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TALKS

ABSTRACTS

A time-resolved *in situ* small-angle X-ray scattering study of silica particles formation in nonionic water-in-oil microemulsion

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During the past decades, colloidal suspensions have been the subject of many papers in the area of soft condensed matter. This interest is attributed to the potential formation of monodisperse systems with tailored average size and with interesting technological features both in the biological and material science field. In particular, water in oil (W/O) microemulsions have been widely used for the production of amorphous silica particles for their wide commercial applications and interesting structural properties. Osseo-Asare and Arriagada [1-3] reported their findings on accurate kinetic studies related to the formation of silica particles produced by the reaction of tetraethylorthosilicate (TEOS) in a NP5/cyclohexane/water system under basic conditions, where NP5 is a Triton X100 nonionic surfactant. This method of synthesis produces highly monodisperse spherical silica particles with a size of 5 to 100 nm. The reactions involved include the hydrolysis of TEOS and the condensation of hydrolyzed silica species in the presence of ammonia. The overall process can be viewed as a sol-gel synthesis that takes place inside the water pool, whereby the micelles act not, only as a reactors, but also as steric barriers against aggregation.

Even though the authors report a detailed investigation about the formation of the silica particles, a complete picture of the entire system in solution which includes micelle contribution has not yet emerged. Most of the previously reported experimental techniques used for monitoring the formation of silica particles were not able to give the complete picture of the growth process, in contrast, small angle X-ray scattering (SAXS) offers the possibility to measure directly the nanostructure of colloidal particles as they form in addition to observing the evolution of the whole system. In this paper we report *in situ* time-resolved SAXS measurements for the evolution of the system proposed in ref [1], taking into account, at the same time, both the formation of silica particles and the evolution of the empty micelles.

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The growth of metallic nanoclusters on porous cellulose fiber surfaces part 1: growth on flat and wedged surfaces

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Recently, it has been shown that Cu and Ni-nanoclusters can be synthesized on cellulose matrix. In this case there are indications that the porosity of the organic cells or fiber surfaces may affect the nanocluster formation, because the nanocluster formation seems to be occurring at the pores or crevices on the cellulose fibers [1, 2]. We have studied these systems using x-ray diffraction, x-ray small-angle scattering and x-ray absorption spectroscopy.

The growth process of metallic nanoclusters on cellulose matrix is assumed to be rather complex, affected not only by the properties of the clusters themselves, but essentially depending on the cluster-fiber interfaces as well as the morphology of the fiber surfaces. The final favored average size for nanoclusters, if such exists, is most probably a consequence of these two competing tendencies towards size selection, one governed by pore sizes, the other by the cluster properties. We develop a model for the growth of metallic nanoclusters synthesized on porous fiber cellulose (or inorganic) surfaces, which is physically reasonable but still mathematically tractable in order to be able to gain insight on the experimentally observable properties of the nanocluster formation. The first step in our study was to evaluate the special case of how the growth proceeds on flat or wedged surfaces.

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Direct Observation of Nucleation and Growth of a Micelle in the Milli-second Range by Synchrotron Small Angle Scattering

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Diblock copolymers spontaneously self-assemble into well-defined micellar structures in selective solvents, i.e. solvents that are good for one block but poor for the other. Starting from a homogeneous mixture of single polymers, this process is theoretically believed to occur via fast nucleation and consequent grow of the micelles by fragmentation/fusion and/or unimer exchange processes. However since the self-assembly typically occur on a short time scale (sub second range), no experiments have been performed capable of properly resolving these processes both in space and time simultaneously.

In this work we have taken advantage of the high brilliance offered by ID02 beamline at ESRF coupled to an ultra-fast stopped-flow apparatus to study directly the structural evolution characterizing micellization in the milli-second range. This can be done employing a tuneable model system represented by poly(ethylene -propylene) - poly(ethylene -oxide) (PEP-PEO) in water/dimethyl formamide (DMF) solvent mixtures. This system is ideally suited for studying this system the solvent mixture allows a continuous tuning of the interfacial tension (between 46 - 8 mN/m), and most importantly, as in pure DMF only unimers exist, micellization can be induced simply by adding water. The time scale is here limited by the transport time after the mixing (less than 4.5 ms) and the time needed for a measurement frame (20 ms). Because of the excellent reproducibility of the system, in addition stroboscopic measurement series could be added to fill an extended time range. The results show that the micellization kinetics is very fast and highly dependent on the solvent composition. At high water content the micelles were observed to freeze into sizes that essentially depends on mixing (non-equilibrium) while at lower interfacial tensions (more DMF) the kinetics proceed towards equilibrium. These results seem to correlate intimately with the existence of molecular chain exchange mechanism previously studied and found to be active only for micelles with low interfacial energy.

