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A. Chemistry

Reactions of 2-bromo-2*H*-azirines with stannanes: explicit Stille couplings or not?

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Classic Stille reaction consists in the C-C bond formation between stannanes and halides or pseudohalides in the presence of catalytic amount of Pd-complex. In certain cases, copper or aurum salts alone are able to catalyze Stille-like cross-coupling reactions without the assistance of palladium [1].

In this study, we have found the reaction between 2-(tributylstannyl)pyridine derivatives and 2-halo-2*H*-azirines, which doesn't require to use of any catalyst at all (Fig. 1). Such transformation can be directly implemented under the heating of starting compounds in toluene. As a result, 2-(pyridin-2-yl)-2*H*-azirines have been obtained in high yields. The reaction tolerates to wide range substitutes in azirine framework. It is obvious, that the reaction has absolutely different from classic Stille or Stille-like reaction mechanism due to the absence of a catalyst. Based on the DFT calculations and control experiments, the mechanism of this reaction was also proposed.

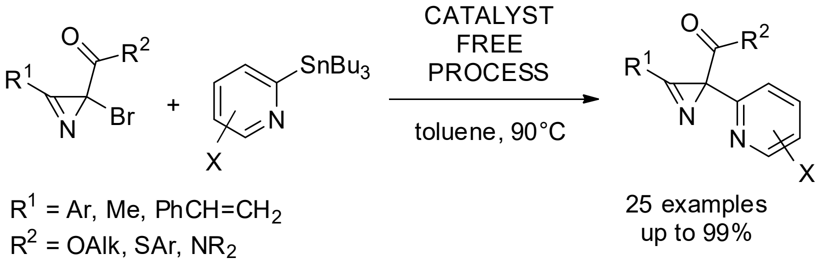

Fig. 1. Synthesis of 2-(pyridin-2-yl)-2H-azirines.

Acknowledgments. This work was supported by the Russian Science Foundation (project № 20-13-00044). This research used recourses of the Magnetic Resonance Research Centre, Chemical Analysis and Materials Research Centre, Centre for X-ray Diffraction Studies, Chemistry Education Centre, Computing Centre of St. Petersburg State University.

References

1. C. Cordovilla et al. // ACS Catalysis, v. 5, p. 3040–3053 (2015).

Electrochemical Platform for NeuroNet Analysis of Zn in blood and urine

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Deficiency of vitamins and minerals (trace elements) is a severe global health problem, partly because of logistical difficulties in assessing the state of trace elements in a population. Zinc is an essential trace element (micronutrient) which plays an essential role in human physiology.

Stripping voltammetry (SV) analysis is a powerful and straightforward tool for continuous monitoring of trace target metal species. The determination of zinc in biological samples is usually carried out by the method of anodic SV(ASV). As working electrodes (WEs), carbon, copper, bismuth, and glassy carbon modified with mercury salts are used [1].

For zinc detection by the method of ASV in biological fluids, various methods of sample preparation and signal acquisition are used. Deproteinization of samples by sodium ethylenediamine-tetraacetate (EDTA) was proposed by Zakharchuk et al. Such a method has the advantage of eliminating the matrix effect of biological molecules and breaking up zinc from complexes. The Metexchange solution (ESA Inc.), which is a mixture made up of chromium chloride (1.07 wt %), calcium acetate (1.43 wt %), and mercuric ions, was used for Zn detection by stripping it on the Bi electrode. Screen-printed modified electrodes without sample preparation for the Zn SV detection in sweat are demonstrated.

Carbon fiber (CF)21,22 is an outstanding class of carbon materials, with carbon atoms bonded together into crystals that are aligned parallel to the long axis of the fiber. Aligning the crystals gives the fiber a high strength to volume ratio.

We propose an electroanalytical platform ElectroSens for zinc detection based on a CF electrode modified with water-soluble PEs [polyethyleneimine (PEI) and poly(sodium 4-styrenesulfonate) (PSS)] and mercury nitrate, as well as a cheap and stable Ag/AgCl reference electrode (RE) based on the CF and the adsorbed layers of PEs. Such a platform is prospective for a wide range of analyses.

References

1. Konstantin G. Nikolaev, Evgeniy V. Kalmykov, Daria O. Shavronskaya, Anna A. Nikitina, Anna A. Stekolshchikova, Ekaterina A. Kosareva, Artemiy A. Zenkin, Igor S. Pantiukhin, Olga Yu. Orlova, Anatoly V. Skalny and Ekaterina V. Skorb // ACS Omega 2020, 5, 18987−18994.
2. Stephen A. Wring, John P. Hart // Analyst, august 1992, vol. 117.

Effect of microporosity on gas adsorption in CMK-3

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Gas separation methods based on physical adsorption in ordered mesoporous carbons are considered as a promising technique, which can be used in different industrial and environmental processes. Molecular simulation is a powerful tool for determining the mechanisms of adsorption phenomena, provided the models used properly represent the properties of the system, especially, adsorbent structure.

Previous studies showed that the model of carbonaceous mesoporous material CMK-3 constructed according to the experimental data on material structure does not provide reasonable agreement with experimental data on gas adsorption. Most probably, defects (in fact, micropores) in CMK-3 structure, which were not taken into account in simulations, significantly influence the adsorbent behavior.

Thus, the initial model of CMK-3 material (Fig. 1) was augmented by cylindrical micropores with various radii and inter-pore distances. The surface of the adsorbent (including micropores) was activated with oxygen-containing functional groups. To examine the enhanced model, adsorption of CO_2, N_2 and CH_4 was studied by grand canonical Monte Carlo simulation at 298 K and pressures up to 50 atm.

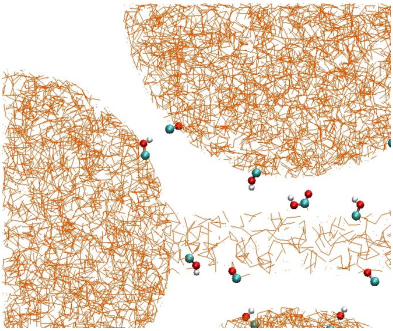

Fig. 1. Initial model of CMK-3. Color map: orange – amorphous carbon, cyan – carbon from functional groups, red – oxygen, white – hydrogen.

Modification of CMK-3 model has led to significantly better agreement of the calculated gas adsorption isotherms to the experimental data.

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Calcium phosphate biomaterials for targeted drug delivery

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Each implanted material must be biocompatible, which means that there must be no inflammation or reaction to a foreign body in the living system and tissue. For this reason, calcium phosphate materials are very perspective for bone replacement because calcium phosphates can dissolve in body fluids and are present in large quantities in solid forms [1].

Besides, excellent biocompatibility, calcium phosphate materials are of considerable interest as drug delivery agents. The systems based on calcium phosphates, especially hydroxyapatite and tricalcium phosphate, have different stoichiometry, functionality, and dissolution properties, making them suitable for delivery into cells. Their chemical similarity to bones and therefore their biocompatibility contribute to their controlled release properties. The inclusion of active molecules can be used to increase the ability of a material to regenerate bone tissue or to target specific skeletal disorders or pathologies [2].

The aim of our research is to obtain calcium phosphate systems for drug delivery. We will be focused on calcium phosphate patterns loaded with model antibiotics such as gentamicin or tetracycline to study the targeted release rate and their influence on cells (Fig. 1). These calcium phosphate materials could be used for bone replacement surgery.

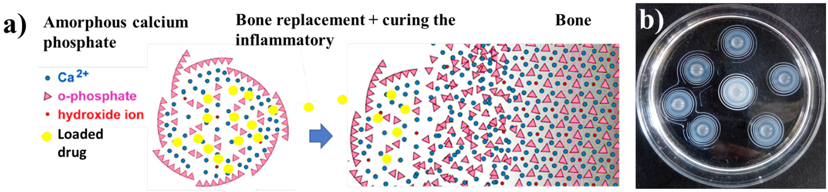

Fig. 1. a) The scheme of our approach; b) the photo of the calcium phosphate patterns.

Acknowledgments. Authors acknowledge RSF grant no. 19-79-10244.

References

1. Jeong, J., Kim, J.H., Shim, J.H. et al. Bioactive calcium phosphate materials and applications in bone regeneration // Biomater Res 23, 4 (2019).
2. Bose S., Tarafder S., Edgington J. et al. Calcium phosphate ceramics in drug delivery // JOM 63, 93–98 (2011).

Synthesis of azide-containing copolysiloxanes for click chemistry reactions

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The development of polymer functional materials has aroused considerable research interest owing to their promising applications as highly stretchable sensors, actuators, additive manufacturing, self-healing materials, coatings and etc.

Polymers are the key components of flexible optoelectronic devices, especially for the light-emitting diodes based on arrays of inorganic nanowires [1]. Among polymers, silicones with photo- and electroactive centers are of particular interest because of their extremely high flexibility, heat-resistance, biocompatibility, etc. The development and optimization of new approaches to fabricate silicone functional materials is a challenging task.

The goal for the current study is a functional copolysiloxane's synthesis. Dichlorodimethylsilane and 3-chloropropylmethylsilane were used as starting reagents for the ring-opening anionic polymerization [2]. The product was azidized to give the final polymer.

These copolysiloxanes can be used as precursors to obtain functional materials with photo- and electroluminescence centers in the main chain by click chemistry reactions [3].

Acknowledgments. The work was supported by the Russian Science Foundation (project 20-19-00256).

References

1. Neplokh V. et al. Modified silicone rubber for fabrication and contacting of flexible suspended membranes of n-/p-GaP nanowires with a single-walled carbon nanotube transparent contact //Journal of Materials Chemistry C 8, 3764–3772 (2020).
2. Kihara Y. et al. Synthesis of alkyne-functionalized amphiphilic polysiloxane polymers and formation of nanoemulsions conjugated with bioactive molecules by click reactions // Polymer Journal 46, 175–183 (2014).
3. Binder, W. H., Sachsenhofer R. "Click" chemistry in polymer and materials science //Macromolecular Rapid Communications 28, 15–54 (2007).

Organoboron derivatives of 1,8-bis(dimethylamino) naphthalene

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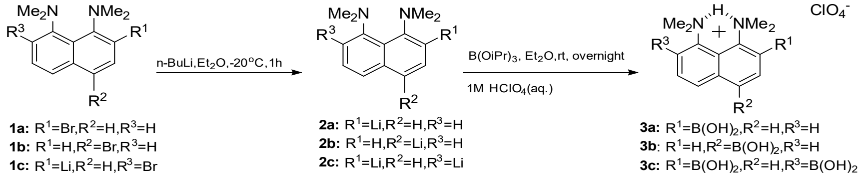
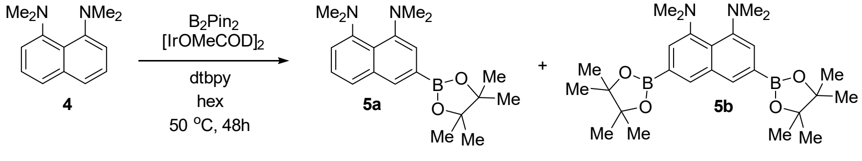
1,8-bis(dimethylamino)naphthalene (DMAN), also known as naphthalene proton sponge attracts the attention of researcher for many years due to its outstanding high basicity combined with low nucleophilicity. Multiple reported methods of DMAN derivatization are generally based on electrophilic substitution, while organometallic approaches are way less developed. We succeeded in the preparation of first organoboron derivatives of DMAN. Treatment of organolithium derivatives **1a-c** with trialkylborates leads to the formation of corresponding boronic acids **2a-c** (Scheme 1). Obtained boronic acids were tested in Suzuki cross-coupling. It was demonstrated, that *ortho*-boronic acids **3a,b** surprisingly undergo deborylation under classical reaction conditions.



Scheme 1.

Direct iridium-catalysed borylation of DMAN **4** with B_2Pin_2 was successfully used for the preparation of *meta*-substituted boronic esters **5a,b** (Scheme 2). Obtained organoboron derivatives open almost unlimited possibility for the further functionalisation.



Scheme 2.

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Synthesis of 2-dichloromethyl-5-aryl-2*H*-tetrazoles and noncovalent interactions in their crystal structure

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Polynitrogen heterocyclic structures are the leading pharmacophores in terms of the combination of biological activity and lack of toxicity. Tetrazoles containing 4 endocyclic nitrogen atoms have been successfully used as such pharmacophores [1]. In turn, the dichloromethyl group is often found in antibacterial drugs, for example, in chloramphenicol [2]. Thus, the dichloromethyl derivatives of the tetrazole ring can be considered as analogs of antibacterial agents containing a dichloromethyl fragment.

A series of 2-dichloromethyl-5-aryl-2*H*-tetrazoles was synthesized in high yields by the reaction of 5-aryl-NH-tetrazoles with trichloromethane in strong organic basic condition (Fig. 1). The obtained compounds were isolated by column chromatography. Structure and composition of products were described by means of various physical and chemical methods: NMR and IR spectroscopy, mass spectrometry and single-crystal X-ray diffraction. The X-ray diffraction data made it possible to reveal the presence in the structure of the studied compounds of intramolecular nonspecific interactions caused by the polarization of π-orbitals and the formation of the so-called π-hole.

The developed synthesis method provides access to a new class of promising compounds that not only potentially have biological activity, but can also serve as intermediate compounds for further alkylation of halogen and the introduction of various fragments into the structure of the compound.

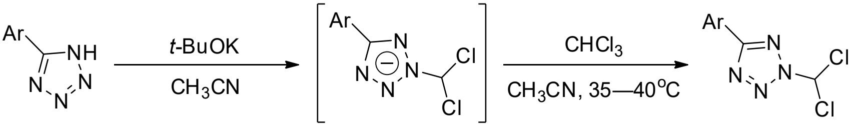

Fig. 1. Reaction scheme.

References

1. V.A. Ostrovskii, E.A. Popova, R.E. Trifonov // Adv. Heterocycl. Chem., 123 (2017).
2. G.P. Dionis, C.M. Athanassopoulos, D.A. Missiri, P.C. Giannopoulou, I.A. Vlachogiannis, G.E. Papadopoulos, D. Papaioannou, D.L. Kalpaxi // Antibiotics, 5 (2016).

Determination of acidity constants (pKa) of cyclic and aliphatic amines by the DFT method and the solvatation model

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The acidity constant (pKa) is a fundamental quantity for the understanding of chemical and biochemical processes. It provides a direct measure of the thermodynamic feasibility of proton transfer reactions found in many chemical and biochemical reactions. It also determines the amount of protonated and deprotonated species at a given pH, for example at physiological pH. The prediction and theoretical calculation of acidity constants is a subject of great interest in the field of chemistry [1].

In DFT-continuum treatments, the free enthalpy (ΔGaq) in phase aqueous is usually expressed as a sum of terms based on a thermodynamic cycle.

When we know that the thermodynamic values ΔGaq, ΔGgas and ΔGsol can be calculated at various theoretical levels (DFT) in conjunction with different solvation methods (solvent effect), a large choice of calculation strategies for pKa can be applied [2].

Cycle C

$$\begin{tikzcd}
BH^+_{(gaz)} \arrow[d, "\Delta G_{sol}(BH)"'] & + & (n+1)H_2O_{(gaz)} \arrow[rr, "\Delta G_{gaz}"] \arrow[d, "\Delta G_{sol}(H_2O)"] & & B(H_2O)_{n(gaz)} \arrow[d, "\Delta G_{sol}(B(H_2O)_n)"] & + & H_3O^+_{(gaz)} \arrow[d, "\Delta G_{sol}(H_3O^+)"] \\
BH^+_{(sol)} & + & (n+1)H_2O_{(sol)} \arrow[rr, "\Delta G_{aq}"] & & B(H_2O)_{n(sol)} & + & H_3O^+_{(sol)}
\end{tikzcd}$$

Fig. 1. The thermodynamic cycles used in the calculation of the absolute values of the pKa.

References

1. A.V. Marenich, C.J. Cramer, D.G. Truhlar // J. Phys. Chem. B 113 (2009) 6378.
2. Kallies B., Mitzner R. // J. Phys. Chem B 101 (1997) 2959.

Application of potentiometric multisensor system and chemometrics for identification of paracetamol formulations origin

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Counterfeit drugs are undoubtedly a great problem across the globe. Approximately a third of the drugs prescribed all over the world are counterfeit drugs [1]. It is known that counterfeit drugs are often produced in different countries in contrast to those labeled on their packages. Thus, a potential tool for identification of such mislabeling is of high interest. Fast and inexpensive analytical tools for identification of pharmaceutical formulations origin are important to ensure consumers' safety. This study describes application of potentiometric multisensor systems ("electronic tongues", or ET) for this purpose.

Paracetamol is a common medication employed to treat pain and fever in many countries. Hence, we have chosen it as an object to study. 72 paracetamol samples purchased in different countries and produced by various companies were studied via infrared spectroscopy (IR), near infrared spectroscopy (NIR), nuclear magnetic resonance spectroscopy (NMR) and potentiometric multisensor system (ET). A variety of chemometric tools was applied to explore and compare the information yielded by these methods. It was found that ET is capable of distinguishing paracetamol formulations from different producers. The chemical information derived from potentiometric sensor responses has something in common with that derived from NIR and IR; however, it is orthogonal to that from NMR. ET can be a valuable tool in express quality assessment of drugs.

References

1. World Health Organization. A study on the public health and socioeconomic impact of substandard and falsified medical products. Available at: https://www.who.int/medicines/regulation/ssffc/publications/SE-Study_EN_web.pdf?ua¼1. (Accessed September 15, 2020).

The selective deposition of silver particles by interference pattern of laser beam

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The development of novel materials consisting of Ag nanoparticles (NPs) has become an important research field in recent years. The unique optical properties of such nanostructures, attributed to the quantum-size effect and the resonance surface plasmon absorption, are of fundamental and practical interest for photonic application [1].

Laser deposition from solution of metalorganic complex was chosen as a way of metallic NPs creation. Scanning electron microscopy showed a regular spatial distribution of Ag nanoparticles from solution $C_7H_7AgO_3$ of metalorganic complex with a periodicity governed by laser deposition parameters and the spatial intensity distribution due to interference pattern of laser beam (Fig. 1). It was found that the average size of nanoparticles can be controlled by the wavelength and laser intensity as well as the exposure time and composition of the solution.

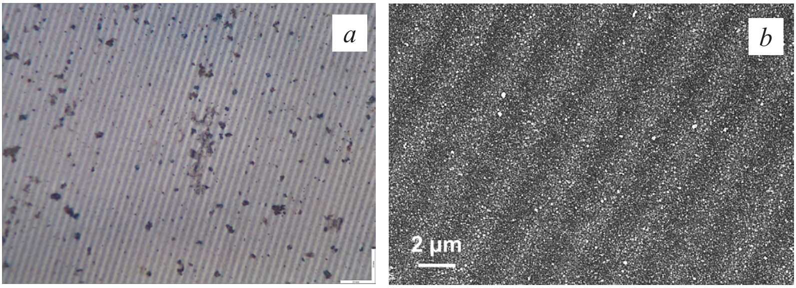

Fig. 1. – a) SEM image of the grating, b) magnified SEM image of the diffractive of the grating, in which the Ag NPs are located.

Acknowledgments. This work was supported by RFBR-DFG (RFBR project № 20-58-12015).

References

1. T.N.Smirnova, L.M.Kokhtych, A.S.Kutsenko, O.V.Sakhno, J. Stumpe // Nanotechnology 20 (2009).

A novel supramolecular solvent system based on primary amines for microextraction application

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Supramolecular solvents (SUPRASs) have gained great importance due to their relevance to the concept of green chemistry. The SUPRASs are water-immiscible liquids generated through two self-assembly processes: aggregation of amphiphile providing supramolecular assembly (I), and coacervation process producing a supramolecular solvent phase (II) [1]. Depending on the type of amphiphile and the trigger causing coacervation process, both polar and non-polar analytes can be separated using supramolecular solvents.

In the present research it was found that SUPRASs can be formed in aqueous solutions containing primary amines with the long hydrocarbon chain and monoterpenoid compounds [2]. When the monoterpenoid was dissolved in primary amine isotropic solution the spontaneous in situ formation of SUPRAS-rich phase was observed (Fig. 1). The developed approach was utilized for the separation of polar sulfonamide antibiotics: sulfamethoxazole, sulfamethazine and sulfapyridine from biological fluids followed by the HPLC-UV determination.

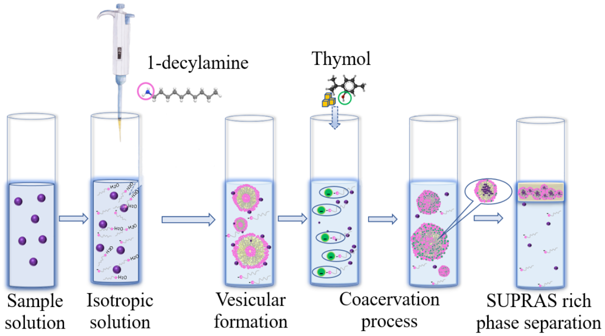

Fig. 1. The mechanism of supramolecular solvent microextraction with the use of primary amine and monoterpenoid phenol.

References

1. A. Ballesteros-Gomez, M. D. Sicilia, S. Rubio // Anal. Chim. Acta, v. 677, p. 108–130 (2010).
2. P. Bogdanova, A. Pochivalov, C. Vakh, A. Bulatov // Talanta, v. 216, 120992 (2020).

The investigation of structure, and dispersity of ternary $86ZrO_2$-$9CeO_2$-$5TiO_2$ precursors

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Ternary tetragonal zirconia based solid solutions are important materials for novel thermal barrier coatings (TBCs) design. The stabilization of zirconia using undersized Ti^{4+} and oversized Ce^{4+} can be used to obtain relatively large stable non-transformable tetragonal phase in ternary TiO_2–CeO_2–ZrO_2 system and thus to achieve the improved thermal and mechanical properties of TBCs [1]. So the aims of this work were the optimization of synthesis parameters and study the physical and chemical properties of the ternary system of $86ZrO_2$-$9CeO_2$-$5TiO_2$ precursor. Using the potentiometric titration the competing processes of the hydrolysis and precipitation during sol-gel synthesis in ternary system were investigated. Microstructure of precursor was studied by BET (ASAP 2020MP). The precursors were obtained using sol-gel synthesis, freeze-drying and calcination at 600-1350 °C for 3 hours. Using PSD analysis (Horiba, LA-950) the data on agglomerate distribution and mean particle size dependence on temperature were obtained. Thermal evolution, phase transition temperatures and water losses were studied by STA (STA 409 Jupiter NETZSCH). The enthalpies of phase transition were calculated from STA data. According to the XRD data (Shimadzu XRD6000) the phase formation $5TiO_2$-$9CeO_2$-$86ZrO_2$ system in the temperature range of 600-1350 °C was studied. Via ESCA (ESCALAB 250Xi) it was shown that Ce^{4+} only present after calcination at 1000 °C. All studies were carried out under the supervision of the scientific supervisor Dr. Kurapova O.Yu. and with the active assistance prof. V.G. Konakov. ESCA, DSC, EDX data were obtained Centres for Thermogravimetric and Calorimetric Research, studies in surface science and GEOMODEL at SPBU Research park.

Acknowledgments. The work was supported by the Council on grants of the President of the Russian Federation, grant number 75-15-2019-210.

References

1. Kurapova O.Y., Glukharev A.G., Borisova A.S., Golubev S.N., Konakov V.G. Phase formation, stability and heat capacity of ternary TiO2–CeO2–ZrO2 solid solutions // Materials Chemistry and Physics. 2020. T. 242. C. 122547.

Deep eutectic solvents based on terpenoid compounds and fatty acids as extractants in liquid-liquid microextraction of tetracyclines from food samples

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In recent years, a novel medium – deep eutectic solvents (DESs) – with properties similar to ionic liquids but with additional advantages has been reported. These solvents are presently getting increased attention from researchers in many areas of science and technology.

In this research DESs based on monoterpenoid compounds and fatty acids were investigated for liquid-liquid microextraction of antibiotics from food samples. It was found that DESs formed by thymol and fatty acids (C6-C9) provided efficient extraction of tetracyclines. The switchable hydrophilicity behavior of the synthesized DESs was found and utilized for dispersion of extractant in aqueous phase. The developed approach was applied to the antibiotic extraction from food samples for subsequent HPLC-DAD determination. The microextraction procedure assumed mixing sample solution with thymol-based deep eutectic solvent and phase separation by centrifugation. A microextraction mechanism was investigated, and microextraction procedure optimization was performed.

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Deep eutectic solvents as a medium for laser-assisted synthesis of electrode materials for non-enzymatic glucose detection

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In this work we propose a completely new approach for producing conductive metallic and polymetallic nanostructured materials that can be used as working electrodes for electrochemical detection of bioanalytes such as glucose, hydrogen peroxide, and certain neurotransmitters [1]. It consists of a combination of cheap, environmentally friendly and effective solvents - deep eutectic solvents (DES) and laser-induced metal deposition technique [2].

DES based on choline chloride and carboxylic acids can be successfully used for dissolving copper salts and for laser-assisted synthesis of nanostructured copper electrodes on the surface of glass ceramics and oxide glass. The relationship between the composition, physical and chemical characteristics of DES and the functional properties of electrode materials obtained in the process of direct laser writing is studied. This approach also allowed us to develop fundamental ideas about the processes that occur in eutectic solvents under the influence of laser radiation [3].

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References

1. Shishov A.,Gordeychuk D., Logunov L.,Tumkin I. High rate laser deposition of conductive copper microstructures from deep eutectic solvents // Chemical Communications (2019).
2. M.S. Panov, I.I. Tumkin, A.V. Smikhovskaia, E.M. Khairullina, D.I. Goreychuk, V.A. Kochemirovsky // Microelectron. Eng., 2016, 157, 13–18.
3. Abbott A.P., Capper G., Davies D.L., Rasheed R.K., Tambyrajah V. Novel solvent properties of choline chloride/urea mixtures //Chem. Commun. (Cambridge, U. K.) 2003, (1), 70- 71.

Potentiometric Sensors for Scandium and Yttrium

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Scandium and yttrium are exclusively produced as the by-products of mining of other metals. The miscellaneous and growing applications of them in high technology fields make them important for analytical chemistry [1].

Potentiometric sensors for quantitative determination of metals offer advantages over conventional methods such as inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) methods [2], mainly due to their reasonable precision, affordable price and the possibility of real-time measurement [3,4].

Measuring of scandium and yttrium is the missing link in application of potentiometric sensors, inasmuch as it has not yet been performed by this method. In this work we have studied 18 different plasticized polymeric sensor membrane compositions with respect to their potentiometric sensitivity towards scandium, yttrium, and lanthanides. The sensor membranes were designed using various organic ligands suggested in liquid extraction for separation of actinides and lanthanides in hydrometallurgical processes. The sensitivity of the sensors to scandium and yttrium was studied at pH=2 in the concentration range 10^{-7} to 10^{-3} M. The results on sensitivity and selectivity of the sensors to scandium, yttrium, and lanthanides will be discussed in the presentation.

References

1. Pyrzyńska K. et al. Separation and purification of scandium // Separation and Purification. Rev. 00, 1–13 (2018).
2. Zhernokleeva K. et al. Analysis of Pure Scandium, Yttrium and Their Oxides Using Methods of Inductively Coupled Plasma Atomic Emission.
3. Spectrometry and Inductively Coupled Plasma Mass Spectrometry // Inorganic Materials, 47, 1627–1634 (2011).
4. Legin A.V. et al. Cross-sensitive rare earth metal ion sensors based on extraction systems // Sensors and Actuators B 131 29–36 (2008).
5. Oleneva E. et al. Potentiometric multisensor system for tetra- and hexavalent actinide quantification in complex rare earth metal mixtures related to spent nuclear fuel reprocessing // Sensors Actuators B. Chem. 288, 155–162 (2019).

Ni(II)-pyridinedicarboxamide-*co*-polydimethylsiloxanes as new materials for flexible electronic devices

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(*Co*)polysiloxane complexes with electroactive centers play an important role in the creation of new self-healing and stimuli-responsive materials for flexible sensors, actuators and coatings [1,2]. Nickel(II)-pyridinedicarboxamide-*co*-polydimethylsiloxanes (Ni-Py-PDMSs) are interesting air-stable silicone materials (Fig. 1). Mechanical properties of Ni-Py-PDMSs change by controlling metal to macroligand molar ratios of 1:(1–8), and by the polymer chain length. A decrease of the Ni(II) content and an increase of the polydimethylsiloxane chain length lead to higher elongation at break up to 1800% and lower hysteresis (less than 3%). Ni-Py-PDMSs exhibit autonomous self-healing performance. The self-healing efficiency reaches 92.5% at room temperature. The glass transition temperature of Ni-Py-PDMSs is from -123 °C to -112 °C, and the electroconductivity is from 10^{-13} to 10^{-11} $S{\cdot}cm^{-1}$. These properties make Ni-Py-PDMSs new potential self-healing materials for flexible electronic devices.

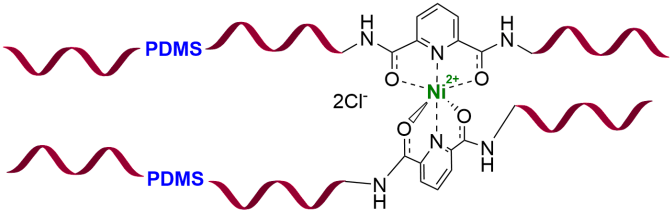

Fig. 1. Ni-Py-PDMSs.

Acknowledgments. Synthesis of polymer materials was financially supported by the Russian Foundation for Basic Research (project № 19-33-90134). Assessment of mechanical, self-healing and electrical properties of the synthesized silicone rubbers was supported by the Russian Science Foundation (project № 20-19-00256). Measurements were performed at Chemical Analysis and Materials Research Centre, Thermogravimetric and Calorimetric Research Centre, and Centre for Innovative Technologies of Composite Nanomaterials (all in Saint-Petersburg State University).

References

1. X. Liu, C. Lu, X. Wu, X. Zhang // J. Mater. Chem. A., v. 5, № 20, p. 9824–9832 (2017).
2. J.Y. Oh, Z. Bao // Adv. Sci., v. 1900186 (2019).

Development of novel sodium alginate membranes for the pervaporation dehydration using bulk and surface modifications

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The most perspective field of sustainable processes is membrane separation technologies due to their characteristics: environmentally friendly, low-energy, with compact equipment and waste-free. Pervaporation is one of the promising membrane processes for separation of low molecular substances effectively applied for the separation of azeotropic and isomer mixtures, close-boiling and thermally unstable substances. This method also is especially important for the dehydration purposes. The rapid development of pervaporation requires the significant improvement of the transport properties for polymeric membranes. It can be easily achieved by the application of bulk and surface modifications of a given polymer network.

In the present work sodium alginate was chosen as green membrane material for further functionalization by bulk and surface modifications with the aim to get novel highly effective membranes for the dehydration of water-organic mixtures. The bulk modification was carried out by the introduction of water soluble fullerene derivative - polyhydroxylated fullerene as modifier and cross-linking agent into sodium alginate matrix, while surface modification was done by the deposition of nanosized polyelectrolyte layer on the supported membrane surface using layer-by-layer assembly method. The structural features of the developed modified membranes were studied by various analysis methods (FTIR spectroscopy, scanning electron (SEM) and atomic force (AFM) microscopies, and contact angle measurements). Transport properties of the modified supported membranes were tested by pervaporation for separation of model isopropyl alcohol – water mixture in the wide concentration range. It was found that only the combination of both bulk and surface modifications for sodium alginate membranes significantly improved transport characteristics.

Acknowledgments. This work was supported by Russian Science Foundation [project No 19-73-00105]. The experimental work was facilitated by equipment from the Resource Centers for Nanotechnology, Magnetic Resonance, X-ray Diffraction Studies, Thermogravimetric and Calorimetric Research Centre, Chemical Analysis and Materials Research Centre, Cryogenic Department and Centre “Nanofabrication of Photoactive Materials (Nanophotonics)” at the St. Petersburg State University.

Hybrid polymers based on modified hydroxyethyl cellulose and hydride-terminated polysiloxane

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Glycosilicones are hybrid polymers composed of saccharide and (poly)siloxane [1]. There is a special interest in cellulose-based glycosilicones as they can be used in microfluidics [2] and cosmetics. However, their synthesis is a problem due to poor compatibility: polysiloxanes are hydrophobic and saccharides are hydrophilic. One of the methods to overcome this complication is to perform synthesis heterogeneously, but use effective and high-yield reactions, such as catalytic hydrosilylation.

This work is dedicated to synthesis of cellulose-based glycosilicones with hydrosilylation, catalyzed by Karstedt's catalyst (complex of platinum(0) and divinyltetramethyldisiloxane) or (acetylacetonato)dicarbonylrhodium(I). The first time glycosilicones were obtained from hydroxyethyl cellulose and hydride-terminated polydimethylsiloxane. The compounds are insoluble in water, but swell in organic solvents. Catalysis with rhodium complex allowed to obtain polymers with higher contact angles (131°) compared to cellulose (30°) what is in accordance with the mixing calorimetry experiments ($-4.9\ \mathrm{J \cdot g^{-1}}$ and $-30.3\ \mathrm{J \cdot g^{-1}}$, respectively). Cytotoxicity tests indicated lesser toxicity of hydrosilylation-obtained glycosilicones towards *Paramecium Caudatum* and *Chlorella Vulgaris* compared to those obtained via CuAAC from hydroxyethyl cellulose and epoxy-terminated polydimethylsiloxane.

Acknowledgments. The synthesis and characterization of glycosilicones was funded by the Russian Foundation for Basic Research (project 19-33-90130). The synthesis of the catalysts for glycosilicones was supported by Russian Ministry of Education and Science (State Contract 14.W03.31.0014, Megagrant). Measurements were performed at Center for Magnetic Resonance, Center for Chemical Analysis and Materials Research, Thermogravimetric and Calorimetric Research Centre, Centre for Culture Collection of Microorganisms, Centre for Innovative Technologies of Composite Nanomaterials.

References

1. S. Boileau, B. Boury, F. Ganachaud // Silicon Based Polymers, Springer Netherlands (2008). doi:10.1007/978-1-4020-8528-4.
2. L. Yang, L. Li, Q. Tu, L. Ren, Y. Zhang, X. Wang, Z. Zhang, W. Liu, L. Xin, J. Wang // Anal. Chem., № 82, p. 6430–6439. doi:10.1021/ac100544x.

Stability of hydrophobic deep eutectic solvents

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Deep eutectic solvents are increasingly used as effective extractants for the separation of various polar and non-polar components from various objects. Moreover, the so-called hydrophobic eutectic solvents are most often used recently for extraction of non-polar components from aqueous or solid-phase samples. The most common representatives of this class are solvents, where either natural terpene (menthol or thymol) or quaternary ammonium compounds (tetrabutylammonium or tetraoctylammonium) are used as a hydrogen bond acceptor, and fatty acids or long chain alcohols are most often used as hydrogen bond donors. The combination of such donors and acceptors allows to create a hydrophobic solvent capable of efficiently extracting non-polar compounds. However, information on the instability of hydrophobic eutectic solvents based on ammonium components has recently appeared in the literature. Therefore, the aim of this work is to study the stability of the two most widely used types of hydrophobic eutectic solvents.

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Development of nanocomposite materials for electrodes of lithium-sulfur batteries based on salen-type nickel polymer complexes and molecular layering technology

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Lithium-sulfur batteries are one of the possible breakthrough solutions in the field of modern energy. For example, the specific capacity of sulfur is about 1678 milliampere-hours per gram, and the best cathode materials for lithium-ion batteries are about 220-260 milliampere-hours per gram, that is, an increase in capacity by more than 500% [1].

However, they have two main disadvantages. The first drawback is that sulfur is washed out from the cathode material, which significantly reduces the stored capacity with each cycle. The second major problem is the formation of dendrites, which leads to a short circuit in the battery.

At the moment, both of these problems have not been effectively resolved to the end, there is no data in scientific articles demonstrating the level of solutions sufficient for real industrial application.

The advantage of our solution is that, firstly, we can create a composite anode material with the participation of Schiff bases, where the attached carboxy group will “trap” lithium from the solution, preventing it from forming dendrites.Such material is not patented for these purposes, and its potential for solving similar problems is shown in the article [2]. Moreover, this polymer material can maintain its electrochemical stability for more than 1000 charge-discharge cycles.
Secondly, we will protect the cathode material using molecular layering technology, that is, we will encapsulate the cathode. This techology has the advantage of greater precision in the application of layers, as well as in greater possibilities for controlling the process, thus obtaining dense crystalline films.

Acknowledgments. Thanks for the support of the project to the Fund for the Promotion of Innovations.

References

1. Zhi Wei Seh, Weiyang Li, Judy J. Cha, Guangyuan Zheng, Yuan Yang, Matthew T. McDowell, Po-Chun Hsu , Yi Cui // Nature Communications volume 4, Article number: 1331 (2013).
2. S.A. Samokhvalova, V.A. Ershov, D.A. Lukyanov, P.S. Vlasov, O.V. Levin // Russian Journal of General Chemistry, 89/4, (2019).

Fabrication and characterization of novel membranes based on polybenzoxazinoneimide and its prepolymer

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Pervaporation has shown explicit advantages over conventional methods in case of the separation of mixtures with similar boiling point or azeotropic compositions, like enriching ethanol from biomass fermentation broth. The membrane material highly affects the separation performance. Polyimide membranes proved themselves to be an appropriate material exhibiting high mechanical and thermal resistance.

The objects of this study were polymers of heteroaromatic structure: polyamic acid imide-containing (PAAI) and polybenzoxazinonimide (PBOI), which are the products of the same synthesis. The heat treatment of PAAI (250 °C) followed by dehydration and cyclization leads to the formation of polybenzoxazinoneimide (PBOI) which combines the valuable qualities of two polymer classes - polyimides and polybenzoxazinones (Fig. 1).

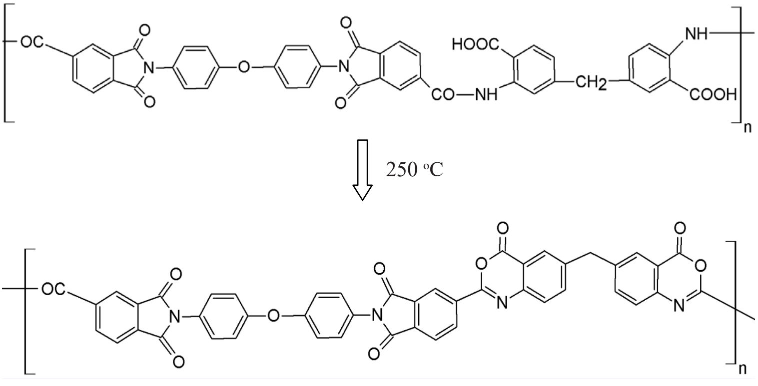

Fig. 1. Thermal conversion of PAAI to PBOI.

Complex research of membranes structure and transport behavior was performed. Pervaporation data demonstrates that PBOI membrane is much more efficient in separating water/ethanol mixture while PAAI is not promising for ethanol dehydration.

Acknowledgments. Membrane formation studies were funded by the President of RF grant [grant MK-1280.2020.3].

Base-promoted cyclization of 4-alkyl-2-azabuta-1,3-dienes into 1-pyrroline derivatives

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The five-membered ring of 1-pyrroline is an important structural fragment in organic chemistry. Compounds containing the pyrroline ring have a wide biological activity and are used in pharmaceutical industry. In addition, the 1-pyrroline fragment is included in some natural compounds. There are a lot of ways for the construction of 1-pyrroline moiety. Most of them are rather cheap and convenient and allow to obtain pyrrolines in good yields. However, only several methods could be used for insertion of substituents in 3 and 4 positions of the pyrroline ring [1].

In this work, a novel method for the synthesis of 1-pyrroline derivatives via the base-promoted 1,5-cyclization of 4-alkyl-2-azabuta-1,3-dienes has been developed (Fig. 1). The method makes possible the introduction of various substituents at the 2-5 positions of the pyrroline ring. The starting compounds for the synthesis of 2-azabuta-1,3-dienes – 2*H*-azirines and diazo compounds – are quite readily available [2]. The synthesis of 2-azabuta-1,3-dienes proceeds in most cases under Rh(II) catalysis, but in some cases it is possible under blue light irradiation.

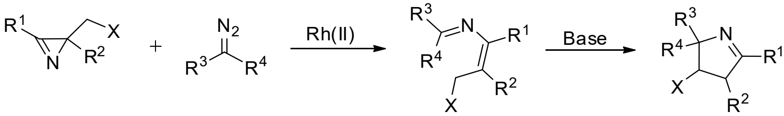

Fig. 1. Reaction scheme.

Acknowledgments. We gratefully acknowledge the financial support of the Russian Science Foundation (19-73-10090). This research used resources of the Magnetic Resonance Research Centre, Chemical Analysis and Materials Research Centre of the Research Park of St. Petersburg State University.

References

1. N.S. Medran, A. La-Venia, S.A. Testero // RSC Adv., v. 9, p. 6804–6844 (2019).
2. I.P. Filippov, M.S. Novikov, A.F. Khlebnikov, N.V. Rostovskii.// EurJOC, v. 19, p. 2904-2913 (2020).

Enhanced photocatalytic activity of Tb-SnO2 nanoparticles with different morphologies for antibiotic degradation

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At the moment there is an acute problem of water pollution by organic matter, in particular cyclic organic compounds, which poses a threat to the environment. For the cleaning process, cheapness, environmental friendliness and the absence of need to use complex equipment are important. In this regard, the process of semiconductor photocatalysis is becoming a growing trend. Among a large number of semiconductor materials, tin dioxide stands out with a rutile-type structure, which is tolerant to substitution of dopants in the crystal lattice. To increase the photocatalytic characteristics and the possibility of shifting to the visible region of the spectrum, we propose to dope the SnO2 matrix with Tb^{3+} ions.

Spherical nanoparticles (NPs) were synthetized by coprecipitation method, followed by hydrothermal treatment to initiate formation of cubic NPs. All samples were characterized by XRD, TEM, FTIR, Raman spectroscopy and SSA estimation. The band gap was calculated from absorption spectra. The organic dye Methylene Blue (MB) solution was taken as a model system for studying photodegradation. According to the kinetic dependences of MB photodegradation and mass-spectroscopy data, the most effective for photocatalysis are cubic NPs with Tb 15 mol % (70% of MB decomposed in 60 minutes).

To create experimental conditions close to real ones, we carried out photocatalytic decomposition of non-colored solution of oxytetracycline (OTC, an antibiotic with a condensed four-cyclic system in its structure). The degradation coefficients were estimated by spectrophotometry and chromatography methods. It was shown that the values obtained by the two methods correlate with each other. This makes it possible to use spectrophotometry for quantitative assessment of photocatalysis, as the most rapid method. The most optimal catalyst for the decomposition of OTC is a sample with hydrothermal treatment with a Tb^{3+} content of 25 mol% (75% decomposed in 60 minutes). Thus, depending on the shape of particles and the concentration of dopant, it is possible to effectively decompose organic pollutants using available technical means.

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Extraction into deep eutectic solvents as an alternative to the microwave decomposition of plant samples for elemental analysis

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Deep eutectic solvents (DES) are a mixture of two or more components capable of self-association, most often through the formation of hydrogen bonds, with the formation of a eutectic mixture, the melting point of which is significantly lower than the melting point of individual components [1]. In analytical chemistry, DESs have proved to be effective extractants, including for the separation of metals from various samples.

Today, to determine the content of trace elements in solid samples, preliminary decomposition of the sample is used with such aggressive substances as concentrated hydrogen peroxide and nitric acid [2-3]. This study demonstrates a new approach for the separation of metals such as Ba, Ca, Cr. Cu, Fe, Mg, Mn, Mo, Na, Ni, Pb, Sn, V and Zn without preliminary decomposition of tobacco samples into deep eutectic solvents. Deep eutectic solvents based on natural components such as choline chloride and malic acid were used as extractants. This approach completely eliminated the need to use aggressive oxidants and acids by using an environmentally friendly eutectic solvent as an extractant.

Acknowledgments. The authors are grateful to the Russian Science Foundation (project No. 20-73-00043) for funding the research.

References

1. Abbott A.P., Capper G., Davies D.L., Rasheed R.K., Tambyrajah V. // Chemical Communications. 2003. T. 1, P. 70-71.
2. Edgar Pinto, MarianaCruz, Patrícia Ramos, Agostinho Santos, Agostinho Almeida. Metals transfer from tobacco to cigarette smoke: Evidences in smokers' lung tissue // Journal of Hazardous Materials. 2017, V. 325, P. 31-35.
3. Syed Ghulam Musharraf, Muhammad Shoaib, Amna Jabbar Siddiqui, Muhammad Najam-ul-Haq, Aftab Ahmed . Quantitative analysis of some important metals and metalloids in tobacco products by inductively coupled plasma-mass spectrometry (ICP-MS) // Chemistry Central Journal. 2012, V.6.

Reaction of 2-halogen-2*H*-azirine-2-carboxylic acid derivatives with trimethylsilylazide as a pathway to 2-azidoazirines

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2*H*-Azirines are convenient synthetic blocks used in the synthesis of nitrogen-containing heterocyclic compounds. For further synthetic modifications, various functional substituents are often included into azirines' structure.

In this work, we present a new method for the preparation of 2-azidoazirines **2** via the reaction of 2-halogen-2*H*-azirine-2-carboxylic acid derivatives **1** with trimethylsilylazide in the presence of triethylamine. Unfortunately, it isn't possible to isolate 2-azidoazirines **2** in pure form due to their instability.

Nevertheless, preparation of azirines **2** with an azide function at the sp^3-hybrid carbon atom allow further modifications of this group in order to obtain new functional derivatives of azirine. Within this context, one of the most promising modifications of the azide group is the 1,3-dipolar cycloaddition reaction catalyzed by Cu(I) (CuAAC). This reaction usually proceeds in high yields and can allow the fixation of azidoazirines **2** in a stable form of triazolylazirines **3**, which can also be introduced into further transformations.

After a series of optimization experiments, we managed to achieve yields of triazolylazirines **3** up to 80% in two stages of one-pot process. The presented method makes it possible to vary the substituents over a wide range in both azirine and acetylene fragments.

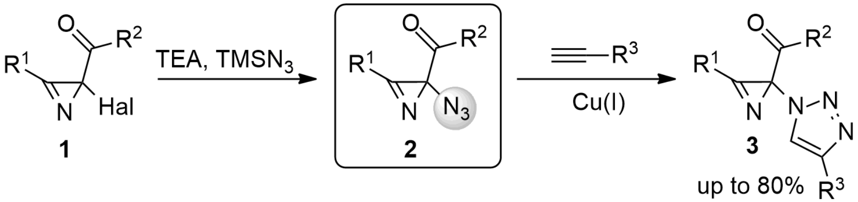

Fig. 1. Scheme for the preparation of azidoazirines and triazolylazirines.

Acknowledgments. This work was supported by the Russian Science Foundation (project № 20-13-00044). This research used recourses of the Magnetic Resonance Research Centre, Chemical Analysis and Materials Research Centre, Centre for X-ray Diffraction Studies of St. Petersburg State University.

Reactions of 3-phenylpropynonitrile and its transformations under superelectrophilic activation conditions

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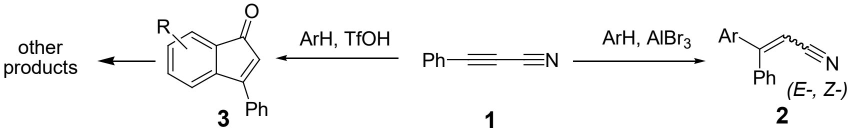
It has been recently shown, that substituted 3-arylpropenenitriles react with various arenes under the action of Brønsted superacid TfOH (CF_3SO_3H) or strong Lewis acid $AlBr_3$ forming two types of compounds, 3-aryl-3-phenylpropanenitriles and 3-phenylindanones [1]. We plan to continue this study and investigate reactions of 3-phenylpropynonitrile **1** under the same conditions with TfOH (CF_3SO_3H) and $AlBr_3$ (Scheme 1). Nitrile **1** was obtained from the corresponding amide of 3-phenylpropynoic acid in the presence of $POCl_3$,

In reaction of 3-phenylpropynonitrile **1** with arenes and $AlBr_3$ one can expect a formation of unsaturated 3-aryl-3-phenylpropenenitriles **2**. In TfOH, this transformation may lead to indenones **3**, which can be undergone further transformations.



Scheme 1. Reactions of 3-phenylpropynonitrile with arenes in TfOH or $AlBr_3$.

Acknowledgments. This work was supported by the Russian Foundation for Basic Research (project No 18-33-0017\18).

References

1. Gorbunova Y., Zakusilo D.N., Boyarskaya I.A.,Vasilyev A.V. // Tetrahedron , 2020, V. 76, № 131264.

An alternative approach to the hydrated imidazoline ring expansion (HIRE) of diarene-fused [1.4]oxazepines

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Although compounds based on medium-sized (8- to 11-membered) ring systems are considered particularly valuable small-molecule tools for drug discovery the development of compound libraries has been hampered by such ring sizes being notoriously difficult to construct via synthesis. Traditional end-to-end cyclisation reactions of long linear precursors are typically unpredictable and impractical processes. In contrast, the expansion of smaller ring systems is an attractive alternative way to synthesize such compounds [1].

In this work we have proposed a fundamentally new approach to the construction of diversely substituted imidazolinium-fused diarene [1,4]oxazepines previously shown to undergo a facile 'hydrated imidazoline ring expansion' (HIRE) [2] to produce ten-membered lactams. The approach relies on the respective *NH*-lactams and secondary 2-hydroxyethylamines (Fig. 1). We have shown for the first time that insufficient electron deficiency of the nitrogen-bound aromatic ring in these systems may change the course of the putative 'hydrated imidazoline' evolution and to deliver *N*-aminoalkyl derivatives as a second or the sole product.

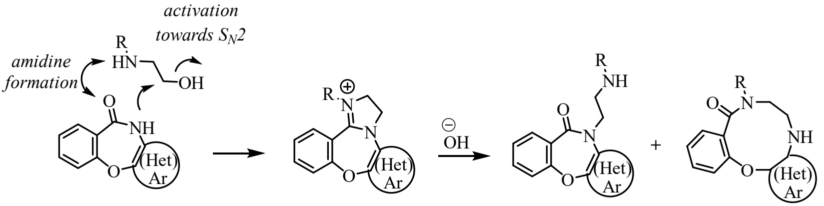

Fig. 1. Alternative HIRE approach explored in this work.

References

1. J.R. Donald, W.P. Unsworth // Chemistry–A European Journal, v. 23, № 37, p. 8780-8799 (2017).
2. E. Reutskaya, A. Osipyan, A. Sapegin, A.S. Novikov, M. Krasavin // The Journal of organic chemistry, v. 84, № 4, p. 1693-1705 (2018).

XRD determination of metals in biodiesel fuel using deep eutectic solvents

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In recent decades, as fossil fuels have become more sustainable, there has been a trend towards green and renewable energy sources. Biodiesel fuel can be used as an alternative to fossil fuels for modern engines without the need of major modifications. The advantages of biodiesel fuel are its low toxicity, renewability and lower emissions of carbon monoxide, nitrogen oxides and other harmful gases in the process of use compared to diesel fuel of petroleum origin.

