and thermodynamic characteristics of Ni–Cr-Si-B+TiC (WC) systems in the atmosphere of various plasma-forming gases in a wide temperature range.

The investigation was carried out using the thermodynamic modeling method and the TERRA and Thermo-Calc software packages. The simulation was carried out in the temperature range of 300 – 6000 K at a total pressure of P=105 Pa in the atmosphere of a plasma-forming gas. As the plasma-forming gases argon, nitrogen, air, the mixtures "air + propane" and "air + methane" were considered. The initial composition of the simulated system corresponded to the composition of the powder self-fluxing material PGSR-2 based on nickel (wt.%): Ni - 79.3, C - 0.5, Cr - 15, Si - 3.2, B – 2 with additions of carbides of tungsten (WC) and titanium (TiC). The content of additives in relation to PGSP-2 varied from 0 to 30 wt. %. When preparing the initial data for modeling, the averaged technological parameters of the plasma spraying unit were taken into account: the plasma–forming gas consumption was 1 l/s, the powder consumption was 1 g/s, 5 g/s and 10 g/s.

The temperature dependences of the equilibrium composition and integral thermodynamic characteristics (enthalpy, entropy and Gibbs energy) are calculated. It is shown that the change in the initial content of the powder material, the percentages of PGSR-2 : WC (TiC) and the composition of the plasma-forming gas has a significant effect on the distribution of the components of the condensed and gas phases and the values of the thermodynamic characteristics of the systems under study.

The obtained results allow us to estimate the composition of the condensed phase formed during equilibrium heating of the studied systems, to predict the behavior of materials under extreme conditions.

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# DEVELOPMENT OF SCHEME OF CALCULATION OF PHASE TRANSITION AND SOLUTION ENTHALPIES OF ANISOLES WITH INTRAMOLECULAR HYDROGEN BONDS

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The enthalpies of vaporization and sublimation are the fundamental quantities necessary to characterize the energetics of the "liquid-steam" equilibrium. Research in the field of thermochemistry of phase transition processes is necessary for the implementation of industrial separation of substances, the prediction of the solubility of pharmaceuticals and the volatility of chemical reagents.

In this research, we propose a method of evaluation of the phase transition and solution enthalpies of anisoles. These compounds are used as precursors in the production of drugs, preservatives, flavors, solvents and reagents for organic synthesis. Many important parameters, such as boiling and melting points, vapor pressure, solubility and biological activity of chemical compounds depend on the number and position of functional groups.

The transpiration method was used as the classical method for measuring the enthalpies of vaporization and sublimation of substituted anisoles at 298.15 K [1]. The enthalpy of fusion and melting point of 1,3,5-trimethoxybenzene and 4-nitroanisole were measured using differential scanning calorimeter. The thermal effect of solution was measured by solution calorimeter. The experimental procedures were verified by measuring the enthalpy of solution of propanol-1 in water. The average value of the enthalpy of solution measured in 5 experiments was in good agreement with the recommended value.[2] Comparison of data of the enthalpy of phase transition of anisoles at 298.15 K obtained by transpiration method and solution calorimetry showed that the obtained values are in good agreement to each other.

In this work, we developed method for calculating the enthalpy of phase transition and solution of anisoles capable of forming intramolecular hydrogen bonds. New data of anisoles phase transition were obtained at 298.15 K, which were successfully checked for mutual consistency.

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# THEORETICAL STUDY OF THE POLYMERIZED IONIC LIQUIDS AT CHARGED ELECTRODE

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The discovery of polymerized ionic liquids (PILs) led to a number of electrochemical applications, where they can be used either as an alternative to the monomeric ILs or in combination with them to achieve necessary mechanical and thermal properties. Such modifications are the basis for the development of PIL-based gel and solid-state electrolytes, proton exchange membranes and supercapacitors. Nevertheless, theoretical investigation of the electrochemical properties of PILs near the charged electrodes similar to those existing for the monomeric ionic liquids is practically absent in literature. We developed [1] a self-consistent field theory of PIL on a charged electrode. We applied Lifshitz theory to describe the conformation entropy of polymerized cations and took into account the electrostatic and excluded volume interactions of ionic species within the asymmetric lattice gas model. Such a model led to a system of self-consistent field equations for the local electrostatic potential and average concentrations of monomers and counterions. By solving them in the linear approximation, we have derived a new analytical expression for the linear differential capacitance of the electric double layer, which depends on the molecular parameters of the polymerized cations, in contrast to the similar formula for monomeric ionic liquids, previously proposed by Kornyshev [2]. Numerical solution of the equations with two boundary conditions corresponding to different cases of the surface-monomers interactions, allowed us to analyze the behavior of differential capacitance as a function of the applied voltage. For the case of the indifferent surface and pure PIL we obtained a bell-shaped capacitance profile, resembling the monomeric IL's one, which decreases with the same power law at rather high voltages. For the same boundary condition and the case of the PIL solution we discovered a strongly asymmetric camel-shaped capacitance profile with a rather high peak at negative voltages compared to the one predicted for the monomeric ILs. In the case of the hard-wall boundary condition describing the strong short-range repulsion between the surface and the monomers, the pure PIL demonstrated the asymmetric camel-shaped capacitance profile, which strongly differs from the one obtained for the indifferent surface boundary condition. The behavior of each capacitance profile is analyzed on the basis of the local monomers and anions concentrations as a function of the potential drop. The proposed theoretical model can potentially be extended to take into account the size asymmetry of the ions and monomers, include short-range specific interactions, static polarizabilities or the permanent dipole moments of the monomers.

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# CLASSICAL DENSITY FUNCTIONAL ASSISTED COMPUTATION OF SUPERCRITICAL FLUID CROSSOVER REGION

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As it is known from literature, the investigation of the solids' solubility in supercritical fluid leads to an observation of interesting behavior: solubility isotherms intersect at two points at the so-called lower and upper crossover pressures. Phenomenologically it is understood that in these points the opposing influence of the solute sublimation and solvent density on the solubility compensate each other. Thus, in the area between the lower and upper crossover pressures solubility decreases with the isobaric temperature increase, because the solvent density effect prevails over the solute sublimation one. And below lower and above upper crossover pressures the dependence of solubility on temperature is direct. The knowledge of the shape and location of this area is essential part of the successful design and utilization of supercritical procedures. Despite the fact that it is accepted that isotherms intersect in single point, careful examination of the experimental data may convince one that the location of the observable in practice upper crossover pressure is smeared to a certain extent, especially when investigation is conducted in a wide temperature range. To investigate this phenomenon theoretically we calculated the solubility of a number of compounds in $scCO_2$ via the approach, based on the application of the classical density functional theory. We located the corresponding crossover areas and discovered that their forms differ from the expected ones [1]. The lower and upper crossover pressure points move with the change in temperature and tend to a limiting pressure value at certain temperature.

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# ENTALPIES OF 1-ETHYL- AND 1-BUTHYL-3-METHYLIMIDAZOLIUM ACETATES FORMATION AND VAPOURIZATION

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Ionic liquids have several distinguished properties superior to those of traditional organic solvents such as low vapor pressure, nonflammability, large liquidus range, high solvating capacity. Among all kinds of ionic liquids, acetic acid ionic liquids with the characteristics of strong solubility and good catalytic property have attracted considerable attention from both academic community and industry. They can be used for enzyme-friendly co-solvent for resolution of amino acids, cellulose dissolution and so on. The objects of the present study are two ionic liquids 1-ethyl-3-methylimidazolium acetate [$C_2$MIm][OAc] and 1-butyl-3-methylimidazolium acetate [$C_4$MIm][OAc].

In literature information on thermochemical properties of [$C_2$MIm][OAc] and [$C_4$MIm][OAc] are fragmentary presented. It is known that these substances do not crystallize upon cooling, but have a glass transition about 200 K [1]. The authors [1, 2] studied the heat capacity of the compounds in the glass and liquid states. Data on the enthalpies of [$C_2$MIm][OAc] and [$C_4$MIm][OAc] formation and vaporization could not be found in the literature. The aim of the present work is determination of thermochemical properties of these ionic liquids: standard enthalpies of formation in the liquid and gaseous state and enthalpies of vaporization at 298.15 K.

In the present study commercial reagents of ionic liquids manufactured by «Sigma-Aldrich» with initial purity 98.3 weight % and 97.6 weight % for [$C_2$MIm][OAc] and [$C_4$MIm][OAc] correspondingly, were investigated. Before experiments samples were dried under vacuum for constant weight. The purity of the ionic liquids was confirmed by elemental (C, H, N, O, Br) and 1H NMR analysis.The enthalpy of solution of ionic liquids were measured in water at 298.15 K by calorimeter 6755 Parr Instrument Company. The enthalpies of [$C_2$MIm][OAc] and [$C_4$MIm][OAc] formation in the liquid state at 298.15 K were determined by Hess law on the basis of the experimental data and [$C_2$MIm]$^+$, [$C_4$MIm]$^+$(aq) [3] and ][OAc]$^-$(aq) [4] enthalpies of formation. The gas phase enthalpies of formation of [$C_2$MIm][OAc] and [$C_4$MIm][OAc] were calculated assuming the existence of these ionic liquids in the vapor in the form of ion pairs. The conformational analysis was performed by considering the possible structures of the [$C_2$MIm]$^+$ and [$C_4$MIm]$^+$ cations and taking into account the different arrangement of the [OAc]$^-$ anion around them. The B3LYP-D3(BJ)/def2-TZVPP method was used to optimize the geometry and calculate the oscillation frequencies. Based on the calculated vibration frequencies, the correction for zero vibrations and the thermal correction were estimated. The energy of the most stable conformers [C2MIm][OAc] and [C4MIm][OAc] was calculated by the DLPNO-CCSD(T1)/CBS method. The theoretical values of the gas phase enthalpies of formation of [C2MIm][OAc] and [C4MIm][OAc and the experimental values for liquid compounds were used to estimate their enthalpies of vaporization.

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# PHASE EQUILIBRIA IN THE DI-(2-ETHYLHEXYL)PHOSPHORIC ACID – TOLUENE (*N*-DODECANE, *N*-HEPTANE) – DI-(2-ETHYLHEXYL) SAMARIUM PHOSPHATE (EUROPIUM, GADOLINIUM) SYSTEMS

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Di-(2-ethylhexyl)phosphoric acid (D2EHPA) with different diluents is a promising extraction reagent for the separation of rare earth elements (REE). The extraction process can be complicated by the appearance of a third phase, which one is a solid complexes – di-(2-ethylhexyl) phosphates ($[Ln(C_{16}H_{34}PO_4)_3]$, $LnA_3$). To implement and optimize the extraction process in industry, a thermodynamic model of multicomponent system should be constructed. For such model parametrization experimental data on the thermodynamic properties and phase equilibria in the organic phase are required.

Phase equilibria in systems D2EHPA – organic diluent (*o*-xylene) – $LnA_3$ (Ln = Sm, Eu, Gd) and in their binary subsystems are presented in paper [1]. Data on the volume properties of the systems $LnA_3$ (Ln = Sm, Eu, Gd) – D2EHPA – solvent (toluene, n-heptane, n-hexane) at different temperatures are given in paper [1].

**The purpose** of this work is to obtain experimental data on phase equilibria in the $LnA_3$ (Ln = Sm, Eu, Gd) – D2EHPA – diluent (toluene, *n*-heptane, *n*-dodecane) systems at 298.15 K.

The complex ($LnA_3$) was synthesized from $Ln(NO_3)_3$ in acetone solution and di-(2-ethylhexyl)phosphoric acid sodium salt (NaL). Elemental analysis, X-ray powder diffraction (XRD), infrared spectroscopy (FTIR), thermal analysis was used to identify the product.

The solubility of REE di-(2-ethylhexyl)phosphates in mixed diluents (D2EHPA – toluene, *n*-dodecane, *n*-heptane*)* was determined at 298.15±0.5 K. Accurate weights of the of $LnA_3$, solvent, and D2EHPA were placed in glass containers with lids and these mixes were kept to until equilibrium with constant stirring. The concentration of the rare earth element in the equilibrium compositions was found using multistage re-extraction of the lanthanide from the organic into the aqueous phase. The resulting aqueous solutions were analyzed by inductively coupled plasma mass spectrometry (ICP-MS). The composition of the organic equilibrium solutions was refined using ICP-MS data (REE content) and dependences of solution density on composition obtained in our early work [2].

In this work it was shown, the solubilities of the $LnA_3$ complexes (Ln = Sm, Eu, Gd) in mixed diluents (D2EHPA – toluene, *n*-dodecane, *n*-heptane) are within the experimental error in the region of dilute solutions and differ significantly in the region with more high content of complexes. The highest solubility of all studied complexes ($LnA_3$) in a mixed solvent is observed in systems with *n*-heptane.

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# ASSIGNMENT OF THE ENAMEL INSULATION GLASS TRANSITION TEMPERATURE BY DSC

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During optimization of curing conditions for polyesterimide enamel PL-955, used in PEEA-155 enameled wire with aluminum core, we've faced with the problem of laboratory determining the enamel curing degree [1]. We suggested to perform such a control by DSC, measuring the glass transition temperature. Unfortunately, enamel on the wire surface is poor object for investigation by DSC method: enamel mass is minor in comparison with metal mass, cylindrical form of the wire doesn't allow to provide good thermal contact between enamel and crucible bottom. This task couldn't be solved by means of one-furnace heat-flux DSC with heating rate 50 °C/min at the most. But it could be solved by means of two-furnace power-compensation DSC 8500 (Perkin Elmer) with accuracy of calorimetric measurement <±0,2% and repeatability of calorimetric measurement <±0,03% with heating rates up to 750 °C/min.

We've started from determining the temperature range of enameled wire constant weight using the TGA method with air medium. Enameled wire kept constant weight up to 270°C. Performing the DSC experiments we used the following range of heating rates: 20, 50, 100, 200 и 300 °C/min. As expected it was impossible to find out the glass transition of polyesterimide enamel PL-955 in the experiment with heating rate of 20 °C/min. Glass transition became more prominent with increasing of heating rate and it could be detected reliably at heating rate 100 °C/min and higher – see Figure 1. Further increasing of heating rate results in small expansion of transition width and noticeable drift of transition in the high-temperature region: from 154°C (for 50 и 100 K/min) to 168°C (for 300 K/min).

Thus the heating rate 100 °C/min was selected for determination of PEEA-155 wire enamel glass transition temperature by the DSC method. We also proved functionality of the test in the range of sample masses from 4 to 20 mg while working with enameled wire diameter from 0.10 to 0.45 mm.

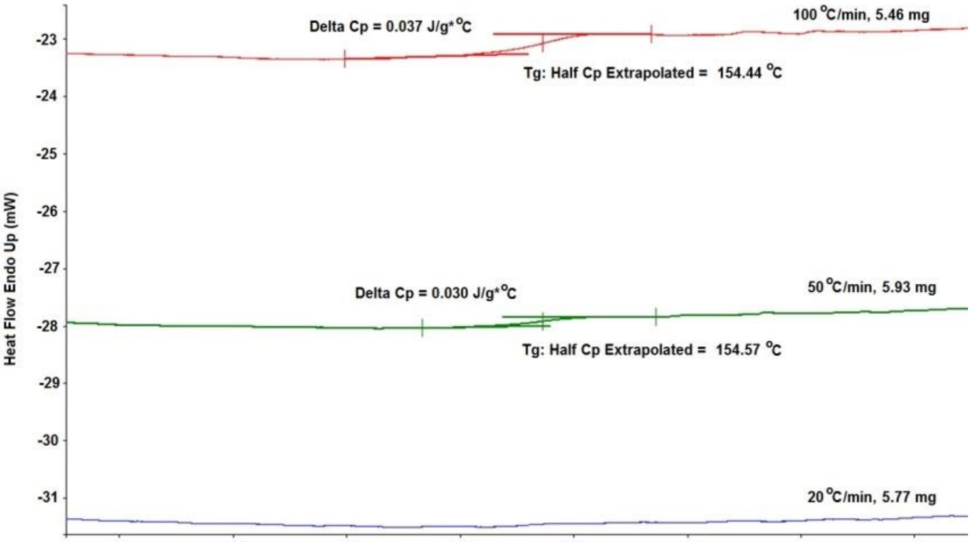

Figure 1 – Thermograms of second heating of PEEA-155 wire
with heating rates of 20, 50 and 100 C/min

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# ТЕПЛОЕМКОСТЬ И ТЕРМОДИНАМИЧЕСКИЕ ФУНКЦИИ НАНОСТРУКТУРИРОВАННОГО МЕДНО-ЦИНКОВОГО МАНГАНИТА $LaK_2CuZnMnO_6$ В ИНТЕРВАЛЕ 298,15-673 К

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Большой интерес в последнее время у ученых вызывают синтез и исследование физико-химических свойств манганитов редкоземельных элементов, допированных оксидами s- и d- элементов, в связи с их уникальными физико-химическими свойствами [1-3]. На основании вышеизложенного, нами методом высокотемпературного отжига из $La_2O_3$, CuO, ZnO, $Mn_2O_3$ и $K_2CO_3$ в интервале 800-1200 °С синтезирован поликристаллический медно-цинковый манганит состава $LaK_2CuZnMnO_6$, из которого измельчением на вибрационной мельнице получены его наноструктурированные частицы, кристаллизующие в кубической сингонии [4].

Далее на калориметре ИТС-400 в интервале 298,15-673 К исследованы температурные зависимости теплоемкости $LaK_2CuZnMnO_6$. На основании полученных опытных данных установлено, что зависимость $C_p° \sim f(T)$ описывается следующим уравнением [Дж/(моль · К)]:

$$C_p° = (402 \pm 25) + (357{,}6 \pm 22{,}2)\cdot 10^{-3}T - (212{,}9 \pm 1{,}3)\cdot 10^{5}T^{-2}. \qquad (1)$$

С учетом опытных данных по $C_p°(T)$ и расчетного значения S°(298,15), вычисленного по методу ионных инкрементов [5], рассчитаны температурные зависимости $C_p°(T)$ и термодинамические функции (таблица).

Исследование финансируется Комитетом науки Министерства образования и науки Республики Казахстан (грант № ИРН AP08855601).

**Таблица.** Термодинамические характеристики $LaK_2CuZnMnO_6$ [$C_p°(T)$, S°(T), $Ф^{xx}(T)$, Дж/(моль · К); H°(T)-H°(298,15), Дж/моль]

| T, K | $C_p°(T)$ | S°(T) | H°(T)-H°(298,15) | $Ф^{xx}(T)$ |
|---|---|---|---|---|
| 298,15 | 269 ± 17 | 310 ± 9 | - | 310 ± 29 |
| 300 | 272 ± 17 | 312 ± 29 | 540 ± 30 | 310 ± 29 |
| 350 | 353 ± 22 | 361 ± 33 | 16300 ± 1010 | 314 ± 29 |
| 400 | 412 ± 26 | 412 ± 38 | 35490 ± 2200 | 323 ± 30 |
| 450 | 457 ± 28 | 463 ± 43 | 57260 ± 3560 | 336 ± 31 |
| 500 | 495 ± 31 | 513 ± 47 | 81110 ± 5040 | 351 ± 32 |
| 550 | 528 ± 33 | 562 ± 52 | 106720 ± 6630 | 368 ± 34 |
| 600 | 557 ± 35 | 609 ± 56 | 133860 ± 8310 | 386 ± 36 |
| 650 | 584 ± 36 | 655 ± 60 | 162390 ± 10080 | 405 ± 37 |
| 675 | 596 ± 37 | 677 ± 62 | 177140 ± 11000 | 415 ± 38 |

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# ТЕПЛОЕМКОСТЬ ТИТАНО-МАНГАНИТА ЛАНТАНА И МАГНИЯ $LaMgTiMnO_6$ В ИНТЕРВАЛЕ 298,15-673 К

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Открытие эффекта гигантского и колоссального магнитного сопротивления в манганитах типа $La(Ca, Ba)MnO_3$ со структурой перовскита послужило началом работ в области синтеза и исследования новых, ранее не известных соединений [1]. Также соединения на основе оксида титана $TiO_2$ обладают уникальными физико-химическими свойствами [2]. В связи с этим для объединения соединений, обладающих с уникальными свойствами в единую фазу нами методом керамической технологии синтезирован кубический титано-манганит состава $LaMgTiMnO_6$ из $La_2O_3$, $MgCO_3$, $TiO_2$ и $Mn_2O_3$ со следующими параметрами решетки: $a = 13{,}58 \pm 0{,}02$ Å; $V^0 = 2504{,}0 \pm 0{,}06$ Å$^3$; $Z = 4$; $V°_{эл.яч} = 626{,}00 \pm 0{,}02$ Å$^3$; $\rho_{рент.} = 4{,}02$ г/см$^3$; $\rho_{пикн.} = 4{,}01 \pm 0{,}01$ г/см$^3$;

Методом динамической калориметрии в интервале 298,15-673 К на калориметре ИТС-400 измерены изобарные теплоемкости синтезированного $LaMgTiMnO_6$ (таблица).

На основании результатов исследований установлено, что наблюдается резкое падение теплоемкости при 323 К, затем появляется аномальный пик при 423 К с дальнейшим понижением $C_p°$ при 473 К и повышением теплоемкости до 673 К. Все эти аномальные скачки теплоемкости, вероятно связаны с фазовыми переходами II-рода. С учетом температур фазовых переходов выведены уравнения температурной зависимости теплоемкости $LaMgTiMnO_6$.

На основании полученных экспериментальных данных по $C_p°(T)$ и расчетного значения $S°(298{,}15)$ $LaMgTiMnO_6$ вычислены температурные зависимости термодинамических функций $S°(T)$, $H°(298{,}15)$-$H°(T)$ и $\Phi^{xx}(T)$.

Работа проведена в рамках программно-целевого финансирования НТП «Создание новых композиционных материалов с высокими эксплуатационными свойствами на основе редких и редкоземельных элементов» Комитета индустриального развития Министерства индустрии и инфраструктурного развития Республики Казахстан.

**Таблица.** Опытные значения теплоемкости $LaMgTiMnO_6$ [$C_p \pm \bar{\delta}$, Дж/г·К; $C_p° \pm \overset{o}{\Delta}$, Дж/(моль·К)]

| T, K | $C_p \pm \bar{\delta}$ | $C_p° \pm \overset{o}{\Delta}$ | T, K | $C_p \pm \bar{\delta}$ | $C_p° \pm \overset{o}{\Delta}$ |
|---|---|---|---|---|---|
| 298,15 | 0,5432 ± 0,0130 | 197 ± 13 | 498 | 0,8141 ± 0,0209 | 295 ± 21 |
| 323 | 0,4827 ± 0,0070 | 175 ± 7 | 523 | 0,9055 ± 0,0171 | 328 ± 17 |
| 348 | 0,6017 ± 0,0073 | 218 ± 7 | 548 | 0,9972 ± 0,0143 | 361 ± 14 |
| 373 | 0,6484 ± 0,0095 | 235 ± 10 | 573 | 1,0411 ± 0,0232 | 377 ± 23 |
| 398 | 0,7802 ± 0,0174 | 282 ± 17 | 598 | 1,0605 ± 0,0168 | 384 ± 17 |
| 423 | 0,8642 ± 0,0132 | 313 ± 13 | 623 | 1,1022 ± 0,0220 | 399 ± 22 |
| 448 | 0,7746 ± 0,0175 | 280 ± 18 | 648 | 1,1501 ± 0,0180 | 416 ± 18 |
| 473 | 0,7015 ± 0,0139 | 254 ± 14 | 673 | 1,1818 ± 0,0192 | 428 ± 19 |

Примечание: $\bar{\delta}$ – среднеквадратичное отклонение для удельной теплоемкости, $\overset{o}{\Delta}$ – случайная составляющая погрешности для мольной теплоемкости.

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# THE VAPORIZATION OF SOME d-ELEMENTS PERFLUOROBENZOATES ACCORDING TO HIGH-TEMPERATURE MASS SPECTROMETRY DATA

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The vaporization of two d elements perfluorobenzoates - silver and zinc - was studied by the Knudsen effusion method with the mass spectral analysis of the gas phase. Being coordinately unsaturated both studied compounds contained additional ligands: perfluorobenzoic acid for silver, water and pyridine for zinc, so the initial complexes were $[C_6F_5COOAg\cdot 0.5C_6F_5COOH]$ and $[Zn(H_2O)_{0.5}(C_6F_5COO)_2(Py)_2]$. It was found that their vaporization starts the same way by the elimination of solvates with removing acid in one step for silver (1) and sequential elimination of pyridine (2) and partial hydrolysis (3) for zinc:

$C_6F_5COOAg\cdot 0.5C_6F_5COOH\ (s) \rightarrow C_6F_5COOAg(s) + 0.5C_6F_5COOH\ (g)$, T=375 K (1)
$[Zn(H_2O)_{0.5}(C_6F_5COO)_2(Py)_2]\ (s) \rightarrow Zn(C_6F_5COO)_2\cdot 0.5H_2O(s) + 2\ Py(g)$, T=273 K (2)
$4[Zn(C_6F_5COO)_2\cdot 0.5H_2O](s) \rightarrow 3\ Zn(C_6F_5COO)_2(s) + Zn(OH)_2(s) + 2C_6F_5COOH(g)$, T=446 K (3)

The following stage is significantly different. $C_6F_5COOAg$ at the temperature of 425 K thermally decomposes with the formation of crystalline silver and the transition to the gas phase of molecules of perfluorobiphenyl $C_{12}F_{10}$ and carbon dioxide $CO_2$, whereas zinc perfluorobenzoate sublimates congruent with the formation of free $Zn(C_6F_5)_2$ and $CO_2$ molecules.

$C_6F_5COOAg(s) = Ag(s) + 0.5\ C_{12}F_{10}(g) + CO_2(g)$ (4)
$Zn(C_6F_5COO)_2(s) \rightarrow Zn(C_6F_5)_2(g) + 2\ CO_2\ (g)$ (5)

The decomposition (4) is characteristic of almost all silver compounds, which is associated with a low metal–ligand binding energy. As expected, the decomposition of the zinc complex (5) is accompanied by the formation of zinc pentafluorodiphenyl, for which the metal–ligand bond energy is much higher than for silver complexes.

The absolute values of the partial pressures of the molecules (Table 1) were calculated. The standard enthalpies of sublimation of the components of the saturated vapor were determined by analyzing the temperature dependencies of the ion current intensities according to the Clausius–Clapeyron equation by the least-squares method and were equal to $\Delta_rH°_T(4) = 154.2\pm19.6$ kJ/mol (T=375-405K), $\Delta_rH°_T(5) = 424.5\pm11.3$ kJ/mol (T=450-520K).

Using the 2nd and 3rd laws of thermodynamics, the standard enthalpy of formation of silver perfluorobenzoate was found to be $\Delta_fH°_{298}(C_6F_5COOAg,\ sol) = -1195.6 \pm 15.7$ kJ/mol, the standard enthalpy of formation of the pentafluorobenzoic acid radical was estimated to be $\Delta_fH°_{298}(C_6F_5COO\bullet,\ sol) = -878.6 \pm 25.0$ kJ/mol, the standard enthalpies of formation of zinc perfluorobenzoate was estimated to be $\Delta_fH°_{298}(Zn(C_6F_5COO)_2,\ sol) \leq -2634.1\pm32.2$ kJ/mol, $\Delta_fH°_{298}(Zn(C_6F_5)_2,\ g) \leq -1422.6\pm31.3$ kJ/mol.

Table 1. Absolute values of partial pressures of saturated vapor components [Pa].

| Condensed phase | T,K | Condition of the evaporation | $P_{Zn(C6F5)2}$ | $P_{C12F10}$ | $P_{CO2}$ |
|---|---|---|---|---|---|
| $C_6F_5COOAg$ | 425 | Knudsen<br>closed cavity | - | $9.4\times10^{-2}$<br>$9.5\times10^{-2}$ | $6.8\times10^{-2}$<br>$4.8\times10^{-2}$ |
| $Zn(C_6F_5COO)_2$ | 503 | Knudsen<br>closed cavity | $3.2\times10^{-2}$<br>$1.2\times10^{-2}$ | - | $5.1\times10^{-2}$<br>$4.2\times10^{-2}$ |

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# THERMODYNAMICS CHARACTERISTICS
# OF ALKALI PIVALATES

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The thermodynamic properties of alkali metal pivalates $(CH_3)_3CCOOM$, where M= K, Na, Rb, Cs, have been studied by mass spectrometry, thermogravimetry, and differential scanning calorimetry. Thermogravimetric studies were carried out on a NETZSCH TG 209 F1 thermobalance with a heating rate of 10 K/min in a dynamic nitrogen atmosphere. DSC studies were carried out on a DSC 200 F3 Maya differential scanning calorimeter manufactured by NETZSCH. The vaporization was studied by the Knudsen effusion method with the mass spectral analysis of the gas phase. Molybdenum Knudsen cells with a ratio of vaporization surface area to effusion surface area of ~600 were used. A detailed description of the procedure and device is available in the literature [1].

According to thermogravimetry and DSC data were shown the decomposition of all compounds proceeds in two stages: after the initial dehydration, the decomposition of the pivalates follows. The heats of fusion are determined: NaPiv – 629K, KPiv – 613K, RbPiv – 592K, CsPiv – 618K.

Gas phase of investigated pivalates has complicated character and consists of polynuclear molecules $(MPiv)_n$ (n=1-6) with dominated by $(MPiv)_2$, $(MPiv)_4$ molecules for sodium and potassium pivalates and (MPiv), $(MPiv)_2$ molecules for rubidium and cesium pivalates. The absolute values of the partial pressures of the molecules and their dependence on temperature were calculated (Table 1). The standard enthalpies of sublimation of the main components of the saturated vapor were determined (Table 2). The complex composition of the gas phase over potassium pivalate and the double interpretation of the mass spectrum lead to increasing error in the enthalpy of sublimation of monomer molecules.

Table 1. Absolute values of partial pressures of saturated vapor components [Pa].

| | Na (T=584K) | K (T=565K) | Rb (T=565K) | Cs (T=565K) |
|---|---|---|---|---|
| MPiv | $5\cdot10^{-5*}$ | $1.6\ 10^{-2}$ | $2.8\ 10^{-2}$ | $1.1\ 10^{-1}$ |
| $M_2Piv_2$ | $3,2\cdot10^{-2}$ | $1.4\cdot10^{-2}$ | $1.0\ 10^{-2}$ | $3.1\ 10^{-2}$ |
| $M_4Piv_4$ | $4.9\cdot10^{-3}$ | $3.9\cdot10^{-3}$ | $4.9\ 10^{-4\,*}$ | $3.0\ 10^{-4\,*}$ |

$^*$ estimate

Table 2. Values of enthalpies of sublimation of saturated vapor components in the temperature range 500–585 K [kJ/mol].

| | Na | K | Rb | Cs |
|---|---|---|---|---|
| MPiv | 204.3 ± 3.4 | 192 ± 21 | 165.6 ± 8.9 | 158.6 ± 4.4 |
| $M_2Piv_2$ | 197.8 ± 2.8 | 190.7 ± 7.0 | 168.6 ± 5.2 | 179.2 ± 7.7 |
| $M_4Piv_4$ | 239.7 ± 6.7 | 228.9 ± 5.0 | 164.0 ± 4.1 | 192.4 ± 7.2 |

The thermodynamic characteristics of alkali metals' pivalates allow us to recommend them as precursors in CVD method for obtaining thin films.

**Acknowledgements** This work was supported under a state assignment for basic scientific research for the Kurnakov Institute of General and Inorganic Chemistry.

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# PENETRATION OF THE ANTITUMOUR DRUG DIOXADET THROUGH A LIPID BILAYER: A MOLECULAR DYNAMICS STUDY

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Dioxadet is a drug developed at the Petrov Research Institute of Oncology in St Petersburg, which has undergone all clinical trials and is used in chemotherapy for ovarian, colorectal and liver cancer. The aim of this study is to reveal the mechanism of dioxadet penetration through the cell membrane using the molecular dynamics method.

Previously, several models of dioxadet were created and their ability to dissolve in water was analyzed. Dioxadet was shown to be readily soluble in water and to form associates. In this work, we first performed the classical molecular dynamics simulations of a dioxadet molecule together with DOPC and DSPC lipid membranes in water for two dioxadet models, ATB and B3LYP, at temperatures of 323, 310 and 300 K. In all cases, the drug molecule spontaneously settled on the membrane, being initially in bulk water, and then remained in contact with the membrane for hundreds of ns. For temperatures of 323 and 310 K with the DOPC membrane, the dioxadet molecule dipped inside the membrane below its surface.

To estimate the probability of the drug molecule to penetrate through the membrane, the Gibbs free energy transfer profiles of the dioxadet molecule through the DOPC membrane at different temperatures of 300, 305 and 310 K were calculated. Also the effect of adding a second dioxadet molecule to the membrane was studied. The calculation result, namely, a negative sign of $\Delta G$ in the membrane indicates a preference for dioxadet to be inside the membrane; also in the midplane of the membrane there is an energy barrier whose height depends on the temperature. From the temperature dependence the entropic and enthalpic contributions to the free energy were obtained. The position of the dioxadet in the membrane is entropically disadvantageous, but overall it is advantageous due to the enthalpy gain. Probably, this is due to the rather large charges on the atoms of the aromatic ring of dioxadet and the corresponding Coulomb interaction with polar heads of lipids. The data set for the umbrella sampling technique also allowed us to calculate the diffusion coefficient profile in the way we described and tried out in [1, 2] as well as the resistivity profile. In the process of permeation of the studied molecule, the highest resistance is found on the membrane surface at the entrance and exit of the membrane. Membrane permeability for the studied molecule is $P = (0.6 \pm 0.1)\cdot 10^{-3}$cm/s at T=300 K. The presence of a second drug molecule inside the membrane almost doubles the permeability by reducing the resistance of the membrane surface.

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# STUDY OF THERMOCHEMICAL PROPERTIES OF VOLATILE PALLADIUM PRECURSORS AND METAL PHTHALOCYANINES IN ORDER TO PREPARE THEIR HETEROSTRUCTURES

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Metal phthalocyanines (MPc) are among the most demanded sensor materials that attract the attention of researchers because of their ability to exhibit a chemiresistive sensor response via changing conductivity in the presence of various gases at room temperature with a recovery time of no more than a few minutes, as well as because of their high thermal and chemical stability compared to most organic materials [1]. Noble metal nanoparticles (NP) and nanostructures are known to be widely used to improve the performance of chemiresistive sensors for the detection of various gases. Recent reports highlighted the advantages of sensors based on heterostuctures (MPc/NP) for the detection of such gases as $NH_3$, $H_2$, $H_2S$, and NOx due to the synergistic effect of their components [2].

The advantages of using gas-phase methods for the deposition of phthalocyanines or metal layers and nanoparticles on the surface of organic semiconductors to create sensing layers with good sensor performance have been shown [3]. The methods of metal-organic chemical vapor deposition (MOCVD) and physical vapor deposition (PVD) for the preparation of hybrid materials open up new possibilities for the creation of sensors with the desired characteristics. The properties of the deposited coatings are significantly affected by the physicochemical properties of the precursors, such as a noticeable saturation vapor pressure at relatively low temperatures (volatility), thermal stability, and the temperature interval between sublimation and vapor decomposition. Therefore, the study of the thermal properties of volatile precursor complexes is necessary for successful application in gas-phase processes.

In this work, a series of new Pd complexes was synthesized to study the effect of the length of the fluorinated substituent chains and the combinations of donor atoms in the ligand on the structure and thermal properties of Pd complexes. Interplay between saturated vapor pressure and crystal structure for cobalt and iron phthalocyanines derivatives also investigated. The saturated vapor pressure of MPc was determined as a function of temperature by the Knudsen effusion method, and the standard thermodynamic parameters $\Delta H_T$ and $\Delta S_T^0$ of the sublimation process were determined. Finally, heterostructures based on MPc(M=Co, Fe)/PdNP were obtained and investigated.