In the presentation we will discuss the equilibrium and non-equilibrium kinetics in light of different theories and present a model for micellization based on a nucleation and growth model. We will also discuss the general interplay between kinetics and structure highlighting the importance of non-equilibrium effects.

The interplay between surface and solution behaviour of complex mixed surfactant systems (di-alkyl chain cationic / nonionic surfactant mixtures).

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Abstract.

Understanding the complex surface and solution behaviour of di-alkyl chain cationic and nonionic surfactant mixtures is important for a wide range of applications, which include detergents, shampoos, and conditioners. Furthermore, by analogy, it has wider implications for membrane solubilisation, a key technique in biochemistry, and for the manipulation of membrane properties.

Neutron reflectivity, small angle neutron scattering, light scattering, and surface tension have been used to characterize the surface and solution behaviour of the di-alkyl chain cationic surfactant, di-hexadecyl dimethyl ammonium bromide, DHDAB, with a range of different nonionic surfactants, from $C_{12}E_3$ to $C_{12}E_{12}$.

The solution phase behaviour for the different cationic / nonionic mixtures has been determined in some detail. For the nonionic surfactants $C_{12}E_6$ and $C_{12}E_{12}$ the nonionic rich region of the phase diagram is comprised of mixed globular micelles. For the cationic rich composition the predominant microstructures are bi-lamellar to multi-lamellar vesicles and L_β lamellar phase. At intermediate compositions there exists a region in which both micellar and planar structures coexist. For $C_{12}E_3$ the phase behaviour is different and shows an evolution of different planar structures with composition.

The surface behaviour is characterised by a marked departure from ideal mixing which is more extreme than is normally encountered in surfactant mixtures. For solutions rich in cationic the surface adsorption is dominated by the cationic surfactant, and the nonionic only competes for the surface for solutions rich in the nonionic surfactant. It is shown how this surface behaviour is correlated with the solution phase behaviour which is determining the relative monomer composition and concentrations.

Scattering from Soft Matter at the ESS-S

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The European Spallation Source will offer exciting new possibilities to scientists: the large gains in neutron flux and data collection rates, and the scientific environment around the neutron facilities will make the ESS the world leading neutron science centre. The reference design for ESS comprises a 5MW proton accelerator delivering proton pulses to a liquid metal target. A suite of more than 20 instruments will receive the thermal and cold neutrons produced during the spallation process in the target. The suite of Day-One instruments contains neutron instruments which are very much relevant to soft matter science (neutron reflectometry, small angle scattering and high resolution spectrometry). Should Lund be selected as the ESS site, the scientific environment will add strong value to the ESS: the proximity of synchrotron facilities (MaxLab in Lund, Petra-III, Flash and XFEL in Hamburg) and the strong links with research centres and Universities in Scandinavia will create a vibrant scientific site.

SAXS and Applications at Anton Paar GmbH

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Small-angle X-ray scattering (SAXS) is a well-established method for structural investigations in the size regime of 1 nm to 100 nm. With state-of-the-art laboratory instruments, structural information of soft and complex materials can be acquired, such as

- (1) Size distribution
- (2) Particle shape and internal structure
- (3) Surface-to-volume ratio
- (4) Degree of crystallinity

A huge variety of applications in research and quality control are addressed by SAXS. The most prominent systems and application fields are

- **Nanoparticles:** proteins, viruses, clay particles, paints, micelles, vesicles
- **Biomaterials:** wood, cellulose, biomineralization products (bones, sea shells, etc.)
- **Polymers:** block copolymers, semi-crystalline polymers
- **Drug Delivery:** Characterization of nano-devices (micelles and vesicles),
- **Screening of storage conditions:** Determination of the porosity and crystallinity,
- **Stability of dispersions:** Particle sizing of colloidal dispersions.

In this presentation we will show a few examples of the above mentioned application areas.