Various metals may be present in the resulting product, which negatively affects its properties. They can come from raw materials or during synthesis and purification. In such case, deep eutectic solvents can be considered as suitable extractant of metals from biodiesel fuel for their future determination. Currently, there are various methods for the determination of metals in biodiesel fuel, but most of them require the use of toxic organic solvents or aggressive oxidizing acids for mineralization of the sample. In this paper, for the first time, a technique for the determination of metals in biodiesel fuel using deep eutectic solvents for subsequent XRD analysis is presented.

Acknowledgments. The study was supported by a grant from the President of the Russian Federation MK-1154.2020.3. Scientific research was partially performed at Chemical Analysis and Materials Research Centre of Saint Petersburg State University.

Stability of mixed $CH_4/N_2/CO_2$ hydrates: molecular simulation

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Methane has a number of significant advantages over other fossil fuels, so the search for its new sources is an important task. Large amounts of methane can potentially be obtained from naturally occurring methane hydrates, but this process should be carried out carefully in order to avoid the catastrophic collapse of gas hydrate deposits.

Molecular dynamics simulations in NVT-ensemble were used to study the stability of CH_4/N_2, CH_4/CO_2, N_2/CO_2 and $CH_4/N_2/CO_2$ gas hydrates. The compositions of mixed hydrates were obtained from preliminary Monte Carlo simulations at a temperature of 270 K and pressure of ca. 90 atm.

The melting point of each gas hydrate was determined based on the observed changes in their thermodynamic, structural (Fig. 1) and dynamic properties.

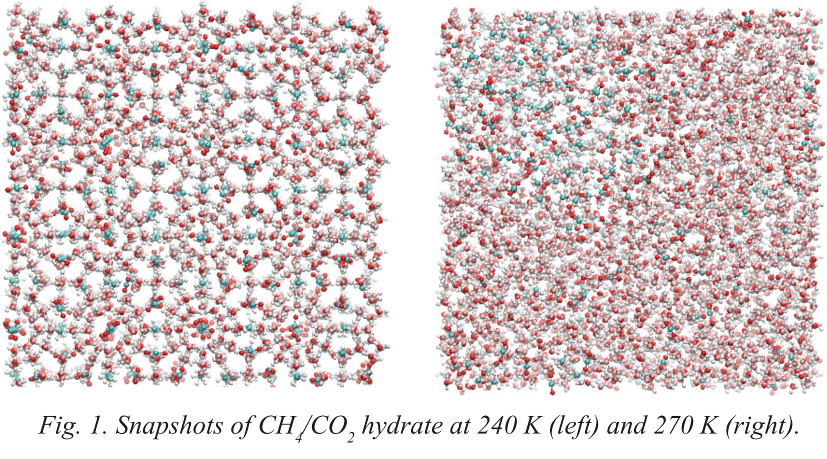

Fig. 1. Snapshots of CH_4/CO_2 hydrate at 240 K (left) and 270 K (right).

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Self-healing complexes of copolysiloxanes with $FeCl_3$

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Synthesis of new (co)polysiloxanes and creation on their basis materials with the most important properties (self-healing, electrical conductivity, flexibility, bioinertness, etc.) is challenging task [1].

In the study polymer-metal complexes of (co)polysiloxane with Fe(III) were synthesized. The poly(dimethylsiloxane) with 2,6-pyridinedicarboxamide groups was prepared by condensation reaction between bis(3-aminopropyl)-terminated poly(dimethylsiloxane) and 2,6-pyridinedicarbonyl dichloride to give a colourless viscous liquid with Mn=32000 g/mol and 40000 g/mol. The obtained (co) polysiloxanes were subsequently cross-linked into the anhydrous solid by Fe(III) chloride.

The obtained polymer films exhibit high stretchability. To demonstrate the self-healing capability the polymer film was cut into two pieces and subsequently put together. Self-healing efficiency was 96 % after 72 h at room temperature.

The redox-active properties of polymer-metal complexes of (co)polysiloxane with Fe(III) using cyclic voltammetry were established. The values of the minimum and maximum potentials were (–300 ÷ 600) mV.

Electrophysical characteristics of the synthesized polymer-metal complexes of (co)polysiloxane with Fe(III) were investigated using high-frequency impedance (conductivity 10-13 Sm/cm at 1 Hz). The metal content in the polymer-metal complexes was 0.68 % (EDX method).

Acknowledgments. The work was supported by the Russian Science Foundation (project 20-19-00256). Measurements were performed at the Center for Magnetic Resonance, the Centre for Innovative Technologies of Composite Nanomaterials (all in Saint Petersburg State University).

References

1. C.H. Li, C. Wang, C. Keplinger, J.L. Zuo, L. Jin, Y. Sun, P. Zheng, Y. Cao, F. Lissel, C. Linder, X.Z. You, Z. Bao // Nat. Chem. 8 (2016) 618–624.

Synthesis of substituted cyclohexanes by the reaction of linear conjugated enynones with malononitrile

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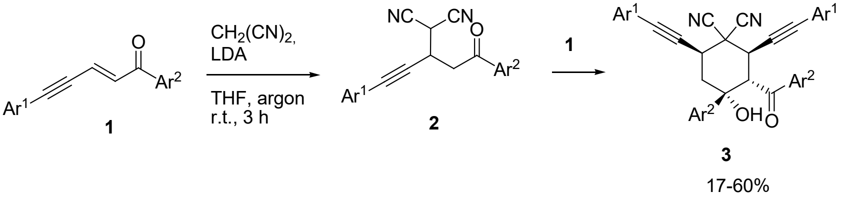
Linear conjugated enynones have a great importance in organic chemistry due to their high reactivity. Reactions of enynones with nucleophiles proceed well, this fact is conditioned by the acceptor effect of the carbonyl group.

LDA-catalyzed reactions of linear conjugated enynones, 1,5-diarylpent-2-en-4-yn-1-ones **1**, with malononitrile resulted in the formation of compounds **2** of Michael addition of the malononitrile to enynone system. Compounds 2 were further transformed into "dimeric" products **3** of cyclohexane type, which formed as a result of interaction of **2** with the second enynone molecule. The obtained substituted cyclohexanes have four stereocenters, that means that theoretically 16 stereoisomers of this compound can be obtained. However, the only one isomer of **3** was formed; the reaction proceed highly stereoselectively.



Scheme 1. Reactions of 1,5-diarylpent-2-en-4-yn-1-ones with malononitrile catalyzed by LDA.

A simple approach to the reliable comparison of kinetic parameters of charge transfer processes in electrode materials for lithium-ion batteries

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Charge transfer processes in electrode materials for lithium-ion batteries, which are described by kinetic parameters quantitatively, are strongly dependent on the surface area of the electrodes. Based on general descriptions [1], surface area of the electrode is assumed as full electroactive area of the electrode (area of electroactive particles), or real surface area (RSA). Nevertheless, in numerous works determination of kinetic parameters is carried out based on the visible surface area [2, 3]. This does not allow to compare kinetic parameters for a single type of electroactive grain in cases of its different amounts per electrode area unit (mass loadings), e.g. for electrodes with different thickness.

In this work, a simple approach to evaluate kinetic parameters more reliably was proposed. This approach assumes that the real active surface area is defined as the total surface of all particles of the active component. In case of particles with normally distributed sizes, their surface area is proportional to the mass of electroactive grains. Determination of kinetic parameters from mass-normalized impedance spectra (or calculations of RSA from mass loading and Brunauer-Emmet-Teller measurements) gives the basis for a more reasonable comparison of the results of various works.

This approach has been identified as reasonable for electrode materials based on $LiMn_2O_4$ with various thickness. It has been shown that the large difference in the values of charge transfer resistances and lithium diffusion coefficients for electrodes with various thickness becomes insignificant after normalization of impedance spectra to mass loading.

Acknowledgments. The financial support from the St Petersburg State University (grant № 26455158) is gratefully acknowledged. The authors would like to thank the Interdisciplinary Center for Nanotechnology of Research Park of St Petersburg State University.

References

1. J.P. Meyers, M. Doyle, R.M. Darling, J. Newman // J. Electrochem. Soc., vol. 147, p. 2930 (2020).
2. C. Zhu, Y. Zhang, X. Yu, P. Dong, J. Duan, J. Liu, J. Liu, Y. Zhang // Chem. Sus. Chem., vol. 13, p. 803–810 (2020).
3. C.G. Han, C. Zhu, G. Saito, T. Akiyama // Electrochim. Acta, vol. 209, p. 225–234 (2016).

Structure, diffusion and self-diffusion coefficients of proton substituted β-alumina

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Nowadays the development and the implementation of green energy sources is becoming extremely important. Here, H-β-Al_2O_3 is regarded as an attractive material for the use as a proton conducting solid electrolyte (SE) in low-temperature fuel cells. Thus, the aim of this work was to study the phase composition, structure, and transport properties of H-β-Al_2O_3 ceramics. Precursor of $Na_2O\cdot 6.5Al_2O_3$ composition was manufactured via pyrolysis, compacted into the pellets at pressure 10 tons/cm^2 and annealed at 1520 ºC for 2 hours. The H-β-Al_2O_3 SE was obtained by ion exchange technique of Na-β-Al_2O_3 pellets in HNO_3 and H_2O at room temperature. Ion exchange was controlled by conductometry (inoLab Cond7110) and atomic emission spectroscopy (ICPE-9000). Structure of H-β-Al_2O_3 SE was examined by XRD (SHIMADZU XRD-6000), SEM and EDX techniques (Hitachi S-3400N). The transport properties of SE were investigated using EMF method. The Na^+ to H^+ exchange results in the peaks intensity enhancement in the XRD pattern without their position shift, corresponding to the protonated β-alumina phase. Via SEM and EDX it was found that both β- and β″-alumina present in the SE structure. Na^+ is exchanged by a H^+ in the β-alumina phase only, no substitution occurs in sodium β″-alumina phase. It was suggested that proton transport is carried out through the H-β-alumina and Cl^- transport takes place through sodium β″-alumina. Diffusion and self-diffusion coefficients calculated from the EMF data. The values obtained correlate well with the literature [1]. SEM and EDX data were obtained at «GEOMODEL» center and AES measurement was performed at «Center for Chemical Analysis and Materials Research» at SPBU Research park.

References

1. Yao Y.F.Y., Kummer J. Ion exchange properties of and rates of ionic diffusion in beta-alumina // Journal of Inorganic and Nuclear Chemistry. 1967. V. 29. №. 9. P. 2453-2475.

1,3-Dipolar cycloaddition of nitrones to 2-(2-oxoindolin-3-ylidene)acetate

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A lot of biologically active alkaloids, such as dactilicapnosinine and dactilicapnosine, contain isoxazolidine fragment. The derived isoxazolidines possess a wide spectrum of biological properties including antiviral, antibacterial and antitumor activities. Spiroisoxazolidine fragment is widely known as a structural part of pharmaceutically important substances and naturally occurring compounds [1].

The synthesis of complex spiroisoxazolidines of high efficiency and selectivity can be carried out using the reaction of 1,3-dipolar cycloaddition of nitrones to exocyclic double bonds. Our research group has recently reported the example of the cycloaddition reactions of nitrones to *N*-arylitaconimides. The reactions proceed regioselectively and with high diastereoselectivity to form isoxazolidines as a single 5-spiro regioisomers [2].

The aim of this work is to investigate regio- and stereoselectivity of *C*-carbamoyl nitrones cycloaddition to (E)-methyl 2-(2-oxoindolin-3-ylidene)acetate.

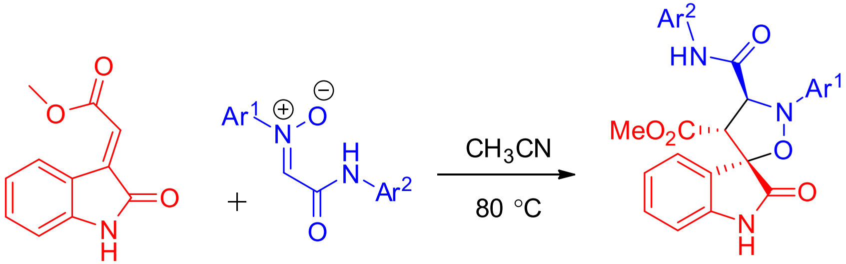

Fig. 1. 1,3-Dipolar cycloaddition of nitrones to 2-(2-oxoindolin-3-ylidene acetate.

The reactions of 2-(2-oxoindolin-3-ylidene)acetate with *C*-carbamoyl nitrones resulted in the regio- and stereoselective formation of new highly functionalized spiro-(indoline-isoxazolidines) with good yields. Further, we are planning to study the possible transformations of the obtained cycloadducts.

References

1. M. Berthet, T .Cheviet, G. Dujardin, I. Parrot, J. Martinez // Chem. Rev., 116, 15235 (2016).
2. P.S. Teterina, M.M. Efremova, E.V. Sirotkina, A.S. Novikov, O.V. Khoroshilova, A.P. Molchanov // Tetr. Lett., 60, 151063 (2019).

DNA encapsulation in melamine – cyanurate supramolecular assembly

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The direction of research in the field of synthetic biology about DNA encasing is not novel, but in the present work for the first time we have proposed and performed encapsulation in melamine – cyanuric acid supramolecular assembly of single stranded DNA marked with fluorescent compound TAMRA.

Our inspiration is in gel-based reaction – diffusion system. To fabricate it, for every single experiment we made three gels with different concentrations of melamine, DNA, cyanuric acid, and magnesium ions. When samples prepared and joined, in the center of DNA-containing gel, a noticeable white line of assembled melamine – cyanurate particles appears.

To obtain data the central line was visually examined using fluorescence microscopy. We gained an interesting result to share of how concentration of magnesium ions affects the spatial distribution of DNA inside the capsules.

The start the research in this direction opens a wide avenue toward area in synthetic biology with developing an artificial cell, molecular-based computation, and data storage. Our approach also could be useful in application of the system in solving a “real-world” problem through preparation of a high – sensitive antibiotics test system quantification.

Self-assembly of *bis*isocyanide complexes of platinum(II) based on halogen bonds

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The main problem in crystal engineering is to control the direction of self-assembly of structures. Platinum(II) complexes with halogen-substituted arylisocyanides are promising supramolecular building blocks in crystal engineering for the formation of 1D, 2D, and 3D structures of a given structure [1-2].

We synthesized dihalide *bis*isocyanide complexes of platinum(II) $[PtX_2(CNC_6H_3\text{-2-F-4-I})_2]$ and $[PtX_2(CNC_6H_3\text{-2-I-4-Br})_2]$ (X = Cl, I). contain, A halogen atom in phenylisocyanide is a halogen bond donor in the resulting complexes. A region with a positive electrostatic potential in halogen atom determines the direction of self-assembly of supramolecular structures (Fig. 1).

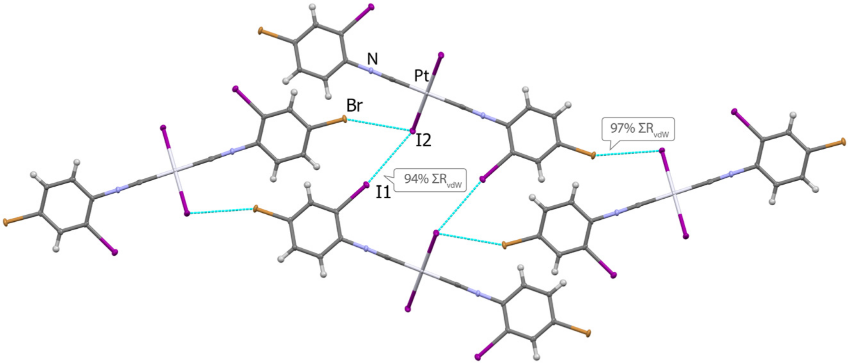

Fig. 1. The structure of the complex trans-$[PtI_2(CNC_6H_3\text{-2-I-4-Br})_2]$. On picture dotted line – halogen bond.

Acknowledgments. These studies were funded by the Russian Foundation for Basic Research (18-33-20073) Measurements were performed at the Center for Magnetic Resonance, the Center for X-ray Diffraction Studies, the Center for Chemical Analysis and Materials Research, and the Chemistry Educational Centre (all belong to Saint-Petersburg State University).

References

1. M.A. Kinzhalov, M.V. Kashina et al. // Angew. Chem. Int. Ed., 57, 12785, (2018).
2. M.V. Kashina, M.A. Kinzhalov et al.// Asian J. Chem., 14, 3915, (2019).

Effect of laser radiation on the bioactivity of thiazolotriazole and aminomalonate compounds

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The ability to control the biological activity of compounds opens up broad prospects for the use of compounds for medical purposes. The search, development and study of the properties of such compounds is an urgent modern trend. We present recently synthesized organophosphorus compounds belonging to the phosphonate class. Due to their ability to inhibit enzymes of the cholinesterase group, the compounds can be used in the treatment of neurodegenerative disorders.

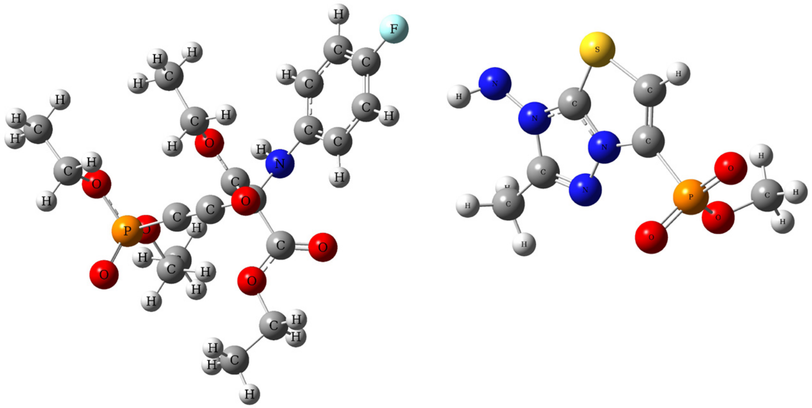

Fig. 1. Structural formulas of phosphorylated aminomalonate and thiazolotriazole compounds.

The investigations of the properties of the compound was carried out using absorption, Raman, FTIR spectroscopies and enzymatic method demonstrated possibility of laser-induced modification of physicochemical and functional properties of this substance.

When studying the biological photo-optical properties of compounds of the phosphonate class, it was established that these properties are photo-controlled. Both compounds show different directions of changes in biological activity as a result of laser exposure. The studies obtained open up the possibility of using the compounds as photopharmacological agents, for example, for carrying out a dark therapeutic regime and then switching off the drug effect, or vice versa.

Reactions of 2-(1'-Me$_3$SiO-1'-trifluoromethyl-alkyl) benzofuranes with arenes in CF_3SO_3H

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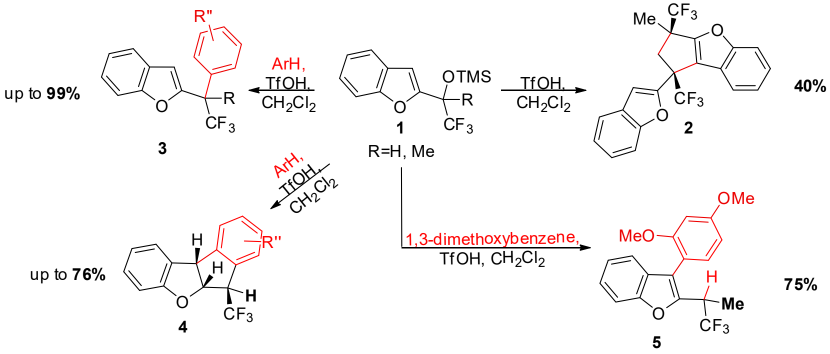
Both five-membered heterocycles and fluoroorganics are widely used in drug discovery due to a wide range of biological activities of these compounds [1, 2]. Therefore, fluoro-containing heterocycles of the series of furan also appear to be promising for application in medicinal chemistry.

In the superacid CF_3SO_3H (TfOH) in the absence of arene molecules, as external nucleophiles, 5-(1'-Me$_3$SiO-1'-trifluoromethyl-alkyl)benzofuranes **1** are transformed into products of electrophilic "dimerization" **2** (Scheme 1). Apart from "dimers", the products of the benzofuran side chain arylation **3** and new fused heterocycles **4** were formed in reactions with arenes. Moreover, interaction with 1,3-dimethoxybenzene resulted in formation of heterocyclic ring arylation product **5** in good yield. It is worth mentioning that significant diastereoselectivity in products formation was observed.



Scheme 1. Reactions of 2-(1'-Me$_3$SiO-1'-trifluoromethyl-alkyl)benzofuranes with arenes in TfOH.

References

1. J.J. Li // Angew. Chem. Int. Ed., 52, 1351 (2013).
2. D. Banner, S. Bendels, M. Kansy, B. Kuhn, K. Müller, U. Obst-Sander, M. Stahl, H.J. Bohm // ChemBioChem., 5, 637 (2004).

Organo-inorganic derivatives of layered perovskite-like oxide $HCa_2Nb_3O_{10}$ with monoethanolamine and aminoacetic acid

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The products of intercalation of organic compounds into the interlayer space of layered perovskite-like oxides are of interest both by themselves and because of the possibility of their use in the synthesis of hybrid materials modified by covalently bound organic groups (grafting), potentially having many practical applications [1, 2].

This work is devoted to the development of a procedure for the synthesis and characterization of organo-inorganic derivatives based on protonated and hydrated niobate $HCa_2Nb_3O_{10} \cdot yH_2O$ with monoethanolamine ($HCa_2Nb_3O_{10}\times$ Gly) and glycine ($HCa_2Nb_3O_{10}\times$MEA) with different types of binding of embedded molecules in the interlayer space. The development of the synthesis procedure was carried out under the conditions of a standard laboratory experiment with varying temperature, time and concentration of reagents, as well as using microwave and hydrothermal synthesis methods. The obtained compounds were characterized using the methods of X-ray phase, thermogravimetric and elemental analysis, as well as ^{13}C NMR spectroscopy. The report focuses on qualitative and quantitative analysis.

The resulting compounds can be indexed in the tetragonal system. The composition of the obtained samples, calculated from the results of thermogravimetric analysis and CHN analysis, corresponds to the formulas: $HCa_2Nb_3O_{10} \cdot 0.3H_2O \cdot 0.75Gly$ and $HCa_2Nb_3O_{10} \cdot 0.35H_2O \cdot 0.9MEA$.

Acknowledgments. The research was carried out using the equipment of the Science Park of St. The authors thank the RC “X-ray diffraction research methods”, RC “Thermogravimetric and calorimetric research methods”, RC “Methods of analysis of the composition of matter”, RC “Magnetic resonance research methods”. The study was supported by the Russian Foundation for Basic Research (Grant No. 18-03-00915).

References

1. K.G.S. Ranmohotti, E. Josepha, J. Choi, J. Zhang, J.B. Wiley. Topochemical manip-ulation of perovskites: low-temperature reaction strategies for directing structure and properties //Adv. Mater., vol. 23, no. 4, pp. 442–60, Jan. 2011.
2. A.J. Jacobson, J.W. Johnson, J.T. Lewandowski. Interlayer chemistry between thick transition-metal oxide layers: synthesis and intercalation reactions of $K[Ca_2Na_{n3}Nb_nO_{3n+1}]$ (3 .ltoreq. n .ltoreq. 7) // Inorg. Chem., vol. 24, no. 23, pp. 3727–3729, Nov. 1985.

Hydrogen peroxide influence on luminescence of melamine barbiturate particles

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There is an advanced direction in supramolecular chemistry today that is aimed to functional materials development. One of the most discussed organic self-assembly is melamine cyanurate because of its rare stability [1]/ It is a complex held together by hydrogen bonds like some other close analogs with different acids.

There are several studies about melamine and its derivatives complexes as a functional material. Melamine barbiturate is supposed to be an encapsulating host-guest system for oxygen radical [2]. The trapping effect is observed only in case of binary system as well as a luminescence of the melamine barbiturate particles.

Melamine barbiturate self-assembly shows luminescence in opposite to melamine and stronger luminescence than individual barbituric acid. Three different channels were used: FITC, DAPI, RHOD. Due to a proposed radical trap function several experiments with hydrogen peroxide are performed. In case of 3% H_2O_2 existence melamine barbiturate particles show a luminescence increase in FITC channel (Fig. 1) that circumstantially proves peroxide radical trapping.

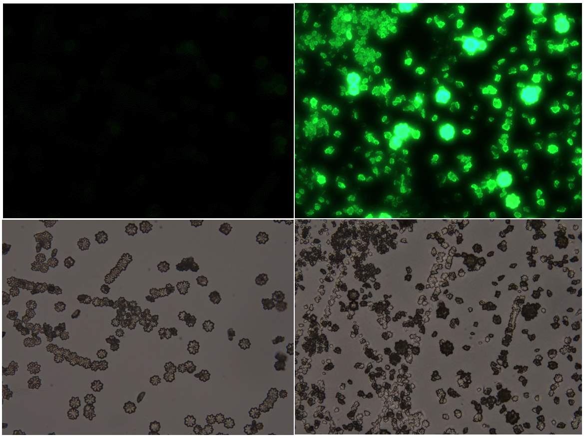

Fig. 1. Luminescence of melamine barbiturate in FITC channel with H_2O_2 (right) and without (left).

References

1. G. Whitesides, J. Mathias, C. Seto // Sci. 254, 1312–1319 (1991).
2. Shilovskikh V.V., Timralieva A.A., Belogub E.V. et al. Radical Activity of Binary Melamine-Based Hydrogen-Bonded Self-Assemblies // Appl Magn Reson (2020).

Novel Denitrogenative Transannulation of 1-Alkyl-1*H*-1,2,3-triazoles with Diazo Esters

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Transannulation reactions of 1*H*-1,2,3-triazoles are rather popular strategy for the construction of nitrogen heterocycles. However, the range of the substrates suitable for the aforementioned transformation is limited to 1-sulfonyl-1,2,3-triazoles, 1-perfluoroalkyl-1,2,3-triazoles and [1,2,3]triazolo[1,5-*a*]pyridines. Here, we developed a method for the synthesis of densely substituted 4-pyrrolin-2-ones **1** by Rh(II)-catalyzed denitrogenative transannulation of 1-alkyl-4-aryl-1*H*-1,2,3-triazoles with diazo esters. The reaction proceeds via an attack of the rhodium-bound carbene derived from the diazo ester at the N2 atom of the triazole and the formation of unstable 3,4-dihydro-1,2,4-triazine. The subsequent Rh(II)-catalyzed denitrogenative triazine ring contraction leads to pyrrolin-2-one and it is also catalyzed by the rhodium complex. The method is inapplicable to 1,2,3-triazoles with primary alkyl substituent at C4, which under the same conditions, in contrast, afford stable 1,2,3-triazol-3-ium ylides **2** as main products.

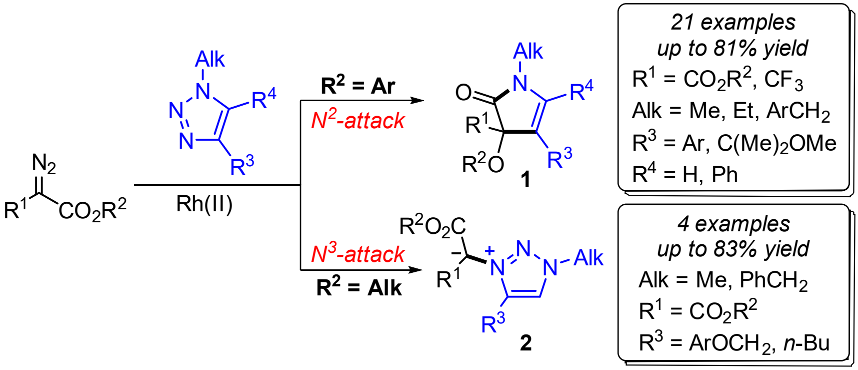

Fig. 1. Reaction between diazo esters and 1-alkyl-1H-1,2,3-tirazoles.

Acknowledgments. We gratefully acknowledge the financial support of the Russian Science Foundation (20-13-00044). This research used resources of the Magnetic Resonance Research Centre, Chemical Analysis and Materials Research Centre, Centre for X-ray Diffraction Studies, Computing Centre, and Chemistry Educational Centre of the Research Park of St. Petersburg State University.

Hydrogen bonds formed by arsinic, stilbinic and bismuthinic acids: investigation by means of quantum chemistry

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Species containing XOOH group (X = C, P, As, Sb, Bi) can participate in hydrogen bonding both as donors (by XOH moiety) and acceptors (by X=O moiety). Carboxylic RCOOH and phosphinic RR'POOH acids are widely explored by experimental spectral techniques [1 - 4] as well as by quantum chemistry methods [1-3].

At that time the ability of acids RR'XOOH (where X = As, Sb, Bi) to participate in hydrogen bonding arepractically unexplored. This work is devoted to the quantum-chemical investigation (MP2/def2-TZVP) of structure, geometry, energy and spectral parameters ofhydrogen bonded complexes formed by arsinic H_2AsOOH, stilbinic H_2SbOOH and bismuthinic H_2BiOOH acids as hydrogen bond donors and acceptors (Fig. 1).

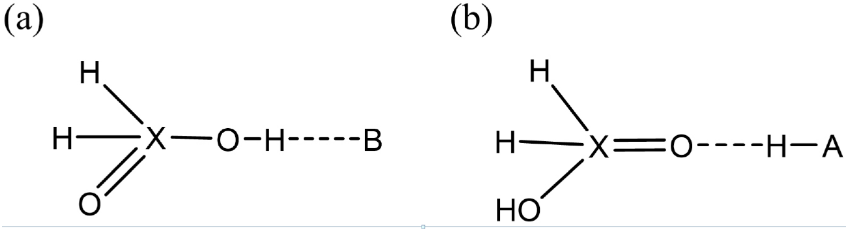

Fig. 1. Schemes of studied complexes: (a) H_2XOOH as a H-bond donor, (b) as a H-bond acceptor. X = As, Sb, Bi; B = base; HA = acid.

References

1. B. Koeppe, S.A. Pylaeva, C. Allolio, D. Sebastiani, E.T.J. Nibbering, G.S. Denisov, H.-H. Limbach, P.M. Tolstoy // Phys. Chem. Chem. Phys., 19, 1010 (2017).
2. S. Pylaeva, C. Allolio, B. Koeppe, G.S. Denisov, H.-H. Limbach, D. Sebastiani, P.M. Tolstoy // Phys. Chem. Chem. Phys., 17, 4634 (2015).
3. V.V. Mulloyarova, I.S. Giba, M.A. Kostin, G.S. Denisov, I.G. Shenderovich, P.M. Tolstoy // Phys. Chem. Chem. Phys., 20, 4901 (2018).
4. I.S. Giba, V.V. Mulloyarova, G.S. Denisov, P.M. Tolstoy // J. Phys. Chem.A., 123, 2252 (2019).

Optimization of creatinine, L-histidine and 3-methyl-L-histidine separation in human urine via ion-exchange high performance liquid chromatography

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The amino acid 3-methyl-L-histidine(3-MH) is a component of muscle fiber. During the muscle catabolism, 3-MH is released into bloodstream and then quantitatively excreted via renal clearance. As a rule, the content of urine metabolites is presented as a relation to the content of creatinine (CR), since the latter is a marker of glomerular filtration rate. Therefore, simultaneous determination of 3-MH and CR in urine can serve as a metric for muscular stress, presenting an interest in means of clinical laboratory diagnostics and sports medicine.

In this work, we proposed a procedure based on ion-exchange high performance liquid chromatography (IO-HPLC) with UV-detection as a solution for 3-MH and CR separation and simultaneous quantitation in human urine. Throughout the method development several stages were completed:

- Choice of the optimal conditions for UV-detection of analytes. The wavelength of 212 nm was selected. L-histidine (His) was considered to be main interfering compound and thus included in the model mixture;
- Full factorial experiment design and optimization of IO-HPLC conditions on a model solution of three components (CR, His, 3-MH). The optimal conditions were: mobile phase H_3PO_4 12 mM aquatic solution, isocratic elution; flow rate 1 $ml \cdot min^{-1}$; column temperature 35°C;
- Chromatographic separation of 3-MH and CR in presence of His and 1-methyl-L-histidine as an additional interfering compound;
- Optimization of the urine sample processing prior to the analysis. A simple filtration and dilution were found to be enough;
- Generation of a calibration curve and 3-MH and CR determination in a human urine sample. Full elution of a urine sample took 7 minutes. The validity of the result was estimated via recovery experiments of spiked samples.

The developed procedure is rather simple, unlike many reversed-phase HPLC procedures widely utilized in the analysis of biological fluids. Our method is also fast, requires simplistic detector and the minimal amount of rather cheap reagents.

Acknowledgments. This research was supported by grant of the St. Petersburg University Alumni Association. The Authors are grateful to Chemistry Educational Centre of the SPbU Research Park for providing access to their facilities.

Unusual Reactivity and Photophysical Properties of the Pt(II) Pincer Complexes Containing 6,6'-diphenyl-2,2'-bipyridine ligands

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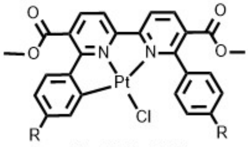
The phosphorescent Pt(II) complexes are extremely attractive for scientists, owing to their potential application as agents in bioimaging. For these purposes, the complexes must be stable, biocompatible and non-toxic, as well as have a wavelength of excitation and emission in the specified range. In this regard, it is important to develop methods for tuning these photophysical parameters of a complex compound.

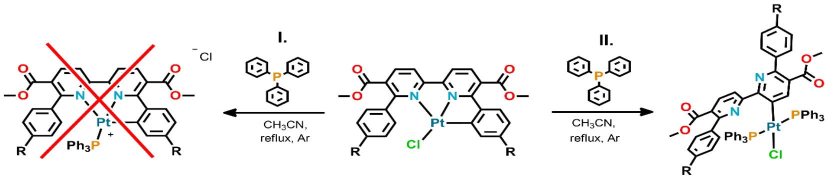
In resent research platinum (II) complexes with NNC-cyclometallic ligands based on 6,6'-phenyl-2,2'-bipyridine fragments were studied (Fig. 1). For all complexes were obtained experimental and calculated absorption and emission spectra. They were compared with each other in detail. Moreover, electronic transitions were analyzed using NTO (natural transition orbitals).



R= OMe, H, F

Fig. 1. Schematic structure of new Pt(II) complexes.

Then we tried to replace the chloride ligand with triphenylphosphine to improve the properties of the compound. However, instead of substitution, the tridentate ligand re-coordinated, the chloride kept bonding to platinum and two phosphine ligands entered in the coordination sphere. The calculation of the Gibbs free energy showed that the resulting product is thermodynamically more stable than the desired one (Fig. 2).



[Pt(NNC-H)$(PPh_3)_2$Cl], (**1a**), 79%
[Pt(NNC-F)$(PPh_3)_2$Cl], (**2a**), 85%
[Pt(NNC-OMe)$(PPh_3)_2$Cl], (**3a**), 82%

Fig. 2. Scheme of synthesis of complexes with triphenylphosphine.

Acknowledgments. This research has been supported by grant of the RSF 19-73-20055.

Development of analytical techniques for ferrate (VI) quantification during its continuous electrochemical production in a mobile water purification plant

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Ferrates are the high-valent iron-based compounds. Among these ferrate (VI) is relatively stable and easy to synthesize. Ferrate (VI) (FeO_4^{2-}) is an emerging disinfectant and oxidant for treating water. Another advantageous property of ferrate (VI) is that its decomposition produces Fe (III) hydroxide, which is an excellent coagulant for removal of metals and radionuclides from contaminated water:

$$4FeO_4^{2-} + 10H_2O \Rightarrow 4Fe(OH)_3\downarrow + 8OH^- + 3O_2.$$

Three different preparation methods are known for Fe (VI) synthesis in laboratory [1]. These are: dry oxidation of iron at high temperature, wet oxidation of iron (III) using chemical oxidizing agents and an electro-chemical method. The latter has an advantage of easy synthesis and automation [2]. For facilitating of efficiency of electrochemical production of ferrate (VI) is necessary to develop analytical techniques for ferrate (VI) quantification during the process of synthesis. The peculiarity of this group of compounds is instability consequently there is a necessity of its production at the point of application.

A new analytical monitoring system of measuring Fe (VI) in aqueous solution during its continuous electrochemical production was developed. Flowing spectrophotometry cell made it possible to determine the concentration of ferrate (VI) in real time in the concentration range between $4*10^{-4}$ M and 0,4 M. But this method has some limitations related to the particulate matter that form during the electrochemical generation of ferrate (VI). Therefore, direct potentiometry method was used as a reference method to spectrophotometry aiming to improve reliability of the system. For the laboratory determination of ferrate, the amperometric titration method was used.

References

1. Tiwari D., Lee S.-M. Ferrate(VI) in the Treatment of Wastewaters: A New Generation Green Chemical // Waste Water - Treatment and Reutilization, 2011, 241-276.
2. E.N. Arakcheev et al. Complex electrolytic unit for producing anode liquor and ferrate to treat waters contaminated by oil-refining products and harmful admixtures // Chemical and Petroleum Engineering, vol. 52, no. 2, pp. 143–148, 2016.

Synthesis of organically modified layered perovskite-like titanates $H_2Ln_2Ti_3O_{10}$ (Ln = La, Nd) and their photocatalytic activity towards hydrogen production from aqueous methanol

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In light of global environmental problems and depletion of fossil fuels, creation of new highly efficient photocatalysts for hydrogen generation from water and water-organic media appears to be one of the most actively developing areas of chemistry [1].

The present research is devoted to synthesis and systematic investigation of photocatalytic activity of inorganic-organic derivatives based on layered perovskite-like titanates $H_2Ln_2Ti_3O_{10}$ (Ln = La, Nd) in the reaction of hydrogen production from the model 1% (mol.) aqueous solution of methanol.

During the photocatalytic experiments, it has been established that organic modification of the interlayer space of the titanates is an efficient way to improve their photocatalytic activity. The rate of increase in the activity compared to that of the initial protonated titanates is up to 117 times and additional coating of the surface with Pt nanoparticles as a cocatalyst allows reaching quantum efficiency of more than 40%. In addition, the hydrogen generation rate over most active photocatalysts is stably maintained throughout the entire measurement time. Photocatalytic activity of the titanates and their derivatives correlates with the hydration degree of their interlayer space, which is considered a separate reaction zone in photocatalysis [2]. Introduction of organic components substantially enhances its availability for reactants that, probably, explains observed multiple increase in the activity.

Acknowledgments. The study was conducted using the equipment of the Saint Petersburg State University Research Park: Centre for X-ray Diffraction Studies, Centre for Optical and Laser Research, Centre for Magnetic Resonance, Centre for Chemical Analysis and Materials Research, Centre for Thermal Analysis and Calorimetry, Interdisciplinary Centre for Nanotechnology, Centre for Innovative Technologies of Composite Nanomaterials.

The work was supported by grants of Russian Foundation for Basic Research (18-03-00915) and Russian Scientific Foundation (20-73-00027).

References

1. A.V. Puga // Coord. Chem. Rev., v. 315, p. 1–66 (2016).
2. W. Cui, L. Li, S. Ma, Y. Liang, Z. Zhang // Catal. Today, v. 207, p. 44–49 (2013).

Efficient liquid exfoliation of layered perovskite-like titanates $HLnTiO_4$ and $H_2Ln_2Ti_3O_{10}$ (Ln = La, Nd) into nanosheets

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Over the past decades, two-dimensional (2D) nanomaterials, such as nanosheets and ultrathin films, have attracted great attention due to superior mechanical, electrical, optical and chemical properties, which can significantly differ from those of three-dimensional (3D) bulk counterparts because of specific nanoscale effects [1]. Most promising application fields of 2D nanomaterials include creation of membranes, supercapacitors, nanoelectronic devices, thermoelectrics, photovoltaic cells, catalysts, and chemical sensors.

The present work is focused on quantitative liquid exfoliation of the Ruddlesden-Popper titanates $HLnTiO_4$ and $H_2Ln_2Ti_3O_{10}$ (Ln = La, Nd) as well as their *n*-alkylamine derivatives into perovskite nanosheets. It is established that whilst protonated titanates practically do not undergo lamination, their amine derivatives with broadened interlayer space can be successfully exfoliated via the stage of tetrabutylammonium hydroxide (TBAOH) intercalation followed by sonication. Propensity of the derivatives for quantitative lamination is found to strongly depend on the intercalated amine length. Despite the greatly enlarged interlayer distance, the titanates modified with long chain amines demonstrate a relatively poor ability to liquid exfoliation as compared with that of the modified by short chain ones. It is also shown that the sonication role probably consists in initiation of the layered structure lamination whose completeness greater depends on the exposure time in the TBAOH solution rather than on the duration of ultrasonic treatment. Successful obtainment of perovskite nanosheets is confirmed by means of electron and atomic force microscopy allowed establishing their average lateral sizes of 30–100 nm and thickness of 3–6 nm.

Acknowledgments. The study was conducted using the equipment of the Saint Petersburg State University Research Park: Centre for X-ray Diffraction Studies, Centre for Optical and Laser Research, Centre for Magnetic Resonance, Centre for Chemical Analysis and Materials Research, Centre for Thermal Analysis and Calorimetry, Interdisciplinary Centre for Nanotechnology, Centre for Innovative Technologies of Composite Nanomaterials.

The work was supported by grants of Russian Scientific Foundation (20-73-00027) and President of Russian Federation (MK-480.2020.3).

References

1. R. Hinterding, A. Feldhoff // J. Phys. Chem., v. 233, №1, p. 117–165 (2019).

Novel thin-film composite chitosan/PAN for isopropanol dehydration by pervaporation

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Pervaporation is one of the dynamically developing methods of the membrane technologies, which seems to be high-potential in the separation of liquids in the different industries. The competitive advantage of the pervaporation over the classical separation methods is the ability to separate azeotropic mixtures, mixtures of thermally unstable components and isomers. Besides high selectivity, pervaporation is an environmentally-friendly and low energy consuming process with inexpensive and compact equipment. The high development of the pervaporation requires the search for new membrane materials with tailored properties.

In this work, thin-film composite membranes (TFC) with a thin selective layer based on chitosan (CS) were developed with various approaches to improve the characteristics: (1) varying the concentration of the CS solution; (2) changing the porosity of substrates from polyacrylonitrile (PAN); (3) deposition of the additional ultrathin layers on the surface of the selective CS layer using interfacial polymerization and layer-by-layer assembly. The developed TFC membranes were studied using fourier-transform infrared spectroscopy, scanning electron microscopy, atomic force microscopy, measuring of water contact angles and porosity. Transport properties of the developed TFC membrane were studied in pervaporation for isopropanol dehydration in a wide concentration range (12–100 wt.% water in the feed) and for dehydration of the azeotropic isopropanol/water mixture (88/12 wt.%) at various temperatures (28, 35, 50 °C). It was found that the use of different approaches leads to improved performance of thin-film membranes based on chitosan.

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Development and study of novel pervaporation green membranes based on sodium alginate modified by Zr-MOFs

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One of the most popular membrane processes for the separation of low molecular weight components is the pervaporation, which allows the separation of azeotropic mixtures, mixtures of isomers and thermally unstable mixtures. Nowadays, the essential improvement of the transport properties of pervaporation membranes can be achieved by the modification of an polymer matrix by an inorganic filler that yields in developing the mixed – matrix membranes (MMMs). The introduction of inorganic filler in the polymer matrix of the membrane allows getting tailoring properties.

In the present work the novel membranes based on biopolymer sodium alginate (SA) were prepared by introducing the three metal-organic frameworks (Zr-MOFs): UiO-66, UiO-66(NH_2)-EDTA and UiO-66(NH_2)-AcOH into the SA matrix. The improvement of the transport properties of polymer membranes occurs due to the porous structure of the metal-organic frameworks. The developed SA and SA-Zr-MOFs membranes were studied using Fourier-transform infrared spectroscopy, and nuclear magnetic resonance, scanning electron microscopy, atomic force microscopy, X-ray diffraction analysis, thermogravimetric analysis, and swelling experiments. The transport properties of the developed membranes were studied by pervaporation separation of the mixture water/isopropanol mixture. All developed membranes were highly selective for water (more than 95 wt.% water in the permeate). The introduction of Zr-MOFs into the SA matrix leads to significant changes in properties of membranes based on sodium alginate.

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Transport characteristics of porous glass membranes modified with bismuth (III) oxide

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Glassy bismuth-containing materials (GBM) are promising for the creation of optical fibers with lasing in spectral ranges that are inaccessible to traditional materials with rare-earth ions. Developments of the ISCh RAS have shown that high - silica nanoporous glass (PG) is a promising medium in which it is possible to effectively control the chemical equilibrium of luminescence centers (bismuth active centers - BACs) [1]. For directed synthesis of GBMs with controlled BACs, it is necessary to study how the colloidal-chemical properties of the pore space surface of the synthesized composites change when the initial matrices are modified. In this regard the study and comparison of the transport characteristics (counterion transport numbers, surface conductivity, streaming potential) of micro- and macroporous (MIP and MAP) glasses, as well as on microporous glass heattreated at 750°C (MIP-750), containing (or not) Bi_2O_3 in 10^{-1}-10^{-4} M KNO_3 solutions were carried out. For obtain composite materials, a part of PG matrices were impregnated in 0.5 M $Bi(NO_3)_3$ solution prepared based on 2 M HNO_3 solution; and the other part of the matrices, in 2 M HNO_3 solution for 3 days (three-stage treatment) with intermediate drying at 50 °C. After impregnation the PG samples were heat-treated to the temperature T = 650 °C, as a result of which $Bi(NO_3)_3$ decomposed in the pore space to form Bi_2O_3.

From the measured streaming potentials values for all the porous membranes under study, the values of the zeta-potentials (ζ) were calculated taking into account the electrical conductivity of the pore solution and the electrical double layer overlapping. It is shown that the efficiency coefficient (which is equal to the ratio of the specific electrical conductivities of pore and free solutions), counterion transport numbers and $|\zeta|$ values for membranes impregnated in saline or acidic solutions and heat treated are close to each other and less than for the initial matrices.

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References

1. M.A. Girsova, S.V. Firstov, T.V. Antropova // Glass Phys. Chem., 45 (2), 98 (2019).

Electrokinetic characteristics of nickel-containing glasses in 1:1 and 2:1 charging electrolytes

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The problem of the modern technologies' progress puts forward the task of developing the scientific basis of direct synthesis of composite metamaterials with specified functional characteristics. Glassy materials are successfully used as matrices, which have such advantages as low cost, thermal, chemical and microbiological resistance, transparency in the visible region, etc. In the present work, nickel-containing glasses (Ni-1 and Ni-2) were obtained by introducing nickel oxide into the batch during the melting of basic alkali borosilicate glass (8V). There was of interest to determine the effect of the modifying agent NiO on the parameters of the phase interface (electrophoretic mobility of particles, position of the isoelectric point, IEP) in solutions of 0.01 M indifferent NaCl electrolyte, as well as in the presence of specifically sorbed ions Ni^{2+} ($NiCl_2$).

According to the elemental analysis of Ni-1 and Ni-2 glasses, which was carried out on 10 × 10 × 1 mm^3 plates before contact with electrolyte solutions by energy dispersive X-ray spectroscopy (EDX), the composition (wt%) of the sample Ni-1 are: 56.21 O, 5.04 Na, 14.33 Si, 24.41 Ni; sample Ni-2 are: 63.40 O, 4.18 Na, 12.42 Si, 20.00 Ni.

Measurements of the electrophoretic mobility of glass particles, found by laser Doppler electrophoresis, were used to calculate the electrokinetic potential (ζ^S). The electrokinetic potential of glasses in NaCl solutions is positive in the acidic region, then at pH 2.1 (8V), pH 2.8 (Ni-1 and Ni-2) passes through the isoelectric point and becomes negative. In nickel chloride solutions, the position of the isoelectric point pH 2.8 (8V) pH 3.1 (Ni-1 and Ni-2) and the ζ - pH curves (at pH> 4) are located lower than in the sodium chloride solution. The observed shift of the IEL to the alkaline region during the transition from an indifferent electrolyte NaCl to an electrolyte containing specific ions Ni^{2+} is consistent with the theoretical concepts of the electric double layer arrangement. Thus, it can be seen that the modification of the matrix has a more significant effect on the electrokinetic characteristics in a NaCl solution than in a $NiCl_2$ solution.

Acknowledgments. The reported study was funded by RFBR according to the research project № 20-03-00544a. The studies were carried out using the equipment of the Interdisciplinary Resource Center in the direction "Nanotechnology". Glass samples were synthesized in the Institute of Silicate Chemistry of the Russian Academy of Sciences by I.N. Anfimova.

Electroconductive particles for sensor application

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The development of electrically conductive polymers for the creation of sensors is an urgent task of fundamental science. Such polymers coupled with various electrical engineering techniques, can be used to detect a wide range of compounds (such as toxic ions, or biological molecules).

The aim of this work is making a material which will form a good film as well as have electroconductive properties. Hence the core/shell particles were obtained. The core are particles based on poly(4-styrene sulfonic acid) obtained by inverse polymerization in cyclohexane with emulsifier using. For particles obtaining the concentration of cross-linking agent and emulsifiers as well as the monomers/cyclohexane ratio were variated.

Obtained particles were used for PEDOT shell forming. PEDOT were obtained without using external oxidant at room temperature [1]. Such method of polymerization without oxidant coupled with obtained water soluble PEDOT make such form of PEDOT promising for using in biosensor application.

Electrochemical properties were measured by electrochemical impedance (EIS) spectroscopy both in electrolyte with different anions and in phosphate-buffered saline. Although in the literature [2] there is a state that reduction form of PEDOT almost does not interact with biomolecule compare with oxidized from but in our work, according to X-ray photoelectron spectroscopy, PEDOT is exactly in the reduction form but anyway we can see the good interaction between bacteria E. coli and PNaSS/PEDOT films. The real clinic sample is complex object that contains a lot of proteins that can influence on electrical signal of EIS and the EIS in the presence of human serum albumin showed that such a form of PEDOT is fouled via proteins in a small extent.

References

1. E.Tomšik, I. Ivanko, J. Svoboda, I. Šeděnková, A. Zhigunov, J. Hromádková, J. Pánek, M. Lukešová, N. Velychkivska, L. Janisová // Macromol. Chem. Phys . 2000219 (2020).
2. B. Cao, C.J. Lee, Z. Zeng, F. Cheng, F. Xu, H. Cong, G. Cheng // Chem. Sci. №7, p. 1976-1981 (2016).

Investigation of the rearrangement of *N*-acyl derivatives of *N*-aryl(heteroaryl)ethylenediamines

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Lactams condensed with an aryl fragment and containing an aminoalkyl side chain at the nitrogen atom can regroup under basic conditions with the expansion of the lactam cycle by 3 links. As was shown earlier in the study of our research group, this reaction can be successfully used for the synthesis of medium-sized rings [1].

In this research, we performed a kinetic study of the described rearrangement on model systems, which were *N*-acyl derivatives of *N*-aryl(heteroaryl)ethylenediamines **3**.