**Acknowledgements** This work was supported by the Russian Science Foundation (project No 21-73-10142).

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# DECIPHERING POLYMER CHEMISTRY FROM THE STATISTICAL DATA ON TRANSLOCATION EVENTS

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This works aims at developing techniques for characterization of polymer molecules from the statistical data on polymer translocation through a narrow opening under electrostatic or hydrostatic forces. We assume that the polymer translocation is described by the Fokker-Plank equation, and the statistical data on translocation time distribution can be used to determine the polymer length and chemistry. The deciphering methodology is based on active machine learning scheme, which queries the FP calculation with the specific length and free energy profile and finds the optimal match in a Bayesian optimization algorithm

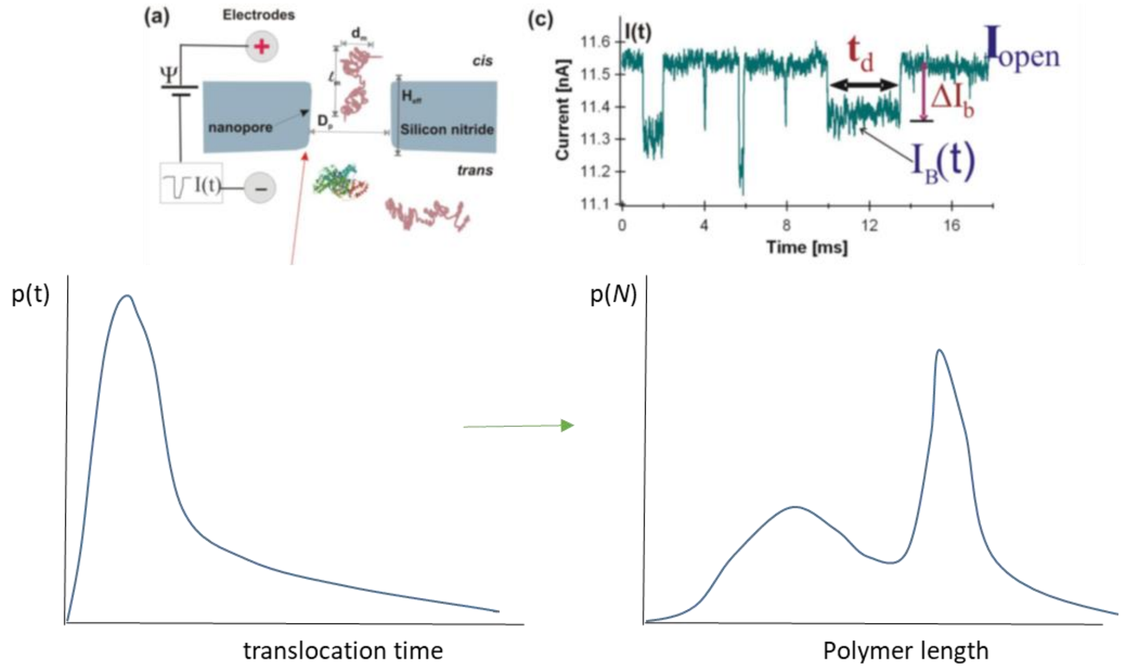

**Figure 1.** Top left [1] : experimental setup: polymers are driven through a pore by electrostatic field. Top right: the dependence of the transient current on time, from which the translocation time. Bottom left: from the fit to the translocation time distribution, the polymer length distribution or free energy profile is determined

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# HYDROGEN STORAGE BY N-CONTAINING HETEROCYCLES. THERMODYNAMIC EQUILIBRIUM OF HYDROGENATION-DEHYDROGENATION REACTIONS

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Hydrogen technology is considered a promising approach to meet future energy needs; however, its development is constrained by the problems of hydrogen production and the development of efficient hydrogen storage system. Liquid organic hydrogen carriers (LOHC), which can undergo reversible hydrogenation and dehydrogenation, are considered promising systems for hydrogen storage. Since at a given pressure and temperature the amount of hydrogen released depends on the reaction equilibrium of the hydrogenation/dehydrogenation reaction, the equilibrium composition of a given LOHC system is one of the key parameters for the reactor and process design of hydrogen storage and evolution units.

In this study we focused on two approaches in investigating the thermodynamics LOHC: experimental study and in silico metods.

A LOHC systems that has attracted our attention are indoline and 1-methylindole. This choice is justified by low dehydrogenation temperatures as well as the liquid state of the sample in fully hydrogenated and dehydrogenated forms. The purpose of this work was to study the thermodynamic characteristics and equilibrium state of hydrogenation-dehydrogenation reactions of systems involving indoline and 1-methylindole, which are necessary for evaluating the possibility of their use as LOHC.

The report summarizes the results of the study of chemical equilibrium for hydrogenation-dehydrogenation reactions of indoline and 1-methylindole. The experimental chemical equilibrium constants for hydrogenation-dehydrogenation reactions served as the basis for calculating the enthalpies and changing the entropies of the reactions. The paper also presents the measurements of the thermochemical properties of indoline and 1-methylindole, theirs partially and fully hydrogenated derivatives.

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# PHASE DIAGRAM OF THE ETHYLENE GLYCOL – ACETONE SYSTEM

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The ethylene glycol (EG) - acetone (AC) system was studied by differential scanning calorimetry in the temperature range 133 K -313 K with two types of devices: TA Instruments Q100 DSC and Mettler TA4000. A low-temperature melting at ~175 K attributed to the eutectic of the system was registered. The effect of devitrification of rapidly cooled samples in the region of low AC concentration (up to 20 mol%) was found. The glass transition temperature was determined to be ~ 153K. The liquid phase of the system was studied by IR spectroscopy. A comparison with the $H_2O$-AC phase diagram has been made.

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# DECOMPOSITION *vs* EVAPORATION: A CASE OF EMIMPF$_6$ IONIC LIQUID

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Heating of alkylimidazolium ionic liquids (ILs) with highly electronegative anions ($BF_4^-$, $PF_6^-$, etc.) is characterized by competing evaporation and decomposition. Knowledge of peculiarities of these processes is very important to practical application of such ILs. This work is devoted to complex investigation of vapor composition of 1-Ethyl-3-methylimidazolium hexafluorophosphate (EMImPF$_6$) by Knudsen effusion mass spectrometry.

Experiments were carried out on sector magnetic mass spectrometer MI1201, equipped by molybdenum Knudsen cell, at different evaporation conditions: 1) Knudsen cell having a small effusion orifice (equilibrium conditions), 2) open surface of IL placed on a metallic substrate (non-equilibrium conditions), and 3) open Knudsen cell (intermediate conditions). Background subtracted mass spectra were recorded in the 464-524 K range with 20 K step. Additionally, ionization efficiency curves, temperature dependencies of ion currents, and mass spectra at low energy (12 eV) were measured.

Analysis of the obtained data reveals complex vapor composition of the IL studied. Moreover, vapor composition is strongly affected by evaporation conditions: decomposition dominates at equilibrium conditions while evaporation of IL in the form of neutral ion pairs is preferable at non-equilibrium conditions. Decomposition of EMImPF$_6$ onto imidazole-2-ylidene, ethylimidazole, methylimidazole, and ethylmethylimidazole was found. The relationships among decomposition routes are also depend on conditions: the closer conditions to equilibrium the higher imidazole-2-ylidene pressure. ethylmethylimidazole is dominating among imidazoles and ethylimidazole has the lowest vapor pressure. Calculated relative mole fractions for the main vapor species at equilibrium and intermediate conditions are shown in Fig. 1.

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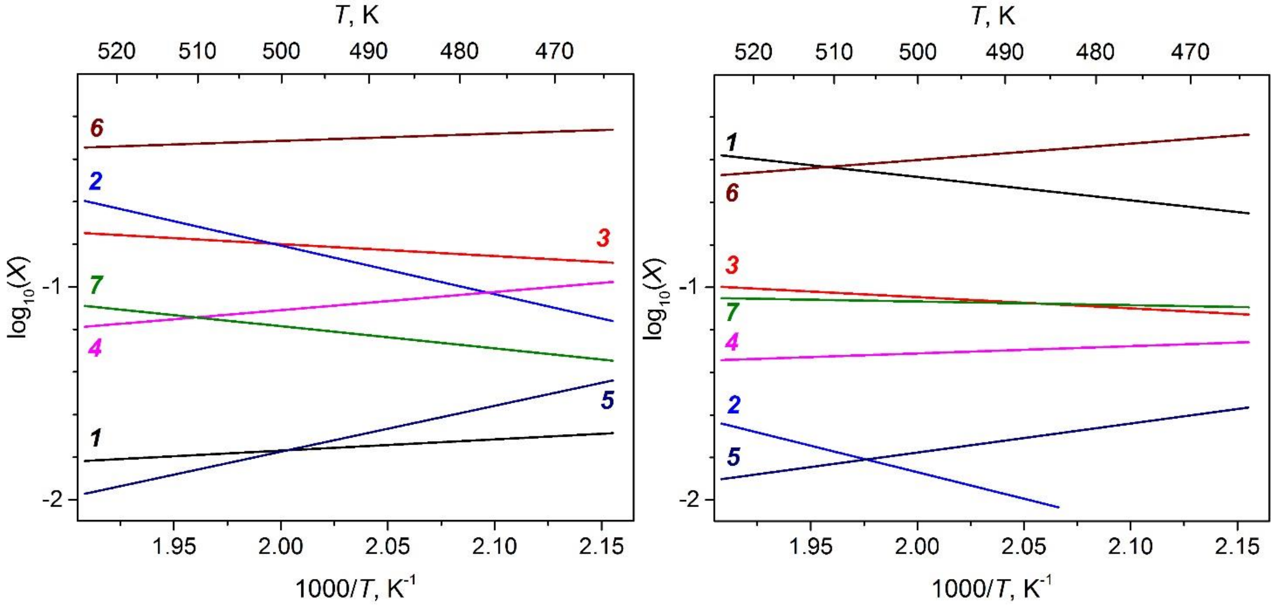

**Figure 1.** Relative mole fractions of vapor species over EMImPF$_6$ at equilibrium (left) and intermediate (right) conditions: 1 – neutral ion pairs; 2 – imidazole-2-ylidene; 3 – ethylmethylimidazole; 4 – methylimidazole; 5 – ethylimidazole; 6 – HF; 7 – PF$_5$.

# ENERGETICS OF RARE EARTH CARBONATES CRYSTALLIZATION

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Amorphous substances and materials are interesting for researchers from various fields. A rigorous definition of “amorphous” is challenging, but an operational definition is often taken to be a material that shows no significant Bragg peaks in its powder X-ray diffraction pattern. Although this definition underplays effects associated with short and mid-range order, it is useful in distinguishing materials with long-range order from much more disordered materials. Amorphous materials can be prepared by a variety of methods: quenching from a melt to form a glass, vapor deposition, radiation damage, and low temperature synthesis from aqueous solution. The last method provides precursors for further synthesis of crystalline materials. Amorphous precursors are usually the first to nucleate and then precipitate from supersaturated solutions; they can sometimes persist without crystallizing at ambient temperature for years, but in many other cases, they crystallize rapidly. Controlling their persistence and directing their crystallization toward desired products are important tasks for nanotechnology. Fundamental knowledge of the structure, thermodynamics, kinetics and reaction pathways linking amorphous precursors and crystalline products is essential to attain such control.

In this work, we studied amorphous precursors of rare-earth carbonates. They were synthesized from aqua solutions at specified conditions and characterized by powder X-ray diffraction, DSC, TG with mass spectrometric analysis of the evolved gases. High temperature oxide-melt solution calorimetry at 700 °C was used to derive enthalpies of formation from oxides and from elements. Enthalpies of possible transformation of amorphous precursors to various crystalline products were calculated and discussed. We conclude all reaction paths to be sensitive to the partial pressure of water and carbon dioxide. The formation of specific phases in ternary system $RE_2O_3$-$H_2O$-$CO_2$ may be caused by competition between thermodynamic and kinetic factors, but thermodynamics dominates the dependence of products formed on temperature and partial pressure of $H_2O$ and $CO_2$.

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# INVESTIGATION OF SHORT-RANGE ORDER IN MULTICOMPONENT ALLOYS WITH THE USE OF MACHINE-LEARNING INTERATOMIC POTENTIALS

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Multicomponent alloys, such as high-entropy alloys or multi-principal element alloys, are promising structural materials. However, the vast range of possible chemical compositions and long annealing times of some of the phases of interest offer an opportunity for their study with ab initio methods. The major drawback of ab initio methods is their huge computational costs.

In this work we address this drawback by developing efficient data-driven interaction models with accuracy close to those of ab initio methods, namely the low-rank interatomic potential (LRP) [1]. They are used in a Canonical Monte Carlo algorithm as an “on-lattice” model that can take into account local lattice distortions in multicomponent alloys. As we have shown [2], local lattice distortions stabilize the solid solution phase of the equiatomic NbMoTaW alloy from 600 – 800 K down to room temperature.

In this work, our approach is used to investigate the equiatomic fcc VCoNi and bcc AlNbTiV systems. The first one represents a medium-entropy alloy with a distorted fcc lattice which leads to outstanding strength-ductility relationship as reported in [3]. We simulate this system by including, implicitly, magnetism into LRP by fitting on spin-polarized DFT calculation. The accuracy fitted LRP has the error of about 1-3 meV/atom and is used to study the formation of the short-range order. Important to notice that in our investigation an M3V structure, where one of four fcc sublattices is fully occupied by V, was observed and later in work [4] the structure from [3] was resolved as (CoNi)3V+ $\sigma$ phase. One can find the details of VCoNi in [5].

The main interest of bcc AlNbTiV investigation was about order-disorder phase transition. Commonly used methods, that are based on aggregation of experimental and thermodynamic data for binary systems point to direct formation of B2(AlNb)(TiV) while cooling solid solution. In [6] we showed that at first B2(AlNbV)(TiNbV) phase is formed. The latter means that relatively high entropy stays in the structure and makes it more stable.

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# QSPR-METHOD OF PREDICTION OF VAPORIZATION ENTHALPIES. THERMOVAP PROGRAM

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The Thermovap program is designed to calculate the enthalpies of vaporization and change heat capacities of the “liquid – vapor” for a number of classes of organic compounds: alkanes, alcohols, ketones, ethers and esters, haloalkanes.

A program is based on the own QSPR-method and modified Randič indices. Unlike the previous version, the program includes halogens (F, Cl, Br, I) and the calculation algorithm has been changed.

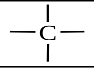
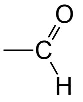
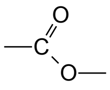
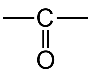
The calculation procedure is based on the linear dependence $\Delta_{vap}H_m{}^o(298.2)$ and $\Delta_l^g Cp^o(298.2)$ of total index ${}^{0-3}\chi$ determined by equation: ${}^{0-3}\chi = {}^{0-3}\chi_f + \chi_{MM}$

The index ${}^{0-3}\chi_f$ is the contribution from the molecular structure estimated by connectivity indices from zero to the third order ${}^{0-3}\chi_f = {}^0\chi + \frac{{}^1\chi}{2} + \frac{{}^2\chi}{3} + \frac{{}^3\chi}{4}$, ${}^0\chi = \sum_1^n \delta_i$ - is the zero order connectivity index and determines the contribution of atoms or a group of atoms; ${}^1\chi = \sum_1^m \delta_i\delta_j$ - is the first order connectivity index and determines the contribution of two valently bonded atoms; ${}^2\chi = \sum_1^p \delta_i\delta_j\delta_k$ - is the second order connectivity index and determines the contribution to the three successively located atoms; ${}^3\chi = \sum_1^r \delta_i\delta_j\delta_k\delta_l$ - is the third order connectivity index and determines the contribution to the four successively located atoms.

The index $\chi_{MM}$ is the contribution from intermolecular interactions determined by equation: $\chi_{MM} = \left(-3.249 \cdot Ln\left(m \cdot {}^{0-3}\chi_{alk}\right) + 14.806\right) \cdot (n-1)$ for esters and $\chi_{MM}$ =11,3 for alcohols. For other classes $\chi_{MM}$ is zero.

Values of descriptors present in table 1.

Table 1. The values of descriptors.

| Descriptor | Value | Descriptor | Value | Descriptor | Value |
|---|---|---|---|---|---|
| $-CH_3$ | 1.4773 |  | 7.5949 | —O— | 1.6062 |
| $-CH_2-$ | 1.6201 |  | 1.1319 |  | 1.1467 |
| $-\underset{\vert}{CH}-$ | 2.3685 | —OH | 1,2115 |  | 1.1664 |
| F | 1.3513 | Cl | 1.1680 | Br | 1.1333 |
| I | 1.1042 | | | | |

A vaporization enthalpy $\Delta_{vap}H_m{}^o(298.2)$ and difference of the molar heat capacities of the gaseous and the liquid phase $\Delta_l^g Cp^o(298.2)$ were estimated by equations:

$$\Delta_{vap}H_m{}^o(298.2) = 1{,}6883 \cdot {}^{0-3}\chi + 2{,}0781 \qquad \Delta_l^g Cp^o(298.2) = -2.416 \cdot {}^{0-3}\chi - 11.0$$

# CHARACTERISTICS OF RETENTION, SATURATION VAPOR PRESSURE AND ENTHALPY OF VAPORIZATION OF MESITYL OXIDE ETHERS AND LINEAR ALCOHOLS $C_1$-$C_5$

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In recent years, more and more new technologies based on renewable raw materials have been developed in the world. Technologies for biobutanol production by fermentation is economically viable in comparison to the petrochemical pathway. The acetone is formed as by-product in an amount of up to 30% of the amount of butanol. In addition, acetone is a product of large-scale production of phenol based on isopropylbenzene. There is a problem of overproduction of acetone. Acetone production volumes exceed the volumes of the sales market. An interesting direction in the processing of acetone can be esters based on mesityl oxide and monobasic alcohols. The ether and keto groups in the molecule of compound presumably contribute to high solubility, low boiling points and high octane number. These properties make it possible to use ethers of mesityl oxide and monobasic alcohols as solvents, depressants and oxygenates.

In the work the experimental determination of thermodynamic properties by gas chromatography of ethers of mesityl oxide and monobasic alcohols with organic acids $C_2$-$C_6$ was carried out.

Isothermal retention indices were calculated by the Kovacs equation:

$$I_x = \frac{\lg(\grave{t}_x) - \lg(\grave{t}_z)}{\lg(\grave{t}_{z+1}) - \lg(\grave{t}_z)} \cdot 100 + 100z \qquad (1)$$

where $t'_x$ and $t'_z$ are the corrected retention times of the ester and *n*-alkanes with numbers of carbon atoms *Z* and *Z* + 1, respectively.

The vapor pressure of obtained ethers was calculated using the equation (2) provided that the infinite dilution activity coefficient for the test compound and the corresponding alkanes are equal:

$$ln(P_x) = Ln(P_z) + \frac{(100*z - I_x)*Ln(P_z/P_{z+1})}{100} \qquad (2)$$

where $P_Z$ и $P_{Z+1}$ – vapor pressure the reference n-alkanes.

The vaporization enthalpy ($\Delta_{vap}H(298.2)$ was derived from the temperature dependence of vapor pressures using equation (3, 4) and was calculated using the own QSPR prediction method:

$$R \times \ln p_i = a + \frac{b}{T} + \Delta_l^g C_p \times \ln\left[\frac{T}{T_0}\right] \quad (3) \qquad \Delta_{vap}H \quad (T) = -b + \Delta_l^g C_p \times T \quad (4)$$

where $\Delta_{\mathrm{l}}^{\mathrm{g}} C_{p,m}^{\mathrm{o}}$ is the difference of the molar heat capacities of the gas and liquid phases respectively; *To* is an arbitrarily chosen reference temperature (To = 298.15 K) and R is the molar gas constant (R = 8.31446 $J \cdot K^{-1} \cdot mol^{-1}$).

The values of the change in internal energy and enthalpy of sorption at the average temperature of an experiment were determined using the dependences (5, 6):

$$ln\left(\frac{k}{T}\right) = C - \frac{\Delta_{sorp}\bar{U}}{RT} \quad (5) \qquad \Delta_{\mathrm{sorp}}H(T_{av}) = \Delta_{\mathrm{sorp}}\bar{U} - RT \quad (6)$$

where *R* is the universal gas constant (8.314 J/(mol K)) and *k* is the retention factor, calculated using retention times of the ether and column dead time.

They were reduced to the standard temperature (298.2 K) using the equation (7):

$$\Delta_{sorp}H(298{,}2) = \Delta_{sorp}H(T_{\mathrm{av}}) + \left(-\Delta_l^g C_p^\circ\right)\left(298{,}2 - T_{\mathrm{cp}}\right) \qquad (7)$$

The excess mixing enthalpy was calculated by the equation (8)

$$\Delta H^{E,\infty}(298.2) = \Delta_{vap}H(298.2) + \Delta_{sorp}H(298.2) \qquad (8)$$

The research results showed that the experimental and calculated values $\Delta_{vap}H(298.2)$ are in good agreement with each other. The values $\Delta H^{E,\infty}(298.2)$ decrease depending on the number of carbon atoms in the alcohol substituent molecule.

# *IN SILICO* STUDY OF PROTEIN TYROSINE PHOSPHATASE BINDING WITH DRUGS

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Molecular binding in solutions plays one of the important roles in the running of many technological and vital processes. Correct experimental determination and / or accurate calculation of the characteristics of this process comparable with experimental data is of great importance for predicting the properties of various compounds including biomolecular ones. Biomolecules, consisting of hundreds and thousands of atoms, are especially difficult for such studies. In vivo, they are involved in a large number of intermolecular interactions such as the interactions with water, with each other, with ions present in the media, or with ligands. Their biological activity essentially depends on the specifics of the manifestation of these interactions. However, in many cases an experimental investigation of biomolecules presents a significant problem, not only technical but also the financial one. The use of numerical approaches makes it possible to narrow down the field of experimental search and give a fast estimation of the parameters of the above interactions.

In this contribution we present the results of *in silico* study of protein-ligand binding, namely, protein tyrosine phosphatase 1B (PTP1B) binding with drugs, 2HB1 (4-Bromo-3-(carboxymethoxy)thiophene-2-carboxylic acid) and 2QBP (5-(3-{[1-(Benzylsulfonyl)piperidin-4-Yl]amino}phenyl)-4-Bromo-3-(Carboxymethoxy)thiophene-2-Carboxylic Acid) as the ligands. PTP1B consisting of 4800 atoms is a protein from the group of enzymes. The ligands, 2HB1 (number of atoms is 17) and 2QBP (number of atoms is 60), were selected according to the PDB (Protein Data Bank)-bank where PTP1B is indicated as a target for these drugs. The thermodynamic and structural data for protein-ligand binding were obtained by the integral equation method in the framework of the 3D-RISM (Reference Interaction Site Model) approach [1]. The protein–ligand binding free energies and binding constants were calculated at $T$=298 K, $p$ = 0.1 MPa and shown a good agreement with the available literature data. In addition, the changes in the solvent structure in the region of the protein-ligand contact was studied. As established, amino acid residues play a key role in PTP1B-ligand complex formation.

**Acknowledgements** This work was supported by the Russian Science Foundation (project No. 22-23-00184, https://rscf.ru/en/project/22-23-00184/).

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# SELF-ASSEMBLING SYSTEMS BASED ON IMIDAZOLIUM AMPHIPHILES WITH CLEAVABLE URETHANE FRAGMENT FOR CONSTRUCTION OF SOFT NANOCONTAINERS

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Numerous practical applications of surfactants cause their active investigation for a long time. Cationic surfactants are of particular importance, since they can be used as non-viral vectors, nanocontainers for drugs, and modifying agents for liposomes. [1]. Optimization of the cost and toxic properties of compositions based on cationic amphiphiles is the driving force for the search for new types of surfactants. As a part of our work, novel cationic amphiphiles, N-(2-ethylaminocarbonyloxyethyl)-N-alkylimidazolium bromides (IAC-n), have been synthesized (Figure 1). Their aggregation properties, solubilization capacity, antimicrobial activity, membranotropic properties and ability to modify liposomal nanocontainers have been investigated.

Using tensiometry, conductometry and fluorescence spectroscopy it has been demonstrated, that that introduction of urethane moiety into amphiphile structure results in the 2-3-fold decrease in critical micelle concentration in comparison with their unsubstituted counterparts. Aggregates with hydrodynamic diameter in the range of 4-10 nm have been obtained. Transmission electron microscopy technique allows us to establish the spherical shape of aggregates formed. These amphiphiles were shown as effective solubilizers for hydrophobic azo dye. All compounds exhibit high bacteriostatic and bactericide properties preferably toward gram-positive strains, as well as they have low hemolytic activity at the concentrations under study.

Also, based on the hexadecyl derivative (IAC-16), modified cationic liposomes were developed that can penetrate the blood–brain barrier and deliver the reactivator of acetylcholinesterase (AChE) pralidoxime chloride (2-PAM) into the brain. To obtain the composition optimized in terms of surface charge, stability, and toxicity, the molar ratio of surfactant/lipid components was varied. Physicochemical parameters, release profiles of the substrates (Rhodamine B and 2-PAM) *in vitro*, hemolytic activity and ability to cause hemagglutination were evaluated. Analysis of 2-PAM pharmacokinetics and *in vivo* AChE reactivation showed that modified liposomes readily pass into the brain and reactivate brain AChE of rat poisoned with paraoxon (POX) by 27%.

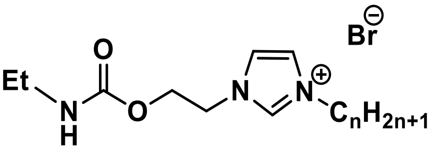

**Figure 1.** Chemical structure of homologous series of IAC-n amphiphiles (n=14, 16, 18).

**Acknowledgements** This work was financially supported by Russian Science Foundation (project № 19-73-30012).

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# DICATIONIC IMIDAZOLIUM SURFACTANTS: AGGREGATION BEHAVIOR AND CATALYTIC ACTIVITY

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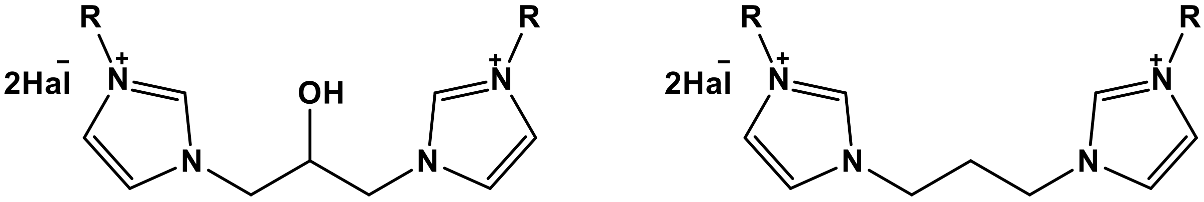
Dicationic surfactants are the wide class of compounds that have two hydrophobic tails and two positively charged head groups covalently linked by a spacer. These surfactants are superior to monocationic analogs in many key properties: they more effectively reduce surface tension, have an order of magnitude lower critical micelle concentrations (CMC), possess high wetting and solubilization effects and are used as drug carriers.

In this work, we studied homologous series of dicationic imidazolium surfactants with a trimethylene spacer fragment, including those functionalized with a hydroxyl group.



R = $C_8H_{17}$, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$; Hal = Cl, Br.

The aggregation behavior of these surfactants in water was studied by methods of tensiometry, conductometry and spectrophotometry. The kinetic parameters reflecting catalytic effect of the dicationic imidazolium surfactants on the alkaline hydrolysis of 4-nitrophenyl esters of phosphonic, phosphoric, and toluenesulfonic acids have been determined. It has been shown that the micellar effect increases both with a growth in the length of the surfactant alkyl chains and with the hydrophobicity of the substrate. A significant increase in the catalytic action is observed when an OH group is introduced into the spacer fragment: the acceleration of the process observed in this case can exceed three orders of magnitude.

**Acknowledgements** This work was supported by the Russian Science Foundation (grant no. 19-73-30012).

# THERMODYNAMIC PROPERTIES AND PHASE EQUILIBRIA IN THE $Na_3PO_4$ – $K_3PO_4$– $H_2O$ SYSTEM

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Aqueous systems containing alkali metal phosphates are found in many fields of modern chemistry: from the search for new compositions of thermal storage materials [1] to nuclear waste treatment [2]. There is a need for a comprehensive description of phase equilibria and thermodynamic properties of phosphate brines. It can be achieved by thermodynamic modeling. However, the last should be based on reliable experimental data.

Historically, more attention was paid to systems formed by mono- and dibasic phosphates. As a consequence there are practically no thermodynamic and phase equilibrium data about the $H_2O$ – $Na_3PO_4$ – $K_3PO_4$ system. To our knowledge, data on salt solubility are limited only to the position of the co-saturation point [3,4]. Information about the activity of the components was not previously reported at all. Nevertheless, the study of this system remains relevant since it is promising for the development of thermal storage materials.

**Thepurpose of this work** is to determine thermodynamic properties and phase equilibria in the $Na_3PO_4$ – $K_3PO_4$– $H_2O$ system.On the first stage we investigated phase equilibria at 298.15 ± 0.02 K with the method of isothermal solution. The compositions of the solid phases were determined by the wet residue analysis. Accurate weights of water, potassium and sodium phosphates are mixed in containers with tight-fitting lids and kept for at least 14 days with constant stirring until equilibrium was attained. The concentrations of the components in equilibria phases were measured by the inductively coupled plasma mass spectrometry (ICP-MS).

On next stage we measured the saturated vapor pressure of water over a series of solutions by static method at three temperatures (288.15, 298.15, and 308.15 K). Before measurement, the solutions were degassed during 8 hours. The compositions were selected using solubility data. The experimental of coefficients of activity of water were calculated from data on vapor pressure.

Thermodynamic data on this ternary system are presented for the first time. The obtained results can be used in thermodynamic modeling.

**Acknowledgements**The financial support of RFFR grant № 21-33-70031

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# STUDY OF 5,10,15,20-TETRA(4’-X-PHENYL)PORPHYRINS (X: H, F, Cl, Br) AND PLATINUM (II) 5,10,15,20-TETRAPHENYLPORPHIRINATE SUBLIMATION

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The vapor composition and sublimation enthalpy of four 5,10,15,20-tetra(4’-X-phenyl)porphyrins ($4C_6H_4X$-$H_2P$; X= H, F, Cl, Br) with free coordination core and platinum II complex of 5,10,15,20-tetraphenylporphyrin ($4C_6H_5$-PtP) were determined by Knudsen effusion method with mass spectrometric monitoring. Magnetic mass spectrometer MI 1201 [1,2] modified for thermodynamic studies was used. The apparatus resolution allows the record of ion masses with an accuracy of ± 2 amu within the range (2 to 850) amu at an accelerating voltage of 5 kV and the range (2 to 1050) amu at 4kV in the temperature range 273-1500 K. The cell with investigated samples was heated in a resistance furnace, and the temperature was measured using a tungsten-rhenium thermocouple WRe-5/20.

Saturated vapors of the $4C_6H_4X$-$H_2P$; X= H, F, Cl, Br, and $4C_6H_5$-PtP were studied in the temperature ranges of 510-560, 550-618, 555-611, 600-660, 568-615 K respectively. The most intensive peaks in mass-spectra correspond to the singly charged parent ions $[4C_6H_4X\text{-}H_2P]^+$ (X= H, F, Cl, Br); $[4C_6H_5\text{-}H_2PtP]^+$. The sublimation enthalpies were determined by the second law of thermodynamics based on the Clausius-Clapeyron equation by the linear regression method. The temperature dependences $\ln(IT)=f(1000/T)$ of ion currents for compounds follow a linear trend. Experimental data treated by the second law of thermodynamics yielded the following sublimation enthalpies (kJ $mol^{-1}$): $4C_6H_5$-$H_2P$ – 212(4), $4C_6H_4F$-$H_2P$ – 233(4), $4C_6H_4Cl$-$H_2P$ – 225(4), $4C_6H_4Br$-$H_2P$ – 243(4), $4C_6H_5$-PtP.

Table 1. Conditions of Knudsen experiments

| | $4C_6H_4X$-$H_2P$ | $4C_6H_4F$-$H_2P$ | $4C_6H_4Cl$-$H_2P$ | $4C_6H_4Br$-$H_2P$ | $4C_6H_5$-PtP |
|---|---|---|---|---|---|
| $U_{ion,}$ V[a] | 45 | 45 | 45 | 45 | 45 |
| $U_{acc,}$ kV[b] | 5 | 5 | 5 | 4 | 4 |
| $T_{min}$-$T_{max}$ [c], K | 510-564 | 550-618 | 555-611 | 600-660 | 568-615 |
| tg α [d] | -25.39282 | -28.0206 | -27.03411 | -29.1825 | -26.75637 |
| r [e] | -0.99989 | -0.99978 | -0.99985 | -0.9994 | -0.99956 |
| Number of experimental points [f] | 26 | 96 | 66 | 51 | 57 |
| Parent ion, amu | 614 | 686 | 753 | 930 | 807 |
| $\Delta H_{sub}$, kJ/mol | 212(4) | 233(4) | 225(3) | 243(4) | 223(4) |

[a] – ionization voltage;
[b] – acceleration voltage;
[c] – lower and upper limits of the studied temperature range;
[d] – approximation function slope $\ln(I \cdot T)=A+ \text{tg}\alpha\ (1000/T)$;
[e] – correlation coefficient;
[f] – number of the measurements of molecular ion intensity.

**Acknowledgments** The financial support of RSF according to the research project № 20-13-00359

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# PARTITION AND THERMODYNAMICS OF TRANSFER OF MACROCYCLIC PHOTOSENSITIZERS FOR PHOTODYNAMIC THERAPY IN THE 1-OCTANOL/PHOSPHATE SALINE BUFFER BIPHASIC SYSTEM

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Photodynamic therapy (PDT) has proved to be an efficient and safe treatment of many socially significant diseases such as superficial malignancies of different etiology and localized antibiotic-resistant microbial infections [1, 2]. This unique technique consists of three essential components, *viz.* photosensitizer (PS), molecular oxygen and red light which taken together lead to destruction of tumor or microbial cells. The human body can be viewed as a series of lipid-like barriers dividing aqueous filled compartments. Hence, affinity of PS molecules towards an aqueous and lipid-like environment strongly influences their binding to serum proteins and passive transport through cellular membranes. The simplest model of the inner core of a lipid membrane is 1-octanol (OctOH) which we used here to study partition of different PSs (see thel structures shown in the Figure) between OctOH and saline phosphate buffer (PSB) at 298-318 K.

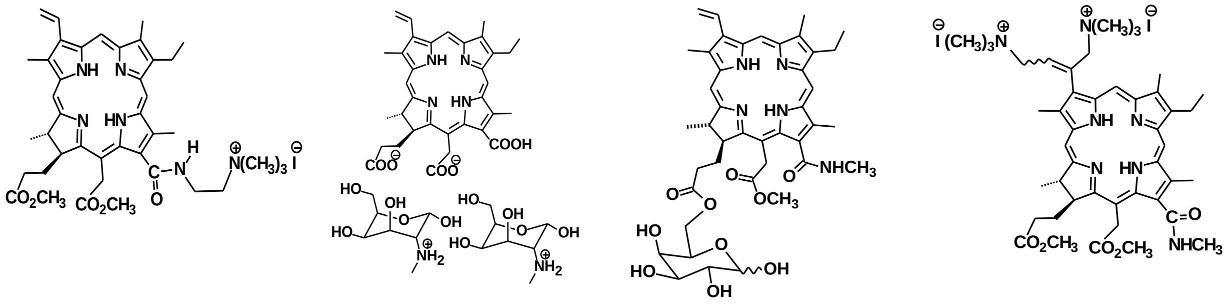

**Figure.** The structures of several chlorin PSs.

Our results indicate that for di- and tricationic chlorins as well as for trianionic chlorins, *viz.* Fotoran $e_6$ and Fotoditazin the partition coefficients are small ($P$~1-2) and almost temperature independent. The partition coefficients for neutral, zwitterionic and monocationic PSs are much larger and usually increase at elevated temperatures. These solutes are localized mainly in a lipid-like phase. The free energy of transfer from PSB to OctOH is negative for all solutes excepting the most hydrophilic tricationic chlorin, where it approaches zero. The enthalpy term is usually positive indicating that solvation of PSs is more exothermic in PSB compared to OctOH due to attractive interactions between solute polar/charged groups and water molecules. In contrast, the entropic term is negative and favors solute transfer to a lipid-like phase in the temperature range studied.

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# KNOWLEDGE ABOUT THE THERMAL BEHAVIOR – IMPORTANT ASPECTS FOR AN APPLICATION OF THE CHARGE TRANSFER COMPLEXES

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The series of new α-diimine-Ni$^{II}$-catecholate type complexes [1] with various ligands' electronic properties were explored in terms of their thermochemical behavior in presented study.

Being the compounds which are distinguished by an effective photoinduced charge transfer between the differently charged redox-active ligands in near-infrared field, α-diimine-Ni$^{II}$-catecholate complexes can act as the perspective chromophore materials. Moreover, a fine tuning of transfer's energy through the varying of the ligands' electronic characteristics due to their functionalization should extend a range of possible practical tasks solved with the participation of similar charge transfer complexes. The possible applications of above complexes - photovoltaics, optics, electrochromic devices - require a thermal stability and clear knowledge towards a composition and a thermal stability, peculiarities of sublimation process and vapor phase composition. Nevertheless, a comprehensive investigation of the thermochemical characteristics for the charge transfer complexes was performed only for *o*-iminobenzoquinonato Mg, Zn, Sr, Cd [2] and Ni, Co [3] derivatives, and carried out for the α-diimine-Ni$^{II}$-catecholate species for the first time within current research.

In particular, the thermal behavior of the solid state phase were investigated, a vapor phase composition was established, the measurements of the saturated vapor pressure with an evaluation of the thermal stability and volatility were performed by TGA, DSC, EI-MS, the Knudsen effusion method with the weight registration of the sublimated substance, and DFT-study.

As a result, studied compounds are characterized by the thermal stability and volatility, which are sufficient for their use as the working material in the applications with the layer deposition through the evaporation-condensation processes, for instance photovoltaics.

**Acknowledgements** The work was carried out with the support of Russian Science Foundation (grant no. 22-13-00351).

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# CRYSTALLIZATION KINETICS AND GLASS-FORMING ABILITY OF SULFONAMIDES

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Increasing the bioavailability of poorly water-soluble drugs is an urgent task of modern pharmacy. One of the methods to improve bioavailability is converting the drug into an amorphous form. On a laboratory scale, the melt quenching method can be used to quickly obtain the amorphous state of drugs.

At the same time, amorphous substances are known to have low kinetic and thermodynamic stability. Over time, amorphous drugs can crystallize, which compromises the bioavailability and shelf life of the dosage form. Thus, investigating stability of the amorphous drug forms is an important research topic. The primary method for determining kinetic stability is differential scanning calorimetry (DSC), however, it allows supercooling only for slowly crystallizing compounds. Amorphous forms of rapidly crystallizing drugs can be obtained using fast scanning calorimetry (FSC), which is based on chip sensor technology. By miniaturizing the sample (typical sample mass of about 100 ng), high cooling/heating rates of up to $10^6$ K/s can be achieved.

In the present work, the kinetic parameters of cold crystallization of sulfaguanidine, sulfadimidine, sulfapyridine, sulfamethoxazole, sulfamerazine, sulfadiazine were determined using non-isothermal kinetics approaches using DSC and FSC methods. Crystallization times at temperatures close to room temperature were predicted based on isoconversional and model-based approaches. The obtained values were confirmed by isothermal kinetics data. The critical cooling rates were 5 K/min for sulfaguanidine and sulfadiamidine, 10 K/min for sulfapyridine and sulfalene, sulfamethoxazole 3 K/s, sulfamerazine 350 K/s sulfadiazine 2000 K/s. The kinetic fragility of the amorphous compounds was 51 for sulfalene, 53 for sulfaguanidine, 47 for sulfapyridine, 61 for sulfadiamidine, 36 for sulfamethoxazole, 40 for sulfamerazine and 48 for sulfadiazine.