Phase Behavior and Temperature-Responsive Molecular Filters Based on Self-Assembly of Triblock Copolymer Hydrogels

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ABSTRACT

This work describes the thermo-responsive transition in polystyrene-*block*-poly(*N*-isopropylacrylamide)-*block*-polystyrene, (PS-*block*-PNIPAM-*block*-PS), triblock copolymer hydrogels, as observed by both direct and reciprocal space *in-situ* characterization. The hydrogel morphology was studied both in the dry and wet state, at temperatures below and beyond the coil-globule transition of PNIPAM, using vitrified ice cryo transmission electron microscopy (cryo-TEM), *in-situ* freeze drying technique, and small angle X-ray scattering (SAXS).

Classical lamellar, cylindrical, spherical, and bicontinuous double gyroid morphologies were observed in the dried state. In aqueous solutions, the glassy PS domains act as physical crosslinks and hydrogels were therefore formed. The bulk block copolymer morphology had a strong effect on the degree of swelling in aqueous solutions upon cooling below coil-globule transition temperature of the PNIPAM midblock. Bulk compositions with spherical PS-domains and PNIPAM continuous phase swelled in water up to 58 times by weight, whereas composition having cylindrical PS domains or bicontinuous gyroid structure in bulk swelled 20 or 10 times by weight, respectively

By combining SAXS and cryo-TEM techniques, it was demonstrated that (i) PNIPAM form physically connected networks in spherical structures and bicontinuous morphologies in the gyroidal phase, (ii) that in PNIPAM chains strands are strongly stretched above the polymer coil-to-globule transition, and that, (iii) surprisingly, upon the gel swelling process, the PS domains undergo extensive plastic deformation although temperature is always maintained well below the PS glass transition bulk temperature.

Additionally our laboratory X-ray apparatuses (SAXS, MAXS/WAXS) are briefly introduced.

**Effects of Electrostatic Interactions on the Temperature-Induced Formation of
Micelle-Like structures of New Amphiphilic Block Copolymers.**

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A combination of turbidity, light scattering, and steady shear viscosity experiments has revealed that aqueous solutions of an amphiphilic diblock copolymer or a negatively charged triblock copolymer, both containing poly(*N*-isopropylacrylamide), can undergo a temperature-induced transition from loose intermicellar clusters [1,2] to collapsed core-shell nanostructures. Turbidity, light scattering, and viscosity results of these short-chain copolymers disclose transition peaks at intermediate temperatures [3]. At high temperatures, the compact core-shell particles from the diblock copolymer aggregate; whereas no renewed interpolymer association is observed for the triblock copolymer or for the solution of the diblock copolymer with added sodium dodecyl sulfate (SDS) because the electrostatic repulsive interactions suppress the tendency of forming interpolymer clusters. The temperature-induced building up of intermicellar structures and the formation of large aggregates at high temperature in the solution of the diblock copolymer is significantly reduced under the influence of high shear rates. Effects of SDS addition to solutions of the uncharged diblock copolymer will be discussed and new results from rheo small angle light scattering measurements will be presented.

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Formation of discrete complexes between DNA and PAMAM dendrimers and their interaction with phospholipid bilayers

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Gene therapy has in recent years been focused towards the complex formation between cationic specimen and DNA. This has been studied extensively as a way of replacing viral vectors as gene carriers for in vivo gene transfer. Surfactants like CTAB or DODAB, histones as well as synthetic polymers like poly (amido amine) (PAMAM) dendrimers, polylysine or poly (ethylene imine) are a few examples of those specimen used (1-7). The cationic specimen cause the DNA to form more compact aggregates resulting in a higher degree of transfection compared to free DNA (8-10).

In our work, PAMAM dendrimers have been used as the vehicle for the condensation of linear DNA (4331 bp). The structural parameters of the formed aggregates have previously been studied in dilute solutions using dynamic light scattering, fluorescence spectroscopy, Cryo-TEM as well as SANS. It has been concluded that cooperativity is present in the complex formation process since discrete aggregates of a fixed size were in coexistence with free DNA at low ratios of dendrimer/DNA (1).

The objective of this work forms part of a larger project, Neonuclei that aims not only to design a module for DNA packaging but also to reveal how this module interact with the cell and its membrane. The eukaryotic nucleus has long been known to be composed of a double membrane made of phospholipids and protein. The intranuclear space itself however, also contains lipids with a composition thought to be dominated by phosphatidyl choline (PC). One possible function of these intranuclear lipids is the stabilization of the DNA double helix (11, 12, 13).