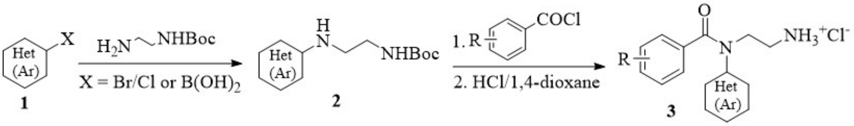

Fig. 1. The general scheme of synthesis.

It is shown that the electronic structure of the aryl (heteroaryl) and acyl fragment in **3** is the key factor determining the possibility of flow and the rate of rearrangement. Electron-acceptor groups significantly accelerate the conversion of precursors; electron-donating groups lead to a decrease in the rate of the studied rearrangement.

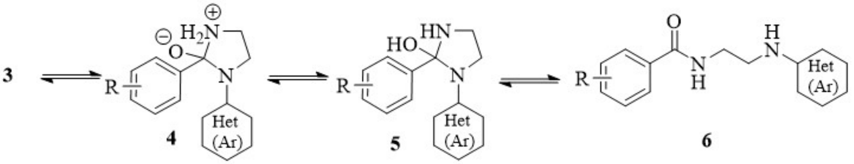

Fig. 2. Mechanism of the rearrangement reaction.

We also performed a quantum-chemical study of this rearrangement and established a correlation between the calculated effective rate constants of the studied rearrangement reaction and the Gibbs free energy for intermediate hydrated imidazolines **5**.

Acknowledgments. This research was supported by the Russian Foundation for Basic Research (RFBR) (Project Grant 18-03-01081).

References

1. E. Reutskaya, A. Osipyan, A. Sapegin, A. Novikov, M. Krasavin // J. Org. Chem., v. 84, № 4, p. 1693-1705 (2019).

Surface modification of titanium alloys to fabricate the functional coatings on dental implants

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Over the past decades, dental implants have become one of the most commonly used biomaterials to replace one (or more) missing teeth. Modern titanium dental implants have proven their safety and effectiveness in a large number of patients. However, there are several problems in the field of dental implants. Implant-related infections are dangerous complications and can cause serious illness with the hematogenous spread of bacteria and secondary infections. Also, lactic acid, which is produced by bacteria in the oral cavity, has a strong effect on the degree of corrosion of the metal [1, 2].

In our work, we consider various methods for modifying the titanium surface to increase the level of bioresorption of the material and its corrosion resistance. Specimens modified by the ultrasonic method and heat-treated were examined. Spider silk proteins were used to modify the titanium alloy surface by a Layer-by-layer assembly. The corrosion resistance has been studied for various types of titanium. The biocompatibility tests were carried out using human postnatal fibroblasts.

Acknowledgments. Authors acknowledge RSF grant no. 19-79-10244.

References

1. Guillaume B. Dental implants: a review //Morphologie, 100, 189–198 (2016).
2. Kulkarni M., Mazare A., Schmuki P. et al. A. Biomaterial surface modification of titanium and titanium alloys for medical applications //Nanomedicine, 111, 111. (2014).

One-pot route to *N*-acyl ureas: a formal four-component hydrolytic reaction

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N-acyl ureas represent an important class of organic compounds because of their broad utilization in materials chemistry and synthetic organic chemistry. These species also attract substantial interest in view of their great potential for pharmacological and agrochemical applications. The one-pot route to *N*-acyl ureas based upon easily accessible aminonitrones, isocyanides and Et_3N was developed. The urea species were isolated in moderate to good yields (44–95%) (Fig. 1).

DFT calculations based upon XRD data indicated that the quasi-cyclic conformation of *N*-acyl ureas is caused by moderate strength (6.2–7.8 kcal/mol) intramolecular resonance-assisted hydrogen bonding, while their solid-state dimerization is determined by the collective action of intermolecular N–H···O (4.1–7.5 kcal/mol) and C–H···O (1.6–4.7 kcal/mol) hydrogen bonds. Results of the kinetic study accompanied by DFT calculations confirmed that the generated 2-substituted 1,2,4-oxadiazolium salts are significantly more reactive toward nucleophilic additions than corresponding 1,2,4-oxadiazoles [1].

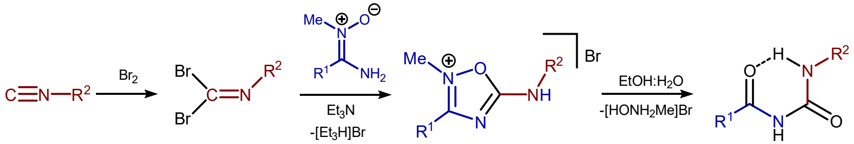

Fig. 1. Preparation of N-acyl ureas.

Acknowledgments. This work was financially supported by the Russian Foundation for Basic Research (grant 19-03-00044).

References

1. M. Il'in, L.A. Lesnikova, D.S. Bolotin, A.S. Novikov, V.V. Suslonov, V.Yu. Kukushkin. One-pot Route to N-acyl Ureas: a Formal Four-Component Hydrolytic Reaction Involving Aminonitrones and Isocyanide Dibromides // New J. Chem., 2020, 44, 1253-1262.

Regiospecific Silver-Catalyzed [3+2] Cycloaddition of Aryl-, Alkyl- and Aminosulfonyl Diazomethanes with Arenediazonium Tosylates

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The 2,5-disanstituted tetrazole moiety is an important synthetic scaffold that found broad application in medicinal chemistry. Compounds containing the tetrazole ring exhibit diverse biological activities such as antibacterial, antiviral, anticancer etc. However, in spite of the significance of tetrazoles, sulfones and sulfonamides moieties in drug design, 2-aryl-5-sulfonyl-2*H*-tetrazoles and 2-aryl-2*H*-tetrazole-5-sulfonamides with promising biological activity were either rare or not reported in the literature.

In the present work a silver-catalysed regioselective [3+2]-cycloaddition reaction of arenediazonium salts with aliphatic and (hetero)aromatic sulfonyldiazomethanes and diazo sulfonamides is reported. The reliance on these two classes of diazo compounds led to a new straightforward synthetic approach to a broad set of rare 2-aryl-5-sulfonyl-2*H*-tetrazoles and hitherto not described 2-aryl-2*H*-tetrazole-5-sulfonamides in moderate to high yields (Fig. 1). Merits of this approach include available starting reagents, wide functional group compatibility and mild reaction conditions. Furthermore, the impact of $AgNO_3$ catalysis on products' yields and regioselectivity of the cycloaddition was showcased [1].

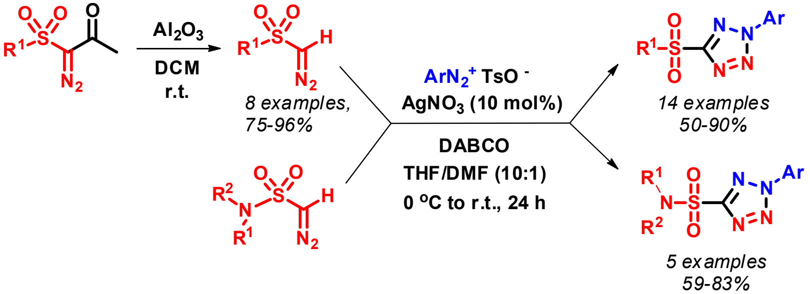

Fig. 1. Synthesis of diazomethyl sulfones and 2,5-disubstituted tetrazoles.

Acknowledgments. This research was supported by the Russian Foundation for Basic Research (project grant 18-33-20194).

References

1. E. Levashova, O. Bakulina, D. Dar'in, A. Bubyrev, S. Chuprun, M. Krasavin //Eur. J. Org. Chem. 2020, 27 4239.

Direct laser writing of conductive copper microstructures from deep eutectic solvents

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The increasing demands for eco-friendly processes, which comply with the principles of green and sustainable chemistry has led to search for alternatives to conventional organic solvents, among which deep eutectic solvents (DES) are the very perspective candidates. Despite this fact, the potential advantages of DES in the field of laser synthesis and laser material science remain almost completely unexplored. This study is focused on the process of laser-induced reduction of metals in DESs to develop simple and effective approaches for synthesis of conductive nanostructured deposits on the surface of dielectrics.

In this work, DESs were used as effective solvents for laser deposition of copper on surface of ceramics and oxide glass. Different DESs based on choline chloride and organic acids were synthesized. The use of eutectic solvents made it possible to greatly simplify the procedure of metal deposition and increase the deposition rate by more than 150 times compared to the use of aqueous solutions. The resulting structures were analysed using a scanning electron microscope and X-ray diffraction (Fig. 1).

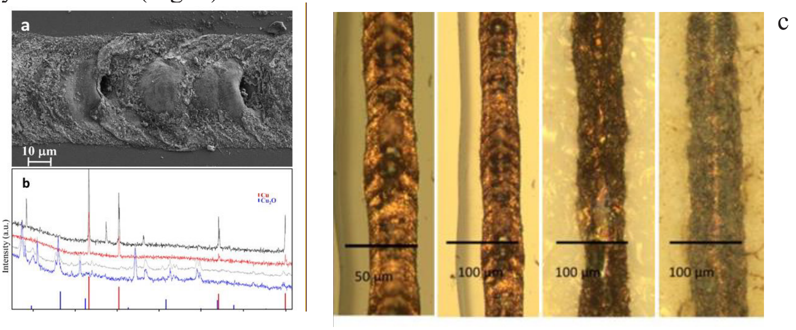

Fig. 1. (a) SEM image, (b) XRD patterns, (c) optical image of copper microstructures synthesized from DES based on choline chloride.

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Novel green pervaporation membranes based on sodium alginate modified by fullerene derivative for dehydration

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Currently, the problem of environmental pollution becomes really important. Therefore, the development of membrane processes, which are related to sustainable processes, is one of the most urgent and important directions. One of the most promising methods for separation of liquid mixtures with low molecular components is pervaporation, which allows easily and effectively separating azeotropic mixtures, mixtures of close-boiling and thermally unstable substances. The fast development of pervaporation requires the creation of novel green membranes with tailored transport characteristics for more efficient separation. An excellent way to solve this problem is the modification of well-known polymer by carbon nanoparticles to create mixed matrix membranes that combine the properties of an organic polymer and an inorganic modifier. In this work biopolymer sodium alginate was chosen as a green polymer network, and water-soluble fullerene derivative with arginine was chosen as a modifier and a cross-linking agent.

The aim of the work was to develop of novel green membranes based on sodium alginate (SA) modified by fullerene derivative with arginine (C_{60}-Arg) with improved transport properties for pervaporation dehydration. The optimal content of the modifier and the optimal method for cross-linking of SA membranes for their application in separation of dilute solutions were selected. The structure of developed membranes was studied by FTIR spectroscopy, scanning electron and atomic force microscopies. The transport properties of obtained mixed matrix membranes were evaluated in pervaporation dehydration of isopropanol in a wide concentration range.

It was shown that modification of SA membranes by fullerene derivative with arginine nanoparticles led to the improvement of the transport characteristics due to significant changes in structure, morphology and surface properties.

Acknowledgments. This work was supported by Russian Science Foundation [project No 19-73-00105]. The experimental work was facilitated by equipment from the Resource Centers for Nanotechnology, Magnetic Resonance, X-ray Diffraction Studies, Thermogravimetric and Calorimetric Research Centre, Chemical Analysis and Materials Research Centre, Cryogenic Department and Centre “Nanofabrication of Photoactive Materials (Nanophotonics)” at St. Petersburg State University.

Usage of choline chloride based deep eutectic solvents for separation of azeotropic mixtures

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Nowadays chemistry tries to solve actual environmental problems. Particularly, there is a certain request for an emission of different volatile compounds reduction, creating new sustainable methods of water purification and energy production. In all these cases scientists can reach the solution using deep eutectic solvents too [1]. Deep eutectic solvents (DESs) are mixtures based on donor and acceptor of hydrogen bond. Such interactions cause the much lower melting point of DES comparing with the individual components. In fact, DESs represent a new wide-spreading kind of solvents, it made mostly from quaternary ammonium salts (especially choline chloride) and different HBDs likewise glycerol, urea and ethylene glycol. Fortunately, developing in this field of searching variety of components state the possibility to construct relevant solvent in exact conditions.

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 – ethylene glycol deep eutectic solvent. 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.

Acknowledgments. This study was supported by the Russian Science Foundation (project no. 19-73-00092). The experimental work was facilitated by the equipment of Magnetic Resonance Research Centre at St. Petersburg State University. Authors are grateful for support for Committee for Science and Higher Education of the Government of St. Petersburg.

References

1. C. Florindo, F. Lima, B.D. Ribeiro, I.M. Marrucho // Curr. Opin. Green Sustain. Chem., v. 18, p. 31-36, (2019).

Application of glow discharge time-of-flight mass spectrometry with combined hollow cathode cell for depth profiling

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With the development of materials science and engineering tasks, there is a high demand for direct and sensitive quantification and depth profiling of a wide range of elements in varied solids. There are a variety of different methods suitable for this task [1]. Nevertheless, with gradual progress in material sciences, lower limits of detection are required for reliable profiling of dopants and impurities in thin films, for example, in photovoltaics. The aim of the current study was to investigate the capabilities of glow discharge time-of-flight mass spectrometry with combined hollow cathode cell for depth profiling with special attention to the alteration of depth resolution during the sputtering and the effect of discharge parameters on the crater shape for different solid samples.

Various thin film and multilayer coatings with different conductivities of the layers and supports were considered for the cause. Fragments of silicon wafers were used for the optimisation to obtain a flat-floored crater shape and acceptable level of intensity and sputtering rate.

In order to achieve the optimal sputtering levels, the effects of discharge pressure, voltage, pulse duration, and auxiliary cathode material on the crater shape and depth resolution were studied [2]. Optimised parameters were selected to obtain the best flat-bottom crater shapes. The crater shape was discovered to be affected, first of all, by the discharge cell pressure. The possibility to undertake depth analysis for multilayer semiconductor-dielectric and dielectric systems was also investigated. Several sample preparation strategies were considered. The prospect of quantitative profiling was demonstrated. High depth resolution was obtained for the coatings from several tens of nanometers to several micrometers.

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References

1. L. Lobo, B. Fernandez and R. Pereiro // J. Anal. At. Spectrom., 32, p.920–930 (2017).
2. A. Gubal, V. Chuchina, Y. Lyalkin, V. Mikhailovskii, V. Yakobson, N. Solovyev, A. Ganeev // J. Anal. At. Spectrom., 35(8), p.1587-1596 (2020).

Modified hydroxyapatite nanoparticles for a dispersive micro-solid phase extraction of tetracyclines

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Green sample preparation techniques play an important role in modern analytical chemistry. Natural materials become popular in chemical analysis due to their biocompatibility and environmental friendliness. Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (HAp) is among green and natural sorbents [1]. The crystalline structure of HAp and its surface atoms of calcium could potentially form complexes with chelating agent. It is known that tetracycline antibiotics are able to form complexes with different metal ions including Ca^{2+} [2], hence, tetracyclines could be selectively adsorbed on HAp. Such possibly has been applied for the determination of tetracyclines antibiotics in complex sample matrices.

A dispersive micro-solid phase extraction has been utilized to promote high masstransfer and increase extraction efficiency. The procedure includes adsorption of the analytes into the modified HAp nanoparticles at the alkaline medium followed by the elution with a formic acid and HPLC-UV determination (Fig. 1). Main parameters such as eluent type and its volume, time of adsorption and elution, as well as amount of the modified HAp nanoparticles have been optimized. Linear concentrations ranges were from 0.1 to 20 mg L^{-1} for oxytetracycline, tetracycline and chlortetracycline.

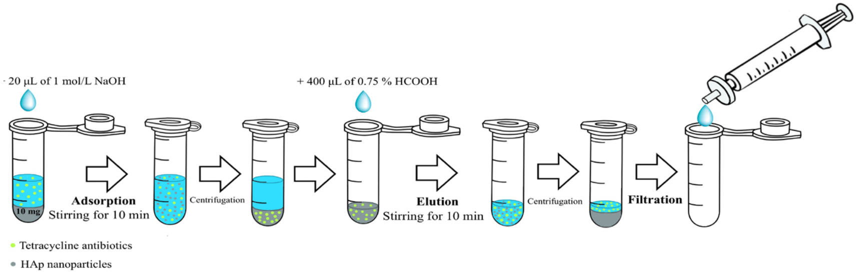

Fig. 1. Scheme of the experiment.

References

1. M. Ibrahim, M. Labaki, J.M. Giraudon, J.F. Lamonier // J. Hazard. Mater., v. 383, 121139 (2020).
2. M.O. Schmitt, S. Schneider // Phys. Chem. Comm., v. 9, p. 42 –55 (2000).

Synthesis and characterization of YVO_4:Ti, Ni particles

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Today, the production and study of materials with luminescent properties are gaining great popularity among scientists. One part of these materials has the ability to luminescence due to the presence of impurity ions in specific matrix, and one of the most promising matrices for these needs are metal oxides due to their stability of properties and chemical inertness. In this work, as the matrix was taken YVO_4, which also has own luminescence.

Ions of transition metals possess luminescence properties in IR region, such as characteristic absorption and emission bands. Doping of oxide matrix with by such ions will result in changing of matrix parameters such as cell volume and coherent scattering region, and the appearance of specific luminescent properties in the material.

In this work powders of YVO_4 doped with Ti and Ni were synthesized with using developed modified Pechini method [1]. The results of the X-ray diffraction analysis (XRD), morphology (SEM), absorption and luminescence spectroscopy were obtained and analysed.

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References

1. Medvedev V.A. et al. Synthesis and luminescence properties of YVO_4: Nd^{3+}, Er^{3+} and Tm^{3+} nanoparticles //Inorganic Chemistry Communications. – 2020. – T. 118. – C. 107990.

On application of artificial neural networks for the analysis of vapor-liquid equilibria in multicomponent systems

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Recently the development of the methods of thermodynamic modeling has allowed achieving the significant scientific results. These approaches include such models as NRTL, UNIFAC, PC CAFT and many others. These methods of thermodynamic modeling have proved to be particularly effective in evaluating and calculating phase equilibria, which are the scientific basis of separation process technologies. At the same time, the method of artificial neural networks (ANN), which is a new and independent tool for evaluating and calculating the parameters of complex systems, has been successfully used in recent years to solve a number of practical problems. Interest in the development of qualitatively new approaches has led to the appearance of a number of works related to the application of ANN for the calculation of phase equilibria, including the vapor-liquid equilibrium.

In our work, we studied the opportunities of using of ANN to describe vapor-liquid equilibria (VLE) data in the systems with different types of deviations from ideality. The objects of our research are ternary and binary subsystems of quaternary system ethanol- acetone-chloroform-hexane. The main problem with using ANN for VLE analysis is related to small volumes equilibrium data. It is known that the best results of the using ANN (in the case of such standard approaches as a multilayer perceptron) were obtained for very large data sets. To overcome these difficulties, we used the Focke method, which allows working with smaller data volumes. This approach was recently proposed in the paper [1]. Our results show that the accuracy of calculations depends significantly on the physical-chemical nature of the systems: with large deviations or complex intermolecular interaction, the calculation errors increase. Note also that ANN-based analysis and approximation, in contrast to thermodynamic models, being relatively simple, leave open the problem of physical validity of the results.

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References

1. I. Argatov, V. Kocherbitov. A note on artificial neural network modeling of vapor-liquid equilibrium in multicomponent mixtures // Fluid Phase Equilibria, 502 (2019), 112282.

UV-Vis Study of barbituric acid Knoevenagel condensation

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Barbituric acid has an active methylene group located at the C-5 position in molecule. This position is a reaction center and can be easily involved in condensation reactions with aldehydes or ketones that do not contain an α-hydrogen. This general type of reaction is known as the Knoevenagel condensation reaction [1].

Knoevenagel condensation in which an active methylene group in a molecule enters into condensation reactions with aldehydes or ketones, is an important and widely used method for the formation of carbon-carbon bonds in organic synthesis with numerous applications in the synthesis of carbocyclic and heterocyclic compounds of biological significance.

In the last years, different methods have been applied to demonstrate chemical kinetics in the lab. Among these methods, detecting chemical reaction kinetics in dilute aqueous solution using spectrophotometry is most used due to its safety and simplicity [2].

It was found that reaction between barbituric acid and vanillin as aldehyde type substance is reaction with color changing. Two colorless solutions of individual substances become bright yellow after mixing, and kinetic of the reaction is studied by UV-Vis spectrophotometry method. Characterization peak is observed on wavelength 404 nm, intensity of absorption increases in the first hour.

References

1. D. Neumann // University of New Orleans, P.132.(2004)
2. Zh. Dai, G. Flatberg, H. A. Preisig, L. Deng // J. of Laboratory Chemical Education, 6(5), p. 141-147 (2018).

The effect of subcritical and critical conditions of hydrothermal treatment on the phase formation and dispersity of $4Y_2O_3$-$96ZrO_2$ and $8Y_2O_3$-$92ZrO_2$ (mol.%) precursors

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The search for new materials for solid electrolyte is an important task for the development of SOFCs. One of the most promising materials for solid electrolytes in SOFCs are solid solutions based on ZrO_2 [1]. There are several ways of synthesis, but the hydrothermal method has a number of advantages for the oxydes synthesis, such as precise stoichiometry control of the resulting solid solutions, as well as the particle size distribution of the resulting oxides, their morphology and crystal structure [2].

The processes were investigated in the critical and subcritical conditions. Gels of stabilized zirconia were obtained by sol-gel synthesis method in the reverse co-precipitation variance and synthesis conditions were T = 1-2°C, pH = 9-10. Then, the initial solutions, freshly prepared gel and freeze-dried amorphous powders were subjected to hydrothermal synthesis in the temperature range 160-280 °C and, further, dried to constant weight at 110°C. Precursors obtained were comprehensively investigated using STA, XRD, SEM and PSD analysis.

It was found that hydrothermal synthesis from the initial solution results in the direct crystallization of needled shaped crystals of the baddeleyite phase. Precursors obtained from freshly prepared gel were found to be cubic phase. The beginning of crystallization in critical conditions is observed after hydrothermal treatment at 200 °C. Precursors from freeze-dried amorphous powders received in subcritical conditions up to 280 °C remain amorphous. The average agglomerate size in powders lies in the range of 0.97-1.36 μm.

References

1. Chen G. et al. Effect of A site deficiency of LSM cathode on the electrochemical performance of SOFCs with stabilized zirconia electrolyte // Ceramics International, 2017, V. 43, №. 1, pp. 1304-1309.
2. Zhu H. et al. Hydrothermal synthesis and characterization of zirconia nanocrystallites // Journal of the American Ceramic Society, 2007, V. 90, №. 4., pp. 1334-1338.

Molecular 2D-membrane for the exchange of cations from crystal structure

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Membranes are fundamental in many areas of science and technology, from water treatment to cell functions. At present work, we did a novel composite membranes, based on graphene oxide (GO) and polyanions. Membrane was characterized by atomic force microscopy (AFM), transmission electron microscopy (TEM), X-ray diffraction (XRD). Present membrane acts as cation sponge for cations, that's was also proved by quartz crystal microbalance (QCM). Premeability of water and ions were controlled by synergistic electrostatic effect that could be achieved due to interactions between the monolayers of polyelectrolytes and GO flakes.

We investigate the electrochemical behavior of membranes with a nickel hexacyanoferrate (NiHCF) to evaluate its potential. Electrochemical studies of the NiHCF covered by membrane showed comparable electrochemically switched ion exchange capability and selectivity for alkali cations with respect to NiHCF. Moreover, we found that the repeated potential cycling. The membrane showed electrochemically switched ion exchange capability for K and Li.

Acknowledgments. This work was carried out with the financial support of the Russian Science Foundation (RSF) (grant 19-19-00508).

References

1. S. Porada, A. Shrivastava, P. Bukowska, P.M. Biesheuvel, K.C. Smith // Electrochimica Acta, v. 255, p.369-378 (2017).
2. R.K. Joshi, P. Carbone, F.C. Wang, V.G. Kravets, Y. Su, I.V. Grigorieva, H.A. Wu, A.K. Geim, R.R. Nair // Science, v. 343, №6172, p.752-754 (2014).

Synthesis of rare-earth metal based luminescent metal-organic frameworks

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Luminescent materials are widely used in science, technology and medicine. Many compounds of rare earth metals have pronounced luminescent properties, however, due to the fact that f-f electronic transitions are characterized by low extinction coefficients, their direct excitation is often difficult. One of the solutions to this problem is the use of a sensitizer that efficiently absorbs light followed by energy transfer to the rare-earth metal ion and radiative transition to the ground state.

In this work we synthesized metal-organic frameworks based on mixed terephthalates of optically inactive gadolinium (III) and lutetium (III) with luminescent ions of europium (III) and terbium (III). Salts of terephthalic acid intensively absorb ultraviolet light promoting the terephthalate anion into a singlet excited state, which then undergoes to the triplet state by intersystem crossing due to the presence of a heavy ion of gadolinium (III) or lutetium (III). Excitation of europium (III) or terbium (III) ions occurs through energy transfer from the triplet state of the terephthalate anion to the f-f excited electronic state of these ions followed by luminescence.

The structure and luminescent properties were studied using photoluminescence spectroscopy, XRD powder diffraction, X-ray energy dispersive spectroscopy (EDX), and IR spectroscopy. The analysis of EDX spectra showed that the ratios of rare earth elements correspond to initial concentrations of their chlorides taken for the synthesis. The X-ray diffraction analysis demonstrated that Eu-Gd and Tb-Gd mixed terephthalates (1,4-bdc) are isostructural to $Tb_2(1,4\text{-bdc})_3{\cdot}4H_2O$, whereas Eu-Lu and Tb-Lu mixed terephthalates are isostructural to $Tb_2(1,4\text{-bdc})_3{\cdot}4H_2O$ only at low concentration of lutetium (III), and new crystalline phase is formed at high concentration of lutetium (III). Upon 280-nm excitation, luminescence spectra of all samples containing Eu^{3+} and Tb^{3+} contained pronounced bands of Eu^{3+} and Tb^{3+} radiative transitions.

O_2-induced segregation as an efficient tool for fine-tuning the intermetallic Pd-In/HOPG surface structure

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Bimetallic catalysts often demonstrate improved catalytic selectivity, activity and stability in comparison with monometallic ones. The formation of the specific surface composition of bimetallic particles plays a crucial role in the synergistic effects. The chemical composition and structure of active sites are determined at the preparation step. However, it can be deliberately modified by specific treatment of the surface sample in the reactive gas atmosphere for fine surface composition tuning and consequent optimization of catalytic properties in low temperature reactions [1, 2].

Model bimetallic Pd-In/HOPG catalysts with size-selected particles and different metal atomic ratios have been prepared using the successive thermal vacuum metal deposition. Intermetallic Pd-In nanoparticles formation and their post-synthesis transformation upon oxidative treatments have been investigated by the combination of synchrotron radiation-based X-ray photoelectron spectroscopy and scanning tunneling microscopy. It was shown that the reversible RedOx transformation $\text{Pd-In}_{\text{intermet}} \leftrightarrow \text{Pd}^{\circ} + \text{InO}_x$ can be efficiently used to deliberately tune the nanoparticles surface composition/structure and respective catalytic characteristics.

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References

1. I.S. Mashkovsky, N.S. Smirnova, P.V. Markov, G.N. Baeva, G.O. Bragina, A.V. Bukhtiyarov, I.P. Prosvirin, A.Yu. Stakheev // Mendeleev Commun., 28, 603-605 (2018).
2. P.V. Markov, A.V. Bukhtiyarov, I.S. Mashkovsky, N.S. Smirnova, I.P. Prosvirin, Z.S. Vinokurov, M.A. Panafidin, G.N. Baeva, Y.V. Zubavichus, V.I. Bukhtiyarov, A.Yu. Stakheev // Kinet. Catal., 60, 842-850 (2019).

Composition and thermal stability of acetonitrile and pyridine complexes with oxo- and thiophosphoni-um Lewis acids

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Recently, the development of "metal-free" catalysts has attracted considerable attention, and therefore Lewis acids based on main group elements are of particular interest. Since phosphonium Lewis acids exhibit catalytic activity in hydrodefluorination of fluoroalkanes [1] and, as part of FLP, in the hydrogenation of olefins [2], a study of tricoordinated complexes of oxo- and thiophosphonium Lewis acids (Fig. 1) with various donors is of a particular interest.

In this work, using a tensimetry method [3], the 1:1 composition and the thermal stability up to 500 K of the complex of oxophosphonium Lewis acid with pyridine was estabtished. Measurements indicated the absence of complexation of oxo- and thiophosphonium Lewis acids with acetonitrile; the desolvation enthalpies for solvates of oxo- and thiophosphonium acids with acetonitrile were determined.

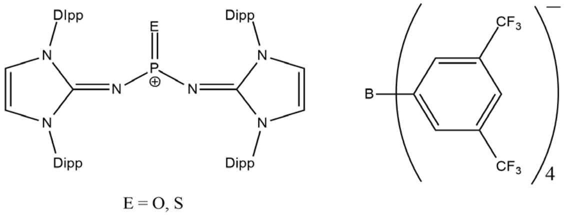

Fig. 1. Chemical formula of oxophosphonium (E = O) and thiophosphonium (E = S) Lewis acids.

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References

1. C.B. Caputo, L.J. Hounjet, R. Dobrovetsky, D.W. Stephan //Science 2013, 341, 1374. DOI: 10.1126/science.1241764.
2. T. vom Stein, M. Pérez, R. Dobrovetsky, D. Winkelhaus, C.B. Caputo, D.W. Stephan //Angew. Chem. Int. Ed. 2015, 54, 10178-10182. DOI: 10.1002/anie.201504109.
3. E.I. Davydova, D.A. Doinikov, I.V. Kazakov, I.S. Krasnova, T.N. Sevastianova, A.V. Suvorov, A.Y. Timoshkin //Russ. J. Gen. Chem., 2019, 6, 843–859. DOI:10.1134/s0044460x1906004x.

Ion-selective carbon fiber electrodes based on polyelectrolyte for early diagnosis of urolithiasis

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Urolithiasis is one of the relevant problems of modern medicine due to the prevalence, features of development and a current. For the last decades increase in frequency of this disease associated with an increase impact of a number of adverse environmental factors on a human body. Given the above, it is necessary to develop an express and accurate method for diagnosing the early stages of urolithiasis.

It is known that ion-selective electrodes based on polymer membranes have found widespread applications in a variety of fields, especially in the area of clinical diagnostics [1].

This research is aimed on the development simple and cost-effective sensors for monitoring selected parameters in urine. We propose the use of ion-selective electrodes based on carbon fiber with immobilized polyelectrolyte layers as a transition layer in the form of an internal solution. The use of carbon fiber is justified by its low cost, availability and the possibility of using for measurement in microvolumes of the samples. Ion-selective membranes with the addition of conducting polymers provide high selectivity and good signal stability [2, 3].

Ion-selective carbon fiber electrodes based on polyelectrolyte were developed selective to potassium ions, sodium, calcium and hydrogen (pH) and tested in model solutions. In the future, the developed electrodes will be used in biological fluids to determine the main parameters reflecting changes in the composition of urine.

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References

1. E. Bakker, P. BuÈhlmann, E. Pretsch // J. Electroanalysis 11, No. 13, p. 915-933 (1999).
2. H.-R. Lim, Y.-S. Kim, S. Kwon, M. Mahmood, Y.-T. Kwon, Y. Lee, S. Lee, W.-H. Yeo // Sensors 2020, 20, 3297.
3. J.E. Zachara, R. Toczyłowska, R. Pokrop, M. Zagórska, A. Dybko, W. Wróblewski // Sensors and Actuators B 101 (2004) 207–212.

Peptides that bind vascular endothelial growth factor

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To the date, antibodies and soluble receptors are widely used in ophthalmology for the treatment of the age-related macular degeneration (AMD), which is a growing health problem worldwide and the major cause of visual impairment in industrialized countries. They act by blocking the interaction between the receptors and their ligand VEGF (vascular endothelial growth factor). Therefore, the design of small VEGF inhibitory peptides may represent a turning point in the development of new drugs that can be used for anti-angiogenic therapies, such as in the case of the treatment of tumors and ocular diseases such as AMD [1].

Peptides, compared with other small molecules, show very high activity and selectivity, no accumulation in organism and low toxicity, and represent very promising class of pharmaceuticals. Peptides and proteins, in particular, monoclonal antibodies, are successfully used for the treatment of various diseases [2-3].

The aim of this work is the synthesis of anti-VEGF peptides. Using the phage display technique, libraries of peptides were built, which were then tested to evaluate their activity against VEGF.

References

1. Avery R.L., Pieramici D.J., Rabena M.D., Castellarin A.A., Giust M.J. // Ophthalmology, 113 (3), 363-372 (2006).
2. Sabatino G., Guryanov I., Rombecchi A., Zanon J., Ricci A., Cabri W., Papini A.M., Rovero P. // Expert Opin. Ther. Pat., 26, 485-495 (2016).
3. Chames P., Van Regenmortel M., Weiss E., Baty D. Br. J. // Pharmacol., 157, 220-233 (2009).

Determination of trace elements in human hair samples by optical emission spectrometry with inductively coupled plasma

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Chemical elements play an important role in the human body [1]. By monitoring the trace element composition, it is possible to assess the general condition of the body, as well as to identify a number of diseases. For biomonitoring purposes, various samples are used, among which hair has a number of advantages: it can be easily collected, transported, and stored for a long time [2].

The aim of this work is to select the optimal method for sample preparation (digestion) of human hair samples, which allows for the subsequent determination of a wide range of elements in mineralizates by optical emission spectrometry with inductively coupled plasma (OES-ICP).

Before analysis, hair samples were crushed and cleaned, then subjected to acidic, incl. microwave mineralization, and dry ashing. The OES-ICP method (spectral device Shimadzu ICPE-9000) was used to determine the content of trace elements. The concentration was determined using calibration curves constructed using a standard multielement solution CertiPUR IV.

In this study various schemes of digestion were tested: acid decomposition with nitric acid and a mixture of nitric acid and hydrogen peroxide, microwave decomposition, dry ashing followed by dissolution of the residue in acid solutions. From the studied methods, the optimal one was selected, which allows determining a large number of elements with minimal time, resource and labor costs. This scheme was used to determine the content of trace elements in hair samples, the results obtained were compared with the literature data.

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References

1. Orlov D.S. (1998). Trace elements in soils and living organisms // Soros Educational Journal, (1), 61-68.
2. Skalnaya M.G., Demidov V.A., Skalny A.V. (2007). The relationship between body mass index and the content of chemical elements in hair in women of childbearing age. Trace elements in medicine, 8 (1), 5-8.

Visible light activated photocatalysts based on Co-doped SnO_2 nanoparticles for organic dyes and antibiotics degradation

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The aim of this research was the study of the possibility to provide a photodegradation process of cyclic organic pollutants, such as dyes and antibiotics under visible light irradiation, using doped wide band gap semiconductor nanoparticles with different morphology. To clarify this aspect, we synthesized Co-doped SnO_2 nanospheres and nanorods by precipitation and hydrothermal methods, respectively, with dopant concentration 11 mol% and 33 mol%. The influence of crystallite size (regulation is achieved due to the induction of slow and fast processes of NP formation) on photocatalytic activity is also under discussion.

As expected, XRD data demonstrated rutile SnO_2 peaks only (PDF 01-072-1147), the crystallite sizes varying from 1.6 to 2.3 nm depending on the synthesis conditions. According to TEM and SSA data, the nanosphere diameter do not exceed 4 nm and nanorod thickness is about 4 nm. XPS data confirms the valence state of Co and Sn atoms. In addition, the concentration of structural defects and oxygen vacancies was determined using Raman spectroscopy and XPS, respectively. The band gap values were determined by UV-adsorption spectra. The band structure of the as-prepared NPs was calculated using quantum-mechanical approach. The photocatalytic activity of the samples was tested using colored methylene blue (MB), non-colored tetracyclines (TC) and visible light source with predefined different emission spectra (683 nm, 1.8 eV). The "dark" adsorption of organic molecules on the surface of the samples has been studied. It has been established that photocatalytic properties depend on the structure of nanoparticles; in this case, for an optimal Co-doped sample 33 mol% HTS, 80% degradation of TC was achieved after 30 minutes using visible radiation, while for Co-doped sample 11 mol% HTS, 90% degradation of MB was achieved after 60 minutes.

Based on the results we assume that organic pollutant degradation process is going through several stages including coordination on the surface of the photocatalyst.

Acknowledgments. The authors are thankful for the financial support provided by the RFBR (no. 20-03-00762 A). Scientific research was performed using the equipment of the Research Park of St. Petersburg State University (Centre for X-ray Diffraction Studies, Chemical Analysis and Materials Research Centre, Centre for Physical Methods of Surface Investigation, Centre for Optical and Laser Materials Research, Interdisciplinary Resource Centre for Nanotechnology).

Palladium(II) and platinum(II)-mediated coupling of mercaptoazoles with coordinated isocyanides

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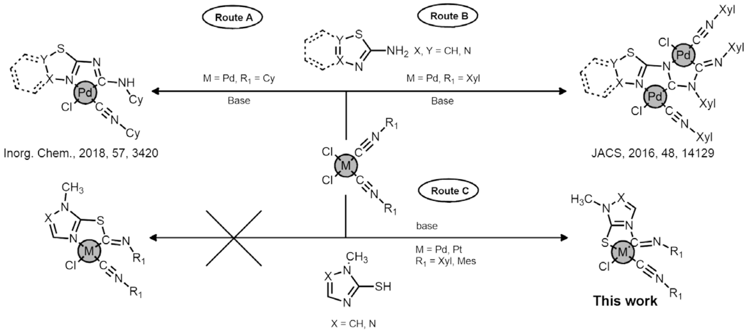
In recent decades, transition metal complexes with aminocarbene ligands have taken a special place in coordination chemistry due to their wide application in catalysis, material design and medical chemistry. One of the promising methods for generating of complexes with various types of aminocarbene ligands is metal-mediated addition of nucleophiles to coordinated isocyanides.

Recently in our research group, it was found that the reaction of Pd^{II} isocyanide complexes with ambident nucleophiles such as aminazoles leads to mono- and binuclear *C,N*-chelate carbene complexes (Scheme 1, Route A, B) [1, 2]. In the present work, we have studied the coupling of *bis*(xylil- and mesitylisocyanide) Pd^{II} and Pt^{II} complex with the another type of nucleophile – mercaptoazole (Scheme 1, Route C) leading to *C,S*-chelate carbene complexes which do not undergo to the formation of binuclear products.



Scheme 1. Coupling of bis(cyclohexyl-, xylil- and mesitylisocyanide) Pd^{II} and Pt^{II} complex with amino- and mercaptoazoles.

Acknowledgments. This work was supported by the Russian Foundation for Basic Research (grant 19-13-00008 mol_a). Physicochemical studies were carried out at the resource centers of St. Petersburg State University "Magnetic resonance imaging methods", "X-ray diffraction research methods" and "Methods for analyzing the composition of the substance."

References

1. Mikherdov A.S. et al. //J. Am. Chem. Soc. 2016. V. 138. N. 42. P. 14129.
2. Mikherdov A.S. et al. //Inorg. Chem. 2018. V. 57. N. 11. P. 6722.

Synthesis of isoxazole-based S-ylides

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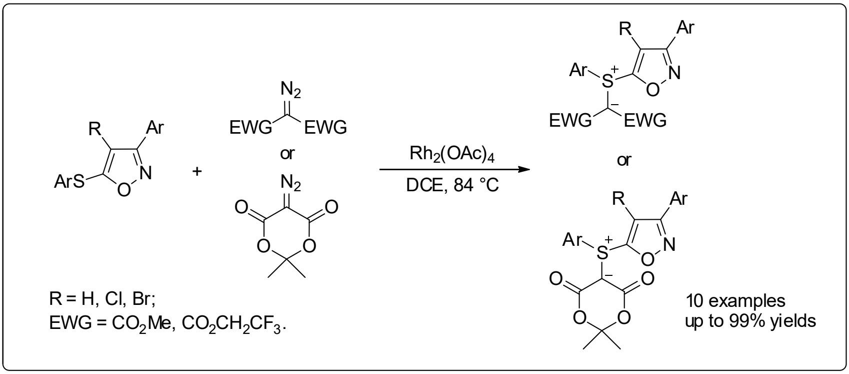
Sulfur ylides are organosulfur zwitterionic compounds, where the positive charge is localized on the sulfur atom and the negative charge is localized on the nearest carbon atom. In our current study, we have synthesised a new type of sulfur ylides based on the isoxazole frameworks. These compounds can be obtained in the reaction of 5-(arylthio)isoxazoles [1] with acyclic or cyclic diazo compounds in the presence of $Rh_2(OAc)_4$ as an effective catalyst. Such an approach allows introducing a wide range of aryl substitutes in the isoxazole framework.



The next step of the investigation will consist of the searching useful synthetic transformations of the ylides.

Acknowledgments. This work was supported by the Russian Science Foundation (project № 20-13-00044). This research used recourses of the Magnetic Resonance Research Centre, Chemical Analysis and Materials Research Centre, Centre for X-ray Diffraction Studies of St. Petersburg State University.

References

1. N.V. Rostovskii, A.V. Agafonova, I.A. Smetanin, M.S. Novikov, A.F. Khlebnikov, J.O. Ruvinskaya, G.L. Starova // Synthesis, v. 49., p. 4478–4488 (2017).

The using of *N*-aminoalkyl derivatives of thiazepinone dioxides in the HIRE reaction

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Compounds based on medium-sized (8-12 membered) cyclic scaffolds have a great potential in drug discovery [1]. Unfortunately, they are poorly represented in modern screening libraries due to the lack of efficient methods for their synthesis [2].

Previously, we reported a novel synthetic methodology for the assembly of medium-sized cyclic scaffolds. It is based on a ring expansion strategy involving the expansion of thi(ox)azepinone-fused hydrated imidazoline (HIRE) [3].

In this study, we developed an effective method for increasing N-aminoalkyl derivatives of thiazepinones reactivity. This approach is based on the oxidation of the sulfide group to sulfone, which promotes the stabilization of the leaving group. In this way, we have synthesized medium-sized cycles, which were previously unobtainable by HIRE methodology. Furthermore, the comparative study of conversion rates in HIRE reaction of oxidized and non-oxidized forms of substrates was performed.

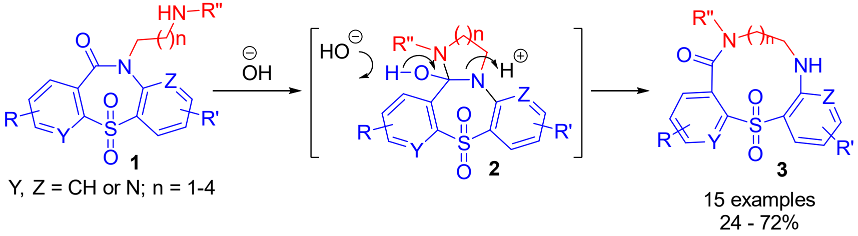

Fig. 1. HIRE reaction of N-aminoalkyl derivatives of thiazepinone dioxides.

Acknowledgments. This research was supported by the Russian Foundation for Basic Research (RFBR) (Project Grant 19-33-90010).

References

1. T. Rezai et al. // J.Am. Chem. Soc., vol.128, p. 2510 (2006).
2. F. Kopp et al. // Nat. Chem. Bio., vol. 8, p. 358 (2012).
3. E. Reutskaya et al. // J. Org. Chem., vol. 84, p. 1693-1705 (2019).

Research of innovative membrane material modified with layered perovskites for the isolation of valuable products from aqueous and organic mixtures

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Polymer membranes have drawn considerable research attention in the field of membrane separation methods due to their high stability and low cost. Considering the advantages of polymer membranes, the inclusion of inorganic nanoparticles in a polymer matrix may be an interesting solution for the development of membranes with improved operational and transport properties.

The main aim was comprehensive research of membranes with the addition of perovskite-like layered oxides in polymer matrix. Particular attention was paid to the study structures of hybrid membranes by SEM and AFM methods, which revealed various compositions of the upper and lower surfaces of perovskite-containing membranes. The effect of inorganic modifiers on thermal properties, surface hydrophilicity and film density was evaluated.

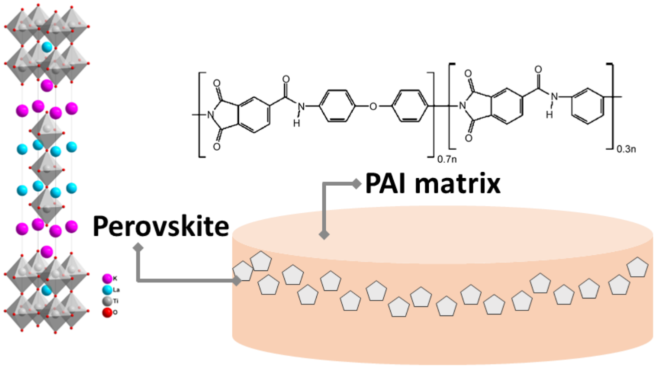

Fig. 1. Scheme of the composite membrane.

Among the processes of membrane separation, pervaporation is an efficient way of separating liquid mixtures, especially in the case of close-boiling and azeotropic ones since it allows to reduce the need for energy and additional components. Transport behavior and separation properties were investigated in the pervaporation process of water/organic separation.

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Study of the influence of cation-exchanger type on the sensitivity of potentiometric sensors to lanthanides

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The advantages of potentiometric sensors are their ease of production, affordable price and simple measuring procedure. One of the fields where such sensors are being actively developed now is a technological analysis in spent nuclear fuel (SNF) reprocessing. It was already demonstrated that potentiometric sensor arrays can be applied for process control in this challenging media [1], however, the development of novel sensors with controlled sensitivity patterns is needed for such arrays. One of the important components of plasticized sensor membranes is an ion-exchanger, which suppresses a counter-ion penetration into the sensor membrane, facilitates the ion exchange, decrease electrical resistance of the membrane and can stabilize the binding of target ion by ionophore [2]. Typically the following ion-exchangers are employed to construct the sensors for SNF analysis: tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), and chlorinated cobalt dicarbollide (CCD). In extraction it was shown that CCD allows in some cases to achieve a non-additive increase of lanthanides extraction – so called synergistic effect [3]. In the field of potentiometric sensors with plasticized sensor membranes, the presence of such effects has not yet been confirmed. In addition, there has been no study of the effect of the cation-exchange additive type on the sensitivity of sensors to lanthanide ions so far. The purpose of this study was to fill this gap. The results of lanthanide sensitivity comparison for CCD and NaTFPB based sensors will be presented.

References

1. M. Agafonova-Moroz, J. Savosina, Y. Voroshilov, S. Lukin, A. Lumpov, V. Babain, E. Oleneva, A. Legin, D. Kirsanov // Journal of Radioanalytical and Nuclear Chemistry (2020) 323:605–612.
2. P. Bühlmann, E. Pretsch, E. Bakker // Chem. Rev. (1998) 98, 1593.
3. M.Y. Alyapyshev, V.A. Babain, I.V. Smirnov, Extractive properties of synergistic mixtures of dipicolinic acid diamides and chlorinated cobalt dicarbollide // Radiochemistry, (2004) 46, 3, 270–271.

Regulation of HAp nanoparticles morphology and thermal properties using surfactant assistant hydrothermal process

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The latest market trends of multifunctional cosmetics popularity growth boost a request for a new material design. Multifunctional cosmetics possess a combination of decorative function, for example, bright color, and additional properties, such as skin care effect. As a white basis for multifunctional materials biocompatible nanoparticles (NPs) can be considered. Today, the range of these proper materials is extremely low, as they should also provide a number of properties, such as biodegradation and biocompatibility. We suppose, that hydroxyapatite (HAp), the main component of bone tissue, appears to be a promising substance.

The functional properties of NPs are affected by their morphological parameters, which, in their turn, depend on synthesis conditions. One of the approaches to control the morphology, as well as to modify the surface, is the addition of surfactants in the reaction mixture. However, to the best of our knowledge, it remains unclear, how surfactants affect NPs morphological parameters and how the latter change NPs functional properties, in particular thermal properties.

In this work, HAp nanoparticles were synthesized by a scalable hydrothermal method at two temperatures (180°C and 240°C) and a significantly lower holding time (2h), than was previously described in the literature. Non-capped and non-ionic (PVP) and anionic (STRN, SDS) surfactant capped NPs were obtained. The morphological parameters of all the samples were characterized by XRD, TEM, SSA, FTIR methods and DFT calculations. In the case of non-capped samples aspect ratio was 2 and 3 for lower and higher temperatures, respectively, and for capped NPs it varied from 3 to 5.5 for different surfactants.

The surfactant impact on NPs formation process at all the stages – from the unit cell to crystallite size and nanoparticle sizes and shape - was shown, and the key roles of HLB values on surfactant molecule size and NPs morphology regulation was demonstrated. TGA-DSC data show that surfactant surface layer prevents NPs sintering and shifts the decomposition temperature to higher values. In addition, it was established for the first time that for HAp NPs thermal stability depends not on the NPs sizes, but on crystallite size and whether the NPs are mono or polycrystalline.

Acknowledgments. Scientific research was performed in the research park of St. Petersburg State University educational resource center of chemistry: Centre for X-ray Diffraction Studies, Centre for Innovative Technologies of Composite Nanomaterials, Chemical Analysis and Materials Research Centre.

Synthesis of Azirine-containing Dipeptides and Depsipeptides by Multicomponent reactions of Azirine-2-carboxylic acids

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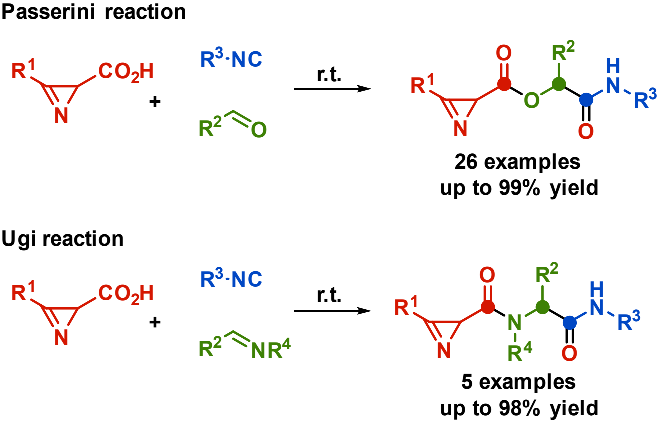
2*H*-Azirines are the smallest unsaturated nitrogen heterocycles. Most importantly, some of the azirine derivatives are bioactive, for example, azirinomycin, motualevic acid F, and other azirine-2-carboxylic acids. Additionally, azirines are widely used in organic synthesis due to the high reactivity of the strained three-membered ring, especially for the synthesis of various heterocycles. Taking into account the biological potential of azirine derivatives indicated above and their significance in synthesis, access to more complex biologically compatible functionalized azirines is of great importance.

In this work, we focused on the synthesis of azirine-containing dipeptides and depsipeptides using the Passerini and Ugi reactions (Fig. 1). A wide range of the desired azirine-containing molecules has been synthesized in good yields at room temperature. In some cases, the product yields in above multicomponent reactions were quantitative. Further transformations and antibacterial activity of azirine-containing dipeptides and depsipeptides were also studied.