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# THERMODYNAMICS OF SOLVATION OF NONPOLAR SOLUTES IN PROTIC AMMONIUM-BASED IONIC LIQUIDS

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Protic ionic liquids (PILs) are ionic liquids produced via direct acid-base interaction and having at least one acidic hydrogen atom in the cation. Many PILs have an advantage of the ease and low cost of synthesis. Acidity can also benefit the use of PILs as catalytic media for a number of organic reactions. An interesting feature of some ionic liquids and particularly alkylammonium PILs is their ability to form nanoheterogeneous domain structure in the bulk phase. The presence of such structure affects the solvation properties.

In this work, the Gibbs free energy of solvation $\Delta_{solv}G^o$ of nonpolar solutes (n-alkanes and alkylbenzenes) in several alkylammonium PILs (nitrates, hydrogen sulfates and thiocyanates) was determined. For the liquids with the same anion, the Gibbs free energy of solvation of hydrocarbons increases in a row butyl- < propyl- < 2-methoxyethyl- < 2-hydroxyethylammonium. The introduction of a hydroxyl group into the cation disrupts the domain structure of the liquid, which leads to a huge increase of $\Delta_{solv}G^o$ . Methoxy group has a weaker destabilizing effect on the domain structure. For hydrogen sulfate ionic liquids, the Gibbs free energies of solvation are greater than those for nitrates and thiocyanates. This difference can be attributed to the acidic nature of hydrogen sulfate anion and larger concentration of the hydrogen bonds in the bulk phase.

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# WATER - N-METHYL-2-PYRROLIDONE MIXTURE: VOLUMETRIC PROPERTIES, DFT, IR, MD ANALYSIS

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Hydrogen bonds between peptide groups play a key role in the conformational stability of protein molecules in solution. Amides are one of the simplest model molecules for the study of peptide bonds, repeating fragments in biological macromolecules of proteins. A combined approach of computational chemistry, vibrational spectroscopy experiments, and density measurements was employed to study the structural properties of water-N-methyl-2-pyrrolidone mixtures over the whole concentration range. The structure of N-methyl-2-pyrrolidone dimers and hydrogen-bonded complexes of N-methyl-2-pyrrolidone with water molecules has been studied by the quantum chemical method based on the density functional theory. The vibrational spectra of aqueous solutions of N-methyl-2-pyrrolidone were recorded. Based on quantum chemical calculations, the bands of the vibrational spectrum were identified, which made it possible to trace the change in hydrogen bonding in the system. At increased N-methyl-2-pyrrolidone concentration, the hydrogen bond network is rearranged. The number of hydrogen bonds between water molecules decreases, water molecules bind to N-methyl-2-pyrrolidone molecules, changing the nature of its environment. Aqueous mixture containing N-methyl-2-pyrrolidone shows strong deviations of volumetric properties from ideality. For a deeper analysis of the data obtained, molecular dynamics simulation of this system was carried out at various temperatures and pressures. It has been shown that the resulting hydrogen bonds are medium strength bonds, but their strength depends on the water molecule environment, which are proved by NBO and QTAIM data. A network of hydrogen bonds is formed in N-methyl-2-pyrrolidone aqueous solution, which is noticeably destroyed with an increase in temperature and slightly changes with an increase in pressure.

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# SUBMERSIBLE ADIABATIC CALORIMETERS

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Низкотемпературные адиабатические калориметры классического типа представляют собой крупногабаритные и сложные вакуумные криостаты с размещенными внутри адиабатическими экранами и калориметрической ячейкой и требующее постоянно работающей системы вакуумирования.

Представляемая нами серия малогабаритных базовых криостатов адиабатических калориметров непосредственно погружается в транспортный сосуд Дюара с жидким азотом или гелием и не требующий постоянной откачки. Одного заполнения сосуда Дюара достаточно для проведения измерений в течении двух-трех недель. Поддерживание высокого вакуума в течении измерений осуществляется внутренним крионасосом. Размещаемые в криостате быстросменные калориметрические ячейки предназначены для измерения теплоемкости различных типов образцов в диапазонах температур от 5К до 500 К.

Калориметр работает полностью автоматически под управлением компьютерно-измерительной системы АК-11

Для разных диапазонов температур и объемов калориметрических ячеек используются три типа базовых криостатов:

БКТ-19 – диаметр 44 мм. Диапазон температур 2.3К-373К
БКТ-20 – диаметр 22 мм. Диапазон температур 5К-373К
БКТ-23 – диаметр 70 мм. Диапазон температур 80К-500К

На стенде представлен действующий адиабатический калориметр на базе БКТ-20.

# FORMATION THERMODYNAMIC PARAMETERS DETERMINATION FOR CARBAMAZEPINE COCRYSTALS WITH BENZAMIDE DERIVATIVES

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The key parameter used to evaluate the stability of a two-component crystal in relation to the original substances under given conditions is the standard Gibbs energy of formation ($\Delta G_f$) [1]. One of the most frequently used methods allowing the evaluation of the thermodynamic functions of cocrystal and complex formation in a solution is the method of phase solubility diagrams. However, since this method is rather time-consuming and costly, researchers often plot phase diagrams only for 1 or 2 temperatures and determine only several parameters: solubility product, complexation constant or Gibbs energy of cocrystal formation. We have recently proposed applying the cocrystal solubility method to determining the thermodynamic parameters of multi-component crystal formation [2]. The essential difference between these methods of investigating formation thermodynamics is that the cocrystal solubility method cannot be used to evaluate the contribution of complexation between the constituents in a solution. However, both of these methods allow a quantitative evaluation of cocrystal/salt stability. In 2016 a competitive cocrystal reaction was proposed as a qualitative method for evaluating the relative stability of multi-component crystals [3]. A new method for the formation thermodynamics of two-component crystals estimating based on melting points and sublimation data was proposed by us at 2017 [4].

In this work, we aim to check the accuracy of determining thermodynamic parameters of formation of multi-component crystals by the cocrystal solubility method (form 293K to 313K), by the method based on melting points and sublimation data and to compare the obtained results with those of competitive reactions. The objects of our investigation are carbamazepine cocrystals with several para-substituted benzamide derivatives. The obtained formation thermodynamic parameter values were discussed in the context of the peculiarities of the packing of molecules in the crystal lattices of cocrystals.

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# HEAT CAPACITY AND THERMAL EXPANSION OF GADOLINIUM-STRONTIUM PHOSPHATE

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Silicates, germanates, phosphates, and vanadates with the structure of the mineral eulytite, $Bi_4(SiO_4)_3$, are used as the basis of promising low temperature co-fired ceramic devices for high-frequency electronic equipment, optical isolators, matrices for solid-state phosphors, as well as crystalline materials for the localization of waste from nuclear technologies. The availability of thermodynamic data for these compounds is very scarce, despite its inherent importance.

In the present study the results of synthesis, calorimetric and XRD studies of $Sr_3Gd(PO_4)_3$ representative of this structural family are presented.

Polycrystalline $Sr_3Gd(PO_4)_3$ powder was synthesized by the method of coprecipitation of salts from an aqueous solution followed by heat treatment. The sample was characterized by XRD on a Shimadzu XRD-6000 diffractometer. IR spectra of the compounds were recorded on a Shimadzu FTIR 8400S spectrometer. It’s elemental and phase compositions were examined using a JSM-7600F SEM equipped with a microanalysis system OXFORD X-Max 80 Premium. Thermal expansion was studied on the same diffractometer using an Anton Paar TTK 450 temperature attachment in the range from 298 to 523 K. An adiabatic calorimeter BCT-3 was used to measure heat capacity in the range 6–350 K. A DSC 204 F1 Phoenix differential scanning calorimeter was applied to measure the heat capacity in the temperature range (330−1273) K.

The results of electron microprobe analysis have shown that the sample is homogeneous and its composition is close to the theoretical value calculated for the formula $Sr_3Gd(PO_4)_3$. Taking into account, that the X-ray pattern of the sample contains only sharp diffraction peaks without asymmetry and also the absence of significant noise and amorphous diffuse halo, we may conclude that the studied phosphate is totally crystalline. X-ray results confirmed phase purity of the studied phosphate (not less 0.99 mass fraction of the main substance) and its crystallization in the eulytite structural type (space group $I\bar{4}3d$, $a$ = 10.0883(2) Å).

Having cubic symmetry, the material expands uniformly in all directions with increasing temperature and has a positive coefficient of thermal expansion ($a_a = 12.1\cdot10^{-6}$ K$^{-1}$). The heat capacity of the sample rises gradually with increasing temperature, and no phase changes or thermal decompositions occurred. The experimental points of $C_p{}^0$ at $T > 6$ K were fitted by means of the least-squares method using power and semilogarithmic polynomial dependences. The experimental data were used to calculate the standard thermodynamic functions: $C_p{}^0$, $H^0(T)–H^0(0)$, $S^0(T)$ and $G^0(T)–H^0(0)$. Standard entropy of formation at 298.15 K was estimated for the phosphate.

# HYDROGEN PRODUCTION FROM DECALIN OVER SILICA-SUPPORTED PLATINUM CATALYSTS: A THERMODYNAMIC STUDY

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Hydrogen is one of the most promising energy carriers nowadays, but its efficient storage is still a challenge. One of the high-potential technologies is the reverse storage of hydrogen through its chemical bonding in molecules of organic compounds (liquid organic hydrogen carrier – LOHC) [1,2].

LOHCs are high boiling organic molecules that can be easily and reversibly hydrogenated and dehydrogenated during the catalytic processes. There are several requirements for LOHC systems: thermal stability, a suitable melting point, favorable thermodynamics of dehydrogenation, wide availability, low toxicity, and a reasonable price [3]. Decalin is often considered in the literature as a promising candidate among polycyclic aromatic compounds because it meets most of the requirements for LOHC. The advantage of decalin dehydrogenation is that the theoretical amount of hydrogen obtained from one mole of decalin is 5 moles of $H_2$, which corresponds to 7.3 wt%. The final product of the dehydrogenation of decalin is naphthalene, which can be easily converted back to decalin by catalytic hydrogenation using a well-studied industrial process.

The kinetic and thermodynamic parameters of the decalin dehydrogenation reaction over Pt catalysts supported on different types of silica were investigated. The dehydrogenation of decalin includes four reversible reactions: in addition to the sequential dehydrogenation of decalin through tetralin to naphthalene, isomerization of the *cis*-*trans* isomers of decalin also occurs. It creates additional difficulties in implementing the process because the *cis*-isomer's activity significantly exceeds the activity of the *trans*-isomer in the dehydrogenation reaction. Under thermodynamic reaction control, the equilibrium constant of *cis*- into *trans*-decalin isomerization decreased with temperature. Consequently, high temperatures will favor dehydrogenation, and low temperatures will favor the isomerization of *cis*-decalin to *trans*-decalin. Therefore, hydrogen production from decalin requires kinetic control.

The catalysts supported on mesoporous silica SBA-15 and MCM-48 showed a significantly higher catalytic activity during dehydrogenation compared to the catalyst supported on amorphous $SiO_2$. The high surface area and small pore size of these supports have a positive effect on Pt particles' dispersion and result in the production of high-active catalysts for dehydrogenation of decalin to naphthalene. The obtained data can be used for the design and optimization of the dehydrogenation-hydrogenation reaction of potential liquid organic hydrogen carriers.

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# PHASE PROCESSES AND CHEMICAL EQUILIBRIA IN THE QUATERNARY SYSTEM ACETIC ACID – AMYL ALCOHOL – AMYL ACETATE – WATER AT 293.15 K, 303.15 K, 313.15 K AND 323.15 K

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Esterification reactions are applied for the synthesis of various esters in both laboratory and industrial conditions. Esters are important substances for different purposes, for instance, amyl acetate is used in production of varnishes and paints, also as an additive to biodiesel etc. Accordingly, the data on phase and chemical equilibrium for the system with amyl acetate synthesis reaction are significant for the optimization of processes, but this important information is rather limited.

In this report we present some results of the study liquid-liquid equilibria (LLE) and chemical equilibria (CE) for the system acetic acid – amyl alcohol – amyl acetate – water at 293.15 K, 303.15 K, 313.15 K and 323.15 K. The mutual solubility for the quaternary system and all the ternary subsystems was investigated by isothermal titration method. The procedure was similar to the well-known cloud point technique but the fixation of the titration end point was carried out both by heterogenization and homogenization of the mixture [1]. The obtained data on solubility gave opportunity for presentation of liquid-liquid (LL) envelope in composition simplexes. The determination of the LL tie-lines for the quaternary and ternary systems at four temperatures was performed using gas chromatography method [2]. The data sets both for LL envelope and coexisting phase compositions tend to be in good agreement with each other and with literature data as well [3]. Finally, based on the data obtained, the location of ternary and quaternary critical points and curves in the composition tetrahedron was estimated. A local composition model (NRTL) and a group model (UNIFAC) were applied for data correlation and LLE modeling. CE compositions for the quaternary systems were also determined by gas chromatography method. Good correlation between obtained data and our results for 318.15 K [4] was observed.

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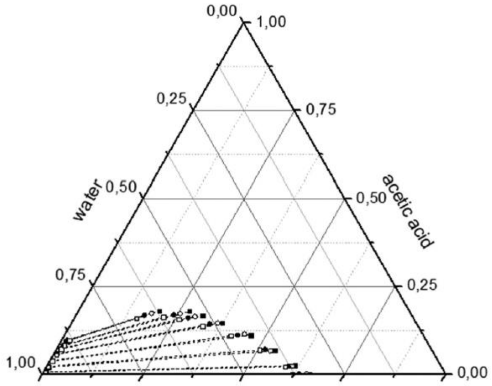

**Figure 1.** The diagram of LLE of ternary acetic acid – *n*-amyl alcohol –water system at atmospheric pressure (mole fractions): ■ – 293.15 K, ○ – 303.15 K, ● – 313.15 K, □ –323.15 K.

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# METROLOGICAL ASPECTS OF ISOTHERMAL TITRATION CALORIMETRY

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Isothermal Titration Calorimetry (ITC) is a commonly used method that allows to simultaneously determine several thermodynamic parameters in a single experiment and has become widespread in studies of molecular-level interactions. Currently more than 500 publications a year include results derived from ITC experiments. These results are crucial for chemical, medical and biological research, therefore particular attention is drawn to ensuring their quality, reliability and uniformity. This work focuses on analyzing several issues that were previously reported in literature concerning metrological aspects of ITC, and sets further research objectives.

Baranauskienė in [1] compared the results of titration experiments using different calorimeters designed by major manufacturers (Microcal, TA Instruments) and concluded that some calorimeters are more reliable than others, due to inconsistency of results among calorimeters and in comparison with literature data. Similar concerns can be drawn from interlaboratory comparisons, in which standard deviations for enthalpy change of 10-20 % were reported, significantly exceeding the individual precision estimates. The issue of underestimating uncertainty, not considering systematic errors and other methodological problems have also been addressed in other studies [2, 3].

Considering the above, though the unit traceability in ITC is established by using an electric heater for calibration, additional metrological tools and procedures should be used in order to correctly evaluate measurement uncertainty and ensure reliability. But, unfortunately, a system for metrological maintenance of ITC has not been firmly set up by now, albeit considerable effort have been put in finding possible solutions.

Some researchers focused on developing procedures for correct evaluation of uncertainty [4, 5] but none of these procedures have been standardized, so they are not widely applied by end-users.

IUPAC and ITC manufacturers reported that differences in heat distribution in the system during electrical calibration can be subject to significant error and suggested conducting chemical calibration or validation using commonplace chemicals or manufacturer's test kits to perform a standard reaction [5, 6]. In the absence of certified reference materials intended for this purpose, an assigned value and its uncertainty could be questionable since there is no information on the method of establishing this value, its traceability and the set of data that is being used. Moreover, it is unclear if homogeneity and stability of those chemicals and test kits have been confirmed.

Despite of these efforts there is still a lack of accessible tools and procedures for metrological maintenance of ITC. To address this challenge VNIIM calorimetry lab started a project on improvement of the State Primary Standard of heat quantity in the field of solution and reaction calorimetry GET 133. The main goal of the project is to develop a new calorimetric complex in order to broaden functional capabilities and measurement range of the GET 133 Primary Standard. By the end of 2022 it is planned to manufacture a reference microcalorimeter, study its characteristics and perform a thorough uncertainty evaluation. In the next phase the objectives will be to develop calibration procedures, study candidate substances for reference materials and obtain precise data for standard reactions.

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# REVERSE MICELLES OF TETRAETHYLENE GLYCOL MONODODECYL ETHER IN SYSTEMS WITH HEPTANE AND NILE RED

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The research of the aggregation of nonionic surfactants of the CnEm type (C is hydrocarbon units, E is an oxyethylene group) in non-polar and weakly polar media is of scientific interest due to insufficient knowledge of the mechanism of reverse micelles formation in the absence of water, and in practice – the need to use the results of the study in various technological processes [1-4]. For reverse micelles, the question of the CMC existence important is still debatable [3,4].

The aggregation processes in the systems tetraethylene glycol monododecyl ether (C12E4) - n-heptane (1) and C12E4 - Nile red - n-heptane (2) have been studied by electron absorption spectroscopy. In addition, a commercial analogue of C12E4 – Brij 30 with a base substance content of 98% and less than 1% water has been studied.

The study of the C12E4 - Nile red - n-heptane system by absorption spectroscopy showed the possibility of forming reverse micelles without a noticeable water addition. The CMC itself in system 2 tums out to be lower than the CMC in system 1, which corresponds to the predictions of the theory [5]. The observed difference in the CMC values for C12E4 and Brij 30 in n-heptane, measured in the presence of Nile red, may be due to the influence of water, which is present in the preparations in insignificant but different amounts, on the processes of aggregation of surfactant molecules in n-heptane.

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# SOLUBILIZATION OF PHTHALOCYANINE AND NILE RED IN AQUEOUS SOLUTIONS OF SURFACTANTS

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The study of the solubility of hydrophobic compounds in aqueous solutions of surfactants is of scientific interest due to insufficient knowledge of its mechanism, depending on the structure and properties of the components in the system. The objects of the study were octa[(4'-benzo-15-crown-5)oxy] of magnesium phthalocyanine (Mgcr8Pc), the synthesis and purification of which are described in [1], and 9-Diethylamino-5-benzo[α]phenoxazinone, commonly known as Nile red (NR)– has acquired much attention during the past few decades owing to its intense fluorescence in various media and its solvatochromic behavior. Despite the widespread use of NR as a hydrophobic probe, very little attention has been given to its aggregation [2].

To realize the effect of Mgcr8Pc monomerization using surfactants dictated by the conditions of possible use of the drug in medicine [3], sodium dodecylsulfate (DSN), alkyltrimethylammonium bromides (C14TAB, C16TAB) and alkyltriphenylphosphonium (C14TPPB, C16TPPB) were used. The effect of surfactants on the solubility of NR in an aqueous medium was studied using the example of DSN and C14TAB.

The well-known phenomenon of transition from Mgcr8Pc dimers to monomers in DSN solutions during solubilization has been studied in more detail by the method of electron absorption spectroscopy [1]. It was found that Mgcr8Pc monomerization begins at concentrations much lower than the critical concentration of micelle formation (CMC) of the studied surfactants, and at an even lower content of surfactants, specific micelles with the participation of Mgcr8Pc dimers are formed.

Based on experimental data obtained in saturated solutions of Mgcr8Pc and NR (under conditions of thermodynamic equilibrium of a solution with a solubilizate precipitate) in the presence of surfactants, the thermodynamic characteristics of solubilization are determined: the solubilization capacity of micelles, the coefficient of solubilisate partition between micelles and an ambient solution, and the standard solubilization affinity.

A comparison of the thermodynamic parameters of solubilization in micellar solutions of DSN and C14TAB shows that in the case of NR, their values are higher than for Mgcr8Pc, which has a more complex molecular structure. C16TPPB, having the same length of the hydrocarbon radical as C16 TAB, has higher mobilization characteristics, which indicates the exceptional role of the bulky polar group of the C16TPPB molecule. The found values of the solubilization capacity, as calculated per one molecule of Mgcr8Pc, in micelles of DSN, C14TAB and C16TAB lead to abnormally large aggregation numbers. This fact may be explained by possible development of a bimodal distribution of micelles, at which solubilisate-containing micelles coexist with “empty” micelles; as a result, the average number of solubilisate molecules in a micelle may appear to be smaller than unity

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# RELAXATION PROCESSES IN Al-R (R = Ce, Sm) GLASS-FORMING MELTS

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Amorphous and nanocrystalline alloys based on Al-R system represent a class of new materials with unique combination of mechanical, electric and magnetic properties. However, their physical properties in liquid state are practically unknown. In this work we investigated density, viscosity and electrical resistivity, of Al-Ce(Sm) alloys in a wide temperature range.

Viscosity temperature and time dependences were measured on an automated setup using torsion oscillation method from liquidus temperature up to 1400 °C with the accuracy of ± 4%. Density was determined using the absolute variant of gamma-absorption method on an automated installation with the accuracy of ± 1% starting from room temperature up to 1500 °C. Electrical resistivity was studied by contactless method in rotating magnetic field in the range 25 – 1400 °C. The accuracy in resistivity values determination is estimated to be ± 3%.

It was shown that in liquid state in the range from liquidus to t = 1250 °C, long-term relaxation takes place in $Al_{91}Ce_9$ and $Al_{90}Sm_{10}$ melts: the measured properties reach their equilibrium values within several hours. Above 1250 °C, the relaxation time decreases sharply and becomes shorter than the measurement time (2 min). The relaxation was observed while measuring viscosity and density, and it was invisible on the electrical resistivity. Since in the alloys investigated electronic properties are determined by local order, one can conclude that the relaxation is the process of large-scale inhomogeneities decay.

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# THERMODYNAMIC STUDY OF MIXED-LIGAND MAGNESIUM COMPLEXES BASED ON BETA-DIKETONATES FOR MOCVD PURPOSES

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Mixed-ligand magnesium complexes $[Mg(Q)(L)_2]$ based on beta-diketonate L = $(RCOCHCOR')^-$ ligands represent a beneficial attractive class of precursors for obtaining $MgF_2$ and MgO functional coatings by Metal-Organic Chemical Vapor Deposition (MOCVD). In fact, the known complexes of this class are synthetically available, stable in air, and have vapor pressure sufficient for MOCVD processes [1]. Non-fluorinated complexes are favorable for MgO production, while deposition of $MgF_2$ requires a special co-reagent [2]. The presence of fluorinated beta-diketonates increases the temperature of obtaining the oxide phase, but makes it possible to prepare $MgF_2$ directly [1]. The main advantage of this class is the possibility of precise tuning of thermal properties through the variation of terminal substituents R,R' in beta-diketonate and a bidentate neutral ligand Q.

To implement this feature, the understanding the effect the ligand structure on thermal properties of complexes based on quantitative measurements is needed. Two complexes with N,N,N',N'-tetra-methylethylenediamine, $[Mg(tmeda)(L)_2]$ where L = thd (R = R' = $^t$Bu) [3], tfac (R = $CF_3$, R' = Me), were previously studied in such a way. Herein, we aimed to the detailed thermodynamic study of mixed-ligand complexes, considering the influence of terminal substituents and neutral diamine.

For this purpose, we have synthesized the complex with ethylenediamine, $[Mg(en)(thd)_2]$ and the fluorinated series (R = $CF_3$), $[Mg(tmeda)(L)_2]$, L = hfac (R' = $CF_3$), ptac (R' = $^t$Bu), btfac (R' = Ph). The samples were carefully characterized by powder XRD, CHNF analysis and NMR-spectroscopy.

The thermal behavior of complexes in the condensed phase was studied by DTA/TG (NETZSCH) in a helium flow and DSC in vacuum (SETARAM). The characteristics of the melting process (*m.p.*, $\Delta_{melt}H_{m.p.}$) have been obtained. For the *ptac*-complex, as for its *thd*-analogue earlier [3], a solid-state transformation was found; however at the noticeably lower temperature (44.5 ± 0.5°C).

The static method with glass membrane-gauge manometers was used to measure the pressure of saturated and unsaturated vapor. After processing the experimental data, the temperature dependences of the saturated vapor pressure for the processes of sublimation and evaporation were obtained and the thermodynamic characteristics of these processes were calculated ($\Delta_{sub}H°$, $\Delta_{sub}S°$, $\Delta_{vap}H°$, $\Delta_{vap}S°$). The presented data were used to evaluate the thermodynamic characteristics of the melting (*en*-complex) or solid-solid transition (*ptac*-complex). The results obtained are in good agreement with the calorimetric data.

The studies of the unsaturated vapor pressure showed that the compounds pass to the gas phase with the preservation of their molecular form. The decomposition of complexes at high temperatures was revealed by the change in the molecular weight of the vapor phase and by irreversible pressure changes with rising temperature. The thermal stability of the fluorinated hfac- and ptac-complexes turned out to be close: decomposition begins at 213±2°C и 214±2°C, respectively.

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# THE EFFECT OF LIGANDS WITH DIFFERENT BINDING AFFINITY ON ALBUMIN FIBRIL FORMATION

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There are different possible treatment strategies for amyloidoses including prevention of the pathogenic proteins synthesis, inhibition of protein oligomerization at various stages of fibril formation, and breaking up already formed pathogenic assemblies. Some compounds inhibiting fibrillation of certain proteins have been introduced into the clinical practice. Known inhibitors usually bind to the fibril-forming protein and/or its oligomers. Upon binding, they prevent fibril nucleation or slow down fibril growth [1]. The primary task is to understand the link between the structure of ligand, its binding to protein monomer, oligomers and large fibrillar aggregates, and inhibiting activity.

In our work, the effect of binding of several ligands to bovine serum albumin on the kinetics of fibril formation at denaturing conditions is studied. The considered ligands are clinical drugs with different binding constants to albumin: relatively strong binders (naproxen, ibuprofen, warfarin) and weak binders (isoniazid, ranitidine).

Using a complex of experimental methods (thioflavin T fluorescence binding assay, Congo red binding assay, circular dichroism spectroscopy, differential scanning calorimetry), it was shown that relatively strong albumin binders with different molecular structure suppress the formation of amyloid fibrils while weak binders do not. These strong binders act as thermodynamic inhibitors reducing the equilibrium amount of formed fibrils, but not the rate constants of fibril growth. The inhibiting activity as measured by the amount of formed fibrils was shown to be governed by the fraction of the unfolded protein form. Thus, stronger inhibition can be achieved by stronger ligand-protein binding, larger number of ligand molecules capable of binding with different sites in the protein molecule, and higher ligand concentration.

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# HEAT CAPACITY AND THERMODYNAMIC FUNCTIONS OF NEODYMIUM STANNATE

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Stannates of rare earth elements are of great interest to researchers in various fields of science and technology. Important multifunctional properties, such as high ionic conductivity and thermal stability, ferroelectricity, and exotic frustrated magnetism, open up broad prospects for their use as phosphors, photocatalysts, gas sensors, and ionic electrical conductors.

$Nd_2Sn_2O_7$ crystallizes in the cubic structure of pyrochlore (Fd-3m), in which rare-earth ions form a network of regular tetrahedra with common corners. The heat capacity of neodymium stannate was previously studied only up to 4 K. It was found that at $T_c \approx 0.91$ K [1], a magnetic phase transition occurs in the so-called "all-in–all-out" magnetic structure, when all four magnetic moments of a tetrahedron are directed either inwards or outsides [2].

A polycrystalline neodymium stannate was prepared by a solid-state method at 1623 K. The phase and chemical purity of the sample prepared were confirmed by X-ray powder diffraction and X-ray fluorescence spectroscopy. The low-temperature heat capacity of $Nd_2Sn_2O_7$ was measured by relaxation calorimetry using a Physical Properties Measurement System (Quantum Design) and adiabatic calorimetry using an adiabatic vacuum calorimeter BKT-3 ("Termis", Russia). To measure the heat capacity of $Nd_2Sn_2O_7$ in the temperature above 320 K, a simultaneous thermal analyzer STA 449 F1 Jupiter (Netzsch) was used.

Heat capacity of neodymium stannate: a) comparison with literature data, b) consistency of data obtained by different methods. Based on the smoothed values of the heat capacity $C_p^o(T)$ of $Nd_2Sn_2O_7$, the temperature dependencies of the standard thermodynamic functions (entropy $S^o(T)$, enthalpy change $H^o(T)–H^o(0)$ and reduced Gibbs free energy $\Phi^o(T)–\Phi^o(0)$) were calculated in the temperature range from 0 to 1400 K.

**Acknowledgements** This work was supported by the Ministry of Science and Higher Education of the Russian Federation as part of the State Assignment of the Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences

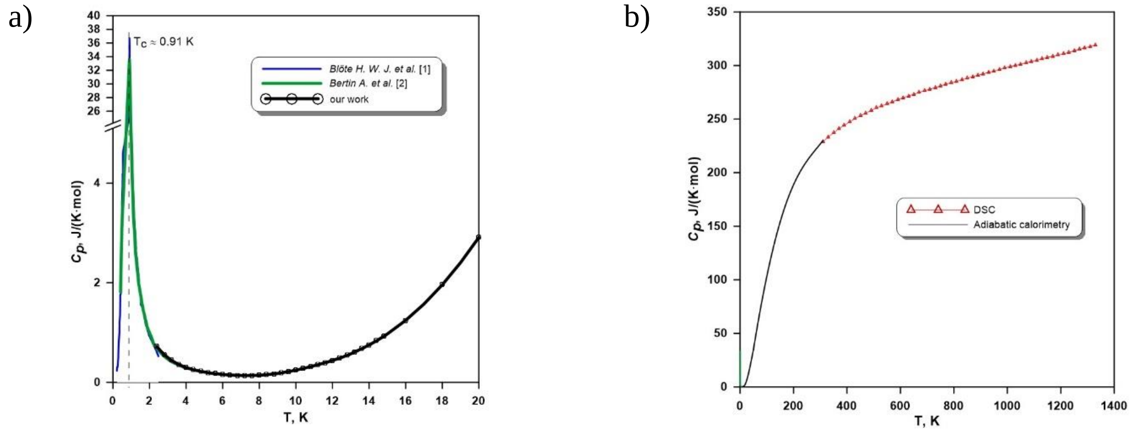

**Figure 1.** Heat capacity of neodymium stannate: a) comparison with literature data, b) consistency of data obtained by different methods.

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# SIMULATION OF WATER-ALCOHOL SOLUTIONS WITH THE CONCENTRATION-DEPENDENT OPLS FF PARAMETERS CORRECTION

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Aqueous alcohol solutions have extremely wide applications. In addition, they are often used as model systems for the investigation of structural features that can be transferred to solutions of other amphiphilic or hydrophobic molecules. Today, the molecular dynamics (MD) simulation of alcohol-water solution structure is a very prospective method for research.

The significant problem of the MD simulations is the choice of correct parameters for the force field (FF) used. This is especially important if it is necessary to change the parameters with the concentration of the solution. Such a need arises for water-alcohol mixtures, where the dielectric constant of the solution changes significantly with concentration. That affects the charge distribution on the molecules in the medium. The standard parametrization of OPLS FF represents well the properties of pure substances (say alcohol). When working with solutions, however, the accuracy of some calculated structural and thermodynamics properties is insufficient. The problem can be solved by a correction of the FF parameters with concentration. We have suggested a simple method for such correction for small monoatomic alcohols (methanol, ethanol, 1- and 2-propanol) in aqueous solutions. The idea is to change the charges, which were ascribed to the alcohol atoms in the standard FF. We have found out that it is enough to use a scaling factor that depends linearly on concentration. Thus, the method is very simple: starting with the OPLS charges, we pick up the values of the charges to describe well the density of the solution at several fixed concentrations and obtain the linear scaling factor coefficients.

MD simulation of the mentioned aqueous alcohol solutions was performed with a small concentration step of 1%, on a range from 1 to 40% for methanol and ethanol and from 1% to 20% for propanols (in molar fraction). The Gromacs package was used for simulation. Our method has reproduced experimental values of density and other volumetric characteristics on the whole concentration range much better than using the standard OPLS parameters. Moreover, we have shown that some other thermodynamic parameters coincide also with the experiment very well. An improvement was obtained for the dielectric constant, excess molar enthalpy of solution, and even for chemical potential calculated by the Kirkwood-Buff approach. A concentration-dependent shift of a peak on the radial distribution function for alcohol oxygen atoms is observed on the improved models of the methanol solutions. This interesting feature demonstrate the weakening of H-bonds between alcohol molecules with the concentration increase.

**Acknowledgements** The financial support of the grant RSF No. 22-23-00620 and RFBR No. 9-33-90205 is gratefully acknowledged.

# MAKING CHEMICAL REACTION THERMAL RATE CONSTANT CALCULATIONS RELIABLE: APPLICATION TO OH + HBr → Br + $H_2O$

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In the present work, we accurately calculate the thermal rate constants of the OH + HBr → Br + $H_2O$ chemical reaction at different temperatures (200, 300, and 500 K). For this aim we use a combination of the most reliable among available methods, (1) Ring Polymer Molecular Dynamics (RPMD) for quantum dynamics simulations [1] and for calculations of thermal rate constants [2,3] and (2) machine-learning interatomic potentials, namely, Active Learning (AL) of Moment Tensor Potential (MTP) [4,5] for accurate construction of the underlying full dimensional global potential energy surface (PES) used in the RPMD simulations. Previously, the combination of RPMD and AL-MTP methods was successfully validated for three representative chemical reactions where MTP was parameterized to the data from previously generated analytical PESs [6,7]. Here we parameterize MTP to the data obtained with the high level of quantum-mechanical theory, namely, the spin-unlimited method of explicitly correlated coupled clusters with allowance for double and partial allowance for triple excitations (UCCSD(T)-F12a). By comparing thus obtained RPMD-AL-MTP rate constants with the ones reported previously using the quasi-classical trajectories (QCT) and the POTLIB PES as well as with the experimental rate constants obtained at the temperature of 5-500 K [8], we demonstrate that the RPMD rate constants are systematically closer to the experimental rate constants than the QCT ones. We conclude that the proposed methodology based on combining best practices for electronic structure calculations, PES construction, and dynamic simulations makes theoretical estimation of rate constants reliable and can be with certainty extended to more complex chemical reactions in future.

**Acknowledgements** The work was supported by the Russian Foundation for Basic Research (grant number 20-03-00833).

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# DYNAMIC SURFACE PROPERTIES OF FULLERENE MIXED FILMS WITH POLYMERS

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Fullerenes have a great potential in various branches of industry and medicine due to their unique properties. At the same time, the complexity of formation of regular thin surface films of unmodified fullerenes seriously limits their direct use in technology, and the extremely low solubility in water limits their use for medical purposes. To overcome this problem one can use the formation of mixed films of fullerenes with amphiphilic polymers [1]. The properties of mixed films of fullerene $C_{60}$ and polyvinylpyrrolidone (PVP) or poly(N-isopropylacrylamide) (PNIPAM) were investigated by the methods of dilatational surface rheology, surface tensiometry, ellipsometry, Brewster angle microscopy and atomic force microscopy. Two methods to form mixed films at the air / liquid interface have been used. In the first case, the both components were spread onto to the water surface from volatile solutions (toluene and ethanol) dropwise. The second method consisted in the fullerene spreading onto the surface of a polymer solution. The observed dependencies of the dynamic surface elasticity on surface pressure had one or two local maxima corresponding to different steps of the formation of the mixed film. A synergistic effect of these components on the dynamic surface elasticity was detected at low surface pressures. The spreading of fullerene from a solution in toluene onto the surface of PNIPAM solution resulted in partial fullerene dissolution in the bulk phase occurs. In case of fullerene spreading onto the surface of PVP solution, fullerene remained at the interface. The properties of $C_{60}$ films on the water surface and on the surface of polymer solutions differed noticeably. In the latter case, a more uniform structure was formed, which allowed formation of regular fullerene structures on a solid substrate using the Langmuir-Blodgett method.

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# VAPORIZATION THERMODYNAMICS OF THE HOMOLOGOUS SERIES OF *N*-ALKYL BENZOATES AND *N*-ALKYL PHENONES

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Vaporization thermodynamics quantitatively describes the liquid-vapor equilibrium, due to which it is used in the purification of compounds, the study of the distribution of molecules in the environment, and many other areas of science and industry. It is difficult to overestimate the importance of studying the thermodynamics of evaporation that confirming by growing number of experimental methods and estimation schemes for vaporization characteristics.

Alkylaromatic compounds are a huge class of compounds and are widely used in industry and everyday life. Alkyl benzoates and phenones are typical compounds of this class. However, there is a quite limited information about vaporization thermodynamics of these compounds, that is typical for most low-volatile compounds. Moreover, the experimental study of all compounds of these classes is a time-consumable procedure required tremendous efforts and a combination of a number of experimental methods rarely available in one laboratory. On the other hand, group additive schemes that make it possible to predict the properties of a substance from its structure are still underdeveloped and poorly describe large molecules.

