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# Annual Report 2009

~ Physical Chemistry, Lund University, Sweden ~

*Physical Chemistry*

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Cover: Fluorescence microscopy image of a DPPC monolayer at  $\Pi_i = 11$  (LC/LE coexistence) with ssRNA present in the subphase. Injection of ssRNA drives the monolayer to formation of interconnected domains/foam-like structures at the surface.

Paula Leckius, Media-Tryck is gratefully acknowledged for the cover design.

## MAX IV AND ESS

On April 27th a Memorandum of Understanding was signed between the Swedish Research Council (VR), the Swedish Governmental Agency for Innovation Systems (VINNOVA), Lund University and Region Skåne, defining the start of the project to build a new, next generation, synchrotron, MAX IV, in Lund. A month later, close to midnight on the 29 of May, Europe's Ministers of Research and Education, representing stakeholders in the European Spallation Source (ESS) to the surprise of many of us finally with a large majority reached the decision to build the next generation neutron source in Lund. These large research infrastructures will obviously have an enormous impact on the region, on Lund University, and on the division of Physical Chemistry. We now have to act so that we also will be able to have an impact on these large laboratories. Strong local user groups can both take advantage of having the large infrastructures in the vicinity, as well as contributing to the further development of the various beamlines of the facilities. These new advanced instruments at the various beamlines, even more so than in the past, require also supporting labs with state of the art lab instruments. Thanks to a generous grant last year from The Knut & Alice Wallenberg Foundation, obtained with the strong support from the management of MAX lab and the ESS, we are during 2010 able to start build a "State-of-the-art Laboratory for Experimental Studies of Molecular Assembly". Within the division of Physical Chemistry, neutron and X-ray scattering have been important experimental techniques for the past 20 years. The relatively close distance to the Risø National Laboratory in Denmark helped building up our competence in small angle scattering. Since then, the use of neutrons and X-rays within the division has gradually increased and represent now core techniques. During 2010 we will do neutron experiments at the ILL in Grenoble (France), at PSI in Villigen (Switzerland), at ISIS near Oxford (UK) and at NIST in Gaithersburg, Md (USA). Furthermore, we will do synchrotron experiments at the ESRF in Grenoble (France) and at Elletra in Trieste (Italy), in addition to the extensive use of the small angle scattering beamline at MAX-lab in Lund. Current methods involve mainly small angle and surface scattering techniques, where we also note that interestingly Sweden has, through a GDR contract, a 30% part of the new Super Adam neutron reflectometer at ILL in Grenoble. However, we also seek to gradually broaden our competence in these techniques. For example, we can foresee an increasing interest in studying dynamics, for which neutron spin-echo and quasi-elastic scattering techniques will be useful, as well as the strongly emerging X-ray photon correlation spectroscopy technique. Other interesting techniques are the use of polarized neutrons for reflectometry, coherent X-ray diffraction and tomography. We look with excitement to the next coming years where we will continue to strengthen our competence regarding the use of neutrons and synchrotron light. We will also continue to play an active role within the Science Faculty as well as with the two fantastic and exciting new facilities MAX IV and the ESS. Welcome to Lund!

Tommy Nylander and Ulf Olsson

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## RESEARCH PROJECTS

### Theroretical work - statistical mechanics

#### **Dynamics of polymer adsorption** (Contact person: Per Linse)

The dynamics of the adsorption of uncharged homopolymers in good solvent appearing in systems composed of a polymer solution placed near attractive, but initially polymer-free, surfaces have been determined by Brownian dynamic simulations, and equilibrium properties of corresponding systems by Monte Carlo simulations. The properties of the systems have been analyzed by monitoring the number of adsorbed polymers, bead density profiles, time and frequency of polymer attachments, spatial extension of polymers perpendicular and parallel to the surface, and configurational characteristics and nematic order of adsorbed polymers.

After a diffusion of the polymer to the vicinity of the surface, four succeeding phases were identified: distortion, attachment, spreading, and final contraction phase. In the distortion phase, the polymer starts to experience the potential of the surface and becomes elongated perpendicular to the surface. In the attachment phase, the polymer makes direct contact with the surface and becomes contracted perpendicular to the surface and starts to spread on the surface. In the extended spreading phase, the polymer continues to spread on the surface. Finally at long times, for flexible polymers the extension of the polymer coils parallel to the surface was reduced, and the perpendicular extension was increased, with associated changes of the number of beads residing in tails, loop, and trains, whereas for stiff polymers a nematic ordering of adsorbed polymers was obtain. This final process is connected to the slow relaxation of the number of adsorbed polymers,

In the first sub-project, the effect of polymer chain length and polymer density of flexible polymers was investigated, and it was found the adsorption process was fastest for shorter polymer at higher density. In the second sub-project, polymers with different flexibility and attractive segment-surface interaction were considered. Large differences in equilibrium structure and adsorption structure and dynamics were found. In the final sub-project, adsorption from solution comprising two different types of polymers was investigated. Polymers with different chain length and/or flexibility were considered. Generally, an initial adsorption layer dominated by short chains that later was replaced by longer chains was observed. (P. Linse and N. Källrot)

#### **Microemulsions** (Contact person: Per Linse)

Structural equilibrium properties of transient networks formed by microemulsion droplets and ABA-triblock copolymers in solution have been studied by Monte Carlo simulation. The droplets were represented by soft spheres, and the polymers were represented by junctions connected by harmonic bonds with an angular potential regulating the intrinsic chain stiffness. The interaction parameters were selected such that the end A-blocks were localized inside the droplets and the middle B-block in the continuous phase.

The influence of (i) the droplet volume fraction, (ii) the droplet radius, and (iii) the contour length of the middle B-block on the formation and the structure of the microemulsion-polymer network at three-fold excess of the polymers were investigated. A universal behavior of the properties investigated was found when examining the results versus the length ratio of the polymer end-to-end separation and the surface-to-surface separation between neighboring droplets for a hypothetical homogeneous

droplet distribution. At a length ratio of 0.5, few polymer bridges between droplets were established and only clusters with a small number of droplets were found. However, at a length ratio of ca. 1.5 a connected network was formed and most of the polymers formed bridges between two droplets. (P. Linse, J. Sarragua and A. A. C. C. Pais (University of Coimbra, Portugal))

Project completed 2009.

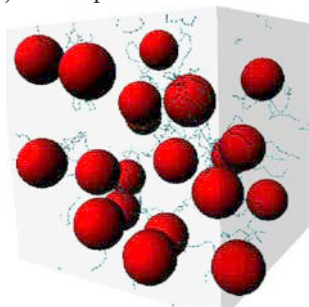


Illustration of microemulsion droplets connected by ABA triblock copolymers.

### **Structural properties of polar liquids** (Contact person: Joakim Stenhammar)

The long-range structural properties of liquids composed of molecular dipoles are a question of long-standing interest within many fields of chemistry and physics. The long range of the dipole-dipole interaction makes the structure of dipolar systems notoriously difficult to probe using computer simulations, although many techniques have been proposed to overcome these problems. Within the present project, we combine the use of dielectric continuum theory with computer simulations to try to elucidate some fundamental properties of polar liquids.

The theoretical analysis is based on electrostatic fluctuation formulas based on the dielectric approximation. These describe the magnitude of the fluctuating electric multipole moments within spherical volumes inside a polar liquid, as a function of the radius of the volume and the dielectric constant of the fluid. The predictions from these formulae are compared with the results of computer (Monte Carlo and molecular dynamics) simulations of strongly polar liquids. The project is aimed at i) elucidating how accurately these liquids are described by dielectric continuum theory, and ii) investigating the accuracy of different schemes used to handle the long-range electrostatic interactions in computer simulations. The research during 2009 was divided into four different sub-projects:

1. Development of electrostatic fluctuation formulae for bulk polar liquids using dielectric theory. These were compared with results from computer simulations of a weakly coupled polar liquid, yielding an excellent agreement.

2. Investigating how well the electric fluctuations in a strongly coupled dipolar system simulated using the Ewald summation and reaction field techniques correspond with the predictions from bulk dielectric theory. In this context, we found strong non-dielectric effects arising from the use of periodic boundary conditions within these two methods.

3. As in 2, but instead using a simulation method based on the use of image charges and dipoles, thus not employing periodic boundary conditions. Here, we found that very large system sizes are needed to reach the full dielectric behavior,

and that surface effects from the dielectric discontinuity are significant for small and intermediate system sizes.

4. Development of dielectric fluctuation formulae for polar liquids under confinement, and comparison with simulation results obtained from a droplet of dipolar particles. The agreement between theory and simulation is very good, and both investigations showed that the fluctuations are greatly reduced as the sampling volume is moved towards the cavity surface. Moreover, the fluctuations perpendicular to the surface are more strongly reduced than those parallel to the surface. (J. Stenhammar, G. Karlström and P. Linse)

**The dielectric approximation.** (Contact person: Luis Pegado)

In the theoretical description of surface forces an aqueous medium is typically described as a dielectric continuum. This often leads to quantitatively accurate descriptions. However, the continuum description of the solvent breaks down at short separations and one must turn to a molecular picture. Through computer simulations we study the relation between the continuum and the fully molecular description of charged surfaces interacting at short range in a dipolar solvent. (L. Pegado, B. Jönsson, G. Karlström and H. Wennerström)

**Dielectric and retardation behavior of dipolar liquids** (Contact person: Per Linse)

A long-standing challenging property of dipolar liquids is their attenuation of Coulomb interaction between ions and how that depends on the orientational structure of the fluid. Extensive Monte Carlo simulations have been performed to address two central questions: (i) development of a novel approach to extract the dielectric property of a molecular polar fluid and (ii) the effect of the retardation on the orientational structure, which is coupled to the dielectric response of the dipolar fluid.

General expressions for two-center electrostatic potential fluctuations and its use to determine (i) the effective interaction between simple ions in a dipolar solvent and (ii) the dielectric permittivity of the solvent are proposed. Such two-center potential fluctuations were determined from Monte Carlo simulations of spherically confined dipolar particles embedded in a dielectric medium described by using an image charge approximation. The deduced dielectric permittivities increased with increasing dipolar moment, and at large dipole moments the effective interaction displayed an attractive first minimum.

A strongly coupled dipolar fluid confined in a sphere has been examined by Monte Carlo simulations using a modified distance-dependent pair interaction to emulate retardation effects. The effective dipole-dipole interaction and a property closely related to Kirkwood's  $g$ -factor have been analyzed for potentials with different distances at which the retardation effects became effective. The retardation effects were found to brake the otherwise long-range orientational ordering occurring in strongly coupled dipolar fluids. (P. Linse, G. Karlström and C. Woodward (University College University of NSW Australian Defense Force Academy, Canberra))

**Portal for statistical-mechanical computation and software.** (Contact person: Per Linse)

Through the web-portal [www.fkem1.lu.se/sm](http://www.fkem1.lu.se/sm), launched 2003, softwares for solving general problems in mainly statistical mechanics are accessible. The softwares were primarily developed as research tools, but have frequently been used in advanced

undergraduate classes and in national PhD courses. From the web-portal, further information about each software can be obtained, reference manuals and sample input files can be retrieved, and the softwares can be executed for test purposes. The software's are:

**DIELEC** is a software for calculation of the electrostatics in the presence of spherical dielectric discontinuities. First version 2008.

**MOLSIM** is package of four integrated and general programs for molecular dynamics, stochastic dynamics, and Monte Carlo simulation for molecular, colloidal, and polymer systems, including polarizable potentials, with extensive static and dynamic analyses. With contributions from Anna Akinchina, Fredrik Carlsson, Samuel Edgcombe, Yoshikatsu Hayashi, Niklas Källrot, Vladimir Lobaskin, Thomas M. Nymand, Alberto Pais, Jurij Rescic, Stefanie Schneider, Marie Skepö, Joakim Stenhammar, Anders Wallqvist, and Per-Olof Åstrand. First version 1990. Parallel version employing MPI since 1997.

**NR** is a software for simulation and analysis of neutron reflectivity data. First version 2007.

**OZ** is a software for solving the Ornstein-Zernike equation with a closure (MSA, PY, HNC, RY, ZH, and RHNC) for systems with central forces. First version 1985.