Passerini reaction

Ugi reaction

Fig. 1. Passerini and Ugi reactions of azirine-2-carboxylic acids.

Acknowledgments. We gratefully acknowledge the financial support of the Scientific Council of the President of the Russian Federation (MK-2698.2019.3). This research used resources of the Magnetic Resonance Research Centre, Chemical Analysis and Materials Research Centre of the Research Park of St. Petersburg State University.

Exploring the possibility of using commercial Ca^{2+} ionophores as the ligands for lantanide sensors

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Developing chemical sensors with pronounced sensitivity towards lanthanides and actinides is a very important task related to analytical control of spent nuclear fuel (SNF) reprocessing. The ligands typically employed for construction of such sensors are mainly adopted from liquid extraction, where different extracting agents were suggested for separation of lanthanides and actinides. Various diamides of organic acids were shown to be very effective for such applications [1], and they were also successfully applied for construction of potentiometric sensors with plasticized sensor membranes yielding high sensitivity towards typical SNF components [2]. The chemical structures of some of these diamides are very similar to those suggested in 80's as Ca^{2+} ionophores, that were subsequently commercialized by Fluka company (now a part of Merck corporation). We have hypothesized that calcium ionophores II and IV can provide noticeable potentiometric sensitivity towards lanthanides due to these structural similarities.

In order to confirm this hypothesis we have prepared a series of PVC-plasticized sensor membranes containing Ca-II and Ca-IV commercial ionophores in combination with two cation-exchangers: chlorinated cobalt dicarbollide and tetrakis[3,5-bis(trifluoromethyl)phenyl]borate. The content of ligand was set at 50 mmol/kg and the content of cation-exchanger was 10 mmol/kg. The membranes were plasticized with *o*-nitrophenyl octyl ether. We have studied the potentiometric sensitivity of these membranes towards a broad variety of metal ions in the concentration range $10^{-7} – 10^{-3}$ mol/L. It was found that commercial Ca-ionophores indeed yield pronounced sensitivities to lanthanides. The particular values depend on a ligand, a cation-exchanger and metal ion. The details will be provided in the presentation.

References

1. M. Alyapyshev et al. 1,10-Phenanthroline-2,9-dicarboxamides as ligands for separation and sensing of hazardous metals // RSC Adv., vol. 6, no. 73, pp. 68642–68652 (2016).
2. E. Oleneva, J. Savosina, M. Agafonova-Moroz, A. Lumpov, V. Babain, I. Jahatspanian, A. Legin, D. Kirsanov // Sensors & Actuators: B. Chemical 288, 2019, 155–162 (2019).

Precipitation of biomimetic hydroxyapatite in the presence of amino acids

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Nature is known to create various patterns to achieve the re-quired material properties. Nature's ability to manipulate the structure of calcium phosphate is important for design of biomimetic materials [1, 2].

Understanding the process of calcium phosphate precipitation is of great interest for various fields of science. Phosphates are formed in the presence of various dextrorotatory or levorotatory α-aminoacids, enzymes and hormones in living organisms. Due to the fact that α-aminoacids contribute to the formation of bone tissue, it is possible to predict what structures are obtained by studying bone formation in the presence of α-aminoacids. Accordingly, the study of these processes helps to develop the techniques to obtain and to design of these structures [2, 3]. Thus, studying the process of the periodic pattern formation in the presence of alpha-amino acids is an actual task.

The aim of our research is to develop a model system to study the hydroxyapatite formation in biopolymer matrix in the presence of α-amino acids.In this work, we analyze the effect of different amino acids (glutamic -acid, L-cysteine, L-ascorbic acid, and D- and L-tyrosine) on the calcium phosphate precipitation under diffusion limited aggregation. The α-aminoacids were used at different concentrations in a range of $10^{-2} \div 10^{-8}$mol/L. Different analytical approaches have been used to characterize precipitations.

The obtained results could be used for the fabrication new biomimetic materials for bone regeneration medicine.

Acknowledgments. Authors acknowledge RSF grant no. 19-79-10244.

References

1. Li T., Song J., Zhao X. et al. Anisotropic, lightweight, strong, and super thermally insulating nanowood with naturally aligned nanocellulose // Sci.Adv., 4, eaar3724 (2018).
2. Jiang W., Pacella M.S., Vali H. et al. Chiral switching in biomineral suprastructures induced by homochiral l-amino acid. // Sci. Adv., 4, eaas9819 (2018).
3. Hood M.A., Landfester K., Muñoz-Espi R. The Role of Residue Acidity on the Stabilization of Vaterite by AminoAcids and Oligopeptides // Cryst. Growth. Des., 14, 1077–1085 (2014).

Synthesis and characterization of $CaWO_4$: Nd, Er and Tm particles

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Luminescence materials have a wide range of applications in contemporary world. Rare earth ions are most often used as effective luminescence centers. Embedding of these ions into different hosts (glass, ceramics, monocrystals, composite and nanomaterials) allows creation efficient materials for different applications: lasers, light-emitting diodes (LEDs), color displays, lighting devices, optical thermometry, biomarkers, sensors, solar panels, etc [1]. Despite the extensive database on optical properties of REI, new appearing scientific directions require a more detailed investigation of the luminescence properties of REI doped materials. Different tasks have been successfully solved by using complex optical systems containing several types of active ions in the structure.

In this work, triply doped $CaWO_4$:$Nd^{3+}/Er^{3+}/Tm^{3+}$ powder was synthesized by Pechini sol–gel method [2]. The structural properties of powders are studied by SEM, X-Ray diffraction and luminescent spectroscopy. Mutual effect of matrix and doping REI ions on the luminescence properties of $CaWO_4$:$Nd^{3+}/Er^{3+}/Tm^{3+}$ powder was demonstrated.

Acknowledgments. Authors are grateful to “Interdisciplinary Resource Centre for Nanotechnology”, Resource Center "Innovative technologies of composite nanomaterials”, “Thermogravimetric and Calorimetric Research Centre”, “Research Centre for X-ray Diffraction Studies” and “Centre for Optical and Laser Materials Research” of Saint-Petersburg State University Research Park. The research has been partially funded by the Russian Science Foundation № 20-79-00101.

References

1. A.N. Meza-Rocha, R. Lozada-Morales, A. Speghini, M. Bettinelli, U. Caldiño. White light generation in Tb3+/Eu3+/Dy3+ triply-doped Zn(PO3)2 glass // Opt. Mater. (Amst). (2016).
2. Pang, M. L. et al. Luminescent properties of rare-earth-doped CaWO4 phosphor films prepared by the Pechini sol–gel process // Journal of Physics: Condensed Matter 15.29 (2003): 5157.

SERS of diamino- and dimercaptostilbenes on gold bipyramidal nanoparticles hydrosol up to nanomolar concentrations

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Over the past two decades, the surface plasmon resonance (SPR) effect has been deeply studied theoretically and has found many practical applications. [1].

The present study is devoted to the development of methods for the synthesis and further modification of new SERS nano tags based on conjugates of gold nanoparticles with Raman reporters such as 4,4'-dimercaptostilbene (DMS) and 4,4'-diaminostulbene (DAS). We have implemented the so-called seed method, which made it possible to obtain nanoparticles of bipyramidal shape [2], which have a plasmon resonance peak in the spectral range 600-700 nm.

Investigation of Raman labels by the SERS method showed the appearance of a characteristic signal up to a concentration of 10^{-9} M in the hydrosol of bipyramidal gold nanoparticles. (Fig. 1). The dependence of the signal on the concentration is practically constant until the concentration of the modifier becomes less than the capacity of one monolayer. The results were reproduced thrice. Thus, we offer these conjugates as a novel strong optical signal SERS tags analytical chemistry and biotechnology purposes.

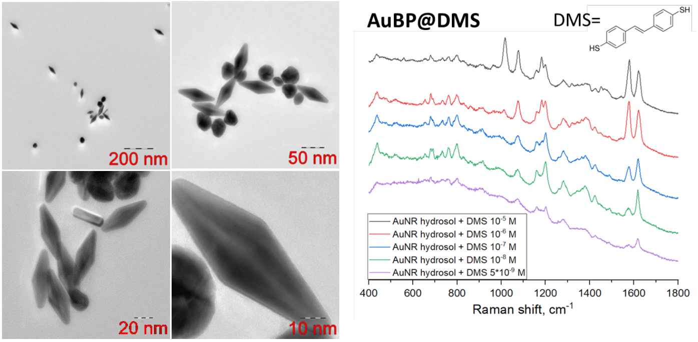

Fig. 1. TEM microphotographs of bipyramidal nanoparticles (left) and Raman spectra of different concentrations of DMS (right) in AuNB hydrosol.

Acknowledgments. The authors thank the Interdisciplinary Center for Nanotechnology and Magnetic Resonance Research Centre.This work was supported by SPbU - SUT Joint Program (ID Pure 60256182).

References

1. J. Langer et al. // ACS Nano. Am. Chem. Soc., 14, № 1. p. 28–117 (2019).
2. E. Le Ru et al. // Nano Lett. Am. Chem. Soc., 11. p. 5013–5019 (2011).

Relationship between polymorphism and non-covalent interactions in crystal structure of cyclometalated platinum(II) complexes with isocyanide ligands

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Supramolecular systems involving metal species are widely used in catalysis [1], molecular recognition [2] and other relevant areas. The modulation of photophysical properties is also possible by constructing supramolecular structures using non-covalent interactions (e.g., hydrogen bonding (HB), π–π-stacking etc.), which are applied for selective assembly of supramolecular structures [3]. The crystallization of a certain polymorph can be regarded as a supramolecular reaction involving formation of energetically suitable aggregates due to non-covalent intermolecular interactions [4].

For this study were synthesized isocyanide complexes [Pt(ppy)Cl(CNR)] (**2a-c**) (Hppy = 2-phenylpyridine, R = C_6H_4-4-Br (**a**), C_6H_3-4- I (**b**), C_6H_3-2-F-4-I (**c**), with 70–90% yields). Single crystal X-ray diffraction method shows that complexes **2a-c** crystallise in two different polymorphic forms aggregated in polymeric chains through weak interactions and halogen bonding (Fig. 1).

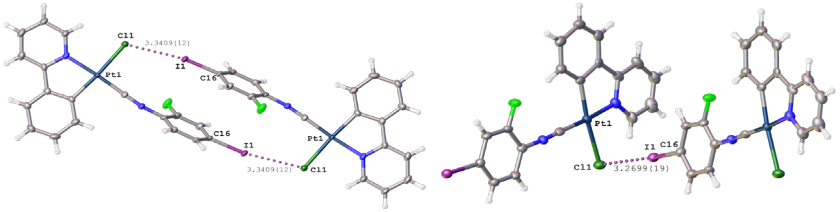

*Fig. 1. Halogen bonding in two polymorphic crystals **2c-K** (left panel) and **2c-Th** (right panel).*

Acknowledgments. These studies were funded by the President of Russian Federation (MK-1476.2019.3). Measurements were performed at the Centre for Magnetic Resonance, the Centre for X-ray Diffraction Studies, the Centre for Chemical Analysis and Materials Research, and the Chemistry Educational Centre (all belonging to Saint Petersburg State University).

References

1. D. Fiedler, R.G. Bergman, K.N. Raymond // Angew Chem Int Ed Engl – 2004 – 43(48) – p. 6748-51.
2. Langner A. et al. // Proc Natl Acad Sci U S A – 2007 – 104(46) – p. 17927-30.
3. Kashina M.V. et al. // Chem Asian J – 2019 – 14(21) – p. 3915-3920.
4. Santhiya K. et al. // J Org Chem – 2018 – 83(18) – p. 10770-10775.

Elemental analysis of fluorine-rich ionic conductors by pulsed glow discharge mass spectrometry

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Dopants in ionic conductors play a crucial role in achieving the required electrochemical properties of the developing crystalline material. A slight variation in their concentration considerably affects crystal conductivity and its applicability as ionic conductor or laser material. Recently, a group of fluorine-containing superconductors, with a general formula of $R_{1-x}M_xF_{3-x}$ (where R = La-Lu; M = Ca, Sr, Ba, etc.), has attracted a special attention since these may be widely used in various electrochemical setups and laser instrumentation [1]. To ensure the growth of high-quality fluoride crystals, adequate approaches for the quantification of matrix and admixture/dopant components are required.

For this purpose a panel of SrF_2- and GdF_3-doped LaF_3 single crystals was investigated. Pulsed glow discharge mass spectrometry (GDMS) was used to simultaneously quantify fluorine, strontium, lanthanum, and gadolinium in the crystals. The electrical conductivity of the crystals was measured using impedance spectroscopy in the frequency range 100 Hz-1 MHz to control for crystal quality. X-ray fluorescence, scanning electron microscopy-energy dispersive X-ray spectroscopy, and arc optical emission spectrometry were used for validation.

During the investigation quasi-periodic intensity drifts under sputtering of the ionic conductors were observed and attributed to F- redistribution on the sample surface, affecting surface conductivity and sputtering rate [2]. Several sample preparation protocols were tested to address that effect. Full coating of the sample with a layer of silver several micrometers thick provided stable and effective sputtering. The parameters for the GDMS determination of F, Sr, La, and Gd were optimised. The elements' distribution was studied in different parts of the crystals.

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References

1. S. Kitajima, K. Yamakado, A. Shirakawa, K.I. Ueda, Y. Ezura, H. Ishizawa // Opt Lett., 42(9), p. 1724-1727 (2018).
2. V. Chuchina, A. Gubal, Y. Lyalkin, O. Glumov, I. Trefilov, A. Sorokina, S. Savinov, N. Solovyev, A. Ganeev // Rapid Commun. Mass Spectrom., 34(11), e8786 (2020).

Electrochemical Determination of Encephalitis Virus Antigen Using Polyelectrolyte-based Screen-Printed Electrode

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Early and accurate diagnosis of viruses is critical to curbing its spread and improving health outcomes. Current methods used for detection of viruses demand on equipment and personnel, and, moreover, diagnosis of infection lasts hours to days. Given the above, finding methods for rapid, sensitive and selective detection of the virus in the environment, body fluids and tissues is still challenging [1].

With these considerations in mind, we are designing an electrochemical immunosensor system for the detection of Encephalitis virus antigen as a model system that can be performed with simple instruments.

Describes in this work system combines the advantages of optical ELISA and electrochemical methods. Compared with traditional optical immunoassays, electrochemical immunosensors are characterized by simplicity, speed, low cost, portable and easy to use instrumentation, greater possibilities of miniaturization and continuous monitoring in real-time, as well as usability for multiplexing.

Suitable immobilization of a biorecognition element, such as an antigen or antibody, on a transducer surface is essential for development of sensitive and analytically reliable immunosensors.

There are different strategies of antibody functionalization for specific, quantitative antigen detection. We hypothesized that polyelectrolyte multi-layers could be used to control the antibodies and antigens adsorption in each step of development electrochemical immunosensors, leading to improvements in the sensitivity of immunoassays. Also, polyelectrolytes hold significant advantages for the effective control of protein adsorption and cell adhesion [2].

In this study, it was found that polyelectrolytes effectively improved the sensitivity of the immunosensors, compared with an antibody-only modified electrode. The hydrophilic properties of polyelectrolytes not only suppressed nonspecific protein adsorption, decreasing the magnitude of the noise signal even in the absence of a blocking reagent adsorption step, but also increased primary antibody adsorption on the substrate, thus increasing the specific detection signal.

References

1. Krejcova L., Hynek D., Adam V., Hubalek J., Kizek R. //Int J Electrochem Sci, 7(11), 10779-10801 (2012).
2. Lai X., Gao G., Watanabe J., Liu H., Shen H. // Polymers, 9(2), 51. (2017).

Automated dispersive liquid-liquid microextraction as an efficient sample treatment technique for the HPLC-FL determination of PAHs in tea

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Polycyclic aromatic hydrocarbons (PAHs) are a large class of organic compounds, which consist of two or more condensed aromatic carbon rings. Being a food contaminant, some of them can be potentially genotoxic and carcinogenic to humans [1]. Therefore, the PAHs residue monitoring in foods and drinks is an important challenge of analytical chemistry.

Taking into account, that PAHs concentrations in foods and beverages are located at micro-levels, there are quite numerous various extraction and preconcentration techniques combined with different instrumental methods for their determination. The most simple and widely used extraction technique is the dispersive liquid-liquid microextraction (DLLME). In the current study, a novel automated DLLME approach for the HPLC-FL determination of PAHs was developed. A surfactant-based DLLME assumes the mixing of aqueous sample phase and homogeneous mixture of hexanoic acid and acetonitrile in a certain ratio in a syringe of flow system with following supramolecular solvent phase formation and rapid and simple PAHs extraction. The conditions of automated in-syringe surfactant-based DLLME and HPLC-FLD analysis have been investigated and optimized. A linear working ranges up to 0.05 – 50.00 $\mu g\ L^{-1}$ with limits of detection in the ranges of 0.02 – 0.04 $\mu g\ L^{-1}$ were found. The advantages of the proposed technique are the rapidity, simplicity and high sample throughput. The reported procedure has been successfully applied to the HPLC-FL determination of PAHs in tea.

References

1. EFSA – European Food Safety Authority. Polycyclic aromatic hydrocarbons in food, Scientific opinion of the panel on contaminants in the food chain // The EFSA J., v. 724, p. 1-114 (2008).

SERS of azamacrocycles adsorbed on silver and gold nanoparticles

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Crown ethers and their derivatives are well known to be great complexing agents for a wide range of metal cations. Their analogs, cyclenes - cyclic compounds with 4 and 6 nitrogen atoms form strong complexes with transition metals and, thus, can be used to determine the concentrations of various cations [1]. At the same time, they possess aza groups which means that they can potentially serve as molecular linkers of silver nanoparticles.

The purpose of this study was to determine the surface enhanced Raman scattering (SERS) response of cyclens adsorbed on the surface of silver and gold nanoparticles. The formation of dimers was detected, as evidenced by the appearance of an absorption peak in the long-wavelength region of visible spec-trum (Fig. 1). This correlates with the SERS studies, that showed significant signal amplification to the overlap of the electromagnetic fields of the nanopar-ticles in the dimers (so-called Hot Spots Effect).

The results of this study open up new opportunities for using cyclens to cre-ate ultrasensitive plasmonic nanosystems for analytical applications.

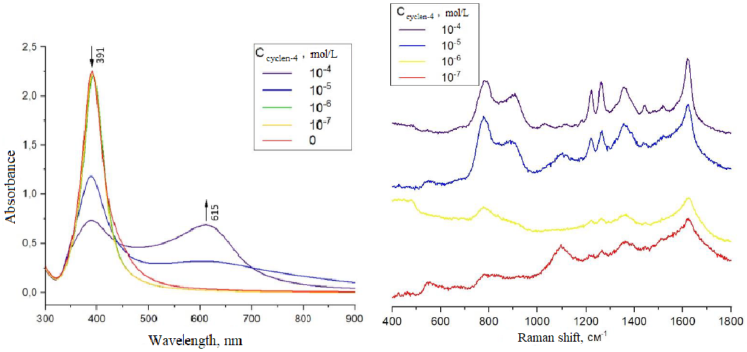

Fig. 1. UV-Vis spectra of cyclen-4 in Ag hydrosol (left). SERS spectra of cyclen-4 in Ag hydrosol (right).

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References

1. A. Bianchi et al. // Coord. Chem. Rev., 110, №. 1, p. 17–113 (1991).

Development of novel membranes based on polyphenylene isophtalamide modified by UiO-66(NH_2)-EDTA for highly efficient methanol isolation

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Membrane separation processes are widely used due to such advantages as environmental friendliness, the use of compact equipment and low energy consumption. The rapid development of membrane methods requires the search for new membrane materials and ways of its modification.

In the present work, the development of highly methanol-permeable pervaporation membranes based on poly-m-phenylene isophthalamide (PA) is achieved by two strategies: (i) modification of PA by novel synthesized and characterized highly stable metal-organic framework UiO-66(NH2)-EDTA particles and (ii) development of supported membranes with thin selective layer on the regenerated cellulose substrate.

The structural features of the membranes based on PA modified by Zr-MOF were studied by molecular dynamics simulation, nuclear magnetic resonance, FTIR, XRD, and SEM. Contact angle was using to study the surface properties of the membranes. The degree of swelling was study by the gravimetric method at 25°C. The transport properties of the developed membranes were studied in the separation of azeotropic 72 wt.% methanol /28 wt.% toluene mixture by pervaporation. It was found that the dense PA/UiO-66(NH2)-EDTA(15%) membrane had the optimal transport properties: 0.473 kg/(m2h) permeation flux, 95.8 wt.% methanol content in the permeate.

Acknowledgments. This work was supported by Russian Science Foundation [grant number 17-73-20060]. The experimental work was facilitated by equipment from the Interdisciplinary Resource Centre for Nanotechnology, Magnetic Resonance Research Centre, Thermogravimetric and Calorimetric Research Centre, Centre for X-ray Diffraction Studies, Chemical Analysis and Materials Research Centre, Nanophotonics Centre, Cryogenic department, Centre for Diagnostics of Functional Materials for Medicine, Pharmacology and Nanoelectronics, and Centre for Geo-Environmental Research and Modelling at St. Petersburg State University. The authors gratefully acknowledge A.V. Bildyukevich and T.V. Plisko for provided membrane samples from regenerated cellulose. Synthesis of MOF samples was performed in the laboratory "Photoactive nanocomposite materials" supported by SPbU.

Tetrachloroplatinate(II) as a promising square-planar halogen binding tecton for crystal engineering

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The construction of supramolecular aggregates based on halogen bonding (XB) are of considerable interest due to the fact that the synthesized systems exhibit a number of useful properties. A number of supramolecular XB tectons for the crystal engineering based on organic species and metal complexes were described earlier, however, squared-planar platinum(II) complexes are poorly studied in this way.

In our work, we showed that the $[PtCl_4]^{2-}$ anion is able to act as an XB-acceptor with a neutral XB donor in the $(PPN)_2[PtCl_4]\bullet(1,4\text{-}C_6F_4I_2)$ (PPN^+ is $Ph_3P{=}N{=}PPh_3{}^+$; $1,4\text{-}C_6F_4I_2$ is FIB) adduct, and in the salt $(Ph_3PCH_2I)_2[PtCl_4]$ with a cation, which also incorporates an XB donor center. X-ray diffraction (SC-XRD) data were obtained and analyzed for these substances. XB of C-I···I-Pt type was found in both structures base on the geometrical criteria. The existence of this bond was confirmed by appropriate theoretical calculations.

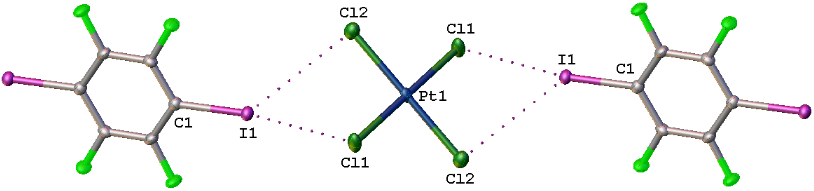

Fig. 1. Tetrachloroplatinate anion with a neutral XB donor.

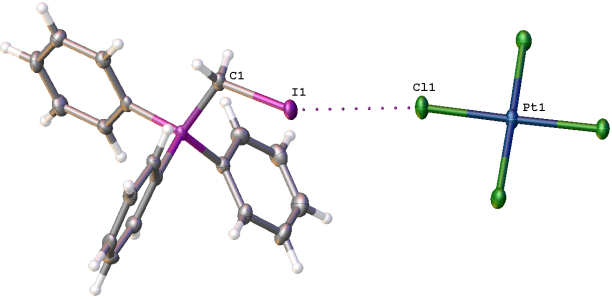

Fig.2. Tetrachloroplatinate anion with cationic XB donor.

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Microextraction of Cr (III) and Cr (VI) from water samples using quasi-hydrophobic deep eutectic solvent

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A sensitive, rapid and simple procedure for the determination of traces of chromium species in natural and waste waters after microextraction using quasi-hydrophobic deep eutectic solvent based on tetrabutylammonium bromide and hexanoic acid was developed. The total chromium concentration was determined after the oxidation of Cr (III) to Cr (VI) with potassium permanganate. In the developed procedure the precursors of deep eutectic solvent played a dual role. During the mixing aqueous phase and quasi-hydrophobic deep eutectic solvent dissolution of tetrabutylammonium bromide in aqueous phase took place. Tetrabutylammonium bromide acted as an agent for the formation of a compound with chromium (VI) in aqueous phase followed by its extraction in hexanoic acid. The organic phase containing chromium (VI) complexes was analyzed by atomic adsorption spectrometry with electrothermal atomization. The limit of detection calculated from a blank test, based on 3σ, was 5 ng L^{-1}.

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Determination of enantiomeric chemicals like as D- and L-tyrosines by using machine learning

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Natural amino acid based synthetic polymers have limited applicability as biomaterial due to several unfavorable material and engineering properties. L-amino acids are the more common in nature, and are the type found in proteins. D-amino acids are less common in nature, and are never found in proteins.

L-Tyrosine is a conditionally indispensable amino acid required for the production of the neurotransmitters dopamine, adrenaline, and noradrenaline, as well as for the skin pigment, melanin. Noradrenaline (norepinephrine) and adrenaline (epinephrine) are the main actors in the body's response to acute stress and, along with dopamine, help to support a positive mood and mental alertness. In addition, L-Tyrosine is especially critical for the normal function of the thyroid gland. On the other hand, D-tyrosine has been the precursor of many different anti-inflammatory [1]. Thus, a simple and reliable method for determining D- and L-tyrosines in pharmaceutical formulations is highly desirable as such, chiral resolution of enantiomers plays an important role in the pharmaceutical industry.

There are different ways of determination of enantiomeric chemicals D-, L-tyrosines. We hypothesized that machine learning could be shown proof-of-concept in the following can be applied for miniaturized test-systems with potential application in the field [2]. Machine learning method uses database and does not need calibration each time. Also, the method is fast, versatile, cheap, robust, and sustainable.

New simple and sensitive electrochemical method has been developed and validated for the determination of L-tyrosine and D-tyrosine in pharmaceutical formulations. This study describes that determining the qualified and quantified enantiomeric chemicals tyrosines based on the current-voltage data for the data processing using machine learning model, which results more admirable and usable in different areas of biomedical. Such machine learning system demonstrates a new approach for the identification and determination of tyrosines which is effective in pharmaceuticals.

References

1. Basheir B.E.A., Elbashir A.A. Spectrophotometric methods for the determination of L-tyrosine in pharmaceutical formulations // Chem Xpress, 8(2), 95-101. (2015).
2. Wang J. Analytical Electrochemistry // Hoboken. (2006).

Crystal growth control of melamine barbiturate through Ni (II) complex formation

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Amount of barbiturates is performed in previous years due to its biomedical activity [1]. Also, barbituric acid is supposed to form self-assemblies based on hydrogen bonds.

Melamine barbiturate as a supramolecular assembly has a host structure ability. The preparation of melamine barbiturate powder goes in aquas solution, then the precipitate is centrifuged and dried at room temperature. Melamine barbiturate exists as 8-pointed star aggregates with sharp edges that is confirmed by optical, fluorescence and scanning electron microscopy. The crystal formation depends on a chemical rate, and in case of solution it is complicated to control diffusion of compounds.

Barbituric acid easily involves in coordination complexes as a ligand because of deprotonated oxygen [2, 3]. Complex with Ni (II) is observed by potentiometric titration.

The one-stage synthesis of melamine barbiturate is proposed. Coordination complex with Ni (II) forms due to a mixing of compounds and slowly decomposes with barbituric acid release. The acid links to melamine with delay, so a low-defect crystal growth is observed as well as a size increase. There is also no insertion of Ni (II) in the crystal structure of melamine barbiturate.

References

1. J.A. Richter, J.R. Holtman Jr. //Progress in Neurobiology, 1982, 18, 4, 275.
2. Zh. Dai, G. Flatberg, H.A. Preisig, L. Deng // J. of Laboratory Chemical Education, 6(5), p. 141-147(2018).
3. N.M. Korotchenko, N.A. Skorik // Russian Journal of Inorganic Chemistry, vol. 45, no. 12, pp. 1945–1948, 2000.
4. Naciye T., Suat A.M. // International Journal of Analytical chemistry, 2014, 1-5.

Photochemical transformation of azidoacrylates into dihydropyrimidines and pyrimidines

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Vinyl azides are highly reactive compounds with great synthetic potential. The methods for preparation of indoles, 2*H*-azirines, pyrazines from vinyl azides have already been described [1]. However, only one example of preparation of pyrimidines from azidoacrylates has been reported until this year [2].

Recently, our group has elaborated a facile light-induced method for the preparation of dihydropyrimidines and pyrimidines from azidoacrylates (Fig. 1) [3]. The reaction starts with photolysis of azidoacrylate **1** to form 2*H*-azirine, which under the same conditions undergoes further dimerization to form diazabicyclohexenes **2**. The latter, without preliminary isolation, were isomerized to dihydropyrimidine **3** at room temperature under basic catalysis. Subsequent oxidation of compound **3** furnishes the target pyrimidine molecule **4**.

The compounds obtained were tested for antibacterial activity against ESKAPE pathogens, only compounds **3** and **4** with Ar = *p*-$CF_3C_6H_4$ showed low activity (against *E. Cloacae*).

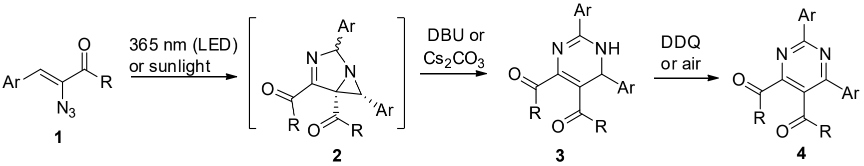

Fig. 1. Our synthetic route to dihydropyrimidines and pyrimidines.

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References

1. J. Fu, G. Zanoni, E. A. Anderson, X. Bi. // Chem. Soc. Rev., 2017, 46, 7208–7228.
2. O. Meth-Cohn, N.J.R. Williams, A. MacKinnon, J.A.K. Howard // Tetrahedron, 1998, 54, 9837–9848.
3. T.K. Nguen, G.D. Titov, O.V. Khoroshilova, M.A. Kinzhalov, N.V. Rostovskii // Org. Biomol. Chem., 2020, 18, 4971-4982.

Structure-Directing (Cyanamide)···Arene Noncovalent Interactions in Cocrystals of Copper(II) Clusters with Arenes

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Polynuclear clusters [1] and noncovalent interactions [2] play an important role in determining the structure, properties, and reactivity of organic and organometallic species. In this report crystallization of newly prepared copper(II) tetranuclear clusters $[Cu_4X_6O(NCNMe_2)_4]$ (X = Cl **1**, Br **2**) and their adducts from toluene and styrene solutions afforded crystalline substances: **1**·4PhMe, **1**·4PhCH=CH_2, **2**·4PhMe, and **2**·4PhCH=CH_2, which were characterized by physicochemical methods including XRD, IR and AAS. Inspection of the X-ray structures of (**1**–**2**)·4(arene) and the appropriate Hirshfeld molecular surface analysis allowed the recognition of the previously unreported π-hole···arene interactions involving the cyanamide ligands.

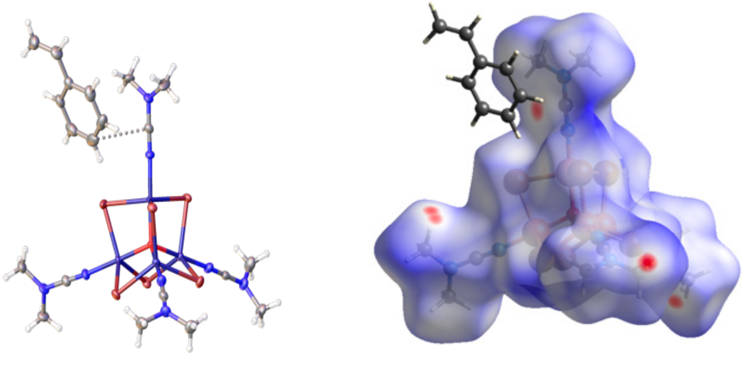

Fig. 1. View of the structure of **2***·4PhCH=CH_2, short C···C contact is given by dotted line (left) and the Hirshfeld surfaces for* **2***·4PhCH=CH_2 (right).*

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References

1. Hobza P., Rezac J. Introduction: Noncovalent Interactions // Chem. Rev., 116, 4911–4912 (2016).
2. S. Sung, D.C. Braddock, A. Armstrong, C. Brennan, D. Sale, A.J.P. White, R.P. Davies // Chem. Eur. J., V. 21. P. 7179 (2015).

Determination of acrylamide by liquid chromatography with deep eutectic solvent

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Acrylamide is a chemical compound that is naturally formed during the heat treatment process in the preparation of foods such as coffee, chocolate, almonds, fries, crackers, chips, cereals and breads. Acrylamide is formed when acrylic acid is heated and is carcinogenic. In extreme doses, it can be toxic, affects the nervous system, liver and kidneys. Therefore, the development of an optimal method for the determination of acrylamide in solid samples became the primary task.

In this work, it was decided to use deep eutectic solvents (DES) in the sample preparation process. Today, they have become an eco-friendly innovation in the scientific industry, for example it could be used such as solvents as analogues of often used organic toxic substances [1]. All this is due to the composition, low cost and new properties. Using these solvents and acrylamide will be released from solid samples. Further, acrylamide absorbed by solvents will be investigated by high-performance liquid chromatography.

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References

1. Abbott A.P., Capper G., Davies D.L., Rasheed R.K., Tambyrajah V. // Chemical Communications. 2003. V. 1. pp. 70-71.

Laser-induced deposition of different types of metal nanoparticles on nanostructured anodic aluminum oxide surfaces

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Method of laser-induced deposition of different types of metal nanoparticles is an approach based on photo-induced decomposition of molecules of organometallic precursors under laser irradiation with subsequent formation of mono- or bimetallic nanoparticles. One of the powerful advantages of this method is the possibility to obtain nanoparticles on different types of substrates including nanostructured ones like anodic aluminum oxide membranes.

Anodic aluminum oxide nanostructured templates are perspective material for creating of composite structures with defined architecture on its base. High aspect/ratio of these oriented tubes makes them attractive in constructing of small devices with high surface area which may be applicable in electrochemistry.

To develop the system applicable in electrochemical measurements it is necessary to cover anodic aluminum oxide template with conductive material to provide the electrical contacts through the system. Polyaniline in form of emeraldine salt is an optima material for such systems because of it biocompatibility and chemical stability.

In this study demonstrated the possibility of Ag, AgAu@C, AgPt@C nanoparticles formation on the top and in the pores of anodic aluminum oxide templates covered with polyaniline. Such systems may find its application in electrocatalysis of glucose oxidation reaction and hydrogen evolution reaction.

Acknowledgments. This work was supported by RFBR-DFG (RFBR project № 20-58-12015, DFG project BA 4277/16-1); RFBR project № 19-33-90239, by the "Scholarships of the President of the Russian Federation to young scientists and graduate students (Competition SP-2019)", project number СП-2368.2019.1. Authors are grateful to "Centre for Optical and Laser materials research", "Centre for X-ray Diffraction Studies" and "Interdisciplinary Resource Centre for Nanotechnology" of Research Park of Saint-Petersburg State University.

Synthesis of luminescent $NaYF_4$: Eu^{3+}, Gd^{3+}/Lu^{3+} nanoparticles

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Luminescent nanoparticles are actively used in different areas of science and technology, such as nano- and optoelectronics, space technologies, biology, and medicine. For example, in medicine and biotechnology, they are as luminescent labels for studying the structure of cells and diagnosing diseases. Rare earth metal compounds are known to demonstrate pronounced luminescent properties. Among the compounds of rare-earth elements, fluorine-containing compounds, for example, ReF_3 or $NaReF_4$, exhibit the brightest luminescence, and the phase composition and morphology of particles critically affects the luminescence properties.

The nanocrystalline phosphors with mixed crystal matrix ($NaY_xEu_zF_4$, $NaY_xGd_yEu_zF4$, $NaY_xLu_yEu_zF_4$) were synthesized by the hydrothermal method at 180 ^0C. The morphology of the nanoparticles was studied using scanning electronic microscopy (SEM). All samples consist of the particles that have shape of hexagonal prisms with the diameter of 50 - 800 nm. The substitution of yttrium by europium, gadolinium or lutecium results in size reduction. The X-ray diffraction analysis demonstrated that all samples have β-$NaYF_4$ crystalline phase. The substitution of yttrium by europium, gadolinium or lutecium results in the increasing the cell volume.

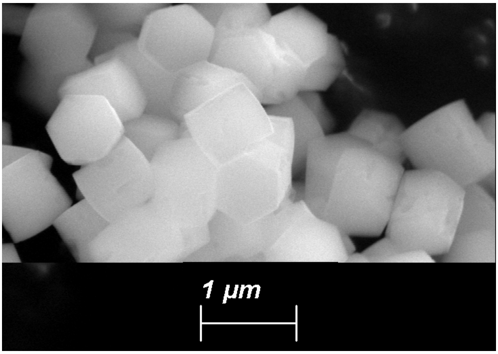

Fig. 1. SEM image of the $NaYF_4$ sample.

Upon 393-nm excitation, samples with Eu^{3+} demonstrated luminescence bands with maxima at 590, 615, 649, 690 and 696 nm. Mole fraction of Eu^{3+} equal to 0.03 relative to rare earth elements correspond to the maximal luminescence intensity. Also, the luminescence intensity slightly depends of the concentration of gadolinium and lutecium.

New hybrid redox-conducting material for organic batteries

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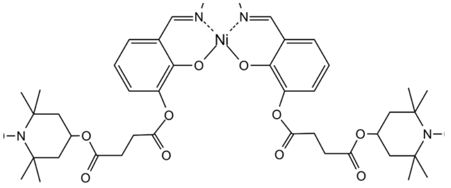
Nowadays lithium-ion batteries are the most widely used class of energy storage devices for both portable electronics and electric vehicles. Unfortunately, the technology of Li-containing current sources is nearly depleted of development possibilities. Currently used inorganic electrode materials, suitable mainly for lithium-containing electrolytes, lead to gradual increase in the mining volume to satisfy the growing demand. The production of such batteries, as well as their disposal, requires much more energy than they can store, and generates a large amount of thermal and CO_2 emissions [1]. This problem of ecological safety stimulates the creation of new environment friendly energy technologies that would be devoid of the disadvantages of the commonly used batteries [2].

Redox-active nitroxyl-containing polymers are promising candidates for replacement of inorganic-based energy storage materials, due to their high energy density and fast redox kinetics [3]. Herein the first implementation of the new TEMPO-containing polymer based on bis(salicylideniminato) nickel (NiSalen) conductive backbone (Fig. 1) as a cathode material for ultrafast-charging organic batteries is reported.



DiTS

Fig. 1. Structure of new hybrid monomer molecule.

Acknowledgments. Scientific research was partially performed at the Center for Geo-Environmental Research and Modelling (GEOMODEL), Chemistry Educational Center, Interdisciplinary Center for Nano-technology, Center for Chemical Analysis and Materials Research, Research Center for Magnetic Resonance of Research park of St. Petersburg State University. The synthetic work was supported by the Russian Science Foundation, grant #16-13-00038. Analysis of the results was funded by RFBR, project number #20-33-90122.

References

1. Majeau-Bettez G., Hawkins T. R., Strømman A. H. // Environmental science & technology, 45(10), 4548-4554 (2011).
2. Poizot P. et al. // Chemical Reviews, 120 (14), 6490–6557 (2020).
3. Muench S. et al. // Chemical reviews, 116 (16), 9438-9484 (2016).

Electrochemical Characterization of Molybdenum Disulfide with Conductive Polymer Binder as Anode Material for Lithium-Ion Batteries

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Molybdenum disulfide (MoS_2) is a promising material for anodes in lithium-batteries. This stems from its two-dimensional structure and high theoretical specific capacity (ca. 670 mA h g^{-1}). MoS_2 layers resemble those of graphene and their interlayer spacing provides paths for lithium ions diffusion. However, low conductivity, significant volume change during cycling, self-aggregation, and complex conversion mechanism hinder its application [1].

The attempts to circumvent these drawbacks rely on interlayer expansion, preparation of MoS_2-graphene composites, fine-tuning of synthesis procedures, and various other techniques. One approach is inclusion of conductive polymer into electrode composition, which has proven useful previously [2].

PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate))/ CMC (carboxymethylcellulose) conductive polymer binder increases specific capacity and cyclic stability of MoS_2-based anodes for lithium-ion batteries, compared to analogous composition with PVDF binder. Further investigation may lead to a more facile and greener production of anodes.

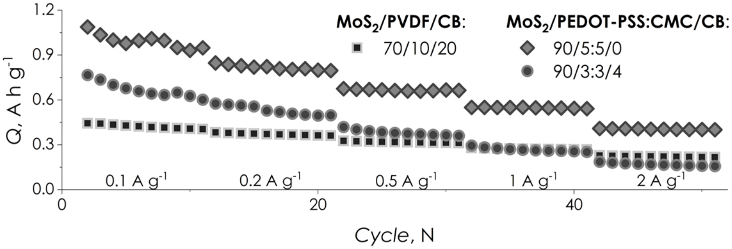

Fig. 1. Cyclic stability of electrodes depending on their composition.

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References

1. J. Wu, F. Ciucci, J.-K. Kim // Chem. Eur. J., v. 26, № 29, p. 6296-6319 (2020).
2. S.N. Eliseeva, M.A. Kamenskii, E.G. Tolstopjatova, V.V. Kondratiev // Energies, v. 13, №9, p. 2163 (2020).

A voltammetric determination of Pb2+, Cd2+ in edible oil using deep eutectic solvent

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Trace element level is important criteria for the assessment of quality of edible oils. The contamination of edible oils with heavy metals such as cadmium or lead is dangerous due to their high toxicity and their ability to accumulate in human bodies. It is well known that cadmium is able to accumulate in the liver and kidneys, increasing the risk of cancer, cardiovascular disease, etc. In turn, lead is a neutrotoxic element and is capable of causing a delay in development and contributes to the occurrence of anemia. Thus, there is a need to control the content of these elements in oils.

Nowadays, electrochemical analysis has emerged as an efficient tool for the determination of trace metals, but determination in samples of edible oils is a difficult task due to the low concentrations of analytes and to the complexity of the matrix. For efficient extraction of heavy metals from a complex matrix, various microextraction techniques are often used, in particular, the most common procedures is liquid-liquid microextraction (LLME) and deep eutectic solvents (DES) are increasingly used as an extractant. DESs, as a subclass of ionic liquids, show comparable characteristics; they are cheaper and easy to be produced due to lower cost of the raw materials, less toxic and often biodegradable.

In this study, effective LLME approach was developed for the extraction of trace elements from edible oils using DES and determinations by voltammetric tools. All experimental variables were optimized.

Acknowledgments. The study was supported by a grant from the President of the Russian Federation MK-1154.2020.3. Scientific research was partially performed at Chemical Analysis and Materials Research Centre of Saint Petersburg State University.

Preparation of inorganic-organic hybrids based on layered perovskite-like niobate $HCa_2Nb_3O_{10}$ and study of their photocatalytic activity towards hydrogen evolution from aqueous methanol

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The depletion of fossil fuel resources has led to stimulating searches for alternative energy sources and hydrogen obtained by the photocatalytic method from water and water-organic solutions is considered their promising substitute [1].

The present research is devoted to the synthesis and comprehensive study of new hybrid photocatalysts based on layered perovskite-like oxide $HCa_2Nb_3O_{10}$, modified with *n*-alcohols.

It was found that modification of the interlayer space with *n*-alkoxy groups of various length leads to a noticeable increase in the activity of photocatalysts in the reaction of hydrogen production. The rate of increase in activity between the initial compound and inorganic-organic derivatives reaches 10 times and the addition of Pt as a cocatalyst gives an increase in rate up to 15 times. Since interlayer space of layered perovskites is considered a separate reaction zone in photocatalysis, it is reasonable to assume that introduction of organic components substantially enhances its availability for reactants providing multiple increase in the activity [2].

Acknowledgments. The study was conducted using the equipment of the Saint Petersburg State University Research Park: Centre for X-ray Diffraction Studies, Centre for Optical and Laser Research, Centre for Magnetic Resonance, Centre for Chemical Analysis and Materials Research, Centre for Thermal Analysis and Calorimetry, Interdisciplinary Centre for Nanotechnology, Centre for Innovative Technologies of Composite Nanomaterials.

The work was supported by grants of Russian Foundation for Basic Research (18-03-00915) and Russian Scientific Foundation (20-73-00027).

References

1. I.I. Moiseev // Russ. Chem. Rev., v. 82, p. 616–623 (2013).
2. W. Cui, L. Li, S. Ma, Y. Liang, Z. Zhang // Catal. Today, v. 207, p. 44–49 (2013).

Effect of different binders on electrochemical properties of Co_3O_4 anode materials for lithium-ion batteries

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Lithium-ion batteries (LIBs) play an important role in modern world. Transition metal oxides, which characterized by high specific capacity, are considered to replace the graphite anode in LIBs [1]. Particularly, cobalt oxide Co_3O_4 has a sufficiently high theoretical capacity (890 mAh/g), which is almost twice higher than theoretical capacity of graphite (372 mAh/g). Due to the limited resources of lithium, it is also interesting that Co_3O_4 can be a suitable material for sodium-ion batteries. Nevertheless, the practical use of Co_3O_4-based anodes is difficult due to a significant decreasing of capacity during long-term cycling of electrodes and low utilization at high currents. It is established that different binders have a positive effect on electrochemical properties of different materials [2,3]. The aim of this work is to study the electrochemical properties of Co_3O_4 with different binders and to find the best composition of electrode material with cobalt oxide.

For the manufacture of electrodes, the components were taken in the following ratios (wt%): Co_3O_4 – 70, graphite – 20, binder – 10. Polyvinylidene (PVDF), the mixture of polyacrylic acid and carboxymethyl cellulose (PAA/CMC) (1:1) and mixture of poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) and CMC were chosen as binders. After preparation, the electrodes were dried at 60°C under vacuum. The materials were tested in coin-cell 2032 against metallic lithium in the potential range 0.01 – 3V by the galvanostatic charge/discharge method in the current range 0.2 – 1 C and cyclic voltammetry at scan rate 0.1 mV/s.

It was found that Co_3O_4 electrodes with water-soluble binders demonstrate higher specific capacity than theoretical ($\approx 1100\ mAh \cdot g^{-1}$ at 0.2 C). Furthermore, it is observed better stability in comparison with Co_3O_4 with PVDF (5% fading during 50 cycles for Co_3O_4 electrode with PEDOT:PSS/CMC, 25% for Co_3O_4/PAA/CMC and 37% for Co_3O_4/PVDF).

References

1. Reddy M.V., Subba Rao G.V., Chowdari B.V.R. // Chem. Rev., v. 113, № 7. p. 5364–5457 (2013).
2. Wang R. et al. // Nanoscale Res. Lett. Nanoscale Research Letters, v. 12. (2017).
3. Eliseeva S.N. et al. // Mater. Lett. Elsevier, v. 161. p. 117–119 (2015).

Oxidation of triphenylpnictogens in the synthesis of diphenylpnictogenic acids

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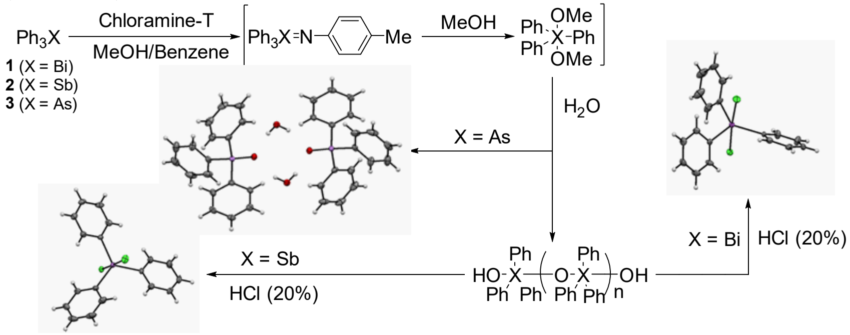
Previously it has been demonstrated by Ogawa et al. that oxidation of triarylbismutines with chloramine-T leads to the formation of corresponding diarylbismuthinic acids [1]. The latter are of significant interest for the investigation of noncovalent forces stabilising their self-associates: while organophosphoric acids are well investigated, hydrogen bonding and structure features of organobismuthinic, -antimonic and -arsenic acids remain unclear. However, our attempts to reproduce abovementioned synthesis for the diphenylbismuthinic acid demonstrated that reported reaction proceeds differently and leads to the formation of triphenylbismuth oxide **4** as a polymeric substance. Similarly, oxidation of triphenylantimony **2** and triphenylarsine **3** leads to the formation of corresponding oxides **5** and **6** (Scheme 1).



Scheme 1.

Via the treatment with hydrochloric acid polymeric oxides **4** and **5** can be easily converted to monomeric dichlorides **7** and **8**, respectively, which was confirmed by X-Ray Structural analysis. Thus, it has been proven that oxidation of triphenylpnictogens (XPh_3) with chloramine-T does not involve the cleavage of X-C bond.

Acknowledgments. This work was supported by the Russian Foundation for Basic Research (project 20-03-00231).

References

1. Ogawa T., Murafuji T., Iwata K., Suzuki // Chem. Lett. 1988, 17, 2021-2024.

Chemical logic devices based on photoelectrochemical photocurrent switching effect (PEPS) in nanotubes of titanium dioxide

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Titanium dioxide is widely used in the design of solar cells and photocatalytic applications. In this report, photoelectrodes based on TiO_2 nanotubes, are considered as the basis for logic devices. The effect of photoelectrochemical photocurrent switching (PEPS) is utilized to perform basic logic calculations. This effect consists in the fact that with the appropriate external polarization and/or illumination by photons with the appropriate photon energy, switching between the anodic and cathodic photocurrent can be observed [1]. We observed the PEPS effect on unmodified Ti/TiO_2 obtained by anodizing Ti plates.

UV irradiation (365 nm) gave a positive photocurrent for all investigated potentials in the range from -0.6 V to 0.6 V vs. Ag/AgCl reference electrode. The dependence of the current on the potential under blue irradiation (405 nm) had a different character. At a more negative potential (-300 mV vs. Ag/AgCl, for example), we observed an anodic photocurrent during irradiation with UV light, while blue irradiation produced cathodic one. Thus, the photoelectrode activity of unmodified titanium dioxide nanotubes can be switched from anodic to cathodic and vice versa.

Considering illumination as input signals and resulting photocurrent as output, photoelectrochemical behavior of Ti/TiO_2 under various illumination can be described in terms of logic gates. This effect allows us to annihilate two input signals and implement an optoelectronic XOR gate under simultaneous irradiation bu UV and blue light. XOR logic operation outputs true (1) only when input val-ues are different and yield zero otherwise. Light sources were used as in-puts, if the corresponding light source is turned on and illuminates the sample under study, this input is 1, otherwise - 0. In the same way, we can as-sign logic 0 to the state when photocurrent is not generated and logic 1 to any nonzero photocurrent intensity irrespectively on its polarization.

