Poster Session A
Monday, September 8, 2014

COST CM1101
PA-1 – PA-11

PA-1

Investigation of Nano-coatings Synthesized from Functionalized with Various Metals and their Oxides Natural Aluminosilicate Nanotubes (Halloysite), Deposited on Ceramic Materials and Perfluorinated Membranes

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Halloysite presents unique natural double-walled nanotubes consisting of layers of aluminum and silicon oxides. The inner diameter of the nanotubes is typically less than 15-20 nm, and their length is in the range of 0.5-1 microns. We have shown that under the influence of short-term exposure of the low temperature microwave plasma halloysite nanoparticles do not undergo any significant chemical or physical changes, while metal salts (Fe, Ni, Co, Pt, Pd, Re, etc.), intercalated into their interior, yield different nanoparticles of zerovalent metals or their oxides, depending on plasma-generating gas composition. Furthermore, halloysite nanotubes in microwave plasma conditions are capable to firmly fuse with the surfaces of porous ceramic and other materials to form a tenacious layer on their surface, which retains all the properties of the original halloysite. During the research there was formulated the transport model of monovalent ions through a three-layer system: initial membrane layer MF 4SK, halloysite surface layer with embedded nanoparticles and the diffusion layer solution. Calculations of diffusion and cross-diffusion forces of different metal cations and their comparison with experimental data allowed us to determine the effective diffusion coefficients of the ions and the distribution coefficients of ion pairs in the modified membrane. Study of modified membranes sections by optical methods allowed us to estimate the influence of surface topography on the parameters of the current-voltage curve. We studied in detail voltage characteristics in various experimental conditions, that allowed us to estimate the contribution of interphase boundaries in the overall effects of concentration polarization. The dependence of the diffusion permeability coefficients of new bilayer nanocomposites in different directions from such parameters of composite membranes as the thickness and the hydrophobicity degree of the surface layer was examined.

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PA-2

Permeability of Soft Microgel Particles at Electric Fields

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We study the influence of the charge and ionic strength on the permeability of microgel particles under electric fields. Electrophoresis experiments with pH-ionizable poly(N-isopropylacrylamide)-co-acrylic acid microgels show that particles interestingly behave as permeable spheres when the polymer network is ionized whereas they keep non-permeably in the absence of charge. The friction coefficient strongly reduces as the polymer mesh expands following a power law $g \sim d^{-4}$ for fully charged networks, in contrast to that expected for non-permeable spheres, $g \sim d$. The overall behaviour arises from the motion of counter-ions driven by the external electric field, which causes hydrodynamic flow across the microgels making them permeable to the solvent. The microgel permeability also depends on the ionic strength, c; a salt-dependent local viscosity is proposed as responsible for these permeability changes. The driving mechanism is associated to the presence of strongly hydrated counterions located around fixed charges on the network that induces strengthening of the water confinement, which in turn results in an increased viscosity, $h \sim c^{0.2}$, and consequently reduced permeability.

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PA-3

Effects of Surfactants on the Swelling Transition of pNIPAM Microgels

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We investigate the effects of anionic and cationic surfactants on the volume phase transition of thermo-responsive poly(N-Isopropilacrylamide), pNIPAM, microgels. The influence of both surfactants, SDS and DTAB respectively, is totally different despite their hydrophobic tail is identical. Whereas the cationic surfactant DTAB does not change appreciably the swelling behavior, the addition of the anionic surfactant SDS significantly swells the microgel and shifts the transition to higher temperatures. In addition, the swelling transition broadens and exhibits a two-step swelling process that can be understood by considering that SDS molecules bounds to pNIPAM segments hydrophobically and repel each other via electrostatic interaction. The microgel-surfactant mixture then behaves as an ionic network in which the first step of de-swelling arises from the change in the polymer solubility with temperature whereas the second step is attributed to its competition with the ionic contribution. The experimental results are quantitatively interpreted in terms of the classical Flory-Huggins theory with important modifications to account for the free energy of association of the surfactant molecules with the polymer network and for a swelling-dependent ionic contribution.

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PA-4

Effect of Surfactant Characteristcs and Conditions of Synthesis on the Formation of Periodic Mesoporous Phenylene-Silicas

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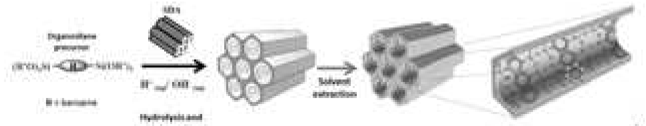
Periodic mesoporous organosilicas (PMO) prepared by self-assembly of bissilylated organic bridge precursors in the presence of template molecules started to be developed in 1999.[1] In 2002, a phenylene PMO possessing both mesoporous and molecular-scale periodicity was synthesized using octadecyltrimethylammonium bromide surfactant.[2] We have shown that it was possible to preserve the 2D hexagonal arrangement of pores together with the order along the wall using alkyltrimethylammonium surfactants with alkyl chain from 14 to 18 as template, Scheme 1.[3]

Here, we present a study of the structural and morphological characteristics of phenylene-PMOs prepared using alkyltrimethylammonium or alkyl methyl-imidazolinium bromide, at different pH, temperature and in presence or absence of additives. PMOs were characterized using N_2 isotherms, XRD, SEM and TEM, solid-state NMR and thermal analyses.



Scheme 1: Typical synthesis of PMOs.

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PA-5

Spreading and Layer Properties in the Case of Pseudo-Partial Wetting of Oil on Surfactant Solution

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We study the spreading phenomena when drops of hydrocarbon oil are placed on aqueous solution of surfactant (CTAB). The rate of spreading depends significantly upon the surfactant concentration (and is zero below a certain threshold). The time evolution of the spread layer and its structure are investigated by ellipsometry. The thickness is determined from analysis of the data for the ellipsometric angles Δ and Ψ. The signal behaviour vs. time, and the pattern of distribution of the experimental points, suggest that a very thin precursor layer (~1 nm) coexists with flat lenses (~100 nm). This features a pseudo-partial wetting of the surfactant solution by the hydrocarbon. In contrast, silicone oil is found to give complete spreading, with layers whose thickness is rather large and non-uniform. The surface pressure is measured with a Langmuir trough, at an A/W interface containing alkane – after a fast initial non-equilibrium spreading of drops of pure oil, saturation of the surface is rapidly reached. The complex spreading behaviour in the studied system can have implications to cases of practical relevance. We have recently shown [1] that the pseudo-partial wetting of the air/ water boundary by oil is of crucial importance for spontaneous formation of nano-droplets: in a fast dynamic process the spreading layer of oil can be dispersed into the bulk aqueous solution during rupture of air bubbles.

[1] Jie Feng et al., Nanoemulsions obtained via bubble bursting at a compound interface, *Nature Physics* 10 (2014) in press.

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PA-6

Complexation Between Poly(allylammonium) Cation and Poly(styrenesulfonate) Anion; Ionic Strength and Electrolyte Type Influence

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Complexation between poly(allylammonium) cation and poly(styrenesulfonate) anion was investigated in aqueous solutions of binary 1:1 sodium electrolytes (NaX, X = F, Cl, Br, I, NO_3, ClO_4) by means of microcalorimetry, dynamic light scattering, electrokinetics and spectrophotometry. The obtained results revealed that at lower molar ratios of monomers charged polyelectrolyte complexes were formed. At molar ratios close to equivalence and at lower salt concentrations (c(NAX) / mol dm^{-3} $\leq$ 0.1) flocculation occurred. The obtained precipitates contained approximately equimolar amounts of oppositely charged monomers. At c(NAX) / mol dm^{-3} $\geq$ 0.5 (X = NO_3, ClO_4) and in the case when the polycation was present in excess, the amount of positively charged monomers in the precipitate was higher than that of negatively charged monomers. In addition, the aggregation of positively charged complexes in concentrated solutions of all investigated electrolytes was noticed. The onset of aggregation was strongly anion specific. However, the aggregation of negatively charged complexes did not occur even at NaX concentration as high as 3 mol dm^{-3}. At 25 °C and c($NaClO_4$) = 1 mol dm^{-3} equilibrium was not reached after two months. By contrast, the supernatants showed no traces of free polyanion chains after being heated for a week at 60 °C. The interpolyelectrolyte neutralization was found to be predominantly entropically driven, irrespectively of the type of reaction products formed (polyelectrolyte complexes, precipitates), electrolyte type and concentration. Nevertheless, a correlation between obtained reaction enthalpies for complex and precipitate formation with anion hydration enthalpies was observed. The product formation was the least enthalpically favourable in electrolyte solutions containing weakly hydrated NO_3- and ClO_4- anions.

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PA-7

Aggregation Rate of Colloidal Particles under Reaction-Limited Conditions at High Concentrations

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Aggregation of colloidal particles plays a key role in a variety of applications. A very common situation is where colloidal particles aggregate in the presence of residual repulsive interaction, a situation commonly known as reaction-limited conditions. In the thirties, Fuchs extended Smoluchowski's equation, developed for the rate of aggregation of colloidal particles under diffusion-limited conditions, to the case of reaction-limited conditions. Nevertheless, its use is limited to sufficiently dilute conditions. In this work we investigate by means of Brownian-Dynamic simulations the rate of aggregation of colloidal particles at high volume fractions, up to 30%. We have developed a correction to Smoluchowski's equation for the rate of aggregation of colloidal particles under diffusion-limited conditions at high concentrations within the framework of trapping theory. This corrected aggregation kernel, accounting for concentration dependence effects, was implemented in a population-balance equations scheme and used to model the aggregation kinetics of colloidal particles undergoing diffusion-limited aggregation under concentrated conditions. It was found that classical Smoluchowski's theory substantially underpredicts the rate of aggregation as well as the onset of gelation, with deviations becoming progressively more severe as the particle volume fraction increases. Similarly, we observed that even under reaction-limited conditions the rate of aggregation of particles under concentrated conditions is substantially higher than that expected from Fuchs-Smoluchowski's theory. An attempt to develop a kernel that corrects for the effects of high concentrations has been made.

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PA-8

Worm-Like Micelles of Polymerizable Surfactants as Template for the Preparation of Rod-Like Polymer Nanoparticles

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The use of particles with anisotropic shape is of significant interest since it allows fabrication of structures with special symmetries and degree of packing, as well as with anisotropic properties. Rod-like polymer particles could have interesting properties and could find many practical applications; however, few methods for the production of such particles are available. In this work we introduced and investigate a method for synthesis of a new class of polymeric nanorods and nanofibrils based on emulsion polymerization using wormlike polymerizable micelles as template. Wormlike micelles are elongated and semiflexible aggregates of surfactant molecules. The equilibrium and dynamics of the micellar structures, however, are determined by a delicate balance of intermolecular forces that can be easily disrupted. In the current study it has been observed that addition of oils or polymers typically reduces the average micelle length and results in a dramatic decrease of the solution viscosity on the microstructure and loss of the highly elongated and entangled micelles. During the polymerization process, the viscosity is reduced by several orders of magnitude to a water-like value, and no viscoelasticity can be observed either visually or rheometrically. These data suggest a transition from rodlike to spherical micellar aggregates. A polymerizable surfactant, cetyltrimethylammonium 4-vinylbenzoate (CTVB), containing a polymerizable counterion, has been prepared and investigated with the purpose of "locking in" the micellar structure over the oil polymerization so that the template is less sensitive to environmental changes. Elongated particles and long polymer fibrils have been formed depending on cross linker concentration used, partially preserving the structure of the parent micelle upon polymerization.

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PA-9

Tuning the Morphology of Cellulose/Hydroxyapatite Scaffolds for Bone Tissue Engineering Application

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The development of polymer based three-dimensional scaffolds which may once solve clinical problems such as the loss of the bone tissue is one of the current challenges in bone tissue engineering. The porous structure of the scaffolds must be precisely designed as it is related with cell adhesion, proliferation, differentiation and vascularization. In this work the porous morphology of the cellulose composites with nanohydroxypatite (particle size ≤200 nm) or microhydroxyapatite (particle size 15-35 μm) was developed by freeze-drying of the prepared gel. For the morphological characterisation of the obtained scaffolds a scanning electron microscopy and micro-computed tomography were used. It was found that a porosity as well as a pore size of the scaffold depended on the solvent in the discontinuous phase of the gel prior the drying process. Changing a concentration of a solvent the morphology of the lyophilized scaffold varied from macroporous to dense. In optimal conditions the matrix of the interconnected porous structure with micro and macro pores was obtained. The porosity of the scaffolds varied from 65 to 72% when microhydroxyapatite and nanohydroxyapatite were used, respectively.
The cellulose/hydroxyapatite scaffold showed a permeable pore network for glucose thus revealing its suitability for fast diffusion of nutrients and metabolites.

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PA-10

Synthesis of Ce- and Zr-doped Alumina Nanoparticles in W/O Microemulsions: Potential Application in Fischer Tropsch Synthesis

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Fischer Tropsch synthesis (FTS) allows the production of valuable long chain hydrocarbons from Natural Gas, Biomass and Coal. The catalytic material for FTS consists of Cobalt nanoparticles well dispersed onto alumina [1]. The nature of the catalytic support influences several important properties of the Co catalysts such as their dispersion, reducibility and electronic structure [2]. We investigated the use of the water-in-oil (w/o) microemulsion method for the synthesis of Al_2O_3 as well as Ce- and Zr-doped Al_2O_3 nanoparticles. This technique offers various advantages such as high control of the nanoparticle size and composition, and high surface area [3]. Zr and Ce ions were chosen as Al_2O_3 promoters, since the first prevents the formation of cobalt-aluminate species that are unfavorable for activity of the catalysts; the second enhances the mechanical property of Al_2O_3 at high temperatures. The aim is to obtain well-defined Al_2O_3, Zr-Al_2O_3 and Ce-Al_2O_3 nanoparticles and to investigate their role as supports for Co nanoparticles in FTS. The synthesis of doped and undoped Al_2O_3 nanoparticles was performed in nonionic W/O microemulsions. The materials were purified, calcined at 550°C, and impregnated with 12wt % cobalt. Characterization by XRD, TPR, BET, chemisorption, TEM and SEM was carried out, in order to investigate the role of doping on the characteristics of the obtained Co supported nanoparticles.

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PA-11

Structure-Activity Relationships for Delivery Agents on the Scaffold of Self-Assembling Cationic 1,4-Dihydropyridines

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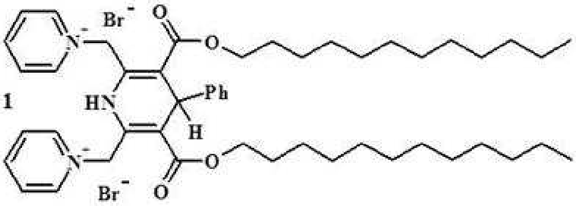
Cationic amphiphiles on the 1,4-dihydropyridine (1,4-DHP) scaffold with self-assembling properties form liposomes and can be used as transport systems. Our initial studies confirmed that some cationic 1,4-DHPs (e.g. comp. 1, Fig. 1) are more active than DOTAP and PEI 25 [1,2]. Last ten years we have been working on the development of compounds as gene delivery systems, studying the influence of lipids head-group on the gene transfection activity [3] and properties of formed liposomes [4]. The previous studies gave background for drawing of final conclusions concerning to relationships of biological and physical-chemical properties of liposomes forming compounds. The aim of the work is to clarify the relationships of biological activity of self-assembling 1,4-DHPs and their physical-chemical properties: for individual compounds and their formed nanoaggregates.



1

Variation of 1,4-DHP molecule:
1) head-group moieties at the 2,6-positions;
2) substituents at 3,5-positions;
3) substituents at the 4-position;
4) substituents at the 1-position;
5) variation of anion;
6) dimerisation.

Fig. 1. Structure of compound **1** and description of structure modifications.

To explore the posed questions we designed and synthesised a group of 1,4-DHP amphiphiles being structurally related to the most efficient delivery agent 1. The amphiphiles were synthesised by targeted modification of the substituents at the 1,4-DHP molecule, physical-chemical analysis of properties of them is performed. Characterisation of nanoaggregates was achieved by atomic force microscopy or transmission electron microscopy and the dynamic light scattering methods. The conclusions would be important for design and development of more efficient delivery agents.

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ECIS Posters
PA-12 – PA-69

PA-12

High Resolution Structure and Dynamics of Virus Self-Assembly

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Viruses are evolved examples of self-assembled structures that are remarkably sophisticated biological machines. Viral capsids and capsid proteins have been used to assemble structures for guided synthesis of inorganic and organic nanostructures, as cages for packaging cargos, and as vectors for gene therapy. The mechanism of packaging even biologically relevant nucleic acids, however, remained unknown. The Simian Virus 40 (SV40) is a small nonenveloped virus belonging to the polyomavirus family. SV40 viral capsid proteins encapsidate a circular double-stranded (ds) DNA genome of 5,200 base pairs compacted by histone octamers forming a minichromosome structure. Using small angle x-ray scattering as well as computer modeling, we wish to reveal the solution structure of Simian Virus 40, as well as its response to different solution conditions.

Recombinant $VP1_5$ (SV40's main capsid protein) also assembles cooperatively around different nucleic acids, to form virus-like particles (VLPs) in a process that appears to follow a rapid kinetic mechanism, in which the capsid geometry, depends on the size and structural features of the nucleic acid substrate. Using Time-Resolved Small-Angle X-ray Scattering we have been able to directly visualize, with a time resolution of 50ms, SV40 $VP1_5$ encapsidating short ssRNA (524 nucleotides) and long dsDNA (5.2 kbp) molecules. The assembly process around ssRNA yields $T = 1$ icosahedral particles comprised of 12 pentamers and one RNA molecule. The reaction follows an extremely rapid, two-state kinetic process with no detectable intermediates. The encapsidation reaction around dsDNA yields a $T = 7$ icosahedral particles similar to the structure of the capsid of SV40. The reaction time scale is of the order of minutes and SAXS indicates the accumulation of intermediates throughout the reaction.

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PA-13

Monitoring the Interaction of Nucleolipoplexes with Cell Membrane Models: from Surface Contact, to Membrane Fusion and DNA Release

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Lipid-based assemblies are the most studied systems for the delivery of nucleic acids for therapeutic purposes. Fundamental research has been directed to the elucidation of the structural features of lipid-DNA assemblies in relation with the experimental conditions, the chemical nature of the lipids and of the nucleic acids. However, the design of efficient nanostructured vectors, implies the comprehension of their behavior in biologically relevant media and interaction with cell mimic systems.

In this contribution we report on the nucleolipid liposomes-DNA complexes (nucleolipoplexes), from the anionic nucleolipid POP-Ade (1-Palmitoyl-2-oleoyl-sn-glycero-3-phosphatidylglycerol) mixed with two zwitterionic helper lipids, POPC (1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine) and DOPE (1,2-dioleoyl-sn-glycero-3-phosphoethanolamine).

We investigated the interaction between POP-Ade nucleolipoplexes and Giant Unilamellar Vesicles (GUVs), taken as cell membrane models through Confocal Microscopy (LSCM) and Fluorescence Correlation Spectroscopy (FCS).

First, we studied the morphology and the structure of nucleolipoplexes through the diffusion of a lipid probe embedded within nucleolipoplexes' lipid structure and of a lipid tag attached to the complexed DNA.

Then, we monitored in real time through LSCM the interaction between nucleolipoplexes and GUVs and membrane fusion occurrence was found dependent on the nucleolipoplexes' liquid crystalline structure and on the surface charge of the target model membrane.

Finally, we carried out FCS studies on the diffusion of fluorescently-labeled lipids and of fluorescently-labeled DNA in nucleolipoplexes-GUVs interaction regions, and on the penetration of fluorescently-labeled DNA inside the GUVs' lumen upon interaction with nucleolipoplexes. The dynamic information on lipid exchange and of DNA diffusion allowed us to elaborate possible hypothesis on the structure of the fusion intermediates and on the interaction pathway between nucleolipoplexes and GUVs from surface interaction, to membrane fusion, to DNA release inside the GUVs.

Costanza Montis, Piero Baglioni, Debora Berti Soft Matter, 2014, 10, 39

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PA-14

Mimicking of Cell Chemotaxis by Oil Droplets

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In the nature, living cells can move preferentially in the direction of the higher concentration of certain chemical and such movement is called as „chemotaxis". In present paper we focus on the study of Artificial chemotaxis" of synthetic objects without any sign of life. Oil droplets consisting of pure decanol are able to move in a gradient of salt in a water solution containing sodium decanoate. We evaluated key parameters of the chemotactic response, namely the induction time and the migration velocity as function of the sodium decanoate concentration and the salt concentration gradient. We have found that this artificial chemotaxis system bears many qualitative similarities with natural chemotaxis systems, namely: *(i)* the ability to perform chemotaxis repeatedly when the chemoattractant gradients are re-created; *(ii)* to perform chemotaxis in topologically complex environments (*e.g.* mazes); *(iii)* to select the chemotaxis direction based on the relative strength of alternative chemoattractant sources; *(iv)* to wait in a dormant state and later respond to a stimuli-responsive chemoattractant release; and finally, *(v)* to deliver a reactive payload towards the chemoattractant source. To the best of our knowledge, this is the first time that an artificial chemotaxis system exhibiting all of the above-mentioned five features has been described.

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PA-15

Cyclosporin A in Cellular Membranes Modeled with Langmuir Monolayers

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Cyclosporin A (CsA) is a hydrophobic cyclic peptide produced by the fungus Tolypocladium inflatum and composed of 11 aminoacids.

It is well known for its high efficiency as an immunosuppressor for transplanted organs and antiinflammatory properties, however, it is also active as antiparasitic (antimalarian) drug [1].

Antimalarian mechanism of CsA action lacks a detailed understanding at molecular level. Due to a high lipophilicity of CsA, it is able to interact with lipids of cellular membranes but molecular targets of this drug are still unknown. To get a deeper insight into the mode of anitmalarian activity of this drug, it is of utmost importance to examine its interactions with membrane components.

To reach this goal, the Langmuir monolayer technique [2], which serves as a very useful, easy to handle and controllable model of biomembranes [3], can be employed. However, the requirement for using this technique is that the molecule of interest must be surface active and capable of stable Langmuir monolayer formation.

Therefore, the aim of this paper is to provide Langmuir monolayer characterization of cyclosporine A and examine itsinteractions with cell membrane lipids, i.e. DPPC, POPC, sphingomyelin and cholesterol.

Differences in interactions between CsA and basic membrane lipids can be helpful in finding molecular targets for its antimalarian activity.

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PA-16

The Effect of Dextran Sulfate on Model Biological Membrane

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Dextran sulfate (DS) belongs to the group of polysaccharides with diverse therapeutic activities. One of the most important function of DS is the anticoagulation effect, causing the reduction of the red blood cell (RBC) aggregation in bloodstream. Due to this property such biopolymer can be used in pharmaceutical therapy as blood plasma substitute [1-3]. It appears that a significant role in the therapeutic efficacy of DS is its effects on the erythrocyte membranes. Although the biophysical properties of DS are studied rather well little is known about consequences of their association with natural lipid membranes. Therefore a study of DS influence on the model erythrocyte membrane is of particular importance.

The aim of the present work was to examine the effect of DS on the lipid organization at the air-water interface. It was possible by analyzing physicochemical properties of Langmuir monolayers, treated as the simplest model of a half of a biological membrane. The analysis of obtained results clearly demonstrates selective influences of examined biopolymer on molecular interactions within model biological membrane.

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PA-17

Characterization of Osteoblasts Cultured on RGD-Peptide Hydrogels

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The need to improve bone regeneration became more dominant in recent decades[1]. A major research strategy to activate a better bone regeneration is to engineer scaffolds that have mechanical, chemical and biological properties. In previous research on bone regeneration carried out in our lab an amphiphilicpeptide hydrogel, abbreviated FD (sequence: Pro–Asp–(Phe–Asp)$_5$–Pro), was used as scaffold. This hydrogel showed a positive result for bone regeneration *in vitro* and *in vivo*[2]. The hypothesis of this research is that enhancement of cell-scaffold interactions in FD hydrogels may further encourage bone regeneration. For this purpose a peptide denoted FD-RGD was incorporated in the matrix of the FD hydrogels. Hydrogels with different FD:FD-RGD ratios (10%, 20%, 30% and 0% as a control) were characterized chemically and in cell cultures. CD results showed that peptide solutions with different FD:FD-RGD rations, maintained the mixed β-sheet and random composition as in FD peptide. Oscillatory rheology assays showed that increasing FD-RGD percentage in the hydrogel lower the storage and loss moduli. More viable cells and cell-hydrogel interactions were found on hydrogels with FD-RGD peptide compared to FD hydrogels. These results highlight the potential advantages in supplementing the amphiphilic and acidic β-sheet peptide hydrogels with specific biologically active motifs.

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PA-18

Bio-based Polyester Colloids

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Aliphatic polyesters derived from bio-based monomers are receiving increasing attention as medical devices for drug delivery and tissue engineering [1]. In our previous work we have synthesized and characterized a series of copolyesters composed of succinic acid, dimerized linoleic acid and 1,4-butanediol. The chemical structure of the monomers used for the synthesis and of the resulting copolyester is represented in Figure 1. Degradable nanoparticles prepared from these polyesters were evaluated as drug delivery nanocarriers [2].

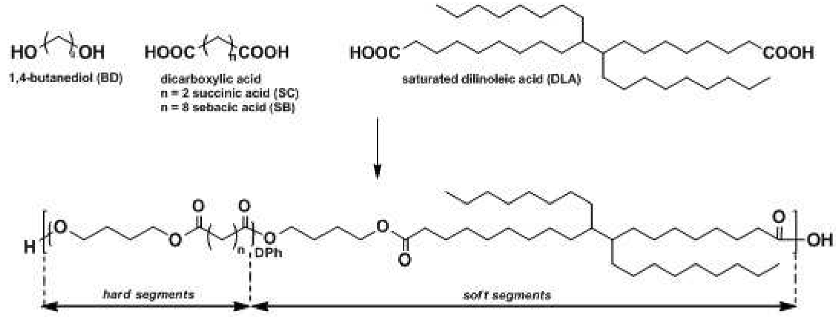

Fig. 1: Chemical structure of bio-based polyesters

In the present work, a high molecular weight (numer average molecular weight M_n ~ 60000 g/mol, dispersities D ~ 1.4-2.0) multiblock copolyesters based on poly(butylene sebacate) (PBS) as the hard segments, and poly(butylene dilinoleate) (PBDL) as the soft segments was synthesized and characterized by FTIR, ^{1}H NMR, SEC, AFM and WAXS.

The novel bio-based copolyesters exhibit very good mechanical properties and thermal stability; with only 5 wt.% of polymer weight loss at 340 – 380 °C. Polyester colloidal nanoparticles with narrow polydispersities were prepared by nanoprecipitation method and investigated by dynamic light scattering and AFM. The mean particle size of nanoparticles in aqueous solutions ranged from 56-170 nm and the size can be tuned by the choice of an organic solvent used for dissolution of the polymer.

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PA-19

Elastic and Viscoelastic Properties of PLL/HA Films Determined by cp-AFM Measurements

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Smart biomaterials have become a highly developed and investigated field of interest in the last decades. One field of smart biomaterials are polyelectrolyte multilayer films (PEM) made of poly-L-lysine (PLL) and hyaluronic acid (HA). Potential applications of $(PLL/HA)_n$ films are located in drug delivery systems (1) and cell adsorption. These applications require a better understanding and control of their mechanical properties, especially separation between elastic and viscous properties.

Mechanical properties of PEM's were determined by using scanning- and colloidal-probe atomic force microscopy (cp-AFM). Elastic properties were determined by single force measurements in liquid at different pH, ionic strength and temperature. While the measured apparent Young's modulus is around 50 kPa for neutral pH, it decreases either by changing the pH to higher/lower values or by increasing the ionic strength. Furthermore separation of pure elastic from viscoelastic properties was determined via creep compliance, stress relaxation and dynamic force measurements, showing a strong viscous behaviour with multiple relaxation mechanisms (3).