**PB** is a software for numerically solving the one-dimensional Poisson-Boltzmann equation for different boundary conditions and symmetries. First version 1982.

**PGSE** is a software for simulation of pulse gradient spin echo attenuations for spins diffusing in restricted spaces of different symmetries with permeable walls. First version 1993.

**POLYMER** is a software for solving lattice mean-field models containing a mixture of solvents and polymers for homogeneous (Flory-Huggins theory) and heterogeneous (Scheutjens-Fleer theory) solutions extended to polymers possessing internal degrees of freedom. First version 1991. (Per Linse)

## Studies of model systems

**Association behavior of block copolymers under the influence of nonionic surfactants and hydrophobically-modified polyelectrolytes.** (Contact Person: Karin Schillén)

A specific group of water-soluble block copolymers that has attracted great interest in the literature is the triblock copolymers of (PEO) and poly(propylene oxide) (PPO), PEO-PPO-PEO. The more hydrophilic copolymers associate into micelles, composed of a hydrophobic PPO core and a PEO corona, established by light, X-ray (SAXS) and neutron scattering investigations. It is well-known that some of these copolymer micelles may undergo a sphere-to-rod transition at elevated temperatures. The underlying principle for this growth is the decrease of the polar PEO headgroup area at higher temperatures because of a transition to the high-energy forms of (non-polar) conformations, which is have a small or no dipole moments. In this project, mixed micelles of PEO-PPO-PEO block copolymers (e.g. P123) and  $C_{12}EO_6$  surfactants are studied, with a special focus on their temperature-induced sphere-to-rod transition at low surfactant content. The change in the shape transition temperature with increasing  $C_{12}EO_6$  content follows the liquid-liquid phase separation temperature of the mixed system (first a decrease, then an increase) was determined using differential scanning calorimetry and visual inspection. This observation is explained by internal structural model of the mixed micelle where the added surfactant molecules lead to

a change in the effective PEO head group area in the micellar corona. The retarded kinetics of the shape transition of mixed micelles of P123 and  $C_{12}EO_6$  is analyzed from simultaneous time-resolved DLS and SLS measurements as well as from time-resolved titration calorimetry and time-resolved rheology and the rodlength may be obtained from depolarized DLS. The internal structure of the mixed micelles has been analyzed by SAXS, confirming that the  $C_{12}EO_6$  reside in the core/corona region of the P123 micelles. The solution behavior of the mixed system consisting of pyrene-labeled poly(acrylic acid) (PAAMePy) and one PEO-PPO-PEO copolymer is investigated by using DLS, steady-state and time-resolved fluorescence spectroscopy. The DLS measurements provide information of the complex formation between PAA and copolymer micelles and the complex structure as a function of pH. (K. Schillén, D. Lóf, T. Costa (University of Coimbra, Portugal), G. Olofsson, W. Loh (University of Campinas, Brazil), A. J. Müller (Simon Bolivar University, Venezuela), O. Glatter (University of Graz, Austria), J. Seixas de Melo, B. Lindman and M. da G. Miguel (University of Coimbra, Portugal))  
Project completed 2009.

**Catalysis of surface-active substrates at interfaces in dispersed media: oil in water emulsions.** (Contact person: Ulf Olsson)

It is known that one efficient way to increase the rate of a catalytic reaction is to accumulate the reagents in a set of micro-reactors, distributed uniformly in the system. We propose another route to concentrate reagents in limited volume, namely, to use the interfacial adsorption of surface-active amphiphilic molecules at the boundaries of immiscible phases in, for example, oil-in-water emulsions. If the adsorbing molecules can react with each other, the interfacial layer becomes a reactor of nano-scale thickness (a "surface nano-reactor"). Computer modeling and theoretical considerations from Khokhlov's group have pointed to a possibility to control the rate of catalytic reactions carried out in emulsions. At a certain size of the emulsion droplets (several hundreds of nanometers) the reaction rate was predicted to exhibit a maximum. This could be simply explained as follows. For small droplet radii, the available surface area is too large and the concentrating effect at the interface is low. On the other hand, for large radii the surface area is too low, thus reducing the probability that the catalyst and the substrate will meet at the interface. The experimental investigation of this possibility is of special interest. Therefore, this project focuses on experiments on catalysis of surface-active substrates in oil-in-water emulsions. (I. Nasimova, U. Olsson, A. Khokhlov (Moscow State University/Russian Academy of Science))

Project completed 2009.

**Diffusive transport in responding membranes.** (Contact person: Emma Sparr)

In a simplified description of membrane transport, one considers a concentration gradient across a static barrier. In a more dynamic approach, the barrier is allowed to respond by changes in lipid phase behavior along the concentration gradient, which motivates the name "responding membrane". In the presence of more than one gradient, this can lead to dramatic effects. It is typical for the rich phase behavior of lipids that small changes in the external conditions can trigger large structural changes with distinctly different diffusion characteristics. It is clear that the abruptness of phase changes can act as a kind of switch for diffusive transport, and thereby introduce non-linear elements to the transport process. In this way, structure and transport are



intimately coupled. This mechanism is highly relevant to biological systems where transport often occurs between regions of profoundly different properties.

In this project we use a combined experimental and theoretical approach to explore the mechanisms for diffusive transport in responding membranes, and how external gradients that induce phase transformations and domain formation can regulate the membrane barrier. The experimental work involves transport studies in model lipid membranes using recently devolved system of so-called double-porous membranes where lipid lyotropic phases are confined inside the pores of a synthetic polymer membrane.

Beside the basic scientific interest in the mechanisms for steady-state transport in responding membranes, several applications in biology and technology can be seen in, for example, the barrier properties of stratum corneum (the upper layer of the skin) and the formation of plastic polymer-surfactant films. (C. Åberg, P. Nilsson, E. Sparr, H. Wennerström, D. Topgaard, F. Costa-Balogh (Coimbra university, Portugal), K. Edler (University of Bath))

### **Interaction between RNA and lipid membranes.** (Contact person: Agnes Michanek)

In the living system, RNA (ribonucleic acid) is present in an environment that contains many substances, which can influence its structure and function. RNA occurs more often than DNA in the single-stranded form, where the apolar parts of the bases are obvious targets for interaction with hydrophobic species in the environment, e.g. lipids in the cell membrane and in the cell nucleus. We aim at revealing the basic features of RNA–lipid interactions. We study the adsorption of nucleic acids to lipid bilayers and monolayers with varying properties, and we study how interaction affect the phase behavior, which in turn provide information of how and where the interaction takes place. For this purpose, we investigated a set of model membrane systems with varying charge density and with fluid or solid acyl-chains together with RNA or DNA of different size and degree of base pairing. We use small single-stranded and double-stranded oligonucleotides (RNA), tRNA and long DNA. Model lipid membrane systems are zwitterionic, anionic, as well as cationic lipids. The system are studied with several techniques, including calorimetry, ellipsometry, quartz crystal microbalance (QCM-D), Neutron reflectometri, fluorescence microscopy and monolayer techniques. (A. Michanek, E. Sparr, T. Nylander, L. Jaeger (University of California, Santa Barbara, USA), F. Höök (Chalmers))

### **How Small Polar Molecules Protect Membrane Systems against Osmotic Stress.**

(Contact person: Emma Sparr)

Urea, under the name of carbamide, and glycerol are standard major components of skin lotions. They are claimed to act as “moisturizers” with seems to imply that have the effect of binding water in excess to what would be the case without the presence of these compounds. Compounds such as urea, glycerol and similar polar substances occur naturally in many organisms to regulate osmotic pressure and to prevent cell damage due to freezing or drying. The question addressed in the project concerns the molecular mechanism(s) behind the role of urea and glycerol in these contexts.

By studying lipid - mixed solvent systems using a range of methods such as sorption calorimetry, sorption balance, X-ray diffraction/scattering and nuclear magnetic resonance it is possible to unravel how the presence of urea and glycerol interacts with phospholipid bilayers. The major conclusions are: i) urea and glycerol shows a

near ideal mixing with water in the lipid lamellar systems. ii) The presence of urea or glycerol has only a minor effect on the gel to liquid crystal transition temperature in the presence of excess solvent. iii) Under conditions of fixed lipid to urea (or glycerol) ratio the transition to a gel state occurs at lower relative humidities than for pure aqueous systems. The “moisturizing” effect of urea and glycerol is, based on these investigations, due to a suppression of a liquid crystal to gel/solid transformation that otherwise would occur under dry conditions. (A. Nowacka, E. Sparr, H. Wennerström, D. Topgaard, F. Costa-Balogh (Coimbra university, Portugal), L. Wadsö (Building Materials, LTH))

**Physico-chemical behavior of aqueous systems containing DNA, proteins and amphiphiles.** (Contact person: Dan Lundberg)

The behavior of systems where DNA coexists with both proteins and amphiphiles is of great biological importance. Most notably, there are indications that interactions between the lipid portions of the cell nucleus with chromatin, which is a DNA-protein complex, are involved in organization of the chromatin and regulation of gene expression. Another example is the finding that the inclusion of proteins in DNA-lipid complexes for gene therapy can greatly enhance the transfection efficiency. The aim of this project is to gain an improved understanding of the physicochemical behavior of such systems. Of particular interest is the structure and composition of aggregates and complexes formed by the components and a multitude of techniques are applied for characterization of these. The work is focused on three classes of systems: 1) model systems of well-characterized proteins, DNA and different types of amphiphiles, 2) systems containing nucleosome core particles (NCPs), i.e. the basic unit of chromatin, which consist of DNA wrapped around a core of eight histone proteins, and different types of amphiphiles, and 3) complexes comprising plasmid DNA, amphiphiles and certain proteins that have been evaluated with regards to their efficiency in transfection experiments. (D. Lundberg, A. Carnerup, J. Janiak, K. Schillén, V. Alfredsson, D. Topgaard, B. Lindman, M. da Graça Miguel, H. Faneca and M. C. Pedroso de Lima (University of Coimbra, Coimbra, Portugal), L. Nordenskiöld and N. Korolev (Nanyang Technological University, Singapore))

**Polymerization in structured media.** (Contact person: Ola Karlsson)

The long-term goal of this project is to study polymers that resemble biomacromolecules in their structure and function. To that end, we study polycondensation reactions in dispersed aqueous systems at ambient or slightly elevated temperatures. The incorporation of active chemical functionalities through polymerization in structured dispersed media will produce new types of polymer. The polymerization reactions that result in such materials include multifunctional monomers, which are often amphiphilic by nature. In order to facilitate the formation of specific molecular sequences, a detailed control of the polymerization loci is a necessity, and the partitioning of the reaction components in the various phases during reaction is crucial. Initially, we study the solubility of the active components and the complex formation between them. We also study how the reaction kinetics are affected by the distribution of the reaction species and by the particle size of the dispersed phase. The project is run in co-operation with MIP Technologies AB, Lund. (J. Bailey, O. Karlsson, L. Piculell)

**Polymerization of polymerizable surfactant counterions** (Contact person: Lennart Piculell)

Polymerization in surfactant systems, typically with the objective of “freezing” or “templating” (making a polymer replica of) the surfactant structure is a very active research field. However, there are notorious problems associated with using “soft” surfactant aggregates to template “soft” polymeric materials, mainly because the polymerization reaction generally strongly affects – and often destroys – the surfactant structure. Two aspects make our approach to this problem unique: 1) We build on our a priori knowledge of the phase behavior of surfactant ions with polymeric counterions in water. 2) We perform the syntheses under conditions where the surfactant aggregates are the sole counterions to the growing chains of the polyion.

We introduce comonomers and/or crosslinkers in the system, with the overall aim to achieve non-random polymeric materials, whose primary structures are affected by the presence of the surfactant aggregates. For example, we synthesize, in cationic surfactant systems, linear copolymers of polyacrylate with neutral comonomers, and also cross-linked gels. Two questions will be addressed in this research:

1) To what extent can we make a soft template that still retains its structure even after the surfactant is removed?