The presented Ti/TiO_2 system is a simple and reliable model of chemical logic valves.

References

1. K. Pilarczyk, P. Kwolek, A. Podborska, S. Gawęda, M. Oszajca, K. Szaciłowski in Advances in Unconventional Computing, ed. A. Adamatzky, Springer, Cham, 2017, pp.429–467.

Cross-sensitive potentiometric sensors based on anti-crown ether $(C_6HgF_4)_3$

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Potentiometric sensors with plasticized polymeric membranes are a popular tool in analytical chemistry both as the components of multisensor arrays and as individual selective sensors. This is due to the simple, fast and typically reagentless measurement procedure, reasonable precision and low detection limits. There is an ongoing search for the novel types of the sensing materials for such sensors in order to improve the performance of the sensors and to extend their applicability domains.

In this work, we have studied the possibility of using three mercury anticrown ether $(C_6HgF_4)_3$ as a membrane-active component for creating polymer plasticized membranes of potentiometric sensors. The choice of anti-crown ether was due to the literature data on such compounds where it was shown that they can form complexes with both cations and anions [1]. Thus we hypothesized that these properties may yield an interesting sensing behavior of corresponding PVC-plasticized membranes.

We have studied the electrochemical sensitivity of polymeric sensor membranes containing a three mercury anticrown in combination with various solvents-plasticizers and ion-exchangers in a wide variety of aqueous solutions of inorganic salts. Based on the results of this study, it can be argued that anti-crown based sensors have cross-sensitivity, which can be used to dvelop novel multisensor arrays.

References

1. K.I. Tugashov, D.A. Gribanyov, F.M. Dolgushin, A.F. Smol'yakov, A.S. Peregudov, M.Kh. Minacheva, L.A. Tikhonova, V.B. Shur // Organometallics, v. 35, p. 2197 (2016).

Fe_3O_4@HAp core-shell nanoparticles as MRI contrast agent: synthesis, characterization and theoretical and experimental study of shell impact on magnetic properties

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Magnetic Resonance Imaging (MRI) is a non-invasive imaging technique that produces three dimensional detailed anatomical images. By now MRI contrast agents have become an indispensable part of MRI procedure for the diagnostic of some diseases. The most common MRI regimes are T1-weighted and T2-weighted scans. In T2-weighted images the diseased tissues that accumulate contrast agents look darker. The main material to produce the T2 contrast agent is the Fe_3O_4 ferrimagnetic nanoparticles.

Nevertheless Fe_3O_4 magnetic nanoparticles are not widely used in clinical practice probably due to the simple surface oxidation process. We chose hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) as a material for the shell production, guided by their biocompatibility and wide use in medicine. Magnetic core-shell Fe_3O_4@HAp nanoparticles with a different HAp amount were synthesized using the co-precipitation method combined with hydrothermal treatment at temperatures range from 140 to 240°C. Nanoparticles morphological parameters were characterized using XRD, FTIR, TEM, SSA, Mossbauer spectroscopy. Computer simulation of blocking temperature dependence on shell thickness revealed the impact of the shell on the anisotropy constant and consequently on blocking temperature. To evaluate the efficiency of the core-shell NPs as contrast agents for MRI, the samples with different HAp amount in agarose matrix were investigated.

The dependence of MRI contrast ability and T2/T1 intensity ratio on shell thickness is not detected. So we can conclude that the shell allow us to protect the magnetite surface from oxidation and does not greatly affect contrast ability. Thus Fe_3O_4@HAp core-shell nanoparticles could be potential candidates for contrast agent.

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Development of novel pervaporation blended membranes based on polyvinyl alcohol-hydroxyethyl cellulose composite

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One of the most popular membrane processes for separating liquid mixtures of low molecular components is pervaporation. This method is applied to separate mixtures of close-boiling components, isomer and azeotropic mixtures. And one of the most important industrial applications of pervaporation is for dehydration, where highly permeable and selective to water membranes are needed. Membranes based on polyvinyl alcohol (PVA) is widely used for these purposes, but it has low permeability. One of the promising methods to improve the productivity of these membranes maintaining selectivity is blending with compatible hydrophilic polymers, membranes based on which has high permeability but low selectivity. By varying polymer ratios in the membrane matrix and preparation conditions, it is possible to obtain the tailored transport characteristics.

In this work novel blended polyvinyl alcohol (PVA) – hydroxyethyl cellulose (HEC) membranes with improved characteristics were developed for pervaporation dehydration. The optimal conditions of chemical cross-linking of membranes with maleic acid (MA) were chosen. Changes in the structural characteristics of PVA/HEC membranes were studied by IR spectroscopy and SEM microscopy. The transport characteristics of developed membranes were evaluated by pervaporation dehydration of isopropanol. It was shown that the addition of HEC to PVA and subsequent cross-linking with MA led to an improvement in transport characteristics of membranes due to structural changes.

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Novel green membranes based on sodium alginate-hydroxyethyl cellulose for pervaporation dehydration

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Nowadays, the development of membrane technology, which is related to sustainable processes, is one the most promising and important directions because these separation processes for liquid and gaseous systems play an important role in various industries and for the environment. In particular, the development of membrane method as pervaporation is important for the chemical and petrochemical industries, where it is actively used for the separation of mixtures of low molecular weight compounds and in particular for dehydration of organic substances. Increasing of requirements for product purity and environmental friendliness of processes in industry requires the search for new green high-performance pervaporation membranes.

In this work biopolymers sodium alginate (NaAlg) and hydroxyethyl cellulose (HEC) were selected for the development of novel environmentally friendly membranes by blending them with improved properties for pervaporation dehydration. It was also important to select optimal method of cross-linking for developed membranes to apply them in separation of dilute solutions. The structure of the blended membranes was studied using by various analysis methods (IR spectroscopy, AFM and SEM microscopies, etc.). Membranes based on NaAlg-HEC were tested in pervaporation dehydration of isopropanol in a wide range of concentrations. It was found that blending of these polymers in a certain ratio led to the improved transport characteristics.

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A new method for determining the absolute instability boundary

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In the framework of this work we propose a new method for determining the absolute instability boundary for binary systems. The boundary of absolute instability in the ethyl propionate - water system under isobaric-isothermal conditions was determined by molecular dynamics methods.

Experimental determination of the absolute instability boundary is difficult due to the complexity of working with metastable compositions. At the same time, using the molecular dynamic's method [1], it becomes possible to observe metastable states and to determine various physical parameters for them within a computer experiment.

The main idea is that after a certain threshold value of the molar fraction of one of the components, the molecules will form 2 phases, and since the experiment time is short (0.5 ns), this value will correspond exactly to the spinodal curve. It is possible to determine whether the system is in a two-phase or single-phase state visually and by the radial distribution functions of the mixture components.

This research is interesting as a theoretical point of view, since it allows one to compare the boundaries of the spinodal with the available theoretical concepts as well as in practical terms to obtain physicochemical values for the metastable region of an industrially significant mixture of ethyl propionate – water [2].

Acknowledgments. The investigation carried out using the equipment of the Resource Center of Computing Centre (Research Park of St. Petersburg State University). Maria Toikka is grateful to the Russian Science Foundation (grant 20-73-10007) for the support of this study.

References

1. Mayo S.L., Olafson B.D.,Goddard W.A. III "DREIDING: A generic forcefield" // J. Phys. Chem., 94, 8897-8909 (1990).
2. Alina Senina, Vladimir Margina, Alexandra Golikova, Nikita Tsvetov, Anna Sadaeva, Maria Toikka. Physico-chemical study of systems involving ethanol, promising for use as a biofuel // Fuel. Vol. 284 (2021) 119099. DOI: 10.1016/j.fuel.2020.119099**.**

B. Geo- and Astrophysics

Effect of velocity uncertainty on microseismic locating

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Velocity model building plays an important role in geological exploration. We propagate data reversely in time in order to focus at proper subsurface locations [1, 2]. Even for strongly perturbed velocity model, we make use of the ray crossing points (Fig. 1). A measure of focusing is estimated by computing their variance around the current focusing point:

$$D(v) = \frac{1}{N}\sum_{i=1}^{N}\left|\boldsymbol{x}_i - \boldsymbol{x}_{focus}\right|^2, \tag{1}$$

which reaches its minimum when the velocity model is correct. x_i – position of the i-th ray crossing. N – number of crossings. x_{focus} – mean value of the ray crossings. Minimizing (1) with respect to parameters describing the velocity model potentially allows for simultaneous source location and velocity model building.

In our studies, we considered a model linearly increasing with depth and placed the seismic source at a point with coordinates $x_s = 1500$ m, $z_s = -3500$ m. 21 receivers were involved with the lateral coordinate ranging from 0 to 4000 m. We perturbed the subsurface model for $0 \le \alpha \le 0.002$ m^{-1} using the same data for backpropagation. As a result, we observed a global minimum of the variance functional at the correct velocity model (Fig. 2).

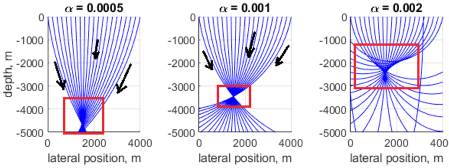

Fig.1. The quality of focusing depending on α.

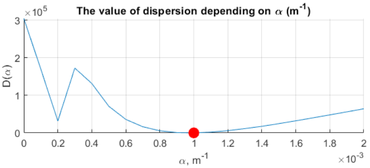

Fig. 2. The value of variance (dispersion) depending on α.

In our opinion, this observation demonstrates potential of using the variance of crossings (Eq. 1) for improving uncertainties in seismic velocity models.

References

1. D. Gajewski, E. Tessmer // Reverse modeling for seismic event characterization (2005).
2. P. Znak et al. // Identification and focusing of edge diffractions with wavefront attributes (2019).

Machine learning applied to the search of edge-on galaxies

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In recent decades many observation surveys which cover a big part of the entire sky have become available. Analysing of these terabytes of images is a very time consuming task. Machine learning methods can help with the automatisation of the data analysis, as they have done successfully in many other fields. We decided to apply a neural network to the search of galaxies in astronomical images.

Disk galaxies have random orientation to the line of sight. Very few of them are viewed from the edge and need to be found among thousands others galaxies in a single image. Whereas the study of galaxies viewed in edge-on position is important because one can accurately measure the thickness of different stellar and gas-dust complexes in such galaxies, and various disk bends manifest themselves in the best way. Research results can confirm or disprove existing ideas about the galaxy formation and evolution. For these reasons, edge-on galaxies are the main focus of our work.

To build a sample of edge-on galaxies we have applied a neural network based algorithm to the images of Pan-STARRS1 wide field sky survey [1]. The neural network was trained on a sample of 6 thousand images of galaxies that was previously found by eye on images [2].

The end result of this research is a catalog of edge-on galaxies found across the sky with reliably measured characteristics such as diameter, thickness, central brightness and the rate of change of these parameters along the radial direction.

References

1. Chambers K.C. et al. 2016, ArXiv e-prints, arXiv:1612.05560
2. Bizyaev D.V., Kautsch S.J., Mosenkov A.V., Reshetnikov V.P., Sotnikova N.Y., Yablokova N.V., Hillyer R.W., 2014, ApJ, 787, 24.

C. Mathematics and Mechanics

Analysis of global stability and oscillations in discontinuous control systems

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Rapid development of analytical-numerical methods in recent years allowed to find limiting dynamical regimes that were not found before and are connected with the theory of hidden oscillations. The classification of oscillations as being hidden or self-excited was proposed in [1]. Hence, it is necessary to revise the applicability limits of classical methods for determining the onset of oscillations in the process of loss of stability that are widely used in engineering practice and to develop special analytical-numerical methods to find hidden oscillations.

One of the most widely used methods for searching and analyzing oscillations in nonlinear control systems is the harmonic balance method that was developed in the 1920-1930s in the works of Krylov and Bogolyubov [3]. For Lurie systems with relay nonlinearity the Andronov point-mapping method (PMM) as well as Tsypkin method and the locus of a perturbed relay system (LPRS) method are applicable to analyze the existence of oscillations. PMM was developed by A.A. Andronov in [4], Tsypkin method was introduced in [5] by Ya.Z. Tsypkin and the LPRS method was developed in [6] and is a further extension of Tsypkin's ideas. In this report we illustrate advantages, disadvantages and limitations of these methods on a number of classical models.

References

1. Leonov G.A., Kuznetsov N.V. Hidden attractors in dynamical systems. From hidden oscillations in Hilbert- Kolmogorov, Aizerman, and Kalman problems to hidden chaotic attractors in Chua circuits // International Journal of Bifurcation and Chaos in Applied Sciences and Engineering, Vol. 23, №1, 2013, art. no. 1330002.
2. Krylov N.M., Bogolyubov N.N. Introduction to nonlinear mechanics (in Russian). AN USSR, Kiev, 1937. (English translation: Princeton University Press, 1947).
3. Andronov A.A., Vitt A.A., Khaikin S.E. Theory of Oscillators (in Russian). ONTI NKTP SSSR, 1937. (English translation: Princeton University Press, 1949).
4. Tsypkin Ya.Z. Relay Control Systems. University Press, Cambridge, 1984.
5. Boiko I.M. Discontinuous Control Systems: Frequency-Domain Analysis an Design. Springer London, Limited, 2008.

Geometric construction of inertial manifolds for non-autonomous dynamical systems

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We present a geometric theory of inertial manifolds for compact cocycles in Banach spaces. The main assumption is a squeezing property with respect to a family of quadratic Lyapunov functionals. In applications such functionals can be constructed with the aid of various versions of the frequency theorem [2, 4]. As a special case, our theory includes the famous theory of inertial manifolds for semilinear parabolic equations developed by C. Foias, G.R. Sell and R. Temam [3], where the main assumption is the Spectral Gap Condition. Other possible applications include nonlinear and non-autonomous ordinary differential equations (with delay), parabolic equations with delay and parabolic boundary control problems [1].

As we will see, the frequency theorem immediately leads to optimal conditions for the existence of such manifolds (unlike it was in pioneering works). For us the main interest is construction of low-dimensional inertial manifolds. This have immediate consequences for the long-time dynamics. This part is inspired by some works of R.A. Smith [5] and his results are also included in our theory.

References

1. Anikushin M.M. A non-local reduction principle for cocycles in Hilbert spaces //J. Differ. Equations, 269(9), 6699-6731 (2020).
2. Anikushin M.M. Frequency theorem for the regulator problem with unbounded cost functional and its applications to nonlinear delay equations, arXiv preprint, arXiv:2003.12499v2 (2020).
3. Foias C., Sell G.R., Temam R. Inertial manifolds for nonlinear evolutionary equations // J. Differ. Equations, 73.2, 309-353 (1988).
4. Likhtarnikov A.L., Yakubovich V.A. The frequency theorem for equations of evolutionary type // Sib. Math. J., 17(5), 790-803 (1976).
5. Smith R.A. Orbital stability and inertial manifolds for certain reaction diffusion systems // P. Lond. Math. Soc, 3(1), 91-120 (1994).

Investigation of shape memory effect and superelasticity in the NiCuTiHf and NiCuTiHfZr alloys

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In this study, the characteristics of the martensitic phase transformation as well as the shape memory and superelastic responses of the $Ni_{44.8}Cu_5Ti_{45.2}Hf_5$, $Ni_{44.8}Cu_5Ti_{40.2}Hf_5Zr_5$, and $Ni_{45.5}Cu_5Ti_{39.5}Hf_5Zr_5$ alloys were investigated. The $Ni_{44.8}Cu_5Ti_{45.2}Hf_5$ alloy showed a maximum recoverable strain of 6.25% with a recovery ratio of 81% upon thermal cycling under tensile stress of 300MPa, while in the $Ni_{44.8}Cu_5Ti_{40.2}Hf_5Zr_5$ alloy, a maximum recoverable strain of about 5% was obtained under 500MPa with a recovery ratio of 86%. The as-cast $Ni_{44.8}Cu_5Ti_{45.2}Hf_5$ alloy showed superelastic response with 0.37% maximum transformation strain at 125˚C. On the other hand, the $Ni_{44.8}Cu_5Ti_{45.2}Hf_5$ alloy showed the best superelastic response at 65˚C with a recoverable strain of about 1.5%. Two-way shape memory strains of 0.85% and 3.30% were obtained in the $Ni_{44.8}Cu_5Ti_{45.2}Hf_5$ and $Ni_{44.8}Cu_5Ti_{40.2}Hf_5Zr_5$ alloys, respectively. The $Ni_{45.5}Cu_5Ti_{39.5}Hf_5Zr_5$ alloy, however, did not show neither shape memory behavior nor superelastic response since the martensitic transformation in the alloy was incomolete and occurred at exteremely low temperatures.

Shape memory effect in the NiTi samples produced by wire-arc additive manufacturing

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Shape memory alloys are widely used in many applications however, their using is limited by difficulty to produce elements with complex shape. In this case, additive manufacturing technologies are taken a great attention because they can allow to reduce the fabrication time and cost of the final products. One of the additive manufacturing technologies is the wire arc additive manufacturing (WAAM) that was previously used to produce the NiTi shape memory alloy. It was shown that the structure of NiTi samples produced by the WAAM was heterogeneous, that affected the martensitic transformations in the layer. The aim of this work was to study the shape memory effect in the NiTi alloy samples produced by WAAM.

A 5-layered sample was deposited on a titanium substrate by WAAM using a Ti-50.9 at wire. % Ni. The bulk sample was cut into plates with a thickness of 0.5 mm, which were used to cut the dog-bone sample with working width and length of 1 mm and 6 mm. The samples were annealed at 450 °C for 10 hours. The shape memory effects were studied using the "Lloyd 30k Plus" testing machine, equipped with a thermal chamber and a video extensometer. Two test schemes were used: in the first scheme, the samples were cooled and heated through a temperature range of martensitic transitions under a constant stress, varied from 50 to 400 MPa. In the second scheme, the samples were deformed at a temperature of 22 °C, unloaded, heated through a reverse transition temperature range to study the shape memory effect, and subjected to a thermal cycle to study the two-way shape memory effect.

The results showed that multilayer TiNi samples produced by WAAM revealed shape memory effects, but the strain variations occurred in several stages. It can be assumed that these stages are caused by the martensitic transformations occur at different temperatures in the layers due to a various Ni concentrations. An increase in stress acting on cooling and heating or the preliminary strain on deformation at 22 ^{o}C increase both reversible and irreversible strains. It is found that an increase in the temperatures of martensitic transitions under stress can be described by the Clausius – Clapeyron like relation.

Acknowledgments. The study was carried out within joint DST-RSF project (RSF #19-49-02014, DST #DST/INT/RUS/RSF/P-36).

On Fredholm boundary problems for the wave equation with conditions on the entire boundary

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We consider the following boundary value problem for the wave equation with the conditions onthe entire boundary. Let M be a smooth compact Riemannian manifold, and Δ be a nonnegativeLaplace-Beltrami operator associated with a Riemannian metric. We fix a positive number τ andstudy the following boundary value problem on the cylinder $[0,\tau]\times M$:

$$\frac{\partial^2 u}{\partial t^2} + \Delta u = f, \tag{1}$$

$$u\big|_{t=0} = g_1, \tag{2}$$

$$Au + B\frac{\partial u}{\partial t}\bigg|_{t=\tau} = g_2, \tag{3}$$

where g_1, g_2 are given functions on M, f is a given function on $[0,\tau]\times M$ (cf. [1, 2]), A and B arepseudodifferential operators on M of orders 1 and 0 respectively.

The main results obtained in this work are the conditions on the coefficients in (3) under whichthe problem (1)-(3) is Fredholm in suitable function spaces. It turns out that these conditions areformulated in terms of the dynamics of geodesic flow on the cosphere bundle of M.We deal with operators associated with groups generated by quantized canonical transformations.The Fredholm property of such operators was studied in the recent papers (see [3, 4]).

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References

1. A.B. Antonevich. Linear functional equations. Operator approach. -Birkhäuser Verlag (1996).
2. S.L. Sobolev. An instance of a correct boundary problem for the equations of string vibration with the conditions given all over the boundary // Dokl. Akad. Nauk USSR, 109, № 4, p. 707-709 (1956).
3. A.Yu. Savin, E. Schrohe, B.Yu. Sternin. Elliptic operators associated with groups of quantized canonical transformations // Bull. Sci. Math. (2019).
4. A.Yu. Savin, E. Schrohe. Analytic and algebraic indices of elliptic operators associated with discrete groups of quantized canonical transformations. ArXiv:1812.11550. (2018).

Modeling and calculation of kinematic diagrams of mechanisms of robotic systems for pipeline diagnostic

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This work investigates the problem of calculating the characteristics of a robotic diagnostic complex (Fig. 1) in an emergency mode, which was designed by the company "SPBU Dynamics" [1] engaged in the creation of science-intensive robotic systems and digital products for in-line diagnostics of pipelines in the heat and power industry.

Fig. 1. The robot model.

We consider the robot with six "legs" with wheels at the ends, moving along the axis of the pipeline and pulling the wire along. The purpose of the work was to calculate the moment on the wheel and the force of pressing the wheel against the pipe in order to move the robot from its place. The control scheme takes into account the possibility of failure of three "legs". Therefore, the calculation of the moment and the pressing force was carried out for the simultaneous control of three wheels and three "legs".

In the course of the work, the equality to zero of the moments and forces of the entire system was used, since the system was initially at rest [2]. After that, auxiliary relations were found from the geometry of the structure. As a result, formulas were obtained for finding the clamping forces and torque, the numerical results of these values, as well as a comparison with the results of the model calculation in the Comsol package.

References

1. Additional information and specification of robot, http://spbudynamics.ru/
2. Polyahov N.N., Zegzhda S.A., Yushkov M.P. // Theoretical Mechanics. Textbook for bachelors. 3rd edition. p. 142-152 (2012).

Machine learning algorithms for evaluation of relaxation terms in state-to-state kinetic equations

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Relaxation terms are the right-hand sides of the set of differential equations for macroscopic gas parameters, describing the flows of multicomponent reacting gas mixtures under conditions of strong vibrational and chemical non-equilibrium [1]. Conventional methods for calculating relaxation terms are computationally expensive, since they imply multiple summations, as well as the calculation of a large number of the rate coefficients of vibrational energy transitions and chemical reactions. In this work, a possibility of evaluating the relaxation terms by machine learning methods is assessed, and the efficiency of several models [2] is compared for the case of **VT** relaxation in the mixture of **N_2-N**. It is shown that the k-nearest neighbours algorithm provides the best accuracy/efficiency ratio and can be recommended for further studies (see Figs. 1, 2).

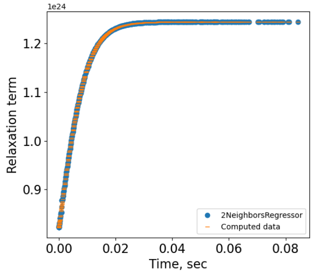

Fig. 1. Comparison of the test data set and data predicted by the 2-nearest neighbors algorithm for the relaxation term for the first vibration level.

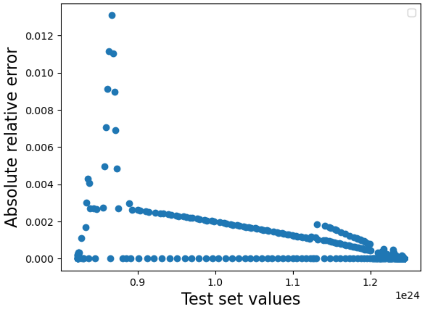

Fig. 2. Absolute relative error for 2-nearest neighbours algorithm corresponding to test set values.

References

1. E.A. Nagnibeda, E.V. Kustova. Kinetic theory of transport and relaxation processes in non-equilibrium reacting gas flows. St. Petersburg: Publishing House of St. Petersb. University, 2003. -272 p.
2. https://scikit-learn.org, scikit-learn project web-site

Effect of Topology upon Relay Synchronization in Triplex Neuronal Networks

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Relay Synchronization in complex networks is characterized by the synchronization of remote parts of the network due to their interaction via a relay. In multilayer networks, distant layers that are not connected directly can synchronize due to signal propagation via relay layers.

In this work [1] we investigate relay synchronization of partial synchronization patterns like chimera states in three-layer networks of interacting FitzHugh-Nagumo oscillators. We demonstrate that the phenomenon of relay synchronization is robust to topological random inhomogeneities of small-world type in the layer networks. We show that including randomness in the connectivity structure either of the remote network layers, or of the relay layer, increases the range of interlayer coupling strength where relay synchronization can be observed.

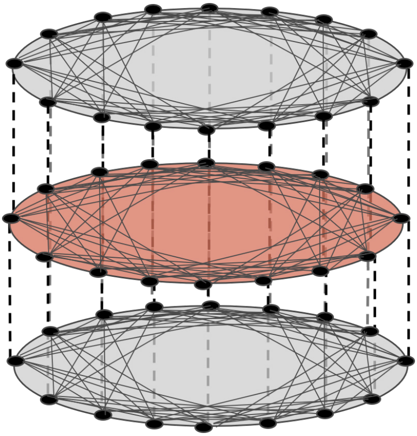

Fig. 1. Illustration of a triplex network with nonlocally coupled ring topology. The remote layers, depicted in grey are connected through the relay layer, marked in red.

References

1. Drauschke F., Sawicki J., Berner R., Omelchenko I., Schöll E. Effect of Topology upon Relay Synchronization in Triplex Neuronal Networks // Chaos 30, 051104 (2020).

Analysis of the cylindrical shell's vibrations under cross-section shape transformation

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Cylindrical shells with a rectangular cross-section are considered in the paper. These shells are used as a model for thin-walled box-shaped constructions which are used in mechanical engineering, chemical industry, and other technical areas. Different kinds of cabins (i.e. elevator cabins, sound booths, etc) belong to these constructions as well. As a part of designing process, frequency analysis can be used to ensure the cabin's unwanted vibrations which may occur during its functioning.

Vibrations of the shells of such a kind can be studied in several ways. In the case of square cross-section modes and frequencies can be found using approximate analytical solution [1] which is obtained by numerical solving of the transcendental equation which is obtained after separation of variables in Germain-Lagrange equation. For strongly rectangular cross-section, finite element method (FEM) or Rayleigh method can be used [2]. When the cross-section shape is close to square, the asymptotical solution [3] can be obtained.

As a particular aspect of this issue, influence of cross-section shape transformation upon vibration modes and frequencies was highlighted [2] for the case, when cross-section shape deviates from square to rectangular. It was revealed that during the shell size transformation the split of the 2nd and the 3rd frequencies occurs, which makes the 2nd one decrease and the 3rd one increase respectively, yet at small transformations they are approximately equal.

The goal of this paper is to study other cases of the cross-shape transformation. In particular, shape transformations from rectangle to parallelogram and from rectangular to trapeze are considered, and frequencies' behavior upon these transformations is analyzed.

References

1. S.B. Filippov, E.M. Haseganu, A.L. Smirnov // Mechanics Research Communications, Volume 27, Issue 4, 2000, P. 457–464.
2. G.T. Dzebisashvili, S.B. Filippov // Journal of Physics: Conference Series, Volume 1479, 2020.
3. A.S. Amosov // Vestnik St. Petersburg University, Mathematics. P. 67-72 (2004).

Strain variation during isothermal holding of the $Ni_{51}Ti_{49}$ shape memory alloy under stress

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It was shown that the $Ni_{51}Ti_{49}$ quenched alloy demonstrated the variation in recoverable strain on holding under a stress of 50 MPa. This effect can be successfully used in actuators, however optimum operating parameters, such as temperature and stress, should be found to provide a maximum recoverable strain variation. The aim of the present work was to study the influence of holding temperature and stress on the recoverable strain variation in quenched $Ni_{51}Ti_{49}$ alloy.

The $Ni_{51}Ti_{49}$ alloy wire samples with a diameter of 1.5 mm and a length of 100 mm were water quenched from 850 ^{o}C for 15 min and subjected to 100 thermal cycles. After thermal cycling, the samples underwent the B2 ↔ B19' martensitic transformations at temperatures of M_s = -43 ^{o}C, M_f = -63 ^{o}C, A_s = -24 ^{o}C, A_f = -9 ^{o}C. To study the effect of temperature and stress on a strain variation during isothermal holding, the following procedure was used: samples were cooled from 100 ^{o}C to the holding temperature T*, kept at T* for a duration of 40 min to stabilize temperature in the sample, loaded by a stress of σ, held for a duration of 60 min under stress and unloaded. A stress was varied in a range of 50 to 300 MPa. The holding temperatures were chosen both within the range of forward martensitic transformation and outside of this range.

Loading of quenched $Ni_{51}Ti_{49}$ alloy at temperature close to M_s induces the B2 → B19' transformation and is followed by strain variation, that recovers on unloading. It is found that isothermal holding under a stress leads to an additional strain variation, which partially or fully recovers on unloading and heating. It was shown that despite stress, an increase in isothermal strain in $Ti_{49}Ni_{51}$ did not depend monotonously on holding temperature and the highest strain growth was found on holding within the range of forward transformation. The dependence of maximum isothermal strain on stress was linear and the maximum value of 5,8% was observed on holding under a stress of 300 MPa.

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Recoverable strain variation during isothermal martensitic transformation in NiTi-based shape memory alloys

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Shape memory alloys exhibit unique properties to recover the initial shape on heating after a preliminary deformation (shape memory effect). This ability is caused by thermoelastic martensitic transformations, which are the first order phase transition. Previously, it was considered that the martensitic transformation was characterized by athermal kinetics. However, for the last decade it was shown, that forward martensitic transformation from austenite to martensite might be realized during the isothermal holding in some NiTi-based alloys and the kinetics of this process was studied [1, 2]. At the same time, the strain variation during the isothermal holding in NiTi-based alloys under a constant stress had never been studied and it was the aim of the present work.

To study the strain variation in $Ni_{51}Ti_{49}$ and $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloys during the isothermal holding under a stress, the samples were loaded in an austenite state, cooled down to T*, held for 60 minutes and heated up. The applied stress σ was 50 MPa for NiTi alloy and 235 MPa for TiHfNiCu alloy. The holding temperature T* was chosen within and outside the temperature range of forward transformation.

It was found that for both alloys the strain increased with time to saturation during the isothermal holding under a constant stress. Since a strain fully recovered on heating, it was concluded that a strain accumulation during the isothermal holding was caused by the isothermal martensitic transformation. The isothermally appeared strain depended on the holding temperature T* in non-monotonic way and maximum values of 0.4 and 2 % for NiTi and TiHfNiCu alloys, respectively, were observed at temperature of $M_s^{\sigma} - 6\ ^{o}C$ (M_s^{σ} – the start temperature of forward martensitic transformation under a stress of σ).

Acknowledgments. The work has been supported by Russian Science Foundation (# 18-19-00226).

References

1. N. Resnina, S. Belyaev, E. Demidova, A. Ivanov, V. Andreev // Mater. Lett., v. 228, p. 348-350 (2018).
2. E. Demidova, S. Belyaev, N. Resnina, A. Shelyakov // J. Therm. Anal Clorim., v. 139, p. 2965-2970 (2020).

Elliptic complexes in relative elliptic theory

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The object of this study is the theory of complexes in relative elliptic theory. This theory was introduced by Sternin [2, 3] as a theory of boundary value problems with conditions on submanifolds of arbitrary dimension.

We consider pairs (*M, X*) of a closed smooth manifold *M* and its submanifold *X*.

Here we deal with complexes of bounded operators acting in Sobolev spaces

$$0 \to \begin{matrix} H^{s_0}\left(M,E_0\right) \\ \oplus \\ H^{t_0}\left(X,F_0\right) \end{matrix} \xrightarrow{d_0} \begin{matrix} H^{s_1}\left(M,E_1\right) \\ \oplus \\ H^{t_1}\left(X,F_1\right) \end{matrix} \xrightarrow{d_1} \dots \xrightarrow{d_{m-1}} \begin{matrix} H^{s_m}\left(M,E_m\right) \\ \oplus \\ H^{t_m}\left(X,F_m\right) \end{matrix} \to 0, \tag{1}$$

where E_j, F_j are complex vector bundles on *M* and *X* respectively, H^{Sj} are Sobolev spaces of vector bundles sections and d_j are morphisms such as

$$d_j = \begin{pmatrix} A_j & C_j \\ B_j & D_j \end{pmatrix} \tag{2}$$

We suppose that (1) is a complex: $d_{j+1} d_j$ for all *j* Here A_j and D_j are pseudodifferential operators (ΨDOs) on *M* and *X* respectively, while boundary and coboundary operators B_j and C_j are equal to

$$B_j = D''_{X,j} i^* D''_{M,j}, \quad C_j = D'_{X,j} i^* D'_{M,j} \tag{3}$$

for some ΨDOs $D'_{M,j}, D''_{M,j}$ and $D'_{X,j}, D''_{X,j}$ on *M* and *X* respectively. Here i^* is a restriction operator such as

$$i^* : H^s(M,E) \to H^{s-\nu/2}(X, E|_X),\ i^* : u \mapsto u\big|_X,\ s > \nu/2 \tag{4}$$

meanwhile i_* is a dual operator defined as

$$i_* : H^{-s+\nu/2}(X, E|_X) \to H^{-s}(M,E),\ s > \nu/2 \tag{5}$$

For such complexes the notion of ellipticity is introduced. For complex (1) the following result is obtained.

Theorem 1. *If the complex (1) is elliptic, then it has Fredholm property.*

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References

1. S.P. Novikov, B.Yu. Sternin. Elliptic operators and submanifolds // Soviet Math. Dokl., 1966, 7(6):1508-1512.
2. B.Yu. Sternin. Elliptic and parabolic problems on manifolds with boundary consisting of components of different dimension // Trans. Moscow Math. Soc., 1966, 15:387-429.
3. B.Yu. Sternin. Relative elliptic theory and the Sobolev problem // Soviet Math. Dokl., 1976, 17(5):1306-1309.

Influence of heat treatment on the mechanical behavior under compression of NiTi alloy produced by wire arc additive manufacturing

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The aim of this work was to study the effect of heat treatment on the mechanical behavior of a 3-layered sample of NiTi alloy produced by wire arc additive manufacturing (WAAM). A 3-layered sample was deposited using a $Ti_{49.1}Ni_{50.9}$ alloy wire with a diameter of 1.2 mm on a titanium substrate. The samples with a size of 2.5x2.5x5 mm were cut from the bulk sample for compression (compression axis was across the layers). The samples were subjected to various heat treatments: quenching from 850 °C (20 min), quenching from 850 °C and annealing at 500 °C for 2, 5 and 10 hours, and annealing at 450 °C for 10 hours (without preliminary quenching). To study the mechanical behavior, the samples were compressed to a stress of 400 - 600 MPa with intermediate unloading. Compression was carried out at different temperatures from 25 to 100 °C, at which the samples were in the austenitic (at high temperatures) or martensite (at low temperatures) states.

At temperatures of 25 °C and 50 °C, compression occurred by the stress-induced martensitic transformation. The martensite phase was stable and did not disappear during unloading. At high temperatures of 75 °C and 100 °C, compression was carried out due to elastic and plastic deformation. The data obtained showed that the smallest residual strain after compression at high temperatures was observed in the sample annealed at 450 °C for 10 hours. This was due to the formation of Ti_3Ni_4 nanoparticles strengthened the NiTi phase and increased the dislocation yield stress, that decreased the contribution of plastic deformation.

The dependence of the phase and dislocation yield stress on temperature was found. The dependence of phase yield stress on the deformation temperature was used to determine the Clausius-Clapeyron ratio. The smallest coefficient was found in the sample without heat treatment, and the highest - in the sample annealed at 500 °C for 2 hours with preliminary quenching. Temperature M_d (the maximum temperature at which the martensite may be induced by stress) grows with an increase in the heat treatment time to 70 °C.

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Global stability and dissipativity in the fractional order Lorenz system

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In the study of dynamical systems given by differential equations of fractional order, due to difficulty of determining derivative operator, more efforts are focused on numerical modeling of the limiting dynamics of such systems.

At the same time, the questions whether the system of differential equations of fractional order actually generates a dynamic system (i.e. whether it is possible to extend the solutions of a system on a half-interval from zero to plus infinity and, also whether there are in phase space of such systems attractors (i.e. invariant, limited, attracting sets) usually remain open. These questions, in particular, are connected with property of dissipativity in the sense of Levinson (or D-property), when in phase space there is a bounded absorbing set, inside which at some point all system trajectories fall and no longer leave.

Thus, if a system of differential equations is dissipative in this sense: first, it produces a dynamic system, and second, it contains a global attractor within the absorbing set. At the same time, if the global attraction is trivial, i.e. consists only of the equilibria of the system, then the system is called globally stable.

In this work, for the classical Lorenz system, generalized to the case of a fractional order derivative, the dissipativity in the sense of Levinson and global stability are proved.

Predicting COVID-19 spreading in Russia based on a learning mathematical model of epidemic

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In December 2019, COVID-19 began to spread, and over the ensuing months caused a global epidemic. The mathematical modeling of infectious diseases is a tool that has been used to study the mechanisms by which they spread, to predict the future course of an outbreak and to evaluate strategies to control an epidemic. The most basic models are SIR and SEIR. They are often used to predict the spread of COVID-19 [1]. More complex models have been developed that take into account the influence of different regions and the duration of the disease [2]. An important step in applying the model is to find more suitable parameters according to available data. Various machine learning methods are used to solve this problem.

This work presents a modified epidemic model. In contrast to the differential models SIR and SEIR, a difference model was used. In the model, Russia was considered as one large region and the number of infected at the moment was investigated. The dependencies of the recovered and the susceptible are not taken into account, the population of Russia is considered constant. Some of the parameters are varied manually, 2-4 parameters are found using the learning algorithm. The "Stripe" learning algorithm was used to train the model. The computer program realizing learning algorithm is implemented in MATLAB environment. The incidence statistics in Russia from 1 April to 31 May of 2019 was used as data for training. For most of the models, a relatively small error was obtained on the initial data. Then the model was simulated with the given parameters from 1 June until 1 August. With some assumptions on more successful models, a forecast is given for July 1 and August 1. Compared to the new data, the forecasts are overstated.

References

1. Tomchin D.A, Fradkov A. L. Partial Prediction of the Virus COVID-19 Spread in Russia Based on SIR and SEIR Models, https://www.medrxiv.org/content/10.1101/2020.07.05.20146969v1
2. Ajitesh Srivastava, Viktor K. Prasanna Learning to Forecast and Forecasting to Learn from the COVID-19 Pandemic, https://arxiv.org/abs/2004.11372

Numerical simulation of coupled problem of determining internal ballistics characteristics in solid rocket motors

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Experimental investigation of physical processes that occur in solid rocket motors (SRMs) is connected with certain difficulties due to their transience and high temperatures and pressures. Hence, numerical simulation methods are essential for examination of such processes [1]. Sufficiently powerful mathematical tools are developed in relation to individual investigated processes (gas dynamics, propellant combustion, material strength, etc.) in high-energy systems by this moment. Based on these tools modern application program packages are implemented. Nevertheless, experimental and calculated high-energy systems parameters often significantly differ in practice. Attempts to define predicted characteristics more precisely using higher order numerical schemes, refined computational grids, reduced integration steps, etc. do not always lead to desired results. In such cases, development of coupled mathematical models that take account of processes with different physical nature can lead to successful results [2]. Determination of internal ballistics characteristics together with tracking the burning surface of solid propellant refers to the class of coupled problems and requires special techniques when implementing numerical model. Mathematical simulation becomes more complicated by the presence of moving boundaries of burning propellant. In this paper we developed numerical algorithm that allows to take consideration of both complex grain geometry and multidimensional combustion products flow pattern. On the basis of given algorithm we obtained and analyzed results for different configurations of SRM including nozzleless rocket motor the nozzel part of which is made of solid propellant and SRM that has design feature in the form of an “umbrella”. We investigated the approximation convergence, showed the dependence of main internal ballistics characteristics on time and provided distributions of flow parameters at some points in time for both configurations. We observed significant burning rate change along the duct axis for nozzleless rocket motor while the results for SRM with “umbrella” are in good accordance with well-known theoretical principles.

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References

1. K.V. Kostyushin, I.V. Eremin, A.M. Kagenov, K.N. Zhiltsov, I.M. Tyryshkin, M.S. Sereda, A.V. Chervakova // J. Phys. Conf. Ser., v. 597, p. 1-6 (2019).
2. S.R. Idelsohn. Numerical Simulations of Coupled Problems in Engineering // Springer, 422 p (2014).

On classical connections in analytical mechanics

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The paper is discussed the concepts of classical holonomic and nonholonomic relations introduced in analytical mechanics. The Hamilton operator and the generalized Hamilton operator introduced by N.N. Polyakhov are used for the vector representation of the connections reactions imposed on the motion of a point. To study the non-free motion of a system of material points system, we use the concept of a Hertzian point. Examples of connections are given, and it is noted that in the case of motion on fixed surfaces, nonholonomic connections are only linear. The concepts of connections are significantly expanded if they can be considered as a program of point movement (program connections) when setting the problem. Examples are given of guidance a point at a target moving according to a given law, using the methods of parallel approach and chase. The concept of connections is extended even further when the motion program is defined as a set of high-order nonhbolonomic connections.

References

1. Polyakhov N.N., Zegzhda S.A., Yushkov M.P. Theoretical mechanics. Moscow: Visshaya shkola. 2000. 592 p.
2. Soltakhanov Sh.Kh., Yushkov M.P., Zegzhda S.A. Mechanics of non-holonomic systems. A New Class of control systems. Berlin Heidelberg: Springer-Verlag. 2009. 329 p.

Deformation of shallow spherical caps under internal pressure

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The work concerns the deformation of shallow nonuniform spherical shells under internal pressure. The effect of anisotropy, material heterogeneity and shallowness on the shell deflection is examined.

The prebuckling state of the shell can sometimes have a strong effect on the critical pressure value if the mode shape of the loaded structure in the prebuckling state differs from the mode shape of the unloaded structure [1].

A mesh-like structure in a human eye called the Lamina Cribrosa may be modelled with shallow spherical shell. Large deformations of the LC can cause edamas and folds at the periphery of the LC, atrophy of the optic nerve fibres and the eventual loss of the sight [2]. This phenomenon can be the result of the axisymmetric equilibrium state buckling of such shell.

It is known that the material of the LC is transversely isotropic or orthotropic. The elastic modulus in the thickness direction is significantly less than the tangential elastic modulus. In this case the prebuckling state of the shells is more accurately described by Ambartsumyan theory. The obtained results are compared with the results of classical theory. In particular, it is shown that Ambartsumyan theory gives larger deflection value.

References

1. D. Bushnell // AIAA Journal, v. 19, № 9, p. 1183-1226 (1981).
2. E.N. Iomdina, S.M. Bauer, K.E. Kotliar. Eye Biomechanics: Theoretical Aspects and Clinical Applications. M.: Real Time (2015).

Simulation of Deformation Effects of NiTi Based Shape Memory Alloy by Means of a Phenomenological Macroscopic Level Model

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Due to simplicity and compactness macroscopic phenomenological models of shape memory alloys (SMA) are most promising for use in Finite Element Analysis (FEA) of smart SMA devices. Further development and improvement of existing macroscopic models still presents a topical problem.

The proposed model is formulated within the framework of the equilibrium thermodynamics. The internal state variables are the volume fraction of martensite Φ and the mean phase deformation tensor Λ_{ij}. Main SMA deformation effects occur due to the direct and reverse phase transformations and the reorientation of martensite. Generalized thermodynamic forces driving these phenomena are calculated as the derivatives of the Gibbs' free energy G:

$$F_{\Phi} = -\frac{\partial G}{\partial \Phi},\ F_{\Lambda_{ij}} = -\frac{\partial G}{\partial \Lambda_{ij}}.$$

To account for the hysteretic nature of SMA's deformation behavior, two dissipation forces $f_{\Phi}^{fr}, f_{\Lambda}^{fr}$ are considered. Equations describing the phase transformations and the martensite reorientation take the form $F_{\Phi}=\pm f_{\Phi}^{fr}$ and $\left\| F_{\Lambda} \right\| = f_{\Lambda}^{fr}(\Lambda_j)$.

Calculated and experimental [1] dependences of the strain on temperature and stress-strain diagrams are compared in Figs. 1 and 2.

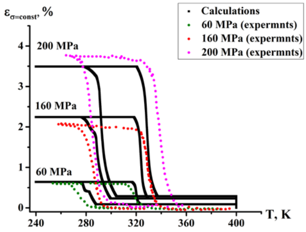

Fig. 1. The strain-temperature curves under constant loads.

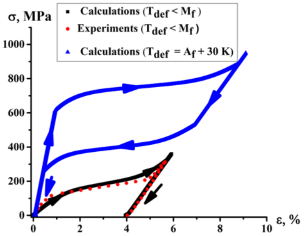

Fig. 2. The stress-strain curves for martensite and austenite.

References

1. Wu X., Sun G., Wu J. 2003. The nonlinear relationship between transformation strain and applied stress for nitinol // Materials Letters 57, 1334–1338. DOI: 10.1016/S0167-577X(02)00983-7.

The lock-in range of a type 2 analog PLL

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Phase-locked loops (PLLs) play an important role in modern telecommunication systems, distributed computer architectures, global positioning systems (GPS, GLONASS), and other applications [1, 2].

Such a concept as the lock-in range was originally introduced in a classical PLL monograph [3]. The author, famous American engineer Floyd M. Gardner stated the following problem (the Gardner problem): to determine the lock-in range corresponding to system acquiring lock within at most one beat between carrier frequency and initial voltage-controlled oscillator (VCO) frequency. A strict mathematical definition of the lock-in range, which were introduced in [4], an extension of Lyapunov theory developed for cylindrical phase space [5] and the well-known KYP-lemma allow one to obtain an analytical estimate of the lock-in range for higher-order type 2 PLLs.

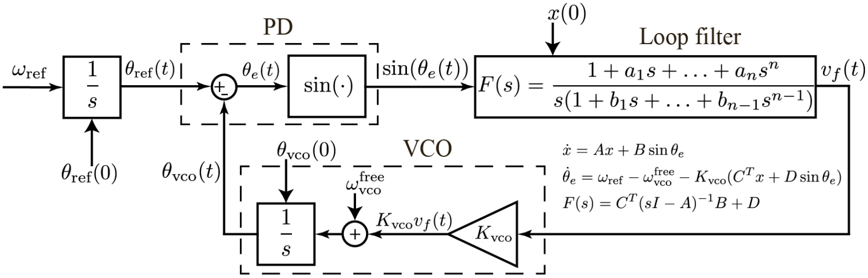

Fig. 1. Baseband model of a type 2 APLL and its closed-form dynamic model.

References

1. Kaplan E.D., Hegarty C.J. Understanding GPS/GNSS: Principles and Applications. Artech House, 3rd edition, 2017.
2. Bakshi U., Godse A. Analog Communication, Technical Publications, 2010.
3. Gardner F. Phaselock techniques. New York: John Wiley & Sons, 1979.
4. Leonov G., Kuznetsov N., Yuldashev M., Yuldashev R. Hold-in, pull-in, and lock-in ranges of PLL circuits: rigorous mathematical definitions and limitations of classical theory // IEEE Transactions on Circuits and Systems–I: Regular Papers, 2015 Vol. 62 № 10 P. 2454– 2464.
5. Kuznetsov N., Lobachev M., Yuldashev M., Yuldashev R. On the Gardner problem for phase-locked loops // Doklady Mathematics, 2019, Vol. 100, №3, P. 568–570.

Synchronization control and bifurcation of coupled two-dimensional Hindmarsh-Rose systems

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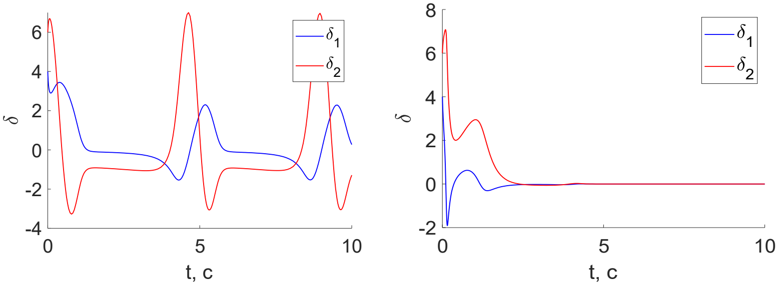
Synchronization is a fundamental non-linear phenomenon and plays an important role in various fields of science and technology [1]. It is very often found in living systems, observed at the level of individual cells, physiological subsystems, organisms, and even at the level of populations.

In this paper, we analyze the bifurcations in two-dimensional Hindmarsh-Rose system (HR) [2], which describes the behavior of an individual biological neuron. Bifurcation is a qualitative change in the behavior of a dynamical system with small change of its parameters. Depending on the parameters the system can be oscillatory or excitable. Here we propose the control algorithm based on the speed gradient method [3] for ensuring the synchronization of two coupled HR systems with known and unknown parameters.



a *b*

Fig. 1. Synchronization transients of error system:without control (a); with control (b).

References

1. Blekhman I.I. Synchronization of dynamic systems. Moscow: Nauka, 1971. –894 p.
2. Hindmarsh J.L., Rose R.M. A model of the nerve impulse using two first-order differential equations // Nature. 1982. Vol. 296, Issue 5853. – P. 162–164.
3. Fradkov A.L. Cybernetic physics: principles and examples. SPb.: Nauka, 2003. – 208 p.

Deformation tensor for BCC-HCP martensitic transformation in TiZr shape memory alloy

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Today shape memory alloys (SMA) are frequently used in various fields of technology and medicine due to their unique properties. The most frequently used SMA is the titanium nickelide alloy (TiNi). However, stricter requirements for medical devices have led to the need to replace potentially carcinogenic nickel in titanium based SMA with other elements such as zirconium, molybdenum etc. The TiZr alloy can be called a high-strength and biocompatible alternative to titanium. This alloy has a high creep resistance at high temperatures and excellent corrosion resistance.

For effective use of SMA in various applications models are needed which allow correctly calculate the deformation of these materials. One of the most important material constants of the microstructure model [1] used in this work is the strain tensor of the crystallographic lattice transformation of the initial high-temperature austenitic phase into a low-temperature martensitic one. In this paper, the strain tensor matrix for BBC ↔ HCP martensitic transformation in the TiZr alloy was calculated. It was assumed that the transformation is performed by shear on the $\{112\}_{BCC}$ plane in the direction of $[111]_{BCC}$ and subsequent atomic shuffle. The deformation gradient and the matrix of Green-Lagrangian deformation tensor were calculated. The deformation tensor matrix was used to model the functional and mechanical properties of this material. The crystallographic resource for this transformation was estimated as the maximum value of the principal strains. The orientation of a single crystal providing the value of strain that is close to the calculated value of the crystallographic resource during realization of the pseudoelasticity effect was found.

Acknowledgments. The study was supported by the Russian Foundation for basic research (RFBR) 19-01-00685. The authors express their thanks to Prof. Aleksandr E. Volkov for useful discussion of the obtained results.

References

1. Belyaev F. et al. A Microstructural Model of SMA with Microplastic Deformation and Defects Accumulation: Application to Thermocyclic Loading // Mater. Today Proc. Elsevier Ltd., 2015. Vol. 2. P. S583–S587.