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PA-20

Biological Synthesis of Conducting Polymer based Nanostructures and Nanoparticles

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Redox enzyme-based reactions were applied for the synthesis of conducting polymer nanoparticles and functional layers [1,2] suitable for the design of electrochemical biosensors. Glucose oxidase (GOx) E.C. 1.1.3.4. from *Penicillium vitale* was applied as biocatalyst, which is forming hydrogen peroxide that initiates polymerization of some conducting polymers. It was shown that this method is suitable for the synthesis of polypyrrole, polianiline and some other conducting polymer based layers and nanoparticles. It was demonstrated that both dissolved and immobilized [1,2] enzymes could be successfully applied for the enzymatic synthesis of conducting polymer-based nanoparticles. We have demonstrated that formed nanostructures and nanoparticles shows good biocompatibility [3]. We have demonstrated that during such kind of synthesis of nanoparticles and/or nanostructured layers the enzymes becomes entrapped within conducting polymer layer. Therefore such nanoparticles and nanostructured layers are suitable for the design of amperometric glucose biosensors, biofuel cells and some other bio-devices.

Acknowledgements:
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PA-21

Interfacial Water Structure and Surface Charging of Colloidal Interfaces

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In many colloids macroscopic properties such as stability are controlled by the inherent interfaces and interactions of the particle surface with the solvent. It is, therefore, of great importance to gain a detailed understanding of the interfacial molecular structure. This is, however, highly challenging since the interface cannot unambiguously be separated from the bulk in most experimental techniques that do not require other experimental constraints. Nonlinear optical techniques and in particular second-harmonic generation (SHG), are inherently surface sensitive and can be powerful tools in interface science. For colloidal particles, second-harmonic scattering (SHS) patterns exhibit distinct angular features that strongly dependent on particle size as well as on the polarization and orientation of molecules at the particle interface. In our study we have applied SHS to address double-layer charging and the orientation of water molecules at the surface of amphoteric particles. The surface potential of these particles can be adjusted by pH-dependent changes in the protonation state of surface groups. The total second-harmonic field generated by the charged particles comprises contributions directly from the interface and contributions whose origin is the surface charge. Both contributions interfere depending on the sign of the surface potential. Hence the second-harmonic field strength depends not only on the absolute value of the surface charge, but also on the direction of the resulting static electric field. The observed interference in the second-harmonic field allows us to determine the net orientation of interfacial water molecules. Additionally, charge screening experiments corroborate our conclusion and have allowed us to determine the surface charge densities of the particles by applying the $\chi^{(3)}$method.[1]

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PA-22

Curable O/W Emulsion for 3D Functional Printing

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In recent years there is a growing need for printable functional 3 dimensional structures such as conductive bridges. 3D printing as an additive fabrication process which is implemented in a variety of fields such as modeling and scaffolds for medical applications. The 3D structures are formed with different polymers or polymeric precursors, while currently the main required function is the structure itself.

The goal of our research is to fabricate 3D porous structures which contain functional materials within the pores. These structures are fabricated by printing a newly developed emulsion ink composed of a curable acrylic monomers mixture as the "oil" droplets in water phase. The printing is performed by the digital light process (DLP) method, in which the structure is formed by local polymerization of monomers. At first stage, the droplets are cured by UV light, and at the second stage, the water phase evaporates away and leaves voids. Currently we focus on impregnating these structures with silver nanoparticles that after a simple sintering process, can connect to form a conductive, continues silver matrix within a solid polymer.

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PA-23

Protein Interactions with Particles Probed by the Patterns of Evaporating Drops

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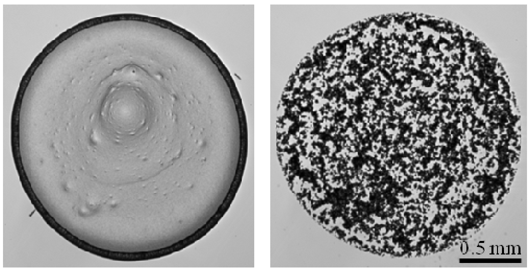
The interactions between proteins and particles are important for many applications, ranging from nanoparticle toxicity to sensors and material biocompatibility. Indeed proteins can either adsorb on particles, followed by structural, dynamic and functional changes [1], or remain free in solution. To investigate this process, we use the "coffee-ring" effect of evaporating drops [2] as a straightforward approach to detect molecular interactions at a macroscopic scale.

Two major blood proteins, hemoglobin and serum albumin, are mixed with polystyrene particles of different sizes and surface charges. 0.8 µL drops of various protein/particle ratios are deposited on a glass substrate and we analyze the deposition pattern after drop evaporation. A marked transition from a coffee-ring to a disk pattern is specifically observed when proteins adsorb on particle surface, thus constituting a macroscopic signature of the molecular protein/particle interaction. Moreover, for an excess in protein concentration, new deposition patterns (e.g. double-ring) are observed and can be interpreted by considering the behavior of proteins at solid/liquid and liquid/gas interfaces [3].



- protein   + protein

Figure. The presence of proteins dramatically changes the deposition pattern of an evaporating drop containing particles from a coffee-ring pattern (on the left) to a disk pattern (on the right). The solution contains negatively charged polystyrene particles (360 nm in diameter) without (left) and with (right) serum albumin.

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PA-24

High-resolution Methodology to Isolate NP-corona Complexes

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Density-gradient ultracentrifugation (UC) is a method widely used in biochemistry and lately has been exploited in nanotechnology to obtain monodispersed nanoparticle (NP) suspensions[1]. It is now known that when NPs come in contact with a biological environment they form protein corona complexes (PCC) [2]. PCCs are new entities composed of NPs coated by multi-layers of proteins. The inner layer, closer to the NP's surface, is the most tightly bound and generates stable objects with a so-called hard corona (HC). HC PCCs mediate the interaction with the cell membrane and affect NPs' fate inside the cell[3]. Isolation and characterization of these NP-protein complexes are important for a rational design of future nanotherapeutics. Here we propose the application of UC as alternative methodology to isolate HC PCCs at a higher resolution than conventional methods, being able to separate HC PCCs of different size and composition present simultaneously in the biological milieu. We systematically studied several NPs different in size, material and surface functional groups in serum and other complex biological fluids in comparison to standard centrifugation protocols. Recovered HC PCCs were characterized by DLS, NTA and SDS-PAGE and applied on lipid bilayers. The interaction between the recovered HC PCCs and lipid bilayer was studied by QCM (Quartz microbalance) and fluorescence microscopy. The technology presented here can be a fundamental preliminary step to investigate further HC PCCs extrinsic behaviour *in vivo* on cells.

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PA-25

Forced Rayleigh Scattering Made Simple: a Photoreactive Dye to Probe Polar and Non-Polar Diffusion Domains and Polymer-Interdiffusion

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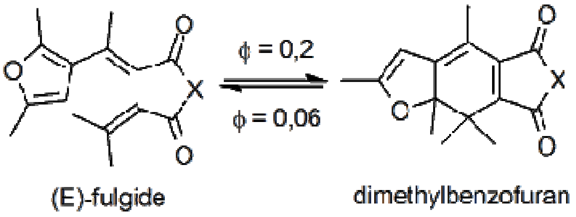
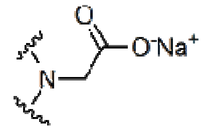
Polymer films serve many applications: from cheap foils and dispersion paints to highly specialized coatings and medical applications. Many desired macroscopic film properties are related to the diffusional behavior of small molecules in the matrix and/or the interdiffusion of the polymer chains.

Forced Rayleigh Scattering (FRS) is a special technique to noninvasively monitor such behavior over length scales from 0.2 to 50 mm and measure diffusion coefficients over six orders of magnitude. Experimentally, a refractive grating is bleached into the sample by holographic writing. The decay of the grating efficiency is measured and attributed to tracer motion in different domains when an appropriate probe is used. Requirements on the probe are high: a photoreaction must trigger a vast change in refractive index without byproducts. Such properties were found in the fulgide moiety (see figure) which, however, needs to be modified into a polar and a polymer-attachable variant bearing similar absorption bands.

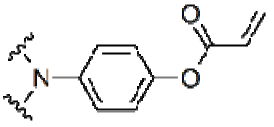
Different synthetic strategies to produce such variants and their results are presented.



X – O
I - Aberchrome 540



II - water soluble variant



III - polymer-attachable variant

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PA-26

Aqueous Dispersions of Paper Surface Hydrophobation Polymers: Interactions and Mechanisms

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For many applications, paper surfaces needto reduce penetration and wetting of liquids, most prominently water. This isoften achieved by surface sizing, i.e. by adsorbing a hydrophobic polymerparticle suspension on the paper surface (1). In the paper making process, theparticle suspension is combined with starch and then the mixture is applied onthe paper surface in the dry-end of the paper machine. It is important, infirst place, to understand the interactions between the different componentsused and how they influence the sizing performance. The interaction study hasfocused on the colloidal behavior of the combination of hydrophobic particlesof different charges and anionic starch. It was found that the cationicparticles form large aggregates with the starch as seen in Fig.1 where atfirst, the addition of starch to the cationic particle suspension induces anincreased turbidity due to destabilization of the system. The stability of thesystem is restored at higher starch concentrations and the particles have thenformed stable aggregates with the starch. The amphoteric and anionic particlesare not affected by the starch addition, however. The effect of ionic strengthwas also investigated.

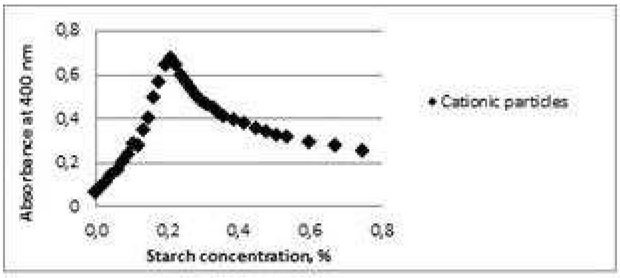

Figure 1.Turbidityplot of the cationic particle suspension at different starch concentrations.

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PA-27

Direct Force Measurements between Negatively Charged Particles in Presence of Ions of Different Valence

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The discovery that the Poisson-Boltzmann (PB) description of the electrical double layer may fail in the presence of multivalent ions triggered renewed interest in the interaction of multivalent ions with interfaces and their influence on interparticle forces. Number of investigations show that in the presence of multivalent ions forces between similarly charged water-solid interfaces may become attractive, whereby the classical PB theory predict purely repulsive forces in such situations.

To clarify the importance of such additional forces, direct force measurements between different types of particles were carried out in aqueous solutions of various inorganic salts containing mono- and multivalent cations with the multiparticle colloidal probe technique based on the atomic force microscope. The theory of Derjaguin, Landau, Verwey and Overbeek (DLVO) is capable to describe well the force profiles in the presence of mono- and divalent cations down to distances of a few nm. For the short-ranged distances (below 3 nm) deviations from the DLVO theory were observed [1, 2]. For more highly charged ions, an additional and more long-ranged (non-DLVO) attractive force was observed, which is attributed to surface charge heterogeneities. Detailed analysis of the intermolecular interactions was performed using direct force measurements for carboxylate latex [1] and silica particles.

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PA-28

Beta-Casein Based Nanovehicles for Oral Delivery of Chemotherapeutic Combinations to Overcome Multidrug Resistance in Gastric Cancer

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The vast majority of chemotherapy is lipid-soluble, administered intravenously. The availability of effective and selective oral delivery system would significantly contribute to patients’ quality of life. Bovine β-casein (β-CN) is an abundant milk protein that has a pronounced amphiphilic structure[1], promoting it's self-assembly to stable micelles in aqueous solutions. β-CN contains 17% proline residues, leading to an open tertiary structure[1] which is easily accessible to gastric proteases. In previous studies we showed the potential of β-CN micelles as oral delivery vehicles for the target-activated release of hydrophobic bio-actives cargo, as chemotherapeutic agents[2], in the stomach[3]. In the current research we explore the possibility to use different combinations of encapsulated hydrophobic anticancer drugs (e.g. Paclitaxel, Mitoxantrone) along with their corresponding encapsulated hydrophobic chemosensitizers (e.g. Tariquidar, Ko143 respectively), which counteract multidrug resistance (MDR) mechanisms, that expel a spectrum of anticancer drugs from cancer cells, based on ATP-driven MDR efflux pumps (e.g. P-glycoprotein/ABCB1, breast cancer resistance protein/ABCG2). Hence, the rationally designed encapsulated pair is expected to display enhanced efficacy and synergy in the overcoming of MDR phenomena in gastric cancer. This novel treatment strategy will significantly promote patient compliance as it would not require medical assistance or equipment, thereby avoiding the need for multiple hospitalizations and enable treatment at the comfort of the patient's home.

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PA-29

Nanoemulsion-templated Polylelectrolyte Multifunctional Nanocapsules for DNA Entrapment and Bioimaging

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The main challenges for the delivery of genetic material (*i.e.* DNA, RNA, etc.) lie in the poor cellular penetration and targeting delivery. For example, negatively charged DNA biomacromolecule cannot be taken up by cell membranes without the aid of transporters or 'vectors' owing to its unfavourable surface charge and hydrodynamic volume. Additionally, the vectors should be equipped with an imaging agent (*e.g.* fluorescent *entity*) to improve the therapeutic DNA localization and its diagnostics. Therefore, in our studies, we entrapped the DNA material (model genetic material from herring) in the newly-designed non-viral vectors, *i.e*, multifunctional nanocarriers obtained by layer-by-layer adsorption of DNA and oppositely charged polysaccharides (dextran or chitosan, DEX/CHIT) on the nanoemulsion core, loaded by cyanine IR-780 (used as the fluorescent marker) and stabilized by gemini *N,N′*-di-n-dodecyl-N,N,N′,N′-tetramethyl ethane-1,2-diaminium dibromide. Firstly, we determined ternary-phase diagrams of the surfactant–oil–water systems by titration method. Then, the stability of obtained nanoemulsion (Ne) with IR-780 solubilized in the isopropyl myristate oleic phase was evaluated by turbidimetry and ζ-potential. In the next step, CHIT, DNA and DEX layers were subsequently deposited on the Ne core. Finally, all IR-780-loaded nanocarriers covered by $(DEX/CHIT/DNA/CHIT)_2$ bilayers *with the size* were subjected to colloidal stability studies and biological analysis on human cancer cell lines (*MCF-7/*WT, A549, MEWO), *i.e.*, cytotoxic activity evaluated by MTT-based cytotoxity assay and bioimaging analyzed by *CLSM* and TIRFM.

Our results prove that the fabricated colloidal stable oil-core multilayer nanocapsules can be suitable as promising multifunctional nanocarriers for gene therapy and cancer diagnostics.

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PA-30

Core-Shell Nanoparticles for DNA Delivery Actuated by Magnetic Fields

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One of the major areas of research in nanomedicine is the design of drug delivery systems with remotely controllable release of the drug. Despite the progress in the field, this aspect still poses a challenge, in terms of selectivity and possible harmful interactions with biological components other than the target. We report an innovative approach for the controlled release of DNA, based on clusters of core–shell magnetic nanoparticles [1]. The coating of magnetic nanoparticles with an external inert shell, such as gold, has been proposed in order to add further properties to the nanoparticles. Moreover, gold provides a platform for the attachment of thiolated biomolecules.

The versatility of DNA as a block molecule for nanotechnologies lies in the unique recognition selectivity and thermal responsivity, which can be coupled to the properties of inorganic nanomaterials.

We have accomplished the conjugation of $Au@Fe_3O_4$ with a thiolated oligonucleotide, whose pairing with a half-complementary strand in solution induces clusterization. The application of a low frequency (6 KHz) alternating magnetic field induces DNA melting with the release of the single strand, based on the hyperthermic heating of clusters [2].

The possibility of steering and localizing the magnetic nanoparticles, and magnetically actuating the DNA release discloses new perspectives in the field of nucleic-acid based therapy.

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PA-31

Magnetocubosomes as Nanostructured Drug Delivery Systems: Encapsulation and Controlled Release of Amphiphilic and Hydrophilic Molecules Studied through Fluorescence Correlation Spectroscopy

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Lipid-based assemblies are the subject of active research for the development of efficient and biocompatible nanocarriers. In particular, cubosomes are submicron lipid particles of bicontinuous cubic liquid-crystalline phase in which lipid bilayers are curved with a cubic symmetry organized to form two non-intersecting continuous water channels. They are characterized by a high surface area compared to bilayered nanoparticles, allowing a higher drug encapsulation efficiency.

In this study we present an investigation on the glycerylmonooleate (GMO) as bulk cubic phase and cubosomes stabilized with Pluronic F127 as nanocarriers. We loaded the bulk cubic phase and the cubosomes with magnetic Fe_3O_4 nanoparticles (NPs), which locally heat and perturb the cubic phase structure when a low frequency alternating magnetic field (LF-AMF) is applied, allowing a spatially and temporally controlled release of the drug. The GMO bulk cubic phase and cubosomes were characterized through SAXS, DLS and Zeta Potential and the same techniques were employed to monitor the incorporation of Fe_3O_4 magnetic NPs within the cubic phase structure.

A study on the encapsulation-release of model drugs by the characterized cubic phase carrier was carried out through Fluorescence Correlation Spectroscopy (FCS). First, we monitored the encapsulation both of a fluorescently-labeled lipid (mimicking an amphiphilic drug) inside the bilayered lipid regions and of a hydrophilic fluorescent probe (mimicking a hydrophilic drug) inside the water channels of the GMO bulk cubic phase and cubosomes loaded with magnetic NPs. Finally, we monitored in real-time the release of the hydrophilic fluorescent probe encapsulated inside the aqueous channels of the bulk cubic phase loaded with Fe_3O_4 NPs, actuated by a LF-AMF.

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PA-32

On the Removal of Polymer Films from Surfaces by Nanostructured Fluids. Microscopic Mechanism and Possible Implications for Restoration of Artifacts

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The removal of polymeric films using amphiphilic solutions is of great interest for colloidal science and for various technological applications in which adhesion phenomena are involved such as conservation science. Understanding the key steps of the cleaning mechanism is the main hurdle towards a more efficient design of these complex fluids; however, due to huge variability of the real substrates and of the nature of the polymeric layer, the factors affecting the interaction between the fluid and the film are not completely understood.

We propose here the innovative use of optical techniques such as confocal laser scanning microscopy and surface methods like atomic force microscopy to highlight the role played by each component of the fluid during the removal process and its main steps. In particular, we focus on the interaction between an ethylmethacrylate/methylacrylate co-polymer and a water/non-ionic surfactant/2-butanone ternary system; we also investigate the behavior of a ternary system containing an anionic surfactant (SDS) to understand the effect of surfactant's chemical nature and of the microstructure of the aggregates on the cleaning mechanism.

Our results indicate a cooperative mechanism between the organic solvent and the surfactant: the solvent rapidly dissolves the outer layers of the polymer film; meanwhile, surfactant micelles penetrate through the polymeric chains inducing conformational changes and promoting the diffusion of solvent molecules. Moreover, the amphiphile decreases the interfacial energy thus polymer removal occurs; the kinetics and the efficiency of the cleaning process can be tuned changing its chemical nature.

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PA-33

Peptide Based NPs for Targeted Delivery of Chemotherapeutics to Mitochondria

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Effectiveness of drug treatment is highly dependent on delivering the therapeutics to the target organ and cells and even to specific intracellular organelles. In several human disorders mitochondria are relevant cellular targets for drug delivery. A challenging problem in the development of drug therapy to treat mitochondrial dysfunction is related to controlling the insertion and distribution of the drug in the cell.

Nanoparticles (NPs) may improve cellular targeted therapy due to their potential ability to deliver payloads directly to specific organelles within cells, while simultaneously enhancing stability and controlling pharmacokinetics.

In this study we developed NPs based on spontaneous co-assembly of γ-PGA, a natural polypeptide and a designed peptide for intracellular chemotherapeutic delivery into the mitochondria. We demonstrated the formation of various NPs in a range of sizes and surface charges. The secondary structure of the peptide has been determined by Circular Dichroism. The NPs were found to be spherical based on AFM measurements with diameter in the nanometric size range that were also confirmed by DLS and SAXS. NPs were loaded with chemotherapeutics such as dequalinium and lonidamine. Moreover, mito-targeted NPs that were developed using peptide coatings, were found by confocal microscopy to localize in the mitochondria of osteosarcoma saos2 cells.

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PA-34

Bioaccessibility and Bioavailability of Hydrophobic Nutraceuticals Encapsulated within Milk Proteins

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The development of effective natural carrier systems, which solubilize, protect and maximize the bioavailability of the ingested nutraceuticals, for promoting human health, remains challenging. The structural and physicochemical properties and the high nutritional value of milk proteins makes them excellent carrier systems for nutraceuticals [1]. The novel use of proteins as vehicles for lipophilic nutraceuticals raises important questions regarding the bioavailability of the entrapped lipophilic nutraceutical. To examine these questions, we focused on vitamin D_3 (VD_3) loaded within re-assembled casein micelles (rCM) as a model system, and 0% fat yoghurt (the most widely consumed nonfat milk product) as a model food. *In vitro* gastric and duodenal digestion of the VD_3 loaded vs. empty rCM was performed to study casein proteolysis and VD_3 bio-accessibility. SDS-PAGE analyses of digesta revealed that the micelles undergo enzymatic degradation in the stomach and enter the small intestine as casein peptides irrespective of their loading with VD_3. A large scale (94 healthy volunteers) double-blind placebo-controlled clinical trial was performed to examine whether the bioavailability of vitamin D_3 would be affected by its delivery in protein nanoparticles, rather than in the fat, and in its absence. The results of this single high dose ingestion trial indicated that the bioavailability of VD_3 in the protein based nanoparticles in the absence of fat did not significantly differ (p0.1) from that in fat. Overall, this work provides pioneering evidence that protein-based nano-vehicles present an excellent alternative to fat for delivery of hydrophobic nutraceuticals in foods.

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PA-35

Plant Protein-Based Nanovehicles for Health-Promoting Bioactives in Clear Beverages

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The solubilization of hydrophobic health-promoting bioactives in clear drinks is highly sought by beverage producers to provide added value for the consumer, but it still imposes tough challenges, particularly in shelf stable drinks. Most food grade surfactants, which may be used for the task, are synthetic, e.g. the Tween series, and thus preclude an "all-natural ingredients" labeling. Other ways to enrich beverages with hydrophobic nutraceuticals are usually expensive, of variable quality and availability, or are using allergenic components.

The currently proposed solution suggests the novel use of a certain plant protein isolate to form co-assembled nanovehicles for delivery of hydrophobic nutraceuticals. This solution is based on natural ingredients only, originating from a widely available inexpensive vegetable protein source. The encapsulation process is simple and inexpensive, and the product would be a readily water-soluble powder. It is non-allergenic and suitable for KOSHER-PARVE products. It is colorless and may be applicable even for completely clear drinks, like vitamin water or fruit flavored soft drinks (carbonated or non-carbonated).

Because the introduction of the protein isolate as a commercially available product is quite recent, and hardly any research has been done about it, this is a highly novel research project, with great commercial potential.

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PA-36

Surface Modification, Colloidal Interaction and the Motion of Particles

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A large portion of the goods transported on earth is transported as granulates and powders. For a good processability of the powders their flow behavior is a dominant parameter. The smaller the particles become, the more dominant is the influence of the inter-particle forces on this flow behavior. The macroscopic behavior of such particulate systems is a complex interplay between the internal properties of the particles, their surface properties and the structure the particles form.

By choosing the appropriate particle chemistry, the interaction between the particles can be tuned from attractive and strongly binding to almost purely repulsive. Using mechanical testing and 3D structural analysis of the sample, correlations between particles interaction and the flowability become visible.

In case the particles are in contact with more than one liquid, the wetting behavior (and thus the surface properties of the particles) plays the dominant role in the particle interaction. When the interfacial energies allow a finite contact angle of the liquid interface on the particles. The wetting dynamics governs the microscopic as well as the macroscopic dynamics of the system.

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PA-37

Printable Conductive Ink Based on Metal Salt Nano Particles

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Fabrication of flexible electronic devices by printing conductive interconnections is of growing research interest, including by many global electronic companies. The main objective is to find ways to fabricate these connections at low cost, by simple processes, including those suitable for plastic substrates. Therefore, during the last decade, several approaches for the sintering of metallic nanoparticles (NPs), mainly silver, at low temperatures, were developed. However, the high cost of silver based nano-inks limits fabrication of low cost plastic devices and therefore inks with other metals, such as copper, are required. However, inks containing copper NPs suffer from stability problems, as these NPs are quickly oxidised, and so lose their conductivity. Therefore, there is an unmet need for a copper ink with a low sintering temperature.

We are researching a new copper ink that will allow the printing of conductors at low temperature. The ink contains a copper salt in the form of oxidation stable nano and sub-micron particles that decomposes at a temperature below 200C. Requirements for a printable ink include small particle size, dispersion stability and viscosity tailored for the printing method. The nanoparticles are formed by a top-down approach: wet ultrafine grinding with a bead mill of the copper salt in presence of a stabilizing polymer. By this process, the size of the particles can be reduced by 3-4 orders of magnitude. Several factors influence the particle size distribution obtained, including the bead size used, milling time, ratios of solids, liquid and dispersing agent.

We have investigated the process of forming the ink, printing it, and finally decomposing the copper salt to obtain a conductive copper pattern.

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PA-38

Colloidal Stabilisation by Unattached Homopolymers, When Does Depletion Repulsion Play a Role?

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It is well known that the addition of non-adsorbing polymers to a dispersion of hard sphere like (HS) colloidal particles introduces short range attraction to the system. This so called depletion attraction can be used to study flocculation or the phase-behaviour of colloidal systems with short range attraction. Beside this polymer-induced (PI) attraction in some cases a PI repulsion can be observed. So far a (re-)stabilisation of a flocced phase by PI repulsion could only be observed in stericaly stabilised particles having thick stabilisation layers. Whether restabilisation can be realised in a true HS system is not yet known. Recently Semenov et al. published theoretical work on colloid-polymer-mixtures[1], where they predicted restabilisation in a HS system in the case of large particles and much smaller polymers, but these predictions have not yet been tested experimentally. To gain experimental access to the influence of PI interactions on particle interactions, we study the osmotic compressibility of HS systems using turbidimetry. So far similar experiments where only carried out on rather small particles, where PI repulsion is of no importance.[2] Thus we are extending the method towards larger particle sizes to check whether the PI stabilisation described by Semenov is able to give a more satisfying description of the data than the classic approaches.

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PA-39

Crowded Colloids in Two Dimensions: Structure and Dynamics

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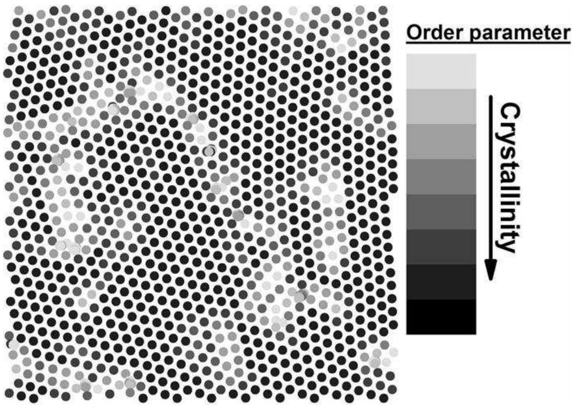
Colloidal spheres confined to two spatial dimensions (2D) provide a unique insight into the fundamental physics of fluids and crystals. These 2D systems, thermodynamically-equilibrated by Brownian motion, are capable to mimic a wide variety of complex interfacial phenomena exhibited by atoms and molecules, such as the phase transitions in Langmuir films and complex relaxation dynamics during atomic deposition, widely used in science and technology. Colloids are visible by direct optical microscopy, allowing their behavior to be studied in a great detail, unavailable for monolayers of atoms and molecules. While 2D colloidal monolayers have been widely studied in the past, in most of these studies the suspending medium was confined to 2D as well, giving rise to significant hydrodynamic interactions between the colloids.