2) Can we make a gel or a polymer that recognizes objects, for instance, such surfactant aggregates as was used for templating? (S. dos Santos, L. Piculell, O. Karlsson and M. Miguel (Coimbra University))

**Soluble complex salts of surfactant ions and polymeric counterions: Composite macromolecular self-assembly.** (Contact person: Karin Schillén)

The aim is to understand the physical chemistry of soluble complex salts in aqueous solution and the intermolecular interactions involved. A complex salt is defined as the neutral salt of surfactant ions (aggregated into highly charged micelles) that interact with a polyelectrolyte chain, which in turn acts as a large counterion (the polyion). The complex salts consist of polyacrylate ( $\text{PA}_y^-$ ) and cationic  $\text{C}_{16}\text{TA}^+$  surfactant ions, denoted  $\text{C}_{16}\text{TAPA}_y$ , where  $y$  is degree of polymerization. At high water contents, the investigated complex salts exhibit miscibility gaps that consist of co-existing phases: a concentrated phase (either cubic or hexagonal internal structure) and a less concentrated phase. In order to make the complex salts soluble, for example forming a composite self-assembled macromolecular aggregate, PEO-containing nonionic surfactants of the type  $\text{C}_i\text{E}_j$  are added. The phase studies on systems containing  $\text{C}_{16}\text{TAPA}_y$  complex salts in water mixed with either  $\text{C}_{12}\text{E}_5$  or  $\text{C}_{12}\text{E}_8$  are carried out by visual inspection of the samples and by using small-angle X-ray scattering (SAXS). They reveal that the solubilization of the complex salts increases with increasing PEO-chain length of the nonionic surfactant. To gain further insight of the dissolution process, isothermal titration calorimetry (ITC) is employed. The solution properties of the composite self-assembled structures at 25° C are investigated by varying the polyion length ( $y=25$  or 6000) and the PEO length of the nonionic surfactant by using dynamic light scattering. SAXS will also be used for structural characterization of these composite aggregates.

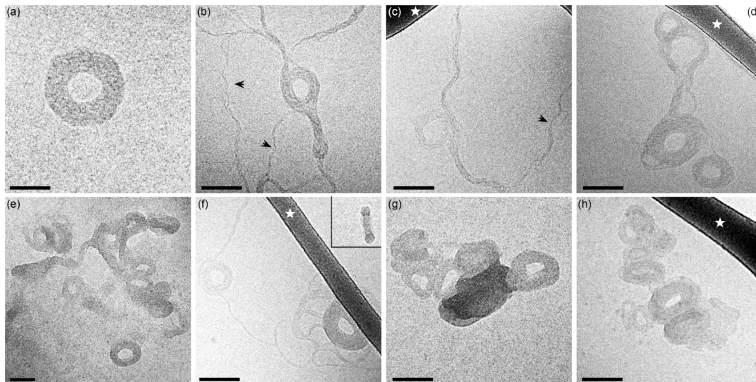
(J. Janiak, K. Schillén, L. Piculell and G. Olofsson, M. Tomšič (University of Ljubljana, Slovenia), O. Glatter (University of Graz, Austria))

## Condensing DNA with cationic dendrimers: means of controlling aggregate morphology.

(Contact person: Karin Schillén)

Upon mixing DNA with poly(amido amine) (PAMAM) dendrimer with an ethylene diamine core and primary amine functional groups PAMAM dendrimers, DNA undergoes a transition from a semi-flexible coil to a more compact compact structure due to the electrostatic interaction present, providing protection against DNase activity and also inhibiting genetic expression. Dynamic light scattering, neutron scattering, cryogenic TEM and steady-state fluorescence spectroscopy are utilized to investigate the interaction between cationic poly(amido amine) (PAMAM) dendrimers and double stranded DNA. The process of compaction is cooperative and kinetically controlled and the structure of the well-defined aggregates strongly depends on the size and charge of the dendrimer and the ionic strength of the aqueous solution. This systematic study reveals how the size, composition and morphology of aggregates formed between DNA and PAMAM dendrimers are affected by dendrimer size and charge. The smaller sized dendrimers, which have a lower total charge per molecule, allow the formation of well-structured rods and toroids. In contrast, globular and less defined aggregates, which are less stable against precipitation, are formed with larger dendrimers. Transient morphologies play an important role during the condensation process with lower generation of dendrimers and both thermodynamic and kinetic factors influence the morphology of the dendrimer/

DNA aggregates in this case. The higher total charge of high generation dendrimers can trap them on the DNA in a non-equilibrium state and the kinetic barrier to overcome for the formation of a complex with the most thermodynamically favored conformation can be large. The electrostatic attraction has to be moderate in order for toroidal aggregates to form, i.e., a balance between mobility and high affinity binding of the DNA to the dendrimer has to exist. (M.-L. Ainalem, A. M. Carnerup, J. Janiak, V. Alfredsson, T. Nylander and K. Schillén)



Time-resolved cryo-TEM images of G2 dendrimers/DNA (G2/DNA charge of 0.5) showing different stages of condensation; (a-d) 1 min, (e,f) 15 min, and (g,h) 35 min. Scale bars are 100 nm except in (a) where it is 50 nm. White stars indicate the carbon support film, and the black arrows indicate supercoiled DNA. (Data from A. Carnerup, Langmuir, 2009, 25, 21, 12466-12470).

**Solubilization of conjugated anionic copolymers by nonionic surfactants in aqueous solution.** (Contact Person: Karin Schillén)

Interaction between the conjugated polyelectrolyte, anionic poly{1,4-phenylene-[9,9-bis(4-phenoxy-butylsulfonate)]fluorene-2,7-diyl} (PBS-PFP), and the non-ionic alkyloxyethylene surfactant n-dodecylpentaoxyethylene glycol ether ( $C_{12}E_5$ ) in water is investigated. Using UV/visible and fluorescence spectroscopy, dynamic light scattering (DLS), small-angle X-ray scattering (SAXS), cryo-transmission electron microscopy (cryo-TEM) and electrical conductivity, a coherent model for this polymer-surfactant interaction is formulated, which is based on the of break-up of the PBS-PFP clusters through polymer-surfactant association and formation of cylindrical micelles containing isolated polymer chains. This process involves a careful balance between electrostatic, hydrophilic and hydrophobic interactions. Strong support for this comes from molecular dynamics simulations, which indicate stable polymer-surfactant structures and also provide support for the tendency of  $C_{12}E_5$  to break up polymer clusters to form these mixed polymer-surfactant aggregates. Radial electron density profiles of the cylindrical cross-section obtained from SAXS results reveal the internal structure of such inhomogeneous species. DLS and cryo-TEM results show that at higher surfactant concentrations the micelles start to grow, possibly partially due to formation of long, thread-like species. (K. Schillén, V. Alfredsson, A. M. Carnerup, H. D. Burrows, S. M. Fonseca, C. L. Silva, A. A.C.C. Pais and A. J.M. Valente (University of Coimbra, Portugal), M. José Tapia (Univeridad de Brugos, Spain), S. Pradhan and U. Scherf (Bergische Universität Wuppertal, Germany), M. Tomšič and A. Jamnik (University of Ljubljana, Slovenia))

Project completed 2009.

**Supramolecular aggregates of amphiphilic gadolinium complexes as contrast agents for magnetic resonance imaging applications.** (Contact Person: Karin Schillén)

Magnetic resonance imaging (MRI) is an imaging technique with cellular resolution that is widely used as a diagnostic tool in clinical practice. In this project, new potential blood pool contrast agents based on amphiphilic gadolinium complexes and amphiphiles that contain a bioactive peptide with target specificity are being developed. The structures of the self-assembled aggregates (lamellar aggregates, vesicles and micelles) in aqueous solution are characterized by means of dynamic light scattering, cryo-TEM and small-angle neutron scattering. (D. Löf, K. Schillén, O. Söderman, M. Vaccaro, L. Paduano, G. Mangiapia, G. Morelli, A. Accardo and D. Tesauro (University of Naples, Italy), E. Gianolio and S. Aime (University of Turin, Italy))

Project completed 2009.

**Microphase separation of diblock copolymers with strongly asymmetric repeating units.** (Contact person: Lennart Piculell)

For a diblock copolymer (polyA-*b*-polyB), the thermodynamic incompatibility between polyA and polyB blocks drives a microphase separation in the melt state where alternating A-rich and B-rich microdomains appear in order to minimize the contact between dissimilar polyA and polyB blocks. The segregated regions of polyA and polyB typically form structures with liquid crystalline ordering. The classical block copolymers (BCs) are conformationally symmetric, meaning that the polyA and polyB blocks have the same persistence length  $l_p$  and that the interaction between the A and B

repeating units can be described by a single interaction parameter. This project seeks to develop experimental model systems of BCs containing strongly asymmetric repeating units. For an asymmetry in  $l$ , we use the poly(ethylene propylene)-*b*-poly(benzyl glutamate) system (the PEP-*b*-PBLG "coil-*b*-rod" BC), with an order-of-magnitude difference in  $l_p$  of the two blocks. For a BC containing amphiphilic repeating units, we use poly(styrene)-*b*-poly(methacrylic acid), PS-*b*-PMAA, where the repeating units of the PMAA block have an amphiphilic nature. Anionic polymerization is used for synthesis of these BCs and small-angle-X ray scattering is utilized for structural analysis. (M. Asad Ayobi, L. Piculell, U. Olsson, A. Khokhlov (Moscow State University/Russian Academy of Sciences), Bo Nyström and Kaizheng Zhu (University of Oslo) and Kristoffer Almdal (Micro- and Nanotechnology, DTU))

### **Water-soluble polymers containing amphiphilic repeating units and their interactions with ionic surfactant micelles.** (Contact person: Lennart Piculell)

The repeating units of water-soluble polymers are usually divided into two classes: hydrophobic versus hydrophilic units. However, it is evident that typical repeating units are actually amphiphilic, since they contain functionalities of both types. Simulations by Khokhlov et al. have shown that conformational properties of polymers containing amphiphilic units are significantly different from those predicted by a model based on uniformly hydrophobic, or hydrophilic, repeating units. The main reason is that amphiphilic units possess a significant surface activity. Both the interfacial activity and the partitioning between water and hydrocarbon solvents are key parameters for a two-dimensional classification of amphiphilic repeating units. In this project we are using the two-dimensional description to classify certain acrylamide monomers with the aim to rationalize the varying tendencies of the corresponding polymers to bind to surfactant aggregates in water. Usually, the tendency of a nonionic polymer to bind ionic surfactant micelles is explained in terms of the polymer hydrophobicity. However, since a large fraction of the micellar surface contains hydrocarbon in direct contact with water, the interfacial activity of the repeating units should also be taken into account. (I. Nasimova, L. Piculell and A. Khokhlov (Moscow State University/Russian Academy of Science))

### **Asymmetric catanionic surfactants.** (Contact person: Ulf Olsson)

Catanionic surfactants are complex salts of surfactant cations and surfactant anions (e.g. dodecyl tetra methyl ammonium dodecyl sulphonate) in the absence of additional simple salts (e.g. NaCl). Symmetric (equal alky chain lengths) catanionics form essentially stable water insoluble crystals at room temperature. In asymmetric catanionics the surfactant film may carry a net charge in mixtures with water because of a mismatch in the aqueous solubility of the two surfactant ions. The chain length mismatch also reduces the Krafft temperature significantly resulting in that these materials are water soluble already at room temperature. If the solubility difference is not too large, these surfactants form a lamellar phase in water which can swell to very high water contents due to the net bilayer charge. However a very interesting aspect is the presence of an unusual miscibility gap within the lamellar phase, which has previously been observed only in a few particular systems. With the addition of an alkane, the lamellar phase is transformed into a water-in-oil droplet microemulsion with spherical, weakly charged droplets of low polydispersity. Using small angle neutron scattering we study the long range droplet-droplet interactions which depend on the concentration dependent effective droplet charge. (B. Silva (Porto), E. Marques (Porto), P. Linse and U. Olsson)