Oscillations in the neuroendocrine system: An event-based regulation model

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The neuroendocrine system enables the brain to regulate activities of the human body, such as reproduction, growth, metabolism, and stress, by controlling hormonal secretion. A hypothalamic–pituitary regulated endocrine system is shown schematically in Fig. 1.The hormones of hypothalamus and pituitary activate secretionof the hormone of the regulated endocrine gland.In its turn, the latter hormone inhibits secretion of the brain hormones. As a result, a homeostasis (a dynamical equilibrium) is attained. Here $x(t)$, $y(t)$ and $z(t)$ are bood concentration of tye recpective hormones.

An impulsive model of the neuroendocrine regulation was proposed in [1]. It combines a Goodwin-type feedback control with impulsive input from neurons located in the hypothalamus. An "integrate-and-fire" scheme was used to model impulses generated in hypothalamic nuclei. Namely, impulses are fired when the integrated membrane potential reaches some threshold, and after the firing the potential resets to zero. Despite the model's simplicity, it exhibits realistic hormonal profiles, including ultradian and circadian rhythms, pulsatile secretory patterns, and occasional chaotic dynamics.

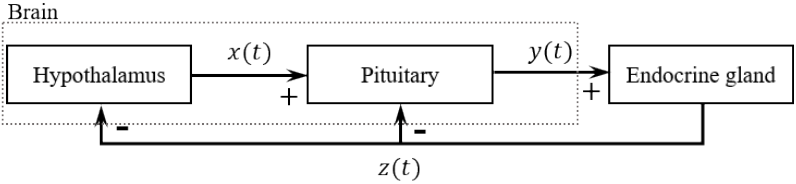

Fig. 1. The neuroendocrine regulation scheme. The plus sign denotes stimulation, and minus – inhibition.

References

1. Churilov A.N., Milton J., Salakhova E.R. An integrate-and-fire model for pulsatility in the neuroendocrine system // Chaos (AIP Journal). 2020.Vol. 30, №8. P. 083132.

Synchronization of the Hindmarsh-Rose neurons via adaptive coupling

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There are many biological systems which can demonstrate synchronous regimes in their behavior. The most important examples of this type of systems are the neuronal populations and their dynamics in a human or an animal brain. Actually, it is well known that the synchronization of a large number of neurons in the central nervous system plays an important role in the formation of the brain waves [1]. Furthermore, it was ascertained that numerous pathological states and diseases of the nervous system, such as essential tremor, epilepsies, Parkinson's and Alzheimer's diseases, relate directly to the anomalous synchronization in the neuronal populations. Today the methods, which rely on suppression of pathological synchronization in the nervous system, are actively used in the therapy of these diseases. Obviously, the development of such methods requires the application of qualitative mathematical tools. Our approach is based on the application of the tools from control theory.

There are many papers which are dedicated to the synchronization of mathematical models of neurons. The majority of these works is devoted to a non-adaptive synchronization [2]. Typically, the results of these studies are some upper bounds of the coupling strength which provide synchronization between the neural models. However, such analytical results are quite rough, which may have negative consequences for a living organism. In our paper we propose to compare the analytical upper bound of the coupling strength with the upper bound which is obtained by the adaptive control algorithm. We apply the adaptive control algorithm which is called the speed gradient method [3]. This method is based on the usage of Lyapunov functions and requires to define the control goal as an objective function.

References

1. Strogatz S.H., Stewart I. Coupled oscillators and biological synchronization, https://doi.org/10.1038/scientificamerican1293-102.
2. Plotnikov S.A., Lehnert J., Fradkov A.L., Schöll E. Synchronization in heterogeneous FitzHugh-Nagumo networks with hierarchical architecture, https://doi.org/10.1103/PhysRevE.94.012203.
3. Fradkov A. L., Pogromsky A. Yu. Speed gradient control of chaotic continuous-time systems, https://doi.org/10.1109/81.542281.

Piloted control: preventing unfavorable pilot-vehicle interactions

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Unfavorable aircraft-pilot coupling events include a broad set of undesirable events of the relationship between the pilot and the aircraft – rare, unexpected and unintended deviations in the spatial position of the aircraft and the flight path caused by anomalous interaction between the pilot and the aircraft [1]. When the dynamics of the aircraft and the dynamics of the pilot connect, the result is called the pilot-induced oscillations (PIO). It is believed that the main nonlinear factor leading to the PIO is the speed limitations on deviation of the aircraft control elements.

The linearization of pilot-vehicle model in a neighborhood of the equilibrium state shows that a closed system is asymptotically stable in a certain neighborhood of zero [2]. But the existence of a hidden attractor in a pilot-vehicle closed-loop system was established.

This report reviews the nonlinear correction method for PIO prevention. The results obtained show that nonlinear correction allows to make possible for a pilot to act with a more aggressive manner, from one hand, and to prevent the PIO, ensuring the flight safety, from another one.

The pilot adapts to the vehicle and forcing function characteristic [3]. Therefore, a functional relationship can be set up between pilot ratings and the objective system factors in terms of the pilot dynamic characteristics alone. Based on this fact, the control system optimization to prevent the nonlinear oscillations is proposed.

References

1. B. Andrievsky, D.G. Arseniev, N.V. Kuznetsov, I. Zaitceva. Pilot-induced oscillations and their prevention // Conf. Cyber-Physical Systems and Control, S-Petersburg, 2019. p. 108-123 (2019).
2. B. Andrievsky, K. Kravchuk, N.V. Kuznetsov, O.A. Kuznetsova, G.A. Leonov. Hidden oscillations in the closed-loop aircraft-pilot system and their prevention // IFAC-PapersOnLine. Vol. 49(14). p. 30-35 (2016).
3. D. McRuer, E. Krendel. Mathematical Models of Human Pilot Behavior. AGARD AG-188 (1974).

Eta-invariant for elliptic operators with shifts on manifolds with cylindrical ends

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The eta-invariant (of Atiyah-Patodi-Singer type, see [1]) plays fundamental role in elliptic theory and appears in many index formulas.

Let a smooth manifold M contain a compact submanifold K with smooth boundary such that the cmplement $M \setminus K$ is diffeomorphic to the cylinder

$$M \setminus K \cong (-\infty, 0) \times \Omega$$

with coordinates (t,x), where the cylinder base Ω has dimension n. Such manifolds are called *n-dimensional manifolds with cylindrical ends*. Let a discrete group $\mathbb{Z}$ act on M by powers of a diffeomorphism $g : M \to M$. The diffeomorphism defines shift operator denoted by T.

We consider the operator

$$D = \sum_k D_k\left(x, t, -i\frac{\partial}{\partial x}, -i\frac{\partial}{\partial t}\right)T^k$$

acting in weighted Sobolev spaces on M, where, for all k, D_k is a pseudodifferential operator, T^k is shift operator in t variable, wherein only a finite number of operators D_k are nonzero. Having applied Fourier transform $\mathcal{F}_{t\to p}$, we obtain a parameter-dependent family of operators

$$D(p) = \sum_k D_k\left(x, -i\frac{\partial}{\partial x}, p\right)e^{2\pi ikp}, \tag{1}$$

where $D_k(p)$ is a parameter-dependent family of classical pseudodifferential operators (see [2]).

For a zero-dimensional base Ω, the winding number of operator (1) has been evaluated. Moreover, using Melrose approach [3] in higher dimensions, the eta-invariant of operator (1) has been defined as an infinite-dimensional generalization of winding number. To this end, certain regularized traces and integrals were introduced. Main properties of the eta-invariant were studied.

Acknowledgments. This work was supported by RFBR, grant № 19-01-00574 A.

References

1. M. Atiyah, V. Patodi, I. Singer. Spectral asymmetry and Riemannian geometry. I // Math. Proc. Cambridge Philos. Soc., v. 77, p. 43-69 (1975).
2. M.A. Shubin. Pseudodifferential Operators and Spectral Theory. Springer-Verlag, Berlin-Heidelberg (1985).
3. R. Melrose. The eta invariant and families of pseudodifferential operators // Math. Res. Lett., v. 2, № 5, p. 541–561 (1995).

D. Solid State Physics

Stabilization of the orthorhombic phase in ferroelectric HfO_2: state and prospects

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Silicon-doped Hafnium Dioxide (HfO_2) is a major alternative tool for ferroelectric nano-devices due to its thermodynamic stability on silicon and the presence of residual polarization. Currently, two main applications of ferroelectric hafnium dioxide are considered: 1) in MIM - a capacitor for DRAM random access memory; 2) in a ferroelectric field-effect transistor FE - FET. A fundamentally important task is to obtain the maximum possible value of the residual polarization (Pr), its stability during cycling and to ensure the largest possible number of rewriting cycles.

To obtain the effect of ferroelectricity, it is necessary to artificially create an orthorhombic phase in the crystal structure of HfO_2. It occurs by doping of Si elements and further annealing after electrode deposition on HfO_2. In previous works, to increase the fraction of the orthorhombic phase, its stabilization and, as a consequence, improve the feroelectric properties, attempts were made to vary the impurity concentration and annealing temperature independently of each other.

In addition, the value of the residual polarization is affected by the quality of the dielectric / electrode interfaces. The problem is in the instability of the polarization reversal cycle, the so-called wake-up effect. It is believed that it is caused by the recharge of defects in HfO_2 (oxygen vacancies) at the interface with the electrodes. However, this question of the influence of the interface with the electrode on polarization is still insufficiently studied.

In view of the above, it seems relevant to study the combined effect of the impurity concentration and the annealing temperature on the stabilization of the FE-HfO_2 orthorhombic phase. It is also worth considering the process of formation and depth distribution of oxygen vacancies in the FE-HfO_2 film.

Isothermal kinetics of the forward martensitic transformation in the NiTi-based shape memory alloys

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Shape memory alloys are widely used due to their unique properties such as strain recovery on heating (shape memory effect). These properties are caused by the thermal elastic martensitic transformations (the first order phase transitions). For a long time, it was assumed, that the martensitic transformations were characterized by athermal kinetics so, the phase change occured on temperature or stress variation and did not depend on time. However, during last 10 years, it has been found that in some NiTi-based shape memory alloys the martensite phase formation may occur during isothermal holding. Although the kinetics of this phenomenon has been studied, its nature remains unclear. To find the mechanism of the isothermal transformation in NiTi, it is necessary to study this phenomenon in the NiTi based alloys with different chemical compositions and it was the aim of the present work.

The isothermal martensitic transformation was studied by differential scanning calorimetry in the binary (Ni-Ti), ternary (Ni -Ti -Cu, Ni- Ti-Cr) and quaternary (Ti-Hf-Ni-Cu) NiTi-based alloys. The isothermal holdings were carried out at start temperature of the forward transformation and holding duration was varied in a range of 1 ÷ 60 min.

It was found that the forward transformation took place during isothermal holding of alloys with non-stoichiometric chemical composition (with high density of point defects). At the same time, isothermal holding of stoichiometric alloys as well as alloys where the precipitates formed during annealing did not lead to the isothermal martensite formation. Hence, it can be concluded, that point defects were crucial condition of the realization of the martensite transformations in NiTi-based shape memory alloys during isothermal holding. The volume fraction of isothermally appeared martensite increased with time up to the saturation, which value depended on chemical composition and holding temperature. The influence of point defect concentration on the maximum of isothermal martensite volume fraction was non-monotonic hence, it might be concluded that there was an optimal concentration of point defects, at which the isothermal martensite formation was more intense.

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Study of interface formation in the Mo/Be structure without/with B_4C buffer layer

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Currently, much attention is devoted to the technology of extreme-ultraviolet lithography as a route to microelectronics manufacturing. Some systems use as many as ten normal-incidence reflections between the source and the wafer, so, high-reflective and stable multilayer mirrors for wavelengths in the region 10–15 nm is crucial. Mo/Be demonstrates high theoretical reflectance (about 70%) with 11.3-nm illumination. In practice, however, reflectivity is lower. This is largely related to formation of interlayers (beryllide compounds with different stoichiometry depending on the film order) at the interfaces Mo and Be layers. Mo/Be reflective coatings are also demanded in space telescopes for solar astronomy, since wavelength region 11.1–12.4 nm, containing emission lines of solar corona, is still uncovered by other multilayers.

This work is devoted to study formation of an interface region in the multilayer periodic Mo/Be mirrors using X-ray photoelectron spectroscopy. The impact of a barrier B_4C layer on the interdiffusion at both interfaces of the Mo/Be mirror (Mo-on-Be and Be-on-Mo) was analyzed in details paying particular attention to the interaction of the barrier B_4C layer with the Mo and Be layers. It was established [1] that the barrier B_4C layer: i) reduces the total amount of the beryllides at the interfaces, compensating by the appearance of MoB; ii) limits the formation of the Be-rich $MoBe_\alpha$ beryllide at the Be-on-Mo interface making this interface more sharp; iii) facilitates the formation of beryllium carbide Be_2C at both interfaces.

Acknowledgments. The present work was supported by RSF grant 19-72-20125.

References

1. Elena O. Filatova, Sergei S. Sakhonenkov, Sergey A. Kasatikov, Aidar U. Gaisin, Elizaveta S. Fateeva, Ruslan M. Smertin, Vladimir N. Polkovnikov // J. Phys. Chem. C (2020) (in print).

The experimental differences in the values of the magnetic gap in the intrinsic magnetic topological insulator $MnBi_2Te_4$

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Topological insulators are materials that are insulating in bulk but have conductive states on the surface. These surface states are formed as a bond between two topologically nonequivalent phases and are protected from non-magnetic perturbations. These unique materials become especially interesting when magnetic order is added to the topological order [1].

Nowadays there is the first intrinsic antiferromagnetic topological insulator $MnBi_2Te_4$. The Dirac point band gap of 88 meV was predicted for this compound [2], which significantly exceeds previously observed one — for other magnetic topological insulators. The gap is the most important parameter that determines the temperature of the magnetic transition and, consequently, the temperature range of corresponding effects due to magnetic order such as quantum anomalous Hall (QAH) or magnetoelectric effects.

For example, it was found that the QAH effect in $MnBi_2Te_4$ can be achieved at 6.5 K, which is significantly higher than the previous ones (about 1K for Cr-doped topological insulators) [3].

However, there is still ambiguity in experimental data for $MnBi_2Te_4$ and related materials. We found that the size of the Dirac point band gap in different samples varies significantly from theoretically predicted values of 88 meV up to almost 0 meV. Here we will present our latest results of $MnBi_2Te_4$ measurements by means angle resolved photoemission spectroscopy (ARPES) with ultrahigh energy resolution. We studied numerous of $MnBi_2Te_4$ samples at different experimental stations (with laser and synchrotron light photoexcitation), above and below the magnetic transition temperature (~ 25 K). We will discuss possible reasons of the Dirac point gap size deviation in experiments from the theoretical predictions.

References

1. C.-Z. Chang, J. Zhang, X. Feng et al., Science 340, 167 (2013).
2. M.M. Otrokov, I.I. Klimovskikh, H. Bentmann, D. Estyunin et al. // Nature 576, 416 (2019).
3. Y. Deng, Y. Yu, M.-Z. Shi et al // Science 367, 6480 (2020).

Ion-induced defects in hexagonal boron nitride

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Hexagonal boron nitride (h-BN) is one of wide-band-gap semiconductors [1]. This material is a promising material for the production of single photon emitters [2]. To study luminescence properties of native defects and ion-induced defects in h-BN we use cathodoluminescence (CL) method.

This work is an experimental study of ion-inducted defects in a thin h-BN single-crystal. CL investigation was performed using SEM Zeiss SUPRA 40VP with Gatan Mono CL3+ detection system. Defects were created with focused gallium ion-beam (FIB). Ion irradiation was performed with various ion doses using cross-beam system Zeiss Auriga. Luminescence spectra were registered within a spectral range 200 nm–700 nm. Electron acceleration voltage was 5kV.

In obtained CL spectra we observe sharp peak at energy of 2.9 eV and broad bands at energies of about 1.9 eV and 4.0 eV. We can attribute observed features of the spectra to the defects in h-BN such as carbon replacing nitrogen (C_N), nitrogen vacancies (V_N), oxygen impurities replacing nitrogen (O_N), boron impurities replacing nitrogen (B_N) or their complexes [1, 3].

We found that the ion beam has a significant influence on the intensity of CL. A comparison of the experimental results and numerical simulation (with the Monte-Carlo method) shows that ion irradiation leads to the appearance of nonradiative recombination centers.

References

1. Cassabois G., Valvin P., Gil B. Hexagonal boron nitride is an indirect bandgap semiconductor // Nature Photonics. – 2016. – V. 10. – №. 4. – P. 262
2. Bourrellier R. et al. Bright UV single photon emission at point defects in h-BN // Nano letters. – 2016. – V. 16. – №. 7. – P. 4317-4321.
3. Ngwenya T.B., Ukpong A.M., Chetty N. Defect states of complexes involving a vacancy on the boron site in boronitrene // Physical Review B. – 2011. – V. 84. – №. 24. – P. 245425.

Graphene intercalated with Mn monolayer on metallic and semiconducting substrates

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Currently, graphene had been established as the one of the most interesting material for researchers, due to the linear dispersion of electronic states, the so-called Dirac cone. Owing to its two-dimensional crystal structure, graphene properties strongly depend on the interaction with the various types of substrates. The contact of graphene with different materials and the functionalization of graphene make it possible to change its electronic structure of π-state dispersion near the K point of the Brillouin zone.

Some studies of the band structure of graphene on metal substrates show that due to the strong interaction between C $2p_z$ and d-states of the metallic substrate, the graphene π-states are in general modified and largely shifted away from Fermi level. Among the strongly interacting systems, the graphene−ferromagnet interfaces are the most exciting due to their perspectives for spintronic applications.

The electronic structure of the graphene−ferromagnet interface can be adapted by intercalation of different species with the purpose to create unusual graphene-based heterostructures. For example, the intercalation of Fe leads to an increase of the induced magnetic moment in graphene [1]; the intercalation of sp-metals decouples graphene from the ferromagnet systems with the controllable modification of the graphene band structure near the K point of the Brillouin zone. Also, in this type of systems it is possible to form unusual magnetic structures. As an example of such an experiment is the formation of a thin layer of Ni_3Mn alloy at the gr/Mn−Ni(111) interface [2].

This work is devoted to the experimental investigation of the electronic structures of the epitaxial graphene on the SiC(0001) substrate after intercalation by manganese atoms and the (CVD)-grown single graphene layer on Co substrate modified through the intercalation of deposited Au and Mn atoms under the graphene monolayer.

References

1. Weser M. et al. // Appl. Phys. Lett., 96, No. 012504 (2010).
2. Voloshina Elena et al. // The Journal of Physical Chemistry C 123.8, 4994-5002 (2019).

Superconductivity of the Bi-Sn eutectic alloy

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Recently, the field of application of traditional superconductors in magnetometers, motors, generators, magnetic resonance imaging systems and other technological applications has been significantly expanded [1]. It is known, that tin-containing alloys are relatively cheap, have low melting points and good wettability. This explains the large number of studies devoted to tin alloys, including Bi-Sn alloys [2-4].

We report thorough studies of superconductivity in the Bi-Sn bulk alloy of the eutectic composition (57 wt.% Bi, 43 wt.% Sn). The temperature dependences of the static (dc) susceptibility were measured by Quantum Design MPMS 3 within a temperature range of 1.8-20 K in magnetic fields up to 20 kOe. In addition, the field dependences of the dc magnetization at different temperatures were investigated.

The study has shown that the bulk Bi-Sn eutectic alloy behaves as a dirty type-II superconductor with a two-stage phase transition which critical temperatures are higher than for pure tin. The high-temperature stage corresponding to the appearance of a weak diamagnetism is presumably due to the formation of a thin layer at the boundary of two phases of the eutectic alloy with a bismuth structure that occurs at high pressure. The second stage is due to the superconducting transition in the phase of the alloy with the Sn structure. The obtained phase diagram H-T demonstrates the presence of a positive curvature of the critical lines at low magnetic fields which was interpreted using the proximity effect model.

References

1. J.H. Durrell, M.D. Ainslie, D. Zhou, P. Vanderbemden, T. Bradshaw, S. Speller, M. Filipenko, D.A. Cardwell // Supercond. Sci. Technol., 31, 103501 (2018).
2. C. Aksoy, T. Mousavi, G. Brittles, C.R.M. Grovenor, S.C. Speller // IEEE Trans. Appl. Supercond., 26, 1 (2016).
3. W.J. Tomlinson, A. Fullylove // J. Mater. Sci., 27, 5777 (1992).
4. B.L. Silva, G. Reinhart, H. Nguyen-Thi, N. Mangelinck-Noël, A. Garcia, J.E. Spinelli // Mater. Charact., 107, 43 (2015).

Electronic and magnetic structure of $MnSb_2Te_4$ topological insulator

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Nowadays new materials with special electronic properties continue to be actively studied. Magnetic topological insulators (TI) could be very useful for future experimental investigations as well as advantageous for their potential spintronic applications. In theory, magnetic topological states have been studied, such as antiferromagnetic (AFM) TI, Weyl semimetals and magnetic Dirac semimetals [1]. The surface states of topological insulators are characterized by a linear dispersion E (k), forming a Dirac cone and are protected from scattering due to the time reversal symmetry (TRS). Magnetic field breaks the TRS lifting the Kramers degeneracy between up and down spins and can open a local gap at the Dirac point. When magnetism is induced into TIs, the gapless topological boundary states are expected to be gapped and various exotic topological phenomena will emerge, including topological magnetoelectric effect, axion insulator and quantum anomalous Hall effect [2].

This work is devoted to study the electronic, magnetic and spin structure of possible ferrimagnetic topological insulator $MnSb_2Te_4$. Lately the electronic structure and magnetism of $MnSb_2Te_4$ have been studied using first-principles calculations. The results show that the $MnSb_2Te_4$ can be an antiferromagnetic or ferromagnetic semiconductor with a trivial or inverted energy gap [1]. Furthermore, it was recently proposed that it is possible to realize FM state in $MnSb_2Te_4$ due to the mixing of Mn and Sb sites. Additionally, anomalous Hall effect had been observed in $MnSb_2Te_4$, supporting the ferromagnetic or ferrimagnetic order in $MnSb_2Te_4$. [2]

The survey was carried out by means of angle- and spin- resolved photoemission spectroscopy with application of synchrotron radiation. The structural and magnetic properties of TI surfaces were investigated by atomic-force microscopy, scanning tunneling microscopy and SQUID.

References

1. Chen Li et al. Electronic structure and magnetism of $MnSb_2Te_4$ // Journal of Materials Science 55.29 (2020): 14292-14300.
2. Zhou Liqin et al. Topological phase transition in layered magnetic compound MnSb2Te4: Spin-orbit coupling and interlayer coupling dependeces. arXiv preprint arXiv:2003.06553 (2020).

Photoluminescence excitation spectroscopy of defect-related states in $MAPbI_3$ perovskite single crystals

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Currently halide perovskite semiconductors are widely used as an active medium in many optoelectronic devices: solar cells, LEDs, micro-lasers etc. [1] The underlying photophysical phenomena in all of these devices are highly dependent on defect states, the energy levels of which are located in the bandgap of the material, since they can interfere with a desired function of a device or originate it.

In this work, we have studied MAPbI3 halide perovskite single crystals at a temperature of 5 K using photoluminescence excitation spectroscopy. Two non-interacting types of states are determined: bound excitons (BE) and defect-related states (D1 and D2) (Fig. 1). Excitation of the crystal with light energy below the bound exciton resonance reveals the complex low-density defects emission, otherwise hidden by the emission of bound excitons. We also propose a method for separating these defect-related luminescence spectra and are carefully studying this emission regime.

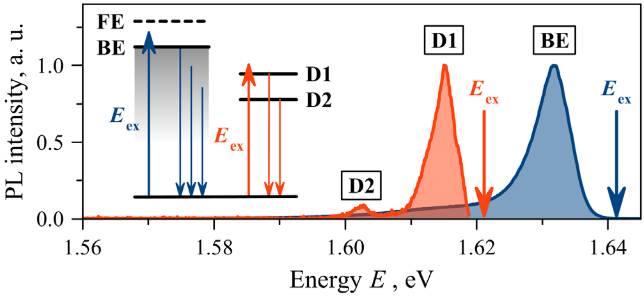

Fig. 1. Normalized PL spectra with excitation above the BE resonance (blue curve) and below the BE resonance (red curve), processed by the proposed method for separating the defect luminescence spectra.

The results of this study lay the groundwork for low-density defects and dopants research in halide perovskite semiconductors.

Acknowledgments. The work was carried out using the equipment of St. Petersburg State University resource center «Nanophotonics» with the support of the Russian Foundation grant 19-72-10034.

References

1. Q. Chen, N.D. Marco, Y.M. Yang, T. Song, C. Chen, H. Zhao, Z. Hong, H. Zhou, Y. Yang // Nano Today, v. 10(3), p. 355-396 (2015).

Excitonic properties of $CsPbBr_3$ halide perovskite single crystal

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Among the many semiconductors, attention is drawn to substances exhibiting excitonic properties, for example, halide perovskites. This work is devoted to the study of the excitonic properties of a single crystal of halide perovskite $CsPbBr_3$, as well as their comparison with the properties of $MAPbBr_3$.

It is known that the binding energy of the ground state of excitons in MAPbBr3 is relatively high: 15.3 meV, while kT at 300 K is 25.8 meV [1]. This makes it possible to create devices based on this single crystal that operate at relatively high temperatures. However, due to methyl ammonium, $MAPbBr_3$ decomposes when heated, opposed to more stable $CsPbBr_3$.

In the course of the work, the photoluminescence spectra of the $CsPbBr_3$ sample were obtained at various temperatures from 110K to 4K. The obtained spectra allow us to say that the studying sample has similar properties to the $MAPbBr_3$. For example, the exciton resonance energy at 4,6K in $CsPbBr_3$ is 2.320 eV, while in $MAPbBr_3$ similar quantity is 2.250 eV. $CsPbBr_3$ has better processability, which makes its use in electronic and optical devices preferred.

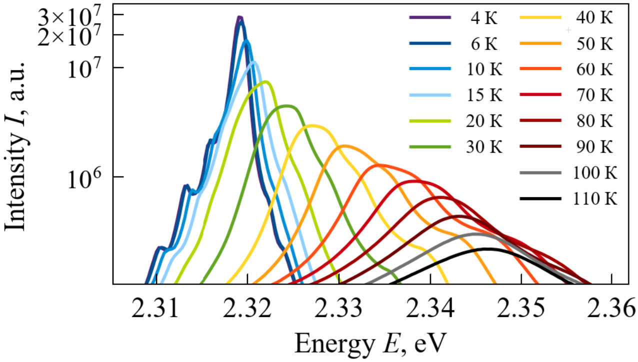

Fig. 1. Photoluminescence spectra of the $CsPbBr_3$ single crystal at different temperatures represented in logarithmic scale.

Acknowledgments. This work was carried out on the equipment of SPbU Resource center “Nanophotonics” and was supported by the Russian Science Foundation (project 19-72-10034).

References

1. O. Lozhkina et al. // J. Phys. Chem. Lett., 9, p. 302–305 (2018).

Free excitons in one-dimensional halide perovskite-like PyPbI$_3$

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The study of the specific features of the behavior of quasiparticles under dimensional quantization in a new one-dimensional perovskite-like PyPbI$_3$ (where $[Py]^+ = [C_5H_5NH]^+$) makes it possible to trace the effect of crystallography of low-dimensional structures on their excitonic properties. The crystal structure of a PyPbI$_3$ single crystal is one-dimensional chains of PbI$_6$ octahedra. Its the photoluminescence and photoluminescence excitation spectra demonstrate a fortyfold increase in the exciton binding energy and a twofold increase in the band gap as compared to the indices of a bulk MAPbI$_3$ single crystal [1].

In the photoluminescence spectrum of PyPbI$_3$, we see three emissions, which were attributed to STE (self-trapped excitons), LE (localized excitons) and FE (free excitons), correspondingly. The temperature dependence of this spectrum reveals the presence of an energy barrier between LE, FE and STE states. The value of the barrier can be determined using a model described by kinetic equations.

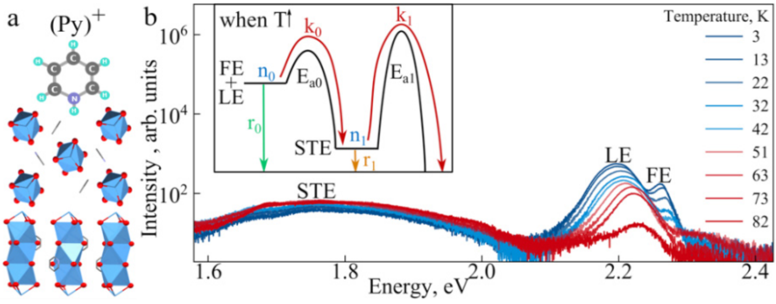

Fig. 1. (a) Crystal structure of PyPbI$_3$. (b) PL-spectrum upon heating PyPbI$_3$.

Acknowledgments. This work was financially supported by the Russian Foundation for Basic Research (19-03-00836-a) and performed on the equipment of the resource center «Nanophotonics».

References

1. N.I. Selivanov, Yu.A. Rozhkova, R. Kevorkyants, A.V. Emeline, D.W. Ahnemann // J. Dalton Trans., 49, 4390-4403, (2020).

Long-living dark optical coherence from excitons in InGaAs/GaAs quantum well revealed by photon echo

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The photon echo (PE) is an optical analogue of the spin echo and it is the coherent response of the system to the successive action of two pulses. The prospect of studying this effect is mainly due to the wide potential of application in the field of optical information processing [1].

In this paper, we investigate the photon echo from excitons in an InGaAs/GaAs quantum well in a magnetic field. The investigated sample P551 contains a 3 nanometer $In_{0.04}GaAs/GaAs$ quantum well.

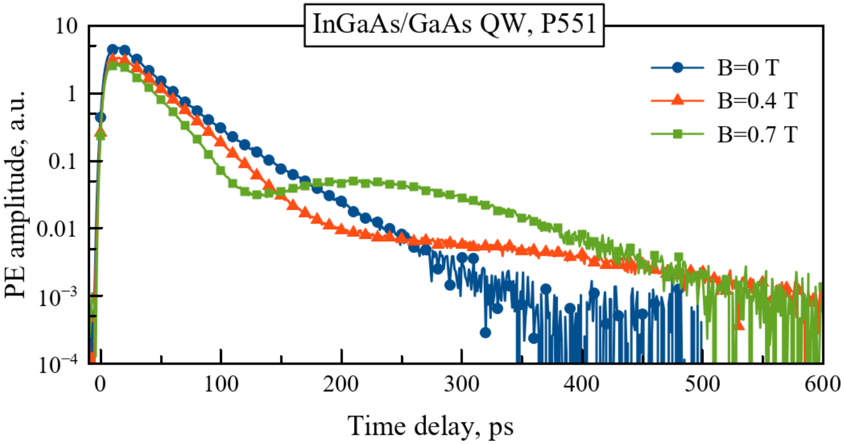

Fig. 1. Decay of PE signal at a different magnetic fields.

The behaviour of PE can be described in terms of five-level system, which has one ground state, two bright excitons with S = ±1 and two dark excitons with S = ±2. Bright states can be excited by $\sigma\pm$ polarized light, whereas dark states do not interact with light. We measured PE, and it turned out that at low magnetic fields effective irreversible phase relaxation time T_{2d} increases up to 240 ps.

Acknowledgments. This work was carried out on the equipment of SPBU resource center "Nanophotonics" and it was supported by RFBR grant 19-52-12046 nnio_a.

References

1. L. Langer, S.V. Poltavtsev et al. // Nature Photonics 8, p. 851–857 (2014).

E. Electromagnetic and Acoustical Processes

Electrical diagnostics of surface dielectric-barrier discharge with coaxial configuration

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Cold atmospheric pressure plasma jets (APPJ) are the subject of intensive studies. The bactericidal properties of cold plasma and the relatively high resistance of cells and tissues to its effects have already been identified [1]. It means that cold plasma is valuable in medicine for sanitizing surfaces, including for disinfection and treatment of human wounds.

A coaxial electrode configuration with surface dielectric barrier discharge was designed to generate a cold plasma jet flowing out into an ambient air [2]. A technique for determining the plasma region extension based on measuring average current and applied voltage has been proposed. The discharge cell is a quartz tube, inside which we mounted a coaxial electrode system insulated by fluorine. Alternating high voltage is applied to the electrode system to generate APPJ. The discharge develops along the free surface of the fluorine insulation from the edge of the grounded electrode (Fig. 1, right).

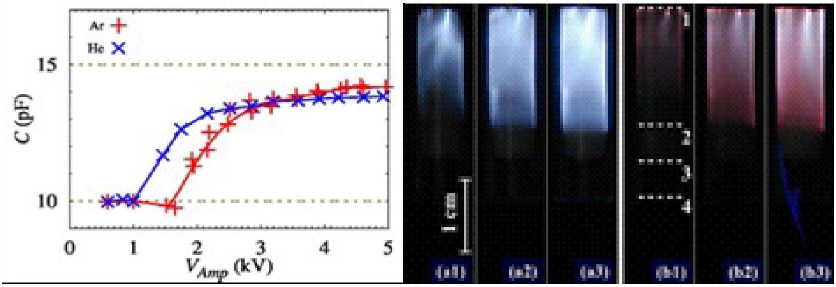

Fig. 1. Capacitance of the discharge electrode system vs amplitude voltage (left) and the photo of the discharge region in helium and argon (right)

Acknowledgments. The work has been supported by the Russian Science Foundation (project 18-79-10048) and Institute for Electrophysics and Electrical Power of the Russian Academy of Sciences.

References

1. S.A. Ermolaeva, F.A. Varfolomeev et al. // Journal of Plasma Medicine, vol. 60, issue 1., p. 75–83, 2011/
2. O.M. Stepanova, O.V. Rybalchenko, M.E. Pinchuk, A.M. Astafiev et al. // Plasma Medicine, vol. 7, n 3, p.187-200, 2017.

Features of the interaction between two types of electrohydrodynamic phenomena: droplet electrodeformation and conduction pumping

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Electrodeformation is the process of changing the shape of a liquid droplet immersed into another liquid under the effect of the strong electric field. Electrohydrodynamic (EHD) flow is a kind of the process in which the fluid moves because of the electric field. One of the kinds of the EHD phenomena is related to the conduction pumping. Charge layers emerge due to the electric-current passage through a low-conducting medium. The phase electrifies because the balance between dissociation and recombination is disturbed and the electric charge appears. The charged liquid accelerates under the effect of the electric field.

These works are important both from academic and practical points of view, especially for designing microfluidic systems and electrostatic dehydrators for crude oil. To our best knowledge there are no studies in which electrodeformation be carried out simultaneously with conduction pumping. The present research is devoted to estimating the effect of conduction EHD flow on the electrodeformation degree of a conductive droplet is suspended in a liquid dielectric.

The study bases on a numerical simulation using the finite-element method and COMSOL Multiphysics software package. The two-phase medium is described using the so-called arbitrary Lagrangian-Eulerian (ALE) method, also referred to as the moving boundary or moving mesh method. The computer model describing the process of a droplet electrodeformation is complemented with the Nernst–Planck equation for describing the effect of the electric field on a liquid dielectric.

The emergence of the EHD flow and the charged layers affect the transient processes and the steady-state degree of the eletrodeformation. The effect on the stationary value can be as high as decades of percent, depending on the combination of the material properties and the applied voltage.

Measuring viscous and elastic characteristics of phantoms biological tissues

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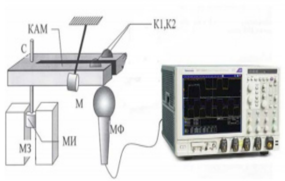
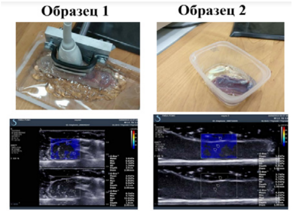
Yung's modulus and shear modulus in soft biological tissues, as well as their direct comparison of their measurements, are important diagnostic parameters in medicine associated with the early detection of various neoplasms.

In the resech proposed a technique for measuring the viscosity coefficient by the damp-ing of tuning fork vibrations (it allows to reduce the sample volume to 1 ml or less). Drops of the investigated liquid are applied to its surface of the tuning fork. The tuning fork vibrations are ex-cited with a hammer and recorded using a Brüel & Kjær 4189 microphone connected to a TEKTRONIX DPO 4034 oscilloscope. The data recorded on the oscilloscope is processed on a computer in the MATLAB software environment. After that, the damping decrement and the de-sired viscosity coefficient are calculated.

We also measured the elastic characteristics (Yung's modulus) of cream-like phantoms and sam-ples containing pus. The measurements were carried out using an ultrasound tomograph of an expert class Supersonic Aixplorer at the Privolzhsky District Medical Center (POMC) using the Supersonic Shear Imaging (SSI) technology.





From the results obtained, it was concluded that viscous inclusions, on the one hand, correlate with elastic characteristics (on the example of samples with pus), although, on the other hand, the example of measuring cream-like phantoms shows that additional studies are required.

References

1. Ultrasound in medicine. Ed. K. Hill, J. Bamber, G. ter Haar. M.: //Fizmalit, 2008.
2. Zhdanov A.G., Pyatakov A.P. Measurement of dynamic viscosity of liquid on damping of tuning fork oscillations // Physical education in universities. 2002, T. 8, No. 4, P. 117-126.

Numerical simulation of nonlinear acoustic waves in a medium with a power-law dependence of the absorption coefficient on the frequency

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The process of propagation of an intense ultrasonic wave is described by the evolution equations. At high coefficients of nonlinearity of the medium, wave propagation is accompanied by their intense self-action, which leads to distortion of the wave profile.

In this paper, we consider numerical modeling of the evolution equation of propagation of nonlinear acoustic waves-the burgers equation (given for a one-dimensional problem in a dimensionless form) [1]

$$\frac{\partial U}{\partial z}-\frac{\partial G(U)}{\partial \tau}=L\left(\frac{\partial}{\partial \tau}\right)U \qquad (1)$$

For media with quadratic nonlinearity $(G(U))=U^2$ and attenuation $L=\mu \partial^2 U / \partial \tau^2$ spectral scheme for solving equation (1) for the nonlinear wave spectrum C(ω,z):

$$C(w,z+\Delta z)=C(\omega,\ z)-i\omega\frac{1}{2}\Delta z F\left(\left[F^{-1}\left(C(\omega,\ z)\right)\right]^2\right)-\mu\omega^2\Delta z C(\omega,\ z) \qquad (2)$$

To implement the solution scheme (2), a program was written in the Python programming language using standard library functions.

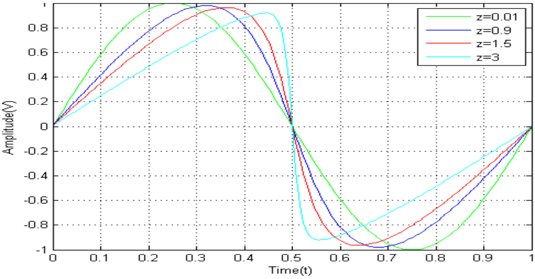

Fig.1. Evolution of the initial sinusoidal wave profile in a medium with quadratic nonlinearity and attenuation μ=0,1.

In this case, the original sinusoidal signal, as it propagates (z increases), not only acquires a sawtooth shape, but also there is a gradual decrease in the amplitude. With further propagation, the nonlinear effects will begin to weaken.

References

1. S.N. Gurbatov, O.V. Rudenko, A.I. Saichev. Waves and Structures in Nonlinear Nondispersive media. General Theory and Applications to Nonlinear Acoustics. Springer and Higher Education Press, 2011, -500 p.

The iterative method for obtaining the height-temperature profile of the solar atmosphere over an active regions on the Sun

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Many works were devoted to the attempts of the reconstruction a model of the atmosphere over the sunspots. In several papers the models were developed based on spectra of extra-ultraviolet and X-ray emission, with focus in these models being given to photosphere [1, 2]. There were several papers in which the atmosphere above the sunspots was investigated in microwave range because it has some advantages in comparison with X-ray and ultra-violet ranges [3, 4]. In the paper [5] the iterative method for the reconstruction of the temperature vs. height dependency was developed.

In this work this method was significantly renovated. The objective of the work was to develop an iterative method for modelling the radiation spectrum of the sunspot and obtaining the height-temperature profiles of the solar atmosphere from comparison of modelled and real spectra. The spectra used by us as input data was obtained on the radio telescope RATAN-600 on the frequencies of 3-18 GHz. There were chosen two active regions and comparison of the real and modelled spectra was conducted. It is shown that the discrepancy between real and modelled spectra is about 2-3% and we can conclude that the method can be successfully used for the reconstruction of the solar atmosphere parameters.

References

1. Fontenla J., White O.R., Fox P.A., Avrett E.H., Kurucz R.L. // Astrophys. J. 518, 480 (1999).
2. Avrett E., Tian H., Landi E., Curdt W., Wülser J.-P. // Astrophys. J. 811, 87 (2015).
3. Alissandrakis C.E., Kundu M.R., Lantos P. // Astron. Astrophys. 82, 30 (1980).
4. Kaltman T.I., Kochanov A.A., Myshyakov I.I., Maksimov V.P., Prosovetsky D.V., Tokhchukova S.K. // Geomagn. Aeron. 55, 1124 (2015).
5. Stupishin A.G., Kaltman T.I, Bogod V.M., Yasnov L.V. // Solar Phys. 293, 13 (2018).

Numerical modeling of behavior of skeletal muscle under a variety of external stresses

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Muscle contraction is a vital function of the body. Skeletal muscles largely determine the process of vital activity of the entire human body. It is main functions are mechanical. Muscle diseases in most cases are associated with changes in mechanical characteristics. In this regard, the prediction of dynamic and kinematic characteristics has great potential in the diagnosis of pathologies and in assessing the condition of people experiencing extreme loads.

In the work by O.V. Rudenko, A.P. Sarvazyan [1] the nonlinear system of equations (1) for studying and modeling of shock and impulse impact on the muscle was formulated, which is the modernized model of Descherevsky.

At numerical modeling of shock impulse influence on a muscle the program on solution of system of nonlinear differential equations (1-3) by means of Runge-Kutt method has been realized. The modeling was carried out for the tailor frog muscle, the program is written in the Python programming language.

System equations (1)

$$\frac{dn}{dt} = (k_1 a_0 \beta) l - k_1 (n + m) - \frac{1}{\delta} n \frac{dl}{dt} \qquad (1)$$

$$\frac{dm}{dt} = -k_2 m + \frac{1}{\delta} n \frac{dl}{dt} \qquad (2)$$

$$P = f(n - m) \qquad (3)$$

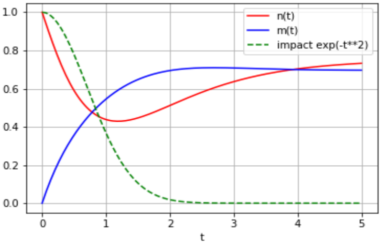

Fig. 1. Results of modeling muscle behavior under influence in the form of Gaussian impulse.

Fig. 1 shows that the number of pulling bridges (n(t)) for a relaxed muscle starts to decrease sharply - this leads to an increase in the number of pulling bridges (m(t)) and then, when the impact stops, n and m go into stationary mode.

References

1. O.V. Rudenko, A.P. Sarvazyan // Acoustical Physics. № 6. 2006. P. 833.

The numerical model of the discharge activity between isolated conductive zones on the insulator surface

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The work considers partial discharge activity on the insulator surface that happens between isolated conductive zones. When high-voltage equipment is exposed to climatic conditions, such as rain or fog, either water films on the entire surface (for hydrophilic material) or drops and conductive zones (for hydrophobic material) appear on the insulation surface. The field increases significantly at the water edges and this can lead to discharge activity, namely, partial discharges.

A discharge is characterized by the magnitude of the apparent charge passing through the system when the conductive zones short out with a spark. The present work shows how various configurations of conductive zones affect the mean interzone electric field and the apparent charge.

The research is carried out with the help of computer simulation using Comsol Multiphysics software package. The results show that the characteristic apparent-charge value indicates the state of the insulator surface.

Research of subthreshold laser-initiated microwave discharge in supersonic airflow

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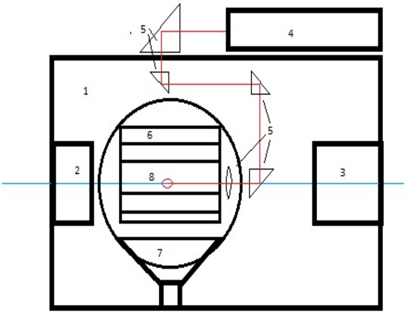
The possibility of applying laser radiation with an intensity below the breakdown threshold (~ 106 V/cm) to initiate microwave discharge in a supersonic airflow is being investigated in the pressure range of 40-760 Torr. The experimental setup [1] uses a microwave generator based on a Mi-505 magnetron (9.6 GHz; 200 kW) with a pulse duration of 0.5-3 μs, a two-pulse Nd: YAG laser EverGreen - 145 (532 nm; 145 mJ) with a pulse duration of 6 ns, and a supersonic ejector-type wind tunnel. The quasi-optical focusing system provides a microwave field strength in focus up to 3.6 kV/cm. Registration of discharges and gas-dynamic processes are performs by a high-speed camera with a resolution of 1024×1024 points, and a shadow system based on the IAB-450 device. The main goal of the experiment is to determine the minimum values of the energy and duration of the laser energy input, which ensure the excitation of microwave breakdown of air at different pressures. The experimental results can be of practical interest, for example, in the problem of controlling the aerodynamics of hypersonic aircraft [2].

Fig. 1. Experimental setup scheme: 1 – wind tunnel; 2 – nozzle; 3 – diffuser; 4 – two-pulse laser; 5 – optic system; 6 - quasi-optical focusing system; 7 - microwave supply; 8 – microwave and laser focus area.



Acknowledgments. This work was supported by RFBR grant 18-08-00707.

References

1. Khoronzhuk R.S., Karpenko A.G., Lashkov V.A., Potapenko D.P., Mashek I.C. Microwave discharge initiated by double laser spark in supersonic airflow // J. Plasma Physics, Vol. 81, No. 03, June 2015.
2. Knight D., Kolesnishenko Y.F., Brovkin V., Khmara D. 46th AIAA Aerospace Sciences meeting and Exhibit // High Speed Flow Control Using Microwave Energy Deposition. Reno, Nevada. 2008. pp. AIAA 2008-1354.

Determination of the elastic characteristics of a skeletal muscle phantom using shear wave elastography

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The point shear wave elastography (pSWE) method is used in ultrasound medical diagnostics for qualitative and quantitative analysis of the elastic properties of tissues. In the pSWE method shear waves are generated by the action of a strong focused ultrasonic pulse on the medium. In this method an intense short acoustic pulse is focused into the medium within one ultrasound ray and creates a sufficiently high radiation pressure there. The energy of this pressure is transferred to the environment and shear waves arise in it and propagate in the investigated soft biological tissue [1]. O.V. Rudenko [2] proposed a string model of skeletal muscle: a thin-layered medium was simulated by periodically alternating layers of thickness h_1 and h_2, the shear elasticities and densities of which were equal to μ_1, ρ_1 and μ_2, ρ_2, respectively. The equations of motion for such a medium were obtained and the shear wave velocities along and across the direction of propagation of the shear wave (position of the ultrasonic sensor) were determined.

$$C_{PAR} = \sqrt{\frac{h_1\mu_1 + h_2\mu_2}{h_1\rho_1 + h_2\rho_2}} \quad C_{ORT} = \sqrt{\frac{\mu_1\mu_2(h_1+h_2)^2}{(\mu_1 h_1+\mu_2 h_2)(h_1\rho_1+h_2\rho_2)}} \qquad (1)$$

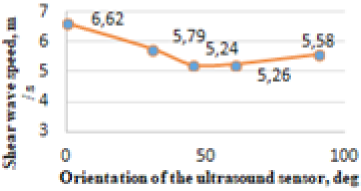

Fig.1.Shear wave velocity versus ultrasound probe orientation

The string model needed to be compared with the experimental results, therefore, the study of the shear properties of skeletal muscles on the Verasonics multichannel acoustic system (Verasonics Inc., USA) became an important stage in the development of the string model. For the experiments a muscle phantom was created with a 10 × 10 matrix of stretched fluorocarbon lines (diameter 0.12 mm) filled with a 7.5% gelatin gel. The picture shows the average values of the shear wave velocity in a string phantom depending on the position of the sensor relative to the fibers. The difference in the values of the velocity and shear modulus along and across the fibers was recorded. The values measured at angles of 30º, 45º, 60º to the fibers and measured across were similar.

References

1. Khalitov R.Sh., Gurbatov S.N., Demin I.Yu. // Physics of Wave Phenomena. № 1. 2016. P. 73.
2. Rudenko O.V., Tsyuryupa S.N., Sarvazyan A.P. // Acoustical Physics, V.62, № 5. 2016. P. 608-614.

F. Optics and Spectroscopy

Ozone adsorption on TiO_2: experiment and DFT calculation

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Despite the great importance of ozone for ecology and industry, the mechanism of its adsorption and decomposition in surface reactions is not clear. To find out the way of its interaction with TiO_2 we have studied adsorption of O_3 isotopic mixtures by means of FTIR spectroscopy at 77 K and DFT calculation.

The band of $\nu_1+\nu_3$ combination mode of chemisorbed ozone was found to split into 8 peaks (Fig. 1), indicating symmetry lowering on interaction with surface site. Calculation of O_3 complex with TiO_2 molecule as a simplest fragment of the solid has shown that ozone forms a complex bound to Ti atom by one of terminal oxygen atoms. The calculated vibrational frequencies of certain identified isotopomers are close enough to the positions of band maxima.

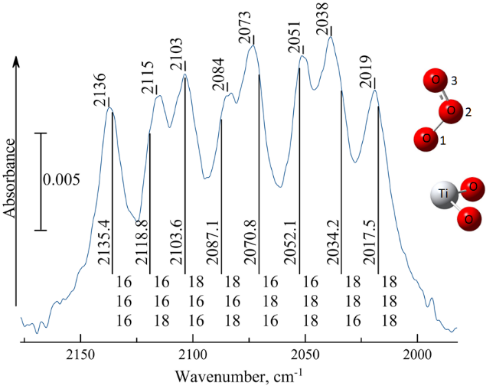

Fig. 1. Experimental spectrum (solid curve) and calculated wavenumbers (vertical lines) of model structures, shown in the scheme, with different isotopic content.

Having the frequencies of $\nu_1+\nu_3$ combinations and the observed positions of ν_1 band it was possible to calculate the values of ν_3 vibrations, which form as expected a group of four unresolved doublets as earlier observed for CeO_2, but closed by bulk absorption of TiO_2.

The obtained results can be used in the experiments of resonant excitation of certain ozone isotopomers to initiate isotopically selective reactions.

Acknowledgment. I would like to thank the Computing Center of Research park of St. Peterburg State University for the computing power provided, Irina Krauklis for support in the calculations. The work was supported by RFBR and CITMA, grant No. 18-53-34004.