We form a two-dimensional suspension of colloidal PMMA spheres in a solvent[1]. The spheres, density mismatched with the solvent, form a 2D fluid at the bottom of the container, pre-coated by polyhydroxystearic acid to avoid particle immobilization. Importantly, while the colloidal spheres in our samples are confined to a single 2D plane, the solvent is unconfined, contrasting with the previous studies. Moreover, by slight tilting of these samples, employing a special stage, we fine-tune the rate and the direction of the in-plane drift of our particles under gravity.
We track individual particles in fluids and crystals and quantify the interparticle correlations in these 2D colloidal systems, both under static conditions and when flowing, driven by an external field. Some results are compared with computer simulations, allowing a deeper insight into the physics of collective phenomena in 2D to be gained.

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PA-40

Anomalous Diffusion in Polyelectrolyte Multilayers

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Polyelectrolyte multilayers (PEM) represent a universal and versatile means for engineering interfaces. They have found applications, just to name a few, in sensing, in encapsulation, and as delivery devices. Most of these applications are based on the specific transport properties of molecules within these relatively dense polymer assemblies. For example, the response time of a sensor located inside a PEM will strongly depend on the diffusion behaviour of the analyte within the multilayer. Therefore understanding the diffusion of molecules in these nanosized heterogeneous and amorphous assemblies is of utmost importance both from a practical and a fundamental point of view. While the permeation of water soluble molecules through multilayers can be studied relatively easily, it is much more difficult to explore diffusion within PEMs. We therefore designed a novel colloidal particle based diffusion assay. Colloids are coated with containing reporter molecules, the fluorescence of which changes upon interaction with a diffusing species. With flow cytometry the time course of fluorescence can then be recorded. For example, NBD (7-nitrobenz-2-oxa-1,3-diazol-4-yl) coupled to poly(allyl amine hydrochloride) (PAH) is irreversibly quenched by dithionite. The quenching kinetics of NBD independent of multilayer composition, thickness, pH and ionic strength were not consistent with normal diffusion. Instead, strongly anomalous diffusion, (subdiffusion) was observed. This behaviour was attributed to the binding properties of dithionite to PAH. The analysis of experiments requires the theoretical description of normal and anomalous diffusion in layers with nanosize thicknesses. Analytical and numerical solutions of the corresponding reaction-diffusion systems are presented both for the normal and the subdiffusion case. Different regimes can be identified depending on quencher and reporter molecule concentrations.

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PA-41

Antibiofouling Properties of Polyelectrolyte Multilayer Thin Films

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Anitbiofouling is defined as the adsorption of biological life-forms and matter onto artifical surfaces. This adsorption of biological components can cuase huge problems like the increase of drag of ships by 80% which causes a comarable increase in fuel consumption.[1] Current antibiofouling systems focus on the utilization of self-polishing layers, which release tinorganic compounds to poision the biological species, which introduces heavy metal and organic compounds into the water.[2] Novel alternatives to this system mainly focus on the fouling release, in which surface energy and mechanical properties are minimized, however such approaches only work on vessels that regularly move.[3] The presented poster shows the results of a systematical study of different PEM structures (hydrophilic, hydrophobic, nanoheterogenities, soft, hard, strong and weakly charged, positive or negatively terminated) and silicone rubber (PDMS) based on their antibiofouling properties in freshwater, their protein repulsion properties and their abilities for symbiotic biofouling.

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PA-42

Magnetic Field Assisted Assembly of DNA Coated Colloids

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Self-assembly of long, straight, mesoscopic scaffolds can be utilised for building more complicated structures [1,2]. Using the right combination of DNA, it is possible to tune the melt temperatures for single, two and three component systems of DNAcc. We present an approach for creating novel superstructures via magnetic field-assisted assembly of DNA coated colloids (DNAcc). Recent publications show chains of short lengths [3–5] and/or short persistence lengths [6]. Introducing superparamagnetic beads as one of the components allows us to manipulate their assembly via an externally applied magnetic field. Ring like and long coaxial skeletons of smaller colloids around larger superparamagnetic cores are demonstrated in a two component system. Proof of concept is demonstrated for further stabilizing these structures by adding a suitably functionalized third component. This could pave the way for novel superstructures such as mesoscopic straight coaxial scaffolds, where a bilayer of different colloids is attached to a rigid primary support. These superstructures could also be developed for lossless RF transmission at macroscales or utilized as template materials in supercapacitors.

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PA-43

Supramolecular Amphiphilic Systems Based on Calix[4]arene Platform for Controlled Self-Assembly

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The self-assembly inducing the formation of different supramolecular assemblies has been widely explored as a kind of facilitated nanocontainers. The success of this application requires the development of a versatile mechanism of a self-aggregation for producing the nanocontainers with controlled functions and structures. There are several strategies for their creation, and alternatively, a nanocontainer structure can be achieved through the self-assembly of macrocyclic platforms. Within the latter methodology, the calix[4]arene platform has demonstrated its potential for building up these systems.

We report the novel classes of self-assembling nanoparticles formed with two types of calix[4]arene compounds, namely resorcin[4]arene cavitands and calix[4]resorcinarenes. Cavitand assemblies are designed via "click" chemistry to form self-assembled noncovalently connected aggregates through counter-ion displacement. Another type of assembly are created from calix[4]resorcinarenes and surfactants with the formation of super-amphiphiles, which further self-assemble into ordered aggregates. The way of controlling the super-amphiphile formation depends on the ionic nature of surfactant. A supramolecular system based on the calix[4]resorcinarene sulfonatoalkylated at lower rim and amine-methylated at upper rim and the cationic surfactant can be derived spontaneously by electrostatic attraction. However, this is not so in the case of anionic surfactant since pH-induced signal generation is required for the super-amphiphile formation. Importantly, in all cases the supramolecular amphiphilic systems with controlled structure and binding behavior could be fabricated. These self-assembling particles can be used as nanocontainers with controllable binding capacity toward hydrophobic compounds and find their applications in delivery system.

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PA-44

Interfacial Interaction in the Oxyethylated Calix[4]arene - Polymer Systems

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Analysis of the current scientific literature shows a significant interest of researchers to the oxyethylated calix[4]arenes (OC), which function as a surfactant. Study of surface phenomena involving OC promotes evidence-based finding ways to improve efficiency and optimize their actions on polymers. However, the question of establishing a boundary layer in contact with a solid surface in the presence of OC, the mechanism of regulation of wettability and spreadability of compositions remain unelucidated. Effects of degree of ethoxylation on the observed surface effects are poorly understood. In addition, the changes in the surface free energy of the cured materials obtained in the presence of OC are not appreciated.

The purpose of this study was to investigate the addition-agent effect of OCs with varying degrees of oxyethylation ($n = 8$-20) on the surface energy characteristics of the cured compositions. The polytetrafluoroethylene and polyethylene terephthalate were used as the polymer surface. It was shown that the content of the polar groups in the polymer surface layer and the length of the oxyethylene chain additively influence the wetting ability and the work of adhesion. Good wetting and adhesion abilities of the OC – polymer systems are observed for all systems, but maximum contact angle value depends on the degree of ethoxylation of OCs, their concentration and polymer surface type. As it follows from the results obtained, OCs may be used in processes of preparation and modification of the surface properties of polymeric materials, which is rather sufficient for further systematic research in this field.

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PA-45

Morphologically Tunable Coassembly of Double Hydrophilic Block Polyelectrolyte with Oppositely Charged Fluorosurfactant

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The formation and structure development of polyelectrolyte-surfactant complexes, PE-S, of double hydrophilic block copolymers poly(sodium 2-sulfamate-3-carboxylate isoprene)-block-poly(ethylene oxide), PSCI-PEO and cationic fluorosurfactant, N-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)pyridinium chloride, HFDPCl, were studied by means of isothermal titration calorimetry, atomic force microscopy, cryogenic transmission electron microscopy and small-angle neutron scattering, in dilute aqueous solutions. Two samples of block copolymers differing in comonomer composition and polyisoprene block modification degree, PSCI171-PEO1261 and PSCI521-PEO612,1,2 were investigated and found to significantly influence the self-assembly process. In the case of PSCI171-PEO126, the gradual increase in the HFDPCl concentration first leads to the formation of spherical micellar complexes, which tend to aggregate into beds-on-string structures and finally into well-defined core-shell cylindrical nanoassemblies with the diameter of ~25nm and the length of up to several hundreds of nanometers. In the case of PSCI521-PEO612 at significantly lower PE to S molar ratio, well-defined vesicular structures with diameters ranging from 40 to 160 nm having membrane thickness of 5 nm are formed, while further addition of surfactant leads to the vesicles collapse and formation of sponge-like structures.With respect to the biocompatibility of both components of the studied coassembly, the prepared nanoparticles are prospective materials in nanomedicine as markers in 19F MRI.

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PA-46

Role of Amphiphilic Additives on Cellulose Dissolution in Newly Developed Alkali Based Solvents

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Cellulose has many industrial applications and is the most used biopolymer in the world. The estimated amount of cellulose and derivatives used each year, exceed 75 million tons[1]. Many important cellulose applications involve, at some stage, dissolution and, for different reasons, this task is normally complicated. The development of cheaper, environmentally and human friendly alternatives, without toxic compounds, to the solvents used nowadays is thus of great interest in the industrial circle.

In this work, we have developed new promising alkali based solvents, showing good dissolution ability of cellulose with reasonably high molecular weight. The addition of amphiphilic molecules (such as urea and surfactants) to the alkali based cellulose solutions results on an increase of the solubility of cellulose in solution and also in a decrease of the viscosity of the system [2,3]. Additionally, these amphiphilic additives also prevent time dependent gelation of the solution.

These cellulose solutions are a very promissory for fiber spinning (e.g. textile applications). Finally, cellulose regeneration under the form of transparent films was achieved from cellulose solutions using simple coagulations systems such as water, ethanol or acidic solutions.

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PA-47

Investigation of Hybrid Systems made of Thermoresponsive Microgels and Gold Nanoparticle

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Microgels that can reversibly switch between a collapsed and expanded state in respond to external stimuli (pH and temperature) are attractive for applications such as sensoric and drug delivery systems. These microgels can be loaded with metal nanoparticles introducing new functionalities and enlarging the field of application to catalysis, medicine and nanoreactors [1][2]. Usually, pNIPAM microgels are prepared in a batch precipitation polymerization leading to a highly crosslinked core and a less crosslinked shell of the microgel particles [3]. This inhomogeneity is caused by the variation in the reactivity of the monomer and the crosslinker. A more homogenous internal crosslinking distribution is reached in a semi-batch polymerization with a constant feed of the monomer components [4]. Here, we present the results of the kinetic and morphological studies on the microgel particles prepared by both methods. Additionally, hybrid microgels containing gold nanoparticles are prepared and characterized in terms of uptake depending on the preparation method of the microgel and their response to temperature.

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PA-48

Cellulose Hydrogel and Solution Dispergation in Water/Ionic Liquid Mixtures

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Cellulose solutions and hydrogels serve as a starting material for the preparation of cellulose beads - spherical particles having a diameter ranging from hundreds of nanometers, up to the millimeter scale. These may be used in many advanced applications such as chromatography over solid supported synthesis, protein immobilization and controlled drug delivery. Hydrogel shaping into spherical particles is realized by different methods: solution dropping into a coagulant, jet cutting, spinning drop atomization, spraying, ultrasonic dispersion techniques, etc.

We investigated the preparation of cellulose hydrogel dispersions in water or water/ionic liquid mixtures, fabricated either from cellulose solutions in ionic liquid or from macro-scale pure cellulose hydrogels of different concentrations.

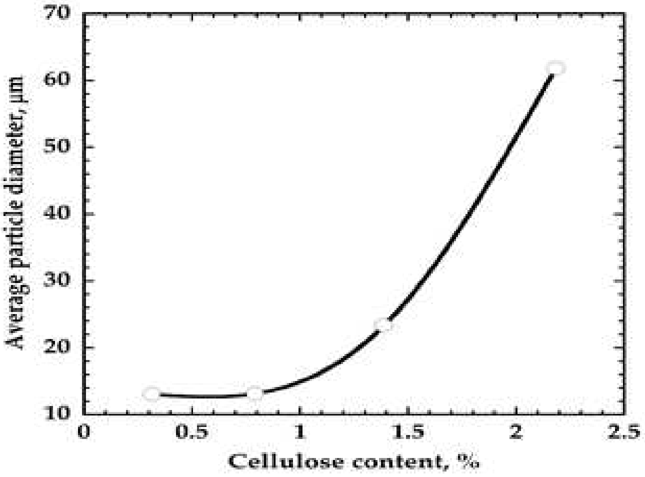

Fig. 1 Influence of cellulose concentration in the initial solution on the particle size of the hydrogel/dispersions in water

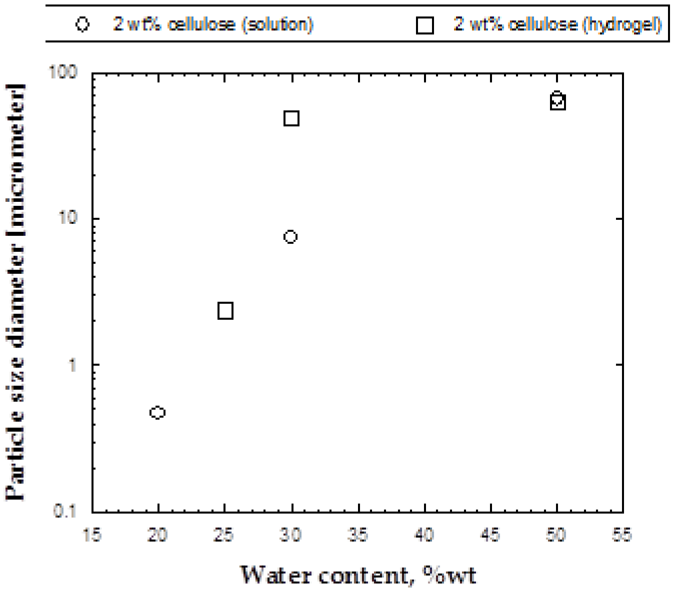

Fig. 2: Influence of water content in ionic liquid/water emulsification medium on the dispersion average particle size for cellulose solution and pure hydrogel.

Based on our results, we can conclude that the most fine cellulose hydrogel dispersions can be obtained using a low concentration cellulose solutions (less than 2 wt. %) or hydrogels with a low cellulose content (less than 2 wt. %) in a dispersion medium consisting of an ionic liquid containing no more than 15 % of the water.

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PA-49

Gold Nanoparticle-Polymer Brush Composites with Tunable Interactions

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Polymer brushes are polymers tethered to a surface or interface by one end, which, at the appropriate conditions, show a stretched conformation away from the surface. Due to their responsive behaviour, they have many potential applications, so understanding their behaviour in the presence of nanoparticles has a great technological interest and, in order to efficiently design new materials or devices, the role of all relevant parameters must be well understood [1].

To isolate the contribution of the geometric factors, such as particle size, brush grafting density or length, non-steric interactions should be removed. However, a strong attractive interaction facilitates incorporation within the brush of the particles in solution in the synthesis phase. This dicotomy can be solved by using a responsive particle capping [2]. Electrostatic interaction between the nanoparticles and the brush can be strengthened during synthesis, to facilitate incorporation of the particles, and decreased afterwards while carrying out the characterisation, to minimize this interaction and better determine the effect of the geometric factors on the composite behaviour.

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PA-50

Preparation of Soft, Responsive Nanogel Particles with Controlled Internal Structure

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The synthesis of responsive nanogel particles has attracted a considerable interest in the last decade. To meet the challenges of nanotechnology, there is compelling need to develop synthetic methods for controlling the internal structure of the nanogel beads. In this contribution we provide information about the synthesis of soft, responsive poly(N-isopropylacrylamide) based nanogel particles with controlled internal structure. To achieve this goal the monomer conversion during the polymerization of pNIPAm nanogel particles has been investigated. Our results indicated that in agreement with literature results the formed nanogel beads have inhomogeneous internal structure, which is the consequence of the different monomer reactivities. Based on our kinetic data we were able to control the internal structure of the prepared nanogel beads in a single pot reaction by controlling the monomer concentrations in the reaction mixture during the particle synthesis. This allowed us to prepare both nonagel particles with homogenous internal structure and unique core/shell particles, (i.e. pNIPAm particles with pure acrylic acid shell). Our investigations clearly indicated that the particle internal structure has a profound effect on the particle properties.

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PA-51

Crystallisation of Nanometer-Sized Micellar Cores in a Series of Well-Defined n-Alkane-PEO Polymeric Micelles

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In this work we study the crystallization of n-alkane confined in small micellar cores formed by a series of well-defined n-Alkyl-PEO (C_nH_{2n+1}-PEO5 with n = 21,24,27,28) polymers in water. By using a range of techniques including small-angle X-ray scattering (SAXS), densiometry [1] and differential scanning calorimetry (DSC) we show that n-alkane crystallizes within the core microdomains.

By varying the temperature we find a discontinuity in the scattering behaviour at high Q with SAXS. We show that this discontinuity can be attributed to a change in contrast. The specific volume confirms the latter by exhibiting a jump at the same temperature. From both results a first-order phase transition is suggested. Hence due to crystallization the specific heat capacity (Cp) shows a clear peak and thus put forward an order-disorder phase transition that can be associated to the melting of the n-alkanes. Interestingly, the melting points are very much reduced with respect to those of the pure n-alkane.

In the presentation we will further discuss the relation between crystallization versus recently observed exchange kinetics revealed by time-resolved small-angle neutron scattering (TR-SANS) [2,3].

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PA-52

Quatsomes: Vesicles Formed by Self-Assembly of Sterols and Quaternary Ammonium Surfactants

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There is a large interest in finding non-lipid building-blocks or tectons, which self-assemble into stable vesicles, and which satisfy the quality standards required in pharmaceutical formulations.[1]

Here we show the ability of quaternary ammonium surfactants and sterols to self-assemble forming stable amphiphilic bimolecular building-blocks with the appropriate structural characteristics to form, in aqueous phases, closed bilayers, which we named quatsomes. When prepared by using compressed fluids (DELOS-SUSP method)[2], these colloidal structures are stable for periods as long as several years, their morphology do not change upon rising temperature or dilution, and show outstanding vesicle to vesicle homogeneity regarding size, lamelarity and membrane supramolecular organization.[3]

Phase behavior analysis of different aqueous mixtures of the quaternary ammonium surfactant CTAB and cholesterol (Chol) have shown that a pure vesicular phase is only formed at equimolar proportions of both components.[4] Molecular dynamic simulations revealed that the cholesterol and CTAB pair works as a unique supramolecular architecture for the formation of more complex colloidal phases such as vesicles.

Many functionalities can be implemented simultaneously in quatsomes, either by covalent attachment to sterol like molecules, by electrostatic interaction with the cationic ammonium head of surfactant units or by hydrophobic interaction with the bilayer. These possibilities open a broad range of applications in pharmacy,[5] cosmetics and materials synthesis.

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PA-53

Understanding the Structural Role of Aromatic Cosolutes Derived from Cinnamate in CTAB Wormlike Micelles

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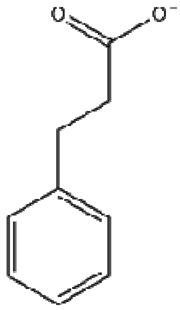
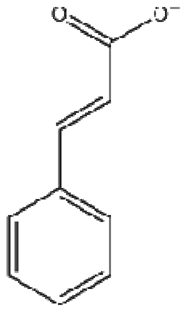
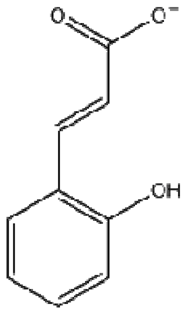
The formation of wormlike micelles by combining cetyltrimethylammonium bromide (CTAB) and aromatic cosolutes such as sodium salicylate is well known.[1] Small changes in the structure of the cosolute affect the rheological properties of the system dramatically, such as a trans-cis isomerization of trans-orthomethoxycinnamate (OMCA).[2] In this work, we have studied the rheological and calorimetric behaviors of a variety of structurally similar cosolutes, derived from cinnamate (3-phenylpropanoate, ortho-hydroxycinnamate, ortho-hydroxypropanoate, ortho-methoxycinnamate), in order to establish a logic between structure and rheology.



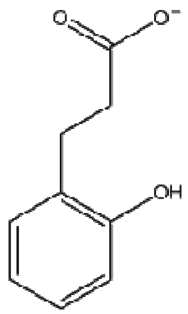
3PPA



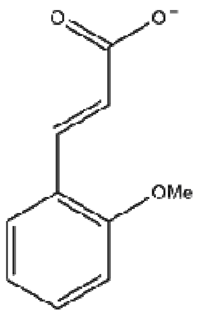
Cinnamate



OHCA

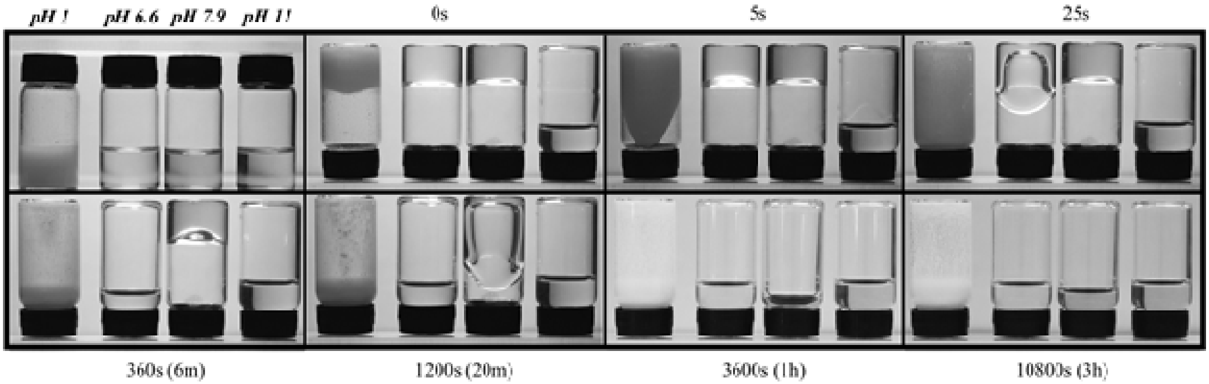


OHPA



OMCA

Additionally, the OHCA wormlike micelles exhibits a stark dependence on the solution pH, where a small increase in pH results on a high increase in apparent viscosity, as can be seen on the picture. Each flask has a solution of 200mM of CTAB and OHCA, on a specific pH, and the flasks were turned upside down at t=0 and then allowed to flow freely due to gravity. At pH 8, the apparent viscosity is much higher than at pH 6.6.



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PA-54

Interaction of Cobalt bis(dicarbollide) Anion with Star-like Copolymers

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The presented study is a part of project concerning the physical-chemical behavior of block copolymer complexes with sodium cobalt bis(dicarbolide) (COSAN) in aqueous solutions. COSAN gives many potential applications, mainly in medical field, as inhibitor of important enzymes. After discovering COSAN interacts with poly(ethylene oxide), poly(2-alkyl oxazoline) and poly(2-vinyl pyridine) blocks via specific interactions, many complexes of polymer-COSAN have been prepared. In this case we chose block copolymers with star-like architecture: 4-arm poly(ethylene oxide)-*block*-poly(2-methyl oxazoline), $[\text{PEO-PMOX}]_4$, in 0.154 M NaCl solution and miktoarm star-like polystyrene-*block*-poly(2-vinyl pyridine), $\text{PS}_{20}\text{-PVP}_{20}$, in 0.1 M HCl. We could observe differences between interaction of COSAN with linear and star-like polymers. It has impact on morphology of the hybrid nanoparticles. While homogeneous nanospheres were formed with linear PEO-PEOX, we detected multicompartment micelles by cryo-TEM in the case of $[\text{PEO-PMOX}]_4$/COSAN. As PVP block forms insoluble complex with COSAN, $\text{PS}_{20}\text{-PVP}_{20}$ micelles were destabilized at elevated concentration of added COSAN. Surprisingly, the micelles were stable in solution up to molar ratio of COSAN 0.1, even though linear PVP precipitated immediately with COSAN. The systems were studied by means of light scattering, NMR, AFM and cryo-TEM.

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PA-55

Self-Assembly of a Tryptophan Substituted Cholic Acid

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The self-assembly of biomolecular building blocks plays an increasingly important role in the discovery of new materials and scaffolds, with a wide range of applications in nanotechnology.[1,2] In particular, peptides and bile acids are widely investigated because of their biological role and their potential as building blocks in the preparation of nanostructured biomaterials. This work comes along with a research field focusing on the preparation of amphoteric compounds merging the bile acid scaffold and hydrophobic amino acids, thus combining the self-assembly properties of both bile acid- and peptide-based compounds. We herein report the study of a novel derivative in which a L-Tryptophan has been introduced in the position C-3 of cholic acid. Such amino acid has been chosen since, together with its well-known self-assembly features, it renders the molecule of special interest as a fluorescently labeled biological compound. The obtained compound is an amphoteric fluorescent labeled bile acid and we demonstrate that it shows a pH-dependent self-assembly, which is extremely different compared compared to the one of its natural precursor. In alkaline conditions it self-assembles forming micelles whereas in acidic conditions it self-organizes in elongated assemblies that grow with time forming a hydrogel. The auto-association process has been investigated by means of circular dichroism, dynamic light scattering, atomic force microscopy, UV-Vis and fluorescence spectroscopy.

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T12. Surfactants, Lipids, Micelles and Vesicles

PA-56

The Role of Aromatic Co-Solutes in Wormlike Micelles Rheological Behavior

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Wormlike micelles (WLM) formed by the threading of different aromatic co-solutes at the micelle palisade of CTAB were systematically studied. For this purpose the aromatics: phenol and derivatives of benzoate and cinnamate were used. Depending on the concentration of the components, the chains of the WLM entangle, forming gel-like systems (see Figure 1). Based on this aspect, some structural characteristics of the aromatic molecules were investigated to correlate with the linear rheology of the WLM formed. The rheological results are explained by considering the relative importance of the electric charge, hydrophobicity and steric hindrance of groups of the aromatic co-solutes. Experiments of SANS produced a complementary panel to understanding the structure of the gels of CTAB containing the aromatics.

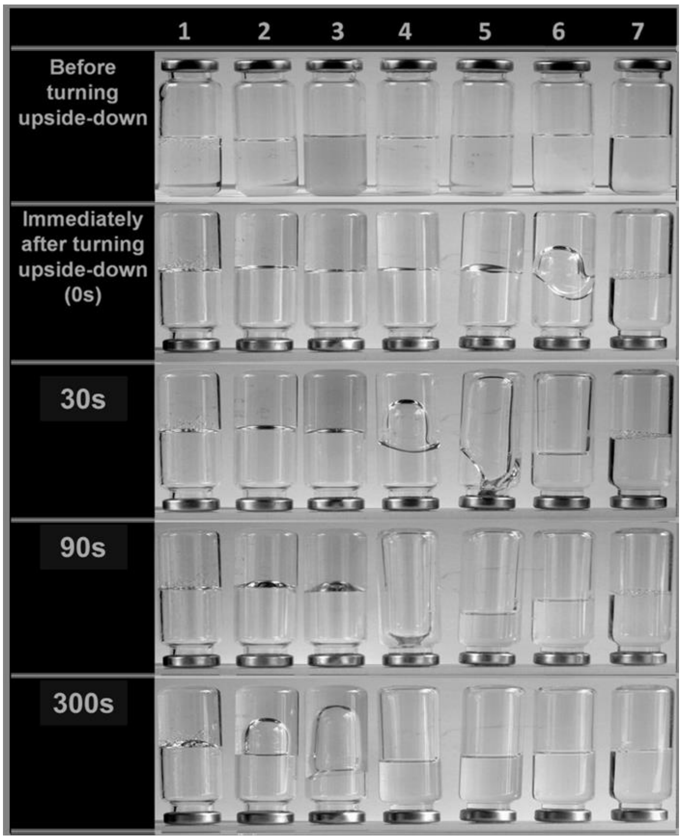

Figure 1. The gravitational effect on gels containing 200 mmol L^{-1} of CTAB and 200 mmol·L^{-1} of: 1 – phenol; 2 – cinnamate; 3 – OHCA; 4 – salicylate; 5 – OMCA; 6 – benzoate; and 7 –ortho-methoxybenzoate . The values (on the left) correspond to the times after the inversion of the vials.