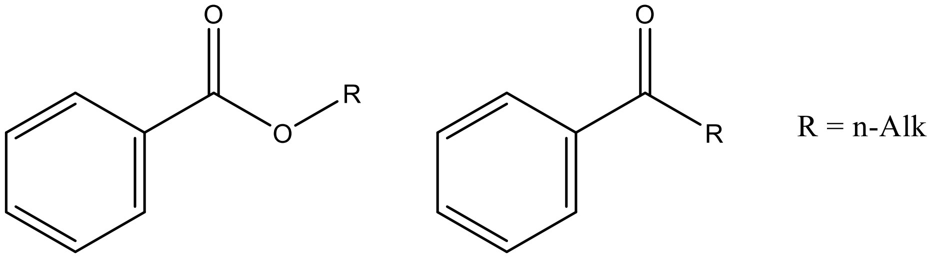

**Figure 1.** General formulas for the homologous series of alkylbenzenes (left) and phenones (right).

In this work, a common approach for comprehensive description of the vaporization thermodynamics for homologous series was proposed and tested. Within it, all available literature information on the vaporization thermodynamics of short-chain benzoates and phenones was collected and critically analyzed. Vapor pressures of moderately and low-volatile compounds were measured using combination of transpiration and TG-FSC methods [1]. Both literature and experimental data were used to analyze the relationship between vaporization characteristics (vapor pressure and vaporization enthalpy at 298.15 K) and the chain length. To estimate difference between ideal gas and liquid state heat capacities, we used a recently proposed empirical correlation between change of the heat capacity and vaporization enthalpy [2].

Combining above ideas, we created and verified a scheme for estimation of vapor pressures in a wide temperature range for C1-C20 homologues, showing an accuracy comparable to the experiment.

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# WATER IN NANOCONFINEMENT OF SILICA NANOPORE. MOLECULAR DYNAMICS SIMULATIONS

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Understanding the interfacial effects on liquid transport behavior through nanopores plays an important role in different areas: the design of nanofluidic devices, the adsorption and separation processes, prediction or controlling fluid transport, reaction pathways and products. The structural and transport properties of water through nanopores were investigated by means of molecular dynamics simulation. We present study of the structure and dynamics of water confined between silica surfaces using β-cristobalite as a model template. The β-cristobalite (111) is the crystalline phase of silica with density and refractive index closest to those of amorphous silica [1]. The β-cristobalite (111) can sustain the two types of hydroxyl groups identified experimentally on the amorphous silica surface, namely, the single silanols (Si-OH), and the geminal silanols ($Si\text{-}(OH)_2$).

Our goal is to investigate the effect of slit-pore width and functionalization (hydroxyl density) of the β-cristobalite surface on the structure and dynamics of the water layers near the surfaces. Slit pores were generated from slabs with three different hydroxyl densities 0, ~2, and ~6 $OH/nm^2$.

The density distribution of water between two solid walls was examined to provide insight into the liquid structure in the vicinity of the interface. The radial distribution function g(r) provides information regarding the structure of water near the silica nanopore surface. Hydrogen bonds (H-bonds) between water molecules as well as with the pore surface hydroxyls are also investigated. To get insights into the dynamics of water molecules confined in the silica nanopores, we have calculated mean square displacement in the direction normal to the pore wall and that in the plane parallel to the pore walls. To compute the self-diffusion coefficient we employed the Einstein relation.

It was found that for hydroxyl surfaces the water density profile did not exhibit strong fluctuations near solid walls. This may be due to the absence of pronounced effects of liquid water stratification, which could be caused by the adsorption of liquid molecules on solid walls. This indicates only a local and limited influence of the surface on the configuration of H-bonds of water molecules, which is consistent with the literature data.

An analysis of the structural and dynamic characteristics showed that the bridging oxygen atoms in silica are weak hydrogen bond acceptors, while the silanol groups are slightly stronger hydrogen bond acceptors.

Method. Classical molecular dynamics simulations were carried out using a software package Gromacs 2019.6. MD simulations have been performed in NVT ensemble. The SPC/E model was used to describe the water interactions. The temperature and density of water corresponded to the liquid state.

**Acknowledgements** The calculations were performed on the supercomputer facilities provided by NRU HSE.

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# MOLECULAR DYNAMICS SIMULATIONS OF IONIC LIQUIDS PROPERTIES UNDER CONFINEMENT

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Room-temperature ionic liquids (RTILs) attract a lot of attention for application in electrochemical double-layer capacitors (EDLCs) that employ porous carbon electrodes due to such advantages as their wide electrochemical window, capability to remain stable up to much higher temperatures than conventional solvents, and at the same time ability of IL-based supercapacitors to operate at extremely low temperatures. Molecular dynamics (MD) simulation of four ionic liquids (ILs) differing from each other by the alkyl chain length of cation (1-ethyl-3-methylimidazolium $[EMIM]^+$ and 1-octyl-3-methylimidazolium $[OMIM]^+$) and type of anion (tetrafluoroborate $[BF_4]^-$ and bis(trifluoromethane sulfonyl)imide $[NTf_2]^-$) in slit charged carbon nanopores of various width (h=1÷15 nm) has been carried out. MD simulations have been performed in the canonical (NVT) ensemble with Gromacs package version 2019.6. A rectangular box was constructed (Figure 1). The graphene layers of the armchair type with an area of 10×10 $nm^2$ making up the nanopore walls were built. Each graphene sheet is separated by 0.335 nm. The innermost graphene sheets are modeled as the cathode by placing negative partial charges on the carbon atoms. The charges were uniformly distributed throughout the pore, the charge density was -0.8 e/$nm^2$ (-12.8 μC/$cm^2$), where e is the elementary charge. The ions were added to the left and right sides of the nanopore model and within the pore using Packmol. The number of IL ions was initially set to correspond to a density equal to the bulk density of the ILs at required temperature and 0.1 MPa. Such characteristics of confined ILs as charge, mass, and number densities inside the pore, radial distribution functions, angle distributions, mean squared displacement of ions, self-diffusion coefficients and electrical conductivity were calculated. The confined ionic liquids were found to have a layering structure inside the pore of less than 5 nm in width. The cations in the layer closest to the charged surfaces are in parallel orientation and form a lamellar-like structure. Our results predict the diffusion coefficients of the ions in ionic liquids to be of the order of $10^{-11}$ $m^2/s$, which is in agreement with other computational and experimental studies. In all cases studied, confinement hindered the diffusion. This is to be expected, since as h goes to infinity, the effect of confinement must be negligible. Increasing the alkyl chain length limits the movement of the imidazolium cations, and so the ILs with longer alkyl chain have lower electrical conductivities than the ILs with shorter alkyl chain. Despite lower ionic diffusion coefficients of $[EMIM][BF_4]$ than that of $[OMIM][NTf_2]$ the former demonstrates higher electrical conductivity than the latter. This is due to its high concentration of charge carriers' density in the pore.

**Acknowledgements** The financial support of the Russian Science Foundation (Grant No. 21-11-00031) and grant of the President of the Russian Federation (project No. MD-341.2021.1.3). The calculations were performed on the supercomputer facilities provided by NRU HSE.

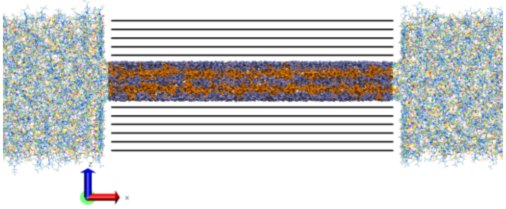

**Figure 1.** Snapshot of the part of the simulation box for [EMIM][NTf2] confined in slit carbon charged pore of width 2 nm. In the pore region iceblue and orange represent $[EMIM]^+$ and $[NTf_2]^-$ ions. Black represents carbon atoms of graphene sheets.

# THERMODYNAMIC PROPERTIES OF THE TERNARY PHASES IN THE Mn(Sn)-Sb-Te SYSTEMS

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After the discovery of topological insulators (Tl) [1], tetradymite-type layered materials which are containing heavy p-block elements stand out as the best candidates for studying many novel Tl properties. Studies also show that ternary phases in the quasi-binary $MTe{\cdot}A^V{}_2Te_3$ (M – Mn, Ge, Sn, Pb; $A^V$-Sb, Bi) systems with the tetradymite-derived structure are experimentally proven three-dimensional topological insulators with robust and unique surface states [2,3].

The knowledge of phase equilibria and thermodynamic data of corresponding systems can provide more reliable information for synthesizing novel complex phases and the development of modern sample-preparation techniques. Therefore the aim of this work is the studying phase equilibria in the Mn(Sn)Te-$Sb_2Te_3$-Te systems and the thermodynamic properties of ternary phases in both systems using EMF measurements under standard conditions.

Alloys of the both system were prepared using pre-synthesized starting binary MnTe, SnTe and $Sb_2Te_3$ compounds and elemental tellurium. All alloys were synthesized at 1000 K for 5 h followed by quenching in icy water. The resulting ingots were furtherly annealed at 700 K for 45 days and 400 K for 5 days to form equilibrium phases, and examined using differential thermal analysis (LINSEIS HDSC PT1600 system) and X-ray diffraction (Bruker D2 PHASER diffractometer) techniques. EMF measurements were performed using a Keithley 2100 6 1/2 Digit Multimeter.

According to XRD results, it is revealed that in the first system, both ternary compounds in the MnTe-$Sb_2Te_3$ section and β-phase based on $Sb_2Te_3$ have a tie-line connection with $MnTe_2$. However, it was found that the $SnSb_2Te_4$ and $SnSb_4Te_7$ ternary compounds, as well as solid solutions based on SnTe (α) and $Sb_2Te_3$ (β) form tie-line with elementary tellurium in second system.

In order to study thermodynamic properties of phases, the concentration cells of

(–) MnTe (solid) | liquid electrolyte, $Mn^{2+}$ | (Mn–Sb–Te) (solid) (+)
(–) SnTe (solid) | liquid electrolyte, $Sn^{2+}$ | (Sn–Sb–Te) (solid) (+)

types were assembled in the 300-450 K temperature interval.

The relative partial thermodynamic functions of MnTe and SnTe in various phase regions of the studied systems were calculated from the measured EMF of concentration cells with respect to the MnTe and SnTe electrodes, respectively. These data together with the corresponding thermodynamic functions of MnTe, SnTe and $Sb_2Te_3$ were used to calculate the relative partial molar functions of manganese and tin in alloys, and also the standard thermodynamic functions of formation and standard entropies of the $MnSb_2Te_4$, $MnSb_4Te_7$, $SnSb_2Te_4$, and $SnSb_4Te_7$ compounds, and solid solutions based on starting compounds.

**Acknowledgements.** The work was supported by the Science Development Foundation under the President of the Republic of Azerbaijan-Grant № EIF-GAT-5-2020-3(37)-12/02/4-M-02.

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# THE DRUG BINDING BY $\{Mo_{72}Fe_{30}\}$ POLYOXOMETALATE

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A large number of research papers are devoted to the development of targeted drug delivery systems. In our laboratory, the possibility of using nanocluster polyoxometalate $\{Mo_{72}Fe_{30}\}$ ($[Mo_{72}Fe_{30}O_{252}(CH_3COO)_{12}\{Mo_2O_7(H_2O)\}_2\{H_2Mo_2O_8(H_2O)\}(H_2O)_{91}]\cdot 150H_2O$) (fig. 1a) as the basis for targeted delivery is being studied [1]. The present study is focused on the one of the stages of creating the targeted delivery systems – binding the drug to the carrier.

We selected two drugs for the study: doxorubicin hydrochloride (antitumor drug) and tetracycline hydrochloride (an antibiotic drug). Using a set of physico-chemical methods, it was determined that selected drugs spontaneously bind to the $\{Mo_{72}Fe_{30}\}$ in an aqueous solution. The ratios of components in complexes are: $\{Mo_{72}Fe_{30}\}$:doxorubicin=1:12, $\{Mo_{72}Fe_{30}\}$:tetracycline=1:4. It is known that both tetracycline and doxorubicin are capable of forming coordinative complexes with metals. By means of FTIR spectroscopy the structures of the complexes were determined (fig. 1 b,c). Under experimental conditions, doxorubicin is a monocation, which provides Coulomb interaction with nanocluster. While tetracycline is a zwitterion (due to the close location of opposite charges, tetracycline can be considered as an uncharged particle when interacting with the $\{Mo_{72}Fe_{30}\}$). It is also worth noting that hydrogen bonds can be formed between some functional groups of drug molecules and the surface oxygens of the nanocluster. Doxorubicin and tetracycline are fluorophores. Therefore, we used the full Stern-Volmer equation (eq. 1) to determine the Gibbs energy of interaction between $\{Mo_{72}Fe_{30}\}$ and the drugs (eq. 2). The quenching mechanism was static (determined by the fluorescence lifetime). The effect of an inner filter for tetracycline-$\{Mo_{72}Fe_{30}\}$ system was taken into account; in the case of doxorubicin, it was not required.

$$\frac{I_0 - I}{I_0} = \frac{[F]_t + [Q]_a + K_d - \sqrt{([F]_t + [Q]_a + K_d)^2 - 4\cdot[F]_t\cdot[Q]_a}}{2\cdot[F]_t} \qquad (1)$$

$$K_{sv}=K_d^{-1},\ \Delta G^{298}=-RTln(K_{sv}) \qquad (2)$$

where $I_0$ – fluorescence of pure fluorophore solution; I – fluorescence of complex $\{Mo_{72}Fe_{30}\}$-fluorophore at 1:1 molar ratio; $[F]_t$ – concentration of fluorophore in solution; $[Q]_a$ – concentration of $\{Mo_{72}Fe_{30}\}$ (quencher); $K_d$ – dissociation constant. The Gibbs energies of interaction are: -37.6 $kJ\cdot mol^{-1}$ for $\{Mo_{72}Fe_{30}\}$-doxorubicin, −24 $kJ\cdot mol^{-1}$ for $\{Mo_{72}Fe_{30}\}$-tetracycline. The larger binding energy for $\{Mo_{72}Fe_{30}\}$-doxorubicin system is associated with the additional contribution of the Coulomb interaction.

**Acknowledgements** This work was supported by the Ministry of Science and Higher Education of Russian Federation (project № AAAA-A18-118020 590 107-0).

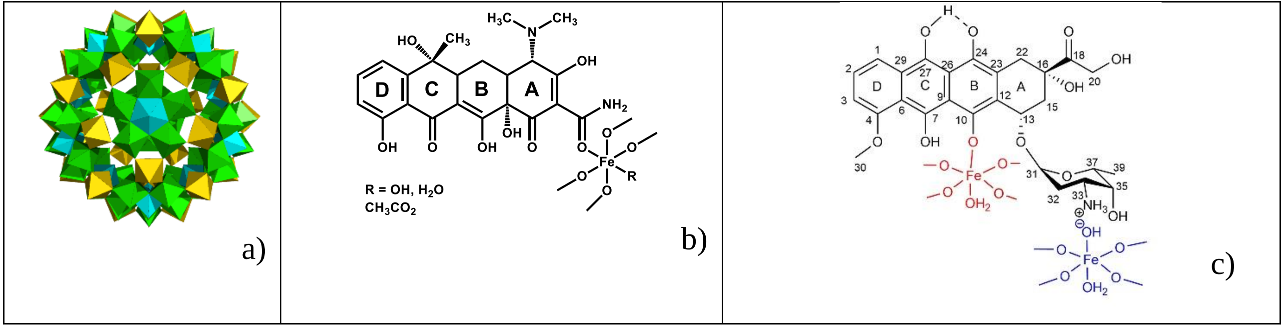

**Figure 1.** The structures of: a) $\{Mo_{72}Fe_{30}\}$, b) $\{Mo_{72}Fe_{30}\}$-tetracycline binding, c) $\{Mo_{72}Fe_{30}\}$-doxorubicin binding.

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# PHYSICOCHEMICAL CHARACTERISTICS OF NANOFORMULATED ROTENONE

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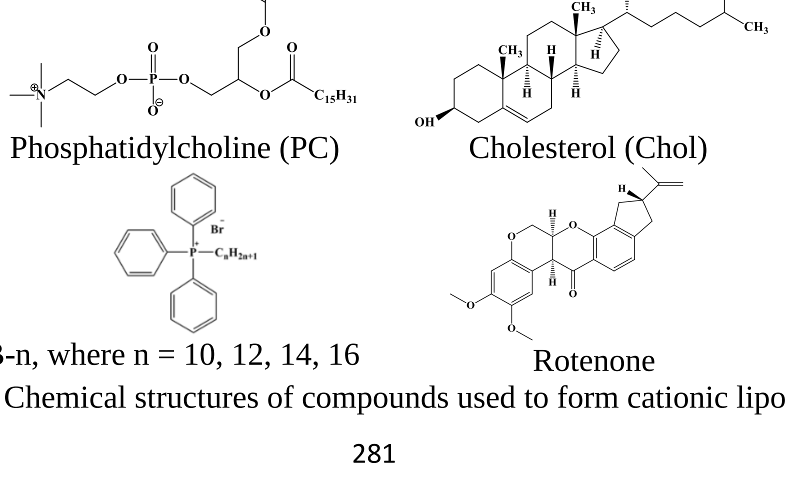
Currently, liposomes are the most versatile drug carriers and can be easily modified with different ligands that give them improved properties, such as organelle targeting. Surfactants, due to their amphiphilic nature, can also be used as liposome modifiers. Cationic surfactants, in particular alkyltriphenylphosphonium bromides, are of great interest. Due to their delocalized and high positive charge, they have been used in mitochondrial medicine. Thus, the main goal of this work was creation of liposomes modified with mitotropic surfactants of the triphenylphosphonium series (fig.1). Mitochondrial poison rotenone was encapsulated in the modified liposomes obtained. Determination of the physicochemical characteristics of liposomes is an extremely important step, since it allows the identification of leader systems for further biological experiments.

The nature of surfactant and the ratio of components in the preparation of liposomes directly affects the physicochemical characteristics of the aggregates and their biological activity. It is known that the zeta potential of liposomes is one of the key factors determining their stability over time. In view of this, to achieve optimal value of the zeta potential, two parameters were varied: the length of the TPPB-n hydrocarbon tail (n = 10, 12, 14, 16) and the lipid/surfactant molar ratio (50/1, 35/1, 25/1). In addition, cholesterol (10%) was included in liposomal composition to give an additional stability to the aggregates. Due to extrusion through membranes with a pore size of 100 nm, the hydrodynamic diameter of liposomes did not exceed 120–130 nm. It has been shown that the incorporation of TPPB-n into the lipid bilayer increases the zeta potential by ≈ +30–40 mV. It should be noted that the lengthening of the TPPB-n hydrocarbon tail and an increase in their amount leads to a slight increase in positive charge. Since the main goal of the work is to obtain mitochondria-targeted liposomes, in order to increase their biological activity, liposomes were loaded with the mitochondrial poison rotenone. It was shown that at a rotenone concentration of 0.1 mg/mL, the encapsulation efficiency (EE) for PC/Chol/TPPB-14 liposomes is 95%, and a further increase in rotenone concentration (0.3, 0.5, 0.7, 1 mg/mL) leads to a decrease in EE. The incorporation of surfactants into the lipid bilayer directly affects the release rate of substrates *in vitro*. In this case, an increase in the amount of TPPB-14 in lipid bilayer resulted in a more prolonged release of rotenone.

**Acknowledgment:** This work was financially supported by Russian Science Foundation (project № 19-73-30012).



Phosphatidylcholine (PC)

Cholesterol (Chol)

TPPB-n, where n = 10, 12, 14, 16

Rotenone

**Figure 1.** Chemical structures of compounds used to form cationic liposomes.

# PROTONIC CONDUCTIVITY OF POLYANTIMONIC ACID BASED ELECTROLYTES

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The development of the scientific basics for the novel membrane materials manufacturing for electrochemical power units i.e. low temperature fuel cells (FC) efficiently working up to 300 °C is a serious scientific problem related to hydrogen energy shift. Polyantimonic acid (PAA) is characterized by high conductivity and thermal stability can be regarded as a prospective proton conducting material. So the goal of the current work was the investigation of the structure, phase stability, and protonic conductivity of PAA based solid electrolytes.

PAA was synthesized using the controlled hydrolysis of $SbCl_5$ in the tenfold excess of water. Then the precipitate was treated by 1n HCl and again washed with distilled water until the negative reaction to clorine ions. Then using 10 and 20 wt.% of fluoroplastic as a binder the cylindrical solid electrolytes (SE) of 30 mm in diameter and 5 mm in thickness were formed by cold uniaxial pressing. Structure of the formed membranes was investigated by thermo-XRD (Rigaku Ultima IV with high temperature equipment "SHT-1500"), SEM and EDX (Supra Zeiss) techniques, STA technique, Raman spectroscopy and hydrostatic weighting. The conductivity of SE in the range 60-300 °C was investigated by electrochemical impedance study in the dry nitrogen, room air and presence of humidity.

Using STA and XRD it was shown that the structure of SE correspond to crystalline $Sb_2O_5 \times 3H_2O$. STA, Raman spectroscopy and thermo-XRD showed that the temperature increase results unit cell shrinkage and crystallinity decrease from ~91 to 75% because of step by step water removal. According hydrostatic weighting, SEM and EDX data, fully dense membranes were obtained, where a binder do not cover PAA grains enabling the ion transport though the grain bulk. Via impedance spectroscopy it was shown that PAA is a great protonic conductor in a presence of moisture. The temperature dependence of conductivity of PAA is complex due to prolonged water losses and the increase of carrier charge mobility with temperature increase.

**Acknowledgements.** This work was supported by the President’s grant for young scientists (research project 75-15-2021-370). SEM and EDX data were obtained at the center for Nanoresearches, thermo-XRD data were performed at the Center for X-ray Diffraction Studies of SPBU Research park.

# PRECURSORS OF N-HETEROCYCLIC CARBENES BASED ON MONO-SUBSTITUTED THIACALIX[4]ARENE DERIVATIVES

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The actual problem in organic synthesis is synthesis of new compounds via C-C or C-HET coupling. It's usually solved by cross-coupling reactions with organometallic catalysts. These catalysts not only accelerate the synthesis but also reduces its temperature and allows to use more green solvents like water. Thiacalix[4]arene derivatives due to the spatial separation of the hydrophilic and lipophilic parts of the molecule are ideal molecules for the synthesis of amphiphilic structures. The use of such structures allows to pursue reactions in water and water-organic systems with both micellar and metallocomplex catalysis.

Monosubstituted derivatives of thiacalix[4]arenes expand the possibilities for step-by-step modification of the molecule to give it the desired properties. However, the production of monosubstituted derivatives of thiacalix[4]arenes by alkylation is not selective due to a small difference in the acidity of phenolic OH groups. An alternative approach is the dealkylation of disubstituted derivatives of thiacalix[4]arenes using tetrabutylammonium bromide (TBAB) [1] or sodium azide [2]. We have obtained monosubstituted derivatives of thiacalix[4]arenes (Fig.1) by quaternization of tertiary amines without the use of TBAB or sodium azide. The synthesis of monosubstituted derivatives of thiacalix[4]arene as well as NHC complexes is discussed.

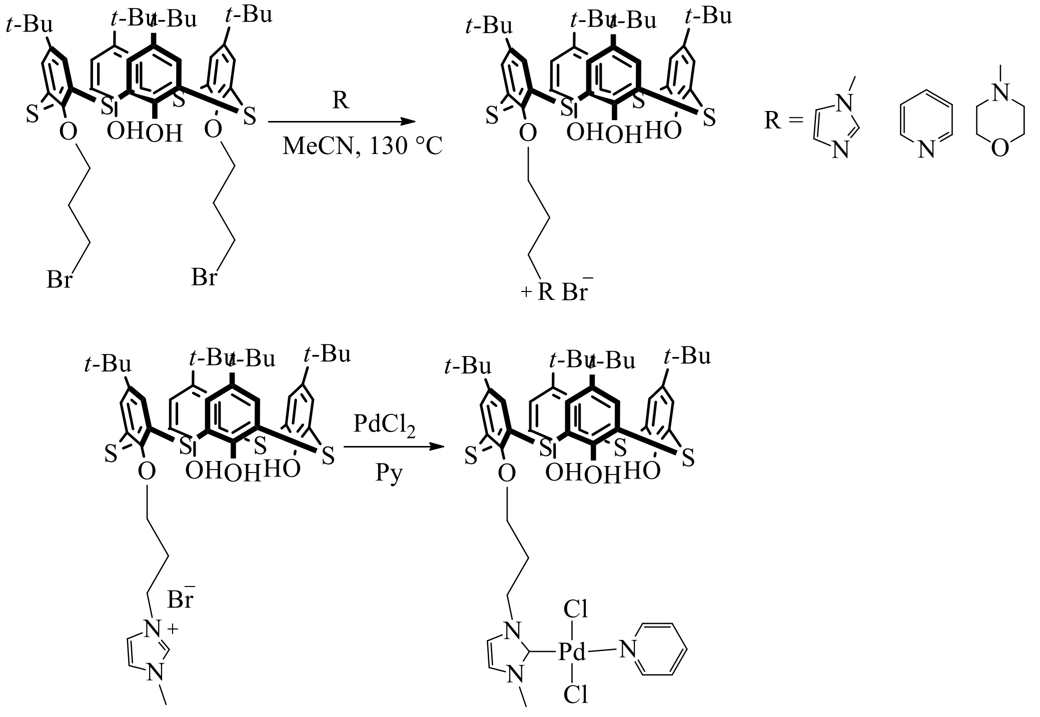

**Figure 1.** Monosubstituted derivatives of thiacalix[4]arenes

**Acknowledgements** *This study was supported by the Russian Science Foundation (Grant No. 21-73-10062).*

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# THERMOCHEMICAL PROPERTIES OF O-IMINOBENZOQUINONATO TRANSITION METAL COMPLEXES WITH EXTENDED CONJUGATED SYSTEMS

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*o*-Iminobenzoquinonato transition metal derivatives have a typical set of applications which are connected with a molecular design, magnetism, catalysis and biomedical issues. In turn, much less attention is paid to the practical fields associated with the thermal behavior. However, knowledge about the thermochemical characteristics is required for the testing of compound as a component of the perspective photovoltaic devices, for instance. At the same time, there are sporadic works devoted to the making of thin-film photovoltaic materials which suggest a layer deposition technology through the evaporation-condensation processes.

This work accumulates the thermochemical study's results towards a wide range of substituted *o*-iminobenzoquinonato complexes with extended π-systems of organic moieties. In particular, it was chosen the *ortho*-substituents (-C(O)Ph, -Ph) [1], *para*-substituents (-Ph) of N-aryl fragments, as well as naphthalene and quinoline parts in the *o*-iminobenzoquinones.

The melting point and thermodynamic parameters of melting were obtained by the DSC method using a differential scanning calorimeter DSC204F1 Phoenix («Netzsch Gerätebau», Germany).

Thermogravimetric study for the solid state samples was performed by means of a Mettler Toledo TGA/DSC 3+ («Mettler Toledo», Switzerland). Mass spectra were recorded with Polaris Q/Trace GC Ultra chromatomass spectrometer with an ion trap mass analyzer («Thermo Electron Corporation», USA), using direct insertion probe.

The temperature dependencies of the vapor pressure were measured by the Knudsen effusion method with the weight registration of the sublimated substance. Vaporization temperature intervals were taken according to the DSC data.

**Acknowledgements** The work was carried out with the support of a grant from the President of the Russian Federation for young scientists - candidates of sciences MK-3402.2021.1.3.

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# THE PATTERN OF CHANGES IN THE THERMAL PROPERTIES OF COMPOUNDS IN THE SERIES $SrLnCuSe_3$ (Ln = La – Lu)

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Complex quaternary selenides of the composition SrLnCuSe3 (Ln = La, Sm, Gd, Er) were synthesized. Compounds were obtained by the ampoule method from binary compounds $Ln_2Se_3$ (Ln = La, Sm, Gd, Er), SrSe, $Cu_{1.999}Se$. Such quaternary selenides are interesting for their semiconductor, thermoelectric, ferromagnetic and ferrimagnetic properties [1,2].

The study of thermal properties was carried out on the device SETARAM Setsys Evolution 1750, PtRh-6%–PtRh-30%. Shooting on the device was carried out under the following conditions: heating rate 5 °C/min, carrier gas – Ar, gas flow rate 50 ml/min. The DSC results were processed using the program SETSOFT 2000.

To study the regularities of the series of compounds SrLnCuSe3 (Ln = La – Lu), compounds were selected from each tetrad of the lanthanide series. $SrLaCuSe_3$ solid phase decomposes (Pic. a), $SrSmCuSe_3$ melts incongruently, SrGdCuSe3 and SrErCuSe3 melt incongruently and have 2 phase transitions each (Pic. b, c). Based on the thermal characteristics of $SrLnCuSe_3$ (Ln = La, Sm, Gd, Er), the dependences of the atomic radius and enthalpy on the thermal transformations are presented. (Pic. d, e). The thermal properties of the system of compounds SrLnCuSe3 are similar to the properties of the system we studied earlier $EuLnCuSe_3$ [1].

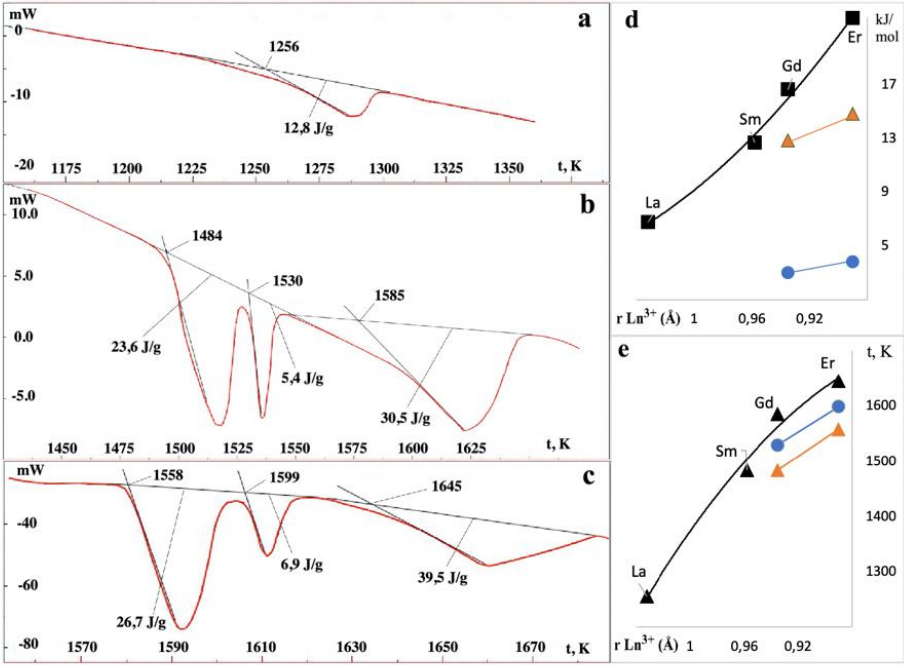

**Figure 1.** Thermograms $SrLaCuSe_3$ (a), $SrGdCuSe_3$ (b), $SrErCuSe_3$ (c), graphs of the regularity of the dependence of the atomic radius (d) and enthalpy (e) on the value of thermal transformations

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# DEVELOPMENT OF APPROACHES TO THE EVALUATION OF INTERMOLECULAR INTERACTIONS IN BINARY AZEOTROPIC SYSTEMS

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It is known that solvents determine the solubility of drugs, crystallization and extraction of many substances, change the rate of chemical reactions [1]. In turn, the use of binary solvents is of particular interest because it opens up the possibility of varying the properties of the medium for practically important tasks [2, 3]. A particular case of binary solvents are azeotropic mixtures, which are widely used in extraction processes and chemical reactions [4].

In this work the enthalpies of dissolution of linear alkanes in binary solvents, including azeotrope, are determined. The deviation of the enthalpies of dissolution of alkanes from the additive value is observed. It is shown that the maximum excess enthalpy of dissolution of an alkane falls on the azeotrope point and depend on the nature and ability of the components of the binary solvent to intermolecular interactions. It is also shown that neither the dipole moment nor the dielectric permittivity of the solvent have a significant effect on the solvation effects in binary mixtures, including azeotropic points.

The heat of vaporization of azeotropic mixtures represents one of the interesting sections of thermodynamics. Attempts have been made both to determine the enthalpy of vaporization experimentally [5] and using various models [6]. However, to date, there is not enough data to make a comparative evaluation of different methods. Therefore, the second part of the work is devoted to the study of solvation of azeotropic mixtures in heptane. The previously developed equation for the dependence of the enthalpy of solvation of nonelectrolytes on their molecular refraction was used. Using the experimentally measured physical properties of the azeotrops, the molecular refractions were determined. Using the equation and enthalpy dissolution data of the azeotropes in heptane, the enthalpies of vaporization of the azeotropes were calculated.

On the other hand, the heats of evaporation in the azeotrope series were studied. Equations for estimating the enthalpy of vaporization for azeotropes in which one of the components is water, alcohol, or alkane have been proposed. The correspondence of the calculated heats of vaporization between these equations is shown.

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# TYPING OF NEAR-CRITICAL RESERVOIR FLUIDS BY INTENSITY OF CRITICAL OPALESCENCE ON THE DEW-BUBBLE BOUNDARY CURVE

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According to the API, there are four types of near-critical reservoir fluids that are in the reservoir before its development in a single-phase state: volatile and very volatile oil, rich and very rich condensate gas. However, a clear criterion for typing these fluids, tied to their phase diagram in the vicinity of the critical point, still does not exist due to the lack of a practical criterion for classifying reservoir fluids as near-critical and critical type.

A new optical method is proposed for identifying the near-critical and critical state of reservoir fluid and, on its basis, for typing near-critical reservoir fluids by the intensity of critical opalescence on the dew-bubble curve (DBC). The idea of the method is to measure the intensity of Rayleigh light scattering in a one-phase region near the liquid-gas critical point and to determine the boundaries of the near-critical and critical regions in the form of contours, where the intensity of light scattering is an order of magnitude and two orders of magnitude higher than the intensity far from the critical point. As the latter, the value of the intensity of light scattering at a critical value of temperature and pressure, say, a few percent higher than its critical value, is taken. The temperatures of the exit points of these contours at the DBC are taking as the temperature boundaries of the critical and near-critical regions, which, together with the critical temperature, determine the temperature intervals corresponding to four different types of near-critical reservoir fluids. The described procedure is illustrated by an example of a recombined reservoir hydrocarbon mixture taken from a real gas condensate field (see Fig. 1).

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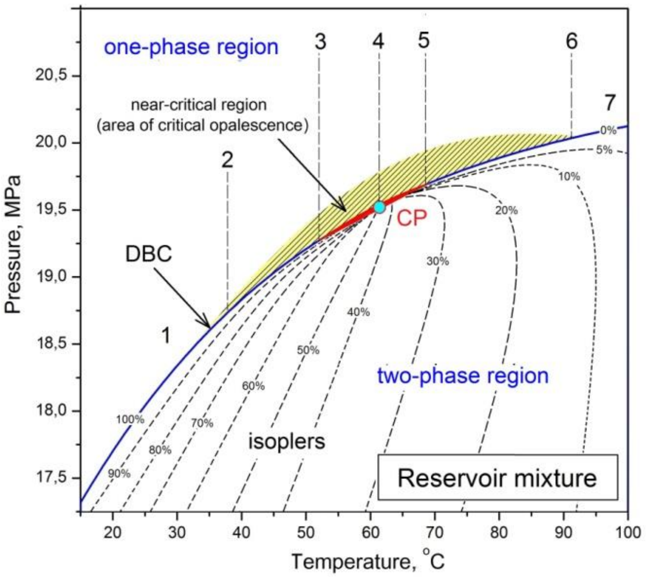

**Figure 1.** Phase diagram of studied reservoir mixture in vicinity of the critical point (CP). Global division of the phase diagram of the mixture in the one-phase region: 1 – slightly volatile (black) oil, 2 – 6 – near-critical and critical (3 –5) reservoir fluids, 7 – lean retrograde condensate gas. Types of near-critical and critical reservoir fluids: 2 – 3 – volatile oil, 3 – 4 – highly volatile (critical) oil, 4 – 5 – very rich (critical) condensate gas, 4 – 6 – rich condensate gas.

# WIDE-RANGING PREDICTION OF PHASE BEHAVIOUR IN THE SYSTEMS OF [$C_x$mim][$BF_4$] AND [$C_x$mim][$PF_6$] ($2 \leq x \leq 12$) IONIC LIQUIDS BY CP-PC-SAFT WITH UNIVERSAL $k_{ij}$ VALUE

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Just a very small part of possible data on the variety of ionic liquids (ILs) and their systems are currently reported in the literature and could be investigated experimentally in the near future. Moreover, the purity of laboratory samples is typically much higher than of industrial solvents, while reaching the equilibria states during laboratory measurements of small samples is controlled more carefully than in large-scale processes. The latter can result in significant differences between the literature data and the actual properties of IL systems employed in industrial equipment. Remarkable, at times they are noticeable deviations even between different laboratory measurements of phase equilibria in the same IL systems. These arguments emphasize a primary importance of developing thermodynamic approaches capable of simultaneous prediction of thermodynamic properties of pure ILs and their systems with reasonable accuracy and in broad range of conditions with the minimal possible referring to experimental data.

This study demonstrates that a Critical Point-based modification of the Perturbed-Chain Association Fluid Theory (CP-PC-SAFT) with molecular parameters generalized as functions of molecular weights can precisely represent the densities of 1-alkyl-3-methyl-imidazolium tetrafluoroborate and hexafluorophosphate ([$C_x$mim][$BF_4$] and [$C_x$mim][$PF_6$]) families of ILs and their mixtures with non-associated compounds in particularly wide ranges of temperatures and pressures. Its predictions of sound velocities are reasonably good as well. Moreover, using the kij value obtained for the system $CO_2$ - [$C_x$mim][$PF_6$], CP-PC-SAFT truthfully predicts VLE, LLE and LLVE in wide variety of systems comprising the considered ILs and non-associating compounds such as oxygen, methane, carbon monoxide, nitrous oxide, propane, vinyl chloride, aliphatic and aromatic hydrocarbons. Distribution rations in ternary systems are considered as well.