**Living polymers and living networks.** (Contact person: Ulf Olsson)

Some surfactants form giant micelles in solution that can be longer than several micrometers. These solutions have properties similar to polymer solutions, however with some significant differences. The size distribution is not fixed but varies with concentration and temperature. Moreover, micelles may break and reform which influences the dynamics. For these reasons they are often referred to as “living polymers”. Furthermore, there are also systems where the micelles form connected (branched) network, similar to a bicontinuous microemulsion. Here the morphology resembles that of polymer gels and one may refer to a “living network”. In this project we compare phase behavior of living polymer and living network systems and we have studied the effect of shear flow on the liquid structure and in particular the shear induced formation of a nematic phase of wormlike micelles. The structural transformation may be followed by small angle neutron scattering (rheo-SANS). In a living polymer system made of reverse, slightly water swollen, lecithin micelles in cyclohexane, the stress relaxation time is around an hour. Hence, the zero shear viscosity is unusually high. The long relaxation times also allow for studying the entangled system's response to fast deformations. Here, the stress strain relationship is similar to that of rubbers. Above a certain critical strain the entangled micellar network fractures, and the micelles align in the flow direction. (U. Olsson, R. Angelico, L. Ambrosone and A. Ceglie (Campobasso), G. Palazzo (Bari), K. Mortensen (Risø, Denmark))

**Bilayer membrane kinetics, including vesicle fusion.** (Contact person: Ulf Olsson)

The phase lamellar-to-“sponge” phase transition involves a topological transformation of a bilayer membrane. In the lamellar phase the bilayer has a planar topology while it is multiply connected in the so-called “sponge” or L3 phase. Topology transformations are believed to involve the fusion or fission of membranes. With nonionic surfactants the phase transformation can occur by a minor change in temperature. Using deuterium as “phase-detection” the transition has been investigated in both directions. The sponge-to-lamellar transition appears to occur via a nucleation and growth process while the opposite transition rather involves a random fusion of adjacent bilayer membranes. To investigate the bilayer structure in more detail, the transitions are also studied by small angle neutron scattering experiments. Nonionic vesicles spontaneously fuse when the monolayer spontaneous curvature is negative, i.e. when the monolayer prefers to bend towards water. In this project, vesicle fusion kinetics is studied using time-resolved static and dynamic light scattering and small angle neutron scattering. In terms of the monolayer spontaneous curvature,  $H_0$ , it was found that vesicles. (S. Bulut, M. Zackrisson, U. Olsson, H. Wennerström, M. Gotter (Köln), M. Baciú Gotter (Köln) and R. Strey (Köln))

**Lamellar phase rheology and shear-induced formation of multi-lamellar vesicles.** (Contact person: Ulf Olsson)

The equilibrium structure and phase equilibria of the lamellar phase are sometimes complicated as noted in already early studies by Ekwall and Fontell. This complication appears to be due to the formation of multi-lamellar vesicles (“onions”) under shear, which can originate simply by shaking the sample. A systematic study is performed on nonionic surfactant- water systems where the structure of the lamellar phase under shear is investigated using small angle neutron and light scattering. Depending on the temperature, that governs the monolayer spontaneous curvature, we can identify

two distinct regions corresponding to “onions” (lower temperature) and planar bilayers (classical lamellar phase, higher temperature). The equilibrium structure at zero shear, however, appears to be the classical lamellar structure. The onion size varies with the applied shear rate or shear stress. In systematic experiments, it was found that the onion states obtained at large strain values are reversible and correspond to true steady states. Oriented (“single crystal”) lamellar phases still contain equilibrium defects that give them a relatively high shear viscosity and in addition make them viscoelastic. In a Couette cell, magnetic resonance chemical shift imaging has shown that the lamellar-to-onion transition takes place homogeneously throughout the sample, while in the onion-to-lamellar transition, the lamellar phase first forms at the inner rotor and the growth of that phase propagates through the gap. (U. Olsson, B. Medronho (Coimbra), M. Miguel (Coimbra), C. Schmidt (Paderborn), M. Imai (Tokyo), Y. Suganuma (Tokyo), P. Galvosas and P. Callaghan (University of Wellington), L. Gentile and C. Oliviero Rossi (Univ. of Calabria))

**PIT emulsification.** (Contact: Ulf Olsson)

In this project we re-examine the phase inversion temperature (PIT) emulsification process using model ternary nonionic surfactant/water/oil systems. This is a low-energy method that uses a physicochemical drive to produce very fine oil/water emulsions in the absence of high shear flows. We find that successful emulsification depends on two conditions. First, the mixture must be stirred at low speed throughout the whole process: this makes it possible to produce emulsions at surfactant concentrations that are too low to form an equilibrium microemulsion. Second, the stirred mixtures must be heated above a threshold called the clearing boundary (CB) and then quenched to lower temperatures. The clearing boundary is determined experimentally by a minimum in the turbidity of the stirred mixture, which results from solubilization of all the oil into swollen micelles. This matches the emulsification failure boundary corresponding to the condition  $R^*C_0=1$ , where  $R^*$  is the spherical radius that results from the oil/surfactant composition for monodisperse spheres and  $C_0$  is the spontaneous spherical curvature of the surfactant monolayer. Thus, we show that such cycles do not need to cross the PIT. In fact, sub-PIT cycles and cross-PIT cycles give exactly the same result. These conditions lead to emulsions that have a narrow size distribution and a mean diameter controlled by the oil/surfactant ratio. The typical range of those diameters is 20-100 nm. Moreover, these emulsions have an excellent metastability, in contrast with emulsions made with shorter oil and surfactant molecules. (K. Roger and B. Cabane (ESPCI, Paris) and U. Olsson)

**Lipid gel phase.** (Contact person: Ulf Olsson)

Double chain cationic surfactants may form vesicles above the chain melting temperature,  $T_c$ . In a vortexed dispersion all chains freeze when the dispersion is cooled below  $T_c$ . However, in a sonicated dispersion it was found from NMR experiments that approximately 50 % of the chains remain in a fluid state even far (20-30 °C) below  $T_c$ . The reason for the stability of this supercooled state, and how frozen and fluid domains are distributed is still unclear. Work is extended to other lipid surfactants and lipids where similar observations have been made. In a more detailed DSC study of the chain melting/freezing process two separate steps involving similar enthalpy changes were observed. One of the processes showed slow kinetics in the freezing direction,, and has therefore not always been recognized. Small and wide angle X-ray scattering (P. Saveyn (Univ. of Gent), P. van der Meer (Univ. of Gent), T. Naraynan (ESRF,



Grenoble), U. Olsson)

**Pickering Emulsions.** (Contact person: Ulf Olsson)

Pickering, or particle stabilized, emulsions have a number of interesting properties. When the particles are properly chosen, they are essentially irreversibly adsorbed at the oil-water interface, which, as a consequence, inhibits Ostwald ripening. In this project we investigate the properties of silica coated particles and their potential for stabilizing W/O emulsions. Furthermore, we want to develop a method to measure the strength of particle adsorption at the oil-water interface. (Y. Sakazaki (Pola Chemical Industries INC, Yokohama) and U. Olsson)

**Complex salts in reverse micelles.** (Contact person: Lennart Piculell)

The complex salt cetyltrimethylammonium polyacrylate is well soluble in short-chain alcohols, such as butanol, where a large L2 phase is formed. The phase diagram is weakly dependent on the degree of polymerization of the polyacrylate, but the rheology of the L2 phase differs dramatically between PAs of 30 and 6000 repeating units. The experimental results seem consistent with a structure of extended inverse micelles (polyion cores surrounded by surfactant counterions), where the length of the polymeric micelle increases with the length of the polyion. The system is investigated by a range of methods including rheology, molecular self diffusion, and cryo-transmission electron microscopy. (L. Piculell, J. Bernardes and W. Loh (UNICAMP, Brazil))

Project completed 2009.

**Nonionic associating polymer-surfactant mixtures.** (Contact person: Lennart Piculell)

Not only oppositely charged mixtures, but also certain nonionic polymer-surfactant mixtures phase separate associatively in water. A well-known case of association involves mixtures of a poly(carboxylic acid) with polyethylene oxide. We have investigated the phase diagrams of mixtures where poly(acrylic acid), of two degrees of polymerization, has been added to aqueous mixtures of the common triblock copolymer EO27PO61EO27 ("Pluronic P104"). At low overall polymer contents, an associative phase separation was observed. At high concentrations of the triblock copolymer, the gradual replacement of water with poly(acrylic acid) made the liquid crystalline phases disappear. A possible explanation of this phenomenon is that polyacrylic acid interacts less selectively than water with the PEO and PPO blocks. (B. Luigjes, S. Santos and L. Piculell)

Project completed 2009.

**Investigation on effect of added drug on a model drug delivery system.** (Contact person: Joakim Balogh)

Here a model drug delivery system consisting of nonionic microemulsions is studied to see the effect when a drug (lidocaine) is added to the system. Both the temperature and concentration dependence have been followed using NMR self-diffusion, Light scattering and the SAXS time awarded on MAX-Lab. It has been shown that not only macroscopical changes occur on the system with changed phase boundaries but also microscopical changes with changed temperature and concentration behavior. The plan is to study the specific interaction the drug has with the surfactant to better understand

the process and to be able to predict what the effect will be in more applied systems. (J. Balogh, K. Schillén, M. Graça Miguel (University of Coimbra, Portugal) and J. Skov Pedersen (i-Nanocenter Aarhus University, Denmark))

### **Determining trends in phase diagrams to assist in making new phase diagrams.**

(Contact person: Joakim Balogh)

Here the extensive amount of published phase diagrams of the nonionic microemulsions of CmEn has been used to determine scalings and trends that are quantitative and not only qualitative as previously. Specially the phase cut with fixed oil to water ratio (1:1 in most cases) called Kahlweit fish cut has been investigated. Using the scalings it is possible with one sample in the three-phase region of the phase diagram to have information about many of the important boundaries. Some of the scalings are applicable to other systems as well but with different numerical values. We are now looking into other systems which will help to get a more general picture. (J. Balogh and H. Burrows (University of Coimbra, Portugal))

### **Cellulose dissolution.** (Contact person: Björn Lindman)

The dissolution of cellulose is important for a number of industrial processes and several solvents and mixtures have been tested. On the basis of an examination of the intermolecular interactions in cellulose novel approaches to cellulose dissolution are attempted. (B. Medronho (Coimbra), L. Stigsson (KIRAM), G. Karlström and A. Holt (Theoretical Chemistry, Lund Univ.) and B. Lindman)

## **Experimental methodologies**

### **Diffusive transport of multivalent ions in cartilage.** (Contact person: Olle Söderman)

Articulate cartilage is a complex material, composed of collagenous fibers, and cells called chondrocytes, all of which are embedded in a firm gel-like ground substance. The chondrocyte cells produce proteoglycans which bind to hyaluronic acid, forming large highly hydrophilic aggregates. These aggregates are entangled with each other and with the collagen fibrils forming what can best be described as a hydrogel that sits within the collagen network. In the general accepted model of the morphology of cartilage, the collagen fibrils associate into columnar structures that extend outward from the bone. The proteoglycans are highly charged due to the presence of sulfate and carboxylic groups. The break-down of cartilage results in a lowering of the concentration of the proteoglycans. It has been suggested to use (Gd-DTPA)<sup>2-</sup> as a contrast in MRI to monitor the concentration of proteoglycans and therefore the state of the cartilage. In healthy cartilage the concentration of (Gd-DTPA)<sup>2-</sup> will be low, while in damaged cartilage it would be high leading to T1-contrast in MRI. There are some fundamental questions in this context. What is the dynamics of the Gd-complex in cartilage? How does one quantify the T1 contrast in terms of the state of the cartilage? On the experimental side, NMR diffusometry and micro imaging techniques will be performed on model system of cartilage made from gel-forming polymers as well as on actual in-vitro samples of cartilage will be undertaken. Theoretical studies on diffusion of large negative divalent ions in models of healthy and damaged cartilage will be carried out. These include Brownian Dynamics simulations, which possibly will be complemented by Dynamic Density Functional Theory calculations. (D. Topgaard, O. Söderman, J. Forsman, J. Svensson (Department of Radiation Physics and the Joint and Soft Tissue Unit at UMAS, Malmö))

**Neutron reflectometri.** (Contact person: Tommy Nylander)

Neutron reflectivity (NR) measurements have been performed on stimulus-responsive polymer brushes containing N-isopropylacrylamide at different temperatures and contrasts using two different brush samples of roughly the same grafting density and layer thickness. The NR data were analyzed using a novel method employing polymer density profiles predicted from lattice mean-field theory augmented with a polymer model to describe polymer solubility that decreases with increasing temperature. The predicted density profiles at the different temperatures were self-consistent with the experimentally observed profiles; hence the experimental data lend credibility to the theory. We found that the brush thickness decreased from 220 to 160 nm and the polymer volume fraction increased from 55 to 75% when increasing temperature from 293 to 328 K. The new evaluation approach involved significantly fewer independent fitting parameters than methods involving layers of uniform densities. Furthermore, the approach can straightforwardly be extended to analyze neutron reflectivity data of grafted, weakly charged polymers that display pH-sensitive behaviour and also to block copolymers and to surfaces with adsorbed polymers. We propose that such accurate model calculations provide a tool to interpret results from NR experiments more effectively and design neutron reflectivity experiments for optimal outcome. (T. Nylander, R. Campbell (ILL, France) and P. Linse.)