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PA-57

Choline as a Green Counter-ion for Alkylsulfates – New, Highly Soluble Surfactants

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It is well-known that surface activity and solubilising power of surfactants, two important features in application, increase by increasing the length of the hydrophobic chain. As a consequence, long chain, water-soluble surfactants are desirable. Unfortunately, with increasing chain length the solubility of the surfactant decreases, which leads to higher Krafft-temperatures. For this reason, sodium alkylsulfates, which are commonly used surfactants in household products, are only applied with a chain length of 12 C-atoms (commercial name: sodium lauryl sulfate). The longer chain alkylsulfates exhibit Krafft-temperatures above room-temperature.

In many papers the decrease of the Krafft-temperature of sulfate- and carboxylate-surfactants is described by using a quaternary ammonium-ion as a counter-ion. The problem is that these ammonium-ions are toxic and consequently inappropriate for application. Choline, also a quaternary ammonium-ion, is a green, non-toxic alternative, which shows the same effect and could be used in formulations.

In the present contribution we will focus on choline hexadecylsulfate (C16) and its Krafft-temperature below room-temperature. As a result of the excellent water solubility, it will be possible to use long chain alkylsulfates (up to C16 and more) in household products, which are applied at room-temperature. This should lead to improved application properties compared to products containing only sodium lauryl sulfate (C12).

Finally, an approach is presented to decrease the Krafft-temperature of longer chain alkylsulfates (C18) below room-temperature, by adding different alcohols as a co-surfactant.

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PA-58

Toward Waterless and Surfactantless Microemulsions

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Since a few years we are working in the field of surfactantless microemulsions [1-3]. These microemulsions are present in a lot of everyday products [4,5]. It even seems, according to our last results, that this kind of structure exists also in systems where water is replaced by glycerol in presence of ethanol and 1-octanol or in deep eutectic solvents, e.g. a mixture of urea and choline chloride (ChCl) with a molar ratio of 2-1, in presence of tetrahydrofufuryl alcohol (THFA) and diethyl adipate. The existence of the nanostructure was detected using dynamic and static light scattering and X-ray scattering.

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PA-59

Diffusion and Precipitation Processes in Ca^{2+}-Based Silica Gardens

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Chemical gardens are plant-like structures produced by a variety of different metal salts when immersed into a solution of certain anions, the most investigated of which is silicate. The resulting precipitates are usually hollow tubules, which have been characterized extensively with respect to morphological and textural aspects. By contrast, only little information is available on dynamic time-dependent processes in these self-assembled systems. In a recent study[1],we have developed a novel procedure to grow cobalt-based silica garden tubes with well-defined macroscopic dimensions, allowing for straightforward sampling and in-situ analysis of the two solutions separated by the tube walls.

In the present work we have extended this approach to prepare silica gardens using calcium salts, as the mechanisms observed in this system are expected to be very similar to those underlying Portland cement hydration. The time-dependent distribution of ionic species in both compartments was traced on-line by pH and potential measurements, while concentration profiles were determined by means of atomic emission spectroscopy and ion chromatography. Further, temporal changes in the structure and composition of the tube walls were monitored by ex-situ characterization methods such as electron microscopy, EDX spectroscopy and X-ray diffraction.The obtained results paint a consistent picture and shed novel light on dynamic dissolution, diffusion and precipitation processes that occur across calcium silicate membranes resembling those found in cementitious materials.

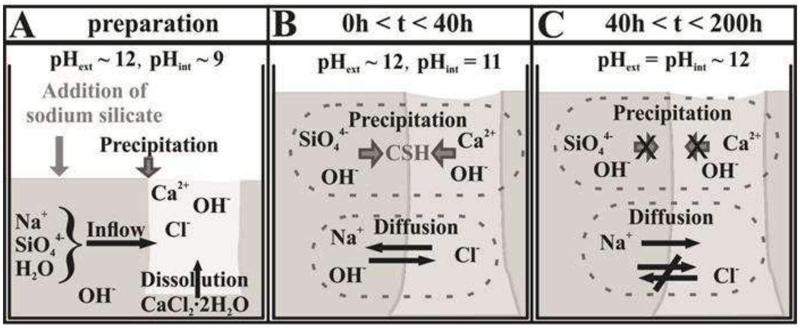

Figure 1: Schematic description of dynamic processes in Ca^{2+}-based silica gardens.

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PA-60

Spheres Becoming Worms: "Filming" the Transition of SDS Surfactant Micelles Using Rapid Stroboscopic SAXS

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Surfactant molecules have the ability to aggregate into a wide variety of highly dynamic nanostructures. The shape and size of the micelles depend on the type of surfactant and conditions such as temperature and solvent composition and have been extensively investigated the last century. However most studies relate to the statics, the structure and macroscopic properties such as surface tension, conductivity, foaming etc. [1]. Concerning the kinetics much less is known and very much limited to near-equilibrium relaxation studies. Here we take advantage of synchrotron-based time resolved small-angle X-ray scattering and follow typical non-equilibrium kinetic processes in surfactant micelle systems at millisecond-time scales [2,3]. We study an archetypical, simple surfactant system consisting of sodium dodecyl sulphate (SDS) in aqueous NaCl solutions and "film" a morphological transition from spheres to worm-like micelles using SAXS combined with stroboscopic stopped-flow schemes. The results show that worms are formed by fusion of globular micelles and short cylinders in a fashion that bears similarities to step-like polymerization mechanisms.

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PA-61

Self-Assembly of Complex Salts Forming Dispersions with Liquid Crystalline Cores

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In this work is reported the use of stimuli-responsive materials on the study of self-assembly systems, exploring their surface anisotropy, for example, as patchy micelles and more specifically, Janus particles, in which responsive properties allow colloidal self-assembly of higher order.

The self-assembly enables the formation of a hierarchical aggregates through the association of anionic block copolymers with cationic surfactants.[1,2] In this case a combination of two different diblocks was used: poly(N-isopropylacrylamide)-b-poly(acrylic acid) and poly(ethylene oxide)-b-poly(acrylic acid) with cetyltrimethylammonium hydroxide (C_{16}TAOH) or dodecyltrimethylammonium hydroxide (C_{12}TAOH). The aggregates were prepared with each diblock as a control and the mixture of diblocks as the main system of study. The surfactant/polymer aggregates are formed by a diffuse shell and a dense core which exhibits a liquid crystalline structure of Pm3n cubic symmetry ($C_{12}TA^+$) or hexagonal structure ($C_{16}TA^+$). Size and aggregation numbers were estimated from a combination of light scattering and small-angle X-ray scattering experiments. It is found that the size of the aggregates decreases by 80% with an increase in temperature (25-45°C, above PNIPAM´s Tc), although the lattice parameter *a* showed little change (1%). This possibly indicates that the attraction and repulsion forces remain the same. As for the thermo-responsive character of the system, when only poly(N-isopropylacrylamide)-b-poly(acrylic acid) is used with $C_{12}TA^+$, after one cycle of temperature the system is not reversible, however the presence of another diblock allows reversibility.

These core-shell aggregates also respond to addition of electrolytes and it was possible to disorder the surfactant mesophase upon addition of salts, which could be reverted upon dialysis.

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PA-62

Transport of Cu(II) Ions in Humic Gels - Influence of Reactive Functional Groups of Humic Acids

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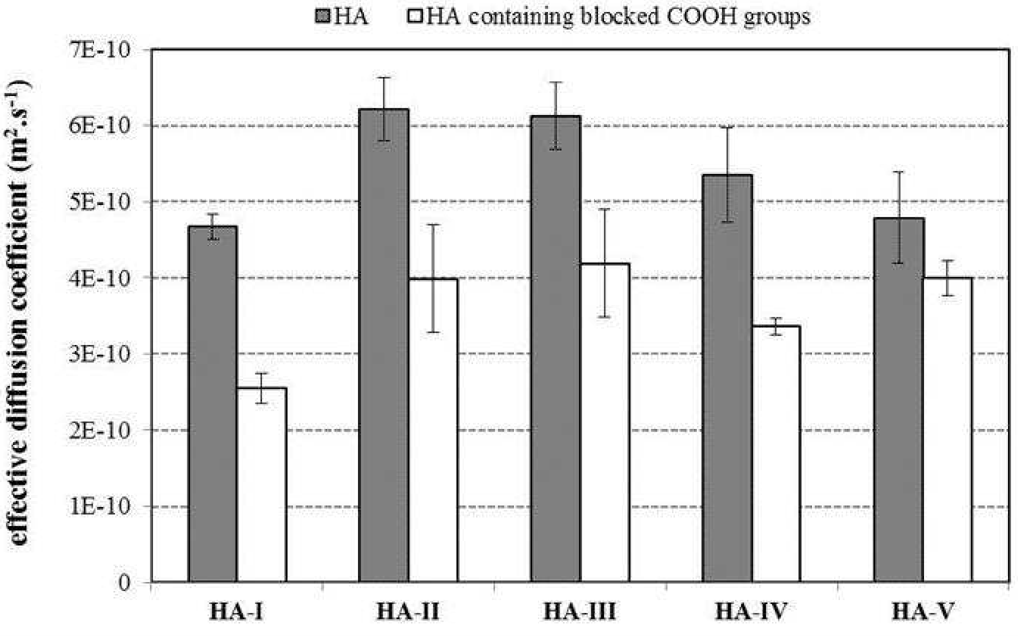
Reactivity and transport properties of metal ions in humic systems are important both for understanding role of humic substances in natural systems and human-driven applications. This work is focused on Cu(II) ions transport and immobilization in hydrogels based on several humic acids differing in isolation conditions and raw materials. Prepared humic gels contained different amounts of reactive functional groups (with different affinity to metal ions) in order to study an effect of structurev and properties of humic acids and selective blocking of carboxylic groups (by methylation) on the mobility and immobilization of Cu(II) ions in gel structure. The experimental arrangement was selected to enable an instantaneous planar source method for data processing based on the determination of concentration distribution of Cu(II) ions in hydrogels. The resulting values of effective diffusion coefficient include both the effect of hydrogels structure and the effect of the reaction between Cu(II) ions and humic acids. The blocking of functional groups reflected in a lower values of diffusivity in comparison to the gels prepared from unmodified humic acids. There was also confirmed the effect of isolation procedure of humic acids and their properties on the diffusivity of Cu(II) ions in hydrogels.



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PA-63

Colloid Transport in Model Porous Media: Effect of Surface Charging of Collectors and Colloidal Particles

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Transport of colloidal particles in a packed bed of collector beads are affected by the hydrodynamic and colloidal interactions between particles as well as between particle and collector. The colloidal interaction depends on the surface charging of collectors and particles. While many researchers have studied on the colloid deposition and transport as a function of ionic strength, experimental investigations examining the effect of surface charge are scarce. To figure out the effect of surface charge on colloid transport in porous media, we have performed the colloid transport experiment in a packed bed of spherical beads. In the present experiment, we used sulfate latex with a constant negative charge and carboxylate latex having pH-dependent negative charge [1, 2] as colloidal particles. Zirconia beads with pH-dependent charge and an isoelectric point around pH 7 were adopted as collectors [2]. The colloid transport experiment was carried out in 1 mM KCl as a function of pH and breakthrough curves of colloid were obtained. Experimental breakthrough curves were analyzed by a convection-dispersion equation including colloid deposition [3], where colloid filtration and dynamic blocking are considered. The results of experiments and analysis show that the maximum surface coverage of sulfate latex is constant against pH change. On one hand, the maximum coverage of carboxyl latex decreases with increasing pH, indicating that increased particle-particle repulsion enhances blocking in later stage of deposition. Hydrodynamic interaction also affects the maximum coverage.

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PA-64

Chemotactic Movement of Oil Droplets in Salt Gradients

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Chemotaxis is defined as an oriented movement along a chemical gradient. Biological chemotaxis is crucial for any living organism, because it represents its ability to locate sources of nutrition and to move towards them. In our present case, we study a non-biological system, where decanol droplets move on a glass substrate, which is covered by a thin layer of sodium decanoate. The droplets exhibit the ability to move towards local additions of NaCl.

The parametric dependence of the chemotactic response with respect to background concentration of sodium decanoate and the strength of the NaCl concentration gradient has been mapped. Several scenarios that utilize chemotaxis - namely migration over a non-linear path, delivery of a chemically reactive cargo, selection of the direction of motion according to the strength of the chemoattractant source, and temperature-triggered release of the chemoattractant - have been demonstrated.

Present poster focuses on experiments and theoretical models that could help us to determine, which forces are primarily responsible for the phenomena of chemotaxis in our respective system. There are few hypotheses, one of them suggests the movement may primarily be caused by convective flows, induced by surface tension gradient and Marangoni effect (the mass transfer along an interface between two fluids towards regions of higher surface tension). Another is based on interaction of droplet with the substrate and the droplet shape changes in concentration gradient (meaning the difference between its advancing and receding angle on a solid surface). In present poster, these and other hypotheses will be discussed.

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PA-65

Nonisothermal Nucleation of Supercritical Droplets in the Vapor-Gas Environment with Inhomogeneities Due to Nonstationary Diffusion onto and Heat Transfer from the Droplets

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An analytical theory of the stage of nonisothermal nucleation of supercritical droplets in a vapor with instantly created supersaturation is formulated with taking into account the vapor concentration and temperature inhomogeneities arising as a result of nonstationary diffusion onto growing droplets and condensation heat release. This theory extends our recent excluded volume approach to isothermal nucleation theory[1] and assumes that the intensity of the nucleation of new droplets is suppressed in spherical non-stationary diffusion regions of a certain size surrounding previously nucleated droplets, and stays at the initial level in the remaining volume of the vapor-gas environment. The value of excluded from nucleation volume depends on the explicit forms of the vapor concentration and temperature profiles in the vapor-gas environment around the growing droplet. To find the excluded volume we use the self-similar solutions of time-dependent diffusion and thermal conductivity equations. The main characteristics of the phase transition at the end of the nucleation stage are found and compared with those in the isothermal and nonisothermal theory of nucleation with homogeneous vapor consumption (the theory of mean-field vapor supersaturation and temperature). It is shown that applicability of the mean-field approach depends on smallness of the square root of ratio of the densities of metastable and stable phases. With increasing the temperature of the vapor-gas environment or for nucleation in liquid or solid solutions, this smallness weakens, and then the excluded volume approach gives a more profound result.

This work was supported by the Russian Foundation for Basic Research (grant 13-03-01049-a) and St. Petersburg State University (grant 11.37.183.2014).

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PA-66

Adsorbate Self-Diffusion in a Microporous Material Studied by Pulsed Gradient NMR Experiments

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The self-diffusion of benzene adsorbed in a Zr(IV)-based metal-organicframework (“UiO-67”) has been studied using pulsed gradient NMR. A low-field instrument operating at 20 MHz(for protons) has been used for this purpose. By varying the observation time,it has been possible to determine parameters that enters a theoretical expression developed by Kärger et al.[1]for analysis of such data.The life-time for the adsorbate within the pores of microcrystallites of the framework is one such parameter. Besides fundamental insight into the dynamic state of adsorbates in microporous materials, such information may also be of relevance in the design of modern catalyzers.

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PA-67

Bicontinuous Microemulsions as Model Systems for Anomalous Diffusion in Crowded Environments

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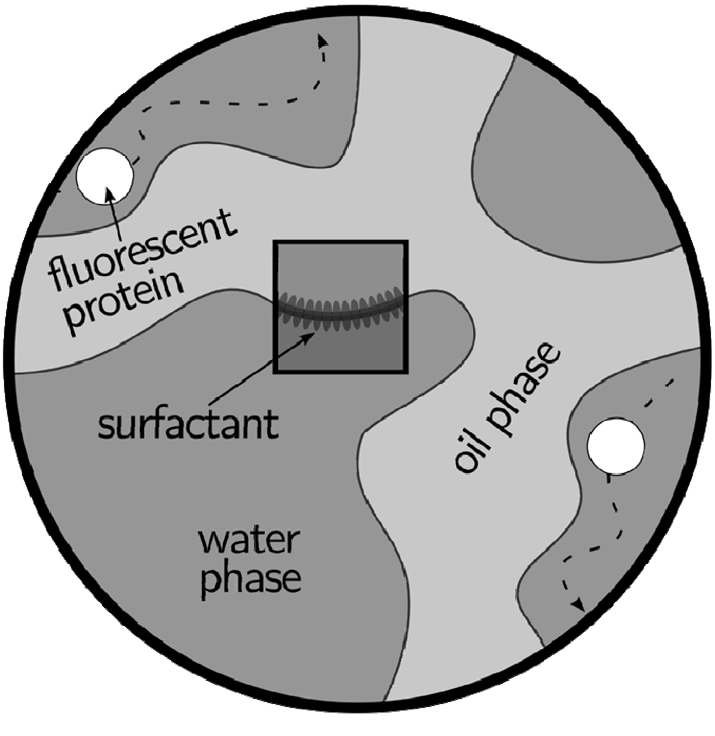
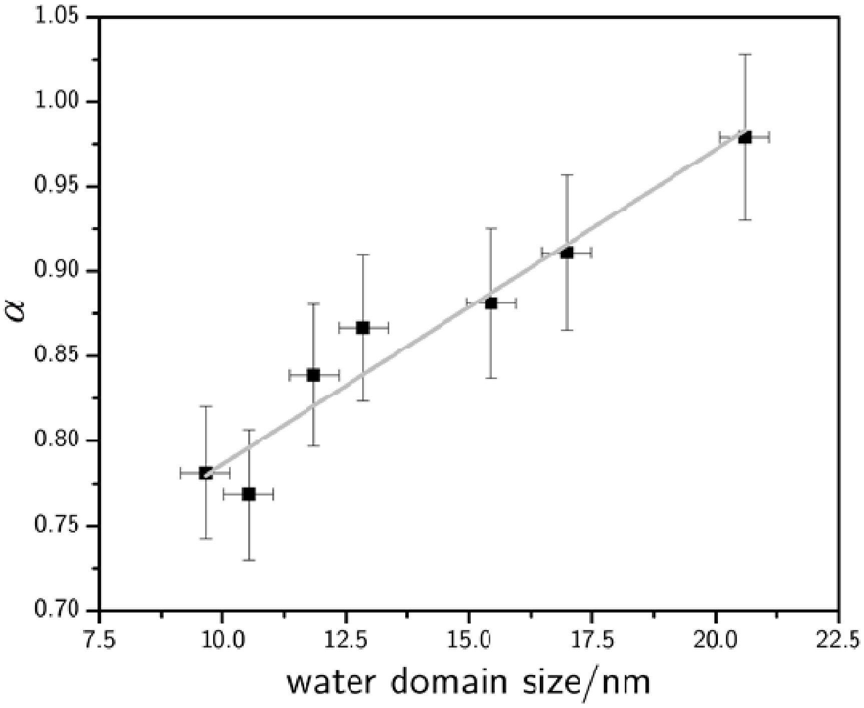
The translational motion of particles in crowded environments, such as living cells or artificial membranes, can differ from the normal Fick type diffusion, where the mean square displacement grows linear in time, but is considered 'anomalous'. To establish a theoretical description and control processes inside these systems, an insight into the diffusive behavior of proteins or catalysts under confining conditions is crucial.

To resolve the dependence of the tracer particle diffusion on the confining environment (left figure), we studied the movement of a fluorescent particle (GFP+) in bicontinuous microemulsions via fluorescence correlation spectroscopy. The size of the confining sponge like network, which is mimics cellular environments, was tuned over a range of several nanometers by changing the composition of the microemulsion and characterized via small angle neutron scattering. The microemulsion slows down the translational movement of the tracer particles with decreasing domain size and changes the diffusiv behavior from 'Fickian' to 'anomalous' in a linear way (rightfigure). Therefore we conclude that the confinment of the protein is only due to the steric interaction with the surrounding microemulsion, which makes the use of this system to model intracellular crowding feasible.





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PA-68

Existence of Three Type of Reverse Aggregates Iin Organic Solvents: Consequences on Observed Cation Distributions between Aqueous and Microemulsion Phases

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Cascade Liquid-liquid extraction is a general technology used to extract valuable and toxic cations for recycling of metals. Exploring new formulations and limiting the harmful emissions is the core objective of the REE-CYCLE project[1]. This requires the development of predictive models for ion extraction and desextraction in phase diagrams of systems containing at least four components: a solvent, a co-solvent, water, an acid or a buffer as well as the salts of cations to be separated. Typical example is to separate rare earths versus iron.

In all efficient processes, the extraction relies on aggregation in the solvent phase, mainly in Winsor-II regime. We will show in this talk that at least three different types of aggregates exist. We present molecular modelling of the three types of aggregates [2]. These can be detected by their scattering signature . We show that it is necessary to take into account long-range interaction in order to be able to evaluate without parameter -for the first time to our knowledge- the large difference between the supra-molecular complexation free energy which is the motor for selective separation between metals[3].and the much lower effective free energy of transfer that is observed in practical applications.

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PA-69

Effect of Ambient Humidity on the Rate of Oil Penetration in a Cellulose Porous Matrix

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Cellulose is a natural hydrophilic polymer used in many applications such as packaging, filtering etc. Furthermore, cellulose is used as a support for different rapid tests using liquids of different polarity. Despite its hydrophilic nature apolar liquid penetration in cellulose is possible via capillary phenomena since under a broad range of conditions the contact angle between cellulose and apolar liquids is 90^o.

This work investigates the effect of ambient conditions and namely the effect of humidity and temperature on the penetration of an apolar liquid in a cellulose fiber porous matrix. For these tests a cellulose fiber porous medium of nominal pore size in the range of 20-25μm and refined sunflower oil were used. During the capillary penetration experiment the porous medium was used dry and in other cases it was equilibrated with water and oil vapors at different temperatures. Furthermore, measurements were performed after fully wetting and subsequently partially drying the porous medium. Depending on the conditions applied the oil penetration rate either increased or decreased respective to the penetration rate of the dry cellulose matrix. It is suggested that the changes in oil penetration rate are due to the changes in the oil-porous medium contact angle and to the partial blocking of pores with water.

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Poster Session B
Tuesday, September 9, 2014

COST CM1101
PB-1 – PB-12

PB-1

Curcumin Loading and Release from Hybrid Nano Vectors of Solid Lipid Nano Particles

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One way to increase the bioavailability and thus the efficiency of an active pharmaceutical ingredient (API) is to appropriately formulate it into a vector. Nowadays challenges in encapsulation technologies for drug delivery applications are the design of nanomatrices that (i) are able to provide sustainable release of poorly soluble drugs in the receiving phase and (ii) respond to changes to external stimuli (*i.e.* temperature, pH). Here we report an original nano-vector by combining solid lipid nanoparticles (SLN) with nano-structured silica materials, for loading and release of curcumin (CU), a hydrophobic API, bearing anti-oxidant and anti-cancer activity. The carrier matrix were prepared by first loading the curcumin into dispersions of SLN in a micellar phase, followed by the silicalization of the colloidal system by sol-gel. [1,2]. The dual templating mechanism afforded a compartmentalized nanovector, with both macro and mesostructured domains. The SLN act as a reservoir of CU while the surfactant present in mesopores is assisting the release (Fig. 1). Moreover, the sustainability of the release depends on the nature of the solid lipid and on the pH of the receiving phase. Cell viability experiments confirm the potentiality of the designed silica-SLN-CU nanovector for drug delivery formulation.

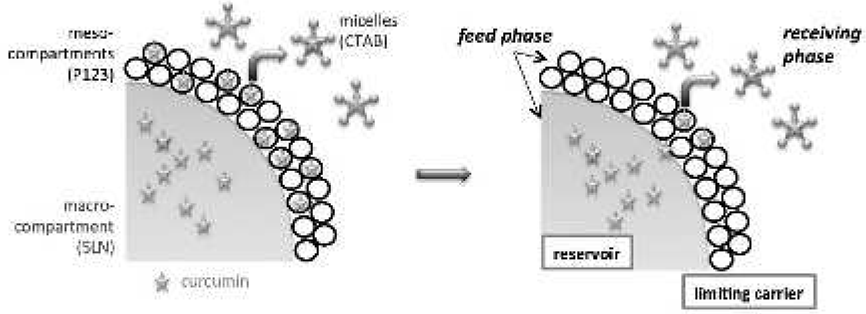

Figure 1: Surfactant-assisted and pH-controlled delivery of cur cumin from compartmentalized meso-macrostructured silica matrix

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PB-2

Structuring and Functional Silica with Siloxane Copolymer (PDMS) Surfactants

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Many small triblock siloxane copolymers belonging to the family of poly(ethylene oxide)−poly(dimethylsiloxane)−poly-(ethylene oxide), PEO_x-$PDMS_y$-PEO_x, are now widely used as lubricants, water repellents, antifoaming and demulsification agents due to their amphiphilic properties.[1] This sort of triblock copolymers have also attracted much interest, especially for their resemblance to the Pluronic® copolymers already used as efficient template in the preparation of organized mesoporous silica materials.

The phase diagram of the triblock silicone copolymer $(EO)_{12}$−$(DMS)_{13}$−$(EO)_{12}$ (I) in water shows direct micellar and hexagonal phases, which are thermally stable. The structural parameters of the hexagonal liquid crystal were determined by SAXS and have been compared with those of micelles[1, 2].

Afterwards, mesoporous materials were synthesized through the self-assembling mechanism with this siloxane copolymer. The resulting molecular sieves are hexagonally ordered mesopores and presented surprisingly perfect spherical morphology with homogeneous size distribution[2].

Then $(EO)_{12}$−$(DMS)_{13}$−$(EO)_{12}$ copolymer was functionalized with triethoxysilane propyl isocyanate through the hydroxyl group carried by PEO side chains to afford (EtO_3Si-$(CH_2)_3NHCOO$-$(EO)_{12}$−$(DMS)_{13}$−$(EO)_{12}$ (F). The later was mixed to the genuine siloxane copolymer at variable ratios in order to obtain mesoporous silica materials with controllable surface chemistry. Thereby, we found astonishingly that the mesoporous particle morphology elongates from spheres to hexagonal rods relatively to the mixture ratio of silicon copolymer and functionalized compound. The morphology and the mesostructure of the mesoporous silica materials were characterized by electronic microscopy (TEM, SEM) and by SAXS.