# STUDY OF TRANSPORT PROPERTIES OF SOLUTIONS WITH INVERSE PREMICELLAR AGGREGATES VIA MOLECULAR DYNAMICS SIMULATIONS

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Surfactants in non-polar solvents can form reverse micelles. In this work, we report results of the study of transport properties of the solution of nonionic surfactant $C_{12}E_4$ in heptane. For all considered systems, we performed all-atom molecular dynamics simulations in NPT statistical ensemble. The all-atom models were created using the CGenFF 4.4 force field [1]. To find the viscosities of colloid systems via molecular dynamics simulations, one can employ the Stokes-Einstein formula [2,3]. Palmer proposed an alternative method [4] based on the calculation of autocorrelation functions of the momentum. We used Palmer's method implemented in GROMACS 2020.1 package [5] to find the viscosities of one-component liquids (water, pentane, heptane, decane) and two-component systems consisting of hydrocarbon (heptane) and a $C_{12}E_4$ aggregate. In particular, viscosities of the systems containing inverse premicellar aggregates with 2, 4, 8, 16 and 25 $C_{12}E_4$ molecules were estimated. Our results for one-component systems are consistent with previous works of other authors. For water systems, the agreement with the results of the molecular dynamics simulation in [6] was observed. The results of the viscosity calculation for pentane matched well those from [7]. For the system containing decane, the agreement with the experimental data from [8] was observed. For the systems containing inverse micelles, we also used the Stokes-Einstein formula to estimate the viscosities. The Stokes-Einstein formula relates the viscosity of the liquid media with the size of a spherical particle in it and the particle's diffusion coefficient. The in-house programs were used to analyze the obtained molecular dynamics trajectories and to calculate the average radii of inverse premicellar aggregates and their diffusion coefficients. Thus, the dependence of viscosity on the total surfactant concentration was obtained by two different methods.

**Acknowledgements:** This work has been supported by the grant from the Russian Foundation for Basic Research (RFBR 20-03-00641_A).

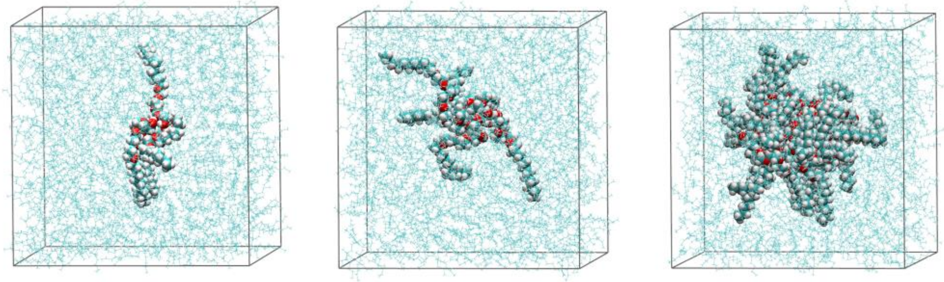

**Figure 1.** Inverse premicellar aggregates of 4, 8 and 25 $C_{12}E_4$ monomers in heptane.

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# EQUILIBRIUM AND THERMODYNAMIC PARAMETERS FOR ESTERIFICATION OF SUCCINIC, MALIC AND CITRIC ACID WITH ETHANOL

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The interest in the production and use of biorenewable chemicals is growing every year. Bio-based chemicals typically are environmentally friendly, possess low toxicity, and have favorable biodegradability, making them prime candidates for replacements of petroleum-based products. The esters of bio-based organic acids fall into the category of benign or green solvents, plasticizers and monomers. Esters of succinic, malic and citric acid attract the greatest attention of researchers. These acids can be esterified with alcohols such as ethanol and n-butanol. It's well known that the reaction esterification is equilibrium-limited and water is formed as a by-product. Design of reactive distillation processes often involves equilibrium-based models in which both phase and chemical equilibrium are achieved on each stage.

Equilibrium constant and thermodynamics parameters usually were determined by analysis of the experimental data at long reaction times. But for slow chemical reaction such as siccinic, malic and lactic esterification the time of the experimental may not be enough to reach equilibrium. So, in this work equilibrium constant and thermodynamics parameters were determinate in a closed system (ampoules) in the temperature range 343.2-373.2 K and long time experiments (15-30 days). The experiment was carried out under conditions of a 5-fold molar excess of ethanol. Samples were analyzed 2-3 times by gas chromatograph equipped with a flame ionization detector and thermal conductivity detector. To calculate the equilibrium constants, the values of the activity coefficients were taken from the literature data on liquid-vapor and liquid-liquid phase equilibrium [1,2].

**Acknowledgements.** The financial support of the Russian Foundation for Basic Research, project no. 20-08-01050_a.

**Table 1.** Equilibrium constant and reaction enthalpies for esterification of succinic, malic and citric acid with ethanol

| Reaction | $\Delta_r H_m^o(liq)$, kJ/mol | T, K | $K_{a1}$ | $K_{a2}$ | |
|---|---|---|---|---|---|
| Succinic acid + EtOH ↔ MES + $H_2O$ (1) | -11,13±0,69 | 343,2 | 8,42 | 4,07 | |
| | | 353,2 | 7,71 | 3,81 | |
| | -12,53±1,79 | 363,2 | 6,91 | 3,35 | |
| MES + EtOH ↔ DES + $H_2O$ (2) | | 373,2 | 6,16 | 2,86 | |
| | | T, K | $K_{a1}$ | $K_{a2}$ | |
| Malic acid + EtOH ↔ MEM + $H_2O$ (1) | -6,05±0,40 | 323,2 | 10,95 | 2,43 | |
| | | 333,2 | 10,33 | 2,28 | |
| MES + EtOH ↔ DEM + $H_2O$ (2) | -7,86±0,45 | 343,2 | 9,63 | 2,11 | |
| | | 353,2 | 9,27 | 1,95 | |
| Citric acid + EtOH ↔ MEC + $H_2O$ (1) | -8,73±0,69 | T, K | $K_{a1}$ | $K_{a2}$ | $K_{a3}$ |
| | | 323,2 | 15,87 | 5,35 | 7,20 |
| MEC + EtOH ↔ DEC + $H_2O$ (2) | -12,63±0,77 | 333,2 | 14,63 | 5,38 | 7,29 |
| | | 343,2 | 13,70 | 4,83 | 6,35 |
| DEC + EtOH ↔ TEC + $H_2O$ (3) | -12,19± 1,53 | 353,2 | 12,33 | 4,27 | 5,84 |

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# SURFACE FREE ENERGY OF CRITICAL CRYSTAL NUCLEI AND CAVITIES: MOLECULAR DYNAMICS SIMULATION

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The kinetics of crystallization and cavitation of a metastable Lennard-Jones liquid was studied using the Direct Forward Flux Sampling (DFFS) method and the seeding approach in molecular dynamics simulation. The calculations were carried out in a system containing from 5 000 to 300 000 interacting particles at a wide range of temperatures and pressures.

We used two ways of determining the surface free energy of critical nuclei (γ). The first was to calculate γ from DFFS data on the nucleation rate and diffusion coefficient of nuclei using the equations of the classical nucleation theory (CNT). The second method involves calculation γ according to the Laplace equation using data on the sizes of critical nuclei (R) from the seeding approach. The use of two methods made it possible to establish the dependence of γ on R for nuclei with radii from 0.9 to 4.4 nm (see Fig. 1).

The surface free energy of critical cavities is directly proportional to the curvature of the interface ($1/R$) and is less than its value at a flat liquid-gas surface. In contrast for critical crystal nuclei the dependence $\gamma(1/R)$ is quadratic and has a maximum, the value of which depends on the temperature.

**Acknowledgments** The investigation has been conducted at the expense of a grant of the Russian Science Foundation (project N. 18-19-00276-P). Computations were performed on the Uran supercomputer at the IMM UB RAS.

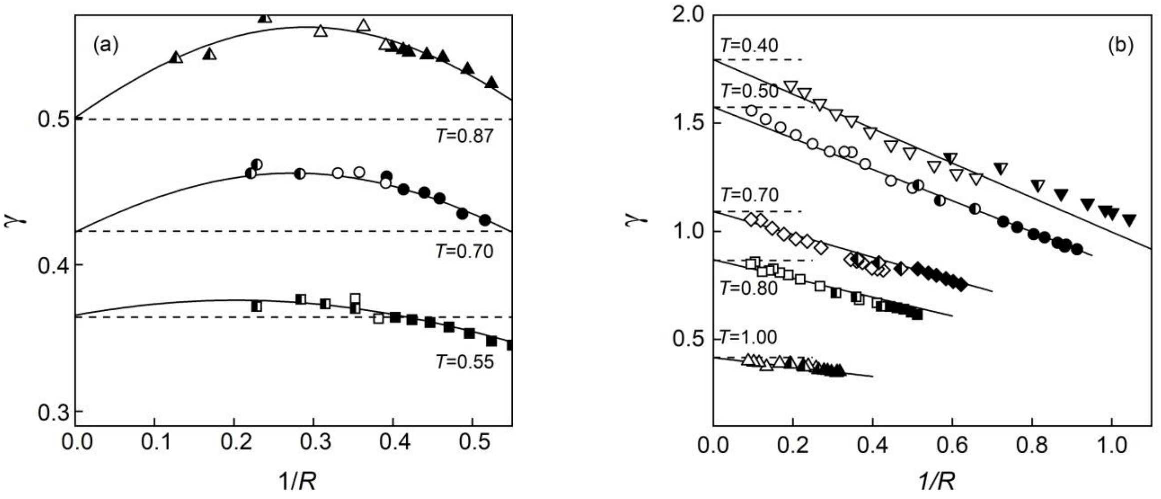

**Figure 1.** Surface free energy of critical nuclei of the crystalline phase (a) and cavity (b). Open points refer to the results of the DFFS, half-filled points refer to the seeding approach, filled points refer to the mean lifetime method. Dashed lines are the surface free energy at a flat interfacial boundary, solid lines are an approximation of the MD data. All quantities are given in a dimensionless form, the reduction units are the parameters of the interaction potential.

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# NUCLEATION IN LENNARD-JONES SOLUTIONS WITH COMPLETE AND PARTIAL SOLUBILITY OF THE COMPONENTS: MOLECULAR DYNAMIC SIMULATION

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The kinetics of homogeneous nucleation of the vapor-gas phase has been studied by the molecular dynamics (MD) method in Lennard-Jones (LJ) systems simulating solutions with partial (*A*) and complete (*B*) solubility of components. Solutions *A* and *B* had the same solvent but different solutes. Calculations were carried out the temperature close to triple point temperature of the solvent, concentrations of the solute $c = 0$, 0.1 and 0.2 and negative pressures $p$. The parameters of phase equilibrium, surface tension at a flat interface liquid-vapor, and pressure as a function of density and concentration are determined in stable and metastable states of solutions. The pressure in the critical bubble has been found from the condition of material equilibrium of the nucleus–solution and the work of formation of the critical nucleus and rate of nucleation have been calculated. At $c < 0.2$ and the nucleation rate $J = 10^{31} - 10^{35}$ m$^{-1}$s$^{-1}$, the ultimate stretching $\Delta p = p_s - p$, where $p_s$ are the saturation pressures, achieved in the MD model of solution *B*, are less than those calculated from the classical theory of nucleation. In solution *A*, at $c > 0.14$, the value $\Delta p$ achieved in the model exceed their theoretical values.

A qualitative difference was established in the formation and growth of a vapor-gas nucleus in solutions *A* and *B* (Fig. 1). In solution *A*, the partial density of the solvent sharply decreases and the density of the volatile component increases at the region of the bubble formation. In solution *B*, at the initial stage of bubble formation, the density of the volatile component inside the bubble remains close to the density in the surrounding phase, and the density of the solvent decreases. This ensures the formation of an equilibrium composition in critical bubbles and interfacial layers.

**Acknowledgements** The authors are grateful to the Supercomputing Center of the Institute of Mathematics and Mechanics of UB RAS for kindly providing the computer facilities for this work. The investigation has been conducted at the expense of a grant of the Russian Science Foundation (project № 18-19-00276-P).

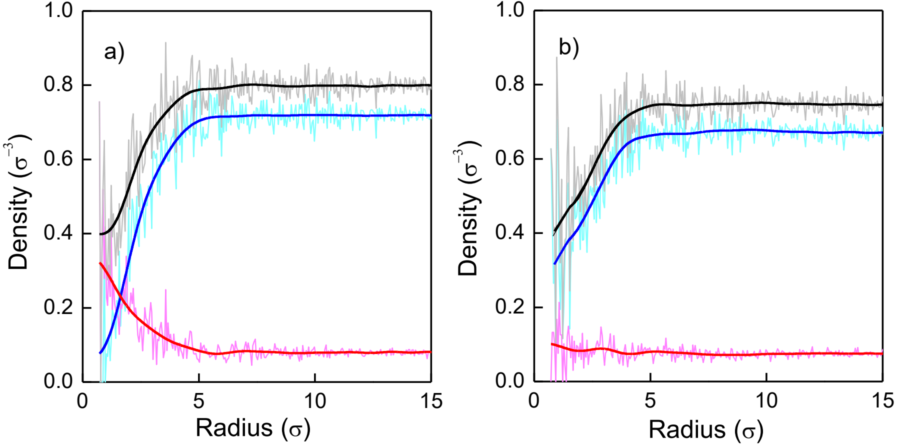

**Figure 1.** Radial density profiles at the places of bubble formation at times preceding a rapid pressure increase in mixture *A* (*a*) and *B* (*b*) at $c = 0.1$ (σ is the linear параметр of LJ potential of solvent). The black lines are the density of the solution, the blue and red lines are the partial density of the solvent and solute, respectively.

# THE EFFECT OF ORANGE OT IONIZATION ON SOLUBILIZATION BY CATIONIC MORPHOLINIUM SURFACTANTS.

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Aggregation behavior of cationic morpholinium surfactants (MS-16 and MS(OH)-16, fig.1) was characterized individually and with various additives to evaluate their hydrotropic and solubilizing potential. The compositions were thoroughly characterized from the self-assembly standpoint, using surface tension and spectrophotometric dye solubilization techniques and evaluated for application in biomedical and other practical areas. It was shown that in the interactions between the surfactant, the solubilized dye and the additive, pH plays a critical role, allowing joint aggregation of the surfactant and dye. [1]

Ethanolamines, owing to their basicity, increase the pH and lead to an order of magnitude of solubilization capacity increase, due to weak acidity of Orange OT phenolic group. Interestingly, on its own, phenol ionization is not sufficient to provide high solubility of Orange OT without the cationic surfactant. As proposed by Holmberg et al. [2], we conclude that cooperative aggregation of surfactant molecules and ionized solubilizate molecules takes place (fig. 2). This work shows similar effects to what was observed before, and suggests a generalization for the increase of solubility of hydrophobic weak acids.

**Acknowledgements** Authors are grateful for financial support from the government assignment for FRC Kazan Scientific Center of RAS.

N-hexadecyl-N-methyl-morpholinium bromide (MS-16)

N-hexadecyl-N-hydroxyethyl-morpholinium bromide (MS(OH)-16)

**Figure 1.** Structural formulas of the studied compounds

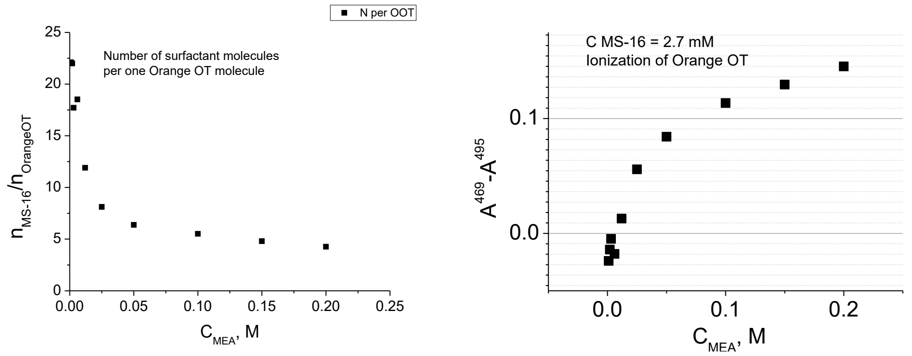

**Figure 2.** (a) Stoichiometry between surfactant and Orange OT at different MEA concentrations. (b) Appearance of ionized state Orange OT absorption band at 469 nm.

[1] R.V Pavlov, F.G. Valeeva, G.A. Gaynanova, D.M. Kuznetsov, L.Y. Zakharova, *Surf. Innov*, 2022, doi: 10.1680/jsuin.22.00006

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# SELF-ASSEMBLY OF CATIONIC SURFACTANTS IN THE PRESENCE OF ATP AS A BIOLOGICAL HYDROTROPE

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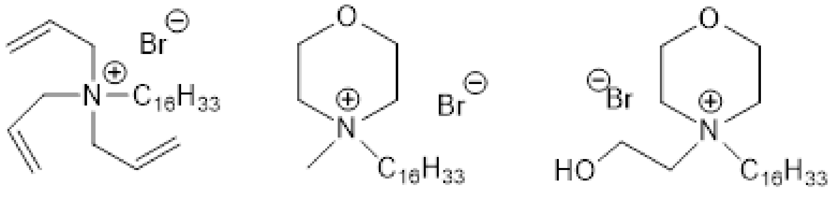
The hydrotropic additives to surfactant solutions make it possible to reduce the concentration thresholds of aggregation, regulate the solubilization capacity of micellar systems, and the dimensional characteristics of the aggregates, which significantly expands the scope of synthetic surfactants. Adenosine triphosphate (ATP) is a major chemical energy source necessary for all biochemical reactions within cells, and also serves as building block of ribonucleic acids. Patel et al. shows that ATP at concentrations found in cells can act as a biological hydrotrope, to help significantly enhance the solubility of proteins. [1-3].

In this regard, it was interesting to study the effect of the biological hydrotrope ATP on the functional properties of cationic surfactants with different structures of the head group (triallyl (TAS-16), morpholinium (MS-16), morpholinium with a hydroxyethyl fragment MS-16(OH)). Structural formulas of the surfactant are given in figure 1. The properties of the mixed systems were studied using a complex of physicochemical methods: tensiometry, conductometry, spectrophotometry, and fluorescence spectroscopy. It should be noted that in the absence of additives, the critical micelle concentration (CMC) of the studied surfactants is 1 mM and practically does not depend on the structure of the head group. All measurements were performed by varying the surfactant concentration at a fixed ATP concentration of 0.5, 1, and 3 mM.

It was shown that the ATP addition to aqueous solutions of amphiphiles at a concentration of 0.5 mM causes a 10-fold decrease in the CMC, and a further increase in its concentration does not affect the aggregation threshold. When ATP was added to aqueous solutions of a morpholinium surfactant with a hydroxyethyl fragment (MS-16(OH)) a strong turbidity was observed, followed by phase separation of the system. It is likely that, in addition to electrostatic interaction, hydrogen bonding is also observed between the components in this case. On the other hand, the solubilization capacity of mixed surfactant-ATP systems with respect to the antifungal drug amphotericin B is controlled by the structure of the surfactant head group.

**Acknowledgements** Authors are grateful for financial support from the government assignment for FRC Kazan Scientific Center of RAS.



**TAS-16** **MS-16** **MS-16 (OH)**

**Figure 1.** Structural formulas of surfactants studied.

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# NONLOCAL ELECTROSTATIC APPROACH TO STABILIZATION OF MONOVALENT CATIONS IN AQUEOUS CAVITY OF ION CHANNEL

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The energy of the image forces $U_{\text{im}}$ acting on $K^+$ in the center of aqueous cavity of ionic channel is calculated in [1, 2] by the Eq.(1), in which $\varepsilon_{\text{cav}}$ and $\varepsilon_{\text{p}}$ are the dielectric permittivity's of the cavity and its environment, $R_{\text{cav}}$ radius of cavity:

$$U_{im} = (e^2/2R_{\text{CAV}})[1/\varepsilon_{\text{P}} - 1/\varepsilon_{\text{CAV}}],\ (1)\ \{[1]:\varepsilon_{\text{CAV}} = \varepsilon_{\text{S}} \approx 80, U_{im}\ \text{Fig.1(b)};\quad [2]:\varepsilon_{\text{CAV}} \approx 5, U_{im}\ \text{Fig.1(a)}\}$$

Let us consider the change in $\Delta\mu$ of the standard chemical potential $K^+$ during its transition from solution to cavity the channel. The $\Delta\mu$ is calculated by Eq. (2), in which $r_{\text{K}}$ is the radius of $K^+$:

$$\Delta\mu_{CE} = (e^2/2r_K)[1-1/\varepsilon_{\text{S}}] - (e^2/2r_K)[1-1/80]\quad (2a),\qquad \Delta\mu_{NE} = W_{NE} - (e^2/2r_K)[1-1/5]\quad (2b)$$

Then the first term in Eq. (2) is the ion's solvation energy in a free solution, and the second term is the solvation energy in the channel cavity. We calculate $W_{\text{NE}}$ in Eq.(2b) according to the formulas of nonlocal electrostatic [3]:

$$W_{\text{NE}} = (e^2/\pi)\int_0^\infty [\sin kr_{\text{K}}/kr_{\text{K}}]^2[1-1/\varepsilon(k)]\,dk,\quad \varepsilon(k) = \varepsilon_o(k) + \varepsilon_S/[kL_D]^2$$

where $k$ is wave number, $\varepsilon(k)$ is the Fourier transform of the dielectric function of the solution with the Debye length $L_{\text{D}}$ ($L_{\text{D}} \approx 8$ Å at $c = 0.15$ M), $\varepsilon_{\text{s}} \approx 80$, $\varepsilon_{\text{o}}(k)$ is the dielectric function of water (see in [3]). The change in the free energy ΔG of the transition of the ion frome the free solution to the channel cavity is calculated by Eqs. (3): $\Delta G_{\text{NE}} = \Delta\mu_{\text{NE}} + U_{\text{im}}$ (3a), $\Delta G_{\text{CE}} = \Delta\mu_{\text{CE}} + U_{\text{im}}$ (3b).

From Fig. 1(a) it follows that for $\varepsilon_{\text{p}} = 3.8$ the change in free energy is zero ($\Delta G_{\text{NE}} = 0$, point on the curve $\Delta G_{\text{NE}}(\varepsilon_{\text{p}})$). Therefore, calculations based on nonlocal electrostatics (NE) explain the stabilization of $K^+$ in a nanometer-sized cavity, in contrast to calculations of ΔG by classical electrostatic (CE) (Fig 1(b)) and conclusions made in [1].

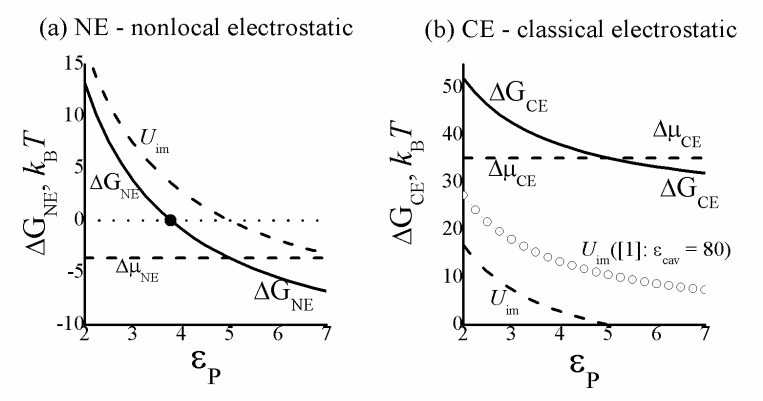

**Figure 1.** Dependence of the change in free energy $\Delta G_{\text{NE}}$ (Eq. (3a), and $\Delta G_{\text{CE}}$ Eq. (3b) (solid curves) of the transition of the $K^+$ cation from a free solution to the center of a spherical water cavity with a radius of $R_{\text{cav}} = 5$ Å on the dielectric constant $\varepsilon_{\text{p}}$ of the medium surrounding the cavity.

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# NONLOCAL ELECTROSTATIC CALCULATION OF ION SOLVATION ENERGY. EFFECT OF THE DISTRIBUTION OF A PART OF THE ELECTRONIC CHARGE OUTSIDE OF THE ION FOR THE CATION AND ANION

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Solvation energy of an ion in nonlocal electrostatics according [1] calculated by: $W = (1/\pi) \int [\rho(k)]^2 [1 - 1/\varepsilon(k)]\, dk$, $(0 < k < \infty)$. (1)
where $\rho(k)$ is Fourier transform of charge distribution $\rho(r)$ of ion, and $\varepsilon(k)$ is Fourier transform of the dielectric function of water was described as a set of three "pole terms": $[1/\varepsilon(k)] = 1 - \{C_1[1+ (k\lambda_1)^2]^{-1} + C_2[1+ (k\lambda_2)^2]^{-1} + C_3[1+ (k\lambda_3)^2]^{-1}\}$ (2)
The idea of paper [2] about effect of cut-out of solution from ion volume was used in [3]. As it was demonstrated in [3] for calculation of solvation energy of an ion on Eq.(1) a charge of ion $e\mathrm{Q}_{\mathrm{cav}}$, localized inside born sphere of an ion (BS, $r_\mathrm{i}$ - its radius), should be carry over on born sphere: $\rho_{\mathrm{cav}} (r, \mathrm{Q}_{\mathrm{cav}}) \rightarrow \rho_{\mathrm{BS}}(r, \mathrm{Q}_{\mathrm{cav}}) = [e\mathrm{Q}_{\mathrm{cav}} /(4\pi r_\mathrm{i}^2)]\, \delta(r - r_\mathrm{i})$, (3) where $e$ absolute value of electronic charge. Now we take into consideration distribution of part of electron's charge outside BS. We suggest that charge $e\mathrm{Q}_{\mathrm{ext}}$ outside BS is negative for cation and for anion ($\mathrm{Q}_{\mathrm{ext}} < 0$). Note, that in theory [1] charge outside BS for cation was positive. Total charge of the ion, $\mathrm{z_i}e$ ($\mathrm{z_i}$ – sign of ionic charge), is composed of these two contributions: $\mathrm{z_i}e = [\mathrm{Q}_{\mathrm{cav}} + \mathrm{Q}_{\mathrm{ext}}]e$. We calculate solvation energies for monovalent ions ($\mathrm{z_i} = 1$ for cation, and $\mathrm{z_i} = -1$ for anion). The electronic charge density $\rho_{\mathrm{ext}}(r, \eta, \mathrm{Q}_{\mathrm{ext}})$ outside the BS may be approximated by Eq. (25) in [3].

$$W(\mathrm{Q}_{\mathrm{ext}}) = \frac{1}{\pi}\int_0^{\infty}[1-1/\varepsilon(k)]\,\{e(\mathrm{z}_i-\mathrm{Q}_{\mathrm{ext}})\sin kr_i/kr_i+(4\pi/k)\int_{r_i}^{\infty} r\rho_{\mathrm{ext}}(r,\mathrm{Q}_{\mathrm{ext}})\sin kr\,dr\}^2\,dk \qquad (4)$$

Eq. (4) is derived from Eqs. (1), (3). Line *4* on Fig. 1 corresponds to experimental data [4]. So, this theory, can explain a difference between solvation energies of cation and anion with equals radii.

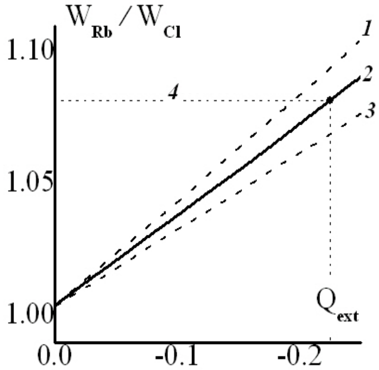

**Figure 1.** Dependence of ration solvation energies W for $\mathrm{Rb}^+$ and $\mathrm{Cl}^-$ calculated by Eqs.(2)-(4) as a function of negative electronic charge $\mathrm{Q}_{\mathrm{ext}}$, which localized outside born sphere of ion. Parameter $\eta$ in $\rho_{\mathrm{ext}}$ for lines *1, 2, 3* equals 0.4, 0.35, 0.3. The radii $r_\mathrm{i}$ of $\mathrm{Rb}^+$ and $\mathrm{Cl}^-$ are taken: 1.63Å and 1.64Å.

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# PHYSICAL PROPERTIES OF Al-Ni-Co-REM GLASS-FORMING ALLOYS IN CRYSTALLINE AND LIQUID STATES

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Aluminum-based metallic glasses (Al > 80 at.%) with 3d-transition metals (TM) and rare earth metals (REM) have unique physical properties, combining high strength and plasticity together with high corrosion resistance. Nowadays these alloys are used as protecting materials in the devices working in aggressive medium. However, their physical properties in crystalline and liquid states are practically unknown. At the same time, the melt state before quenching can influence greatly the structure and properties of solidified materials.

In this work we investigated density and electrical resistivity of Al-Ni-Co-R (R = Nd, Sm, Gd, Tb, Yb) alloys in solid and liquid states with the different Ni/Co ratio.

Density was determined using the absolute variant of gamma-absorption method on an automated installation with the accuracy of ± 1%. Electrical resistivity was studied by contactless method in rotating magnetic field. The accuracy of resistivity values determination is estimated to be ± 3%.

It was found that all the compositions have a wide two-phase zone and specific behavior of properties at liquidus temperature. Hysteresis of density (i.e. incoincidence of heating and cooling curves) was found for all the alloys.

The optimal combinations of Ni/Co ratio and rare-earth elements providing high thermal stability and glass forming ability of the alloys were established. In particular, the alloys with equal amounts of nickel and cobalt demonstrate higher thermal stability and glass forming ability. The regime of melts heat treatment before crystallization/quenching was provided.

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# CALCULATION OF VAPORIZATION ENTHALPIES OF METHANOL – TETRAHYDROFURAN – ACETONITRILE AT ATMOSPHERIC PRESSURE

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The molar vaporization enthalpies ($H_v$) of mixtures are needed to estimate the energy consumption of distillation columns. Experimental data «composition − $H_v$» are limited, so it is necessary to develop computational methods. Such method was proposed for binary systems [1, 2]. For the ternary system, it is used for the first time. The arrays «composition − $H_v$ » arrays are calculated based on *dP/dT* dependence for pure substances $H_{vi}{}^{0}$ (1) and mixtures (2) [1]. $H_v$ are determined from vapor–liquid equilibrium (VLE). VLE was modeled using NRTL equation.

The molar vaporization enthalpies for methanol (M) – tetrahydrofuran (T) – acetonitrile (A) system were calculated at 101.32 kPa. There are three binary azeotropes (min T) in M–T–A system (Fig. 1a). The diagram isolines of vaporization enthalpies constructed according to the calculated data is shown in Fig. 1b.

The array of vaporization enthalpies for M–T–A system was also determinated by additivity. The structure of the excess enthalpy of vaporization diagram is more complex (not given here). The M–T–A system is characterized by positive and negative values of excess vaporization enthalpy, and the latter is adjacent to constituent M–A. The greatest deviations from the additive values were recorded in the composition region nearly A-T. The relative error reach 8.5%.

So it is necessary for non-ideal ternary mixture the excess enthalpy of vaporization to take into account.

$$H_{vi}^{0} = \frac{dP_i^0}{dT}\frac{RT^2}{P_i^0} \qquad (1)$$

$$H_v = \frac{dP}{dT}\frac{RT^2}{P} \qquad (2)$$

**Acknowledgements** This work was financially supported by the Ministry of Education and Science of the Russian Federation (state assignment No. 0706-2020-0020).

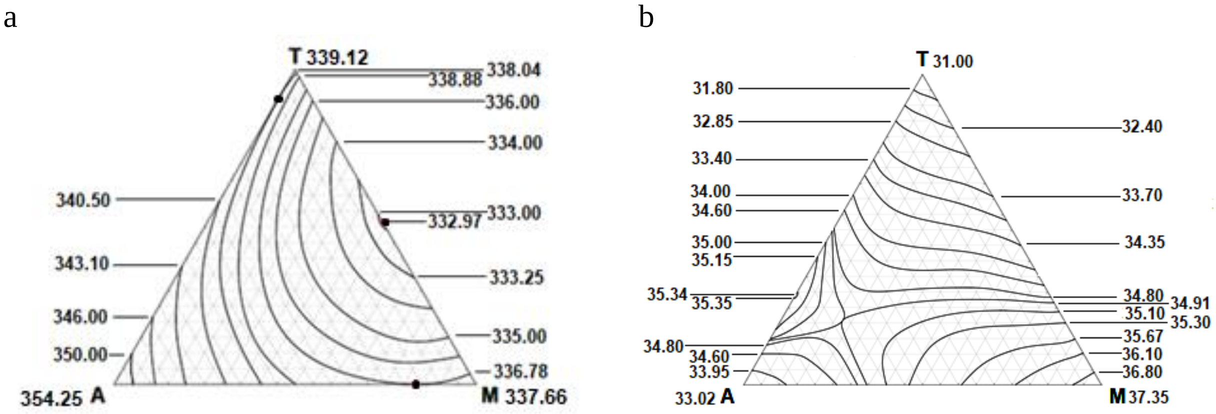

**Figure 1.** Diagrams isoline of methanol (M) – tetrahydrofuran (T) – acetonitrile (A) at 101.32 kPa: a− temperature (K); b − vaporization enthalpy (kJ/mol)

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# HIGH-PRESSURE POLYMORPHISM OF MOLECULAR CRYSTALS – THERMODYNAMIC AND CRYSTALLOGRAPHIC APPROACHES. PERSONAL VIEW

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High-pressure polymorphism of molecular crystal is widely and extensively studied phenomenon. New forms of organic crystals are critical for pharmaceutical industry, due to control of thermodynamic and kinetic properties, such as solubility, dissolution rate, bioavailability, etc.[1] It is also very important for high-energy materials, where high pressures and temperatures may influence combustion rate and other valuable characteristics for energy release.[2] High-pressure techniques help to form and (rarely) preserve these new phases which may be stable or metastable. Moreover, it is stated that investigations of high-pressure behavior result in understanding the nature of molecular crystal formation.

Despite phase transitions has a very strict definitions and classification, this concept is used vaguely and widely for many systems. Researchers usually use single-crystal or powder X-Ray diffraction as well as Raman spectroscopy techniques to monitor and define phase transitions in solid state. Whilst, first Gibbs energy derivative should be monitored to state first order phase transition, diffraction changes are commonly used as a proof of new phase formation. Another option is usage of equation of states to plot volume/pressure graph and control volume change. Final point is DFT calculations which may give phase energies directly. These three techniques are compared in this work to find questionable phase transitions and discuss possible uncertainties. For all techniques limitations and prospects are discussed, showing how combination of them should be used.

Application of different techniques, describing phase transitions are demonstrated for several systems, where new phases may be at least questionable as well as conclusions about phase stability. Such systems as L-serine, L-leucinium hydrogen maleate, di-p-tolyl disulfide and several others are described using all three techniques to show uncertainties in describing new phases, their thermodynamic (meta)stability and some key properties.

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# THERMAL-PHYSICAL PROPERTIES OF POLYMER NANOCOMPOSITES CONTAINING POLY(TANONIUM OXIDE) WITH IMMOBILIZED Au AND Ag NANOPARTICLES

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Powdered $TiO_2$ of anatase allotropic modification is currently one of the most common photocatalysts due to its ability to UV-induced reversible transition of $Ti^{4+}+e^{-}\leftrightarrow Ti^{3+}$ with the generation of electron-hole pairs and the formation of active oxygen forms on the surface. Due to this property, the obtaining materials containing nanostructured $TiO_2$ in a polymeric stabilizer matrix is of practical importance for the development of photocatalytic systems for wastewater treatment of dye production and self-cleaning coatings. In the last two decades, intense research has been conducted to enhance the photosensitivity of $TiO_2$ by immobilizing gold and silver nanoparticles (NPs) on its surface, which expand the working wavelength range of the composites. At the same time, the whole set of material properties is also changed, among which the most important performance characteristics are thermal and physical properties.

In the present work the influence of poly(titanium oxide) (PTO) doping with Au and Ag nanoparticles in the organic polymer matrix of poly(hydroxyethyl methacrylate) on the composites thermal physical properties has investigated. In situ modification of the PTO by Au and Ag nanoparticles was carried out in the process of synthesis of composites from the corresponding precursors. Using the methods of scanning electron microscopy and X-ray scattering at small angles, it was found that Au and Ag nanoparticles were formed in the vicinity of the PTO and had an average size of 8 and 12 nm, respectively. The thermal physical properties of composites were investigated in static and dynamic modes - by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) methods. The first is important for the processing of materials, and the second in terms of their operation. The DSC method established a sharp decrease in the glass transition temperature ($T_g$) of the materials from ~ 151 to ~ 80°C in the presence of even small amounts of NPs. This effect intensifies with an increase in the NPs concentration from 0.01 wt.% to ~ 0.2 wt.%, after which $T_g$ remains practically constant. The downward trend in $T_g$ is coincide with the DMA data. However, it is noteworthy that under dynamic loading conditions a shift of $T_g$ to a lower temperature as compared to the results obtained by the DSC method is observed both for the initial polymer matrix - from 151 to 118 °C, and for nanocomposites based on them - to 56 and 75 °C for Ag and Au NPs, respectively, which is caused not only by the thermodynamic mobility of macromolecules but also by the kinetic one. The observed phenomenon may be associated with a change in the structure of the polymer matrix in the presence of NPs and the differences in their thermal conductivities, due to which a dual mechanism of heat transfer is possible - diffusion and ballistic. Sucrose, heating faster, transfers energy in the form of heat to macromolecules of the organic polymer matrix, facilitating the mobility of its segments adjacent to the transition region between the Sucrose and the polymer volume.

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# ALTERNATIVE METHOD FOR ESTIMATION OF PHASE TRANSITION ENTHALPIES OF ALIPHATIC COMPOUNDS

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Phase transitions play an important role in many chemical and physical processes. Knowledge of the thermochemistry of the processes of vaporization, sublimation and fusion is necessary for calculating the heat balance, thermal stability and parameters of the purification processes of substances. The enthalpies of these processes are used to calculate important physical parameters such as the enthalpies of formation, solubility and vapor pressure.