References

1. K.M. Bulanin, J.C. Lavalley, A.A. Tsyganenko // J.Phys.Chem. 99 (1995) 10294.
2. R. Kevorkyants, Y.V. Chizhov, K.M. Bulanin // Langmuir 36 (2020) 1930.

Isotopic isomerism of adsorbed CO. DFT calculation

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FTIR spectra of CO adsorbed on reduced Ni-containing USY zeolites with Si/Al = 30 show the formation of mono-, di-, and tricarbonyls with Ni^+ centers. Small width of CO stretching bands, with FWMH ~ 1-1.5 cm^{-1} enables us to resolve the band splitting for isotopically mixed dicarbonyl species, due to nonequivalent positions of two CO molecules. As a result, the dicarbonyls exist in two isomeric forms differing in localization of isotopically substituted atoms [1]. This phenomenon, called by us "isotopic isomerism", can be explained either by linkage isomerism, when one molecule is bound via C, and another -via O atom, or by dissimilarity of local environment of molecules in the framework of zeolite.

This effect has been modeled using quantum mechanical DFT calculations.

Table 1. Experimental and calculated data for Ni dicarbonyls in zeolite.

x/y	νCO, cm^{-1}			
	exp. [1]	calc. I	II	III
12/12	2097	2096	2090	2086
	2141	2141	2149	2151
12/13	2065	2056	2043	2039
	2124	2133	2147	2151
13/12	2060	2069	2082	2085
	2129	2120	2107	2103
13/13	2050	2049	2042	2039
	2092	2093	2099	2102
E, kJ/mol		130	-186	-282
Scaling coeff.		1.0249	1.0309	1.0242

The table shows experimental CO band positions and those for three calculated model structures for isotopically mixed Ni+(xCO)(yCO) dicarbonyls. In structure I both the molecules are in sodalite cage, in II one molecule is in sodalite cage, while another is linked to nickel from hexagonal prism via carbon, and in III – via O atom.

The presented data show that i) 13C substitution in positions x and y leads to different results, thus demonstrating isotopic isomerism; ii) the most favorable is structure I, which besides the minimum total energy, better reproduces experimental νCO values.

Acknowledgments. The work was supported by RFBR and CITMA, grant No. 18-53-34004

References

1. R. Belykh, F. Mauge, A. Tsyganenko // Applied Catalysis A. 583 (2019) 117140.

Online tumor margins control via near-infrared fiber optic probe: towards the cancer surgery enhancement

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While cancer surgery is the most common method of solid tumor treatment, there is no convenient tool for accurate online tumor margins assessment by a surgeon [1]. Resecting a tumor, the surgeons mostly rely on their experience; a histological analysis of the excised tumor fragments is generally performed after the surgery. Thus, if the tumor was not completely removed, or, in the other words, the tissue fragment margins are positive for cancer cells, a re-excision surgery is inevitable. The lack of fast and reliable tumor margins assessment method results in extra loading on hospital resources and in higher risk of side effects associated with surgery and anesthesia. Besides, a patient's moral state could be negatively affected; some people tend to choose radical surgery (e.g., mastectomy) as more "certain", even if organ-conserving treatment is available as an option.

Recently, various spectroscopic methods have been extensively studied for tumor margins assessment [2]. Due to the different metabolic processes, occurred in tumor and normal cells, it is possible to distinguish them by specific spectral features (light scattering, peak intensities, etc.). In our work, a near-infrared (940-1800 nm) fiber optic probe coupled with portable spectrometer has been applied for tumor distinction *in vivo* and *in vitro* from normal and pathologically changed benign tissues (e.g., hyperplasia) on various carcinogenesis animal models and on tissue fragments obtained from real patients with cancer. In combination with several multivariate data analysis algorithms, this easy-to-use approach demonstrates promising results in tumor cells distinction with the evaluated limit of detection equal to $3x10^3$ cell units.

References

1. M.S. Moran et al. // Ann. Surg. Oncol. 2014, V. 21 P. 704.
2. V.R. Kondepati et al. // Anal. Bioanal. Chem. 2008, V. 390 P. 125.

Complexation of phosphonic acids: Self-association and hydrogen-bonding with nitrogen bases

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One of the most promising classes of materials for polymer electrolyte membranes (PEMs) is based on polymers containing either phosphonic acid residues, $–PO(OH)_2$ [1], or their combination with heterocyclic nitrogenous base residues [2]. In such materials the protons are transported via a network of OHO and OHO/OHN hydrogen bonds. This work is devoted to the determination of the structure and NMR spectral manifestations of hydrogen bonds in complexes formed by model phosphonic acids either in self-associates (OHO bonds) or in acid-base complexes with nitrogen bases (OHO/OHN bonds).

In the first part of the work we report the results of experimental low-temperature (down to 100 K) liquid-state ^{1}H and ^{31}P NMR study of self-association of *tret*-butylphosphonic acid, *t*BuPO(OH)$_2$, in polar aprotic mixture of liquefied freonic gases, CDF_3/CDF_2Cl. For the first time we prove the formation of tetrahedral tetramers (see scheme in Fig. 1, left; *t*Bu substituents are omitted for clarity) held by eight medium-strong OHO hydrogen bonds.

In the second part of the work we present the results of a computational study of a series of complexes formed by several phosphonic acids, with substituted pyridines (see examples in Fig. 1, center and right). Effects of complex's stoichiometry and structure, as well as bridging proton position in individual hydrogen bonds on ^{1}H and ^{31}P NMR chemical shifts are discussed.

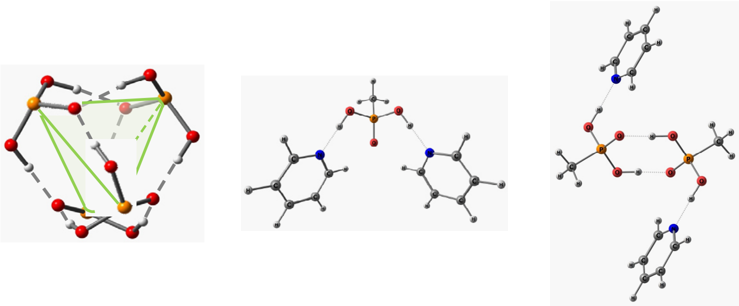

Fig. 1. General view of phosphonic acids complexation.

Acknowledgments. This work has received financial support from the RFBR grant 19-33-90047.

References

1. G. Brunklaus et al. // J. Phys. Chem. B, 113, 6674 (2009).
2. I. Dimitrov et al. // J. Membrane Sci., 450, 362 (2014).

Resonant behavior of the plasma electron component and stratification of a discharge in inert gases

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Stratification of classical glow discharge is one of the fundamental problems in the physics of nonequilibrium plasma, which has been the subject of hundreds of papers over the past decades. Striations are an example of the self-organization of a discharge in the form of ionization waves propagating along the positive column. Recently, significant advances have been made in understanding the stratification mechanism based on the use of nonlocal electron kinetics in spatially periodic sinusoidally modulated inhomogeneous fields.

In this work, we develop a dynamic approach [1, 2] to the analysis of the phase trajectories of electrons. The behavior of the electron component of the plasma is analyzed during energy gain up to the excitation threshold in the absence of elastic impacts. In the kinetic theory, this case is ignored, since the distribution functions are reproduced from period to period, and there is no dissipation. From dynamics, this case is most important, since the spatial scale of the periodic field appears, which is responsible for integer and non-integer resonances. An interpretation of the experimentally observed S-, P- and R-striations is proposed as the fundamental resonance, the second harmonic, and a non-integer resonance corresponding to 2/3 of the fundamental resonance. The dynamic approach eliminates the main difficulties of the kinetic theory associated with the large length of the spatial settling of the distribution function, much exceeding the length of the positive column. The role of small energy losses in elastic collisions is analyzed. The dynamic approach eliminates the main difficulties of the kinetic theory associated with the large length of the spatial settling of the distribution function, much exceeding the length of the positive column. The role of small energy losses in elastic collisions is analyzed. It is shown that in this case the phase trajectories contract to attractors, which in the kinetic theory correspond to resonance trajectories.

References

1. Y. Golubovskii, E. Pelyukhova, F. Sigeneger, V. Nekuchaev // Phys.Plasmas 22, 032105 (2015).
2. Y. Golubovskii, S. Valin, E. Pelyukhova, V. Nekuchaev, F. Sigeneger // Phys. Plasmas 23, 123518 (2016).

Quantum chemical investigation of electronic structure of selenocysteine as a model of antioxidant enzyme glutathione peroxidase in redox reactions

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Selenium is one of the essential micronutrients for a human body. Its deficiency or consumption without medical supervision may lead to serious health problems. Selenium is present in the active sites of proteins (selenoproteins) in the form of one or more residues of selenocysteine (an amino acid that differs from cysteine by replacing the sulfur atom with selenium). Functions of selenoproteins vary significantly. For example, one of selenoprotein families – gluthathione peroxidases GPx – are catalysts for the reduction reaction of hydrogen peroxide to water [1]. The details of its catalytic mechanism remain poorly investigated. In literature a few possible catalytic mechanisms based on experimental observations and common chemical intuition are discussed [2].

This work is dedicated to quantum-chemical investigation of selenocysteine fragments in order to model the potential mechanism of catalytic reactions involving glutathione peroxidase enzyme. We studied the features of the electronic shell of a selenium atom by classical mapping methods: MESP and ELF, which can clarify the most probable directions for nucleophilic attack of peroxide. Moreover, we have calculated a selenium chemical shift, the obtained results uncover a dramatic change of its value during the oxidation cycle. The calculations were performed using Gaussian software package, with a quite high level of theory: CCSD for geometry optimisation and MP2 for NMR parameters calculations with appropriate basis sets.

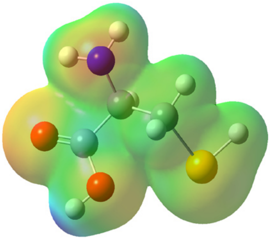

Fig. 1. Isosurface of electron density (isovalue =0.01) mapped with MESP for selenocysteine.

References

1. R. Brigelius-Flohé, M. Maiorino // Biochim. Biophys. Acta., v. 1830, № 5, p. 3289-3303 (2013).
2. B.K. Sarma, G. Mugesh // Org. Biomol. Chem., № 6, p. 965-974 (2008).

Evolution of the band contours in the absorption spectra of SF_6 during phase transitions

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The experimental results on the IR spectra of crystalline thin (4-5 μm) films and liquid in a thin layer (90 μm) of SF_6 in the region of combinational modes are presented. The main goal of the study is to obtain an overall picture of the changes in the band contours upon phase transitions. Three different types of contour behaviour upon phase transitions were found (Fig. 1). The different behaviour of the studied bands is explained by basic mechanisms of band formation, such as resonant dipole-dipole (RDD) interaction and hindered rotation motion. The contributions of these mechanisms were estimated using the apparatus of spectral moments [1].

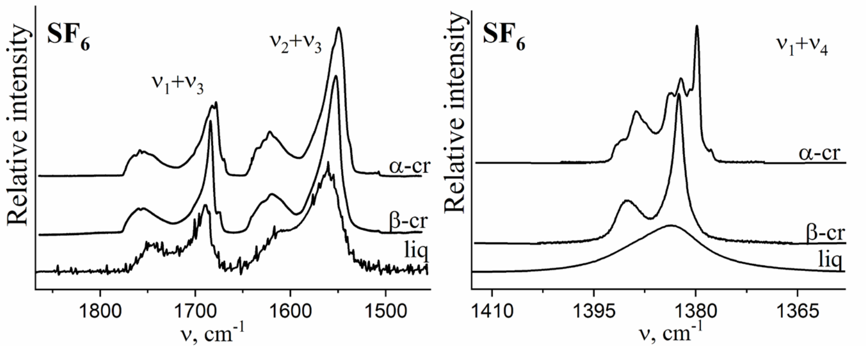

Fig. 1. The band contours of the $\nu_1+\nu_3$, $\nu_2+\nu_3$ bands and $\nu_1+\nu_4$ band in the IR spectra at different phases.

Acknowledgments. The work was supported by the RFBR No. 19-33-90073. The experiment was performed at the center for Geo-Enviroment Reseach and Modeling (GEOMODEL) of Research park of St. Peterburg State University.

References

1. T.D. Kolomiitsova, A.P. Burtsev, V.G. Fedoseev, D.N. Shchepkin // Chem. Phys., v. 238 p. 315–327 (1998).

The study of non-covalent interactions involving models of modern volatile anesthetics by quantum-chemistry calculations and NMR spectroscopy

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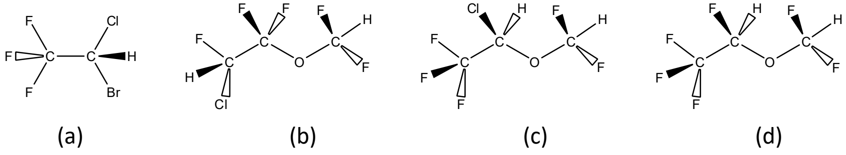
Among the safest and most effective general anesthetics are halothane, enflurane, isoflurane, desflurane (Fig. 1), which are used to induct or maintain anesthesia. Anesthetic effect is based on binding of these molecules to protein targets (such as gamma-aminobutyric acid receptor, GABAA), presumably by forming various non-covalent interaction. However, physicochemical process of binding to target molecules is still poorly understood [1].

Molecule of anesthetics contains C–H and C–Hal groups (Hal = F, Cl, Br), which makes it possible to form one or more hydrogen and halogen bonds [2]. Besides, these bonds could be cooperatively/anti-cooperatively coupled and affect for formation and properties of each other.

In this work, we use quantum-chemical calculations to study the 1:1, 1:2 and 1:3 intermolecular complexes formed by the C-Hal group of model molecules CH_3Cl and CF_3Cl with hydrogen and halogen bond donors (primarily HF and FF molecules). The coupled non-covalent bonds in these complexes were characterized by complexation energies, interatomic distances and NMR chemical shifts of the atoms involved in bond formation. The calculated spectroscopic parameters are compared with experimental ones, measured for halothane dissolved in solvents with various proton/halogen accepting abilities.



(a) (b) (c) (d)

Fig. 1. Structural formulas of halothane (a), enflurane (b), isoflurane (c), desflurane (d).

Acknowledgments. This work was supported by RFBR grant 20-03-00536.

References

1. S.M. Melikova, K.S. Rutkowski, M. Rospenk // Spectrochim. Acta A, 2019, 223, 117363.
2. A.S. Ostras’, D.M. Ivanov, A.S. Novikov, P.M. Tolstoy // Molecules 2020, 25, 1406.

Magneto-optical effects in hyperbolic metamaterials based on Au/Ni nanorods' arrays

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Hyperbolic metamaterials (HMMs) are highly anisotropic uniaxial structures where permittivity and/or permeability tensor components are of opposite signs [1]. Along with the hyperbolic dispersion law, the HMMs possess two important spectral features: the sign reversal (Epsilon-Near-Zero, ENZ) and the appearance of a pole (Epsilon-Near-Pole, ENP) of the real part of the effective permittivity components [1]. It leads to a vast potential of HMMs for the observation of interesting optical phenomena and their applications in nanophotonics. Additional functional properties of the HMMs can arise if a structure contains a gyrotropic material, thus allowing magnetic field control over the «light-HMM» interaction [2]. Here we perform the magneto-optical spectroscopy of HMMs based on ordered arrays of Au nanorods with nickel segments with the emphasis on the spectral vicinity of the ENZ and ENP features.

Samples were prepared by templated electrodeposition of gold and nickel inside the porous anodic alumina. The diameter of Au nanorods coincides with the pore diameter 21 ± 2 nm, their length being 188 ± 8 nm, and the volume fraction of metal in the Au/AAO nanocomposite is about 10%, the length of Ni segments is 70 ± 3 nm. Numerical studies indicate that the ENP and ENZ features are at 520 nm and 780 nm, thus the samples possess the hyperbolic dispersion at $\lambda > 780$ nm. Magneto-optical properties of the HMMs were studied in the geometry of Voight and Faraday effects at various angles of incidence of the probing radiation. We measured the values of magnetic contrast of transmission, while DC magnetic field of 3 kOe was applied to the sample. An enhancement and sign reversal of the magnetic contrast in the spectral vicinity of the ENP and ENZ points was detected. Near the ENP this increase is due to the localization of the electromagnetic field of pump radiation within the structure while near the ENZ the spectral behavior of magnetic contrast is caused by the strong anisotropy of the optical properties of the HMM and giant birefringence.

Acknowledgments. The work was supported by RFBR grant 18-02-00830_a and the Foundation for the advancement of theoretical physics and mathematics "BASIS".

References

1. A. Poddubny, I. Iorsh, P. Belov, Y.Kivshar // Nature Photon., v. 7, p. 948–957, (2013).
2. I.A. Kolmychek, A.R. Pomozov, A.P. Leontiev et al. // Optics Letters., v. 43, № 16, p. 3917–3920, (2018).

IR spectroscopic study of photostimulated CO desorption on the TiO_2 surface

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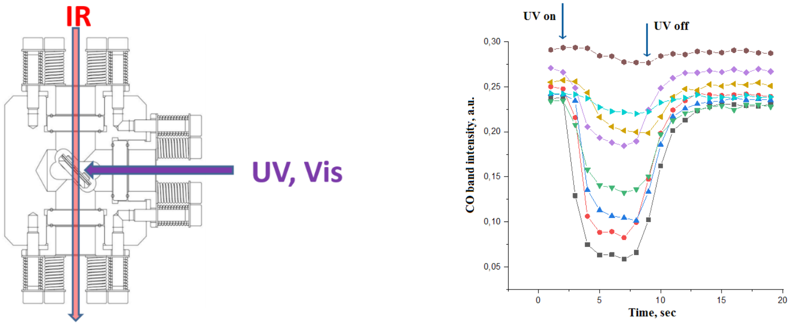
In situ IR spectroscopy is a very suitable method for studying non-stationary processes, including photoprocesses on the surface of photoactive materials [1, 2]. In our work, this technique was applied to examine the process of desorption of carbon monoxide molecules adsorbed on the titanium dioxide surface upon UV irradiation. The obtained data are very important for understanding the mechanisms of such surface processes involving photogenerated carriers as photosorption-photodesorption, photostimulated hydrophilicity, and photoreactions.

The home-made transmission-mode IR cell with dual-beam configuration was used for *in situ* experiments (Fig. 1a). The configuration and operation of the device are presented. The obtained spectroscopic data on photoactivated desorption of carbon monoxide at ambient temperature from the dehydrated TiO_2 surface are presented and analyzed. Fig. 1b shows the kinetics of the intensity changes for the adsorbed CO band during "on-off" experiments with UV irradiation of different light densities. In conclusion, two plausible mechanisms of observed phenomenon are discussed.



a ***b***

Fig. 1. (a) The horizontal cross section of bottom part of IR cell. (b) Changes of the band intensity of CO adsorbed on TiO_2 surface during photoexperiments.

References

1. K.M. Bulanin, D.W. Bahnemann, A.V. Rudakova // Rev. Sci. Instrum., 90, ID 105113, 8 p. (2019).
2. P. Pichat // Catal. Today, v. 224, p. 252-253 (2014).

Gires-Tournois interferometer with a quantum well mirror

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Gires-Tournois interferometers are generally used for chromatic dispersion compensation in lasers as the phase of reflected light is wavelength dependent. Their design is analogous to one of Fabry-Perot's, however they operate in reflection and have a highly reflective second mirror. In this work we investigate a heterostructure of a similar configuration: a thin film consisting of three layers with the first layer's surface being a partially reflective mirror and a quantum well (QW) functioning as a second non-ideal mirror.

Excitonic response observed in reflectance spectra of the structure is dependent of the phase change of reflected light, radiative Γ and non-radiative dampings γ [1]. The ratio of dampings can be tuned by pumping the structure with red light or varying the temperature of the sample (i.e. Fig. 1). Satisfying certain conditions for Fresnel reflection coefficient r one may experience the "absence" of the excitonic response in a spectrum so QW functions as an ordinary mirror however saving abnormal non-linear phase shift Φ arising from it thus allowing us for additional dispersion control.

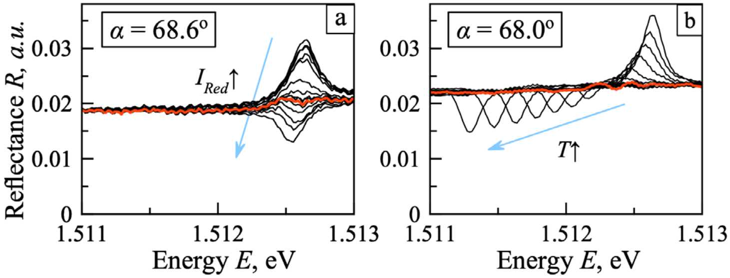

Fig. 1. Experimental reflectance R spectra of $In_{2.5\%}GaAs/GaAs$ *QW structure with QW layer 2 nm thick and first layer 295 nm thick* ($\lambda+\lambda/4$) *at different (a) pump intensities* I_{Red} *of red light (at 10 K) and (b) at different temperatures T from 10 up to 40 K. The spectra of red color are shown at near like conditions of observable "absence" of excitonic response.*

Acknowledgments. The work was carried out at SPbU resource center "Nanophotonics" with the support of Russian Foundation for Basic Research (RFBR 20-32-70163).

References

1. E.L. Ivchenko. Optical Spectroscopy of Semiconductor Nanostructures // Alpha Science International Ltd., ISBN: 1-84265-150-1, (2005) -350 p.

Angular determination algorithm development for autocollimation systems with trihedral reflectors with cylindrical surface

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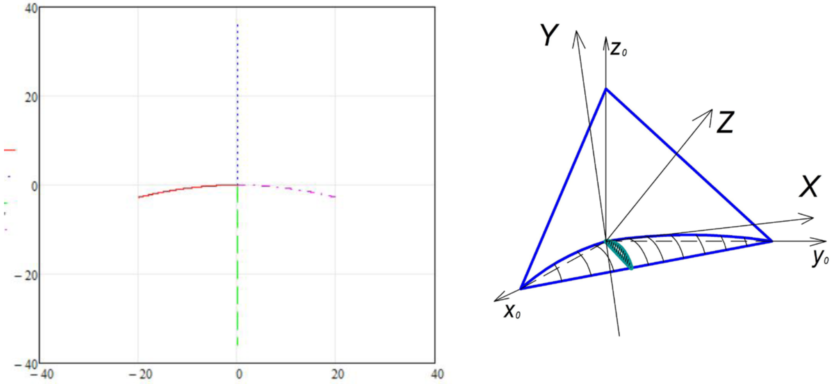
Autocollimation systems are used to measure bearing construction element's deformations, to navigate air, water or space docking crafts, for bend angle determination of tower-type engineering structures. Usually flat mirror is used as an autocollimation systems reflector, but in this case it is impossible to measure angle of rotation about normal. For this purposes trihedral reflector with cylindrical surface can be used [1]. This type of reflector, creates an image (Fig. 1) which parts change their angle due to reflector's angle of rotation. For example, if reflector is tilted about Z axis, image will rotate to the same angle as the reflector, if it's tilted about Y axis, horizontal curve will rotate to angle, proportional to the square root of the rotation angle. This fact justifies the need of angular determination algorithm development for curves on the image.



a *b*

Fig. 1. a) Image from trihedral reflector; b) Trihedral reflector's coordinate system.

References

1. Mikheev S.V. Optical-electronic system for real-time position control of roof's supporting structure / S.V. Mikheev, I.A. Konyakhin, I.S. Stepashkin, A.V. Petrochenko // Proceedings of SPIEE. – 2016. – Vol.9899. – pp.989934
2. Konyakhin I.A., Renpu L., Smekhov A.A., Kleshchenok M.A. Trihedral Reflectors for Three-Axis Angular Autocollimation Measurements // Latin America Optics and Photonics Conference, LAOP 2014, 2014, pp. LTh4A

Resonance IR photochemistry of adsorbed molecules

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Resonance excitation of vibrational states has attracted much attention of specialists for almost 50 years, mainly because of the hope for a selective effect on certain isotopic compounds in order to develop a method for isotope separation [1].

Studies of various surface processes induced by infrared laser radiation demonstrate a real resonant nature of the effect, which occurs only when irradiated in the absorption bands of the studied compound, but the expected isotope selectivity has never been observed, apparently as a result of a relatively fast energy exchange and transfer to other species. Time-resolved spectroscopy and band shape analysis provide data on the energy and phase relaxation of vibrational excitation. Resonant dipole-dipole interaction between adsorbed molecules is a direct energy transfer channel in the adsorbed layer.

Experiments were carried out to start the process of decomposition of adsorbed ozone and its isotopic mixtures by infrared laser radiation on the surface of titanium and cerium oxides with control over the reaction by IR spectra.

Acknowledgments. The work was supported by the RFBR, grant 19-33-90296.

References

1. A.A. Tsyganenko, T.N. Kompaniets, R.G. Novikov, O.S. Pestsov // Curr. Opin. Chem. Eng., v. 24, p. 69–78 (2019).

Combined spectroelectrochemical cell for photoelectrochemical experiment

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Raman-shift spectroelectrochemistry is a precise combined analytical method. It provides an impressive opportunity for biochemical and electrochemical research of various systems, such as polymer-modified electrodes, nuclear acids and other systems, requiring precise qualitative and quantitative analysis. Another advantage of spectroelectrochemical instruments is the probability of in-situ analysis of the electrode and solution during the electrochemical process. Nevertheless, some of existing problems of the method are not yet solved:

- No opportunity to study processes, requiring irradiation of the electrochemical cell. In different fields of research, such as photoelectrochemistry [1], photocatalysis [2], the irradiation of the cell and the electrode is needed. However, the fact of irradiation itself prevents us from this. It means, that processes such as this could not be studied by means of standard spectroelectrochemical procedure.
- All existing hardware design contains potentiostat or requires using certain potentiostat specifically. It means that researcher can not use the device, which is more convenient for the situation being studied instead of suggested.

Existing devices provide continuous registration of the specter during the electrochemical experiment. The proposed scheme assumes short impulses of the irradiation, while which the photometric data is not being collected. The short length of impulse let us to carry the in-situ analysis of nonstationary photoinduced processes (the process is in a sense similar to differential pulse voltammetry. Another part of the solution is to use the modular scheme of the arrangement of the instrument, which allows the researcher to use electrochemical apparatus needed for the certain situation.

The solution will facilitate the photoelectrochemical research, but requires some fundamental research and development work to be done.

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References

1. Dr. Alexander S. Konev, Mikhail Yu. Kayumov, Dr. Mikhail P. Karushev, Yuliia V. Novoselova, Daniil A. Lukyanov, Dr. Elena V. Alekseeva, Dr. Oleg V. Levin // ChemElectroChem, 5, 3138-3142 (2018).
2. Dechao Chen, Prof. Dr. Aixiang Wang, Prof. Dr. Mark A. Buntine, Dr. Guohua Jia // ChemElectroChem, 6 4709-4724 (2019).

A study of CO adsorption on CaY zeolite by DFT calculation

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FTIR spectra of CO adsorbed on Ni-containing USY zeolites show the formation of mono-, di-, and tricarbonyls with Ni^+ cations, characterized by one, two or three well resolved bands which shift in a certain way on ^{13}C substitution [1]. In earlier studies of linkage isomerism of CO adsorbed on CaY zeolite [2, 3] adsorption of two molecules on the same cation was manifested in a shift of CO stretching band with coverage, which does not split in two maxima as expected for the dicarbonyl. Band assignment in the spectra of adsorbed ^{12}CO-^{13}CO mixtures faced some difficulties. For better understanding the experimental results we have carried out a DFT calculation of one or two CO molecules interacting with Ca cation in a cluster modelling a fragment of zeolite framework. The calculated frequency values compared with those observed experimentally in [2, 3] are presented in Table 1. The calculated values of harmonic frequencies were multiplied by scaling coefficients different for C- or O- bonded molecules.

Table 1. Experimental and calculated frequencies for Ca^{++} carbonyls in Y zeolite.

	^{12}CO	$O^{12}C$	^{13}CO	$O^{13}C$
exp. cm^{-1}	2197	2094	2150-2149	2048
calc. cm^{-1}	2198,5	2094,0	2149,2	2047,2
	$^{12}CO^{12}CO$	$^{12}CO^{13}CO$	$^{13}CO^{13}CO$	$^{12}CO^{12}OC$
exp. cm^{-1}	2191	2191	2142-2140	2211?; 2099
calc. cm^{-1}	2197,5; 2188,9			2189,9; 2101,3

Analysis of the obtained results demonstrates a good agreement between the observed and calculated values and shows that due to weaker interaction between the two molecules in dicarbonyls the splitting is small and the second band of CO vibration coincides with that of monocarboonyl. Assignment of a shoulder at 2211 cm^{-1} to C-bonded molecule in dicarbonyl structure, proposed in [3], does not agree with the calculation.

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References

1. R. Belykh, F.Mauge, A.Tsyganenko //Applied Catalysis A. 583 (2019) 117140.
2. A. Tsyganenko, P. Storozhev, C. Otero // Areán. Kinet. Catalysis, 45 (2004) 530.
3. A.A. Tsyganenko. In: Aspects of the Surface Chemistry of Oxidic Systems. Proc. Symp. in Honour of E. Escalona Platero. Torino. 1999, p. 51.

Optical spectroscopy of chitin-based metal-dielectric microstructures

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Optics of spatially periodic media is the object of close attention of researches. In last few decades, active interest to such structures is associated with the studies of photonic crystals (PhC), that possess the period of the structure comparable with the wavelength of light. The main feature of photonic crystals is the presence of photonic band gaps (PBG) where the propagation of light through the PhC is suppressed. It is known that exciting effects appear in the spectral vicinity of the PBG edges, such as slow light, localization of electromagnetic field and others [1]. Different devices like optical filters, waveguides (for example, in fiber-optic communication lines) are created and developed on the basis of PhC; photonic crystals are a part of laser constructions as well.

The special class of photonic crystals are biological photonic crystals that exist on some beetles' back, on surfaces of clamshells, in wings of some dragonflies, butterflies and other organisms [2]. The interconnection between spatial structure of a biological PhC and their optical spectra is of interest, primarily, for modeling of structures with new photonic properties [3]. A special interest is attracted to the possibility of modifying a PC by introduction of different materials in their structure, which can bring up additional PhC features.

In this work, the spectral properties of wings of butterflies Morpho Portis and Morpho Godarti Asarpes covered by thin gold films were studied experimentally. Frequency-angle spectra of the scattered light measured both for the original and Au-covered structures confirm the appearance of the PhC structures in these samples. We show that the deposition of gold allows one to shift the PBG up to 20-50 nm in the long wavelength range as compared to initial wings. Within the transfer-matrix method, we modelled the reflectance spectra of the structures under study and estimated the characteristic parameters of the samples.

References

1. S.G.J. John, D. Joannopoulos, J.N. Winn, R.D. Meade. Photonic crystals: molding the flow of light. Princeton University of press (2008).
2. Comoretto D. (ed.). Organic and hybrid photonic crystals. Switzerland: Springer International Publishing (2015).
3. R.A. Potyrailo, R.K. Bonam, J.G. Hartley, T.A. Starkey, P. Vukusic, M. Vasudev, T. Bunning, R.R. Naik, Z. Tang, M.A. Palacios, M. Larsen, L.A. Le Tarte, J.C. Grande, S. Zhong, T. Deng // Nature communications, v. 6, № 1, p. 1-12 (2015).

Intensities in IR spectra as a measure of FH···X hydrogen bond strength

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Evaluation of a singlehydrogen bond strength is often a quite complicated task (especially for complexes with multiple hydrogen bonds).In this case, it is necessary to use indirect methods - energy estimations based on measurable spectral parameters.

For example, it can be reasonable to use IR parameters such as stretching vibrational frequencyof proton donor group $\nu_s$or its intensity A.The linear relationship $\Delta H = 12.2 \cdot \sqrt{A}$, between hydrogen bond enthalpy ΔH and intensification of proton donor stretching band ΔA was previously proposed by A. Iogansen [1].

In this work, we examined the limits of applicability of this relation through quantum-chemical modeling of complexes with hydrogen bonds FH ··· X(X = F, N, O) in a wide energetic range (0.02–49.2 kcal/mol). We show that the dependence of energy on the intensification of the stretching ν_s vibrationremains linear in the range from 0 to about 15 kcal/mol.

Also, we propose a more universal method for estimationsof the strength of hydrogen bonds from IR spectra, namely, using the quantity $\sqrt{A/\nu_s}$ instead of $\sqrt{A}$, which directly reflects the change of in the transitiondipole moment matrix element.

References

1. Iogansen A.V. Direct proportionality of the hydrogen bonding energy and the intensification of the stretching ν (XH) vibration in infrared spectra // Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 55 (7-8), p. 1585-1612 (1999).

Optical design of microscope objective with an increased working distance

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Change of magnification in one microscope is provided by a revolver with a set of micro-objectives, the magnification of which is closely related to their working distance – a free space between the object under study and the surface of the system's first lens. The greater micro-objective magnification, the shorter it's working distance: starting from 6 mm for 40x lenses and up to the contact versions design, when object under study must come into contact with the first lens of the system [1]. Therefore, traditional problem of 40x and higher objectives is a risk of the sample damaging when operator change or move the microlens. Thus, solving such problem as providing safety of samples is relevant task in the development of optical instrumentation.

However, with an increase in the working distance aberrations in the optical system also increase significantly [2]. Their correction requires carefully selected optical elements: their number and parameters are strictly limited by the requirements for the overall dimensions of the micro-objective.

This paper proposes a structural diagram, which is useful to adhere in optical design of microscope objectives with an increased working distance. The diagram takes into account the specific functional elements which are necessary in development of such systems. The article provides a comparative analysis of frontal lens groups and chromatic correctors that are currently used in optical instrumentation [3, 4]. Analysis is based on modeling of such solutions in CAE systems.

References

1. L.N. Andreev, V.A. Panov. Optics of microscopes. Calculation and design. L.: Mechanical engineering, (1976) (in Russian) -432 p.
2. J.E. Greivenkamp. Field Guide to Geometrical Optics, SPIE Press, Bellingham, WA (2004).
3. N.B. Skobeleva Planapochromatic microlens of medium magnification with long working distances. Utility model patent No. 152835 dated 06.11.2014.
4. T. Toshi, K. Takasago. Microscope objective lens. Useful model patent No. 10281703 dated 07.05.2019.

Photoluminescence spectra modeling of ion beam irradiated $CsPbBr_3$ halide perovskites single crystal

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Although halide perovskites rush into semiconductor physics little over a decade ago, they become one of the most promising materials for future photovoltaics and optoelectronic devices. And one of the most perspective method of creating micro- and nanostructures on semiconductor's surface is focused ion beam milling (FIB) [1].

In this investigation we studied effect of 30 keV Ga^+ ions on photoluminescence (PL) spectra of $CsPbBr_3$ single crystal. Besides of redistribution of intensities of narrow exciton line and wide defect line due to ion irradiation, we registered red shift of wide defect line with dose increasing and blue shift with increasing intensity of optical pumping (Fig. 1).

These experimental results allow us to suggest relatively simple model, which can reproduce described above behavior of PL spectrum. In our model we consider dose-dependent density of defect states. These states could be filled from the free exciton reservoir, and the excitation could be transferred to states with lower energy or recombine radiatively.

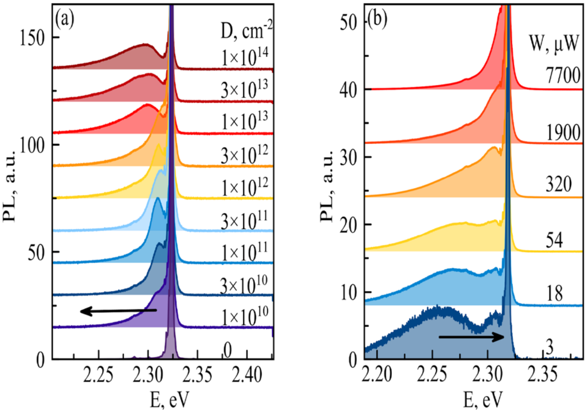

Fig. 1. PL spectra at 4K (a) as function of irradiation dose at 100 μW pumping (b) as function of pump intensity for 10^{14} cm^{-2} dose (normalized on pump intensity).

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References

1. Alias M.S., Dursun I., Shi D., Saidaminov M.I., Diallo E.M. // J. Vac. Sci. Technol. B, 33, 051207 (2015).

G. Theoretical, Mathematical and Computational Physics

Nonresonant corrections for hydrogen atom in modern highly precision atomic physics

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Spectroscopic experiments have long been and remain one of the most precise experiments in physics. Measurements of transition frequencies with extraordinary accuracy in hydrogen atom give us an opportunity to obtain such values as proton charge radius and Rydberg constant. But increasing of the experimental measurements' accuracy in the last decade led to the problem called "proton radius puzzle". Despite the fact that nowadays this problem proposed to be solved [1], it is necessary to give a close theoretical analysis on this challenge.

Such theoretical analysis corresponds to evaluation of the one-photon scattering process on the hydrogen atom. Description given in our work [2] represents exactly the case of the experiment [1]. It was found that arising nonresonant (NR) corrections play an important role in experiments with the accuracy achieved in [1]. Since the NR corrections are process-dependent, it is necessary to consider experiments with different processes.

The most accurate experiments in modern atomic physics are based on the process of two-photon excitation [3] which allows to essentially decrease different broadenings of spectral line. Like in the work [1], using methods of quantum electrodynamics and the theory of spectral line profile [4, 5], the rigorous theoretical analysis presented in our work for the two-photon excitation processes in hydrogen atom has led to the same conclusion: the NR corrections must also be taken into account in spectroscopic experiments based on the two-photon absorption process.

References

1. A. Beyer et al. // Science 358, p. 79-85 (2017).
2. D. Solovyev et al. // J. Phys. B: At. Mol. Opt. Phys., v.53, № 12 (2020).
3. B. de Beauvoir et al. // Eur. Phys. J. D, v. 12, p 61-93 (2000).
4. F. Low // Phys. Rev., v. 88, № 1, p. 53 (1952).
5. O. Yu. Andreev et al. // Phys. Rep., v. 455, p. 135-246 (2008).

Photon-spin-dependent contribution to the P,T-odd Faraday rotation effect for atoms

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The photon-spin-dependent contribution to the ordinary Faraday effect – optical rotation in an external magnetic field $\vec{H}$ is well known. This contribution is proportional to factor ($\vec{s}_{ph}\cdot\vec{H}$) where $\vec{s}_{ph}$ is the photon spin [1].

Recently a P,T-odd Faraday effect – optical rotation in an external electric field $\vec{E}$ – was discussed as a promising tool for observation of the electron electric dipole moment in the intra-cavity absorption spectroscopy [2-5]. In the present work, we introduce the photon-spin-dependent contribution to the P,T-odd Faraday rotation effect. This contribution is proportional to ($\vec{s}_{ph}\cdot\vec{E}$) and has to be taken into account in the calculations of the P,T-odd Faraday effect.

References

1. G.J. Roberts, P.E.G. Baird, M.W.S.M. Brimicombe, P.G.H. Sandars, D.R. Selby, D.N. Stacey // J.Phys. B. 13, 1389 (1980).
2. D.V. Chubukov, L.N. Labzowsky // Phys. Rev. A 96, 052105 (2017).
3. D.V. Chubukov, L.V. Skripnikov, L.N. Labzowsky // Phys. Rev. A 97, 062512 (2018).
4. D.V. Chubukov, L.V. Skripnikov, L.N. Labzowsky, V.N. Kutuzov, S.D. Chekhovskoi // Phys. Rev. A 97, 052515 (2019).
5. D.V. Chubukov, L.V. Skripnikov, L.N. Labzowsky // Pis'ma Zh. Eksp. Teor. Fiz., 110, 363 (2019) [Sov. Phys.JETP Lett. 110, 382 (2019)].

Binding energy, g-factor and QED effects in strong nuclear field

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The energy level of an electron bound by a supercritical charge ($Z > Z_{\mathrm{crit}} = 173$) dives into the continuum of negative energy states. As experimentally accessible systems, one can consider the so-called heavy diatomic quasimolecules, which can be observed in heavy-ion collisions [1]. The relativistic and QED corrections grow strongly with Z and can crucially alter the properties of the bound state in the near-critical regime. In this work, the behaviour of the one-electron binding energy and the g-factor in strong nuclear field is studied right up to the negative-continuum immersion for the 1s, 2s and 2p states. Both single ions and diatomic quasimolecules (such as uranium-uranium) are considered. Moreover, the self-energy corrections to the quantities listed above are calculated within the rigorous bound-state QED approach, using methods from [2].

References

1. W. Pieper, W. Greiner // Z. Phys. 218, 327 (1969).
2. V.A. Yerokhin, V.M. Shabaev // Phys. Rev. A 60, 800 (1999).

Investigation of differential transition probabilities in two-photon decay of *2s* and $2p_{1/2}$ states of one-electron ions

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The two-photon transition is the main decay channel of *2s* state in light and middle one-electron ions. Due to the relative simplicity of the one-electron ions the *2s* state is a unique system for studying two-photon transitions.

In this work we report our results of studying the two-photon decay of *2s* and $2p_{1/2}$ states. The calculations were carried out within the framework of the relativistic theory, in particular, the Dirac wave functions were used.The summation over the full Dirac spectrum was performed using the finite basis set method for the Dirac equation, constructed from B-splines. In the case of 2s state the main contribution to the transition probabilities is given by E1E1 transitions. The higher multipoles with photon angular momentum $J \leq 4$ were also taken into account. The calculations were performed for a large number of Z up to uranium.

In the case of $2p_{1/2}$ state, the main decay channel is one-photon E1 transition. The main two-photon decay channel is E1M1 transitions. All the necessary higher multipoles were also taken into account. The decay of the $2p_{1/2}$ state is more difficult to study experimentally, however it is of particular interest because the emitted photons are different.

The results of our calculations of the total transition probabilities are in good agreement with the results of previous authors [1, 2].

The main goal of the present work is investigation of the various polarizations of the emitted photons and the polarizations of the initial and final states in the process under consideration. Special attention was paid to study of the differential transition probabilities with respect to the angles of the emitted photons. The results of our calculation are in reasonable agreement with the results presented in [3]. The dependence of these properties on atomic nuclear charge Z was investigated. Finally, we compare the two-photon decays of *2s* and $2p_{1/2}$ states in the relativistic and non-relativistic domains.

References

1. L.N. Labzowsky, A.V. Shonin, D.A. Solovyev // J. Phys. B 38, 265 (2005).
2. L. Filippin, M. Godefroid, D. Baye // Phys. Rev. A 93, 012517 (2016).
3. A. Surzhykov, P. Koval, S. Fritzsche // Phys. Rev A 71, 022509 (2005).

P,T -odd Faraday rotation in intracavity absorption spectroscopy with particle beam as a possible way to improve the sensitivity of the search for the time reflection noninvariant effects in nature

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Existence any electric dipole moment(EDM) for any particle violates both space parity (P) and time invariance (T)Therefore the observation of EDM for any particle would mean the existence of T-noninvariant interactions(forces) in the nature. A search for the particles EDMs starts from 1950 when it was suggested to observe the neutron's EDM by the magnetic resonance method. Later it was predicted that the electron EDM (eEDM) should be greatly enhanced in heavy atoms and even greater enhancement should exist in heavy heteronuclear diatomic molecules. In it was also predicted that apart from the P,T -odd effect of interaction of the eEDM d_e with an external electric field another P,T - odd effect should exist: a P,T - odd interaction of the electron with the nucleus in an atom or molecule.

The most restrictive bounds for d_e or d^{eqv}_e were obtained in the experiments with ThO molecule $d_e<1.1*10^{-29}$ ecm. Theoretical predictions for d_e, d^{eqv}_e in frames of the Standart Model (SM) are still far from the experimental bounds. The predicted equivalent eEDM value was $d^{eqv}_e \approx 10^{-38}$ ecm which recently is considered as a benchmark result. This interaction exists at the 3-loop level. For the estimates of the loop integrals again the GIM mechanism was employed. Another 3-loop electron-nucleus P,T - odd interaction model was suggested in as an exchange between the electron and the nucleus by Higgs boson. The estimates obtained were rather uncertain: $d^{eqv}_e \approx 10^{-40}$ ecm – 10^{-45} ecm.

Due to the gap (9 orders of magnitude) between the experimental upper bound for eEDM and the largest theoretical prediction within SM, there are various extensions of SM giving the larger predictions for eEDM. There exists a very vast literature on the subject - see for example. It contains supersymmetric, multihiggs, extra dimensional etc extensions. Some of these extensions, for example one-loop supersymmetric, are already disproved bythe recent experimental bounds. Still there is a possibility that the SM predictions will remain adequate. Therefore the problem of further improving the accuracy of experimental results remain actual. It seems to be important to find new approaches and to suggest new types of experiments for this purpose. One possible attempt in this direction was reviewed.

Quantum Numbers of Four Narrow Ω_b-Baryons within the Quark-Diquark Model

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The LHCb Collaboration have announced an evidence of 4 narrow baryonic resonances with the open bottom and double strange flavors [1] which were identified with excited Ω_b-baryons. Similar resonances with the open charm — Ω_c-baryons — were observed earlier by the LHCb [2] and Belle [3] Collaborations and were interpreted as orbitally excited states. Based on the Heavy-Quark Symmetry and Quark-Diquark Model of hadrons, Karliner and Rosner [4] suggested that the newly found Ω_b-baryons are also orbitally excited states with one (fifth) state is missed experimentally. According to them, the missing state should have the spin-parity either $J^P = 1/2^-$ or $J^P = 5/2^-$. There exist another possibility within this approach to identify all five allowed orbitally excited states with the Ω_b-baryons found by LHCb, assuming that the second peak with $m = 6330.3$ MeV contains two yet unresolved states with the spin-parities $J^P = 1/2^-$ or $J^P = 3/2^-$. The other possibility is that three lightest in mass baryons are orbitally excited states while the heaviest one is radially excited. If so, there should exist one more baryon with $m = 6304$ MeV and spin-parity $J^P = 1/2^-$ which is a good goal for the LHCb for its searching in an updated statistics.

References

1. R. Aaij et al. [LHCb Collab.] // Phys. Rev. Lett., v. 124, p. 082002 (2020).
2. R. Aaij et al. [LHCb Collab.] // Phys. Rev. Lett., v. 118, p. 182001 (2017).
3. J. Yelton et al. [Belle Collab.] // Phys. Rev. D., v. 97, p. 051102 (2018).
4. M. Karliner, J.L. Rosner // Phys. Rev. D., v. 102, p. 014027 (2020).

Relativistic calculations of the ground states energy difference of ^{163}Ho and ^{163}Dy

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Within the Standard Model framework neutrinos are massless particles, however modern experiments on the neutrino oscillations show the opposite. From them only the relative mass difference between neutrino flavors can be extracted [1]. Another type of experiments, which focuses on the edge point of the beta decay and electron-capture spectra, gives the direct estimation of the electron neutrino upper mass bound.

Collaboration ECHo aims to measure the electron capture spectrum in neutral ^{163}Ho atom [2] and analyze it for setting a new restriction on the electron neutrino mass. Studying of this spectrum requires precise knowledge of the mass excess between parent and daughter nuclei, which can be experimentally determined with the sufficient precision only for highly charged ions. Therefore, a conversion from the mass excess of highly charged ions to the mass excess of neutral atoms is necessary for the study. The corresponding are evaluated in the present work for Ar-like and Kr-like ions of Ho and Dy exploiting the configuration interaction method in the basis of Dirac-Fock-Sturm orbitals [3].

References

1. M.C. Gonzalez-Garcia, Y. Nir //Rev. Mod. Phys. 75, 345 (2003).
2. L. Gastaldo et al. // Eur. Phys. J. Spec. Top. 226, 1623 (2017).
3. I.I. Tupitsyn et al. // Phys. Rev. A 68, 022511 (2003).

Local Duality Symmetry in Gauge Field Theories

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The idea of local duality symmetry is developed. Dual invariant Lorentz-scalar electrodynamics Lagrangian is constructed in techniques of Clifford algebra which provides convenient and compact formalism. This Lagrangian is shown to be the same as the usual one in tensor formalism. The duality symmetry is then can be localized in two ways, leading to the appearance of the new fields in Lagrangian. However, these fields would break the gauge U(1) symmetry of electrodynamics. To prevent this, it is proposed to 'stitch' the duality symmetry with the gauge symmetry, allowing to compensate gauge transforms with local duality transforms and vice versa. Possible role of such mechanism of localization of the duality symmetry in QCD and dark matter is briefly discussed.

Electron-positron pair production in strong fields: locally constant field approximation

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We investigate the fundamental phenomenon of electron-positron pair production in the presence of strong electromagnetic fields predicted as early as the 1930s [1-2] and rigorously described by quantum electrodynamics (QED). This process in the non-perturbative regime of a strong coupling, i.e. the so-called Schwinger mechanism [3], has never been experimentally observed. However, the current rapid development of laser technologies could make such studies feasible in the not-so-distant future.

To identify the most promising experimental scenarios, one has to properly estimate the pair-production probabilities in various external-field configurations. To this end, one can employ the closed-form expression derived in the case of a constant uniform electromagnetic field [2-3] and integrate the corresponding local contributions over space and time taking into account the field inhomogeneities. This approximate approach, which is called the locally constant field approximation (LCFA), allows one to perform fast calculations of the particle yield and spectra of the particles produced. On the other hand, the validity of the LCFA is not yet fully understood. Here we identify the domain of the field parameters, where the LCFA is well justified [4].

In order to obtain the exact results, we use two different techniques: Furry-picture quantization in momentum space [5] and the method of quantum kinetic equations [6]. Benchmarking the LCFA predictions against the exact results, we determine the field parameters which justify the applicability of the LCFA.

References

1. F. Sauter // Z. Phys. 69, 742 (1931).
2. H. Euler, W. Heisenberg // Z. Phys. 98, 714 (1936).
3. J. Schwinger // Phys. Rev. 82, 664 (1951).
4. I.A. Aleksandrov, G. Plunien, V.M. Shabaev // Phys. Rev. D 99, 016020 (2019).
5. I.A. Aleksandrov, G. Plunien, V. M. Shabaev // Phys. Rev. D 94, 065024 (2016).
6. S. Schmidt, D. Blaschke, G. Röpke, S.A. Smolyansky, A.V. Prozorkevich, V. D. Toneev // Int. J. Mod. Phys. E 07, 709 (1998).

Free and unfolded surfaces in embedding theory

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The embedding theory is the approach to gravity proposed by Regge and Teitelboim in which 4D space-time is treated as a surface in high-dimensional flat ambient space [1]. The embedding function is considered as an independent variable. Varying the Einstein-Hilbert action we obtain the Euler-Lagrange equations called Regge-Teitelboim equations. The embedding theory can be presented as General Relativity with additional fictitious matter, thus it can be used in explaining the dark matter mystery.

Physically realistic embeddings have to have some specific properties. We introduce the concept of unfolded surfaces. We consider classes of embedding introduced in [2] (free embeddings, q-free embeddings, spatially free embeddings) comparing them with the concept of unfolded embeddings. Unfolded surfaces can be used in Regge-Teitelboim equation linearization .