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PB-3

Hyaluronic Acid, a Useful Tool for Modulation of Cytotoxic Effects of Cationic Surfactants

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CTAB (cetyltrimethylammonium bromide) and Septonex (carbethoxypendecinium bromide) are cationic surfactants known for harmful effects on different cell types (bacteria, fungi, mammal cells, etc.). Colloidal complexes of CTAB or Septonex with oppositely charged hyaluronic acid (HyA) were prepared primarily by their electrostatic interactions with the aim of their potential application in drug delivery. HyA seems to be promising biomaterial of near future due to its broad range of biological functions - combination of its biocompatibility and biodegradability properties and its susceptibility of chemical modifications. HyA can serve as a biocompatible carrier of a delivery system in which the surfactant serves as a solubilizer for hydrophobic active substance (drug). Our data show, that HyA complexes with CTAB or Septonex reduce (in different rate according to used antiseptic and HyA concentrations) cytotoxicity of both antiseptics in all concentrations tested. In addition, a significant role of FBS (important supplement of cell culture medium) in cell recovery under the stress conditions like CTAB or Septonex presence was observed. Taken together, HyA could be a useful tool for modulation of CTAB or Septonex effects on cells at diverse levels.

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PB-4

Self-Assembly Behavior of Negatively Charged Hyaluronan and Oppositely Charged Surfactants

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Physico-chemical interactions between negatively charged hyaluronan and positively charged surfactant result in self-assembly nanoparticles formation. These particles have a core-shell like structure and can be used in targeted delivery of hydrophobic active substances. A hydrophobic inner core contains aggregated surfactant molecules and hyaluronan create a hydrophilic shell layer.

The aim of our study was to prepare and study hyaluronic acid nanoparticles based on electrostatic interactions with oppositely charged surfactant molecules.

Interactions of hyaluronan and surfactants were investigated using dynamic light scattering and Laser Doppler Velocimetry methods. Titration experiments (size distribution and zeta potential measurement and isoelectric point) were utilized to explore the formation of aggregates. Hyaluronan or surfactant was used as titrant for creation of different type of aggregates. Effect of molecular weight of hyaluronan and ionic strength of solvent were investigated.

Aggregates formation is influenced by preparation of system. Different particles are formed if hyaluronan is added to surfactant solution or vice versa. Molecular weights of hyaluronan have inconsiderable effect on interactions of components. If hyaluronan have a role of titrant, final particles are smaller than in the case of surfactant as titrant and can be more suitable for drug delivery applications.

Presence of low molecular weight electrolyte in the system has a significant effect on isoelectric point achievement and stability of the system due to reduction of electrostatic repulsion between oppositely charged components.

Assuming in the isoelectric point is reached compensation of charges of hyaluronan and surfactant, real degrees of hyaluronan dissociation were determined. Concentration of hyaluronan and conformation of hyaluronan in the system have a significant effect on established degree of dissociation.

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PB-5

Fast & Real-time Instrumented Microfluidic System for Complex Fluid's Phase Diagram Determination

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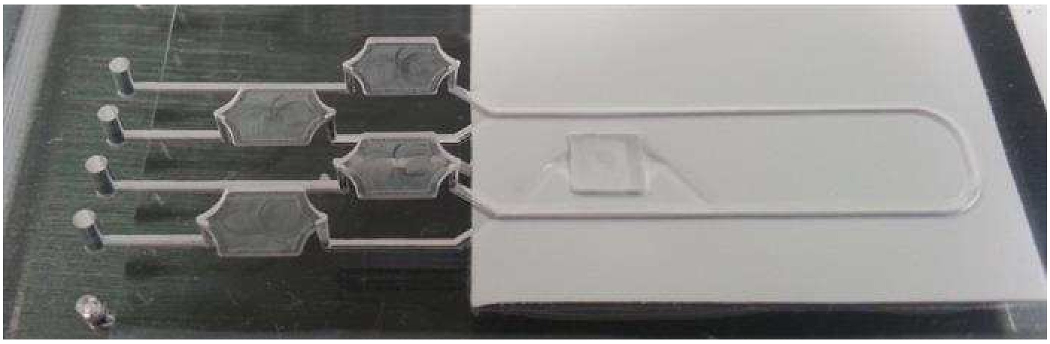
Liquid-liquid extraction, i.e. control of the reversible transfer of cations between phases, is a core chemical process for metal purification and recycling. The objective of the "REE-CYCLE" project (Rare Earth Element reCYCling with Low harmful Emissions)[1] is to develop the fundamental understanding involved in the process' complex fluids (both experimental and theoretical) in order to render environmentally friendly processes economically competitive.

Current technology is based on engineering arts, with a strong input of ienaics[2], the science of control of ion circulation in emulsified complex fluids. In order to develop predictive theories, one needs to acquire experimental data on selectivity, chemical potential differences and solvent activities versus temperature, pH and "modifiers", the engineering trick for process intensification[3].

We describe a microfluidic device enabling for the first time simultaneous fast measurement of the free energy of mass transfer per ion pair between complex fluids as determined by XRF and solvent activity as determined by vapor pressure analysis. Examples will be shown on AOT-HDEHP mixed reverse micelles as model system for which the effect of long-range chemical interactions beyond the first neighbor between metal cations and reverse micelles[4] is important. The four-channel "ionoscope" device described in this talk should be a versatile efficient tool to provide reliable data for meso-scale modeling. Data obtained by XR fluorescence and FTIR spectroscopy will be presented to elucidate the phases.



Microfluidic device with on-line measurement sites.

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PB-6

Joint Endeavor for Rare Earth Element Recycling with Low Harmful Emissions (REE-CYCLE)

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It is a matter of strategic independence for Europe to urgently find processes taking account of environmental and economic issues, when mining and recycling rare earth elements (REE). The objective of the ERC REE-CYCLE project (reecycle-erc.blogspot.fr) is to develop the fundamental understanding involved in the process' complex fluids (experimental and theoretical) concerning liquid-liquid extraction of REE and furthermore using it to design new, cost effective and environment-friendly processes. This is achieved by:

(1) Developing and assembling a new, fastand on-line measurement tool characterizing equilibrium distributions of ions near the macroscopic oil-water interface. This computer-controlled microfluidic device will give access to phase composition, water/oil phase activities and kinetics of ion transfer in controlled and reproducible manner.
(2) Developing advanced semi-analytic simulation of free energy variations and merge it with modeling of microstructures, involved at nano- and meso-scale, into a general colloidal modeling approach.
(3) Assembling a simple device based on pertraction with increased kinetics.
(4) Proposing and exploring new generations of formulations and process windows, based on the newly gained mechanism, kinetics and theoretical knowledge.

It is envisaged implementing findings into a pilot plant and demonstrating the feasibility of the newly proposed triggered lanthanide liquid-liquid extraction from recycled aqueous phases obtained by dissolution of used devices, such as magnets, Li-ion cells, batteries and low-consumption lamps and finally sea-water as non-commercial ultimate efficiency test.

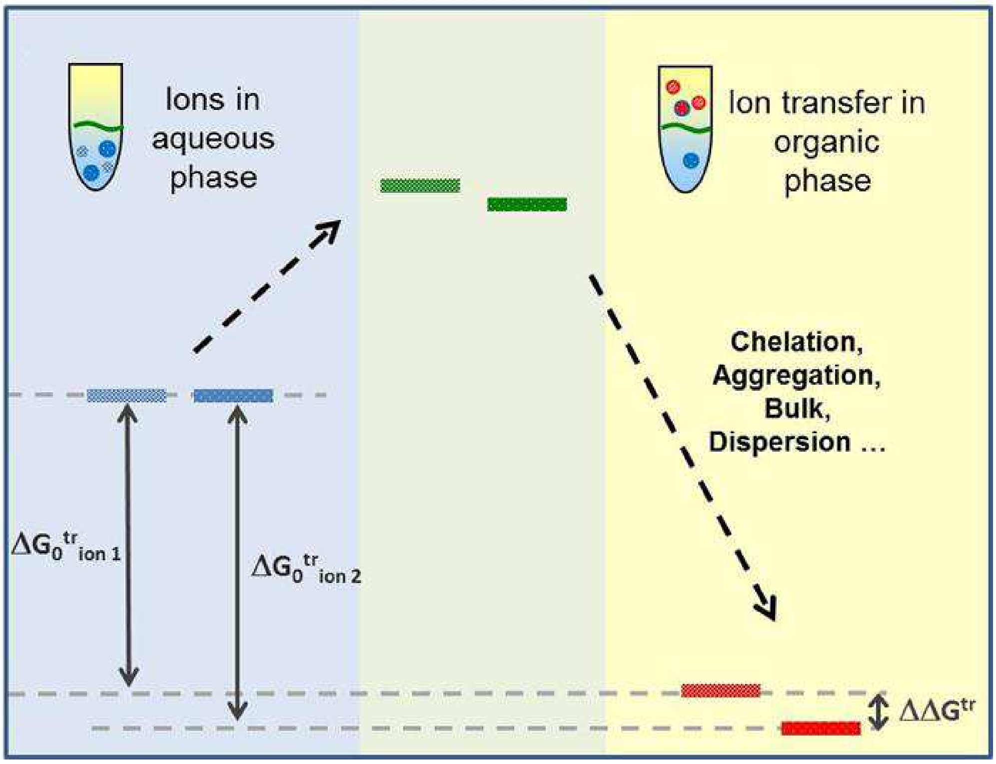

Fig: The reference chemical potential of ion pairs compared in water (left) and in solvent (right). Difference in free energy per ion pair extracted from aqueous to solvent phase is ΔGtr, respectively. The selectivity between the two is the double difference between the two steps i.e. ΔΔGtr.

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PB-7

Stable and Easy Biodegradable Aqueous Foams for Medical or Cosmetic Applications

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Aqueous foams are extremely complex systems with a cellular internal structure, consisting of polydisperse gas bubbles separated by thin liquid films. The foam evolution and its transient stability are functions of drainage and rupture of liquid films between air bubbles.

Our aim was to develop a new technology of generating of bio-inspired, easy degradable, biopolymer based aqueous foams for biomedical application. Thus, the specific objective of this work was to find correlations between surface activity and foaming properties of biopolymers solutions and biopolymers/surfactant mixtures. The foams of the pure biopolymers (proteins like BSA, casein and polysaccharides i.e. methyl cellulose, alginic acid) and solutions of their mixtures with anionic surfactant (lauric arginate LAE) were analyzed.

Foam stability was determined by monitoring the liquid drainage out of the foam volume with two complementary techniques: i) in a classical foam column, where the decreasing of the foam height and variations of the bottom liquid level were measured and ii) in a rotational Hele-Shaw cell (2D foam) for the evolution of the local liquid fraction on various levels of foam. Dynamic surface tension measurements were chosen to investigate the adsorption state in the interface layer under dynamic conditions. Additionally, the rising bubble method was used to determine the concentration of biopolymer and its mixture with lauric arginate that allows a complete immobilization of the bubble surface just after detachment from the capillary orifice.

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PB-8

Adsorption of Esterquat Surfactants and Polyelectrolytes at the Air/Water Interface

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Interaction of oppositely charged surfactants and polyelectrolytes usually leads to formation of surfactant-polyelectrolyte complexes. Surface activity of such complexes depends on the relative concentration and properties of the surfactant/polyelectrolyte pair. Surface active complexes can be used to stabilize emulsions, further used as cores for encapsulation of hydrophobic components, while non-surface active can be utilized as carriers of hydrophilic compounds.

In the present work we consider both experimentally and theoretically adsorption of cationic esterquat surfactants, in the presence of anionic polyelectrolytes (poly(sodium-4-styrene sulfonate (PSS) and sodium alginate (ALG)). We studied derivatives having –O-CO- bond between quaternary amine and hydrophobic tail: N,N,N-trimethyl-2-(dodecanoyloxy)ethaneammonium bromide (DMM-11) and N,N,N-trimethyl-2-(dodecanoyloxy)-1-methylethaneammonium bromide (DMP2M-11)), and derivatives with –CO-O- bond: dodecyloxycarbonyl-methyl-*N,N,N*-trimethyl ammonium bromide (DMGM-12)), and dodecyloxycarbonyl-1-ethyl-*N,N,N*-trimethylammonium bromide (DMALM-12)). These compounds are stable in the acidic conditions but in neutral and basic pH undergo hydrolysis resulting in either dodecanoic acid or dodecanol as surface active products. That influences the surfactant – polyelectrolyte interaction and as consequence the surface activity of their mixtures . The extended "surface quasi two-dimensional electrolyte" (STDE) model of ionic surfactant adsorption was applied for the description of hydrolysis influenced surface activity of surfactants and their mixtures with polyelectrolytes. We found that mixtures of DMGM-12 or DMALM-12 surfactants with polyanions exhibit synergistic effect on the surface tension, decreasing with time as the result of hydrolysis, while in the mixtures of DMM-11 or DMP2M-11 surface active complexes do not form.

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PB-9

New Diamidequat-type Surfactants in Fabrication of Long-sustained Theranostic Nnanocapsules: Colloidal Stability and Bioimaging

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There is increasing interest in development of theranostic nanoparticles that can be applied to transport separately hydrophobic pharmaceuticals (mainly cytostatics for the cancer therapy) as well as imaging agents (organic dyes, fluorescent proteins orfluorescent semiconductor nanocrystals) to the site of disease.

Thus, we have now focused on encapsulation of colchicine (cytostatic drug) and coumarin-6 (fluorescent biomarker) in the oil-core nanocarriers, stabilized by diamidequat-type surfactants and fabricated by the emulsification/solvent-evaporation technique. The titular surfactants, N,N-dimethyl-N,N-bis[3-(alkylamido)ethyl]ammonium methylsulfates (2xC_nA-MS, n=8,10), were synthesized in a technologically convenient three step reaction. In the first step, methyl acrylate was converted in a reaction with methylamine to N-methyl-N,N-bis[2-(methyloxycarbonyl)ethyl]amine (2xC_1E). Then, in reaction of 2xC_1E with n-alkyl amine, N-methyl-N,N-bis[3-(alkylamido)ethyl]amines (2xC_nA, n = 8,10) were achieved. Finally, by quaternization with dimethylsulfate, 2xC_nA-MS (n=8,10)were produced.

The potential of the encapsulated theranostic cargoes was evaluated in cytotoxicity studies as well as in imaging of intracellular localization, accumulation and distribution of cargos delivered to well characterized human cancer cell lines - doxorubicin-sensitive breast (MCF-7/WT), alveolar basal epithelial (A549) and skin melanoma (MEWO) - performed by confocal laser scanning microscopy (CLSM). DLS measurements confirmed the particle diameter below 200 nm, while AFM and SEM - its morphology and shape. Doppler electrophoresis provided a highly positive ζ-potential. UV-Vis was applied to determine the encapsulation efficiencies (ca. 90%), and release profiles.

Our results prove that the studied long-sustained monodisperse oil-core nanocapsules provide suitable nanocarriers for *in vivo* administration and for diagnostic applications.

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PB-10

Streaming Current Study of Biodegradable Biocidal Polymers

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Biodegradable polymers are attracting increasing attention from academia and industry, especially related to medicine and food packaging. Among them, poly(lactic acid) (PLA), polycaprolactone (PCL), and poly(hydroxybutyrate) (PHB), are the most seriously considered for applications. When discussing the mechanism of biodegradation, both chemical and microbial pathways should be considered. In the latter, formation of a biofilm seems to play very important role. On the other hand, for medical and food-related applications, polymers should ideally deter biofilm formation, which is usually achieved by addition of biocides to the polymer. Thus, design of biodegradable biocidal material requires analysis of the factors affecting attachment of polymer-degrading and pathogenic bacteria.

Because of the net negative surface charge of most bacteria, electrostatic contribution is expected to play an important role in bacterial adhesion to the polymer surface. For this reason we characterized the surface of three biodegradable polymers using electrokinetic measurements [1]. For this purpose the streaming current measurements of thin polymer foils were performed by pushing an aqueous electrolyte through a thin channel with walls lined with the polymer. The three biodegradable polymers: PLA, PCL and PHB were analyzed both without and with the addition of biocidal Polyhexamethyleneguanidine Hydrochloride (PHMG) derivatives: sulfanilic acid salt, stearate, and granular PHMG polyethylene wax (1 % w/w). The results show that the ζ-potential vs pH curves obtained from streaming current measurements shift by as high as one pH unit upon addition of the PHMG biocide. Shifting to both lower and higher pH values was observed, depending on the nature of the derivative. The correlation of the ζ vs pH curves with biodegradability and biocidal activity of the three polymers will be discussed.

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PB-11

Microemulsion-Based Organogels Containing Lipase Used Under Continuous Flow Conditions for the Synthesis of High Added Value Products

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Microemulsions have been considered as adequate media for carrying out bioconversions however, their use is limited by the difficulty in isolating products due to the presence of surfactants that hinder phase separation. Nevertheless, microemulsions can be transformed to gels by adding a gelling agent mainly biopolymer such as cellulose derivatives [1], to form the so-called microemulsion-based organogels (MBGs). MBGs are rigid and stable in various non-polar or relatively polar organic solvents, and enzymes immobilized in such media maintain their catalytic activity and stability for long periods [2], therefore, MBGs can be used for the catalysis of interesting synthetic reactions with great biotechnological interest.

In the present work *C. antarctica* and *R. miehei* lipases were immobilized in hydroxyl-propyl-methyl cellulose (HPMC)- MBGs and used for the synthesis of various high added value products under continuous flow conditions. For this purpose, two continuous flow systems have been used based on packed bed reactors: one commercial for the production of monoacylglycerides, and one home-build for the production of lipid and phenolic esters as well as terpene alcohol esters. In all cases, high productivities were obtained as compared to analogue batch reactions. Moreover, the study on the reuse of the system showed that it can be reused 15 times without activity loss, a number two fold higher than for immobilized lipases in batch conditions.

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PB-12

Microemulsions as Antioxidant Carriers. Effect on Enzyme Activity

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Food industry is increasing its interest in formulating biocompatible microemulsions to be used as reservoirs of bioactive substances. The structural characterization of such systems is of great importance, as their physicochemical properties govern their capacity for encapsulation and delivery of bioactive components.

The aim of this work was to formulate a food grade microemulsion based on medium chain triglycerides, isopropyl myristate, lecithin, ethanol and glycerol in order to encapsulate different antioxidant molecules and a subsequent comparative assessment of their antioxidant activity.

Structural characterization of the proposed system was obtained using Dynamic Light Scattering (DLS), Electron Paramagnetic Resonance (EPR) spectroscopy using the spin probing technique [1], and Cryogenic-Transmission Electron Microscopy (Cryo-TEM).

Moreover, the microemulsions loaded with antioxidants were studied for their free radical scavenging capacity [2]. A comparative assessment of a series of encapsulated antioxidants showed gallic acid to have the highest scavenging activity.

Finally, key enzymes encountered during digestion were encapsulated in the microemulsions and tested for their activity in presence and absence of antioxidants.

The developed system could be potentially used as effective carrier of antioxidants in food industry.

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ECIS Posters
PB-13 – PB-68

PB-13

Understanding of Size Selective Precipitation: Achieving Tailored Optical Properties of ZnS Quantum Dots by Classification on a nm Scale

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Colloids like quantum confined semiconductor nanoparticles in the size range of only a few nm are promising materials due to their outstanding electro-optical properties. However, for optimum product dispersity, a post-synthetic narrowing of a particles size distribution often is necessary. This can be realized by size selective precipitation (SSP) where the preferential flocculation of larger particles is induced by addition of a poor solvent. The method is applicable to various colloids, like CdS(e), PbS(e) ZnS(e) or gold and enables a highly efficient classification of particles between 1 nm and 5 nm in diameter.[1-3]
However, the complex interplay between van der Waals interaction and the chemical interaction between the ligand bound to the particle surface and the solvent mixture is still not sufficiently understood. In this contribution a detailed mechanistic study on SSP is presented. It proves that SSP is a highly efficient and robust process that can be applied within a continuous synthesis setup. Moreover, our study allows a theoretical description of the classification based on the separation efficiencies. In conclusion, our work reveals that the in-depth understanding of colloidal interactions is a key-step towards an optimized and knowledge-based process design.

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PB-14

Efficient, Knowledge-Based Design of ZnO Nanoparticles 10 nm in a Modular Microreaction Technology Setup

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During the past years continuous synthesis concepts of colloids using microreaction technology (MRT) devices became more and more attractive. Especially the possibility of a controlled production of larger quantities at high quality is important. However, the modeling of particle formation in MRT based on the mechanistic understanding of nucleation, growth and ripening is still missing.

We use ZnO semiconductor nanoparticles due to their technical relevance and due to the fact that the dispersity of our product is easily derived from absorbance measurements.[1] However, the description of Ostwald ripening of small particles 10 nm is highly challenging because of the strong size dependence of the solubility.[2] We addressed this issue by an implicit numerical scheme which enables a significant reduction of the applied time steps. In fact, several hours of ripening can be predicted within a few minutes on a standard workstation. The subsequent transfer of the batch simulation to the continuous MRT process was realized by means of the experimentally determined residence time distribution. For validation of our model, an excellent agreement with the experimental findings at the reactor outlet was proven. Our methodology is believed to be a very important step for a future process design that enables the continuous larger scale production of complex nanoparticles.

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PB-15

Ink-Jet Printing Dispersions of Fluorescent Seeded Nanorods

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The use of fluorescent semiconductor nanocrystals for ink-jet printing applications is gaining a lot of interest in the last few years. Their unique optical features that are characterized by wide absorption spectrum accompanied by a sharp and narrow emission spectrum, along with their optical and chemical stability, offer interesting advantages for their implementation in different technologies

Although the use of fluorescent spherical semiconductor nanocrystals (quantum dots) is well established in the literature with possible applications in the field of solar cells, electronic devices, biosensing and biomarking, there are no reports for the use of fluorescent nanorods (quantum rods) in ink-jetting applications. Fluorescent nanorods are outstanding candidates for fluorescent inks, due to their relatively low self-absorption, the robust synthesis of mono-dispersed nanocrystals, their high QYs and their intrinsic emission polarization properties.

We report here on the development of dispersions and ink formulations containing CdSe/CdS seeded nanorods. The nanorods are stabilized by polymeric dispersing agents. The advantages of seeded nanorods over quantum dots in inks were examined by conducting a thorough investigation of the optical properties of both structures used in the ink-jet printing. The characteristics of nanorods and quantum dots inkjet printed patterns were compared regarding their quantum yield, fluorescence and more. Seeded nanorods ink formulations show a good dispersion, and are stable both chemically and optically over a long period of time. We show an optimal multi-layer printing of fluorescent inks with high fluorescence quantum yield and a full coverage of the substrates. Using a similar method of production, it is possible to create a wide range of inks that share the same characteristics but produce various colors. These inks are applicable for diverse applications such as signage and RGB displays.

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PB-16

Formation of Colloids with Optical Traps

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During the last decade significant advances in controlling nano objects and polymer/DNA clusters with optical traps have been demonstrated along with the ability to create various phase changes induced by photon pressure.

Here we present a novel method were colloidal particles with controlled size are created when an optical trap is introduced while an emulsion or micro-emulsion polymerization is taking place. Nucleation seeds, oligomers and micelles are attracted to the trap and (under certain parameters) coalesce and polymerize, thus creating a colloidal particle.

To create numerous colloids the optical trap is focused within a microfluidic channel. The size of the forming colloids is determined by the intensity of the laser and the flow rate of the solution. Using Holographic Optical Tweezers (HOT) we create hundreds of traps that are independently controlled and therefor create any kind of colloidal size combination.

The versatility and ease of making various changes to the end product without the need for chemical modifications makes this approach appealing for testing model systems.

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PB-17

Orthokinetic Aggregation of Charged Colloidal Particles in the Presence of Repulsive Double Layer Force: a Trajectory Analysis with Non-Linear Poisson-Boltzmann Solution

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Aggregation rates in a shear flow were analyzed on the basis of trajectory analysis with non-linear Poisson Boltzmann (PB) solution used for the calculation of double layer force. The PB solution enables us to analyze the experimental data of orthokinetic aggregation of highly charged particles[1,2] where linearized PB solution is not valid. Fig.1 shows the capture efficiency, which is defined as the ratio of actual aggregation rate to Smoluchowski's one in shear flow, as a function of KCl concentration for different shear rate, *G*. Symbols are experimental values for sulfate latex particles with a diameter of 1.96 µm and a surface charge density of -60 mC/m^2 taken from Sato *et al.*[1], and lines are the theoretical values calculated with a Hamaker constant of 2.0×10^{-21} J. Fig.1 demonstrates that theoretical calculation qualitatively describes experimental data. However, theoretical values of CCC and capture efficiencies in fast coagulation regime are not quantitatively consistent with experimental ones. These discrepancies might be caused by the additional non-DLVO forces and charge heterogeneity which are not included in the present calculation.

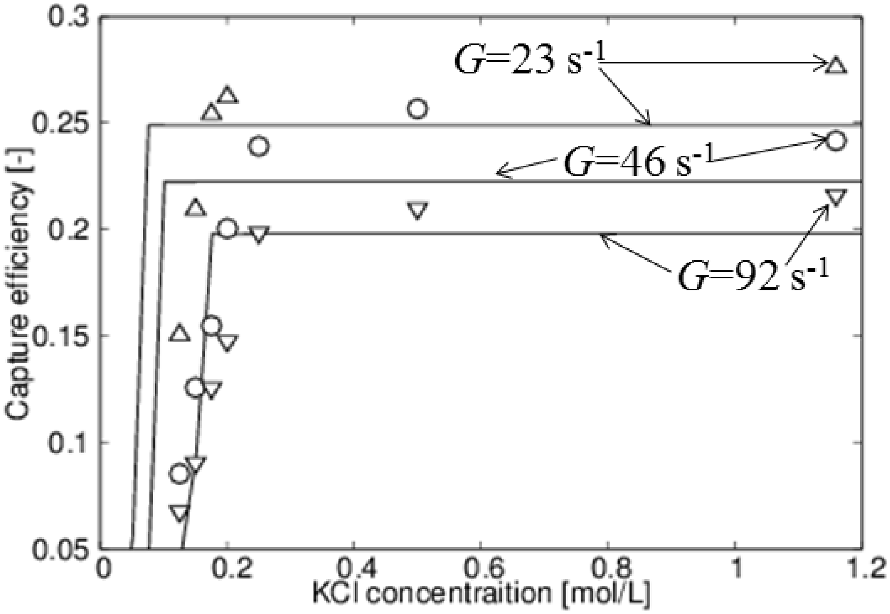

Fig.1 Capture efficiency vs. KCl concentration for sulfate latex with a diameter of 1.96 μm: Symbols and solid lines are experimental values taken from Sato *et al*. (2005) and theoretical values calculated by trajectory analysis with exact PB solution, respectively.

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PB-18

Preparation of Titania-Coated Gold and Gold / Silver Nanorods and Their Photocatalytic Properties

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Photocatalytic systems working under visible and infrared light are of vital importance for efficient utilization of sunlight. Apart from doping of light elements and metal ions to semiconductor particles, combination of metal nanoparticles with semiconductor ones is one of promising systems for this purpose. Gold nanorods are advantageous since they show a broad and large absorption band from visible (l ≥ 520 nm) to near-infrared (l ~1000 nm) regime. Meanwhile, silver nanoparticles exhibit stronger absorption band in contrast to gold ones, although the band is located at shorter wavelengths (l ~400 nm).

Herein gold nanorods of different aspect ratios were employed as core and coated with either directly with titania shell or with an intermediate silver layer and outermost titania shell. The titania layer was formed by utilizing specific interaction between the titanium alkoxide and quaternary ammonium head groups of cationic surfactant (CTAB) bilayers on the gold or gold / silver nanorod surfaces.

The titania-coated gold nanorods showed a significant photocatalytic activity for oxidation of 2-propanol under visible light (l ≥ 420 nm). Intriguingly, they exhibited the photocatalytic activity also under NIR light (l ≥ 720 nm). Meanwhile, a thin silver interlayer was found to enhance the photocatalytic activity. The thickness of titania shell also influence the photocatalytic activity; about 10 nm of the shell thickness was found to be optimal.