Methods for determining the vaporization and sublimation enthalpies can be divided into direct (calorimetric) and indirect (based on the dependence of saturated vapor pressure). Calorimetric methods make it possible to measure these values at 298.15 K, however, they are only suitable for volatile compounds. Indirect methods are associated with the heating of a substance, which causes difficulties in the study of highly volatile, thermally unstable, explosive compounds. Therefore, the development of alternative methods for estimation of phase transitions enthalpies at 298.15 K, suitable for a wide range of compounds, is an actual task.

In work [1] was proposed the solution calorimetry method, which allows to determine the enthalpies of vaporization and sublimation at 298.15 K. This method is based on the following equation:

$$\Delta_{\text{vap/sub}}H^{\text{A}_i} = \Delta_{\text{soln}}H^{\text{A}_i/\text{S}} - \Delta_{\text{solv}}H^{\text{A}_i/\text{S}}$$

(1)

Solution enthalpy ($\Delta_{\text{soln}}H^{\text{A}_i/\text{S}}$) in equation (1) can be measured by solution calorimetry or found from excess enthalpies of mixing. Solvation enthalpy ($\Delta_{\text{solv}}H^{\text{A}_i/\text{S}}$) in this method can be calculated from different approaches [2].

In this work, we propose additive scheme for calculation solvation enthalpies of aliphatic compounds in *n*-heptane:

$$\Delta_{\text{solv}}H^{A_i/S} = \sum_{i=1}^{g} n_i \cdot h_i$$

(2),

where $n_i$ – number of structural parameter ($h_j$).

The standard deviation between solvation enthalpies calculated by the additive scheme (eq. 2) and experimental values (eq. 1) was 0.9 kJ·mol$^{-1}$.

The method for estimation of vaporization and sublimation enthalpies of aliphatic compounds based on eqs. (1) and (2) was proposed. This method was tested on 58 compounds. The standard deviation between evaluated and experimental values was 1.0 kJ·mol$^{-1}$. Proposed method was used to determine vaporization enthalpies for 46 compounds at the first time.

In addition, in this work, was proposed approach for estimation of fusion enthalpies of aliphatic compounds at 298.15 K. Proposed approach was validated on 10 compounds. The standard deviation between calculated and experimental values was 1.1 kJ·mol$^{-1}$.

Thus, in the present work, were developed methods for determination of vaporization, sublimation, and fusion enthalpies of aliphatic compounds at 298.15 K.

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# ON THE PROBLEM OF THE PREDICTION OF STABILITY/INSTABILITY FOR NANOCLUSTERS AND NANOALLOYS: THEORETICAL APPROACH AND COMPUTER SUMULATION

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The problem of stability of nanoparticles and nanostructured materials is of interest from both fundamental and applied points of view. It acquires a technological soundness in recent years. However, to date, the problem of stability/instability of nanoparticles does not even have a clear statement and, accordingly, an exhaustive solution, despite of its significance. In [1-3], conditions for the mechanical stability of isolated nanoparticles and nanoparticles in a solid matrix were obtained and analyzed, which follow from the non-negativity of the second variation of the free energy of the system. The stability/instability of the core-shell nanostructures A@B and B@A where the first component (figuring before symbol @) corresponds to the particle core and the second to its shell was analyzed in the frame of a hypothesis on the relationship between the spontaneous surface segregation of one of the components of binary nanoparticles A-B using the results of the computer simulation [4-6]. Different scenarios of the loss of stability are possible. As a rule it can be observed four such scenarios in computer experiments: (1) transformation of the A@B nanostructure into the alternative B@A one; (2) the core-shell structure can transform into a binary nanoparticle with the uniform (in some approximations) distribution of components; (3) the A@B nanostructure transforms into a Janus structure and (4) the A@B nanoparticle disintegrates into smaller nanoclusters. The mono- and bimetallic nanowires may also demonstrate the structural instability [7]. We also plan to discuss theoretical approaches [8] to evaluation of the size dependence of the surface energy which relates to prediction of stability/instability scenarios. Besides, some visual computer simulation data on structural instability will be presented.

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# THERMODYNAMICS OF SOLVATION IN THE MIXTURES OF ORGANIC SOLVENTS AND INORGANIC SALTS

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Ionic liquids exhibit solvophobic effects which lead to their self-assembly into mesoscopic supramolecular aggregates and a relatively low solubility of nonpolar compounds [1]. It was shown that in aprotic ionic liquids, the Gibbs free energy of solvation of hydrocarbons grows up with increasing concentration of ion pairs in the liquid [2]. Solutions of inorganic salts in organic solvents are quite similar to ionic liquids and can be used as a model to study the influence of ion concentration and other factors on the solvation properties.

In the present work, the solvation of hydrocarbons in solutions of sodium iodide and lithium bromide in methanol and tetrahydrofuran has been investigated. The studied solutes were aromatic and aliphatic hydrocarbons. The Gibbs free energy of solvation was calculated from the values of limiting activity coefficients obtained by headspace analysis.

For all solute+[salt+organic solvent] systems, the Gibbs free energy of solvation increases with increasing ion concentration. The value of the $CH_2$ group increment does not depend on the nature of the salt. This evidences the strengthening of the solvophobic effect with an increase of ion concentration, which is in a good agreement with the tendency observed for the solvophobic effect in ionic liquids.

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# ISOBARIC MOLAR HEAT CAPACITY AND MELTING PARAMETERS OF 1-ETHYL- AND 1-BUTHYL-3-METHYLIMIDAZOLIUM METHANESULFONATES

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Imidazolinium ionic liquids containing methanesulfonate ions are commercially demanded along with ionic liquids containing classical anions such as chlorine, bromine, and acetate [1]. This is since the production of methanesulfonic acid has recently increased by applying one-stage synthesis method with a high yield [2]. It should also be emphasized that methanesulfonates is biodegradable [3], and ionic liquids attract are of interest to scientists and technologists due to unique properties, such as low vapor pressure, high thermal stability, and capability to recovery in solvent possesses. The objects of the present study are two ionic liquids 1-ethyl- and 1-buthyl-3-methylimidazolium methanesulfonates (([$C_2$mim][$SO_3CH_3$]) and [$C_4$mim][$SO_3CH_3$], respectively).

Information on thermodynamic properties of these ionic liquids is fragmentary presented in literature. It is known enthalpies of formation of these substances in the liquid and gaseous state [4]. However, [$C_2$mim][$SO_3CH_3$] and [$C_4$mim][$SO_3CH_3$] are solid at the room temperature. To recalculate the thermodynamic functions of formation from liquid to the solid state, it is necessary to know the melting points, heats of fusion, and the isobaric heat capacity of solid and liquid phases of the compounds. There are data on the isobaric heat capacity of liquid [$C_2$mim][$SO_3CH_3$] [5], ones for solid phase and for another ionic liquid [$C_4$mim][$SO_3CH_3$] are absent. As to fusion parameters, there is only melting point of [$C_4$mim][$SO_3CH_3$] [6].

The aim of the present work is devoted to determination following thermodynamic properties of [$C_2$mim][$SO_3CH_3$] and [$C_4$mim][$SO_3CH_3$]: melting points, heat of fusions and isobaric heat capacity of solid phases. For these purpose DSC 204 F1 Phoenix (NETZSCH GmbH) was applied. Sample purities and fusion parameters were obtained by ASTM E928 at the heating rate 0.5 K·min$^{-1}$. Melting points were corrected to zero contamination by Schroeder's law (Table). Isobaric heat capacity was measured by ASTM E1269 at the heating rate 10 K·min$^{-1}$ in the temperature range from 150 K to the melting point of corresponding substance.

Table. Source, purity and melting parameters of [$C_2$mim][$SO_3CH_3$] and [$C_4$mim][$SO_3CH_3$].

| Formula | Source | Purity/ mol. % | $T_m$/ K | $\Delta_m H^0$ ($T_m$)/ kJ·mol$^{-1}$ |
|---|---|---|---|---|
| [$C_2$mim][$SO_3CH_3$] | «Roth» | 99.14±0.03 | 313.4±0.2 | 15.3±1.1 |
| [$C_4$mim][$SO_3CH_3$] | «Alfa Aesar» | 99.52±0.03 | 349.1±0.2 | 25.2±1.8 |

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# EVAPORATION AND THERMAL DECOMPOSITION OF TWO IMIDAZOLIUM-BASED IONIC LIQUIDS

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The ionic liquids (Ils) based on imidazolium cation are well known at nowadays. It famous fact that such Ils with halogen as anion are characterized by a low thermal stability. The data about thermal stability of 1-ethyl-3-methylimidazolium chloride ([EtMIm]Cl) and 1-butyl-3-methylimidazolium chloride ([BuMIm]Cl) are ambiguous. In the works of last years, thermal stability of these Ils were investigated by thermogravimetric analysis and obtained results are contradictory[1,2]. Moreover, in the last study, it was shown that the observed temperature of the beginning of thermal decomposition (thermolysis) of samples significantly depends on the conditions of the experiment, for example, the heating rate of the sample[3]. The vapor pressures of both Ils are not presented at the literature.

In this study, the vapor pressures of both Ils were obtained by Knudsen effusion mass-spectrometry (KEMS) with using original high temperature ion source with electron ionization (EI, $E_{ion}$ = 70 eV) of vapour components. Commercial MI1201 magnetic mass spectrometer (r = 200 mm, R = 500) was used. In addition, Matrix Assisted Laser Dissociation Ionization Mass Spectrometry (MALDI MS) was applied for qualitative analysis of the composition of the condensed phases – the initial ILs and their evaporation residues.

In first step, the optimal temperatures of experiments and heating rate of samples were customized. Under these conditions thermal decomposition of chlorides [EMIm]Cl and [BuMIm]Cl is dominating process, but the calculation of the vapor pressures is possible. The EI mass spectra shown that the [EMIm]Cl and [BuMIm]Cl decomposition occurs with different ways. Nonetheless, the MALDI mass spectra of the starting samples and residue in the cell were similar. It means that the main decomposition products are volatile under experimental conditions. It was found that during evaporation, thermolysis products do not affect the thermodynamic activity of chlorides [EMIm]Cl and [BuMIm]Cl, and it remains equal to 1. Therefore, the vapour pressures of both Ils were determined under decomposition conditions.

Apart from that, during the complete isothermal evaporation/thermolysis of the samples, experimental dependences of the decomposition products pressures on time were obtained. Using the original procedure for processing of these functions, kinetic curves of chlorides [EMIm]Cl and [BuMIm]Cl decomposition according to established schemes, as well as the rate constants of the corresponding reactions, were obtained.

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# THERMOCHEMISTRY OF COMPOUNDS ON THE BASIS OF BISMUTH OXIDE DOPED BY GADOLINIUM AND DYSPROSIUM

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Compounds based on delta-form of bismuth oxide are possessed of highest ionic conductivity among solid oxides [1]. However, perspectives of using these compounds are constrained by fact that delta-form of bismuth oxide is stable only in narrow temperature range from 1000 to 1100 K. In order to expand stability region of delta-form of bismuth oxide, doping by various elements is used. Some of best results have been obtained with rare earth doping.

In this paper, compounds based on bismuth oxide doped by gadolinium and dysprosium ($Bi_{1.2}Gd_{1.8}O_3$ and $Bi_{1.4}Dy_{0.6}O_3$) were synthesized and their thermochemical properties were investigated. Compounds were synthesized from high purity bismuth oxide (99.99999%, Nikolaev Institute of Inorganic Chemistry) and oxides of gadolinium (99.99%) and dysprosium (99.99%). Synthesis was carried out by solid state reaction at temperatures above 1000 K. Before synthesis, the starting materials were calcined to remove traces of moisture and carbon dioxide. Next, stoichiometric mixtures were mixed in Fritsch Pulverizette 6 mill, pressed into pellets, and annealed in SNOL 4/1200 furnace for 70 h (Fig. 1). Compounds were identified by X-ray powder diffraction. The analysis showed that compounds are individual phases, fluorite structure, space group *Fm-3m*.

To determine thermodynamic characteristics of $Bi_{1.2}Gd_{1.8}O_3$ and $Bi_{1.4}Dy_{0.6}O_3$, solution calorimetry at 298.15 K was applied [2]. The dissolution enthalpies of $Bi_2O_3$, $Gd_2O_3$, $Dy_2O_3$, $Bi_{1.2}Gd_{1.8}O_3$ and $Bi_{1.4}Dy_{0.6}O_3$ were measured by solution calorimetry in 2 M HCl. Based on measured experimental and literature data, the standard formation enthalpies and lattice enthalpies were calculated. It was shown that standard formation enthalpies and lattice enthalpies were increasing in series $Bi_{1.2}Gd_{1.8}O_3$-$Bi_{1.4}Dy_{0.6}O_3$. It connected with decreasing of radii of rare earth elements.

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**Figure 1.** Compound $Bi_{2-x}R_xO_3$

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# THERMODYNAMICS OF HETEROGENEOUS EQUILIBRIA IN THE ZnO-WO3 SYSTEM STUDIED BY KEMS

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The optical and scintillation properties of zinc tungstate make it suitable for use as a sensing element for detecting an ionizing radiation. $ZnWO_4$ scintillators, having very low radioactive contamination of the material, are promising detectors in experimental setups for registering rare events. Physical vapor deposition allows to obtaining the most optically pure scintillation materials. However, its application is complicated by the lack of reliable information on vaporization processes in the ZnO-$WO_3$ system.

In the present work, thermodynamics of heterogeneous equilibria was investigated by Knudsen effusion mass spectrometry at temperatures 1330-1530K. In accordance with XRD analysis, the complex oxide $ZnWO_4$ and equilibrium mixtures [$WO_3$+$ZnWO_4$] and [$ZnWO_4$+ZnO] were obtained by the solid-state synthesis in air at 1173 K. It was found that the $ZnWO_4$ compound evaporated incongruently so that the gas phase was enriched in the more volatile component ZnO relative to the condensed phase.

Vapor of species Zn, $O_2$, $W_2O_6$, $W_3O_8$, $W_3O_9$ and $W_4O_{12}$ were found in the saturated vapor above the two-phase region [$WO_3$ + $ZnWO_4$], and their partial pressures were determined at 1330 K. The vapor above the two-phase region [ZnO + $ZnWO_4$] was represented only by Zn and $O_2$. In addition, the partial pressures of the vapor components and their temperature dependences were determined over the two-phase region [Liquid + $ZnWO_4$] and [Liquid].

Based on the experimental data, the equilibrium constants of heterogeneous reactions involving $ZnWO_4$, $WO_3$ and ZnO and the component activities were computed in different phase fields of the system. The standard enthalpies of heterogeneous reactions and the standard enthalpy of formation of $ZnWO_4$ were also calculated.

Gas phase equilibria $W_nO_{3n} = W_3O_8 + O_2$ (n = 2, 3, 4) were investigated and the standard enthalpies of the corresponding reactions were determined. The enthalpy of formation of $W_3O_8$ was obtained by the second- and third-law calculations. The value calculated by the third-law -1792 ± 120 kJ mol$^{-1}$ was recommended.

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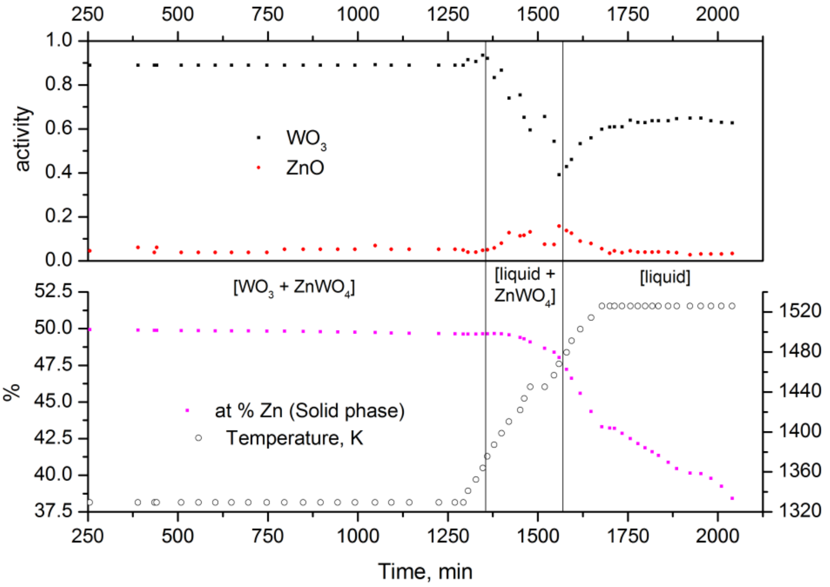

**Figure 1.** Variation in the activities of $WO_3$ and ZnO during the KEMS experiment.

# THERMAL EXPANSION OF PHOSPHATES − ANALOGS OF α-$CaMg_2(SO_4)_3$

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We synthesized isostructural $BiFe_2(PO_4)_3$ and the $Bi_{1-x}Sb_xCr_2(PO_4)_3$ solid solution, the first representatives of phosphates with the α-$CaMg_2(SO_4)_3$ type structure. They are a promising material in the light of their interesting magnetic and dielectric properties. Considering the applications of the phosphate, it is necessary to know its thermal behavior and thermophysical properties.

Using the adiabatic and differential scanning calorimetric methods, the heat capacity of crystalline $BiFe_2(PO_4)_3$ was measured in the temperature range between 5 and 660 K and the thermodynamic functions were determined in the range from $T \to 0$ to 660 K. A phase transition associated with the ordering of magnetic moments in the structure of the compound was detected on the heat capacity curve of the sample at temperatures of 12−32 K. Except for this region, the heat capacity of the phosphate rise gradually with increasing temperature. The study of the sample by DTA showed the presence of an endothermic phase transition in phosphate at a temperature of $T$ = 711 K. The observed endothermic transition is reversible; it reproduced at repeated cooling and heating. A slight change in enthalpy during the transition is associated with a slight restructuring of the structure, accompanied by an increase in the symmetry of the cell. According to the DTA, XRD, and thermogravimetry data, $BiFe_2(PO_4)_3$ congruently melts at (1313±5) K. Phosphates $Bi_{1-x}Sb_xCr_2(PO_4)_3$ ($0 \leq x \leq 1$) are stable up to 1200°C.

The main purpose of the present investigation is to determine $BiFe_2(PO_4)_3$ and the $Bi_{1-x}Sb_xCr_2(PO_4)_3$ thermal expansion coefficients as a function of temperature.

Polycrystalline phosphates $BiFe_2(PO_4)_3$ and $Bi_{1-x}Sb_xCr_2(PO_4)_3$ were obtained by evaporation of the aqueous salt solution followed by heat treatment. The formation of the desired phosphates was confirmed on a Shimadzu XRD-6000 diffractometer. Their elemental and phase compositions were examined using a JSM-7600F SEM equipped with a microanalysis system OXFORD X-Max 80 Premium. To study the thermal expansion of the sample, the X-ray diffraction measurements were carried out on the same diffractometer with increments of 0.02° ranging from 10° to 60° using a temperature attachment (Anton Paar TTK 450) with a discrete mode of temperature variation from 173 to 473 K with a step of 50 K.

$BiFe_2(PO_4)_3$ expands on heating with positive thermal expansion ($\alpha_a = 4.0 \cdot 10^{-6}$ K$^{-1}$, $\alpha_c = -3.1 \cdot 10^{-6}$ K$^{-1}$, $\alpha_{av} = 1.6 \cdot 10^{-6}$ K$^{-1}$) and characterize by opposite in sign and close in value coefficients of linear thermal expansion (LTECs). The studied $BiFe_2(PO_4)_3$ is a low-expanding material.

The minimum anisotropy of expansion at a small value of the average LTEC is characterized by $Sb_{0.5}Bi_{0.5}Cr_2(PO_4)_3$ and $Sb_{0.75}Bi_{0.25}Cr_2(PO_4)_3$, for which $\alpha_{av} = 0.5 \cdot 10^{-6}$ K$^{-1}$ and $|\alpha_a - \alpha_c| = 4.8 \cdot 10^{-6}$ K$^{-1}$. By varying the composition of the solid solution (Table 1), it is possible to obtain materials with controlled small LTECs and expansion anisotropy.

**Table 1.** Thermal Expansion Coefficients and anisotropy for $Sb_xBi_{1-x}Cr_2(PO_4)_3$ ($173 \leq (T$/K$) \leq 473$)

| $x$ | $\alpha_a \cdot 10^6$, K$^{-1}$ | $\alpha_c \cdot 10^6$, K$^{-1}$ | $\alpha_{av} \cdot 10^6$, K$^{-1}$ | $\alpha_V \cdot 10^6$, K$^{-1}$ | $|\alpha_a - \alpha_c| \cdot 10^6$, K$^{-1}$ |
|---|---|---|---|---|---|
| 0 | 4.9 | -4.1 | 1.9 | 5.7 | 9.0 |
| 0.25 | 4.2 | -2.7 | 1.9 | 5.7 | 6.9 |
| 0.5 | 2.1 | -2.7 | 0.5 | 1.5 | 4.8 |
| 0.75 | 2.1 | -2.7 | 0.5 | 1.5 | 4.8 |
| 1 | 4.9 | -5.5 | 1.4 | 4.3 | 10.4 |

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# CALCULATION OF EUTECTIC COMPONENT ACTIVITIES IN WATER-SALT SYSTEMS

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Depending on the history of the liquid phase, crystallization can be of two types: quasi-equilibrium (QEC), practically without overcooling and non-equilibrium-explosive (NEC) with significant overcooling, therefore, it is of interest to calculate the activities of both components both at temperature $T_E$, i.e. at the start of quasi-equilibrium crystallization (QEC), and in the overcooling region at temperature $T_{\min}$ at the start of non-equilibrium-explosive crystallization (NEC).

The activity $a_E^{H_2O}$ and $a_E^{salt}$ in liquid eutectics at $T_E$ (i.e. in the absence of overcooling) was calculated by Schroeder's equation.

$a_E^{H_2O} = \exp[\frac{\Delta H_L^{H_2O}}{R}(\frac{1}{T_L^{H_2O}} - \frac{1}{T_E})]$, (1) $a_E^{salt} = \exp[\frac{\Delta H_L^{salt}}{R}(\frac{1}{T_L^{salt}} - \frac{1}{T_E})]$, (2) where $\Delta H_L^{H_2O}$, $\Delta H_L^{salt}$ - enthalpy of melting ice and salt; $T_L^{H_2O}$, $T_L^{salt}$ - melting points of ice and salt. Activity coefficients $g_E^{H_2O}$, $g_E^{salt}$ under the same conditions were found from the ratios of activities to concentrations of components in eutectic ($X_E^{H_2O}, X_E^{salt}$): $g_E^{H_2O} = a_E^{H_2O} / X_E^{H_2O}$; $g_E^{salt} = a_E^{salt} / X_E^{salt}$ (3).

Next, activation energies in eutectics, both from the water $W_E^{H_2O}$ side and from the salt $W_E^{salt}$ side, were evaluated:

$W_E^{H_2O} = \frac{\Delta H_L^{H_2O}(1 - \frac{T_E}{T_L^{H_2O}}) + RT_E \ln X_E^{H_2O}}{(1 - X_E^{H_2O})^2}$, (4) $W_E^{salt} = \frac{\Delta H_L^{salt}(1 - \frac{T_E}{T_L^{salt}}) + RT_E \ln X_E^{salt}}{(1 - X_E^{salt})^2}$. (5)

Energies $W_E^{H_2O}$ and $W_E^{salt}$ were used to test the values of activity coefficients $g_E^{H_2O}$ and $g_E^{salt}$:

$g_E^{H_2O} = \exp[-(1 - X_E^{H_2O})^2 \cdot W_E^{H_2O} / RT_E]$, (6) $g_E^{salt} = \exp[-(1 - X_E^{salt})^2 \cdot W_E^{salt} / RT_E]$. (7)

Of particular interest is the analysis of the above parameters in the overcooled metastable area at the start of the «explosive» crystallization. Denote the activity at the boundary of metastability $\alpha_E^{H_2O}$, $\alpha_E^{salt}$, the coefficients of activity $\gamma_E^{H_2O}$, $\gamma_E^{salt}$, and activation energy $\omega_E^{H_2O}$, $\omega_E^{salt}$.

In this case, the "Schroeder logarithmic" works and the equations (1), (2), (4), (5) take the following form:

$\alpha_E^{H_2O} = \exp[\frac{\Delta H_L^{H_2O}}{R}(\frac{1}{T_{\min}^{H_2O}} - \frac{1}{T_{\min}^E})]$, (8) $\alpha_E^{salt} = \exp[\frac{\Delta H_L^{salt}}{R}(\frac{1}{T_{\min}^{salt}} - \frac{1}{T_{\min}^E})]$, (9)

$\omega_E^{H_2O} = \frac{\Delta H_L^{H_2O}(1 - \frac{T_{\min}^E}{T_{\min}^{H_2O}}) + RT_{\min}^E \ln X_E^{H_2O}}{(1 - X_E^{H_2O})^2}$, (10) $\omega_E^{salt} = \frac{\Delta H_L^{salt}(1 - \frac{T_{\min}^E}{T_{\min}^{salt}}) + RT_{\min}^E \ln X_E^{salt}}{(1 - X_E^{salt})^2}$.(11)

# LIDOCAINE CONFORMATIONAL PREFERENCES UNDER ISOBARIC CONDITIONS

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One of the effective methods of obtaining new polymorphic forms of drug compounds is conformational polymorph screening based on finding the optimal thermodynamic parameters and other ways of shifting conformational equilibria in fluid systems. As it was shown in works [1-4], which studied small molecules in drug compound compositions, their extraction from a saturated solution leads to the formation of a polymorph with the most probable molecule conformation in the solution. It is supercritical fluid technologies that are currently among the most promising approaches to obtaining new polymorphic forms and studying their nucleation.

This work presents the results of monitoring lidocaine conformational preferences in a $scCO_2$ fluid system. Nuclear Overhauser Effect Spectroscopy (NOESY) data were used to trace the conformational dynamics at different pressure and temperature values. The experiments were carried out under isobaric conditions (10, 20, and 30 MPa) at three temperatures on each isobar (35, 50, and 70°C). Pressure was shown to affect the change in the conformer group ratio in scCO2. For example, on the 10 MPa isobar, the proportion of major conformers changed only by 0.4% depending on temperature, while at pressures of 20 and 30 MPa, it changed by 36.2% and 41.7%, respectively, at the same temperatures. This work demonstrates the unique functionally of NMR spectroscopy in determining conformational distributions of small molecules in $scCO_2$.

The NMR spectroscopy experiment was performed using the molecular fluid spectroscopy facility (http://www.ckp-rf.ru/usu/) of G.A. Krestov Institute of Solution Chemistry of the Russian Academy of Sciences (ISC RAS) (Russia).

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# VAPORIZATION THERMOCHEMISTRY OF LEUCO DYES: MEASUREMENT AND PREDICTION

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The enthalpy of vaporization is one of the most important thermochemical characteristics of a substance due to its wide application in industry and science. Information about the temperature dependence of this quantity is required for solving many problems, both fundamental and applied. The enthalpy of vaporization as a function of temperature can be found using Kirchhoff's law of Thermochemistry, given the difference between the heat capacities of the liquid and ideal gas phase. However, the determination of these values for many compounds is a non-trivial task; therefore, Chikos and coworkers [1] previously proposed a scheme for estimating the difference between the heat capacities of the condensed and gas phases for organic compounds based on the molecular structure, which has been used by researchers for 30 years, despite obvious limitations. Recently, our group has developed methods for estimating the difference between the heat capacities of liquid and gas phases for aromatic [2] and aliphatic [3] compounds based on correlation with the enthalpy of vaporization at 298.15 K. Combining these two approaches with an additive scheme for calculating the enthalpy of vaporization at 298.15 K proposed by in our laboratory [4], we can obtain a universal method for calculating the enthalpy of vaporization of arylaliphatic compounds at an arbitrary temperature based on the molecular structure. The possibility of its application was tested for alkylaromatic hydrocarbons [5], and excellent agreement with the literature data was observed (RMS = 1.9 kJ·mol$^{-1}$), while the use of the Chikos scheme led to significant deviations.

To confirm the correctness of the developed approaches, the thermochemistry of the evaporation of several arylaliphatic compounds was studied using the method of fast scanning calorimetry (FSC). Hardly volatile leuco dyes such as 4,4'-methylenebis(N,N-dimethylaniline), leucocrystal violet, and leucomalachite green were chosen as objects of study.

**Acknowledgements** The financial support of the Russian Science Foundation (Grant No. 21-73-00006) is acknowledged.

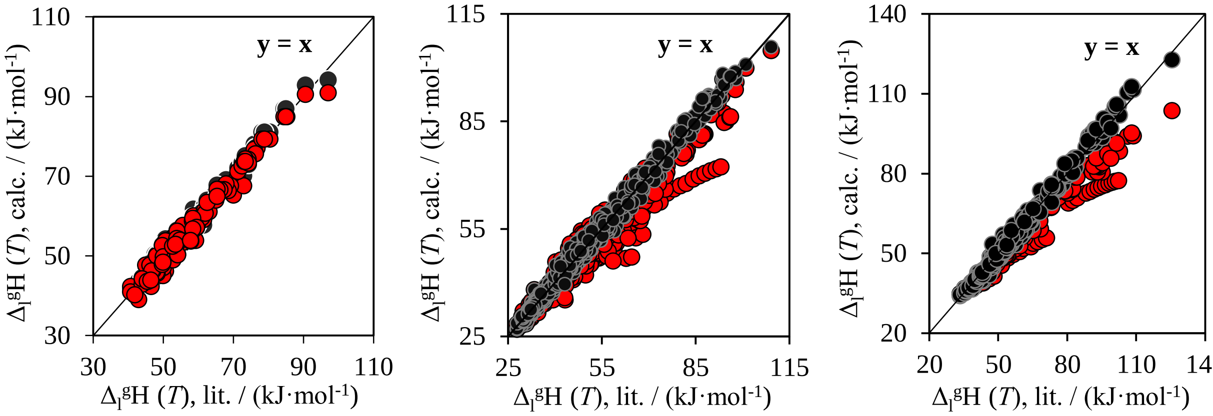

**Figure 1.** Comparison of the calculated vaporization enthalpies (black dots – this work, red dots – *Chickos et al.* scheme) with the literature values for aromatic (left), aliphatic (middle) and alkylaromatic (right) compounds.

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# MOLECULAR THERMODYNAMIC MODELING OF AGGREGATION AND TRASMEMBRANE POTENTIAL FOR VESICLES FORMED BY IONIC SURFACTANT MIXTURES

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Vesicles are spherical bilayer membranes which are widely used as nanoreactors and containers for application in micellar catalysis and drug delivery [1]. Vesicular aggregates commonly self-assemble from mixtures of cationic with anionic surfactants in solution [2, 3, 4]. The molecular thermodynamic aggregation models [2, 5, 6] aim at predicting properties of the self-assembled aggregates based on the molecular parameters of surfactants. The majority of molecular-thermodynamic models of aggregation employ the Poisson-Boltzmann theory to describe the electrostatics assuming electroneutrality of the vesicle's interior. This implies no drop of the electrical potential across the membrane of the vesicle. However, the transmembrane potential is very important because it is the driving force for the transfer of mobile ions across the membranes.

In this work, we discuss the version of the classical aggregation model [5] that leads to an analytical expression for the transmembrane potential [6] within the linearized Poisson–Boltzmann theory. This expression reflects the dependence of the transmembrane potential on the parameters of the vesicle (including its curvature and charge) and on the solution salinity. Maxima or minima of the transmembrane potential may appear in response to variation of salinity. We show that adding salt to solution may lead to the reversal of the sign of the transmembrane potential, and demonstrate that a vesicle brought to equilibrium with an acidic environment may hold an alkaline solution in its interior.

We predict aggregation behavior for catanionic mixtures of classical surfactants (sodium alkylsulfates with alkyltrimethylammonium bromides and sodium dodecylbenzenesulfonate with 1-hexadecyl-3-methylimidazolium chloride) that form vesicles, including distributions of the aggregates over their size and shape (spherical and rodlike micelles, and vesicles), the aggregate's composition and the micelle-to-vesicle transitions. The molecular parameters of surfactants have been taken from the literature [5]. Comparison with SANS and cryo-TEM data [3, 4] shows that the vesicles with the radius of less than 30 nm are reasonably predicted by the model. The predicted values of the electrical potential in the electrical double layer around the vesicles formed by cetyltrimethylammonium bromide with sodium octylsulfate agree with experimental data for the zeta potential [2].

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# THERMODYNAMIC PROPERTIES OF INDOLINE AND BENZOXAZINE BASED SPIROPYRANS

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Spiropyrans are organic photochromic materials. They have spiro-bond and pyran heterocycle in their structure. Under the exposition of ultraviolet light, the spiropyran molecule turns into an opened form and its absorption spectrum changes. In the last few decades interest in the synthesis and properties of photochromic compounds has increased significantly, due to the possibility of their application in molecular photonics. They can be applied as high-density optical drives, image processing, optical switches and signals.

This work is devoted to the research of thermodynamic characteristics of indoline and benzoxazine based spiropyrans. Four spiropyrans were selected as objects of study (NSP-1: 1,3,3-trimethyl-6′- (tert-butyl) -8′-formyl-spiro [indolin-2,2′-2H-chromene]; NSP-4: 1,3,3,8′-tetramethyl-6′-formyl-spiro [indolin-2,2′-2H-chromene]; NSP-7: 1,3,3-trimethyl-8′-methoxy-6′-formyl-spiro [indolin-2,2′-2H-chromene]; NSP-9: 3-methyl-6'-methoxy-8'-formyl-spiro [1,3-benzoxazin-4-one-2,2'-2H-chromene). Thermal analysis, high-temperature mass spectrometry, and quantum chemical calculations were chosen as research methods.

Thermal analysis was used to determine the melting point and decomposition temperature of spiropyrans and also to calculate the enthalpy of melting. Thermodynamic investigations were carried out on a magnetic sector mass spectrometer MI-1201 combined with a Knudsen cell in electron ionization mode. Absence of ions with masses over the mass of the molecular ion means that monomer molecule is precursor of all ions in spectrum. It was also confirmed by measured appearance energies of all main ions. The lowest appearance energy among them has molecular ions.

Intensities of ion currents were recalculated into vapor pressures using the results of Knudsen effusion experiment. Temperature dependencies of vapor pressure were used to obtain sublimation enthalpies at average temperature of experiments. Thermodynamic functions of crystalline state were calculated by integration of temperature dependencies of isobaric heat capacity. Quantum chemical calculations were used to determine the thermodynamic functions of the gaseous state. It became possible to recalculate the sublimation enthalpies to the temperature 298.15 K. All results are given in table 1. It was shown that sublimation enthalpy weakly depends on spiropyran structure even between benzoxazine and indoline types.

**Table 1.** Thermodynamic functions

| Object of study | $\Delta T$, K | $T$, K | $\Delta_s H°(T)$, kJ·mol$^{-1}$ | $\Delta_s S°(T)$, J·mol$^{-1}$·K$^{-1}$ | $\Delta_s H°(298.15)$, kJ·mol$^{-1}$ |
|---|---|---|---|---|---|
| NSP-1 | 340-405 | 370 | 128±3 | 317±8 | 131±3 |
| NSP-4 | 315-360 | 336 | 115±2 | 293±5 | 118±2 |
| NSP-7 | 350-385 | 367 | 128±2 | 310±5 | 132±2 |
| NSP-9 | 335-410 | 369 | 120±1 | 277±3 | 124±1 |

**Acknowledgements** This work was supported by the Ministry of science and higher education of the Russian Federation in the framework of Government order (project No. FZZW-2020-0007). The study was carried out using the resources of the Center for shared use of scientific equipment of the ISUCT (with the support of the Ministry of science and higher education of Russian Federation, project No. 075-15-2021-671).

# VAPORIZATION AND THERMODYNAMIC PROPERTIES OF THE MAX-PHASES CONTAINING $ZrO_2$ AT HIGH TEMPERATURES

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At present, MAX phases, which are a family of layered compounds containing a d-block element (transition metal, M), a p-block element (A), as well as carbon or nitrogen (X), are of the great practical interest for creating materials, which can be applied in mechanical engineering, aerospace sector, and nuclear industry. MAX phases exhibit a unique combination of low density, high thermal and electrical conductivity, high strength, resistance to high-temperature oxidation and thermal shock. MAX phases have high melting temperatures and are stable at the temperatures up to 1270 K and above [1].

Vaporization and thermodynamic properties of $Al_4C_3$, $Ti_2AlC$, $Ti_3AlC_2$, $Zr_2AlC$, $Zr_3AlC_2$, SiC, $Ti_2SiC$, and $Ti_3SiC_2$ as well as the $Ti_2AlC$-$ZrO_2$ and $Ti_3AlC_2$-$ZrO_2$ systems were studied by the high-temperature mass spectrometric method [2]. Vaporization of the samples was carried out from the graphite twin effusion cell placed in a molybdenum shell. Heating of the cell with the samples inside was carried out by electron bombardment. The temperature was measured by the EOP-66 optical pyrometer with an accuracy of ± 10 K.

When $Al_4C_3$, $Ti_2AlC$, $Ti_3AlC_2$, $Zr_2AlC$, and $Zr_3AlC_2$ were heated up to the temperature 1500 K, atomic aluminum began to transfer into vapor while titanium (zirconium) and carbon accumulated in the condensed phase. At a much higher temperature of 1870 K, atomic titanium (zirconium) was observed in the vapor over the studied MAX phases, and, at the temperature 2300 K, $C_3$ vapor species was identified in the gaseous phase. In the gaseous phase over SiC, $Ti_2SiC$, and $Ti_3SiC_2$, starting from the temperature 1900 K, the Si, $Si_2$, $SiC_2$, and $Si_2C$ vapor species were observed.