References

1. T. Regge, C. Teitelboim // Proceedings of the First Marcel GrossMann Meeting, Trieste, Italy, 1975, edited by R. Ruffini, 77-78, 1977.
2. M.D. Bustamante, F. Debbasch, M.-E. Brachet, 2005, arXiv:gr-qc/0509090.
3. M. Pavsic // Phys. Lett. A, 107 (1985), 66-70.

Correlation effects in highly charged ions: g factor and hyperfine structure

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Over the past two decades, significant progress has been made in studies of the g factor in highly charged ions [1, 2]. Modern experiments have reached an accuracy of 10^{-9}–10^{-11} for H-like, Li-like, and B-like ions [3-5]. The g-factor of the ground state of B-like argon was recently measured with an accuracy of 10^{-9} in the framework of the ALPHATRAP project [5]. The experimental value is in perfect agreement with the theoretical one [5]. This work presents theoretical calculations of the g-factor of the ground and first excited states of B-like ions in the range Z = 10 – 92. The first-order interelectronic interaction corrections are evaluated within the framework of a rigorous QED approach. The second-order interelectronic interaction is considered within the Breit approximation. The QED, the nuclear recoil and nuclear size corrections, are also taken into account. Various effective screening potentials are employed to estimate the higher-order interelectronic-interaction effects. The obtained results were presented for B-like ions in the range Z = 10 – 20 [6, 7].

The hyperfine splitting in Li-like bismuth has been measured recently at GSI [8]. Good agreement with theory [9] was found after reevaluation of the bismuth-209 nuclear magnetic moment [10]. We extend the calculations of the hyperfine splitting in Li-like ions to the wide range of Z and further improve the accuracy of the higher-order interelectronic-interaction effects.

References

1. S. Sturm et al. // Atoms 5, 4 (2017).
2. V.M. Shabaev et al. // J. Phys. Chem. Ref. Data 44, 031205 (2015).
3. S. Sturm et al. // Phys. Rev. Lett. 107, 023002 (2011).
4. D.A. Glazov et al. // Phys. Rev. Lett. 123, 173001 (2019).
5. I. Arapoglou et al. // Phys. Rev. Lett. 122, 253001 (2019).
6. V.A. Agababaev et al. // J. Phys. Conf. Ser. 1138, 012003 (2018).
7. V.A. Agababaev et al. // X-Ray Spectrom. 49, 143 (2020).
8. J. Ullman et al. // Nat. Commun. 8, 15484 (2017).
9. A.V. Volotka et al. // Phys. Rev. Lett. 108, 073001 (2012).
10. L.V. Skripnikov et al. // Phys. Rev. Lett. 120, 093001 (2018).

H. Soft Matter
(biophysics, polimerphysics, liquid crystalls, colloids, …)

DNA conformational changes in the presence of bis-(1,10-phenanthroline)-zinc(II) acetate

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Currently, there are a large number of metal complexes that contain transition metal ions. The topicality of the development of metal complexes is associated with their high efficiency as antimicrobial and antifungal drugs. Binding of the metal complex to DNA leads to inhibition of macromolecule synthesis in the cell which gives the opportunity to consider these compounds as potential anticancer.

This work is devoted to study of conformational changes of DNA in the presence of a new compound — bis-(1,10-phenanthroline)-zinc(II) acetate (Zn1). Interaction of this compound with DNA in aqueous-salt solutions was studied by the methods of UV-Vis spectroscopy, spectrophotometric DNA melting and dynamic light scattering. The absorption spectra of DNA solutions in the presence of Zn1 differ significantly from the spectra of the separated components, particularly in the spectral regions corresponding to the absorption bands of metal complexes. The melting temperature (Tm) of DNA shows linear growth at the increase of Zn1 concentration. The hydrodynamic radii (R_h) of the DNA molecule in the presence of Zn1 were measured by dynamic light scattering. Non-monotone dependence of R_h on Zn1 concentration can indicate different modes of the metal complex binding to DNA. The data obtained can be explained by the complexation of bis-(1,10-phenanthroline)-zinc(II) acetate with DNA, presumably not only by monomer, but also by dimer binding, and one of the binding modes is intercalation.

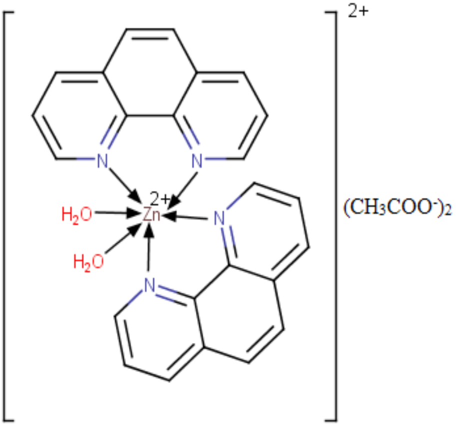

Fig. 1. Bis-(1,10-phenanthroline)-zinc(II) acetate in aqueous solution.

Polymer complexes with detonation nanodiamonds for medical utilization

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Detonation nanodiamonds (DND) which only recently have become commercially available, attract attention for theirs utilization in modern medicine as bioinert and uniform is size nanoparticles. First of all, this is due to a specific surface of DND available for chemical modification due to functional groups that are formed during detonation synthesis. It was shown the possibility of DND application as drug carriers and biomarkers [1, 2]. Aggregation of these nanoparticles in aqueous media and instability of DND suspensions remain a problem limiting its practical application in medicine. One of ways to dissolve the problem is a selection of water soluble polymer as DND carrier.

In this work we have studied aqueous solutions of DND complexes with the biocompatible synthetic polymer polyvinylpyrrolidone (PVP, MM=10^3), as well as the triple complexes PVP-DND-e6, where e6 (chlorine-e6) is a main component of photosensitizer Radachlorin@ applied in the modern photodynamic therapy of certain oncological diseases.

Hydrodynamics and dynamic light scattering techniques were used to determine the stability conditions of the prepared complexes; the spectral methods were used to determine the effect of DND and PVP on the chlorine-e6 properties. The study of luminescence spectra of complexes* showed that PVP increases the intensity of e6 luminescence and the generation of singlet oxygen in solution under UV excitation at a wavelength 405 nm. It was also shown that DND in combination with PVP and e6 are able to transfer excitation energy to the surrounding molecules and enhance the luminescence of singlet oxygen. The detected phenomena can significantly reduce the therapeutic dose of Radachlorin@ by using the PVP-e6 and PVP-DNA-e6 complexes instead of the original drug, thus reducing its toxicity.

References

1. Chen M., Pierstorff E., Lam R., Li Sh.-Y.,Huang H., Osawa E., Ho D. // ACSNano., vol. 3, № 7, p. 2016-2022 (2009).
2. Bradac C., Das Rastog I., Cordina N., Garcia-Bennett A., Brown L. // Diamond & Related Material., vol. 83, p. 38-45 (2018).

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* Spectral studies were conducted at the Center for optical and laser materials research of St. Petersburg State University

Development of a system for multi-element analysis of the composition of petroleum raw materials and products of its processing, as well as environmental control

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The digitalization of objects in the chemical industry and the environment sets the goal of developing compact sensor systems with low energy consumption. The project proposes to qualitatively improve the process of analyzing the composition of oil and oil products, as well as the environment. Using a fundamentally new approach to the simultaneous analysis of multiple nonselective cross-sensitivity sensors. Those. each sensor is sensitive to several substances and there is an intersection of sensitivity ranges between the sensors in the cascade. The received signals from all sensors form a multidimensional data array, which is converted into the required indicators using the principal component method. Accordingly, in one measurement, it is possible to cover the entire spectrum of substances necessary for analysis, with appropriate accuracy and sensitivity.

Coordination polymers and high-temperature enzymes cleaving the carbon-carbon bond are considered as an electrochemically active layer. The measurements are carried out by the method of auto-balancing bridge impedance spectroscopy with an adaptive noise reduction system based on the perceptron model. This approach allows obtaining results of sufficient accuracy without using high-performance equipment, which opens up the possibility of miniaturizing the device.

Acknowledgments. Thanks for the support of the project to the Fund for the Promotion of Innovations.

References

1. Alekseeva E., Stelmashuk T., Danilov S., Yang P., Levin O. Bimetallic Cu/Pt Oxygen Reduction Reaction Catalyst for Fuel Cells Cathode Materials // Catalysts 2020, 10, 667.
2. Lvova L., Yaroshenko I., Kirsanov D., Di Natale C., Paolesse R., Legin A. Electronic tongue for brand uniformity control: A case study of apulian red wines recognition and defects evaluation // Sensors (Switzerland), 18 (8) paper # 2584 (2018).

Conformational and optical molecular properties of poly (hexyl methacrylate) and poly (stearyl methacrylate)

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The study of various comb-like polymers remains one of the most promising directions in the development of modern physical chemistry of high-molecular compounds.

The present work is aimed to determine conformational and molecular (hydrodynamic, optical) characteristics of poly (hexyl methacrylate) (PHMA) and poly (stearyl methacrylate) (SMA). The results were compared with themselves and literature data in order to check the self-consistency and reliability of received data. The scientific novelty of the study is that researched samples have the highest available side chain length which exceeds the length of previously likewise investigated poly (alkyl methacrylate)s. The detailed analysis of the studied samples was performed in dilute solutions in organic solvents by computer simulation and the following experimental techniques: viscometry, velocity sedimentation, dynamic light scattering, densitometry, refractometry, flow birefringence. As a result, the values of intrinsic viscosity, translational diffusion and sedimentation coefficients, and partial specific volume were defined. Based on the calculated molecular masses of the studied samples, the Mark-Kuhn-Houwink equations were received, which enabled us to estimate the thermodynamic quality of the solvent. The equilibrium rigidity and polymer chain diameter were defined using Gray-Bloomfield-Hearst extrapolation procedures. We can note an increase in the value of the equilibrium rigidity of SMA compared with PHMA. Long aliphatic side chain determines the negative intrinsic optical anisotropy of poly (alkyl methacrylate)s. The measured value of the intrinsic optical anisotropy of the monomer unit for SMA can be caused by noticeable folding of the side chains in considered macromolecules. The computer simulation was applied to receive the values of the geometrical dimensions and the intrinsic optical anisotropy of the monomer unit of PHMA and SMA.

It was found that the determined characteristics are in acceptable agreement with each other and the previously received data on aliphatic poly (alkyl methacrylate)s.

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Interpolyelectrolyte complexes of a DNA molecule with synthetic polymers in solution

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Non-viral systems for nucleic acid delivery offer a variety of potential advantages compared to viruses. Such features include relatively low toxicity and immunogenicity, easy production and less stringent vector size limitations. DNA-polymer complexes have been studied widely as non-viral gene vectors and have numerous applications for the diagnosis and treatment of genetic diseases. Unfortunately, these interpolyelectrolyte structures still have some side effects: immune reaction, cytotoxicity. Thus, a new generation of cationic polymers are in development. Biologically active agents such as silver and gold nanoparticles are able to increase their selectivity and efficiency for medical purposes.

Aim of present research was to determine molecular mechanisms of DNA-polymer complexes formation (also with biologically active agents such as dyes and silver nanoparticles). Spectrophotometry, luminescent spectroscopy, low-gradient viscometry and agarose gel electrophoresis methods were applied. The stability of the DNA-polymer systems in a wide range of pH was considered. The charge properties of DNA-polymer complexes were studied using the electrophoresis method. It was shown that 4-AM-DMAEMA copolymer are able to produce complexes with DNA molecules and it was expressed by visible light scattering (observed as opalescence). Also the possibility of DNA-poly(DMAEMA)-silver nanoparticle complexation has been proved.

References

1. Benjamin D. Hornstein 2 Cinnamon L. Hardee, Lirio Milenka Ar evalo-Soliz, Lynn ´Zechiedrich. Advances in non-viral DNA vectors for gene therapy // Genes, p. 3, February 2017.
2. Corey J Bishop Joel C Sunshine, Jordan J Green. Advances in polymeric and inorganic vectors for nonviral nucleic acid delivery // PubMed Central, p. 1-49, April 2014.
3. Spirin A.S. Spectrophotometric determination of the total amount of nucleic acids // Biochemistry, 1958, № 5, p. 656-662.

Programmable soft-matter electrochemical EGaIn interface formation

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Currently, there is a need to create portable wearable and biocompatible electronics. Such devices can be used not only in everyday life, but also for the development of medical technologies, in particular for bioprostheses. However, the creation of such devices requires the development of soft and flexible electronic components [1]. One of the promising materials used for this purpose is the eutectic alloy of gallium and indium [2].

In the present work, chemical system which combines several electrical behaviors is presented. This system is based on eutectic alloy of Gallium-Indium (eGaIn) and hydrogels doped with polyacrylic acid (PAA) and polyethyleneimine (PEI) in presence or absence of phosphate buffer saline (PBS). When current flows**,** oxide and phosphate layers are formed at the phase boundary between the hydrogel and the alloy. Thickness of this insoluble layer determines electric behavior of the system. 4 behaviors were obtained: capacitor, resistor, diode, and memristor. Thickness of oxide and phosphate layer was controlled by applied voltage in range from 20 mV till 5 V. Also, chemical perceptron based on chemical memristors was designed. This system was applied to analyze and determine the compositions and concentrations of various gels. Such soft-matter systems have a potential to become a new approach of creation flexible reprogrammable electronic components.

References

1. C. Wang, C. Wang, Z. Huang, S. Xu // Adv. Mater., v. 30, 1801368 (2018).
2. T. Shay, O.D. Velev, M.D. Dickey // Soft Matter, v. 14, № 17, p. 3296-3303 (2018).

Research of comb-like polyelectrolytes for micellar catalysis

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The topic of the influence of surface-active substances on the course of organic reactions in an aqueous solution is widely covered in the scientific literature. Micellar catalysis can be used in various fields of science and production. For example, it can be used for utilization of plastic and some chemical warfare agents, as well as for investigation of systems for targeted drug delivery and for the study of the properties of surfactants themselves.

The aim of this work was to investigate catalytic effects of comb-like polyelectrolytes in the reaction of esters hydrolysis.

The following polyelectrolytes were synthesized:

poly-11-acryloyloxyundecyltrimethylammonium bromide (C_{11}), as well as its triethyl, pyridine, quinoline and N-methylmorpholine analogues. Rate constants were obtained from UV spectra. From the approximation of the dependence of the constant on the concentration, many physicochemical parameters are extracted, and discussed in the work.

These compounds were used as catalysts in the reaction of hydrolysis of ester of paranitrophenyl butyrate. Fig.1 shows the dependence of the constant of the hydrolysis reaction rate on the concentration of various surfactants.

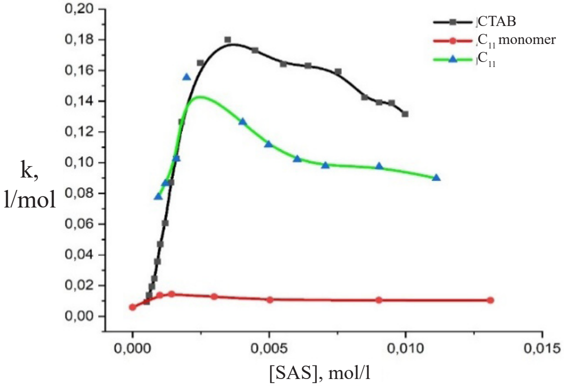

Fig. 1. The dependence of the rate constant of the hydrolysis of ester on the concentration of various surfactants.

Acknowledgments. P.A. Fetin and M. Kadnikov are grateful to the Russian Science Foundation project No. 19-73-00059. The authors are grateful SPBU Research park.

Influence of side chains on conformation of polyamino acids in calcium chloride solution

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Anionic poly(amino acids), such as poly-(α-L aspartic acid) (PASA) and poly-(α-L glutamic acid) (PGA) are used to regulate mineralization, guide nucleation and crystal growth, deliver minerals to organic matricies. Despite similarity, Picker et al. have demonstrated that aspartic acid increases solubility of the initial precipitated phase of $CaCO_3$ while glutamic acid decreases it [2]. Moreover, Thula et al. showed that PGA alone did not yield mineralization of collagen sponges [1].

We have performed atomic MD simulation of PASA and PGA in $CaCl_2$ solutions to determine structural diversity between PASA-Ca^{2+} complex and PGA-Ca^{2+} complex. To overcome high-energy barriers, we used Hamiltonian replica exchange method, adopting similar approach for a-L aspartic trimers [3].

As a result, we have compared radii of gyration of PASA and PGA in various $CaCl_2$ concentrations. Obtained curves of PASA and PGA radii of gyration on $CaCl_2$ concentration agree with theory of semiflexible polyelectrolyte chains in multivalent salt. However, due to longer side chain and therefore ability to increase distance between adsorbed Ca^{2+} ions, PGA stays in collapsed state for a wider $CaCl_2$m concentration range. Therefore, PGA, at the concentration at which PASA has an extended conformation, maintains the conformation of a dense globule. This explain the differences in mineralization of organic matrices using PASA and PGA.

Acknowledgments. The research was performed within the framework of the Project No 19-73-00283 of the Russian Science Foundation (RSF).

References

1. Thula T. et al. Mimicking the Nanostructure of Bone: Comparison of Polymeric Process-Directing Agents // Polymers 2011, 3, 10–35.
2. Picker A.; Kellermeier M., Seto J., Gebauer D., Cölfen H. The multiple effects of amino acids on the early stages of calcium carbonate crystallization // Z. Krist. 2012, 227, 744–757.
3. Lemke T.; Peter C.; Kukharenko O. Efficient Sampling and Characterization of Free Energy Landscapes of Ion-Peptide Systems // J. Chem. Theory Comput. 2018, 14, 5476–5488.

Investigation of interaction of C4-Azo-OC6TMA in cis- and trans-conformations with DNA by molecular dynamics method

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A high-molecular DNA chain in an aqueous solution is a swollen coil, negatively charged due to the content of phosphate groups. Charge compensation, for example, using organic cationic salts, leads to the reversible packaging of DNA in solution.

The aim of the study was to investigate the mechanism of interaction of surfactant cationic salt (C4-Azo-OC6TMA+) and DNA chain fragment. The organic cation contains azobenzene group that can change its conformation under UV-irradiation from trans (hydrophobic) to cis conformation (hydrophilic). This property can make it possible to control the compaction of the DNA. Surfactant molecules in both conformations organize into micelles with reaching of the critical micelle concentration. The trans-conformer is capable of forming complexes with DNA, while the interaction of the cis-conformer with DNA is poorly expressed [1].

The aim of this work was to study the interaction of C4-Azo-OC6TMA with DNA in an aqueous solution using the molecular dynamics method. We considered three systems containing DNA and a surfactant in the trans-conformation, in the cis-conformation, after the transition from the trans- to cis-conformation.

Simulation was carried out using the AKMD program. To describe the interactions of atoms, the OPLS-AA potentials were used, which set the partial charge of the atoms. Periodic boundary conditions were set. The cell was created by sequentially combining three initial ones containing a DNA chain (18 base pairs), surfactant ions, and water molecules. The simulation had a step of 2 fs.

Acknowledgments. The calculations were carried out using the resources of the Computing Center of St. Petersburg State University (www.cc.spbu.ru).

References

1. Kasyanenko N., Unksov I., Bakulev V., Santer S. DNA Interaction with Head-to-Tail Associates of Cationic Surfactants Prevents Formation of Compact Particles // Molecules. – 2018. – Vol. 23, i. 7. – 1576.

Modelling of Transportation Process in Plane Flowswith Stagnation Points

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We study transport of passive tracers by plane laminar flows with stagnation points. This setup serves as a simple model of transport in porous media. Close to stagnation points, the flow velocity is much lower than on the average. Many experimental data [1, 2] disclose that transport through porous media is slower than predictions of the standard advection-diffusion model. Commonly, in descriptions of flows through porous media the heterogeneity of flow is disregarded, and some average velocity is adopted. To model regular arrays of flow patterns with stagnation points, we employ the construction of special flow [3]: a combination of mapping and a sort of ceiling function with singularity. We show that, depending on the type of stagnation points, many experimentally established effects can be reproduced. This includes the linear sorption, usually described by the standard MIM model [4], as well as subdiffusion, described by the fractional MIM model [5]. We also show that slow molecular diffusion does not eliminate the effects of the transport slowdown. The results of this work is presented in the paper [6]

Acknowledgments. The work was partially supported by German-Russian Interdisciplinary Science Center (G-RISC) project No E-2019b-1d.

References

1. M. Bromly, C. Hinz // Water Resour. Res., v. 40, W07402 (2004).
2. P. Gouze, T. Le Borgne, R. Leprovost, G. Lods, T. Poidras, P. Pezard// Water Resour. Res., V. 44, W06426 (2008).
3. M.A. Zaks, A.S. Pikovsky, J. Kurths // Phys. Rev. Lett. V,77, 4338 (1996).
4. M.T. Van Genuchten, P.J. Wierenga // Soil Sci. Soc. Am. J., V.40, 473 (1976).
5. R. Schumer, D.A. Benson, M.M. Meerschaert, B. Baeumer // Water Resour. Res. v. 39 (2003).
6. B.S. Maryshev, M.A. Zaks // Trans. Por. Media., pp. 1-24. (2020) (on-line).

The interaction of sodium hypochlorite with DNA in presence of various antimicrobial drugs

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The spreading of antibiotic resistance raises the importance of research of antimicrobial drugs. One of the ways to inhibit resistance is using antiseptics. Also, the bactericidal effect can be increased by using combination of different medicine.

Sodium hypochlorite is one of the widespread antiseptics (Fig. 1). The hypochlorite is a source of ClO^- with DNA molecule and induces it's denaturation. At the same time hypochlorite modifies nitrogenous bases [1].

In this work we study the interaction of sodium hypochlorite with DNA in presence of different combinations of antimicrobial drugs (betaine, poviargol, dioxidine). The UV-visible spectrometry is used to examine the water-salt solutions contained DNA, sodium hypochlorite and one of the substances under consideration. The results show that betaine inhibits denaturation of the DNA molecule. Poviargol, in contrast, accelerates this process. The influence of dioxidine on interaction of DNA with sodium hypochlorite wasn't detected.

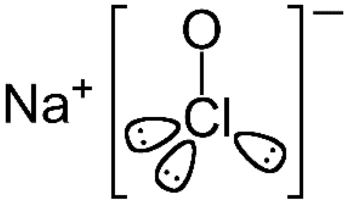

Fig. 1. Sodium hypochlorite.

References

1. Osinnikova D.N., Moroshkina E.B., Mokronosova E.S. Effect of sodium hypochlorite on nucleic acids of different primary and secondary structures // J. Phys.: Conf. Ser., 2019, vol. 1400, 033001, doi:10.1088/1742-6596/1400/3/033001

Small angle neutron scattering investigations of the domain structure of multiblock polyurethane ureas

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Segmented polyurethane ureas (PUU) are widely used in the world today as coatings, adhesives, membranes, sealants, heat-shrink packaging, damping and heat-insulating materials. The widespread use of PUU in such areas is possible due to their ability to microphase separation into hard and soft segments [1, 2].

In this work, as a soft segment in the synthesis of multiblock polyurethane ureas, were used polycaprolactone diols with molecular weights of 530 and 2000 g/mol, and result of the reaction between aromatic diisocyanates and diamines were formed as a hard block.

This work aims to investigate relationship between the domain structure and thermomechanical properties, phase separation and morphology of PUU using small-angle neutron scattering (SANS) method. SANS measurements were performed at the YuMO spectrometer (IBR-2, JINR, Dubna, Russia).

From the analysis of experimental data, it was shown that with increasing length of aliphatic segments in the structure of the polyurethane ureas don’t affect on the size of the hard phase domains, but increases the distance between domains. It was found that the portion of hard segments does not affect the size of domains, but the chemical structure of the aromatic part can be influence to the domain structure. In view of the fact that symmetric diisocyanates promote denser packing of the hard segments, it leads to the enlargement of the domains from units of aromatic nature.

References

1. C. Prisacariu Polyurethane elastomers from morphology to mechanical aspects, Verlag Wien. Springer (2011).
2. K. Gisselfalt, B. Helgee // J. Macromol. Mater. Eng., № 3 p. 288, 265–271. (2003).

Determination of thermodynamic binding parameters of low-molecular compounds to a DNA molecule

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The DNA molecule is a target for a large group of antimicrobial and anticancer biologically active compounds. That is why a lot of attention is being paid to the process of DNA complexation with various low-molecular ligands. In the literature, there are examples of different models of non-covalent drug-DNA binding, and several ways of calculating binding parameters (such as average ligand site size *n*, intrinsic binding constant *K*, and in some cases co-operativity parameter *w*) are suggested. Interestingly, the results gained by application of different approaches to the problem of calculating these parameters are often vary significantly.

In this paper, some of the most widespread of such approaches are discussed and analyzed in details. The work also shows experimentally obtained data on the investigation of binding to a calf timus DNA of three dyes (Fig. 1): ethidium bromide, phenosafranine and acriflavine (representing phenantridine, phenanzine and acridine series respectively). The DNA/dye complexation was studied by UV-Vis spectrophotometric titration and thermal melting in two conditions: 1) 0.1M NaCl, where only one binding type was observed; 2) 0.001M NaCl, where at least two types of binding occur.

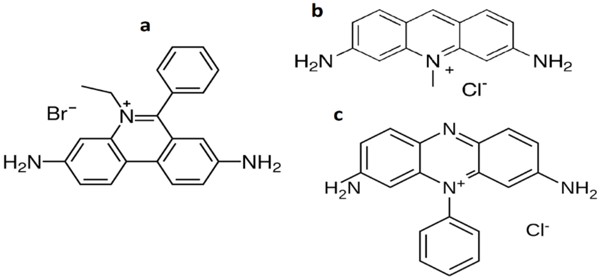

Fig. 1. Ethidium bromide (a), acriflavine (b) and phenosafranine (c).

The analysis of the experimental data was performed applying the three following methods: Double reciprocal plot method, Scatchard equation modeling and McGhee – von Hippel equation modeling. The McGhee – von Hippel equation modeling (for both cases of one and two types of binding occurring) was made through original Matlab R2019b program, which structure is explained in the text. The results of the treatment show that even in relatively simple cases, when only one type of binding to DNA is observed, different binding models and ways of calculation of the corresponding parameters give noticeably different results.

Analysis of IR spectra of blood serum of patients with multiple myeloma.

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Multiple myeloma accounts for about 10% of blood cancers. Multiple myeloma (MM) is an oncohematological disease accompanied by an increase in the of one of the types of immunoglobulin (the so-called M-protein). About 75% of secondary structures of immunoglobulin are β-sheets. Accumulation of the M-proteins suggests an increase in the content of β-sheets. The content of changes in various types of secondary structures can be detected by IR spectroscopy.

IR absorption spectra were recorded using Tensor 27 Fourier spectrometer (Bruker, Germany). The secondary protein structure was analyzed using the spectra obtained from 10 samples of blood serum of patients with MM. Serum samples from 5 healthy donors were also analyzed. Information about the secondary structure was obtained by analyzing the Amide I band (1600-1700 cm^{-1}).

For the blood serum of healthy donors, the secondary structure parameters are characterized by the predominance of α-helical regions, ~ 50%, and β-sheets immerse about 38%. An increase in the percentage of β-sheets is characteristic of the blood serum of patients with MM. The percentage varies from sample to sample. In the limit values: ~ 50% of β-sheets and ~ 36% of α-helical regions. Another limiting case is ~ 40% of α-helical regions and ~ 40% of β-sheet fragments. In general, all samples exhibit the tendency to increase the content of β-sheets.

Based on the results of this work, it can be concluded that IR spectroscopy can reveal differences between the serum spectra of healthy donors and patients with mm due to a qualitative increase in the level of β-sheets.

Acknowledgments. The authors are grateful for the financial support of the Russian Foundation for Basic Research (grant No. 18-08-01500). Part of the work was performed using the equipment of the Research park of Saint-Petersburg State University (Optical and Laser Methods for Studying Substances, Center of Diagnostic Functional Materials for Medicine, Pharmacology and Nanoelectronics, Nanotechnologies, Cryogenic laboratory).

I. Resonance Phenomena in Condenced Matter

Photoinduced defect formation in pristine and doped CsPbBr$_3$ perovskite

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The CsPbBr$_3$ perovskites have great potential in photonics and optoelectronics applications and provide a very promising alternative to organo-metal halide perovskites, taking into account their better long-term stability and impressive radiative efficiency [1]. It has been demonstrated that tuning the optoelectronic properties of perovskites is possible via inclusion or partially replacing Pb with a monovalent cation Ag.

The essential response demonstrated by CsPbBr$_3$ perovskites to irradiation in intrinsic absorption spectral region is photostimulated generation of new defect states. Their formation results in appearance of new corresponding absorption bands in extrinsic absorption spectral region [2]. The analysis of kinetics of photostimulated defect accumulation infers that two different mechanisms are realized: typical for both photoresistant and photosensitive solids. In former case the photostimulated defect formation occurs due to charge carrier trapping by existing defects in perovskites while in latter scenario new lattice defect states are formed due to electronic excitation dissipation. It has been demonstrated that efficiencies of both defect formation photoprocesses are dependent on Ag dopant concentration.

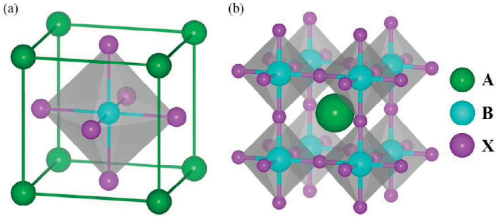

Fig. 1. ABX$_3$ perovskite cubic structure (example: A = MA$^+$/Cs$^+$, B = Pb^{2+}/Sn^{2+}, X = I$^-$/Br$^-$/Cl$^-$). a) Representation of the unit cell and b) the unit cell projection.

We can see in Fig. 1 all perovskite materials have in common the general formula ABX3, where A is a large cation (which can be an atom or a molecule), B is a smaller cation and X is an anion, the A and B sites usually accommodate inorganic cations of various valency and ionic radius and the X site accommodates halogen anions.

References

1. Abdi-Jalebi M., Dar M.I., Sadhanala A., Senanayak S.P., Gratzel M., Friend R.H. Monovalent Cation Doping of CH3NH3PbI3 for Efficient Perovskite Solar Cells // 2017, J. Vis. Exp., 55307.
2. Emeline A.V., Sheremetyeva N.V., Khomchenko N.V., Ryabchuk V.K., Serpone N. // J. Phys. Chem. C 2007, 111, 11456-11462.

^1H and ^{13}C NMR investigation of SLAS in mixtures and SiO_2 dispersions

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Surfactants are widely used in various industries. Therefore, we investigated the aggregation and interfacial behavior of aqueous solution and binary mixtures of anionic (sodium lauroyl sarcosinate, SLAS) and cationic (dodecylammonium bromide, DTAB) surfactants. SLAS, for instance, has unique physical and chemical properties, such as low toxicity, dermatology softness, hydrolysis resistance, and, most important, the fast biodegradability.

We studied the NMR parameters of SLAS in mixtures with DTAB at different molar fractions of both surfactants from 0.5 CMC to 3 CMC and in silica dispersions at different concentration of SLAS. All ^1H and ^{13}C NMR experiments were performed using a Bruker AVANCE 500, with Larmor frequencies 500 MHz for the proton spins, and of 125 MHz for the ^{13}C nuclear spins, respectively.

A splitting of the resonance lines for the N-alkyl groups in the ^1H and ^{13}C NMR spectra has been registered [1-3]. The relative concentrations of the cis- and trans-forms, existing in surfactant molecules, were estimated from the integral intensities of ^1H spectral lines, and we obtained the dependencies of the conformers' amount on the DTAB concentration. Moreover, in the ^{13}C spectra we observed the effect of splitting and merging $11CH_3$ spectral lines in different concentration regions.

References

1. Popova M.V., Chernyshev Y.S., Michel D., Chizhik V.I. ^1H and ^{13}C NMR investigation of conformational and aggregation behavior of sodium N-lauroyl sarcosinate // Journal of Molecular Liquids. 280 (2019) 40-48. https://doi.org/10.1016/j.molliq.2019.02.029.
2. Popova M.V., Michel D. Behavior of sodium Lauroyl Sarcosinate in solution and binary mixtures by means NMR // Appl. Magn. Reson. 45 (2014) 353-364. https://doi.org/ 0.1007/s00723-014-0531-9.
3. Oshimura E., Yamashita Y., Sakamoto K. Conformational Behavior of N-Acylamino Acid Oil and N-Acylamino Acid Surfactant in Aqueous Solution // J. Oleo Sci. 56, 115 (2007) 115-121. https://doi.org/10.5650/jos.56.115.

The influence of the peptide 1B03 on micelle formation in magnesium hexanoate solution

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For computer simulations, the OPLS-AA, CHARMM, AMBER potentials are widely used, in which the charge of the divalent magnesium ion is +2e and the charge of the acid residue of hexanoic acid is -1e. Earlier it was published [1] that the electric charges of ions, specified in the standard file of potentials of atom-atom interactions OPLS-AA, are not acceptable for simulation of concentrated ionic systems. As a result of simulation of micelle formation in an aqueous solution of magnesium hexanoate, the charges calculated by the Mulliken method turned out to be the best suitable: +1.4e for the magnesium ion and -0.7e for the acid residue.

In continuation of that work, the influence of the 1B03 peptide molecule (Fig. 1) to the micelle formation process in an aqueous solution of magnesium hexanoate was investigated. Two model systems were created with different charges on ions: taken from OPLS-AA (system I) and calculated by the Mulliken method (system II). The charge of peptide 1B03 in the second system was scaled 0.7 times.

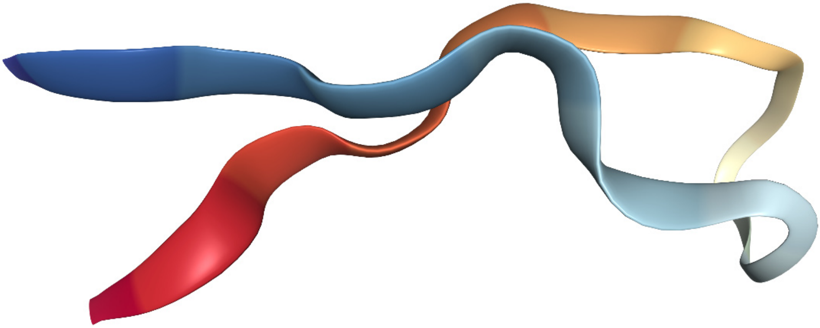

Fig. 1. Schematic representation of the structure of a peptide 1B03.

References

1. N.A. Antonova, A.M. Ryzhkov, A.V. Komolkin. Computer simulation of micelle formation in magnesium hexanoate solution // Magnetic resonance and its applications: Proceedings 16th International School-Conference, Saint-Petersburg, March 31–April 5, 2019. — Saint Petersburg, VVM Publisher, 2019. P. 130-132.

Simulation of an ionic liquid 1,3-di-n-dodecyl-imidazolium chloride in liquid crystal state

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Currently, ionic liquids (IL) containing an imidazole ring are used as electrolytes for fuel cells, as stabilizers for nanoparticles [1, 2].

As a representative of imidazolium IL, [C12-Im-C12] [Cl] is interesting as it has long alkyl chains and, therefore, at some temperatures, it has the properties of not only ionic liquids, but also liquid crystals. This IL was studied in the liquid-crystalline state using the molecular dynamics method in the AKMD program. When processing the results, the most favorable conformations of the [C12-Im-C12] [Cl] cation (Fig. 1) at 370 K and their interaction with chlorine ions and water molecules were considered. Using the probability density for the realization of dihedral angles, the conformations were studied in relation to 3 different bonds. It turned out that the alkyl chains are most likely directed in one direction, moreover, they are orthogonal to the plane of the imidazole ring and this coincides with the initial configuration of the molecule. The radial distribution function of the interaction of the imidazole ring with the chlorine ion and oxygen atom from the water molecule was also considered. The numerical values of this function show that there is one ion and one water molecule per ring, i.e. all water molecules and anions are concentrated around the imidazole rings.

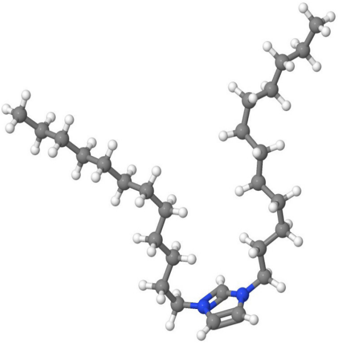

Fig. 1. 1,3-di-n-dodecyl-imidazolium cation.

References

1. Gettanjali S., Anil K. // Ind. J. Chem. 2008, 47(A), 495-503.
2. Bellina F., Bertoli A., Melai B., Scalesse F., Signori F., Chiappe C. // Green Chem. 2009, 11, 622-629.

NMR relaxation of solvent nuclei in solutions of monomeric and aggregated RRM2 domain of TDP-43 protein

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Aggregation of protein is a stochastic process of formation of nm-μm particles comprising polypeptide chains connected by covalent and/or non-covalent interactions. It is relevant to the context of many proteinopathies, biophysical research, and the pharmaceutical industry. At the present moment, the aggregation could be quantitatively studied using methods based on various physical observables (light scattering, fluorescence, electrophoresis, etc.). However, the extraction of the structural features and dynamics information is challenging without structural biology methods. NMR on protein nuclei can provide data on soluble and homogeneous samples, while it is struggling to observe inhomogeneous, dynamic, and slowly tumbling aggregate particles. The NMR relaxation of solvent nuclei paves the way to study protein aggregation under native conditions [1]. The present study aims to illustrate the possibility of ^{1}H, ^{2}H, ^{23}Na, and ^{35}Cl NMR relaxation studies of aggregation in protein systems on the example of aggregate particles formed under conditions of oxidative stress from RRM2 domain of TDP-43 protein [2]. For example, the observed relaxation of water protons could be described as a three-site exchange between (*i*) bulk water molecules, (*ii*) water in hydration of protein, and (*iii*) exchanging protein protons. The study besides comprises the simulations of dependencies for observed ^{1}H relaxation rates on system parameters that respond to protein aggregation. Fitting of experimental data may provide an insight on structural changes upon aggregation (e.g. denaturation, assembly of high molecular weight complexes) and alteration of chemical exchange for protein protons. Complementary studies of relaxation of nuclei of salt ions give information for charge distribution on the solvent-accessible surface of protein aggregates. Information that could be extracted from NMR relaxation of solvent nuclei renders this approach as a worthy companion to structural biology methods that are applicable only for soluble well-behaving protein samples.

Acknowledgments. The reported study was funded by RFBR and CITMA according to the research project №18-53-34003.

References

1. Taraban M.B. et al. Use of Water Proton NMR to Characterize Protein Aggregates: Gauging the Response and Sensitivity // Anal. Chem. 2019. Vol. 91, № 6. P. 4107–4115.
2. Rabdano S.O. et al. Onset of disorder and protein aggregation due to oxidation-induced intermolecular disulfide bonds: case study of RRM2 domain from TDP-43 // Scientific Reports. 2017. Vol. 7, № 1. P. 11161.

Simulation of model system of carbosilane dendrimer of different generations

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Dendrimers are highly branched synthetic polymers, usually organized according to three structural building blocks: the core block as the origin of branching points; repeating blocks and the functional groups as the ending structure. Dendrimers are used in various fields of polymer chemistry, biology and medicine. The study of structural properties of dendrimers is very important for understanding their physical behavior and interactions with the environment and with other compounds [1].

Studied molecule was modeled with GROMACs package [2] in chloroform solution. For each case with different generation and cell size was made an energy minimization and equilibration conducted in two phases – NVT and NPT. After, the MD simulations for 0.1–2 μs, depending on the generation was run.

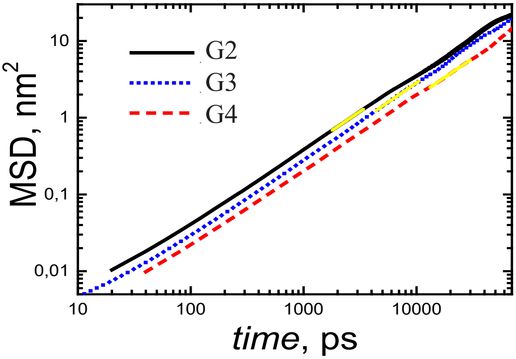

Fig. 1. MSD as a function of time for various generations in double logarithmic scale. The range of the diffusion regime for each generation is marked in yellow.

Acknowledgments. This work is supported by the Russian Foundation for Basic Research (No. 19-03-00715). The simulations were performed in Computer Resources Center of Saint-Petersburg State University.

References

1. Yamamoto K. et al. New Horizon of Nanoparticle and Cluster Catalysis with Dendrimers // Chemical Reviews, 2020.
2. Abraham M.J. et al. Gromacs: High performance molecular simulations through multi-level parallelism from laptops to supercomputers // SoftwareX. 2015.

Water mobility in pillared zeolites with mordenite and ZSM-5 studied by ^{1}H NMR

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During recent years the interest to layered zeoliteshas increased. These materials exhibit a hierarchical porous structure, in which macropores formed by the space between the layers can be filled by guest molecules, e.g. water. Water is an important component in the composition of the substance. Moreover, many chemical reactions are promoted by water. From this perspective the knowledge of water behavior in the confined interlayer zeolite space in highly required. Nuclear magnetic resonance (NMR) is a versatile tool that provides an access to the structure and mobility of water.

Here we report on the results of our study of the dynamics of water molecules inside the interlamellar space of the pillared mordenite and ZSM-5 zeolites.

^{1}H NMR experiments were done using a Bruker Avance IIITM 400 MHz solid-state NMR spectrometer (operating with Topspin version 3.2) using a double-resonance 4mm low temperature magic angle spinning (MAS) probe. The temperature was changed within a temperature range from 173 to 293 K and controlled with accuracy 0.5 K. Spin-lattice relaxation times (T_1) were measured using the so-called inversion-recovery method ($180° – \tau – 90°$).

In zeolites, water can be in various states: bounded to the zeolite surface and bulk. The evolution of the ^{1}H NMR spectra with temperature confirms that the majority of water molecules is situated inside the mesopores.At room temperature water molecules are bounded with the zeolite surface by hydrogen bonds. However, with temperature decreasing one observes disappearing of these hydrogen bonds and formation of bulk water with its further crystallization.The relaxation experiment also evidencesthe complex behavior of water: within the studied temperature range $T_1(T)$points out at existence of at least three regimes of the proton motion with the activation energy of 8.0, 21.0 and 25.9 kJ/mol for the pillared mordenite sample and 5.2, 23.1 and 30.7 kJ/mol for the pillared ZSM-5 sample.

Acknowledgments. The work was supported by the Russian Foundation for Basic Research (project No. 18-53-34004).

References

1. W.J. Roth, P. Nachtigall, R.E. Morris, J. Čejka // Chem. Rev. 114 (2014) 4807–4837.
2. C. Pantalei, R. Senesi, C. Andreani, P. Sozzani, A. Comotti, S. Bracco, M. Beretta, E. Sokol // Phys. Chem. Chem. Phys. 13 (2011) 6022–6028.

The effect of the alkyl chain length on the rotational motion of ions in alkylammonium nitrate ionic liquids. A molecular dynamics simulation study

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Alkylammonium nitrate protic ionic liquids (AN PILs) are considered as perspective electrolytes for advanced fuel cells. In the present study a subset of three alkylammonium nitrate PILs: ethyl-, propyl-, and butylammonium nitrates, was investigated using molecular dynamics simulations.

For each of three AN PILs a model system of 300 nitrate and 300 alkylammonium ions in cubic cell with periodic boundary conditions was simulated in the NPT ensemble at 298 K and 1 atm using the MDynaMix package [1]. The cations were modeled employing the potentials described in Refs. [2-4]. Model nitrate anion was treated as a 4-site planar structure with a central nitrogen atom and three oxygen atoms at a distance of 1.22Å with all O-N-O angles of 120^o [5]. Its intermolecular interactions were described as the sum of Coulomb and Lennard-Jones (6-12) potentials. Three different potential parameters sets, taken from Refs. [6-8], were considered.

To describe the reorientational motion of ions the normalized time autocorrelation functions of various intramolecular vectors were calculated. A special attention was given to the reorientational correlation time of the N-H molecular vectors of the alkylammonium cations. The effect of the alkyl chain length on the dynamical properties of alkylammonium nitrate PILs was studied in details.

References

1. A.P. Lyubartsev, A. Laaksonen // Comp. Phys. Comm., 128, 565-589 (2000).
2. T. Mendez-Morales, J. Carrete, O. Cabeza et al. // J. Phys. Chem. B, 118, 761-770 (2014).
3. V. Gomez-Gonzalez, B. Docampo-Alvarez, O. Cabeza et al. // J. Chem. Phys., 143, 124507 (2015).
4. T. Mendez-Morales, J. Carrete, J.R. Rodriguez et al. // Phys. Chem. Chem. Phys., 17, 5298-5307 (2015).
5. C. Ebner, R. Sansone, S. Hengrasmee, M. Probst // Int. J. Quant. Chem., 75, 805-814 (1999).
6. T. Megyes, S. Balint // J. Phys. Chem. B, 113, 4054-4064 (2009).
7. Y. Umebayashi, W.-L. Chung, T. Mitsugi et al. // J.Comput. Chem. Jpn., 7, 125-134 (2008).
8. A. Laaksonen, H. Kovach // Can. J. Chem., 72, 2278-2285 (1994).

Molecular Dynamics Simulation of [CuCl$_2$(1,2-diaminoethane)$_n$] (n = 1, 2) complexes in aqueous solution

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Medical research shows that many anticancer, antiviral and antiseptic agents work by binding to DNA. This can damage the DNA of cancer cells and kill them [1]. The use of metal-based drugs with transition metals, like Cu (II) or Zn (II), presents the most important strategy in the development of new anticancer and antimicrobial agents [2].

Selection of suitable Force Fields for Molecular Dynamics simulation of EDA-$Cu^{2+}\cdot 2Cl^-$ and EDA_2-$Cu^{2+}\cdot 2Cl^-$ complexes in aqueous solution could be used in further research of anticancer drugs.

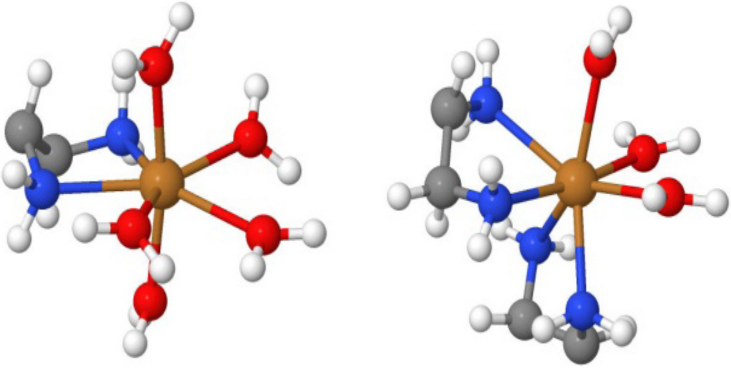

Fig. 1. The structures of EDA-Cu^{2+} and EDA_2-Cu^{2+} aqua complexes.

References

1. N. Raman, A. Selvan, S. Sudharsan. Metallation of ethylenediamine based Schiff base with biologically active Cu(II), Ni(II) and Zn(II) ions: Synthesis, spectroscopic characterization, electrochemical behaviour, DNA binding, photonuclease activity and in vitro antimicrobial efficacy // Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. V. 79. № 5. September 2011. P. 873-883.
2. J.G. Liu, B.H. Ye, H. Li, Q.X. Zhen, L.N. Ji, Y.H. Fu. Polypyridyl ruthenium (II) complexes containing intramolecular hydrogen-bond ligand: syntheses, characterization, and DNA-binding properties // J. Inorg. Biochem. 1999. V. 76 №. 3. P. 265–271.

S. First Steps in Science
(for secondary school students)

The effect of changes in hydration properties of Cl^- anion in aqueous solutions according to NMR-relaxation data

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In order to study the hydration properties of chlorine anion in aqueous electrolyte solutions, the method for determination of solution microstructure parameters, based on the study of concentration dependencies of nuclear magnetic relaxation rates of solvent nuclei [1] at different temperatures, is used.

The first bend of the experimental dependence (see Fig. 1) is connected with the complete filling of all hydrate shells and disappearance of the free solvent structure.

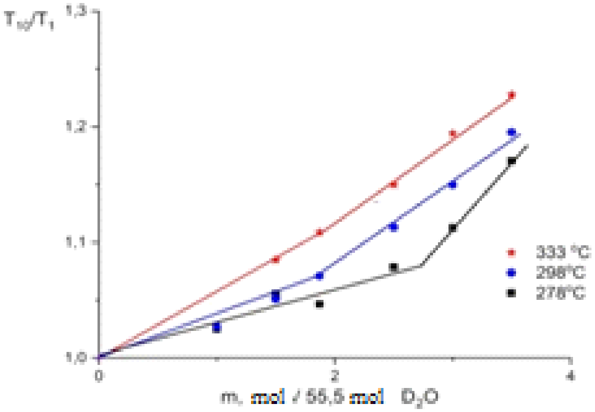

Fig. 1. Isotherms of concentration dependences of relative relaxation rates of deuterons in NaCl-D_2O solutions.

It can be seen that as the temperature increases, the bend shifts to the area of lower concentrations. This is due to the fact that at temperatures below 35 °C chlorine anion coordinates 4 molecules of solvent, and at temperatures above 35 °C – 8 solvent molecules.

Acknowledgments. This research was carried out with the support of the Saint-Petersburg State University (No. 107-11462).

References

1. A.V. Donets. The effect of changes in coordination of chlorine and bromine ions in aqueous electrolyte solutions at temperature variation according to NMR-relaxation data. SPbSU (2007).

Finding soil contamination level by heavy metals in some districts of Saint-Petersburg

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Heavy metals – chemical elements, which have metallicity and high atomic weight. They are Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Mo, Cd, Sn, Sb, Te, W, Hg, Tl, Pb, As, Bi and others. They accumulate in soil, and it is really hard to get rid of them. If they are too much, they can make colossal damage for environment. Soil, plants, animals and human suffer from them.

Purpose of the work was finding concentration of movable forms heavy metals in Krasnogvardeisky, Nevsky, Vasiliostrovsky and Central districts by atomic emission spectral analysis , comparison of results with maximum permissible concentration and scientific literature. Also we found concentrations another metals like Al, K, Li to find interelement correlation.

We took 3 samples from one district. They dried about 2 weeks and then they were grinded up and were made soil extracts with ammonium acetate buffer solution. After preparation we carried out metering in ICPE-9000, which located in resource-center of SPSU. We make calibration dependencies to determine concentration.

We made some conclusions during the work:

Concentration of metals is really various in different samples of one or different districts.

Most samples have one or more exceeding the maximum permissible concentration.

There are too much Pb and Zn in Central, Vasiliostrovsky and Nevsky districts. Also there is too much Cd in Vasiliostrovsky district.

Based on the results, the cleanest samples are samples of Krasnogvardeisky district and the most contaminated samples of Central district.

The highest correlation is observed between Al and Fe.

Table of Content

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