**Polymer-surfactant interaction at liquid and solid interface.** (Contact person: Tommy Nylander)

Considerable effort over the last two decades has been devoted to gaining an understanding of the nature of the interaction between polyelectrolytes and oppositely charged surfactants in the bulk phase as well as at interfaces because such mixtures are used extensively in commercial products such as shampoos and fabric conditioners. These investigations showed that usually a one-phase transparent system forms in the presence of a small amount of surfactant. By increasing the bulk surfactant concentration, the solution becomes turbid, and an associative phase separation occurs (i.e., a concentrated phase enriched in both polymer and surfactant separates from a dilute aqueous phase containing mostly small ions). With further increases in the bulk surfactant concentration, the turbidity may decrease, and redissolution of the polyelectrolyte/surfactant complexes can occur. In practise these system are used under non-equilibrium conditions. In this project we focus on the implications of the non-equilibrium complex formation and aggregation on the structure and properties of the interfacial layer, mainly on liquid interfaces. We exploit ellipsometry in the present project by analyzing fluctuations in the optical signal, features that would most likely not be detected in the relatively slow and macroscopic measurements made using for instance neutron reflectometry (NR). Ellipsometry, surface tension and neutron reflectometry measurements, both with changing bulk composition and evolving time, we can track the relative amount of adsorbed material as well as composition of the formed layer (neutron reflectometry). We have exploited the spatial and kinetic resolution of ellipsometry to monitor the lateral movement of inhomogeneous patches of material in mixed adsorption layers of polyelectrolytes and oppositely charge surfactants at the air/liquid interface. We show that the choice of sample preparation methods can have a profound effect on the state of the interface for chemically equivalent samples. The extent of aggregation in the bulk solution on relevant time scales is affected by specific details of the polymer/surfactant mixing process, which produces varying numbers of aggregates that can become trapped in the interfacial layer, resulting in an enhanced

and fluctuating ellipsometry signal. It is inappropriate in this case to consider the interface to comprise a homogeneous adsorption layer that is in dynamic equilibrium with the bulk solution. Our work shows that it can be helpful to consider whether there are macroscopic particles embedded in molecular layers at the air/liquid interface for systems where there is prior knowledge of aggregation in the bulk phase. (R. Campbell (ILL, France), K. Tonigold, M. Yanez, T. Nylander, L. Piculell, I. Varga and R. Mészáros (Eötvös Loránd University, Budapest; Hungary))

**Diffusion NMR methods for biological tissues.** (Contact person: Daniel Topgaard)

Molecular transport by diffusion is a crucial process for the function of biological tissues. Diffusion NMR is a powerful method to non-invasively study molecular motion on the micrometer length scale and millisecond time scale. By following the self-diffusion of molecules in a cellular system, information about structure and dynamics on the cellular scale can be obtained. Most of the present day diffusion NMR studies use the same basic experiment as in the pioneering works from the 60's. Here we design new protocols for estimating parameters such as the diffusion coefficient of the intracellular medium, the cell membrane permeability, and the length scale at which an inhomogeneous medium, such as brain tissue, start to appear homogeneous. The structure of biological materials, or the transport behavior of molecules within these materials, can often be mimicked by carefully designed colloidal model systems such as emulsions and gels. The new methods are first tested by simulations, subsequently applied to colloidal model systems, simple cellular systems, and excised tissue, and finally implemented in the context of medical MRI. (D. Topgaard, O. Söderman, I. Åslund, S. Lasic, F. Ståhlberg (Medical Radiation Physics, LU) S. Oredsson (Cell- and Organism Biology, LU) K. Bryskhe and A. Stenstam (Colloidal Resource))

**A 12-channel microcalorimeter for use as a monitor of biological systems.** (Contact: Ingemar Wadsö)

The instrument is primarily intended for investigations of microbial activity in soil, of animal (human) cells and tissues and for small animals. The calorimeter is a further development of the earlier 48-channel instrument (cf. AR 2007), which mainly was intended for use in the pharmaceutical industry, at temperatures around 37 °C. The new instrument is designed for use in a wider temperature range, down to 0 °C and has larger vessels. The instrument should be considered as analytical tools (process monitors), which are sensitive (about 10 nW) and stable (days on the  $\mu$ W level), but are not suitable as accurate and versatile thermodynamic tools. (I. Wadsö)

**A 10-channel microcalorimetric system for use in analytical and thermodynamic measurements.** (Contact: Ingemar Wadsö)

The new instrument has a different mechanical design and is intended as a “platform” for different reaction vessels, useful as process monitors or in accurate thermodynamic measurements. As for the 12-channel instrument the goal is to reach highest possible sensitivity and stability, but the useful temperature range will be wider (0-150 °C). Most mechanical parts for the “platform” have been manufactured. Tests will initially be conducted by use of simple static vessels, which are suitable for some biological systems and for stability measurements of technical materials. Later more advanced vessels (of types we earlier have designed for conventional microcalorimeters) will be tested/adapted: vessels with stirring and injection devices (g, l, s), flow vessels and vessels

equipped with analytical sensors such as electrodes for pH and O<sub>2</sub> used simultaneously with the calorimetric measurements. (I. Wadsö)

**Solid-state NMR methods for amphiphile systems.** (Contact person: Daniel Topgaard)

Several types of intermolecular interactions, e.g., steric, electrostatic, and hydrophobic, affect the dynamic behavior of large molecules in a crowded system. NMR offers a unique possibility of resolving different molecules and molecular sites even in rather complex mixtures. For colloidal systems with reduced molecular mobility and sample heterogeneity on the nano- to micrometer scale, solid-state NMR methods with magic-angle spinning are necessary in order to extract high-resolution spectroscopic information. Dynamic and site-resolved information can be correlated in multidimensional experiments. The experimentally determined parameters have simple geometrical definitions and can be estimated using theoretical approaches such as molecular dynamics simulations. The NMR methods are applied to a series of colloidal systems including cationic surfactants with mono-, oligo-, and polymeric counterions, nonionic surfactants with poly(ethylene oxide) or glucoside headgroups, DNA-lipid assemblies, and synthetic analogs of the lipid mixtures in the stratum corneum. (D. Topgaard, E. Sparr, G. Karlström, P. Linse, A. Nowacka, T. Ferreira, D. Lundberg, A. Bilalov, J. Reimer, N. Bongartz, J. Norrman, R.W. Martin, U.C. Irvine, S. Ulvenlund, C. Wende and O. Söderman)

**Cryogenic transmission electron microscopy – imaging lyotropic liquid crystals.** (Contact person: Viveka Alfredsson)

Cryogenic transmission electron microscopy was used in the study of lyotropic liquid crystalline phases. (J. Ruan, A. Carnerup, V. Alfredsson, Y. Sakamoto and O. Terasaki (Stockholm University), M. Mörgelin (Medicin, LU))

Project completed 2009.

## **Colloidal biology**

**Amyloid formation in the presence of lipid membranes.** (Contact person: Emma Sparr)

The starting point of this project is the recent realization that lipid membranes seem to play pivotal roles in the pathogenesis of the protein misfolding disorders, e.g., Alzheimer and Parkinson diseases. An increasing amount of evidence suggests that the process of fibril formation in vivo and the mechanism of toxicity involve membrane interactions. The objective of the project is to explore the basic principles of how aggregating amyloid protein influence the lipid membrane barrier and the underlying interactions between the aggregating protein and the lipid membrane. We use recombinant A $\beta$  and  $\alpha$ -synuclein peptides produced in *Escherichia coli*, which allows us to perform large scale amyloid formation assays with good statistics where the aggregation process is followed in means of thioflavin T fluorescence. The lipid membranes are introduced in the system as unilamellar vesicles (figure). One important goal of the present project is to further understand how the aggregating amyloid protein can influence the membrane barrier properties and thus affect the transport of the protein itself as well as other substances. We also investigate whether transport amyloid can occur over a pure model membrane in the absence of the membrane proteins and uptake systems inherent to cells, and if the aggregating peptide affect the membrane integrity

to diffusional transport of small molecules.

Finally, we study lipid-peptide association using different biophysical techniques, including monolayers technique, confocal microscopy on giant unilamellar vesicles, NMR, ellipsometry, QCM-D, neutron reflectivity and electron microscopy. (M. Grey, E. Sparr, A. Nowacka, D. Topgaard, E. Hellstrand and M. Lundqvist (Biophysical chemistry, LU), S. Linse (Biochemistry, LU), D. Walsh (University College Dublin), P. Brundin and J-Y. Li (Wallenberg Neurocenter, LU), R. Melki (Laboratoire d'Enzymologie et Biochimie Structurales, CNRS, Gif-sur-Yvette, France))

### **Cyclodextrins in DNA decompaction.** (Contact person: Björn Lindman)

Important cellular processes involving DNA, such as transcription and replication, can be strongly affected by the extent of condensation of the chromatin fiber. In synthetic gene delivery systems, the use of cationic lipids can protect and compact the large and highly biodegradable DNA molecule. Once the DNA:compacting agent complex reaches the target inside the cell, the DNA should be decompacted to be accessible to the cell machinery responsible for translating the enclosed information. Obviously, it is desirable to achieve a reversible DNA condensation process in order to control the transfection efficiency. Many chemical agents have been successfully used to compact DNA *in vitro*, thus mimicking the natural process occurring in the cell. Various strategies have also been used in order to decompact the condensed DNA, such as the introduction of non-ionic and anionic surfactants.

In the present study, the efficiency of  $\alpha$ -CD and  $\beta$ -CD, as well as 2-hydroxypropyl- $\beta$ -CD of various degree of 2-HP-substitution, in the DNA decompaction process of DNA previously compacted by CTAB is investigated. The decompaction process, which mechanism is puzzling and yet to be fully characterized, is studied by fluorescence microscopy and fluorescence spectroscopy. Furthermore, the possibility of direct interactions between DNA and CD is studied by thermal melting and circular dichroism. Additionally, macroscopic phase separation and dissociation studies are also being performed. (B. Lindman, J. Carlstedt, R. S. Dias (University of Coimbra, Portugal), A. González-Pérez (MEMPHYS, SDU, Denmark))

### **Controlling the phase behavior of polyion-surfactant ion complex salts by cyclodextrins.** (Contact person: Björn Lindman)

We have previously shown that cyclodextrins can be used to decompact single DNA molecules that were compacted by cationic surfactants. Additionally, macroscopically phase separated DNA-surfactant complexes were shown to be dissociated at sufficient cyclodextrin concentrations. In this study we look at the phase behavior of concentrated ternary systems of polyion-surfactant ion complex salt and cyclodextrins to deepen our knowledge on these interactions. Various parameters, such as polyion hydrophobicity and length, surfactant chain length, as well as salt dependence and type of cyclodextrin is addressed. Preliminary results from a system containing DNA-DTA:2-HP- $\beta$ -CD:water shows a rich and very interesting phase behavior. These studies are both of biological and biotechnological interest and may also be interesting for other industrial applications. (B. Lindman, R. S. Dias (University of Coimbra, Portugal), U. Olsson, A. Bilalov, J. Carlstedt)

**Structure and self-assembly of viruses.** (Contact person: Per Linse)

The project comprises studies of the packaging of DNA inside viral capsids using a density functional theory and constitutes an extension of previous computer simulations of polymers in confined geometries at the Division of Physical Chemistry. Of special interest is to investigate the liquid-crystalline transition in the spherical capsid and elucidate possible conformation transitions of DNA in confined geometry.