The determination of the partial pressures of atomic aluminum, Si, $Si_2$, $SiC_2$, and $Si_2C$ vapor species in wide temperature ranges allowed the equations of the temperature dependences of the logarithm of the partial pressures of the vapor species mentioned over the studied samples to be obtained.

It was found that $Ti_2AlC$ had the greatest thermal stability in the series $Al_4C_3$, $Ti_2AlC$, and $Ti_3AlC_2$ while $Zr_2AlC$ was the most thermally stable compound in the series $Al_4C_3$, $Zr_2AlC$, and $Zr_3AlC_2$. Among the compounds SiC, $Ti_2SiC$, and $Ti_3SiC_2$, $Ti_2SiC$ was the least volatile MAX phase.

In the vapor over the $Ti_2AlC$-$ZrO_2$, $Ti_3AlC_2$-$ZrO_2$, $Zr_2AlC$-$ZrO_2$, and $Zr_3AlC_2$-$ZrO_2$ systems, in addition to atomic aluminum, aluminum oxide $Al_2O$ was present, which was not observed in the vapor over pure carbide MAX phases. The SiO vapor species was identified also in the gaseous phase over the $Ti_2SiC$-$ZrO_2$ and $Ti_3SiC_2$-$ZrO_2$ systems.

As a result of the present study, the limiting temperatures of the thermal stability of the carbide MAX phases as well as the carbides in the presence of $ZrO_2$ were identified. It should be emphasized that, above the obtained limiting temperatures of the carbide thermal stability, the transition of the volatile components into vapor and the change in the composition of the condensed phase may be expected.

**Acknowledgements** The reported study was funded by RFBR and ROSATOM according to the research project № 20-21-00056.

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# STUDY OF EQUILIBRIUM CONDITIONS OF HYDRATE FORMATION IN THE WATER-METHANE-ECTOINE SYSTEM

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Gas hydrates are non-stoichiometric crystalline compounds of gas molecules enclosed in a hydrogen-bonded framework built of water molecules. They are stable at low temperature and high pressure. Since the beginning of the 20th century, the formation of gas hydrates in pipelines has been regarded as a serious problem for the oil and gas industry, as this can lead to emergencies, and, consequently, to a threat to human safety, huge economic losses, and environmental pollution. On the other hand, the development of hydrate-based technologies is important for carbon dioxide capture, desalination, and especially natural gas storage and transportation [1]. To solve various problems associated with the formation of gas hydrates, substances are needed that can affect hydrate equilibrium, namely thermodynamic hydrate inhibitors and promoters. The mechanism of thermodynamic hydrate inhibitors action is to reduce the activity of water in an aqueous solution and, as a result, change the equilibrium conditions towards lower temperatures and higher pressures. These compounds include, for instance, methanol, ethylene glycol and dimethyl sulfoxide [1,2]. Thermodynamic promoters can stabilize the hydrate and shift the equilibrium conditions, on the contrary, to higher temperatures and lower pressures. Known promoters of this type include tetrahydrofuran, cyclopentane, methyl iodide, methyl tert-butyl ether, 1,4-dioxane, 1,3-dioxolane [3]. A substance that effectively alters the water activity (and hence the hydrate equilibrium) may be ectoine (1,4,5,6-tetrahydro-2-methyl-4-pyrimidinecarboxylic acid) which is a natural compound found in several species of bacteria. The peculiarity of ectoine is that it is able to surround itself with a layer of water [4]. Thus, this feature can affect hydrate formation for sure. To study this influence, the high-pressure DSC was employed. First, a system containing water, ectoine, and methane was undergone to a multicycle cooling-heating mode for the complete water-to-hydrate conversion, and then heated stepwise, maintaining a long isotherm every 0.1°C. In the current work, equilibrium conditions of the methane hydrate formation were obtained depending on the ectoine concentration. The enthalpy of hydrate decomposition was determined by DSC and derived from the Clausius-Clapeyron equation as well.

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# HALOGENATED VANADYL PHTHALOCYANINES: CRYSTAL STRUCTURE AND PHASE TRANSITIONS

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Metal phthalocyanines have unique physicochemical properties that define a wide area of their practical application as active layers of electronic devices such as solar cells, organic field effect transistors, and chemical sensors. It is known that the addition of various peripheral substituent atoms to the phthalocyanine ring makes it possible to change the electrophysical, photophysical, and sensory properties of the complex. Among the wide variety of substituents, halogen substituents attract the attention of researchers due to their strong electron-withdrawing character. The introduction of halogen substituents leads to a change in the conductivity level and the magnitude of the sensor response, and in the limiting case, when all sixteen peripheral hydrogen atoms are replaced by fluorine atoms, it makes it possible to change the conductivity type of the phthalocyanine complex from p-type to n-type.

Along with this, it should be taken into account that all these effects can be observed not only due to a change in the electron density of the conjugated macrocycle, but also due to a change in the nature of the molecular packing and intermolecular contacts. Introduction of bulky fluorine and chlorine atoms in place of hydrogen atoms changes the size and shape of the phthalocyanine molecule, which results in halogenated phthalocyanines having completely different packing styles compared to their unsubstituted predecessors.

In this work, we studied the crystal structures and thin films of several halogen-substituted vanadyl phthalocyanines $VOPcHal_x$ (Hal = F, Cl; x = 4, 8, 16), which exhibit a variety of different molecular packing motifs, such as molecular chains, 2D molecular layers and vertical molecular columns. Also a distinctive feature of halogen-substituted vanadyl phthalocyanines is the tendency to undergo phase transitions when heated up to 150÷250 °C. This effect is especially noticeable in thin films and can occur within a few minutes.

*In situ* studies of such phase transitions in thin (less than 100 nm) polycrystalline layers (i.e. the form in which they are of greatest interest) present quite a challenge, mainly due to the low intensity of diffraction reflections the tendency of phthalocyanines to form oriented layers on substrate surface. Diffraction patterns of these samples are usually have only the orders of reflections from the selected crystallographic plane. In this work we implemented 2D Grazing Incidence X-ray Diffraction (2D GIXD) geometry on the basis of standard laboratory single crystal diffractometer, equipped with a microfocus tube, two-dimensional CCD-detector and thermal attachment. Additional diffraction data observed on 2D GIXD patterns allowed us to evaluate the degree of orientation of the crystallites relative to the substrate surface and to study the dynamics of the ongoing phase transition with relatively small frame acquisition time of 60 seconds. Such information allows to reliably interpret the phase transformations occurring in oriented thin layers, in our case when heating sample substrate.

# DISTRIBUTED FREEZING RANGE AND FREEZING-MELTING HYSTERESIS OF THE IONIC LIQUID 1-ETHYLPYRIDINIUM TRIFLATE

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Ionic liquids are substances of active recent interests due to the properties making them promising media for the usage as low-volatile solvents, absorbents, electrochemical compounds, heat transfer fluids, etc. Among the thermodynamic applications, ionic liquids as salt melting at temperatures lower than 100 °C, attract attention as working fluids for absorption heat pump systems. Here we report results of studies of phase transitions for 1-ethylpyridinium triflate, which is considered as one of the prospective substances for the goal mentioned, and still require our better understanding.

At the same time, existing experimental data on the phase state and kinds of phase transitions of this liquid at room range of temperatures are not only extremely scarce but also quite contradictive [1–3].

Herewith we report results of detailed investigations of the phase transition in 1-ethylpyridinium triflate at the room range of temperatures. One of approaches is the time-dependent thermography, which revealed a wide range of solidification temperatures, Fig. 1(left panel), and existence of metastable states dependent on the cooling rate. Another one is the dynamic scanning calorimetry DSC measurements like that shown in Fig. 1(right panel) in order to measure all thermal processes that occur in one measurement run during the slow heating and cooling of ILs. In this case, the melting and solidification peaks and specific enthalpy of fusion and crystallization are evaluated. Additionally, the thermal analysis TGA allowed the decomposition temperature of investigated compound to be determined.

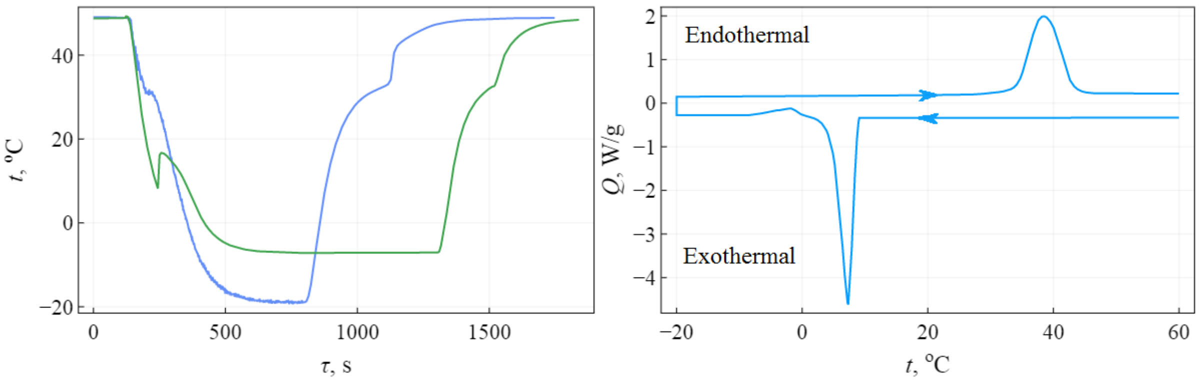

**Figure 1.** Examples of temperature change during cooling and heating with different rates (left panel) and the DSC-based measurements of the phase transition specific heat (right panel).

Finally, the electronic microscopy-based analysis of structures of the substance solidified under different conditions was carried out as well as relation of the reveled phenomena to predictions of different group contribution models.

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# ENTHALPIES OF FORMATION OF 1-ETHYL- AND 1-BUTHYL-3-METHYLIMIDAZOLIUM METHANESULFONATES

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Investigation of the properties of methanesulfonic acid's salts is of interest from the fundamental point of view. The present work is devoted to the study of thermochemical properties of two ionic liquids: 1-ethyl-3-methylimidazolium methansulfonate ([$C_2$mim][$SO_3CH_3$]) and 1-buhyl-3-methylimidazolium methansulfonate ([$C_4$mim][ $SO_3CH_3$]). The choice of object of research is caused by its application as catalysts, reagents for extraction and the perspective solvents able to dissolve biomass and lignocellulosic materials.

Information on the properties of these ionic liquids is given partially in the literature. The only work [1] devoted to the experimental determination of the [$C_2$mim][ $SO_3CH_3$] and ([$C_4$mim][ $SO_3CH_3$]) enthalpies of formation by combustion and solution calorimetry.

In present study commercial reagents of ionic liquids were investigated ([$C_2$mim][ $SO_3CH_3$] - «Roth», ([$C_4$mim][ $SO_3CH_3$]) - «ThermoFisher Scientific», purity >99 weight %). The purity of ionic liquids was checked by DSC (purity of [$C_2$mim][$SO_3CH_3$] and ([$C_4$mim][ $SO_3CH_3$] 99.14±0.03 and 99.52±0.03 mol.% correspondently).

The thermochemical properties of methansulfonates at solid state were investigated by method of solution calorimetry.

The enthalpy of solution of ionic liquids were measured in water at 298.15 K in hermetically sealed swinging calorimeter with an isothermal jacket, similar to that described in [2]. Temperature rise in each run was measured by platinum resistance thermometer. Thermometric sensitivity was $3 \cdot 10^{-5}$ K. The energy equivalent of the calorimeter was determined by electric technique. The enthalpy of formation of [$C_2$mim][$SO_3CH_3$] and [$C_4$mim][$SO_3CH_3$] at 298.15 K was calculated on the basis of the experimental data and [$C_2$mim]$^+$, [$C_4$mim]$^+$(aq) [1] and $SO_3CH_3^-$ (aq) [3] enthalpies of formation. The results are presented in Table. The comparison and analysis of the obtained thermochemical properties with the literature data [1] are carried out.

Table. Thermochemical properties of ionic liquids at 298.15 K

| Sample | $\Delta_{sol}H^0_{298.15}$, kJ · mol$^{-1}$ | $\Delta_f H^0_{298.15}$, kJ · mol$^{-1}$ |
|---|---|---|
| [$C_2$mim][ $SO_3CH_3$] (s) | -5.30±0.49 | -693.1±5.4 |
| [$C_4$mim][ $SO_3CH_3$] (s) | +4.30±0.33 | -742.1±5.1 |

**Acknowledgements** Investigation was performed in framework of Program "Chemical Thermodynamics"(AAAA-A16-116061750195-2) and by financial support of Russian Science Foundation (Grant no.20-73-00211).

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# PECULIARITIES OF OXIDATION OF NANOPOROUS IRON SYNTHESIZED BY DEALLOYING IN MELTEN EUTECTIC LiCl-KCl

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Nanoporous metals are extremely promising materials for a wide variety of applications, ranging from alternative energy to sensors for complex biochemical investigations as well as green chemistry [1]. Only a few works have been carried out to fabricate nanoporous iron, because of it is considered as one of the most capable biodegradable material for implantation in traumatology. In our recent work, firstly, the synthesis of a bi-continuous structure of nanoporous iron was carried out under specially selected conditions: 1) Chloride eutectic LiCl-KCl 2) Temperature 400 C (slightly below of the beginning of recrystallization temperature of a pure iron) 3) rapid quenching of Fe-Mn melt of equiatomic composition [2].

It is of great interest to study the features of the oxidation of nanoporous iron obtained by dealloying in molten salts. This report will present thermochemical data on the features of the oxidation of nanoporous iron in air, as well as their possible interpretation by means of high-temperature X-ray phase analysis.

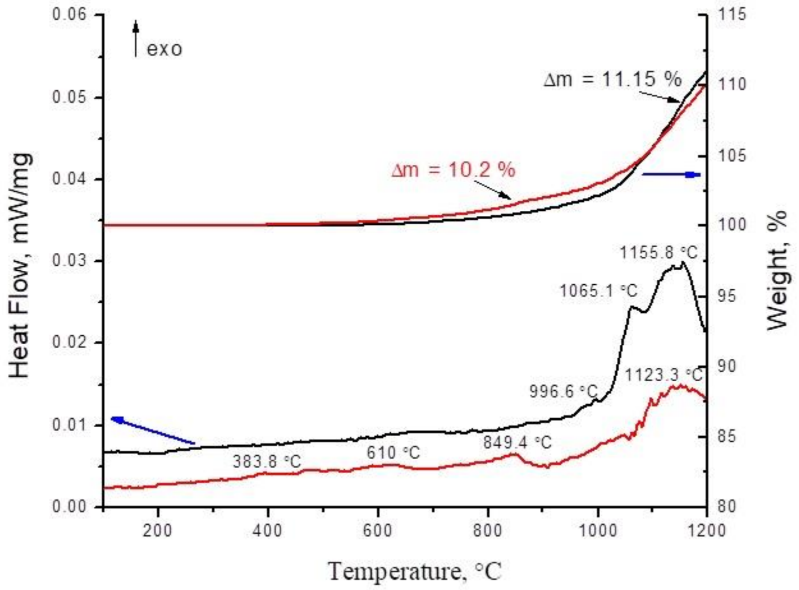

**Figure 1.** DSC results of initial ferro-manganese sample (black) and fabricated nano-porous iron (red) at 10 °C min$^{-1}$

DSC was performed by means of a thermal analyzer Netzsch STA 449 F1 Jupiter at the rate of 10 °C min$^{-1}$ in $Al_2O_3$ crucibles with lids over a 35 – 1000 °C temperature range at the expulsion rate of 20 mL min$^{-1}$ in Air.

**Acknowledgements** The financial support of the Russian Science Foundation № 22-23-20073 and the RFBR № 20-33-90224.

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# SYNTHESIS OF Ba-, Sr-, Mg- SUBSTITUTED HYDROXYAPATITE

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Currently, substituted hydroxyapatite is a perspective material for medical application because hydroxyapatite (HA) is the main inorganic compound from which forms bone tissue. In hydroxyapatite, even a small amount of doping can create a significant alteration of critical properties such as solubility, particle size, morphology, specific surface area, porosity, and aspect ratio. Moreover, the doping elements will eventually be released in vivo making these materials as multi-functional systems for the release of biologically active ions [1]. Our research was concentrated on the synthesis Ba-, Sr-, Mg- substituted hydroxyapatites in order to creation glass-ceramic composite material based on porous glass.

Hydroxyapatite and substituted hydroxyapatite were synthesized by method of deposition from aqueous solutions (reaction 1 and 2). Then sediment was treated into autoclave hydrothermal conditions. The samples were identified by comparing the peak positions of the experimental X-ray powder diffraction patterns with cards of data base ICDD. Parameters of lattice cell was calculated.

$$10Ca(NO_3)_2+6(NH_4)_2HPO_4+8NH_4OH \rightarrow Ca_{10}(PO_4)_6(OH)_2+20NH_4NO_3+6H_2O \quad (1)$$

$$(10\text{-}x)Ca(NO_3)_2+xY(NO_3)_2+6(NH_4)_2HPO_4+8NH_4OH \rightarrow Ca_{10-x}Y_x(PO_4)_6(OH)_2+20NH_4NO_3+6H_2O,$$ где Y-Ba, Sr, Mg; x – 0.33, 0.5, 1 (2)

Hydroxyapatite and Ba-, Sr-, Mg-, BaSr-, BaMg-, SrMg- BaSrMg- substituted hydroxyapatite were synthesized. X-ray diffraction patterns coincide with card of HA № 01-074-0565_$Ca_{10}(PO_4)_6(OH)_2$ from ICDD PDF-2. But Sr-substituted hydroxyapatite coincided PDF card № 01-077-9002_$Ca_{9.045}Sr_{0.955}(PO_4)_6(OH)_2$. Parameters of lattice cell for substituted HA are larger than for hydroxyapatite (№ 01-074-0565 a=9.424Å, c=6.879Å, V=529.09Å$^3$). Parameters of lattice cell for Mg- substituted HA are smaller. Possibly, it is related to the fact, that Mg atomic radius is smaller (0.16 nm) than Ca atomic radius – 0.197 nm. Obtained parameters of lattice for Sr-substituted hydroxyapatite (a=9.477Å, c=6.923Å, V=538.48Å$^{3)}$ are comparable with parameters from PDF card № 01-077-9002 a=9.471Å, c=6.923Å, V=537.77Å$^3$.

To form porous structure glass $Na_2O–K_2O–SiO_2–CaO–P_2O_5–MgO–F_2–Al_2O_3–ZrO_2$ was processed by $NaNO_3$ melt during 5-12 hours at temperatures 400-500°C. Complete exchange $K^+$ ions from glass-matrix to $Na^+$ ions from salting melt was achieved at following parameters: temperature - 450°C and time – 10 hours. And then hydroxyapatite was synthesized inside the glass-porous structure for creating glass-ceramic composite material. X-ray diffraction pattern of glass-ceramic material surface coincided with hydroxyapatite card № 01-074-0565_$Ca_{10}(PO_4)_6(OH)_2$.

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# IMPROVING THE SCIENTIFIC BASIS FOR HIGH-ENTROPY ALLOY COATING BY LASER CLADDING

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The work is aimed at the development of scientific bases for the production of new structural coatings based on high-entropy alloys by methods of additive technologies (primarily by laser cladding), as well as the development of fundamental bases for the processing and operation of such coatings. It should be done a theoretical and experimental study of physical and chemical processes occurring during coatings formation based on high-entropy alloys using laser cladding, as well as the study of the properties of the obtained coatings and how these properties affect the parameters of the coating formation processes.

The following methods and approaches are used for the research:

1. Experimental manufacturing of the samples with the coatings by methods of laser cladding under variation of the production conditions (compositions and geometrical characteristics of the powders, the energy and temperature characteristics of the coating formation). The possibilities of coatings formation based on various high-entropy compositions are studied. An important part of the work on coatings formation is the work aimed at selecting the parameters of coatings formation that allow to obtained them in situ, directly on the coated surface during the deposition/cladding of low-entropy powders (pure metals and/or double and triple alloys). As a substrate for coatings, samples of nickel-based alloys, stainless steels and low-carbon steels are used.
2. Experimental study of the composition and structure of the coatings (by electron microscopy, X-ray microanalysis and X-ray phase analysis). The distribution of various elements in the microstructure of the coatings and their phase composition were investigated.
3. Experimental study of phase stability in the coatings. It was performed by DTA methods to determine the temperature limits of the phase stability of the obtained coatings based on HEA. In addition to the DTA study, phase stability is investigated in the course of experiments on long-term annealing of the obtained coatings in order to determine how many hours of exposure of samples at temperatures from the range of 800-1200 °C affects the elements distribution and the phase composition of the coatings.
4. Thermodynamic and kinetic modeling of the processes of high-entropy phases formation in the laser cladding conditions and possible service conditions. The experimental study of the phase stability in the coatings was form the basis for the construction of thermodynamic and kinetic models of phase equilibria and phase transformations implemented in the formation process, possible heat treatments and HEA coatings service at high temperatures. In this part of the study, modern approaches were used for modeling that allows the implementation of modern software. In particular, thermodynamic modeling was performed using the methods developed within the Calphad approach. Thermo-Calc Software (including DICTRA and TC-PRISMA kinetic simulation software) and FactSage Software are used for this work. The simulation results allow us to draw the conclusions necessary to improve the compositions of the used powders.
5. The results of the experiments are analyzed and compared with the literature data, as well as with the results of the simulation to determine the ways to optimize the coating processes, and determine the possibility of their optimal application.

**Acknowledgements** This work was supported by the Russian Science Foundation (Project No. 20-19-00304).

# THE SYNTHESIS, STUDY OF THE STRUCTURE AND THERMODYNAMIC MODELING OF HIGH-ENTROPY INTERMETALLIC COMPOUNDS

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During the last two decades, development and studies of high-entropy phases and their properties have become one of the most actively developing fields in materials science. At first, the entropy stabilized phases were defined in high-entropy alloys, and then this concept was applied to nitride, oxide and boride high-entropy phases, and their features were increasingly investigated. Nowadays some results have been produced at this area. These results are of interest not only for basic science but are rather advantageous from the point of view of the practical application of high-entropy phases as engineering and functional materials.

The scientific challenge to be solved by the present work is the creation of theoretical foundations for the synthesis and use of a new class of high-entropy phases– high-entropy intermetallic compounds – i.e. multicomponent phases with almost equimolar ratio of main components, in which homogeneous intermetallics structure is stabilized by high mixing entropy. The structure of the phases in the simplest case can be expressed by a formula of the form (A1, A2,...,An)x(B1, B2,...,Bm)y. Chemical interaction is realized between elements (metals) of types A and B and, therefore, such phases are intermetallics. However, within the A or B sublattices, the constituent elements form high-entropy substitution solution, which affects the configurational entropy of the system as a whole, and as a result, the Gibbs free energy of the multicomponent metallic phase to stabilize a single intermetallic phase. From this point of view such compounds are not only intermetallic but also high-entropy phases.

By analysis experimental data produced in the course of the research, it is possible to create a theoretical background for the formation of high-entropy intermetallics. At that, some specific systems are used as examples for investigating regularities of high-entropy intermetallics formation to improve the potential of these materials from the point of view of their practical application and to get new knowledge about under-investigated or not investigated systems.

The experimental data (temperature and concentration limits of solid solutions stability in the systems under the study) are used to make a thermodynamic description of the formation of high-entropy solutions. The principal task is to provide an independent description of temperature and concentration dependencies of Gibbs free energy for high-entropy solid solutions. Reliable information related to low-entropy phases is available in literature and in databases spread on a commercial basis that is accessible for the team.

In the course of the investigation, modern licensed software Thermo-Calc and FactSage completed with the databases are used for thermodynamic modeling, the creation of own databases and optimization of the required parameters. At that, the study results are considered in the process of creation of own databases that are optimized for the description of the specific systems explored in the course of the investigation.

Thermodynamic modeling results are presented both as phase diagrams of various types (depending on requirements of the thermodynamic analysis being carried out) and in the form of diagrams representing results of crystallization process modelling (in particular, with the use of Sheil-Gulliver model).

**Acknowledgements** The reported study was funded by Russian Science Foundation according to the research project № 22-23-00243.

# PHASE DIAGRAM OF POLYMER BRUSHES WITH MOBILE ANCHORS IN A GOOD SOLVENT CALCULATED WITH THE EXPANDED ENSEMBLE METHOD

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This work explores the free energy of "mobile polymer brushes" (MB): the polymer molecules are not chemically bonded to the surface, but can desorb or move. Such brushes form upon adsorption of a surfactant with a very long head segment at a liquid–liquid interface or upon chemisorption of polymers with a weak chemical bond forming between an active endgroup and the surface. In a good solvent the prevailing forces in the system (apart from the attraction between the adsorbed anchor and the surface) originate from the entropic repulsion between the individual chains.

The free energy of the brushes is explored with Brownian Dynamics in conjunction with Expanded Ensemble Monte Carlo simulations. The free energy is calculated as a function of the interfacial lateral density, polymer length, and effective exclusion volume of the segment. The thermodynamic properties were related to the structural features, such as brush height, chain radius of gyration, and the in-plane radial distribution function between the chain anchors.

The dependencies of the concentration profiles, brush height and gyration radii are in a full agreement with the expectations and are similar to those in conventional brushes. Somewhat surprising is the lateral structure. At low density, the chains behave as polymer coils tethered to the interface, and the in-plains RDFs show that their interactions are similar to those between soft spheres or cylinders, which can be expected in a semi-diluted regime. The calculation of chemical potential actually indicates a linear scaling of the excess free energy related to chain transfer from a reference infinitely low-density brush into a brush of a finite lateral density and the same length *N* both with respect to the lateral density and *N*, which disagrees with the common mean-field treatment. From the free energies, we calculate the adsorption isotherm of the polymers at the surface.

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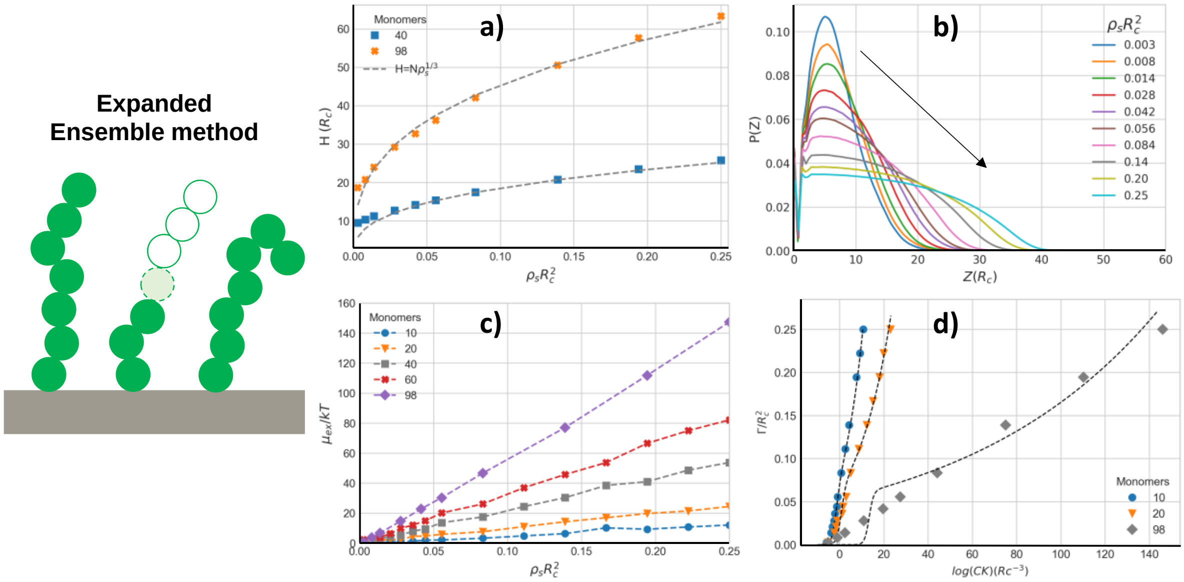

**Figure 1.** The schematic expanded ensemble for MB with a trial chain a) MB height as function of surface density, $\rho_s$; b) density profile for N = 40; c) The dependence of the excess chemical potential, $\mu_{ex}$ on $\rho_s$; d) adsorption isotherm derived from the thermodynamic calculations fitted with Redlich-Peterson equation.

# A NEW APPROACH TO THE CALCULATION OF SOLVATION EFFECTS IN BIOMOLECULAR SOLUTIONS IN THE FRAMEWORK OF THE CLASSICAL DENSITY FUNCTIONAL THEORY

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In the pharmaceutics an estimation of the binding affinity of a ligand (pharmaceutical drug) to a target protein plays a key role for virtual screening since this affinity reflects stability of the formed complex. This is important since a ligand with a higher protein affinity is known to provide a therapeutic effect at a lower concentration. One of the grand challenges for computational chemistry is to estimate the binding affinity (binding constant) of a ligand (L) to a protein (P), i.e., the P–L binding free energy (BFE). To date, there is a large set of non-empirical methodologies for estimating BFE such as virtual screening, end-point approaches, alchemical and pathway methods, etc. If one moves from virtual screening to pathway approaches in this set, an accuracy of BFE calculation increases but their costs also increase. Therefore, despite the abundance of computational methods, the fast and simultaneously inexpensive prediction of P−L BFE with high accuracy (1-2 kcal/mol) remains as one of the grand challenges of computational chemistry.

When calculating the P−L BFE, it is necessary to take into account the free energy of solvation/desolvation (FES) which can make a significant contribution to the BFE. The calculation accuracy of FES directly determines the calculation accuracy of BFE. Computer simulations using the techniques mentioned above are applied for calculating the required solvation term in the binding energy of the PL complex but have the same problem to calculate the BFE quickly and accurately.

In this contribution we present two new ideas on how to increase the efficiency and accuracy of SFE calculations by the statistical mechanics methods in the framework of theory of liquids such as 3D-reference interaction site model (3D-RISM) and renormalized site density functional theory (RSDFT) approaches. The first is realized by calculating the parameters of complex formation of biomolecules in a limited region of their hydration shell to increase the speed of calculations. The second is based on new parameterization of the solvation (hydration) free energy functional to improve the accuracy of calculations. The development of a new approach provides new opportunities for in silico studies of the solvation effects in solutions.

**Acknowledgements** This work was supported by the Russian Science Foundation (project No. 22-23-00184, https://rscf.ru/en/project/22-23-00184/).

# SYNTHESIS AND STRUCTURAL FEATURES OF SILICA-BASED AEROGEL IMPREGNATED WITH MEFENAMIC ACID

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In recent years, close attention has been paid to the problem of targeted delivery of drug compounds. A number of organic systems (for examples micelles, polymer nanoparticles) have been developed to transport drugs to specific organs. However, due to poor thermal and chemical stability, their use is extremely limited. The filling of such objects usually takes place using organic solvents, which can adversely affect the biological effect of the placed substance.

Aerogels offer a biocompatible and stable alternative. They have a developed porous structure and a significant specific surface area. At the same time, impregnation can be carried out in the same medium where the matrixes themselves are obtained - supercritical fluid.

All these properties together allow this class of mesoporous materials to be used for drug delivery.

Mefenamic acid is a non-steroidal anti-inflammatory drug. The compound affects the central and peripheral mechanisms of pain, reduces the local inflammatory process.

In this work, an aerogel based on silicon dioxide was impregnated with mefenamic acid in a supercritical $CO_2$ medium. The results obtained can be used in the field of pharmaceutical chemistry and in areas related to the transportation of medicinal compounds.

**Acknowledgement** This work was supported by the Russian Science Foundation (grant No. 22-13-00257).

# TOPOLOGICAL INVARIANT OF THE LLE DIAGRAMS AS THE BASIS OF EQUIVALENCE CLASSIFICATION

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Qualitative theories of various processes and phenomena are constructed on the basis of topological invariants. Theories of this type allow identifying characteristic properties of a group of objects and predict the behavior of the system. The use of qualitative methods makes it possible to move from the study of individual processes (phenomena) to their equivalence classifications. One of such topological properties is the invariant of the liquid-liquid equilibrium (LLE) diagram.

The boundary space of the phase diagram is homeomorphic to a sphere of the corresponding dimension. The miscibility area is "cut out" from the diagram boundary space. Consequently, a “hole" will appear on the sphere and its Euler characteristic will decrease by the number of such holes [1]:

$$E_B = \alpha_0 - \alpha_1 + \alpha_2 - \alpha_3 + \cdots = (1 - (-1)^{n-2}) - d,$$

where $E_B$ – Euler characteristic for boundary space, $\alpha_m$ – an element of a manifold of m dimension, n – the number of components, d – the number of “holes” on the sphere (coincides with the number of miscibility areas). This property can become the basis for the development of the LLE diagrams classification [2]. The diagram class is a sequence of two numbers: the first is the number of components in the system, the second is the Euler characteristic ($E_B$). The diagram type refers to the number of liquid phase splitting binary constituents. Examples of LLE diagrams of different classes and types for quaternary systems are shown in the figure 1 ($E_B$ can take values from -4 to 2 and the parameter responsible for the diagram type varies from 0 to 6 for quaternary systems). The phase diagram of a homogeneous system will correspond to the sequence 4.2-0. Systems of the same class contain the same number of miscibility areas (Figure 1 (a) and (b); (c) and (d)). Within the framework of one type, a thermodynamic transition between diagrams is possible (Figure 1 (b) and (c); (d) and (e)). It does not make sense to obtain a complete atlas of LLE diagrams, since the basis of equivalence classification is a topological feature (Euler characteristic).

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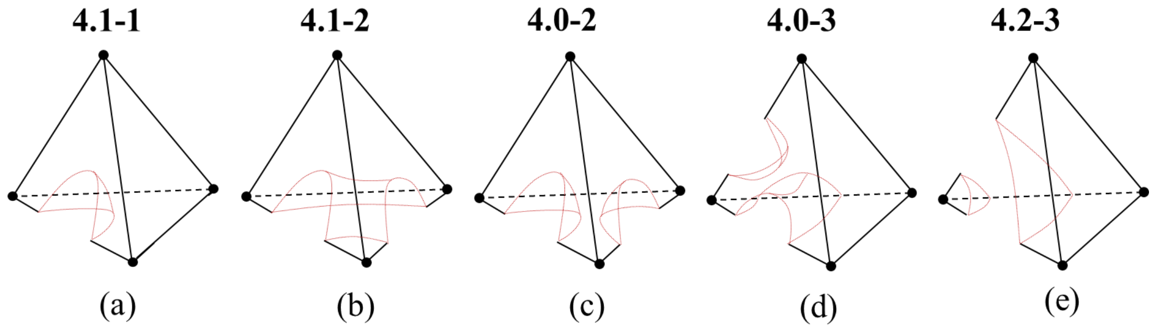

**Figure 1.** Examples of LLE diagrams of different classes and types

[1] A.V. Frolkova, L.A. Serafimov and Semin G.A., *Theor. Found. Chem. Eng.*, 2014, 48, 158.

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# THERMODYNAMIC-TOPOLOGICAL ANALYSIS OF THE VAPOR-LIQUID EQUILIBRIUM DIAGRAM OF A SIX-COMPONENT SYSTEM FOR OBTAINING PHENOL BY THE CUMULUS METHOD

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Thermodynamic-topological analysis (TTA) of phase diagrams is the basis for solving problems related to the structure of the vapor-liquid equilibrium diagram, identification of the limiting possibilities of the distillation process, synthesis of mixtures separation technological flowsheets [1, 2]. It is relevant to establish features of formation of the phase diagram structure of multicomponent systems (with more than three components) and their use to assess the possibility of industrial organic synthesis mixtures separation.

The object of the study is a six-component reaction mixture containing water, phenol, isopropylbenzene, alphamethyl styrene, hydroxyacetone, 2-methylbenzofuran. Phase equilibrium modeling was carried out using the NRTL equation in the AspenTech software package. The system is characterized by the presence of 14 binary azeotropes, including 10 positive, 4 negative. The possibilities of visual representation of the internal space of the six-component system diagram (hexatope) and its scans in a high-dimensional space are significantly limited. Therefore, formulas for enumerating elements that are adjacent to components with specific phase behavior (the presence of azeotrope, separatrix, limited mutual solubility of components) are used [3]. The analysis of these elements makes it possible to simplify the procedure and unambiguously determine the types of phase diagram singular points, to identify points with a minimum and maximum boiling point (at constant pressure) and, most importantly, saddle-type points that generate separatric manifolds as the boundaries of the distillation regions.

A complete TTA of the six-component system considered was carried out. The absence of separatric manifolds of the 4th dimension in the hexatope was proved. Thus, the phase diagram is represented by a single distillation region. At the same time, the difficulties of separating an industrial mixture are associated with the presence of separatric manifolds of the third (second) dimension in five-component (four-component) constituents and negative azeotropes of the target product (phenol) with impurity components (hydroxyacetone and 2-iethylbenzofurane). The products whose compositions belong to these constituents are the balance flows of the proposed technological distillation flowsheets, implementing direct, indirect sequences or sharp distillation at the first stage. Special techniques were used to completely separate mixtures of different compositions: extractive and reextractive distillation. The flowsheets columns operation parameters that ensure the production of products of the desired quality are determined in a computational experiment.

**Acknowledgements**The financial support of Russian Science Foundation (grant RSF 19-19-00620П).

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# INTERMOLECULAR INTERACTIONS BETWEEN IMIDZOLIUM- AND CHOLINIUM-BASED IONIC LIQUIDS: REGULARITIES AND PECULIARITIES

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The increase in the attention to the pharmaceutical products based on biomolecules gives particular importance to the preservation of the activity and, by extent – the native state of biomolecules. It is critical for such biopharmaceutical products as vaccines, allergens, and recombinant proteins.

However, despite the efforts paid to investigate the interactions between ionic liquids and proteins in recent years the quantitative interpretation of the role of intermolecular interactions of ionic liquids in the stabilization of biomolecules was not established.