Neutron reflectivity as well as null-ellipsometry has been used in order to characterize the dendrimer-DNA complexation behavior on macroscopic surfaces. In addition to using bare silica surfaces, the measurements were performed using supported model membranes composed of DOPC (14-15).

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ORDER-DISORDER STATES IN Li⁺-DOPED TRIBLOCK COPOLYMER
POLY(ETHYLENE GLYCOL) DISTEARATETomás S. Plivelic¹, Tito J. Bonagamba² and Iris L. Torriani^{1,3}¹*Laboratório Nacional de Luz Síncrotron (LNLS) - Brazil*²*Instituto de Física de São Carlos/USP - Brazil*³*Instituto de Física "Gleb Wataghin"/UNICAMP - Brazil*

The Li-doped ABA triblock copolymer poly(ethylene glycol) distearate (PEGD) is a potential candidate to be used as solid-state polymer electrolyte substituting liquid electrolytes in rechargeable lithium batteries. Li⁺ mobility takes place in the amorphous phase and its diffusion occurs through a complex mechanism involving PEG segmental mobility. The effects of the PEG chain length and the doping level on the phase behavior of the copolymers were studied by simultaneous and time resolved SAXS/WAXD/DSC experiments. In the amorphous phase and for shorter PEG chain lengths (2, 5 or 9 units), order–disorder transitions were observed when at least one lithium per PEG chain is present. The temperature where the transition takes place increases as a function of the Li-doping level. The ordered state of the systems can be described as being part of a locally lamellar structure. For larger PEG chains (135 units) an ordered phase is obtained for temperatures higher than the melting temperatures of the individual blocks. Increases in doping level seem to restrict the movements of the PEG chains and promote structural organization. The morphology proposed for the ordered state is that of spherical PE/Li-rich PEG core shell domains in a Li-doped PEG matrix.

Bone Nanostructure from SAXS: a New Data Analysis Method

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Bone is a hierarchical material consisting of nanocrystalline hydroxylapatite in an organic matrix predominantly consisting of collagen. SAXS is well-suited for determining the orientation of the crystallites and for determining their width, the crystallites having a size of about 100x50x3 nm. Traditionally, a two-phase model based on determination of the Porod constant at 'large' q has been used in all prior work on bone [1-4]. This model suffers from several assumptions. Therefore we propose a new model based on fitting the q -dependence of the scattering data to a model based the scattering from plates with a Schultz-Zimm distribution of thicknesses. Interparticle correlations are taken into account via a random phase approximation that captures some of the most likely interparticle organizational features in bone. Additionally, larger length scale structural effects are taken implicitly into account through an effective fractal model. The model is discussed through its application to recent laboratory based data.

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In-situ SAXS measurement and modeling following the formation of mesoporous silica**Andreas Berggren¹, Anders E.C. Palmqvist¹, Cristiano Luis Pinto Oliveira² and Jan Skov Pedersen²**¹*Applied Surface Chemistry, Department of Chemical and Biological Engineering, Chalmers University of Technology, SE-412 96 Göteborg, Sweden*²*Department of Chemistry and iNANO Interdisciplinary Nanoscience Center, Aarhus University, Langelandsgade 140, DK-8000 Aarhus C, Denmark*

Mesoporous silica is a material with walls made of silica and pores in the size range of 2-50 nm. Since the silica most often is amorphous, the material lacks short range order but the pores may be arranged in different structures generating a long-range order. The field of mesoporous materials has attracted a lot of attention during the last 15 years. The main reason for this interest is the multitude of possible applications. The main characteristics of mesoporous silica, such as high surface area, ordered structure and tunable pore size, are often desirable properties. Despite extensive studies of different syntheses the molecular mechanisms involved in the formation of these materials are not yet fully understood.

Here we present an in-situ SAXS study of a synthesis of mesoporous silica using non-ionic surfactants as the template. In order to improve the understanding of the formation mechanisms involved the data obtained is also fitted using a newly developed model. This enables us to follow the formation of the material and also study which parameters are affected during this development. This gives new insights to the different processes involved in the formation mechanism.