A density functional theory of the spatial distribution and nematic ordering of polymers of arbitrary length and rigidity inside a spherical cavity is developed. The theory originates from the mathematical apparatus used in the classic theories on nematic ordering of polymers in the bulk. Thereby, the local self-assembly of different segments of the chain can be considered as a nematic phase with a non-constant (distorted) director. The steric interactions are taken into account in the second virial approximation. Our principal results are the polymer density and orientational order distributions throughout the volume of the sphere. It is demonstrated that a short and flexible polymer is located at the center of the sphere and is orientationally disordered. Upon increasing length and/or rigidity of the polymer, it is shifted towards the surface of the sphere and undergoes the nematic transition. The theory proposed can model the behavior of a genome molecule in spherical viral capsids.

During 2009, a new mathematical technique for the minimization of free energy functional describing the arrangement of a polymeric chain in a spherical cavity was implemented. It is based on the expansion of generalized density into spherical harmonic series, which allows the analytical integration of the density functional. As a result, the density functional was reduced to a function of a number of coefficients of the spherical harmonic expansion. Currently, the predictions of the theory are being explored and comparison with experimental data is in progress. (N. N. Oskolkov, P. Linse, A. R. Khokhlov (Moscow State University))

**The skin as a barrier to molecular diffusion.** (Contact person: Emma Sparr)

The upper part of the human skin, stratum corneum, is one important example of a responding barrier membrane in biology. The skin can be exposed to rather extreme gradients in water, temperature and in other species, and these gradients may affect the molecular structure in the barrier membrane. One example of this is that the water flux through skin shows nonlinear response to variations in water activity with a distinct decrease in permeability at water activities below 0.85-0.9. This non-linearity indicates a structural change in the skin that also alter the transport properties in a profound way.

The main goal of this project is to couple stratum corneum barrier properties to stratum corneum lipid structure, and to explore how this is affected by, e.g. hydration, "moisturizers". These studies aim to understand how molecular diffusive transport occurs through the SC and thus how it can be affected.

We aim at the characterization of the lipid component of the stratum corneum and intact stratum corneum under varying conditions, using NMR and sorption calorimetry. This is combined with transport studies of different drugs across intact stratum corneum in the presence several gradients. (S. Björklund, E. Sparr, A. Nowacka, D. Topgaard, J. Engblom (Biofilms; Malmö university), K. Thuresson (Hemocue), L. Wadsö (Building materials, LTH), J. Bouwstra (Leiden university), V. Kocherbitov (Malmö University), V. Burnier (L'ORÉAL, Paris), B. Cabane (ESPCI, Paris))

**DNA-lipid complexes.** (Contact person: Björn Lindman)

Systems containing DNA, cationic cosolutes and phospholipids have a broad biological and biotechnological significance. For example, in the cell nucleus of eukaryotic cells, there is an intricate interplay between DNA, cationic proteins and lipids self-assembling into complex structures. This self-organisation is still far from being understood and in particular concerning the role of the lipids present. Important transfection agents are based on a mixture of cationic amphiphiles (surfactants of lipids) and neutral zwitterionic lipids. Understanding the interaction between the zwitterionic lipids and DNA would give a better basis for designing lipoplex formulations for transfections. In view of this significance we investigate the aqueous phase behavior of the “complex salt” DNA-amphiphilic cation (e.g. dodecyl trimethyl ammonium (DTA)) when mixed with various lipids. The ternary DNA-DTA/water/lecithin system show a rich phase diagram with several liquid crystalline phases. Of particular interest is the first observation of a DNA containing bicontinuous cubic phase. (A. Bilalov (Kazan State Technological University), B. Lindman and U. Olsson)

**Peptide self-assembly.** (Contact person: Ulf Olsson)

The development of modern peptide chemistry has opened for the possibility of custom peptide synthesis that allows for systematically investigating the relationship between a specific oligopeptide molecular structure and the macroscopic phases and structures formed in such systems. Understanding the assembly behavior of peptides is important in not only designing nanomaterials for a desired functionality but also for combating neurodegenerative diseases such as Alzheimer and Parkinson’s disease which are strongly associated with an accumulation of amyloid forming peptides in the brain.

In this newly started project we focus initially on the self-assembly behavior of short simple and synthetic peptides, AnK, where n is varied in the range 4-10 (A=alanine, L=lysine). These peptides allows for a systematic investigation of e.g. the hydrophobicity and peptide length on the self-assembly behavior.

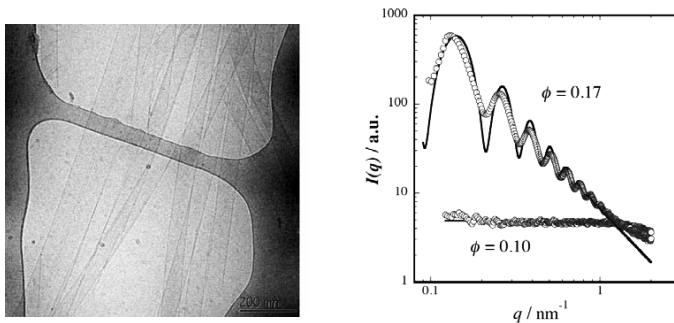


Figure 1. Cryo-TEM image (left) and SAXS data (right) of A6K nanotubes formed in water.

A6K in water forms very long hollow nanotubes with a (monodisperse) diameter of 52 nm, for concentrations above a critical aggregation concentration,  $c_{ac} \approx 11\%$ . Because of the large aspect ratio, the nanotubes form a nematic phase or a hexagonal phase. Work is now proceeding to investigate the self-assembly behavior of the analogue peptides A4K, A8K, and A10K. (C. Cenker, U. Olsson, M. Lund, M. Zackrisson, S. Bucak (Istanbul), I. Hamley (Reading), V. Castelletto (Reading))



**DNA gel particles and cross-linked DNA gels.** (Contact person: Björn Lindman)

Through an interfacial diffusion mechanism DNA particles were prepared and studied with respect to internal structure and DNA release. A large difference in internal structure between different DNA conformations for surfactant systems point to the role of hydrophobic interactions. Release properties of the gel particles, which can be manufactured in the size range from 100 nm to mm, are investigated. DNA gel particles are made from mixtures of DNA with cationic surfactants, proteins and polymers and also for other polymers. DNA molecules, both single- and double-stranded, have been covalently cross-linked to form chemical gels. Addition of electrolytes causes a deswelling of the gels. From the volume changes the association of oppositely charged cosolutes with DNA can be monitored. For cationic surfactants a dramatic compaction is noted as well as the formation of different ordered microstructures. An extensive comparative study of the deswelling of both ss- and ds-DNA gels on addition of several cosolutes- metal ions of different valency, proteins, polyamines and other polycations and cationic surfactants- have been performed. Both thermodynamic and kinetic aspects, as well as reversibility of volume changes, have been considered. The release of DNA and incorporated proteins are investigated, in particular related to triggering release. (M. C. Morán, M. Miguel, D. Costa (Coimbra) and B. Lindman)

**Lipid chain freezing in dilute vesicle dispersions.** (Contact person: Ulf Olsson)

In this project we investigate the thermal behavior of lipids in dilute dispersions of uni-lamellar vesicles. Main focus is on charged lipids. As the main model system, we have chosen the long chain synthetic lipid octadecyl dimethyl ammonium bromide, DODAB. However, also other lipids have been investigated. Lipid bilayers may often undergo several transitions as a function of the temperature. Cooled below the so called main transition,  $T_m$ , the alkyl chains stretch and form a viscous glass-like, still disordered, state. Decreasing the temperature further there may be one or several additional sub-gel transitions where the chains pack in a more ordered lattice. The DODAB system show a main transition at ca. 40 °C and sub-gel transition at ca. 36 °C. The formation of the gel phase is very rapid, and behave essentially as barrier free. In the formation of the subgel phase, on the other hand, a significant barrier is involved, and the gel phase can be super cooled more than 20 °C before the sub-gel formation can be observed. The thermal behavior of charged lipids is also dependent on the vesicle size. A most striking observation is that for small ( $\approx 50$  nm) vesicles there is an incomplete chain freezing when the vesicles are cooled below  $T_m$ . In large vesicles, the gel phase may easily nucleate and grow from several spots along the bilayer, and such vesicles are often found to be faceted or polyhedral shaped, resembling a polycrystalline material, when imaged by cryo-TEM from lower temperatures. In small vesicles, the number of nucleation events are few, perhaps only one or two. When a fl at solid domain grows in a small vesicle, this results in an additional bending deformation the super-cooled remaining fl uid part. If the bilayer bending rigidity is large, as it is for charged lipids, this additional curvature stress may be large enough to terminate the growth of the solid domain, leaving a gel-fl uid coexistence in a single vesicle. The relative fractions of gel and fl uid depends on the vesicle size and on the degree of super cooling. (Pieter Saveyn (Gent University), Ulf Olsson, Malin Zackrisson, Paul van der Meer (Gent University), Teyencheri Narayanan (ESRF, Grenoble))

Project completed 2009.

## Molecular matter for specific functions

**Modeling of the adsorption of bottle-brush polymers onto surfaces.** (Contact person: Per Linse)

A new class of polymers composed of the monomers poly(ethylene oxide) methyl ethyl methacrylate (PEO45MEMA) and methacryloxyethyl trimethylammonium chlorid (METAC) have recently been synthesized by Vareikis and coworkers. Depending on the monomer ratio, polymers continuously ranging from uncharged bottle-brush polymer ( $X = 0$ ) to highly charged polyelectrolyte ( $X = 100$ ) are available. Solution and as well as adsorption properties of this class of polymers are currently of large experimental interest.

To further understand the adsorption mechanism of this class of polymer onto various solid surfaces, we have performed model calculations using a lattice-mean field theory. The bottle-brush polymers were modeled as being composed of two types of main-chain segments: charged segments and uncharged segments with an attached side chain. We have been able to capture the major experimental findings for adsorption on mica and on silica oxide, made predictions that we currently are testing experimentally, and provided further insight into the adsorption.

In our first sub-project, model calculations were made for various main-chain compositions (various value of  $X$ ) for adsorption on mica-like and silica-like surfaces. The mica-like surface possesses a constant negative surface charge density and no special affinity, whereas the silica-like surface has a constant negative surface potential and a positive affinity for the side chains of the bottle-brush polymers. The model was able to reproduce a number of salient experimental features characterizing the adsorption of the bottle-brush polymers for the full range of the composition variable  $X$  on the two surfaces, and thereby quantifying the different nature of the two surfaces with respect to electrostatic properties and nonelectrostatic affinity for the polymer. In particular, the surface excess displays a maximum at  $X \approx 50$  for the mica surface and at  $X \approx 10$  for the silica surface. Moreover, the thickest adsorbed layer is obtained at  $X = 10 - 25$ .