In this work, we aim to find ionic liquids' parameters that determine their effects on the protein properties to find quantitative correlations between the properties of the ionic liquids and their impact on protein stabilityThe intermolecular interactions of imidazolium- and cholinium-based ionic liquids and hen egg-white lysozyme (HEWL) were studied by spectral, thermodynamic, and computational methods. The cholinium- and imidazolium-based ionic liquids: choline chloride [Ch][Cl], choline dihydrogenphosphate [Ch][DHP], choline acetate [Ch][OAc], 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][$BF_4$], 1-butyl-3-methylimidazolium trifluoromethanesulfonate [BMIM][TfO], 1-butyl-3-methylimidazolium acetate [BMIM][OAc] and 1-butyl-3-methylimidazolium methanesulfonate [BMIM][$CH_3SO_3$] were selected. The proton donor and acceptor abilities of ionic liquids were determined based on gas chromatography and solution calorimetry data. The temperature denaturation of HEWL in ionic-liquid solution was observed using capillary differential scanning calorimetry (DSC) and circular dichroism spectroscopy (CD). The interaction of ionic liquids with HEWL at the standard temperature was accessed by monitoring the protein's fluorescence changes. The effect of the ionic liquid on the stability of the native structure of HEWL strongly depends on the proton acceptor ability of ionic liquids. The denaturation temperature of the native structure HEWL is linearly correlated with the enthalpy of the specific interaction (hydrogen bonding) of methanol and trichloromethane in the studied ionic liquids. At the same time, fluorescence data revealed ionic liquid-specific effects, which depend on both ions in the ionic liquid. Both fluorescence and molecular docking data indicate a lack of strong binding between the studied ionic liquids and HEWL.

# MODEL OF CRUDE OIL FOR CALCULATING OIL-BRINE INTERFACIAL TENSION AT RESERVOIR CONDITIONS

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We report experimental investigation of the composition of reservoir oil samples of Yamburg oil fields of Acimovskaya suite and molecular dynamics simulations studies of the interfacial tension between crude oil and water brine. Based in distillation and chromatographic data, we compose a surrogate model of crude oil for molecular simulation studies. The composition of the aliphatic components is described by gamma-distribution and divided into fractions, each of which is presented by one alkane component. Aromatic components of similar boiling temperatures are added to the alkanes in amounts determined by the chromatographic analysis. The resulting surrogate model of separated liquid oil reproduces the experimental distillation curve. The surrogate model is applied in simulation studies of the dependence of the interfacial tension (IFT) between oil and brine on temperature, pressure, brine salinity and the gas content. The gas amount is shown to strongly influence the IFT, which decreases as the gas amount increases. The aromatic content showed almost no influence on the IFT. Based on the simulation results we build a linear model that describes the IFT dependence on the temperature, pressure, gas content, molality of the brine.

**Acknowledgements** This research was supported by PJSC Gazprom.

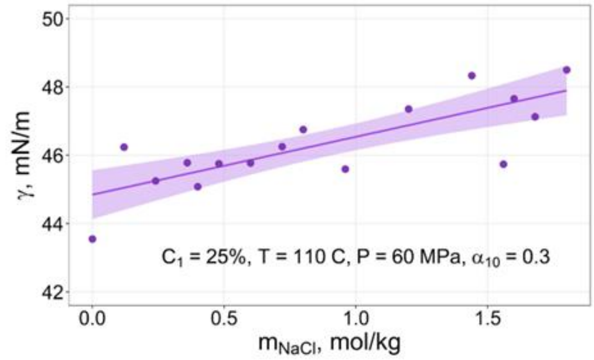

**Figure 1.** IFT in oil-mineral-brine system from brine salinity.

# IFT AND CONTACT ANGLES AT CRUDE OIL-BRINE-MINERAL INTERFACES AT RESERVOIR CONDITIONS

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One of priority tasks of increasing the oil recovery factor is to study the flow of downhole fluid in rocks. Important parameters necessary for modeling filtration are interfacial tension and contact angles in mineral-oil-brine systems under downhole conditions. Experimental and calculated data of these parameters in the special literature are insufficient due to the problems associated with measurements at high pressures, as well as the large differences in the composition of crude oil in different oil wells. In this study we created the model for determining contact angles and IFT in the quartz-oil-brine system. The model allows to use different minerals, including quartz, as one of the most common minerals of reservoir rocks. We took the (001) alpha-quartz surface as the most stable. In this work, models of quartz with different degrees of hydroxylation were created. Complex oil model with 15 components, including aromatic substances, was used for the calculations. We parameterized adsorption interactions using experimental data. The model parameters were determined - the hydroxylation of the quartz surface and the degree of interaction of the quartz atom with CH groups of alkanes. For other minerals only interactions of mineral atoms and CH groups were determined. Dependences of IFT and contact angle on temperature, pressure, amount of methane, salinity of brine and degree of aromatization were found. It was found that the contact angle weakly depends on the temperature, while the surface tension changes significantly at different temperatures. A decrease in surface tension with increasing content of methane in the model oil has been revealed, since it is super-critical component of the mixture. At the same time, a nontrivial dependence of the contact angle on the methane content in the mixture, shown in Fig. 1, was established. The maximum angle (Fig. 1) is achieved at a mass fraction of methane equal to 15%, while the angle and surface tension do not depend on aromatics. It was found that with increasing pressure, the surface tension weakly decreases and the contact angle noticeably increases; with increasing salinity, the surface tension increases. Thus, the work created a model to determine the contact angles and surface tension in the oil-salt-surface mineral systems and removed the main dependencies. In the further researches influence of aromatics will be studied at variation of quantity of methane.

**Acknowledgements** We thank Gazpromneft NTC (St. Petersburg) for financial support

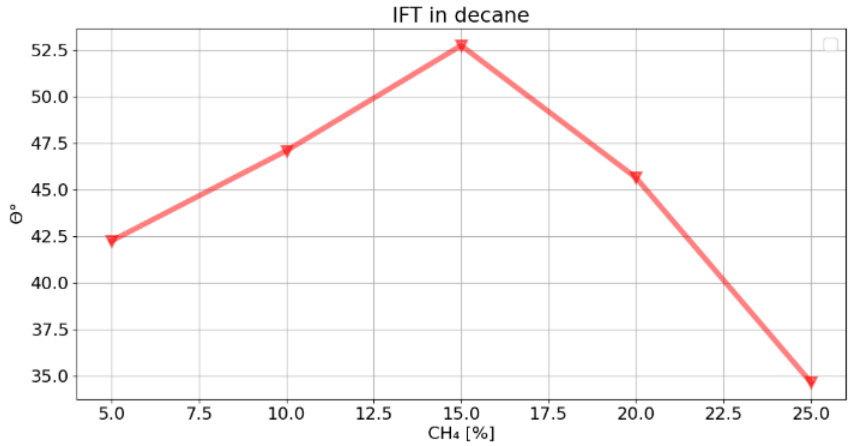

**Figure 1.** Contact angle in oil-mineral-brine system from methane content

# INDIUM(III) β-DIKETONATES AS MOCVD PRECURSORS: SYNTHESIS AND THERMAL PROPERTIES

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Indium oxide is one of the best transparent conductive materials. Moreover, its functional properties such as optical, electrical and ferromagnetic can be additionaly tuned by doping. One of the convenient techniques to obtain films and nanostructures is chemical vapor deposition, where the metal compound (precursor) is transported in gaseous form to the object to be coated (substrate) and converted there to the desired material *via* decomposition, oxidation or other chemical conversions.

To optimize the deposition conditions of functional materials, thermal properties including condensed phase transitions and stability, melting, sublimation and vaporization processes for a volatile metal-organic precursor used are of great importance.

Metal β-diketonate complexes are often used as volatile indium oxide precursors. Even more, the ease of synthesis and air stability as well as a variety of thermal properties depending on ligand composition distinguish metal β-diketonates favorably.

In the current work, several indium(III) complexes with β-diketones with different substituents in ligand (acetylacetone, trifluoroacetylacetone, benzoylacetone, benzoyltrifluoroacetone, dibenzoylmethane, etc.) were synthesized and purified. They were identified by a set of methods – elemental analysis, visual melting point observation, IR spectroscopy, X-ray phase and structural analysis. The data on thermal stability in condensed phase were investigated by thermogravimetry (TG, in helium) and differential thermal analysis (DTA). Saturated vapor pressure was studied by the flow method.

By an example of $In(thd)_3$, the importance of vapor pressure data for optimizing precursor's mass transfer in chemical vapor deposition (CVD) process was shown.

**Acknowledgements** The financial support of the work was provided by the Russian Science Foundation and the Government of the Novosibirsk Region (project no. 22-23-20182).

# THE TRANSFORMATIONS OF THE STRUCTURES OF AN EQUILIBRIUM PHASE DIAGRAMS OF THREE COMPONENT BIAZEOTROPIC SYSTEMS UNDER EXTERNAL CONDITIONS CHANGE

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As is known, the presence of azeotropes in the reaction mixtures of the products of the main organic and petrochemical synthesis complicates the distillation separation of such mixtures and leads to complex and energy intensive schemes for the isolation of the target products. The presence of biazeotropy leads to an increase in the number of singular points, which also leads to an increase in the number of structures of equilibrium phase diagrams (SEPD) of separated mixtures. The biazeotropy generates a non-trivial course of distillation lines in the concentration simplex, accompanied by the appearance of closed separatrix, which is excluded in monoazeotropic systems; this, in turn, leads to an increase in the number of distillation regions. In this regard, it is necessary to analyze the mechanism of SEPD change for biazeotropic systems in order to create the most favorable conditions for the separation of such mixtures by distillation. The objects of this study are three component systems that contain binary biazeotropic components and do not have ternary azeotropes, which belong to the first group of biazeotropic three component systems according to the classification [1].

In the first stage of the study, we analyzed the transformations of SEPD of zeotropic and monoazeotropic systems that belongs to 3.0.0, 3.1.0, 3.2.0 classes of Serafimov's classification [2] in to biazeotropic systems through the stage of forming a binary internal tangential azeotrope under external conditions change (for example, pressure). In total, we obtained 24 possible variants of diagrams transformations and 24 SEPD of three component systems with a binary biazeotropic constituent [3].

The second stage of our study included the analysis of SEPD transformations of monoazeotropic systems that belongs to 3.1.0, 3.2.0 and 3.3.0 classes [2] into diagrams of biazeotropic three component systems through the stage of formation of a binary boundary tangential azeotrope under external conditions change. In this case, the number of possible variants of diagrams transformations and the number of SEPD of three component systems with a binary biaseotropic constituent was 27 and 19, respectively [4].

Thus, we have established the regularities of mutual transformations of the structures of the vapor-liquid equilibrium diagrams of zeotropic, mono- and biazeotropic three component systems under external conditions change, which allows us to choose rational technological parameters for the separation process of biazeotropic mixtures.

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# STUDY OF THE KINETICS OF THE FORMATION OF METHANE GAS HYDRATE FROM WATER FOAM

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The gas hydrate formation process is being studied more and more actively in various kinds of disperse systems, including foamed materials [1-3]. At the same time, only a few works on hydrate formation in the most common type of foams, the aqueous foams stabilized by surfactants, are available. As an example, one can point to the results in [4]. This work shows that the presence of foam in the reactor increases the rate of methane hydrate nucleation by an order of magnitude. Thus, the almost complete absence of experimental data in this field has determined our interest in the study of hydrate formation from surfactant-stabilized aqueous foams.

This work presents experimental studies of methane hydrate formation from aqueous foam stabilized by surfactants. The experiments were carried out in a high-pressure optical chamber [5,6]. It is shown that the process of hydrate formation begins near the chamber walls. The front of hydrate formation propagates through the entire volume of a sample at a rate of ~1 mm/s which leads to the hydrate crust formation on the surface of foam cells, while a liquid layer of surfactant solution remains between the hydrate films. The paper discusses the phase transition criterion, which quantifies the fraction of water that converts into hydrate during the adiabatic process. The following phenomena accompanying hydrate formation in foam are described: (a) deformation of the foam structure behind the hydrate formation front due to a decrease in the gas pressure; (b) subsidence of foam associated with capillary suction of solution through the inter-hydrate media.

**Acknowledgements** This work was supported by the Russian Science Foundation, project no. 22-19-00092.

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# ESTIMATION OF METHANE PRESSURE IN A COAL MASSIF BY MASS TRANSFER PARAMETERS

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Determination of the formation pressure of methane in coal directly in the mining, and not in laboratory conditions, is necessary to predict sudden emissions of coal and gas.

Laboratory methods for studying the kinetics of mass transfer in coal matter are often based on saturation of crushed coal samples with methane and analysis of subsequent degassing [1,2]. They allow us to determine the structural characteristics of coal (porosity), mass transfer parameters (diffusion and filtration coefficients of methane in coal) and the time when the mass transfer mechanism changes. These measurement methods do not allow to determine the initial pressure of methane because coal is subjected to significant multi-stage processing (grinding, vacuuming, drying, etc.).

Consider the configuration of real conditions (Fig. 1), in which it is possible to estimate the reservoir pressure of methane directly in the production, without resorting to laboratory studies.

A probe capable of recording the flow of gas coming out of the well is inserted into the well drilled in the coal massif immediately after drilling. First of all, methane, which was previously contained in closed microscopic pores and cracks destroyed during drilling, will come out of coal quickly enough. $P_c$ can be interpreted as the reservoir pressure of methane (the pressure of methane in the closed pores of coal away from the development zone).

Since the dimensions of the hole are quite small (the length of the hole is 1 m, the diameter is 42 mm), it can be assumed that in the first minutes of gas release, the gas pressure in the filtration channels of the coal substance along the boundary of the hole differs little from the pressure in undisturbed coal. Then the problem of gas accumulation in the hole can be reduced to the standard problem of diffusion in a cylindrical body with a fixed concentration of diffusing (in our case, gas pressure) at the boundary.

To correctly determine the pressure, it is necessary to take into account the fact that gas release into the volume of the hole does not occur through the entire surface area. Since the measurement of the gas flow is carried out immediately after drilling the hole, at this time there is only the release of methane, which was in gaseous form inside the system of open pores of coal.

Thus, with a well length of 1 m, a methane flow of 2 l/min, an open porosity of 0.05, the gas pressure in the reservoir will be estimated at 18 atmospheres.

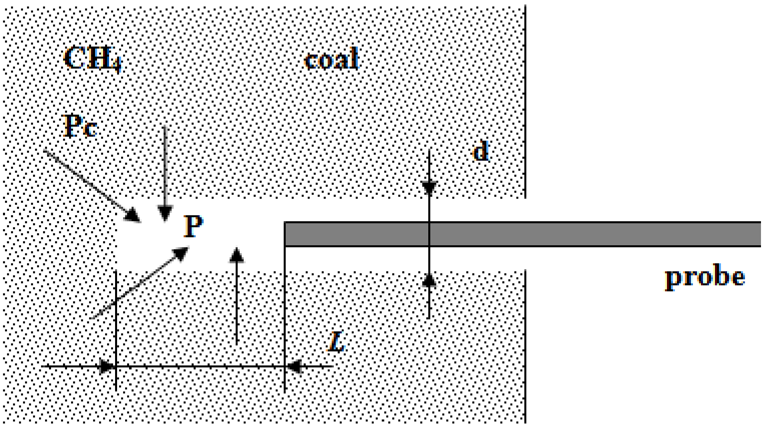

**Figure 1.** Location of the measuring probe in the coal massif

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# EXPERIMENTAL STUDY OF THE PHASE EQUILIBRIA IN THE Tb-Co AND Tb-Co-Fe SYSTEMS

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The rare earth elements (R) with transition metals (TM) form a series of intermetallic compounds, which possess exceptionally interesting magnetic properties such as high Curie temperatures, saturation magnetic moment, and uniaxial anisotropy and very high energy products. As well the alloys from the R-TM systems find the application as magnetostrictive and H-storage materials [1]. However, the lack of data on the phase diagrams of corresponding systems complicates significantly the materials design process.

Phase equilibria in the Tb-Co, and Tb-Co-Fe systems were investigated experimentally by a combination of scanning electron microscopy (SEM), electron probe microanalysis (EPMA), X-ray diffraction (XRD), and differential thermal analysis (DTA). Based on the experimental data from the present work, the Tb-Co system was constructed. The liquidus and solidus projections, the melting diagram, the isothermal sections at 1200 and 1000°C, the vertical sections and the Scheil reaction scheme for the Tb-Co-Fe system over the whole concentration range were constructed for the first time. No ternary intermetallic phases exist in these system, but the continuous solid solutions $Tb_2(Co,Fe)_{17}$, $Tb(Co,Fe)_3$ and $Tb(Co,Fe)_2$ were found and the $TbCo_5$ and $Tb_2Co_7$ phases have extended homogeneity ranges in the ternary system.

In addition to that, the magnetic properties of some Tb-Co phases were measured.

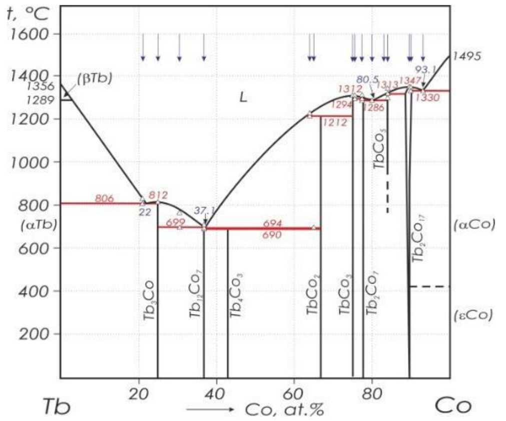

Fig. 1. Phase diagram of the Tb-Co system: △ – DTA data.

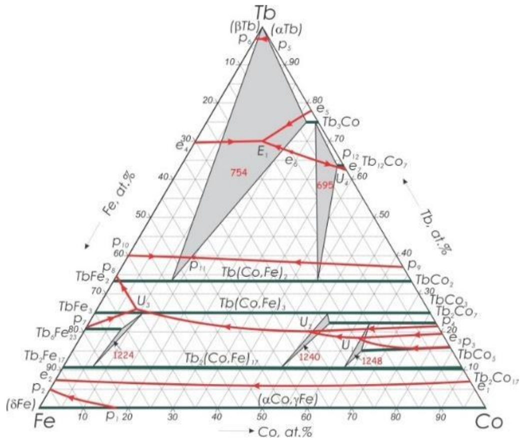

Fig. 2. Phase diagram of the Tb-Co-Fe system.

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# THE EFFECT OF HYDROTHERMAL SYNTHESIS CONDITIONS ON DEHYDRATION, CRISTALLIZATION TEMPERATURES AND PHASE COMPOSITION OF $60CeO_2$-$30ZrO_2$-$10Y_2O_3$ (MOL.%) CERAMIC PRECURSOR

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Cerium dioxide solid solutions are used as catalysts for selective oxidation in biological systems and as anodes and oxygen-conducting membranes for various electrochemical devices. However, such solid solutions crystallize at temperatures of the order of 900°C so there is a need to lower the crystallization temperature. Hydrothermal synthesis has several advantages over the other techniques for oxides synthesis, such as precise stoichiometry control of the resulting solid solutions, as well as the particle size distribution, their morphology and crystal structure. Thus, the goal of the work was to investigate the effect of hydrothermal treatment conditions on dehydration, crystallization temperatures and phase composition of $60CeO_2$-$30ZrO_2$-$10Y_2O_3$ (mol.%). Ceria based gels were obtained by sol-gel synthesis in the reversed co-precipitation version, the synthesis conditions were pH = 9-10, T=1-2°C. The resulting gel was then placed in an autoclave at temperatures of 160-260°C (with a heating step of 20 °C) for 120 minutes. The obtained powders were dried until weight constancy at 110 °C. Precursors obtained were comprehensively investigated using STA, XRD, XPS and PSD analysis. It was found that the use of hydrothermal treatment of gel resulted in the shift of solid solution crystallization from ~900 to 200 °C. The average agglomerate size of hydrothermally-treated powders lies in the range of 180-240 nm. The hydrothermal treatment of the 0.3M solution of nitrates at 260°C results in the direct crystallization of ceria-based cubic solid solutions.

**Acknowledgements.** DSC and TG studies were performed at the Thermogravimetric and Calorimetric Research Centre, SPbU. This work was supported by the President’s grant for young scientists (research project 075-15-2021-370).

# ALKYLAMMONIUM PROTIC IONIC LIQUIDS WITH ANIONS OF SULFONIC ACIDS: THERMAL PROPERTIES AND STRUCTURE

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This work presents a systematic review of the experimental data on thermal properties and the results of quantum chemical calculations of the family of protic alkylammonium salts $R_nH_{4-n}NX$ bearing anions of different sulfonic acid. Protic ionic liquids, as other ILs, have a lot of useful properties, such as good thermal and electrochemical stability, a wide temperature range of liquid state, low flammability, and a simple synthesis procedure, which make them very attractive for a wide range of practical applications. We report the experimental data on thermal properties (decomposition, melting, and glass transition temperatures) and consider the ILs structural features associated with hydrogen bond formation. The effect of the structure/nature of cations and anions on the above-mentioned properties and the structure of these PILs are discussed. In this work, we analyze the properties of alkylammonium salts including both the ones investigated in our laboratory (the new data and results published earlier) and those presented in the literature.

An analysis of the data on decomposition temperatures showed that in salts with the same cation, the $T_{dec}$ value depended on the anion, while in salts with the same anion, $T_{dec}$ was not strongly dependent on the cation. The highest decomposition temperatures were observed for the salts with TFSI and TfO anions. There was no linear dependence between the decomposition and melting points, on the one hand, and the $\Delta pK_a$ values, on the other.

Quantum chemical studies showed that the acid donated the proton to the amine to form ion pairs in most of the PILs. The thermodynamic stability of the ion pairs significantly increased at higher values of the energy of amine affinity with the proton and decreased as the anion affinity with the proton grown. The calculations of the interaction energy between the ions in the ion pairs according to the supermolecular approach showed that the electrostatic interaction mainly determined the energy stability of the ion pairs. The dispersion interaction made a certain contribution to the interaction energy value but it is always less than the H-bonding contribution. The successive substitution of hydrogen atoms for ethyl groups in the ethylammonium cation (EA>DEA>TEA>TetEA) as well as the increase in the alkyl group size in the tertiary cation (TMA>TEA>TPA>TBA) led to a significant decrease in the ion-ion interaction energy and weakening of the H-bonding interactions. The hydrogen bonds in most of the ion pairs with a tertiary ammonium cation were extremely strong, with their energies reaching 140 kJ/mol. For the ion pairs with a TfO anion the $E_{HB}$ values grow in the following series: TBA<TPA<TEA<TMA. A correlation was found between the calculated values of free energy changes of the ion pair formation with the decomposition temperature of PILs. However, no direct correlations were observed between the interaction energy in the ion pair determined by quantum-chemical calculations and experimentally observed melting points, which indicated how important it was to take many-body effects into account.

**Acknowledgements** Ionic liquids tripropylammonium bis(trifluoromethylsulfonyl)imide and tripropylammonium sulfobenzoate were synthesized and studied within the project of the Russian Science Foundation (grant № 22-23-01155).

# QUANTUM-CHEMICAL METHODS FOR ESTIMATING THE THERMODYNAMICS OF ACID-BASE REACTIONS OF PROPYLAMINES WITH DIFFERENT BRØNSTED ACIDS

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Proton transfer in protic ionic liquids is not well understood. Some acid-base reactions do not proceed to the extent that is expected from the difference in the pKa values between the base and acid in aqueous solutions, yet some do. In that regard, we present the results of quantum-chemical investigation of the interaction of propylamine (PrA), dipropylamine (DPrA) and tripropylamine (TPrA) with sulfuric (SA), methansulfonic (MsO) and benzenesulfonic (BSu) acids. All calculations were performed by dispersion corrected density functional theory method (B3LYP-GD3). Relaxed potential energy surface scans with respect to the O−H bond of the acid in all the studied acid-amine systems were carried out. It was found that when PrA interact with sulfuric acid – superacid, the acidic proton moves to the nitrogen atom of the amine and generates the ions held together in the ionic pair not only by electrostatic interactions but also hydrogen bonding. The interaction of MsO and BSu with PrA leads to the formation both of molecular hydrogen bonding complexes and ionic pairs. The increase in the number of propyl groups on the nitrogen atom in the order PrA<DPrA<TPrA strengthens the amine basic properties, which facilitates the proton transfer from the acid to the amine leading to the formation of ionic pairs.

The thermodynamic characteristics of the formation process of the molecular complexes and ionic pairs were evaluated. Negative Gibbs free energy values show that the formations of the complexes and ionic pair are thermodynamically favorable. The $\Delta G_{298}$ values for the ionic pairs PrA/BSu and PrA/MsO are more negative than for their corresponding complexes. We found the dependence of the $\Delta G_{298}$ on the ΔPA parameter (difference in proton affinity of the acid anion and alkylamine), which indicates that the energy tends to decrease with the ΔPA rise.

It was established that the specific feature of the ionic pairs with PrA and DPrA cations is the presence of two hydrogen bonds. Herewith, the ionic pairs with DPrA cation tend to form more symmetrical ring structure of dual hydrogen bonds compared with that in the ionic pairs with PrA cation. A sole N-H…O hydrogen bond is formed in the ionic pairs with TPrA cation because of the lack of other hydrogen atoms of the amino group. The ion-ion interaction energy in the ionic pairs with the same anion decreases with an increase in the cation size PrA<DPrA<TPrA owing to the steric hindrances imposed by large propyl groups, which weakens both electrostatic interactions and hydrogen bonding with the anion. The results also showed that the anion replacement of the hydroxyl group in the hydrogen sulfate anion by the benzene ring (Bsu) and methyl group (MsO) in the ionic pairs with the same cation leads to an increase in the energy of ion-ion interactions. The analysis performed indicated that the increase in the interaction energy, including hydrogen bonding energy, correlates with the increase in the ΔPA values.

We suggest that the ΔPA values can be used as a measure of estimation of the proton transfer degree in the acid-base interactions. The found dependences can also be very useful for predicting the melting and decomposition temperatures and viscosities of new ionic liquids.

**Acknowledgements** This work was supported by the Russian Science Foundation, grant № 22-23-01155.

# THE EQUATION OF STATE OF MOLECULAR GROUPS EMERGING FROM THE CORE OF AN INVERSE MICELLE

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In order to have a stable inverse micelle of a surfactant in a nonpolar solvent, one needs to identify such contributions to the work of aggregation which provide a minimum in this work above the critical micellar concentration (cmc) of the corresponding surfactant in the solvent. It is clear that one of such contributions is given by the electrostatic interaction of polar heads [1] within a core of the inverse micelle, which provides a large negative term in the aggregation work. Positive term in the expression for the aggregation work is associated with the free surface energy of the interface between the micellar core and solution. In fact [1,2], there are several positive terms related to the free surface energy. The obvious one is determined as $gA$ where $g$ is the surface tension for the flat interface between the polar groups phase and the solvent and $A$ is the core surface area depending on the aggregation number $n$. Such a contribution is responsible for appearance of first maximum in the expression for the aggregation work, but it is insufficient to explain the appearance of the subsequent minimum of the work and growth of the work at large aggregation numbers. An additional positive term in the surface free energy in the form $-k_{\mathrm{B}}T\ln\left(1-a_0/a\right)$ (here $a=A/n$ is the area per surfactant molecule at the interface micellar core-solvent and $a_0$ is the cross-sectional area of the surfactant molecule tail, $a_0/a<1$) has been considered in [1]. As said in [1], the term $-k_{\mathrm{B}}T\ln\left(1-a_0/a\right)$, generally, takes into account the effect of the excluded area of the interface (due to finite cross-section of a surfactant molecule) and is important at large aggregation number in a micelle. Nevertheless, this term still turns to be insufficient for appearance of minimum of the aggregation work, and this fact allowed some researchers [1] to consider existence of the cmc and stable inverse micelles in nonpolar solvent as evidence and result of small impurities of water in the solvent. It has been recently shown [2] that the term $-k_{\mathrm{B}}T\ln\left(1-a_0/a\right)$ does not represent a complete account of the effect of excluded interface area. More accurate description of this effect may be obtained with the help of the two-dimensional equation of state of a system of hard disks. One can use the equation for two-dimensional pressure $\Pi$ at the interface from the scaled particle theory [3] in the following form: $\Pi=k_{\mathrm{B}}T/a\left(1-a_0/a\right)^2$ ($k_{\mathrm{B}}$ is the Boltzmann constant, $T$ is the absolute temperature). This equation is known to be a two-dimensional analog of the known Carnahan–Starling equation for hard spheres. It has been noted that, in spite of its analytical simplicity, such equation of state is well applicable at any value of $a$. With the help of the Gibbs–Duhem relation, we find instead of term $-k_{\mathrm{B}}T\ln\left(1-a_0/a\right)$ the following positive contribution $k_{\mathrm{B}}T\left[-\ln\left(1-a_0/a\right)+\left(3-2a_0/a\right)a_0/a\left(1-a_0/a\right)^2\right]$ to the aggregation work. This contribution does provide a minimum and growth of the aggregation work for large $n$ in the case of inverse micelles. It is noteworthy that even more accurate two-dimensional equations of state [5] can also be used.

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# THERMODYNAMIC PROPERTIES OF STRONTIUM FERROMOLYBDATE

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A calorimetric study of the heat capacity temperature dependence of the strontium ferromolybdates $Sr_2FeMoO_{5.82}$ (I) and $Sr_2FeMoO_{5.93}$ (II) in the range of (7 to 370) K was performed.

The polycrystalline samples of $Sr_2FeMoO_{6-\delta}$ were obtained by solid-phase synthesis from initial «puriss. spec.» reagents $SrCO_3$, $Fe_2O_3$ and $MoO_3$. Grinding and mixing of the stochiometric mixture of initial reagents were carried out in a vibrating mill in ethanol for 3 hours. Obtained mixtures were dried at $T$ = 350 K and pressed into pellets. Preliminary annealing was carried out in air at temperatures near 970 K for 20 h. To increase the homogeneity, secondary grinding was used. The final synthesis of the samples I and II was carried out in a gas mixture flow (5 % $H_2$/Ar) at temperatures of 1450 K and 1420 K, respectively, for 25 h, followed by quenching at room temperature. According to the X-ray data, it was established that the obtained samples had a single-phase composition. Based on the complete reduction of the magnet in a hydrogen flow at 1370 K for 20 h to SrO oxide and metals Fe and Mo, it was found that the chemical composition of the samples I and II corresponds to the formulas $Sr_2FeMoO_{5.82}$, and $Sr_2FeMoO_{5.93}$ respectively.

The heat capacities of the strontium ferromolybdates I and II were measured in an automatic vacuum adiabatic calorimeter TAU-10 (Termis, Moscow, Russia). The relative expanded uncertainty in the heat capacity measurements didn't exceed ±0.4 % in the temperature range of (20 to 80) K, ±1 % in the range of (10 to 20) K and ±2 % in the range of (5 to 10) K.

It was determined that the heat capacities of the samples I and II increase monotonically with increasing temperature in the range of (7 to 370) K, while the molar heat capacities of the sample I were almost always higher than those of sample II (from 20 % at 10 K to 5 % at 80 K and on average by 3.5 % in the range of (80 to 370) K). There was only a small temperature region from 20 K to 25 K, where the heat capacities of the two samples coincide within the limits of their determination errors. The differences in the heat capacity of the samples at the lowest temperatures (from 7 K to 15 K) were most significant due to the special sensitivity of the heat capacity to oxygen nonstoichiometry in this region and the features of the cations superstructural ordering. Thus, a decrease in the oxygen content in the sample and a corresponding decrease in the degree of superstructural ordering of cations ($P$ from 88 % to 78 %) leads to a significant increase in the molar heat capacity of strontium ferromolybdates.

On the heat capacity temperature dependence curves of the studied samples, λ-shaped anomalies were found in the region of (159 – 202) K. The nature of the change in the heat capacity of the samples with temperature indicates that the detected transformations are second-order phase transitions (λ-type) and can be explained by the appearance of antiferromagnetic ordering of the ions magnetic moments inside perovskite-like blocks.

It was found that the molar heat capacities of the studied samples of strontium ferromolybdates in the range of low temperatures from 7 K to 15 K don't obey the $T$-cubes law. An analysis of the heat capacities temperature dependences of the oxides in the region of (7 – 10) K indicates a transitional nature of their structure (between layered and three-dimensional).

Standard thermodynamic functions of $Sr_2FeMoO_6$, calculated based on the heat capacity polynomial temperature dependences for the studied samples, were recommended for practical calculations (with the relative expanded uncertainty ± 2%).

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# STUDY OF THE BEHAVIOR OF DIOXADET MOLECULES IN WATER BY MOLECULAR DYNAMICS METHODS

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Dioxadet is a drug designed to treat various types of oncology and was developed at the Petrov N. N. NMRC of Oncology in St. Petersburg. It is a functional analog of cisplatin and has a comparable efficiency and fewer side effects. The drug has passed the second phase of clinical trials and is approved for production and use in clinical practice [1].

Nevertheless, there is no complete information about its physico-chemical properties and, in particular, about its mechanism of action. Therefore, this study is dedicated to characterizing the typical behavior of this drug molecule in water by molecular dynamics methods.

The GROMACS package was used to perform the computer experiments. The parametrization of the molecule was performed using the online resources: ATB, PRODRG, SwissParam, also the AmberTools software package was used. Also the quantum calculations necessary for parameterization were performed in Gaussian by the Harti-Fock method and on the basis of the B3LYP functional with the same 6-31G* basis for both calculations. This resulted in the creation of five different models.

Each of the five models were used to perform the Gibbs free energy calculation of the solvation of one dioxadet molecule in water with alchemistry method and MBAR postprocessing and also by quantum chemistry methods. The Gibbs free energy calculated for a nearly saturated solution is lower than for an infinite dilution, which means the benefits of dissolving several molecules. The enthalpy and entropy of solvation were obtained from the results of $\Delta G$ calculations at different temperatures for the two models B3LYP and ATB. The enthalpy of dissolution was also obtained by the direct calculation of the sum of the potential energy and the work of expansion. The results indicate the hydrophilic nature of the dioxadet. Molecular dynamic simulations of three dioxadet molecules in water were performed. The spatial distribution of the molecules relative to each other showed the preference to form associates with a stack-like structure.

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# LIQUID-LIQUID EQUILIBRIUM OF TERNARY SYSTEMS BUTANOL + WATER + BUTYL LACTATE AND BYTANOL + WATER + BUTYL GLICOLATE

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Last decade, the production of hydroxy acid derivatives from renewable biomass has acquired importance. The reactive distillation stands out is the most promising one technology of recovery volatile acids as well as hydroxy acids from different broths. Still, the main challenges are the conditions and energy optimization of the process to be effective. The industrial production of lactic acid is mainly based on renewable sources since it is estimated that about 90% is produced microbiologically. Glycolic acid is another attractive potential molecules-platform obtained from biorefinery processes.

The esterification reactions of hydroxy acid with alcohols are not only used in the purification process but also in the production of the corresponding esters. Butyl lactate is biodegradable and used as solvent for nitro and ethyl cellulose, gums, oils, dyes, paints, etc.

In the fermentation process hydroxy acid is produced as an aqueous solution. In reaction system components (butanol, water and butyl glycolate or butyl lactate) are characterized by limited solubility. The liquid-liquid equilibrium (LLE) in ternary system was experimentally at 298.15 К and atmospheric pressure. Heterogeneous binary mixture of butanol and water were prepared in glass vessel at room temperature by gravimetric method with accuracy of 0.0001 g using an analytical balance VL-200. Prepared binary mixture was heated up to 298.15 K using a liquid thermostat. The ester was added using Hamilton glass syringes. The system was homogenized stirring with magnetic stir bar. Organic and water phase samples were analyzed 2-3 times by gas chromatograph equipped with a flame ionization detector and thermal conductivity detector.

The butyl lactate and butyl glycolate preferentially dissolve in the organic phase.

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**Table 1.** Experimental data on solubility (W, % mass) in the ternary systems at 298.15 K and atmospheric pressure

| Butanol (1) - Water (2) - Butyl Lactate (3) | | | | | | Butanol (1) - Water (2) - Butyl Glycolate (3) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Organic phase | | | Water phase | | | Organic phase | | | Water phase | | |
| 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 |
| 74,41 | 21,16 | 4,43 | 7,91 | 91,92 | 0,17 | 72,52 | 22,64 | 4,84 | 7,92 | 91,31 | 0,77 |
| 70,43 | 20,89 | 8,68 | 7,86 | 91,73 | 0,41 | 67,87 | 23,00 | 9,13 | 8,04 | 90,78 | 1,18 |
| 66,26 | 21,40 | 12,34 | 7,39 | 92,02 | 0,60 | 64,20 | 22,72 | 13,08 | 6,98 | 91,65 | 1,36 |
| 62,83 | 21,23 | 15,94 | 6,99 | 92,25 | 0,76 | 60,55 | 22,77 | 16,68 | 7,13 | 91,10 | 1,77 |
| 60,00 | 20,83 | 19,17 | 6,78 | 92,27 | 0,94 | 57,80 | 22,28 | 19,92 | 7,00 | 90,92 | 2,07 |
| 57,24 | 20,71 | 22,04 | 6,90 | 91,87 | 1,24 | 54,92 | 22,42 | 22,66 | 6,99 | 90,60 | 2,41 |

# POPULAR THERMODYNAMICS

# CHEMICAL THERMODYNAMICS ON POST STAMPS

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World philately reflects numerous images of scientists who have made a significant contribution to the development of chemical thermodynamics (Fig. 1).

**Figure 1.** Post stamps: a – A. Celsius; b – M. Berthelot; c – H. von Helmholtz; d – F. Haber; e – J.H. van't-Hoff; f – J.W. Gibbs; g – L. Boltzmann; h – J.D. van der Waals; i,j – W.H. Nernst; k,l – M. Planck

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