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PB-19

Functionalized Nanocrystalline Cellulose Particles

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Nanocrystalline cellulose particles (NCC) (also known as cellulose nanocrystals (CNC)) are small rod-shaped particles with a length of 100-200 nm and a width of about 5 nm. They are typically made from cellulose fibers by hydrolysis with H_2SO_4, which breaks down the amorphous cellulose chains into sugars, leaving the nanocrystals which, in suspension, form cholesteric liquid crystals. They have a number of potential applications in color films, reinforcement agents in composites, templates for chiral glasses and many more. The conventional NCC is stabilized by sulphonate groups, introduced during the hydrolysis. It is also possible to liberate the NCC particles by chemical reactions. We have made NCC with protruding DAC (dialdehyde cellulose) or DCC (dicarboxylated cellulose) chains, providing the particles with steric and electrosteric stability respectively. An AFM micrograph of DCC stabilized NCC is shown in the figure. These particles are much more stable than conventional NCC and form much stronger films. Properties of these functionalized nanocrystalline cellulose particles will be discussed.

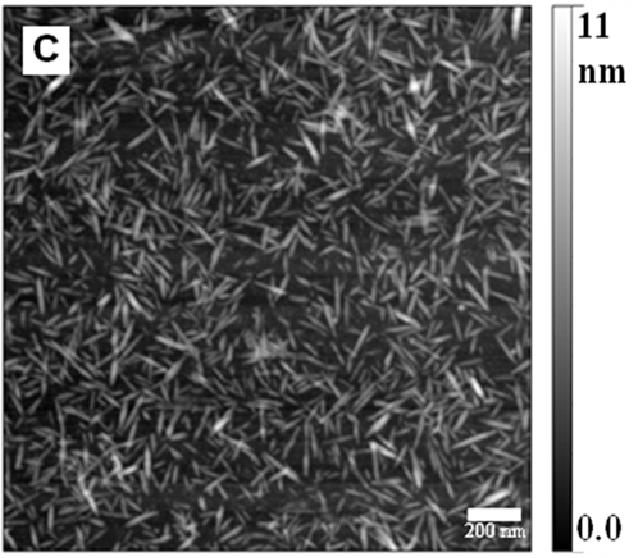

Fig. 1AFM of nanocrystalline cellulose particles stabilized with dicarboxylated cellulose chains

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PB-20

Study of Proteins, Lectins, Glycoconjugates and Colloids Mutual Interactions Using Surface Plasmon Resonance

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Interest in the study of biochemical and biological properties of glycoconjugates is growing. Lectins and glycoconjugates (mainly glycoproteins) have a huge potential for use in biology and medicine as diagnostic and therapeutic tools, and polymers and colloid nanoparticles can ensure controlled distribution for their interaction with targeted cells in organisms. Development of many diseases including cancer is connected with changes in protein glycosylation, and glycans and lectins as substantial components of microbial cell walls are also involved in the interactions with the host cell immediately after pathogen – host first contact leading to infection reaction and immunological response. Biochemical investigations of interactions of isolated or synthesized oligosaccharides linked to protein carriers or other surfaces are so crucial for drug research and vaccine development. On the other side, the interactions of nanoparticles/polymers with individual components of the body can be unwanted with very serious consequences led to the damage of organism. Therefore, the exact study and quantification of such interactions is important for future development and application of involved molecules/substances in diagnostics and therapy. Surface plasmon resonance is a technique routinely used for study of protein - protein interaction. Its employing in studies of mutual interactions between proteins, lectins, glycoconjugates, polymers and colloids is however still limited. We have studied interactions of mannan glycoconjugates with lectins, human proteins with colloidal nanospheres, and DNA with light-switchable polymer using microfluidics surface plasmon resonance as case studies for future biomedical research and possible applications.

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PB-21

Polymer/drug Interactions of PNIPAM-g-PEO and Indomethacin in Aqueous Media

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The effects of the cononsolvent composition and the added drug – indomethacin– on the structure of PNIPAM-g-PEO copolymer aggregates in mixtures of ethanol and water are investigated.New data about the adsorption layer properties at the air/solution interface and the foam film stability are obtained. It is established that higher degree of copolymer grafting results in a remarkable frequency dependence of the surface rheological properties at room temperature and in a pronounced thermal sensitivity of the copolymer-drug formulation at elevated temperatures. Important input is added in view of the optimal composition of the copolymer/drug formulation aimed at possible pharmaceutical applications. It is found for example, that ethanol quantity of 10% (v/v) is the lowest limit of pharmaceutical interest, and the range of 15-20% ethanol quantity is the optimal composition for the specific polymer-drug system. The obtained results add new knowledge about the mechanisms of the drug entrapment and release events, considering the system's composition and different temperatures.

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PB-22

In Vitro Studies of Serum Albumin Interactions with Poly(D,L-lactide) Nanospheres Loaded with a Model Hydrophobic Cargo

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The various polymer-based nanocarriers are very attractive for *in vitro* and *in vivo* bioapplications. A new type of promising drug delivery systems for cancer tissues - poly(D,L-lactide) nanospheres stabilized with Cremophor EL and loaded with hydrophobic cyanines (IR-780 or ZnPc) or curcumin (CUR) were fabricated by the nanoprecipitation method [1]. Obtained Cremophor EL/PLA/water nanospheres demonstrated regular shape, low polydispersity (PdI0.3) and high entrapment efficiency of selected cargo (over 90%). The size of those nanoconstructs below 130 nm are in the desired nanocarriers size range for tumor delivery, that is larger than the renal filtration cutoff and small enough for tumor penetration [2]. Low level of *in vitro* drug release from loaded nanospheres after long-time storage indicates their good stability. The half-life of nanocarriers in the circulation, and their biodistribution after parenteral administration are associated with the ability of plasma proteins adsorption. For these reasons the affinity of the obtained nanospheres for albumin as a major plasma protein was investigated *in vitro*. The binding of nanocarrier containing cyanine IR-780 with albumin immobilized in the wells of polystyrene plate occurred with lower efficiency than analogs loaded with ZnPc or CUR. The formation of albumin/nanosphere complexes was confirmed in ^{1}HNMR DOSY experiments and similar differences of Cremophor EL/PLA/water nanospheres affinity to serum albumin were observed. The changes in diffusion coefficient values revealed that nanosphere-albumin complex dimensions were about twice higher than those for a free nanoparticle loaded with ZnPc or CUR.

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PB-23

Development of Fluorinated Colloidal Gold Nanoparticles as Theranostic Drug Delivery Systems

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In the last decades the use of nanoparticles (NPs) for biomedical applications has attracted a growing research interest, promoting NPs use in imaging, therapy, and drug delivery. [1] The possibility of combining diagnostic and therapeutic properties in unique nano-objects has led to the development of new theranostic systems, [2] which might improve the prognosis of many diseases. At the same time, fluorinated tracers represent a powerful diagnostic tool for *in vivo* imaging through ^{19}F MRI detection. [3] Thus, the use of fluorinated ligands for NPs surface functionalization can bring to the development of innovative theranostic agents to be employed in nanomedicine.

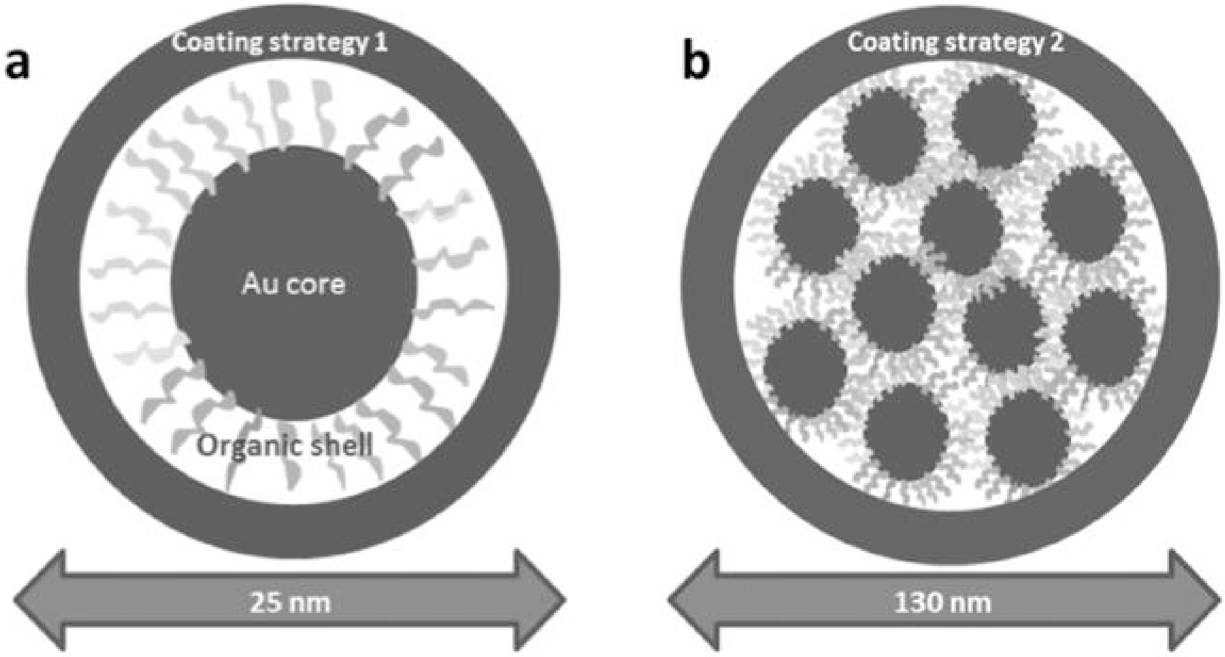

Figure 1: Schematic representation of NPs structure obtained by using coating procedures 1(a) and 2(b)

In this contribution we report on a novel multifunctional nanomaterial based on gold NPs stabilized with highly fluorinated chains or with a mixture of hydrogenated and highly fluorinated ligands. These NPs were successfully transferred into an aqueous environment using two different coating amphiphilic polymers. The obtained nanodispersions were characterized by DLS, zeta-potential, ^{19}F-NMR, FTIR, TEM and UV-VIS measurements. As shown in Figure 1, the two coating strategies produced different hybrid nanostructures. Indeed, in one case we obtained NPs formed by a single Au core coated with a layer of polymer, while in the other the NPs were composed of several Au clusters covered by a coating film. Stability studies in biological fluids such as serum and human plasma were also performed. Overall, these systems can function simultaneously as ^{19}F-MRI contrast agents and as drug delivery systems, resulting in promising theranostic agents for biomedical applications.

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PB-24

Multifunctional Nanoparticles for Biomedical Applications

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Scientific and industrial impact of nanoscience and nanotechnology in analytical chemistry, medicine and pharmacy has been growing. Many different nanosystems have been developed for these purposes. However, the choice of the bioconjugation approach directly affecting the orientation, accessibility, and bioactivity of biomolecules immobilized on these nanoparticles is a very important issue in bionanotechnology [1,2]. There are plenty methods for antibody immobilisation on surfaces. If antibodies acquire an improper orientation, their active sites become inaccessible for antigen, which reduces their biological activity.

Native antibodies and their reduced fragments were immobilized on planar gold, gold nanoparticles and magnetic gold nanoparticles. Antigen capturing efficiency was compared using direct and indirect detection methods and different techniques. Quartz crystal microbalance with dissipation was applied for the investigation of antibody fragment surface mass density on planar gold and gold nanoparticle modified surfaces, and for the evaluation of specific and non-specific interactions [3]. Surface-enhanced Raman scattering-based sandwich immunoassay format was used for the enhancement of analytical signal after the immune complex formation on magnetic gold nanoparticles [4].

Prospects of nanoparticle synthesis, bioconjugation, and application for targeted drug delivery will be discussed.

Acknowledgements:
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PB-25

Development of Soft-Colloid Regulation Method by Self-Assembly for Nanotoxicology and Nanomedicine

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A large number of toxicological and medical papers have suggested the effect of nanoparticles using methods that lack biocompatible nanoparticle-dispersion protocols. Nano-assessment requires careful consideration of biological molecular adsorption on the nanoparticle. However, there is no uniform standard for safety evaluation. The relationship between nanoparticle-physicochemical properties and exact effects remains unclear. Recently, due to the progress of nanoparticle researches, we are coming to understand that the nanoparticle surface is an essential factor for decisions of cellular recognition and response. Hence, it is necessary to broaden our understanding of the biological molecular adsorption mechanism, which can interact with nanoparticles. Biological molecules can adsorb on nanoparticle surfaces with physical forces. However, the mechanism by which this occurs has not yet been clarified. The present study demonstrates physisorption of phospholipids on colloidal nanoparticles using phospholipids with different hydrophilic groups and lengths of saturated fatty acid hydrocarbon chains, and evaluates cellular uptake of phospholipid-adsorbed nanoparticles.

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PB-26

Magnetically Responsive Polyelectrolyte Nanocapsules

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In the past decades nanocapsules gained increasing interest in biomedical applications. They can be used as carriers of the lipophilic, poorly water-soluble, or even water-insoluble drugs. Such carriers can be specifically developed for achieving intelligent drug delivery system. Targeting towards selected pathologically changed tissues/cells would enable delivery of the drug only to the selected tissues. That should not only significantly decrease deleterious side effects, but also may drastically enhance therapy efficiency. Various approaches were proposed to accomplish this goal. The layer-by-layer adsorption of charged species like polyelectrolytes, nanoparticles, proteins, organic molecules, etc. is considered as a convenient method to obtain multilayer nano and microcapsules' shells on colloidal cores. A polyelectrolyte shell of capsules can be functionalized by magnetic nanoparticles to form magnetic carrier which could be guided with magnetic field gradients and therefore, could transport the biologically active matters with an optimum therapeutic concentration of the pharmaceuticals to the desired tissue of the organism, while the total dosage remaining unchanged. The aim of this work was to develop the method of preparation of magnetically responsive, loaded nanocapsules based on a liquid core encapsulation by polyelectrolyte (PE) multilayer adsorption. Magnetically responsive drug nano delivery systems were prepared by the sequential adsorption of polyelectrolytes (layer by layer technique) using biocompatible polyelectrolytes (Poly L-lysine as the polycation and Poly Glutamic acid as the polyanion). The model lipophilic drug, β-carotene, was successfully encapsulated in the liquid core while Fe_3O_4 nanoparticles were embedded into the polyelectrolyte multilayer shell. This magnetically responsive drug nano delivery system may be a promising platform for future targeted therapies (e.g. cancer) or other biomedical applications (e.g. separation systems, diagnostics).

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PB-27

Polyelectrolyte Nanocapsules as an Anticancer Drug Carriers

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The targeted delivery of the drugs is currently one of the main topics in the field of nanomedicine. Many drug-candidate compounds have been found active *in vitro*, but had limited clinical effectiveness partly because of their side effects, low solubility, and/or other limitations of pharmaceutical parameters. Among various approaches to specifically target drug-loaded carrier systems to required pathological sites in the body, two seem to be most advanced--passive (EPR effect-mediated) targeting, based on the longevity of the pharmaceutical carrier in the blood and its accumulation in pathological sites with compromised vasculature, and active targeting, based on the attachment of specific ligands to the surface of pharmaceutical carriers to recognize and bind pathological cells. The aim of our work was to develop the method of preparation of loaded nanocapsules and their surface modification for passive targeting via EPR effect. Nanocapsules containing anticancer drugs (e.g. Taxol, Curcumine), were prepared using a method of direct encapsulation of emulsion droplets in polyelectrolyte multilayer shell. The oil cores containing selected drugs stabilized by an AOT/PLL (Poly L-Lizyne) surface complex were encapsulated with shells formed by layer-by-layer adsorption of polyelectrolytes. The average size of the obtained capsules was 100 nm. Surface of obtained capsules were modified by pegylation for passive targeting. *In vitro* anti-cancer activity of the nanoencapsulated anticancer drugs on CT26 CEA, 4T1 cancer cells was evaluated.

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PB-28

Structured Emulsions as Hydrogels of Complexing Biopolymers

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Work is devoted to the establishment of new fundamental laws that characterize the relationship between the structure, rheology and colloid-chemical properties of structured systems - highly concentrated emulsions as hydrogels. Mixtures of biopolymers - gelatin with polysaccharides (chitosan, alginates, carrageenan) derived from marine hydrobionts have been used as emulsion stabilizers. The highly concentrated emulsions are considered as hydrogels, including microparticles (droplets) of oil. Mechanism of structure formation in such systems has been investigated. The new ideas about the formation of supramolecular structures in the multicomponent systems, determining the nature of the sol-gel transition of biopolymers at concentrations above the threshold of gelation are discussed. The thermostability of mixed biopolymers' gelled systems having fundamental importance is considered.

The main goal is to create methods of directed structural morphology control of gel-like emulsion network and their rheological (viscoelastic) properties by changing the composition (in particular, gelatin/polysaccharide ratio) of the multicomponent systems, including the introduction of micro-heterogeneous agents. Solution of this problem contributes to the development of innovative food technologies aimed at sustainable use of bioresources. These technologies, in particular, would solve the problem of replacing gelatin derived from animals by fish gelatin and polysaccharides of marine origin.

Aqueous dispersions of biopolymers, the formation of polyelectrolyte complexes of gelatin with ionic polysaccharides have been studied. The structure and rheological properties highly concentrated emulsions stabilized by mixtures of gelatin with polysaccharides (chitosan, alginate, carrageenan) of marine origin were investigated.

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PB-29

Food Concentrated Emulsion Systems with Using *Fucus*

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The research is dedicated to the creation of new laws describing the relationship between structure, rheology (viscoelasticity) and colloid-chemical properties of food concentrated emulsions (type "oil-in-water") containing *Fucus* – natural stabiliser derived from brown algae. Two type of *Fucus* (*F.vesiculosus and Ascophyllum nodosum) from Barents Sea* have been used for creating emulsions. This stabilizer contains polysaccharides, such as fucoidan, and also amino acids, microelements, polyunsaturated fatty acids.

Influence of the stabilizer concentration and pH value on stability and dispersity of concentrated emulsions was considered.

Rheological behavior of structured emulsions stabilized by Fucus was investigated under shear deformation. Viscosity was measured in two regimes: at controlled shear stress and controlled shear rate. Viscoelastic properties of emulsions have been studied by a dynamic method. It is shown that increase in the relative content of the stabilizer results in a growth of the system elasticity. The obtained frequency dependence of the elastic modulus is characterized by the existence of a plateau in a wide frequency range with the elastic modulus being always higher than the viscosity modulus.

The idea of control of structural network morphology of concentrated emulsion and their rheological (viscoelastic) properties by changing the composition of the multicomponent systems have been discussing. The solution of this problem contributes to the development of scientific bases for the creation of innovative technologies of food emulsion products. The technology of canned fish products with using sauces has been developed. The main components of sauces prepared on the basis of the concentrated emulsions are water, sunflower oil, *Fucus*, and flavorings.

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PB-30

Formation of Copper Nano-Particles by Copper Complex Decomposition

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Fabrication of flexible electronic devices by ink-jet printing of the conductive patterns is of growing research interest. Ink formulations based on copper has the potential to replace the silver due to its low price and high conductivity.

However, it is difficult to prevent the oxidation of copper nanoparticles, before and after printing, which leads to poorly conductive patterns. Moreover, after printing the copper nanoparticles require a high temperature curing (usually above 200 °C) which prevents their application in low cost, heat sensitive plastic substrates.

To address these challenges, we developed a metal organic decomposition (MOD) ink based on copper amine complexes that undergoes pyrolysis to copper metallic nanoparticles at low temperatures (below 150 °C), and therefore enables printing conductors on heat sensitive plastic substrate (PET and PEN). The ink is stable in air for prolonged periods, without problems of losing functionality which are usually encountered in nanoparticles inks, such as aggregation and creation of copper oxides.

Our observations showed that controlling copper particle size following complex decomposition is possible by controlling the process temperature. The range of particles size obtained was between 10 nm and 2 µm.

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PB-31

Jamming and the Onset of Granulation in a Model Particle System: an Experimental Study

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Granulation is the process of mixing a dry solid powder and a liquid phase in order to produce agglomerates. This method of processing is used in a wide range of industrial applications from food stuffs to pharmaceuticals to produce aggregates with specific physical characteristics such as size and mechanical strength. Much work has been done to try and understand the various parameters that control granule properties; however less progress has been made on mechanistic understanding. At low volume fractions the mixing of solid and liquid produces pastes and suspensions, yet at high volume fractions granules are produced. In this work we present a model system of glass spheres and glycerol that exhibits a stress dependent transition from suspension to granules at a critical volume fraction. Using rheological data we find two divergent viscosity branches corresponding to frictional and frictionless flow. The frictional branch diverges at a volume fraction phi(m), beyond which the system cannot rearrange in response to further stress, but instead fractures and granulates. The frictionless branch diverges at a volume fraction phi(rcp), above which the system will always granulate. Thus we make contact with recent work on the role of friction in suspension shear thickening (Wyart and Cates, Physical Review Letters 112, 098302, 2014).

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PB-32

Interactions of Perfluorohexyloctane with Tetradecane and Water-Thermotropic Phase Behavior and Occluding Effects

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Semifluorinated alkanes (SFA) is a class of molecules which display several unique properties and have been proposed for use in numerous biological applications [1-3]. In this study we have investigated the interaction of perfluorohexyloctane (F6H8) with tetradecane (C14) and water.

F6H8/C14 mixtures were found to display eutectic phase behavior with an eutectic point of -8.5 °C at 6 wt% C14. F6H8 displays two transitions at -42°C (DH=1.0 kJ/mol) and -6°C (DH=16.4 kJ/mol). Due to the low enthalpy value of the first transition in F6H8 it is likely that this corresponds to a transition in solid F6H8 rather than solid-liquid transition. Similar, the main transition point indicates that F6H8 is not fully crystallized in the solid phase but rather partly amorphous. The data indicates that most probably the fluorinated part is crystal while the hydrogenated segment is in amorphous state. Pure C14 has one solid-liquid transition point at 5.9 °C (DH=48.0 kJ/mol). Titration of small amount C14 into infinite volume of F6H8 reveals an enthalpy of solution at infinite dilution of 4 kJ/mol C14.

Further, the low water solubility determined for F6H8 and F6H8-C14 mixtures promotes the ability to form an effective occlusive layer. We have shown that a film of F6H8 or F6H8-C14 mixtures significantly reduces water evaporation from a hydrogel.

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PB-33

Monodisperse Colloidal Gas Aphrons for Oilfield Applications

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Wet microbubble foams (WMF) are of growing interest in various oilfield applications: drilling, completions, water flood monitoring, hydraulic fracturing etc. The most attractive properties of WFMs therein are their low density, high yield-stress rheology as well as their pressure-triggered mobility in porous media. The main complication in the development of a successful oilfield technology lies in the development of WMFs able to survive reservoir pressure and temperature. In respect to such severe environment unique are the properties of the WMFs known as colloidal gas aphrons (CGAs). CGA based fluids consist of microbubbles, the cores of which are composed of a gas surrounded by a thick multilayer surfactant film. Wettability tests show that CGA bubbles have very little affinity for each other or for the mineral surfaces of rock formations.

In the work a procedure for the preparation of monodisperse CGA stable at reservoir pressure is developed. It is based on the modeling of foaming process in gas-oversaturated solution. A set of experiments is conducted in order to validate the model and determine the key factors affecting the properties of the final CGAs.

The behavior of CGA based fluids under pressure variations is studied experimentally by optical microscopy. A high-pressure thermostabilized optical cell is specially designed for use with Carl Zeiss inverted microscope to visualize CGA microbubbles at pressure up to 40 MPa. The CGA images taken with the microscope camera are processed in order to calculate bubble size distribution (BSD).

The CGAs studied are prepared with anionic surfactants sodium dodecyl sulfate and potassium stearate as aphronizers and xanthane gum as polymer viscosifier. The results show that the aprons produced by our method have narrow BSD remaining in other respects common CGAs. The dependence of the final BSD on the gas oversaturation and the pressure release rate are examined in detail.

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PB-34

Characterization and Evaluation of Surface Functionalized Silica Nanoparticles

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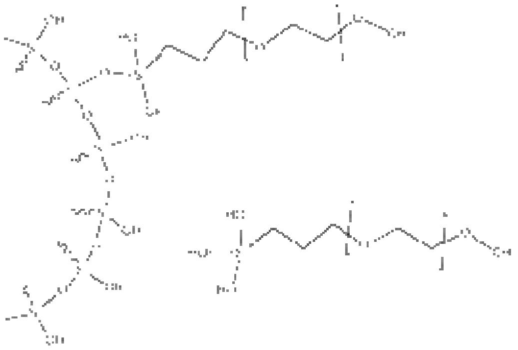
Colloidal particles can spontaneously accumulate at the interface of two immiscible liquids and thereby stabilize disperse systems such as emulsions and foams [1]. Properly designed particles can adsorb irreversibly at the interface of an emulsion droplet, providing an unusually high stability of the system. In emulsion applications surface modified silica nanoparticles with controlled hydrophobicity and surface activity have great potential.

In this work, the properties of colloidal silica with hydrophobic and hydrophilic functionalizations are explored. The particles are evaluated and characterized to obtain knowledge of how they behave not only in dispersion systems, but also in terms of stability of the modification and steric stabilization effects. NMR diffusometry is used to evaluate the surface modification and is an essential tool for the characterization. The figure shows the diffusion profile of methyl polyethylene glycol silane (mPEG silane) grafted on silica particles with a specific surface area of 130m^2/g. These particles are surface active and, at high enough coverage, sterically stabilized.



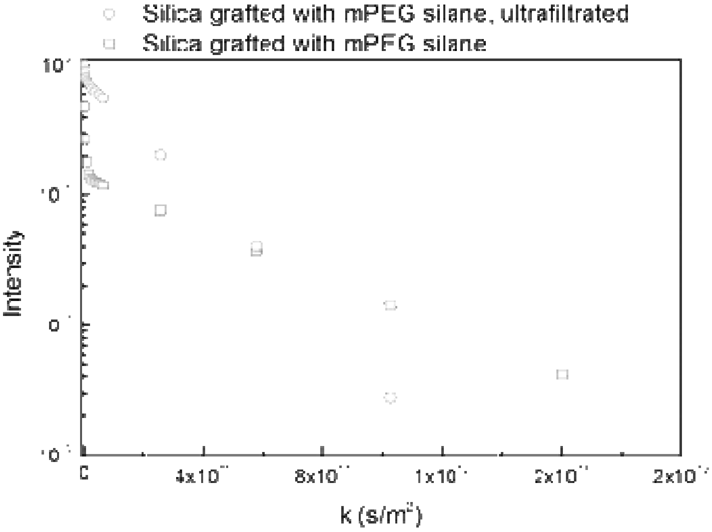


Figure 1: NMR diffusometry measurements (right) of silica particles grafted with mPEG silane (left). Before purification by ultrafiltration, 20% of the silanes (0.2µmol/m^2) are attached to the particles, and after purification 85% of the silanes are attached to the particles. The steeper slope of the filtrated suspension is due to a more diluted sample with a lower viscosity.

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PB-35

Developing and Characterizing Efficient Polycation-Clay Sorbents for the Removal of Diclofenac

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Diclofenac is one of the most frequently detected pharmaceuticals in water bodies since its removal by most conventional wastewater treatment plants is low. Efficient sorbents for diclofenac removal based on the adsorption of a specially synthesized polycation, poly N-methyl 4-vinyl pyridine iodide co styrene (QPVPcS), to montmorillonite, were developed. These composites, at low (0.1 g/g) and high (0.2 g/g) polymer loadings, were characterized by zeta-potential, X-ray diffraction (XRD), FTIR and thermal gravimetric (TGA) measurements. Zeta potential reached charge reversal at both polymer loadings. FTIR measurements suggest that at a low polymer loading the main configuration is as trains while at a high loading it is also as loops and tails. Polymer intercalation was observed by XRD measurements at low and high polymer loading; however, complete exclusion of the intercalated water occurred only at high polymer loadings. Water exclusion at high loadings was supported by TGA measurements which also indicated that the polymer adsorbs in more than one mode. The positively charged composites promoted electrostatic interactions with anionic diclofenac (pKa=4.15). However; studying the effect of ionic strengths on the removal of diclofenac by QPVPcS composites (in comparison to polycation composites without aromatic groups) indicated that in the case of QPVPcS π–π interactions contributed significantly to diclofenac binding. Adsorption isotherms of diclofenac to the composite and to granular active carbon (GAC) were adequately described by the Langmuir equation and did not differ significantly. However, the adsorption kinetics of diclofenac to the composite was significantly more rapid than to GAC. Finally, the fast kinetics of diclofenac binding to the composite was advantageous in filtration and diclofenac removal by composite filters was more efficient than by GAC filters.