In our second sub-project, model calculations were extended to cover bottle-brush polymers with different length of side chains. With the mica-like surface, at low  $X$  the surface excess became smaller and at  $X \geq 25$  it became larger with increasing side-chain length. Hence, the value of  $X$  at which the surface excess displays a maximum increased with the side-chain length. However, with the silica-like surface the surface excess increased with increasing side-chain length at all  $X < 100$ , and the maximum of the surface excess appeared at  $X \approx 10$  independent of the side-chain length. (P. Linse, P. Claesson (KTH, Stockholm))

**Low interfacial tension microemulsions for practical applications.** (Contact person: Ulf Olsson)

The high solubilization capacity and the ultra low interfacial tension exhibited by microemulsions make them desirable for a broad range of applications including enhanced oil recovery, soil and aquifer remediation, consumer and pharmaceutical formulation, chemical reaction media and nanoparticle preparations. In this project we investigate various microemulsion formulations, targeted for practical applications, combining phase diagram and interfacial tension studies. Systems studied include ionic surfactant in combination with oppositely charged hydrotropes with the aim to optimize the overall surfactant efficiency. (I. Kayali and K. Qamhieh (Al-Quds

University, Jerusalem), U. Olsson, L. Bemhert and R. Strey (University of Köln))

**Hydrophobically modified polymers in pharmaceutical tablet formulations.**  
(Contact person: Lennart Piculell)

Hydrophobically modified polymers are water-soluble polymers that contain a small proportion of strongly hydrophobic functionalities attached to the polymer backbone. Such polymers are not traditionally used as excipients in pharmaceutical drug tablets. In this project, we study how the hydrophobic modification as such, and the possible presence of other amphiphilic molecules such as surfactants, affect the drug release properties of tablets made from hydrophobically modified poly(acrylic acid). (P. Knöös, L. Piculell, M. Wahlgren (Food Technology) and S. Ulvenlund (AstraZeneca))

**Interaction between functionalised soft polymer particles and inorganic surfaces.**  
(Contact person: Lennart Piculell)

When water evaporates from a dispersion of polymer particles, the particles are forced together developing a coherent film. Therefore soft polymer particles are widely used as binders in a range of applications, including water based paints, glue, and paper coatings. It is generally found that chemically modified particles have superior properties in films that include inorganic pigment particles, resulting in improved mechanical properties and water resistance of the film. In this project, the effect of the functionalisation of the polymer particles on their film formation and interactions with inorganic surfaces is studied, primarily by atomic force microscopy. (J.K. Dreyer, T. Nylander, L. Piculell, O. Karlsson)

**Phase separation, adsorption behavior and delivery capacity of polyelectrolytes and oppositely charged surfactants at surfaces.** (Contact person: Lennart Piculell)

The concentrated phase formed in dilute mixtures of polyelectrolytes and oppositely charged surfactants can be a precipitate (solid) or a coacervate (liquid) depending on parameters such as the molecular weight and charge density of the polymer, the self-assembly of the surfactant and the charge ratio of polymer vs. surfactant in the mixtures. The phase separation is of practical use in products where it is desired to obtain a deposition on a surface. The polymer-surfactant complexation can also be used to deliver an additional substance to the surface. The aim of the present project is to link the adsorption behavior of a polyelectrolyte-surfactant mixture with the characteristics of the phase separation in the bulk solution. Based on these results, the delivery of an oil-in-water emulsion to a hydrophilic and hydrophobic surfaces are studied. A combination of different techniques is used: in-situ ellipsometry to investigate the adsorption behavior, phase studies and turbidity measurements to look into the bulk properties, dynamic light scattering to determine the size of soluble aggregates and gel swelling experiments to investigate the polymer-surfactant binding. (A. Svensson, O. Santos, M. Clauzel, W. Wei, T. Nylander, L. Piculell and E. Johnson, R. Panandiker and M. Sivik (Procter & Gamble, Cincinnati))

## INSTRUMENTS AVAILABLE AT THE DIVISION

**NMR.** (Contact person: Daniel Topgaard)

Two Bruker Avance II spectrometers are available at Physical Chemistry: one 500 MHz system from 2007 and one 200 MHz system originally installed in 1994 but upgraded in 2006. Both spectrometers are equipped for high-performance diffusion studies. The 500 MHz has accessories for microimaging, solid-state, and high-resolution magic-angle spinning experiments. (Sponsored by VR/KFI.)

**SAXS.** (Contact person: Ulf Olsson)

The instrument is a Kratky compact camera equipped with a linear position sensitive detector (MBraun, Graz), and a Seifert ID 3000 (3.5 kW) generator. Equipped with two separate detectors, the instrument may record, simultaneously, the scattered intensity at both 'low' and 'wide' angles. The wide-angle ( $q$ -range 1.3--1.8 1/Å) scattering reports on short-range correlations and is helpful for example in discriminating between fluid and frozen surfactant chains. (Sponsored by FRN.)

**SAXS at MAX.**

Physical Chemistry, in particular through Malin Zackrisson and Ulf Olsson continue to work with Yngve Cerenius concerning the development of the beam line I711 at Max-lab and the possibilities there for small angle scattering experiments (SAXS). The beamline is now fully operational on SAXS but e.g. sample environment is continuously upgraded, with the aim to develop it into a first class SAXS instrument. For further details on the SAXS instrument see the I711 home page at <http://maxsun5.maxlab.lu.se/beamlines/bli711>.

**Optical microscopy.** (Contact person: Emma Sparr)

The division has a Zeiss Axioplan Universal microscope equipped with differential interference contrast and a High Resolution Microscopy Camera AxioCam MRm Rev. 3 FireWire, Illuminator HBO 100 as well as with a 100W mercury short-arc lamp and a system of filters to allow the fluorescence microscopy observations. The microscope is further equipped with a high-sensitivity SIT video camera and an image processor, AxioVision 4 together with the Macintosh-based image analysis software. (Sponsored by FRN & Crafoord Foundation.)

**Rheometers.** (Contact person: Ulf Olsson)

A Carri-med controlled stress rheometer CSL 100 temperature controlled by a Peltier system. Measuring systems; cone and plate (solvent trap) in acrylic (4 cm, 1° and 6 cm, 1°) and stainless steel (4 cm, 1° and 6 cm, 1°). (Sponsored by Nils and Dorthi Troëdsdson Research Foundation). A Physica UDS 200 controlled stress rheometer. Measuring systems temperature controlled by a Peltier system; cone and plate in acrylic (2.5 cm, 1°, 5 cm, 1°, 7.5 cm, 1°), cone and plate in stainless steel (2.5 cm, 1°, 5 cm, 1°, 7.5 cm, 1°), plate and plate in stainless steel (2.5 cm and 5 cm). Measuring systems temperature controlled by a cylindrical temperature system and an external water bath; cup and bob (2.5 cm) and a double gap measuring device, both in stainless steel.

**Calorimeters.** (Contact person: Gerd Olofsson)

A double twin isothermal microcalorimeter for the simultaneous determination of sorption isotherms and differential sorption enthalpies of vapors on solids. Isothermal titration microcalorimeter 2277 TAM Thermal Activity Monitor System.

**Transmission electron microscopy with cryo facilities.** (Contact person: Viveka Alfredsson)

The national Centre for High Resolution Electron Microscopy (nCHREM) at the Department of Chemistry has two transmission electron microscopes. The Philips CM120 BioTWIN Cryo is a microscope dedicated for cryo-imaging. It is operated at 120 kV. The BioTWIN objective lens gives high contrast and the resolution is 0,34 nm. The microscope is equipped with an energy filter imaging system (Gatan GIF 100) and digital multiscan CCD cameras (Gatan 791). There is an Oxford CT 3500 Cryoholder and transfer system. The JEOL3000F is an analytical high-resolution transmission electron microscope with a field-emission electron source and an operating accelerating voltage of 300kV. The microscope is equipped with video-rate camera, and a 2 x 2 k CCD camera for HR image recording. The structural resolution is 0.17 nm in conventional mode, and 0.13 nm in STEM mode with high-angle annular detector. The microscope has an Oxford XEDS system and a Gatan Imaging Filter (2 x 2 k) for analysis of chemical composition with a spatial precision below 1 nm. Specialised holders for specimen transfer at liquid nitrogen temperature, in-situ heating, scanning tunneling microscopy with simultaneous TEM viewing etc are available. The microscope can be remote-controlled via Internet via a portable knobset. More information about nCHREM can be found at <http://www.materialkemi.lth.se/nchrem/index.html>. (Sponsored by NFR, Crafoord Foundation and Knut and Alice Wallenberg foundation.)

**QCM-D, Quartz Crystal Microbalance with Dissipation monitoring.** (Contact person: Tommy Nylander)

The instrument is from Q-Sense fitted with E4 and E1 module and is able to collect, both the dissipation and the resonance frequency of a quartz crystal. These data can be used to follow the formation of thin films (nm) such as proteins, polymers and cells onto surfaces, in liquid by using a flow system at controlled temperature. The advantage with measurements at several frequencies and the dissipation is that we can determine the adsorbed film is rigid or water-rich (soft). The instrument is equipped with a Q-Sense Ellipsometry Module (for the Q-Sense E1 system), which enables simultaneous QCM-D and ellipsometric measurements on the same substrate. Thus we can determine both the adsorbed amount and the water content in adsorbed layer. (Sponsored by The Knut and Alice Wallenberg Foundation.)

**Ellipsometry.** (Contact person: Tommy Nylander)

The development of a high precision ellipsometer for time-resolved studies of thin adsorbed films has been successful and of great importance to several specific projects. The instrument allows precise and rapid measurements of the ellipsometric angles  $\Psi$  and  $\Delta$ , thus, allowing unique studies of the evolution of both the thickness and density (refractive index) of adsorbed surfactant and polymer layers with time. The possibility of working at different wavelengths provides an additional source of information on complex systems as well as flexibility to optimize the optical contrast of the systems

studied. Continued efforts are invested in upgrading this instrument to improve its potential for studies of fast interfacial processes occurring on the nanometer scale. During 1998 we acquired an additional ellipsometer, an Optrel Multiskop (Optrel, Berlin Germany). This instrument has been fitted with sample cells to measure at the solid-liquid, liquid-liquid and liquid-air interfaces. Apart from doing null-ellipsometry we can also do imaging ellipsometry, Brewster Angle Microscopy, Surface plasmons as well as operate it in waveguide mode. (Sponsored by FRN).

We are currently purchasing a spectroscopic ellipsometer, which will allow a more extensive determination of the properties adsorbed films. This equipment will be in operation during the spring 2010 (sponsored by The Knut and Alice Wallenberg Foundation.)

**Dynamic and static light scattering equipments.** (Contact person: Karin Schillén).

1) Laser light scattering goniometer system from the ALV GmbH, Langen, Germany, is a measuring system for simultaneous angular dependent determination of DLS and SLS. The CGF-8F compact based system includes CW Helium-Neon (He-Ne) gas laser (632.8 nm with a output of 22 mW), laser beam focusing optics including a laser beam attenuator and a Glan laser polarizer prism, a goniometer with a rotary table with the angular range of about 20° to 150°, a cell housing with an cylindrical quartz vat (filled with a refractive-index matching liquid, toluene), a fiber optical near-monomodal detection system (with a possible depolarized light detection), a detection unit comprises of two matched avalanche photodiodes that is put in a pseudo-cross correlation arrangement. For the DLS measurements using photon correlation spectroscopy, the latest ALV-7004 multiple tau digital correlator is utilized to produce the time pseudo-cross correlation function of the scattered intensity. It has an initial real sampling time of 25 ns and a lag time range that extends from 25 ns to up to 54975.6 s, which makes it possible to detect particle sizes from 1 nm up to about 5000 nm. The temperature range of the vat is -12 °C to +140 °C (if the refractive index matched liquid changed) and is controlled to  $\pm 0.01$  °C by a F32 Julabo heating circulator. In addition, also included in the overall set-up, is a differential refractometer with one He-Ne laser from ALV for the determination of refractive index increments necessary for the SLS experiments. (Sponsored by the former Swedish Natural Science Research Council, NFR, and by Knut and Alice Wallenbergs Stiftelse, KAW.)

2) For convenient DLS and SLS measurements and determination of electrophoretic mobility (or zetapotential), a Zetasizer Nano ZS from Malvern Instruments Ltd, Worshestershire, UK, is available. The instruments measures DLS and SLS at a set angle of 173° using the NIBS technology. The zetapotential (or electrophoretic mobility) measurements using M3-PALS technology are performed at 17°. The laser used is a 4 mW He-Ne laser (632.8 nm) and the detection unit comprises an avalanche photodiode. The temperature range of the instrument is 2-90 °C. (Sponsored by Crafoordska Stiftelsen.)