The synthesis of mesoporous silica started with hydrolysis of TEOS in water at pH 2-3. Then the obtained silica solution was mixed with a water solution of the non ionic surfactant Pluronic P123. This reaction solution was then directly transferred to a capillary and the SAXS measurement started within five minutes after the mixing. How fast the formation of the mesostructure proceeds can be controlled by the pH of the silica solution and the time between the hydrolysis and the mixing of the reactants. The conditions used here was a pH of 2,1 and 24 hours between the start of the hydrolysis and the start of the reaction.

The data obtained from the SAXS measurements was fitted using a model based on methods proposed by Förster et al¹ and Freiburger et al². It includes empirical expressions for the form of the silica covered micelles as well as for the ordering of these. The model enables a factorization of the scattering intensity into contributions from the form factor and the structure factor which means that these two contributions can be modeled separately.

The results show that in the beginning of the synthesis there were only small changes with time and no mesoorder was observed. The solution contained mainly Pluronic micelles that might have been elongated due to some interactions with the silica present in the solution. This part of the synthesis was modeled using only a form factor. After ca 100 min some changes in the reaction solutions start to occur and at 200 min the first indications of mesoorder appeared. At this point there were probably also larger aggregates of silica and surfactant present in the solution. The continues improvements of the mesoorder was then followed and after about 1000 min a stable result was obtained showing four diffraction peaks indicating an hexagonal structure. The model describes these experimental data well and this enables a more detailed description of the changes that occurred during the synthesis.

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**Fifth Nordic Workshop on Scattering from Soft Matter Trondheim Feb 6-7 2008
Auditorium R9 Realfagbygget NTNU****Utilizing WAXS to characterize the orientation distribution of clay assemblies
– application to electro-rheological suspensions and weakly-hydrated samples**

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Characterization of platelet-colloid orientations by Small Angle X-ray Scattering (SAXS) is a well-known technique. Here, we use synchrotron Wide Angle X-Ray Scattering (WAXS) data provided by a two-dimensional detector to study the orientational order of various clay assemblies. The building block of these clay systems are nano-stacked particles of Na-fluorohectorite (NaFH) smectite clay. Each particle is a stack of several tenths of 1nm-thick NaFH individual platelets; cations (and possibly, water molecules) intercalated in the inter-platelet space bind two adjacent platelets together. The even spacing between adjacent platelets turn these nano-stacks into quasi-1D crystals, for which X-ray diffraction peaks resulting from the stack structure are much more intense than other types of diffractions peaks. Besides, the intensity of the peaks depends on the orientation of the incoming X-ray beam with respect to the platelets' stacking direction. For assemblies of platelets with axially-symmetric orientation distribution probabilities (ODPs), we analyze the azimuthal decay of WAXS peaks and infer the ODPs[1] from it. The technique is applied to three types of clay assemblies.

The first type of samples are electro-rheological suspensions of the NaFH particles in silicon oil. Under the effect of a strong external electric field, the particles polarize and aggregate into chain bundles parallel to the field direction. At the same time as the aggregate, they reorient so as to have their stacking direction as perpendicular as possible to the external electric field. We monitor the ODPs of the clay aggregates as the field is applied and until they reach equilibrium[1,2]. The amount of orientational disorder is observed to be depended on the nature of the cations intercalated inside the clay nanostacks[2].

The second type of samples are weakly-hydrated clay assemblies obtained by dehydrating an aqueous suspension of particles, under uni-axial constraint. The resulting material possesses both a mesoporosity at the particle scale (100 nm to 1 micron), and a microporosity (10 nm) within the nano-layered clay crystallites themselves. The mesoporous space is anisotropic, with the silicate sheets of the particles being predominantly perpendicular to the direction of the principal constraint applied during dehydration. Under humid conditions, absorption of water occurs in the mesoporosity but also through the swelling of the crystallites by intercalation of water inside them. We study what impact that swelling has on the crystallites' relative positioning inside the material, by monitoring their ODPs while the hydration state is being modified. The width of the angular distribution (ODP) is found to decrease during water absorption, showing that particle swelling goes along with an increased ordering of the assembly[3]. We attribute this phenomenon to steric effects. We further studied samples prepared at two very different magnitudes of the uniaxial constraint (0.25 and 25.00 MPa), and observed that the samples prepared at higher pressures appear significantly less ordered than those prepared at lower pressures [3].

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