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PB-36

Dynamic Interfacial Tension Measurements as Means for Investigating Amylose-Fatty Acid Inclusion Complexes

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Amylose forms complexes with fatty acids under certain conditions. These complexes could be potentially used as delivery systems of essential fatty acids in the human organism. This work uses dynamic interfacial tension measurements as means for investigating such complexes for the first time in the literature. The Whilelmy plate technique and the pendant drop / axisymmetric drop shape analysis method were used for the measurement of equilibrium and dynamic interfacial tension. First the interfacial tension at the water/air interface was measured for three fatty acids (capric, myristic and oleic) in 0.1 N KOH solution at three different concentrations ($6*10^{-2}$, $6*10^{-3}$ and $6*10^{-4}$ g/100ml). The surface tension of amylose in 0.1 KOH solution was measured as well. Then amylose and fatty acid solutions were mixed to fatty acid-to-amylose weight ratios of 10, 1 and 0.1 % and a fatty acid concentration in the final solution equal to the fatty acid solutions without amylose. For all examined systems the dynamic interfacial tension of the mixed amylose – fatty acid solution was significantly higher than this of the fatty acid solution, showing that some of the fatty acid was no longer available to adsorb at the interface and suggesting its inclusion in the complex. Besides, the dynamic interfacial tension of the mixed system was lower compared to the amylose solution indicating that some of the fatty acid did not participate in the complexes and that the fatty acid excess depended on fatty acid-to-amylose ratio.

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PB-37

Molecular Dynamics and Electronic Structure Properties on the Inhomogeneous YVO_4-Pt Photo-catalyst System in Contact with Aqueous Methanol Solution

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The material YVO_4 is known as a promising photocatalyst which can produce both oxygen and hydrogen from water by UV light irradiation. Especially, it possesses a remarkable efficiency in decomposing methanol aqueous solution to produce hydrogen in the presence of a Pt co-catalyst[1]. In this conference we focus theoretical understanding on the role of Pt co-catalyst on the adsorption properties of methanol molecules onto YVO_4 photocatalyst surface in contact with aqueous methanol solution by using first principles molecular dynamics and on the related electronic properties of the inhomogeneous system. Main results of this work are as follows; (1) We have found that, during the 300 K NVT dynamics, a CH_3OH molecule often can be dissociatively adsorbed to the Pt co-catalyst cluster surface and the extracted H atom from the methanol by the O atom of the approaching H_2O molecule forms a hydronium H_3O^+ species. (2) In the case that H_2 molecules are solvated in the methanol aqueous solution, H_2 molecules have the net effect of inhibiting the methanol dissociation. Instead, H_2O molecule can be dissociated on the Pt cluster surface. We also observed the dissociation of H_2 molecule at a Pt site. Such a phenomenon seems to be related to the concentration of hydrogen molecules. (3) In the detailed investigation on the electronic properties of the inhomogeneous systems, we have cleared the role of Pt co-catalyst that it can promote the carrier separation, which would enhance the excited electron life time, and the probability to transfer excited electrons to the protons, thus leading to hydrogen generation.

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PB-38

Adsorption Mechanism of PEO-PPO-PEO Triblock Copolymers on Gold and Hydrophobic Substrates

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The adsorption mechanism of a series of PEO-PPO-PEO triblock copolymer has been studied at the water/hydrophobic interface and water/Au interface by Ellipsometry and Surface plasma resonance (SPR). The copolymer forms monolayer with the middle PPO block anchoring at the surface and the PEO groups either anchoring at the surface or protruding into aqueous phase. Two plateaus have been observed in the adsorption isotherms. At very low bulk concentration, the surface coverage is low and that the PEO segments of the adsorbed copolymer is believed to be fully extended. As the surface coverage increases with the increase of bulk concentration, the extended EO segments on surface become saturated and reach the first pseudo-plateau of the isotherm. By further increasing the bulk concentration the oversaturated EO segments at the interface will then be gradually forced away from the surface and extruded into the bulk solution. Since the free space released by the desorbed EO segment will allow for further adsorption of the copolymer, one observes a 2nd stage increase in the adsorption isotherm. As the coverage increases, EO is increasingly forced away from the surface and finally formed a brush structure provided the bulk concentration and the adsorption affinity of the Pluronics are both high enough. The adsorption state of PPO segment on various surfaces is mainly determined by its affinity with surfaces. The stability of the adsorbed film is also studied by series desorption tests.

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PB-39

Extracellular Glycolipid-Mediated Carbohydrate-Carbohydrate Interactions: Importance of Lipid Raft Domains for Multivalent Binding

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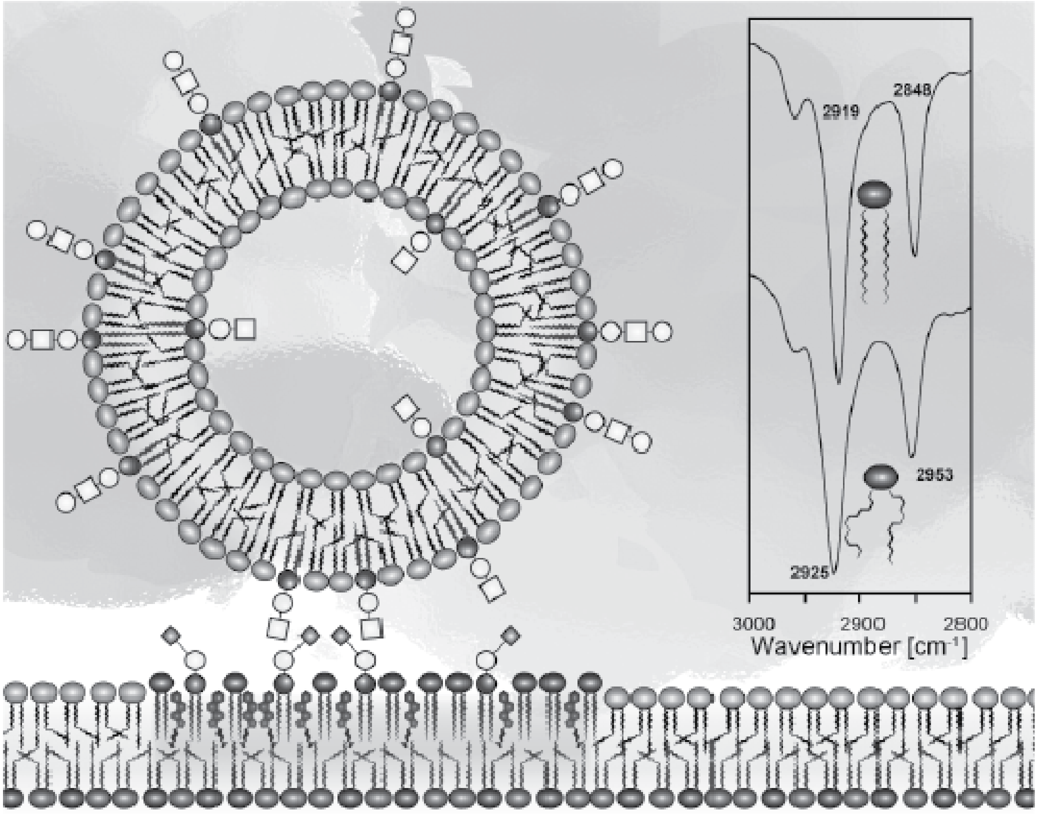
Carbohydrate-carbohydrate interactions in biological systems have recently been recognized as important for cell-cell interactions such as cell-adhesion, proliferation, differentiation as well as for disease processes such as tumour formation and metastasis. In this project, focus is on the last example. Metastasis of melanoma cells, which is initiated by their binding to the endothelium, is directed via the specific interaction between sialosylllactosylceramid (GM_3) and gangliotriaosylcermaide (Gg_3). The existence of this interaction has been a matter of debate due to the very weak interaction strength. However, strong and specific interaction can be realized via the formation of so called lipid raft domains into which the glycolipids become concentrated. This concentration enables multivalent interaction and the raft domains act as communicating and signalling hubs. We are investigating the formation of raft domains containing GM_3 in models of the extracellular leaflet using mainly Langmuir monolayers-based techniques (FRET, GIXD, IRRAS, surface pressure-area/time isotherms and dilatational rheology). More specifically, IRRAS has been used as a non-invasive method to conveniently follow the formation of the raft domains by probing the methylene stretch vibration of the hydrophobic lipid chains. The binding of Gg_3-containing liposomes to monolayers or bilayers containing GM_3 is studied using TIRF spectroscopy and SPR. As a complement, the biological relevance is investigated by cell-binding assays (flow cytometry and confocal fluorescence microscopy) and signal transduction (Western Blot) using GM_3 and Gg_3 expressing cell-lines (murine melanoma B16 and lymphoma L5178-S cells lines respectively).



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PB-40

Stability and Structure of Liquid Interfaces in Foams and Emulsions

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Understanding the properties of adsorbed films at air-liquid or liquid-liquid interfaces is important for formulating stable emulsions and foams in the food, cosmetic, pharmaceutical and coating industries. For example, some proteins are known to denature and form a two-dimensional network at air-liquid and liquid-liquid interfaces. The denaturation process can be examined by measuring the viscoelastic properties of these interfaces. Dynamic rheological experiments are capable of separating the storage (elastic) and loss (viscous) modulus of complex rheologi-cal behavior. Both, area changing (dilatational) and constant area (shear) properties can be measured and give valuable information on the mechanical properties of the interface.

In this presentation, two methods for the study of interfacial protein layers are presented; oscillating drop (dilatational) and interfacial shear rheometry (shear). The study presents results on measuring the viscoelastic properties and the adsorption and network formation of protein solutions to interfaces. Time dependent data shows how to determine the gel point of the systems. It also demonstrates how precise control of surface pressure during a measurement makes it possible to model natural systems like cell membranes.

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PB-41

Integrated Surface Chemistry and Roughness Characterization to Study Wettability and Adhesion

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Both surface chemical and topographical properties are important parameters in many different applications and processes, where wetting and adhesion behavior needs to be optimized. Wettability can be studied by measuring contact angle of the substrate with given liquid. The well-known Young equation describes the balance at the three phase contact of solid-liquid and gas.

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv}\cos\theta_e$$

The interfacial tensions, γ_{sv}, γ_{sl} and γ_{lv}, form the equilibrium contact angle θ_e of wetting. The Young equation assumes that the surface is chemically homogenous and topographically smooth. This is however not true in the case of real surfaces, which instead of having one equilibrium contact angle value exhibit range of contact angles between advancing and receiving values. To define the equilibrium value, surface roughness should be taken into account. Relationship between surface roughness and wettability was defined already in 1936 by Wenzel who stated that adding surface roughness will enhance the chemical wettability of the surface. For example, if the surface is chemically hydrophobic, it will become even more hydrophobic when surface roughness is added.

Until now, it has not been possible to directly combine the surface roughness and contact angle measurements. In this abstract we describe the equipment where these two measurements can be done in conjugation to each other. In addition, with example measurements it will be demonstrated the importance of both surface chemistry and roughness on wetting and adhesion behavior.

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PB-42

Stress Relaxation Mchanism by Strain in the Si-SiO_2 System and its Modification by Laser Irradiation

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It is known that internal mechanical stresses (IMS) due to the differences in the thermal expansion coefficients between films and substrates and lattice mismatch appear in the Si-SiO_2 system during the process of its formation and that point defects (PD) generation and redistribution could be used to reduce partially the surface strains. However, this process on the atomic scale is till not studied. The goal of the present report is to investigate the strain relaxation mechanism in the Si-SiO_2 system and its modification by laser irradiation using EPR, IR absorption spectroscopy, scanning elektron microscopy (SEM) and samples bending measurements. PD density and stresses in the Si-SiO_2 system were varied by oxidation condition (temperature, time, cooling rate, ambient) and by Si_3N_4 deposition on SiO_2. Different sign of the thermal expansion coefficient of the SiO_2 and Si_3N_4 on Si allow to modifay the IMS at the interface. It has been found that samples bending decreases or increases simultaneously with EPR signal intensity depending on the oxidation condition (temperature). At lower temperature (1100^0C) the bending of the samples decreases with the increase of the EPR signal intensity (vacancies) while at a higher oxidation temperature (1200^0C) the bending and EPR signal increase simultaneously. These allows to suggest that at lower oxidation temperature PD reduce the IMS, while at higher oxidation temperature IMS created PD. It has been shown that after laser irradiation the samples bending decrease or increase depending on the laser irradiation intensity.A possible reason for that can be the change of the IMS under laser irradiation and compressive or tensil stresses formation at the interface.

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PB-43

Interactions of Local Anaesthetics with Model Membranes - Langmuir Monolayer Study

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In this study Langmuir monolayer technique is involved in monitoring interactions of selected local anaesthetics (LAs) - lidocaine, prilocaine, mepivacaine and ropivacaine - with monolayers mimicking erythrocyte, mitochondria and nerve membranes.
In the first step of investigations, the interactions of LAs with pure monolayers of 1-palmitoyl-2-oleoyl-phosphatidylcholine (POPC), cholesterol (Chol), sphingomyelin (SM) and cardiolipin (CL) were examined. It was found that the presence of LAs in the subphase increases the area occupied by lipid molecules. From all the drugs studied, the highest expansion was observed for ropivacaine. Among the investigated membrane lipids, the strongest effect of LAs was noticed for cardiolipin.
In the next step, the effect of LAs with model erythrocyte (POPC:SM:Chol=1:0.9:1.3), nerve cell (POPC:SM:Chol=1:0.9:2.6) and mitochondria (POPC:CL:Chol=1:0.35:0.1) membrane was studied. Fluidizing effect on model membranes was observed in all the cases. The strongest influence was noticed for nerve cell membrane.

The Langmuir monolayer investigations have been complemented with other techniques, i.e. PM-IRRAS and BAM.

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PB-44

The Influence of Alkylphosphocholines on Lipid Rafts - a Monolayer Study

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Outer layer of cellular membrane contains ordered domains enriched in cholesterol and sphingolipids, called 'lipid rafts', which play various biological roles, i.e. they are involved in the induction of cell death by apoptosis. Recent studies have shown that these domains may constitute binding sites for some drugs. Some of them are alkylphosphocholines (APC). The mode of action of APC, which are new generation antitumor agents characterized by high selectivity and broad spectrum of activity, has been hypothesized to be linked with the alternation of biophysicals properties of lipid rafts. To get a deeper insight into this issue, interactions between selected APCs (miltefosine and erucylphosphocholine) and a raft model (composed of cholesterol and sphingomyelin mixed in 1:2 proportion) were investigated using the Langmuir monolayer technique.

The obtained results, based on experimental π – A isotherms complemented with visualization method (Brewster angle microscopy), confirm the alteration in physical parameters of raft membrane by APCs. Namely, drug molecules induce a phase separation and fluidize the model raft system.

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PB-45

Polyfunctional Systems Based on Mono- and Dicationic Morpholinium Surfactants

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Cationic surfactants are extensively involved in various nanotechnological strategies focusing on the development of drug and gene carriers, micellar catalysts, emulsifiers, inhibitors of corrosion, etc. Therefore much attention is devoted to the correlation of their chemical structure with aggregation and functional activity. At the present work we focused on the polyfunctional systems based on mono- and dicationic surfactants with morpholinium fragment in their head group. Study of the aggregation behaviour and catalytic activity toward the cleavage of p-nitrophenyl esters of carbonic acids of different hydrophobicity has been carried out in the presence of the surfactants. The catalytic effect increases with the alkyl chain length of surfactants and depends on the structure of the head group. Catalytic effect of gemini surfactants is higher as compared to conventional analogs; it realizes at lower concentrations and is characterized by a marked substrate specificity.

The morpholinium surfactants were used for the complexation of oligonucleotide. The formation of the lipoplex was monitored by the dynamic light scattering and fluorescent spectroscopy. Compaction of oligonucleotide and the neutralization of anionic phosphate groups in the presence of morpholinium surfactants suggest that these compounds may act as nonviral vectors.

It was established that the morpholinium surfactants are effective inhibitors of hydrogen sulfide corrosion. Besides they are characterized by a high bactericidal activity toward sulfate-reducing bacteria and demonstrate a pronounced bacteriostatic and fungistatic effect.

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PB-46

Effect of Small Molecules on Structural Behavior of Self-Assembling Systems

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Self-assembling systems based on ionic surfactants are highly sensitive to the additives of small molecules capable of hydrogen bonding, dipole-dipole, electrostatic interactions and other forces affecting water structure. Two types of such additives are known to be differentiated, i.e. chaotropic and kosmotropic ones. According to simplified interpretation the former disrupt the water structure, while the latter stabilize it. Meanwhile the influence of small molecules on surfactant solutions is markedly determined by chemical structure of additives and may be realized via different mechanisms. Apart from their effect on the water structure low molecular weight additives may modify charge character and surface curvature, thereby affecting critical micelle concentration, size and morphology of aggregates.

In this work, effect of small nonionic molecules and organic electrolytes on the solution behavior of cationic surfactants is studied. Different amphiphiles including typical cationic surfactant cetyltrimethyl ammonium bromide, its gemini analogs and amphiphilic phosphonium salts are involved. As additives organic electrolytes are explored, such as acetic acid salts, sodium tosylate, salicylate, benzoate, etc. Besides, organic and bioorganic nonionic molecules (glucamine, thymol, isosteviol) of different polarity are also used. Aggregation properties, solubilization capacity, viscoelastic behavior and functional activity (catalytic, antimicrobial) of surfactant-additives systems are studied by methods of tensiometry, conductometry, fluorescence spectroscopy, dynamic light scattering, etc. It was found that some of organic electrolytes are able of associating with the formation of their own nanosized aggregates, while such uncharged species as thymol may markedly modify the viscosity of solution.

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PB-47

Molecular Dynamics Simulation of the AOT Reverse Micelles at Freezing

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Molecular dynamics (MD) simulation has been performed to investigate structural, thermodynamic properties of the AOT reverse micelles in nonpolar medium. The modeling is carried out for the aggregates at the temperature from 300 to 160 K. Water molecules are simulated with SPC/E model. Surfactant and oil are treated in a coarse-grained approach.

It was found out the temperature of water freezing is lower than that in bulk water. There are three different types of water molecules in reverse micelle: bulk-like water in the center of the polar core, intermediate state water and molecules in ionic shells. For the first water type the temperature of freezing is close to 270 K. Counterions are moved to the aggregate surface. The second one becomes crystal-like structure at 170 K. The water molecules in ionic shells and oil molecules demonstrate liquid state during the simulation.

Two type of water are considered in pure water clusters in oil. Water molecules are more structured without surfactant. There are more hydrogen bonds at 300 K. The water drop is compressed at this temperature and several molecules are located at the center of the cluster. Water molecules at the surface construct a layer structure with temperature decreasing. Oil molecules without surfactant demonstrate layers as well.

There is sufficient different behavior between water-in-oil system without and at the presence of surfactant. Surfactant aggregates are stable aggregates. Ionic surfactants make a main contribution into the whole energy of the system.

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PB-48

A Computational Microscope: Coarse Grained Simulations of Dense Microemulsions Systems

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Microemulsions are exciting systems that are promising as tunable self-assembling templating reaction vessels at the nanoscale. Determination of the nano-structure of microemulsions is, however, not trivial, and there are fundamental questions regarding their design. We were able to reproduce experimental data for an important microemulsion system using coarse grained simulations involving relatively limited computational costs. The simulation allow visualization and deeper investigation of controversial phenomena such as bicontinuity and ion mobility.

Dense microemulsions of Sodium-AOT/n-heptane/water were simulated using the Martini coarse-grained force field. Sodium-AOT was parameterized by matching the geometry with atomistic simulations. All simulations were based on 800 surfactant molecules in a constant ratio equal to two with oil, while the water content was varied up to 60% in weight. Simulations were 1 us long. From Mean Square Displacement calculation of all species, it was possible to quantify caging effects and ion mobilities. Average diffusion coefficients were calculated for all charged species and conductivity was found in quantitative agreement with experimental data. The scattering function was calculated for the hydrophilic species and matched the experimental data obtained from Small Angle X-ray Scattering measurements. In particular, bicontinuity of water and oil was for the first time computationally visualized. Equilibrated coarse grain simulations were reversed to atomistic models in order both to compare ion mobility and to catch finer simulation details.

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PB-49

A Model System for Understanding the Formation of Mesoporous Silica - the Influence of Surfactant Counterions

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Mesoporous silica can be synthesised with different properties and pore structures [1]. Some properties appear to be dependent on anions present during the synthesis for the cationic system MCM-41 [2]. In an attempt to unravel the significance of the initial interactions between the cationic micelles (the structure directing agent), silica and counterions/anions we designed a model system. The system consists of a small surfactant, $C_{10}TA^+$ $[CH_3(CH_2)_9N(CH_3)_3]$ with Cl^-, NO_3^-, SO_4^{2-} or para-toluene sulphonate (PTS), as counterions, and a small silica species (POSS). The anions were chosen to extend over the Hofmeister series. POSS, a cubic silsesquioxane, $[Si_8O_{20}(N(CH_3)_4)_8]$ forms discrete, negatively charged species in aqueous solutions with tetramethylammoniumions as counterions. This system was chosen to represent an initial snapshot of a mesoporous silica material synthesis.

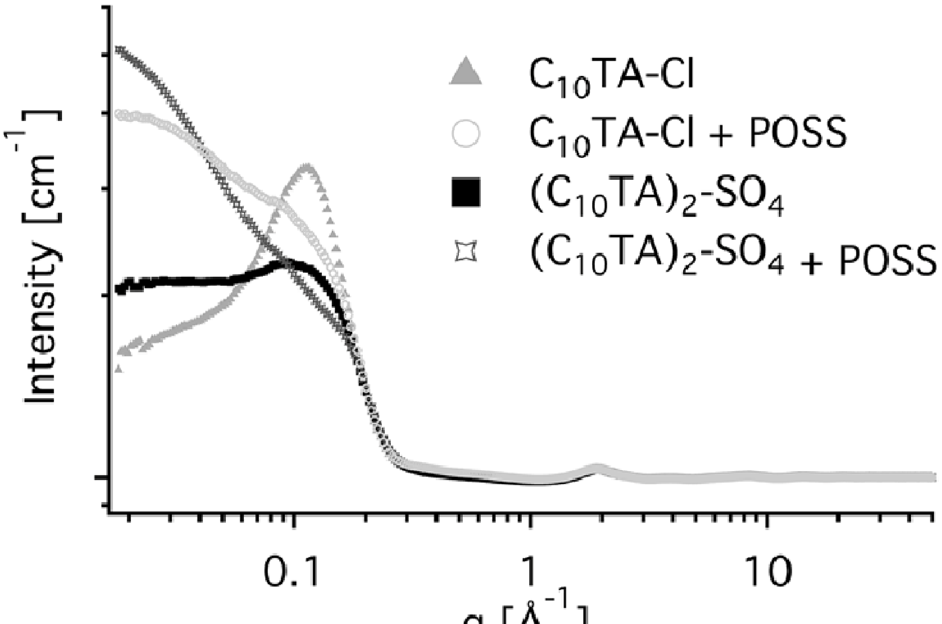

Figure 1: Scattering data (one contrast) of $C_{10}TA^+$ with two different counterions, with or without POSS.

Using a combination of wide q-range neutron scattering and computer modeling [3], Empirical Potential Structure Refinement (EPSR), atomistic details of the system are provided. Our scattering data shows that different anions affect the micellar properties and that POSS interacts with the micelles. Further, this interaction depends on the identity of the anions, see Figure 1.

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PB-50

Impact of Hydrocarbon Nature on the Structure of Triton-X100 Micelles

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The nonionic surfactant p-tert-octylphenoxy polyethylene (9.5) ether (TritonX-100) possesses excellent surfactant performance in detergency, emulsifying and wetting characteristics over a fairly broad temperature range and being readily biodegradable has been widely used for decades. The issue about the TX100 micelle structure, however, is not trivial because at low concentrations it is has a two-layer spherical structure with partially overlapping internal and external layers of Triton X-100 molecules and no distinct hydrophilic-hydrophobic boundary. The effect of oil addition to this structure is not easily predictable. We have studied the evolution of the micelles upon addition of linear and cyclic alkanes by dynamic light scattering, viscosimetry, PFGE-NMR and NOE-NMR. Upon oil addition, the micelles first swell but above a certain critical oil content decrease in size. Such a decrease is due to two effects: a reduction in the aggregation number, and a dehydration of the polyethylene chains.

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PB-51

Small Angle Neutron Scattering Study of Micellar Structure of the Type CiE$_7$ (i =10,12,14) of Surfactants in Dilute Solutions

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The aim of experiment was investigated of aggregation of three non-ionic classic surfactants type CiEj - heptylethylene glycol monodecyl ether ($C_{10}E_7$), heptaethylene glycol mono dodecyl ether ($C_{12}E_7$) and heptaethylene glycol monotetradecyl ether ($C_{14}E_7$) in D_2O solutions by SANS method. The aggregation for such surfactant in water solutions dependence on concentration, temperature and molecular structure of surfactants. The size and shape of micelles in dilute aqueous solutions was determined by small angle neutron scattering (SANS). The SANS results were successfully analyzed with the aid of PCG 2.1 program from Graz University (Austria). For all investigated solutions c=0.17%, 0.5% and 1% and temperatures (10^o,15^o,20^o,25^o,30^o and 35^oC) micelles are two axes oblate ellipsoids which increases slightly with increase concentration and temperature.

The small angle neutron scattering measurements for two surfactants $C_{10}E_7$ and $C_{12}E_7$ were carried out on the "Yellow Submarine" instrument at Budapest Neutron Centre. The sample to detector distance and the mean neutron wavelength were np.1.3m and 3.86A, respectively. The samples were placed in 2mm thick quartz cuvettes and then thermostated to ±0.5K. The scattering experiments covered the scattering vector, q (q=4psin (q/2)/l, q is the scattering angle, l is the wavelength), range 0.02-0.45$Å^{-1}$.

The experiment with small angle neutron scattering method for surfactant $C_{14}E_7$ was made using a YuMO spectrometer of the IBR-2 on pulsed neutron source in the Laboratory of Neutron Physics, JINR, in Dubna (Russia). The Q range was 0.007 – 0.4 $Å^{-1}$. The temperature within the cells was kept constant in a range of ± 0.5^oC by means of a thermostat. Conversion of the scattered intensities into absolute differential cross-sections was done by using an internal calibration standard (vanadium).

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PB-52

The Complex Formation of Eu^{3+} and Tb^{3+} with Amphiphilic ß-Diketones

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Recently, the LB films based on rare earth metals have a high attractiveness for many researchers. Previously, we have studied the complex formation of Co (II) and Ni(II) with the monolayers of octadecane-2,4-dione [1]. In this work, we start study of the complex formation of Eu (III) and Tb (III) with the monolayers of amphiphilic β-diketones (Fig. 1) and prepare the LB films based on this structure.

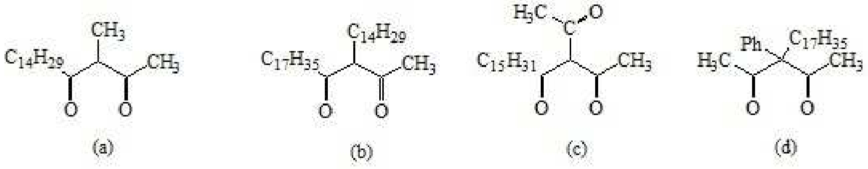

Fig. 1 The structure forms of amphiphilic β-diketones (a - octadecane-2,4-dione; b – 3-tetradecylheptadecane-2,4-dione; c – 3-acetylnonadecane-2,4-dione; d – 3-heptadecyl-3-phenilpentane-2,4-dione

We investigated the complex formation of Eu (III) and Tb (III) ions in the monolayer of β-diketones as a function of concentration of the metal ions in the subphase (pH = 5.9). In the case of the subphase containing Eu^{3+} and Tb^{3+}, the area per molecule was significantly increased compared to metal ions- free subphase. It indicates the formation of the complex in the monolayer. In the monolayer creates the steric strain due to the complexes formation. This can be confirmed dependences of molecular area and collapse pressure of the monolayer β-diketone as a function of concentration Eu^{3+} and Tb^{3+} ion in the subphase. This dependences is clearly illustrate a more broadening of the monolayer of complex Tb (III) than Eu (III).

This work supported by a grant from the Russian Foundation for Basic Research.

[1] Repina I.N., Sokolov M.E., Panyushkin V.T. Investigation of complex formation of cobalt(II) with molecular Langmuir layers of octadecan-2,4-dione // The Journal of Physical Chemistry C. 2012, V. 116, pp. 5554 - 5557.

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PB-53

Composite Lipid/Fe_3O_4/SiO_2 Mesoparticles for Remotely Controlled Release of Active Substances

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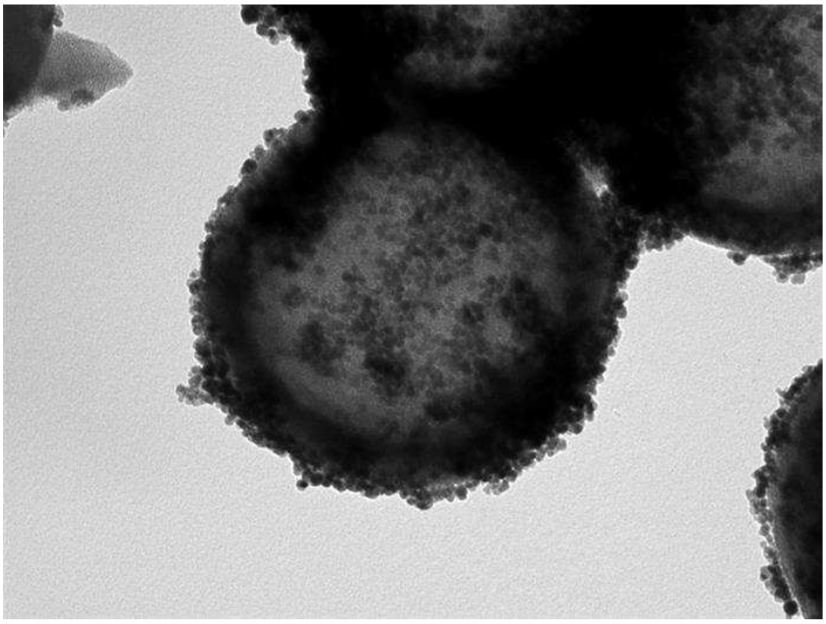
The goal was to prepare composite lipid/Fe3O4/SiO2 mesoparticles from hollow porous silica shell particles (500-600 nm) prepared by emulsion method, superparamagnetic iron oxide nanoparticles (5-20 nm) prepared by co-precipitation method and lipid nanoparticles (30-40 nm) prepared by phase inversion temperature method. First, composite Fe3O4/SiO2 particles were prepared by coating the silica shell by a layer of iron oxide. The composite particles were then loaded by the active substance and coated by a layer of lipid nanoparticles to form a barrier which blocks diffusion in and out of the particles, thus preserving the active substance inside. The particles were characterised using transmission electron microscopy, dynamic light scattering and electrophoretic light scattering.

The release mechanism is triggered by alternating magnetic field in the radiofrequency range, which heats up the magnetic iron oxide particles and melts the lipidic barrier. Pores are no longer blocked and the active substance diffuses into the environment. Release kinetics of the active substance were measured using UV-VIS spectrophotometry. The ability of the particles to be visualised by Magnetic Resonance Imgaging (MRI) was demonstrated.



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PB-54

Phosphate 2.0

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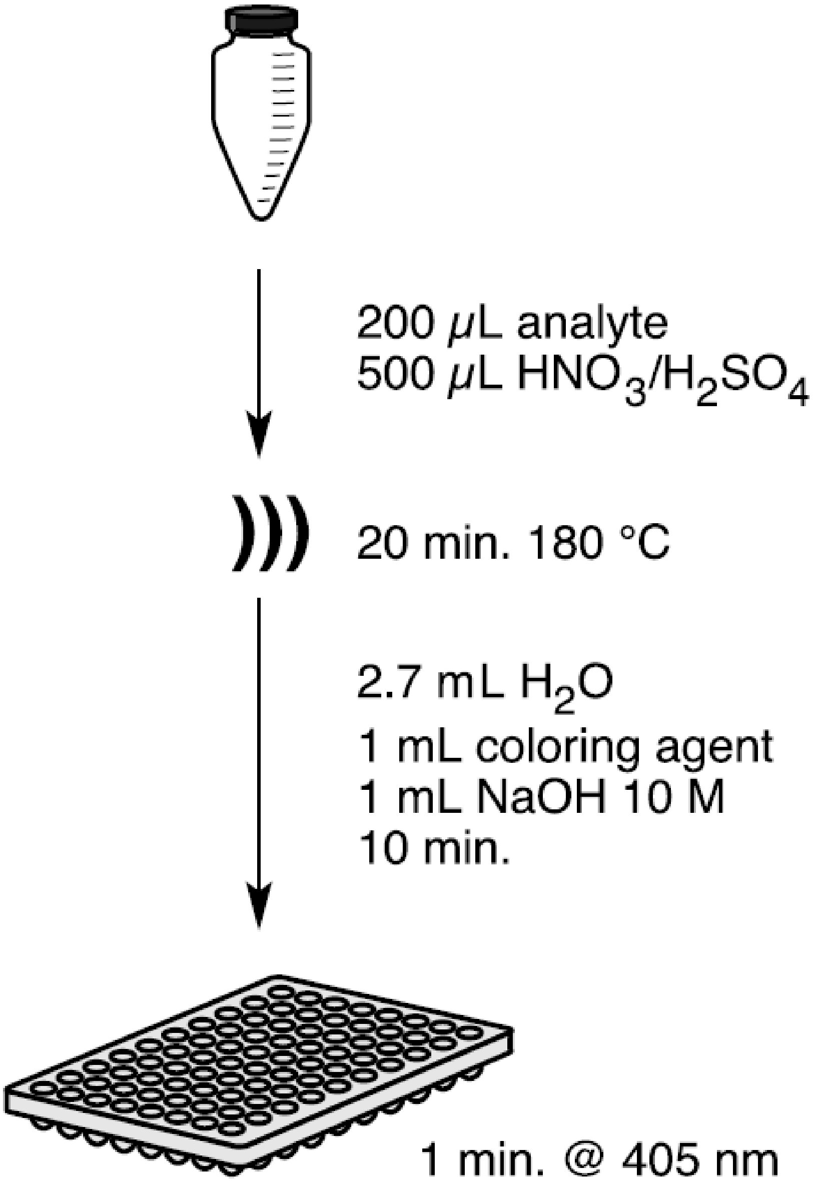
The determination of the phospholipids concentration in liposomal suspensions is a key step in phospholipids science. Standard phosphate tests date back several decades and require extended hands-on time. The procedures consist in a chemical digestion step where the phosphodiester moiety of the phospholipid is oxidized to an orthophosphate. This step is often carried out by heating the phospholipid suspension in the presence of a strong acid or oxidizing agent in a open vessel. Evaporation of solutes calls for an extra, time consuming volumetric step. The orthophosphate is the detected colorimetrically as a metallo complex. Many coloring agents can be used mainly molybdenum compound such as vanadomolybdophosphoric acid, molybdenum blue or phophomolybdenum-malachite green complex[1].

The use of microwave assisted chemical digestion allows skip the volumetric step as no solvent is evaporated during the oxidation of the phospholipids.

Vanadomolybdophosphoric acid has a maximum absorption wavelength (402 nm) close to the standard 405 nm filter found on almost every plate reader. The plate reader allows to analyze several samples in parallel with a high number of replicates. The new phosphate test method has proven to be efficient even for low concentration suspensions (2 µM to 200 µM of phosphate).



Etienne Stalder, Andreas Zumbuehl, CHIMIA International Journal for Chemistry, 67, (**2013**), 819-82.

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PB-55

Control of Release and Enzymatic Reaction Progress inside Magnetic Liposome Microgels

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Many biochemical processes in living cells are regulated by internal structuring of cells, i.e. compartmentalisation. Enzymes and reactants are separated by semi-permeable membranes. In order to mimic this feature we present internally structured alginate gel micro-particles containing thermo-responsive liposomes (filled with reactants) and colloidal iron oxide allowing remote heating of micro-particles by radiofrequency field.

Utilizing these particles we controlled the progress of the oxidation of ABTS (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid)) catalysed by the enzyme laccase. The substrate was encapsulated inside the immobilized liposomes and the enzyme was dispersed within the alginate hydrogel. We were able to dose the substrate by short RF pulses and the product of the reaction was stepwise released out of the gel micro-particles.

However, alginate gel particles are not very stable in isotonic buffers and are dissolved in few hours. Rigidity of such particles is necessary for further bio-adhesive study; therefore, a method of their stabilization in concentrated solutions was developed. The modification utilizes polycationic polysaccharide chitosan as a co-cross-linker of alginate gel. Such particles remain stable and rigid in an isotonic PBS buffer for more than a month.

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PB-56

Transparent and Airtight Silica Nano- and Microchannels with Uniform Tubular Cross-section

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Experimental results on a template-assisted technique to fabricate uniform nano- and micro-channels are presented. Different template materials, polystyrene and poly(vinyl alcohol) electrospun and spider silk fibres were coated with silica. After calcination mechanically stable and transparent channels with uniform tubular diameter were obtained. The diameters ranged between 150 nm and 4 µm, depending on the size of the fibre template. By coating crossed fibres we prepared connected channel junctions that were solvent- and airtight. The channels and junctions remained tight even when applying a pressure above 3 bar as verified by laser scanning confocal microscopy. The flow of liquids in the channels was monitored and described by the Lucas-Washburn equation. We varied the viscosities and surface tensions of the liquids and measured the filling velocities over a distance of several millimeters as well as very close to the channel entrance. The late stage of capillary filling can be well-described by the Lucas-Washburn equation. The early stage was slower than predicted. We attribute the delayed filling to the velocity dependence of the contact angle.

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PB-57

Fluorescence Correlation Spectroscopy Directly Monitors the Equilibrium Chain Exchange Kinetics of Diblock Copolymer Micelles

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Dual color fluorescence cross-correlation spectroscopy was applied to measure the equilibrium chain exchange kinetics of amphiphilic diblock copolymer micelles. As a model system we choose the copolymer polystyrene-block-poly[oligo-(ethylene glycol) methyl ether methaxrylate] (PS-POEGMA) comprising a linear-brush architecture forming micelles with a thin and bulky corona [FIG. 1].

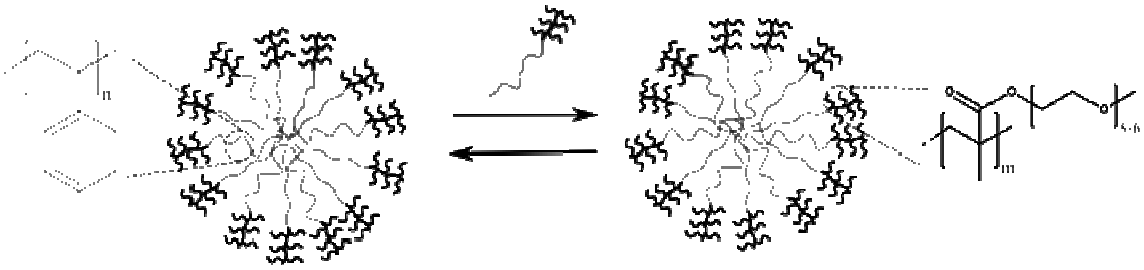

FIG. 1: Scheme of the dynamic equilibrium chain exchange of amphiphilic diblock copolymer micelles formed by PS-POEGMA.

The exchange was monitored in different solvents and at various temperatures showing the reliability of the method.[1] In methanol as a solvent, the exchange persists even at temperatures well below the nominal glass transition of the core forming PS suggesting that the methanol swells the micelle core. At the same temperatures no exchange could be observed when pure water is used as a solvent. Furthermore, even small changes in solvent quality can slow down or fasten the exchange by orders of magnitude. This tremendous impact of solvent quality allows extensive tuning of the exchange kinetics.

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PB-58

Superamphiphobic Particles - How Small Can We Go?

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Water and oil repellent coatings - so-called superamphiphobic coatings - greatly reduce the interaction between a liquid and a solid. So far, only flat or weakly curved superhydrophobic and superamphiphobic surfaces have been designed. This raises the question of whether highly curved structures or microspheres are feasible. Therefore, we coated microspheres with a superamphiphobic layer and measured the force between the spheres and a liquid (*Phys. Rev. Lett.* **2014**, 112, 016101). A qualitatively different dependence of the adhesion force on the applied load for superamphiphobic and smooth spheres is detected. Furthermore, we demonstrate both experimentally and theoretically that superamphiphobicity fails below a critical particle radius, depending on topological details and type of liquid. Therefore, this study sets a fundamental physical limit to the application of superamphiphobic layers for small objects with high curvature.

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PB-59

Super Liquid-Repellent Gas Membranes for Carbon Dioxide Capture and Heart-Lung Machines

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In a gas contactor membrane, gas is transferred between a liquid and a gas through a microporous membrane. The main challenge is to achieve a high gas transfer while preventing wetting and clogging of the membrane. Especially low surface tension liquids and deposits of biological material like proteins and cells pose problems to conventional gas membranes. With regard to heart-lung machines, a good blood-membrane haemocompatibility is also required. To meet these challenges we developed novel membranes based on macroporous metal meshes coated with a super liquid-repellent — or superamphiphobic — layer[1]. The superamphiphobic layer consists of a fractal-like network of fluorinated silicon oxide nanospheres[2]; gas trapped between the nanospheres keeps the liquid from contacting the wall of the membrane. We demonstrate the capabilities of the membrane by capturing carbon dioxide gas into a basic aqueous solution and calculate the mass transfer coefficient. In addition we oxygenate blood, like in heart-lung machines. Usually, blood tends to clog membranes because of the abundance of blood cells, platelets, proteins and lipids. We show that human blood stored in a superamphiphobic well for 24 h can be poured off without leaving cells or adsorbed protein behind.

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PB-60

Liquid Drops Impacting Superamphiphobic Layers

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The dynamics of liquid drops impacting superamphiphobic coatings is studied by high speed video microscopy. Superamphiphobic coatings repel water and oils. The coating consists of a fractal-like hydrophobized silica network. Mixtures of ethanol-water and glycerin-water are chosen to investigate the influence of interfacial tension and viscosity on spreading and retraction dynamics. At low impact velocity the drops completely rebound. However, the contact time increases with impact velocity, whereas the restitution coefficient decreases. We suggest that the drop partial impales the superamphiphobic coating. With increasing velocity the drops pin and an increasing amount of liquid remains in the coating. Drop retraction consists of a fast inertia-dominated phase followed by a slow decrease of the contact diameter. The crossover occurs when the diameter of the retracting drop matches the diameter of the drop before impact. From an estimate of the pressure is can be concluded that impalement is dominated by depinning rather than sagging.

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PB-61

Control of Light Energy Converting Processes into Langmuir Monolayers and Langmuir-Blodgett Films of Conjugated Organic Compounds

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This study is devoted to the revelation of new possibilities to control aggregation structure and structurally dependent photophysical characteristics of organized ultrathin films based on amphiphilic π-conjugated organic dyes.

It is shown, that alteration in subphase cationic composition can directly affect the type and the degree of molecular aggregation in crown-substituted hemicyanine monolayers. The phenomenon of reversible lateral pressure induced excimer formation in such monolayers formed on cation-containing subphases upon the monolayer cyclic compression-expansion is found out. According to UV-Vis spectroscopy and X-Ray reflectivity data, on pure water, two dye molecules arrange themselves in comparatively stable pairs with head-to-tail orientation due to the electrostatic interactions. Such a structure causes rather uniform electron density distribution with long monotonously falling tail. Instead, the presence of barium ions in the subphase leads to the organization of neighboring molecules in head-to-head manner due to the formation of crown-barium-crown sandwich structures at the initial state of monolayer spreading. The structure of the layer manifests itself in a clear electron density distribution with two maxima of crown-ether groups and ClO_4^- ions. Such a structure is responsible for the excimer formation.

Possibility to manage the donor-acceptor excitation energy transfer in mixed monolayers of two naphthalimide type fluorophores is discussed in terms or Forster theory. The extreme character of the dependence of irradiative energy transfer efficiency on the distance between donor and acceptor monolayers is revealed. It is found experimentally, that the optimal efficiency can be achieved when these monolayers are spaced by an inert layer thickness of 5-7 nm.

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PB-62

Influence of the Silane Coupling Agent and of the Temperature of Deposition on the Structure of the Silica Surface Layer

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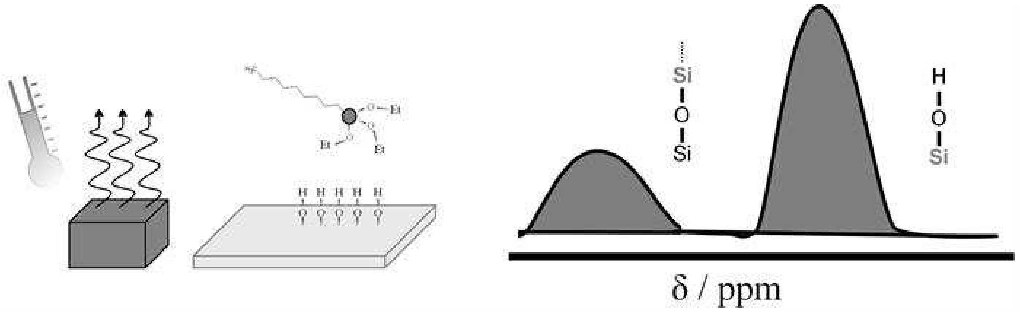
Silane molecules are widely used in literature as coupling agents for the synthesis of composites that involve oxide surfaces (generally glass, silica films or particles). Promising applications are described in many different fields, such as the low cost deposition of transparent conductive layers (like indium thin oxide) on glass[1], the encapsulation of silica particles in polymeric materials to enhance the mechanical properties or the stabilization of oxide suspensions in organic matrixes[2].

Here, vapor phase chemisorptions of different silanes on silica substrates were studied at different temperature (70 – 150 °C). The silane chemisorption was realized both on glass slide and on micrometric silica powders. Silanes with different chemical nature were employed, comparing fluorinated and un-fluorinated molecules. The quality of the layer was tested by an original combination of spectroscopic, electrochemical and surface characterization techniques. Solid state nuclear magnetic resonance (CP-MAS NMR) provides information about the grafting mode of the silane on the surface [3], whereas water contact angle, electrochemical (CV and impedance) and FTIR measurements give information about the role played by the nature of the coupling agents and the growth conditions of the surface layer on the final structure.



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PB-63

Superhydrophobic and Photoactive Films on Polymer Surfaces

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Transparent and flexible polymeric films might represent cheap and versatile materials for applications such as low cost solar cell covers. However, their use is limited by their low mechanical hardness and UV-light sensitivity. The use of oxide coatings has been proposed to enhance the mechanical properties and UV-resistance of polymers[1]. Oxide films might also impart self-cleaning or anti-stain properties to polymer surfaces. This might represent an innovative solution to a common issue for the service life of solar cells, *i.e.* the loss of incident light through scattering or absorption by accumulated dust. As a matter of fact, each g/m^2 of dirt on cell covers reduces their efficiency up to 33%[2]. As installed solar panels are difficult to access, self-cleaning cell covers might be a viable solution. To achieve this goal, the main challenge to overcome is the development of low temperature syntheses for the deposition of active and adhesive oxide films over polymers. In this study, adhesive, antireflective, self-cleaning or anti-stain oxide films are deposited over transparent polymers by a two-step approach. First, the polymer surface is engineered to improve the oxide adhesion by providing a homogeneous distribution of suitable functional groups. Second, a low temperature synthesis is developed to obtain transparent, photoactive or superhydrophobic TiO_2/SiO_2-based films starting from a colloidal oxide suspension grown under microwaves irradiation. The obtained materials are characterized for their optical (UV-vis spectroscopy), mechanical (hardness and adhesion tests), and photocatalytic properties (stain removal). Further, durability tests under environmental conditions and accelerated aging under UV-light are performed.

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PB-64

Fluorescence Spectroscopy Studies on Polymer Blend Films for Photovoltaics

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The polymer TQ1, (poly[2,3-bis-(3-octyloxyphenyl)quinoxaline-5,8-diyl-*alt*-thiophene-2,5-diyl]) [1], exhibits a low band gap, approximately 2.4 eV, and is a popular candidate as donor in organic solar cells. A suitable acceptor molecule together with TQ1 is [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{70}BM$) [1].

We have studied films of TQ1, with and without $PC_{70}BM$, spin-casted from different solvents by fluorescence spectroscopy. The solvents used in this study were chloroform (CF), chlorobenzene (CB), and *o*-dichlorobenzene (ODCB), while 1-chloronaphthalene (1CN) was used as solvent additive. From a spectroscopic point of view, TQ1 acts as fluorescent probe and $PC_{71}BM$ as quencher.

Vertical phase-separation occurs in the blend films and the surface composition depends on the solvent used. All films are polymer-enriched at the surface, and 1CN strengthens this tendency. These morphological differences cause alterations in the fluorescence from TQ1. The degree of quenching is coupled to the morphology through the distance between TQ1 and $PC_{70}BM$ in the film.

The results show that fluorescence spectroscopy can be used as a complementary technique to investigate organic blend film compositions with high sensitivity.

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PB-65

Effects of Salt Ions on the States of Water and Hydration Behavior in Zwitterionic Poly(Sulfobetaine Methacrylate)

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Water hydration behavior on the surface of materials is thought to be the fundamental factor determining subsequent biological responses and bio/blood compatibility of materials. Poly(sulfobetaine methacrylate) (polySBMA), a zwitterionic sulfobetaine polymer, is one of the biomembrane mimetic materials that exhibits excellent bio/blood compatibility. It has been reported that the zwitterionic polySBMA exhibits "antipolyelectrolyte" behavior, which changes polymer conformations and antifouling properties, in solutions containing salt ions. Here, we studied the hydration behavior of polySBMA by thermal analysis of differential scanning calorimetry (DSC) and identified various water hydrated states in different salt concentrations. We clarified the salt effects by adding monovalent (NaCl) /divalent ($MgCl_2$) ions in polySBMA aqueous solutions. The results indicated that with the addition of miniscule salts, ions are attracted to the zwitterionic groups and the hydrated states are significantly changed. The attracted ions promote the incorporation of water molecules into polymer chains and enhance the solubility of polySBMA. Nevertheless, when large amounts of salts are added into the system, the excess ions tend to bind with free water molecules, which may impose an osmotic pressure on the hydrated polySBMA molecules and causes the shrinkage of the molecules. These results demonstrated that salt has a significant effect on polySBMA-water interactions, which may affect the biocompatibility of the material.

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PB-66

Interfacial Tension and Surface $\Delta\chi$-potential of Concentrated Electrolyte Solutions

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A modification of Schmutzer’s model is proposed for the interface between aqueous electrolyte solution|hydrophobic phase. Image and hydration forces are explicitly modeled. The thickness of the ion free layer at the surface is calculated from the thicknesses of the hydrophobic gap and the hydration shell of the ion [1-3]. This model (without adjustable parameters) is used for the calculation of the interfacial tension of systems where the hydrophobic phase is air [1,2], oil or solution of alcohol in oil [3]. It is in good agreement with the experimental data, except for the case where large ions are present (due to the neglected van der Waals and hydrophobic forces). The Hofmeister effect on the interfacial tension of salts of the same valence type is explained with the ion-specific bulk activity coefficient. The interfacial tension of aqueous electrolyte|solution of alcohol in oil is lower than that of an electrolyte solution|oil interface due to the adsorption of alcohol which shifts the Gibbs surface.

Schmutzer’s model predicts also the surface Δc-potential of brines [2]. The addition of salt to the water lowers its dielectric permittivity e; since c ~ 1/e, the surface potential c becomes more negative than that of pure water (i.e., Δc0). For a series of electrolytes, the order of Δc at given concentration follows the order of the electrolyte-specific dielectric permittivity.

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PB-67

Effect of Oleic Acid on the Properties of Protein Adsorbed Layers at Water/oil Interfaces: An EPR Study Combined with Interfacial Tension Measurements

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The aim of the present work was to study the effect of fatty acids on the properties of protein molecules adsorbed at water/oil interfaces. The systems were studied using dynamic interfacial tension measurements by the pendant drop / axisymmetric drop shape analysis method and Electron Paramagnetic Resonance (EPR) Spectroscopy. The proteins examined were β-lactoglobulin and κ-casein. Biocompatible oils (Miglyol 810, 812, 818 and isopropyl palmitate) were used as the oil phase. The concentrations and conditions in the examined systems were selected within the range found in food systems. The EPR study was performed employing the paramagnetic amphiphilic spin probe 5-doxylstearic acid (5-DSA) and provided information on fatty acid molecular mobility. Oleic acid at increasing concentrations was solubilized in the oil phase. When water was introduced in the system, fatty acid molecules were adsorbed at interface and transferred to the aqueous phase thus affecting the spectral characteristics of the spin probe. The same experimental procedure was followed with the addition of proteins in the aqueous phase. The measurement of dynamic interfacial tension of the same systems provided the adsorption characteristics of each molecule as well as the dynamics of combined adsorption at the interface. The combination of results by both methods provides new insight on the adsorption/transfer/molecular mobility characteristics of the examined systems.

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PB-68

Curved Phospholipid Bilayers Supported by Vertically Arrayed Nanowires

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Cellular membrane curvature is involved in many biological processes, with several proteins shown to be responsive to differing curvatures of membranes. But while the diversity of membrane shapes has been implicated in many biomolecular interactions, there few model membrane systems have a curved surface topography. In order to study the interactions of biomolecules with curved lipid membranes, we have investigated the use of vertical arrays of nanowires (NW) as supporting surfaces for lipid bilayers. The surfaces are covered with vertically aligned NWs that are of nano-range diameters and micro-range lengths. We formed lipid bilayers on gallium phosphide NW arrays via *in-situ* fusion of vesicles containing different lipid compositions. Using fluorescence confocal microscopy and fluorescence recovery after photobleaching, we determined the continuity and topography of the bilayer on the surface formed by the planar array of NW tips and found the lipid bilayers to conform to the structured surface. Thus, the high aspect ratio of the NW forest resulted a large surface area covered by a curved bilayer. We used this curved supported bilayer to investigate the binding of two membrane-associated proteins. Since arrays of nanowires are finding their way into biological applications such as measurements of cellular force[1] and transfection[2,3] the hybrid nanowire-bilayer platform shown here can be used to study the influence of lipid membrane curvature on biomolecule adhesion and interaction, as well as further development of nanosensors.

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