3) For characterization of molecular weight and studies of conformation changes or association processes in macromolecular systems, a multi-angle laser light scattering instrument for SLS measurements is available. The instrument is a Dawn DSP-F MALLS photometer (Wyatt Technology Corp., Santa Barbara, California) equipped with a 5 mW He-Ne laser (632.8 nm). The intensity of the scattered light is measured using photodiodes at 18 different angles simultaneously. The instrument is connected to a gel permeation chromatography system for on-line molecular weight determinations

in aqueous solvents but batch analysis may also be performed. (Sponsored by NFR.)

**Surface force apparatus.** (Contact person: Tommy Nylander)

The Surface Force Apparatus allows the direct measurement of the interaction between two molecularly smooth surfaces (usually mica) in a crossed cylinders geometry. The separation between surfaces is measured interferometrically up to 0.1 nm resolution. The force is calculated from deflection of a double cantilever spring with an accuracy of ca 10<sup>-8</sup> N. The SFA is being successfully used to identify and quantify most of the fundamental interactions occurring between surfaces, namely van der Waals, electrostatic double-layer, hydration, hydrophobic and steric forces, in different colloidal systems. (Sponsored by FRN.)

**Surface film balance.** (Contact persons: Tommy Nylander and Emma Sparr)

Three different equipments optimized for different purposes; 1) A Nima technology 611 Langmuir trough with a surface film balance (Wilhelmy plate) was acquired during 1997. The instrument is equipped with a dipper to prepare Langmuir-Blodgett films. It can also be used for dynamic contact angle measurements, while simultaneously recording the surface film pressure. 2) A KSV minitrough was acquired 2000 and used together with the Optrel Multiskop ellipsometer. Both surface film balances are equipped to measure the surface potential. 3) A 20 ml Langmuir micro-trough from Kibron. The equipment include surface pressure sensor, a window in the bottom of the trough for microscopy, a temperature control plate, and a multiwall plate for surface pressure measurements. (Sponsored by Crafoord Foundation and Per-Eric and Ulla Schyberg's foundation.)

**Multimode scanning probe microscope.** (Contact person: Emma Sparr)

A Multimode Scanning Probe Microscopy (Nanoscope-III) was purchased jointly by Physical Chemistry and the Department of Food Technology from Digital Instruments Inc. in April 96. The instrument can be operated as both a scanning tunneling microscope (STM) and an atomic force microscope (AFM). With its many configurations the instrument can scan and image a wide variety of samples with scan sizes from atomic level up to 125 by 125 microns. As an AFM, traditional contact mode experiments in air and liquid and TappingMode experiments in air have been available for many years. More recent equipment purchases allow users to image surfaces with TappingMode in fluid environments, perform lateral force microscopy (LFM) measurements of topography and friction, and make force measurements using a colloidal probe. In the latter mode, a spherical particle is adhered to an AFM cantilever and colloidal forces between the probe and surface in a fluid environment can be studied. Other force measurements are also possible using standard cantilevers or chemically modified cantilevers. (Sponsored by FRN.)

**Fluorescence spectrophotometer.** (Contact person: Emma Sparr)

A Cary Eclipse Fluorescence spectrophotometer for fluorescence, phosphorescence or chemi/bio luminescence was purchased in 2007. The instrument includes both 4-position automatic cell holder with temperature sensor, stirrer and connected water bath as well as a microplate reader. Equipment also include the automated polarizer accessories. (Sponsored by the Crafoord foundation)

**UV-Vis spectrophotometer.** (Contact person: Ingegerd Lind)

A Cary 300 Bio UV-Vis spectrophotometer with 4-position automatic cell holder with temperature sensor, stirrer and connected water bath was purchased in 2007.

## COLLABORATIVE RESEARCH PROGRAMS

### Organizing Molecular Matter

In 2005, the Swedish Research Council (VR) launched a call for proposals of collaborative research efforts from strong Swedish research environments with the prospect of long-term (10 years) “Linnaeus support”. A group of nineteen senior researchers from the divisions of Physical Chemistry, Theoretical Chemistry and Biophysical Chemistry at the Department of Chemistry, Lund University, responded with a proposal called Organizing Molecular Matter (OMM). The program was accepted and was operational from June 2006, with a funding of 7.5 MSEK from VR and 1 MSEK from Lund University. The OMM research program, which can be found together with accounts of ongoing research at the OMM website (<http://www.omm.lu.se>), focuses on intermolecular interactions and their manifestations in a liquid environment. The interplay between theory and experiment is an essential feature of the program. The theoretical basis for the description of intermolecular interactions and their consequences are treated using quantum chemical calculations and statistical mechanical simulations. Carefully selected model systems are studied experimentally, and an important part of the experimental studies is an ongoing improvement of methods. A final part of the program is to apply the understanding obtained in the basic studies for solving applied problems both in the biophysical/molecular biology field and in the industrial area. By the end of 2009, a total of 20 new PhD and postdoctoral projects had been initiated within OMM, and each of these projects typically involves two or more OMM scientists. OMM also contributes substantially to the salaries of four young senior scientists. In addition, OMM organizes a series of weekly seminars, occasional workshops, and two annual meetings.

### SSF–“Porous surface layers through polymer-assisted deposition.”

This project started in July 2009 and is a five-year research programme financed by the Swedish Foundation for Strategic Research (SSF). The goal of the program is to develop a method for a controlled deposition of mesoporous colloidal particles on surfaces and to apply the method on three types of porous particles. The basic strategy is to gradually destabilize an initially stable colloidal dispersion to achieve surface deposition rather than bulk aggregation. For this we use a potentially phase separating polymer to achieve colloidal stability/instability. The transition stability-instability should be smooth, which allows for an ordered equilibrium deposition layer. In one project we model theoretically the process to identify useful tuning parameters. In one experimental project flat mesoporous silica particles are deposited on a surface to give micrometer thick layers with pores of well defined size and orientation. Such layers can be used for separating small solutes from larger ones through a diffusional membrane transport. Another application is in tapes with a graded porous layer to be used as precise meters for relative humidity. In a third project we deposit porous liquid crystalline particles. Such particles can be loaded with an enzyme producing an enzymatically active surface coating. The fourth project aims at synthesizing soft mesoporous gel particles through in situ polymerization. In a surface layer of the particles the porosity



can respond to changes in the properties of the bulk liquid such as pH or salt content. Porous responsive surface layers have a large potential in drug formulation. (L. Piculell, P. Linse, B. Lindman, V. Alfredsson, T. Nylander, H. Wennerström)

## **POLYSURF**

This is a Transfer of Knowledge (TOK) Development Scheme (DEV) funded within the Marie Curie Program of the European Union. The overall objective of the project is to increase the knowledge and research level of the host organisation, Institute of Textiles at the University of Maribor, on the creation of tailored and/or smart fibre forming polymers and materials that would be able to control the release of various active compounds or to create new tailored fibre surface properties for different end applications in the area of technical textiles, such as medical, therapeutic, hygienic and protective textiles. The project will transfer knowledge of innovative fibre surface modification technologies based on (WP2) colloidal micro-hydro-gelation, (WP3) nano-micro-(en)capsulation and (WP4) polymer surface coating. Additionally, (WP1) innovative biotechnological, green-chemistry, chemical and physical catalysis tools, or their combination will be applied to activate and/or modify polymer surfaces and/or colloidal particles/layers created using ecologically and toxicologically suitable processes. According to the diversity of the knowledge and expertise that shall be transferred, the project will build a highly multidisciplinary scientific group, cutting across different established research areas, i.e. textile chemists, physical chemists, biological catalysts and colloidal engineers, that will be able to prepare colloidal particles, coatings and multi-layers, and subsequently apply them to different suitably eco-pre-activated and/or modified natural and synthetic polymer surfaces. The new fibre materials with upgraded properties can be exploited either to enhance the bulk properties of existing products for better performance, or to create new value-added products with smart and/or tailored surface characteristics based on the multi-functionality. The project objective will be realised through training, module-based courses and several research activities by outgoing seconded and incoming recruited more experienced (MER) and inexperienced (ER) researchers that will be able to provide the necessary inputs in these areas. (B. Lindman)

## **Biopolymers based surfactants - stabilization and functionalization of particles and surfaces.**

The COST-project “Biopolymers based surfactants - Stabilization and functionalization of particles and surfaces” aims at increasing the knowledge of processes at surfaces and interfaces and factors tuning them at the molecular scale. An interdisciplinary effort to study the interaction of surfactants, derived from high and low molecular biological sources, with different kinds of substrates, as soft and hard particles and structured polymer surfaces, is envisioned. This activity will focus on the stabilization of the systems and the functionalisation of different surfaces. This has extended social and industrial interest as these results will provide advanced hygienic and technical materials as well as new insight into critical medical field, as for example the biocompatibility of implants. This requires a multidisciplinary approach i.e. synthesis and activation of materials, characterization and understanding of surface properties and processes at the molecular and supramolecular level. A theoretical description of these systems will allow to predict the properties of final products based on their chemical composition

and the structure of the surface active compounds and substrates. Modification of these surfactants as well as the dispersed and macroscopic substrates will change their interaction abilities and functionalities. The results will enable us to understand, and ultimately control, the structure-property relationship and create new materials with excellent surface specificity. (B. Lindman)

## NEONUCLEI

The division was granted a 4 year EU-FP6 STREP in the NEST PATHFINDER project within Synthetic Biology, entitled “Self-assembly of synthetic nuclei: key modules for semibiotic chemosynthetic systems” (Acronyme NEONUCLEI and Contract no.12967) and coordinated by Prof. George Attard, University of Southampton, UK. NEONUCLEI will develop transcription-competent synthetic analogues of cell nuclei. These particles, termed neonuclei, will be obtained through self-assembly/organisation in mixtures of DNA, macromolecules (or nanoparticles), and lipids. The composition of the neonuclei will be chosen to produce particles with internal nano-architectures capable of sustaining gene transcription upon the addition of transcription factors. The DNA of the neonuclei will contain a gene cluster (or tandem repeats of the same gene). The genes will be separated by sequences designed to induce DNA compaction in response to specific chemical or physical stimuli. This will be exploited to establish non-biological control over the transcription of parts, or all, of the DNA. These control sequences offer the opportunity for multiple transcription control strategies and provide the capability of implementing temporally co-ordinated synthesis of multiple gene products. Neonuclei represent a key enabling step in the realisation of semi-biotic systems: these are systems and devices that combine synthetic non-natural functional systems with systems of biological origin. The neonuclei will be integrated with biological systems, or with isolated components, to produce novel semi-biotic devices capable of the controlled in situ synthesis of complex bio-molecules on demand. Physical Chemistry mainly contributes in providing understanding formation, morphology and structure of relevant self-assembly structures, DNA-surfactant/particle interaction, DNA compaction, morphology and structure of formed entities. (T. Nylander, V. Alfredsson, B. Lindman, U. Olsson, H. Wennerström)

## BIOCONTROL

EU Marie Curie research training network “BIOCONTROL” aims at controlling biological functions at, respectively on, bio-interfaces. It is based on the recent recognition of the importance of structure and properties of bio-interfaces, e.g. biological membranes, for a multitude of life processes. We now know that the evolution of atherosclerosis, cancer, immunity and viral infections, neurodegenerative disorders (Alzheimer, Prion diseases, etc.) and aging depend on perturbations of such interfaces. However, we need to improve our knowledge of the underlying molecular mechanisms in order to design efficient drugs and to meet the challenges in regenerative medicine and tissue engineering. This requires a deeper understanding of processes and interactions at bio-interfaces in terms of biology, biochemistry, biophysics and structure. The two major scientific objectives of BIOCONTROL are to: Provide fundamental knowledge of the forces and molecular mechanisms that regulate the interactions and biological processes taking place in and around biological membranes. Construct bio-mimetic surfaces and self-assembled structures that enable external

control of biological and biotechnological processes, such as, cell adhesion and cell cycle regulation. Real progress in the field can only be achieved by breaking traditional academic borders. This requires the education of new researchers that are trained in cross-disciplinary and collaborative work. Therefore the major educational objective of BIOCONTROL is to train of a new category of 'life science' experts who can work across disciplines. This will be achieved by an unprecedented interdisciplinary training programme comprising (bio)physicists, biologists, (bio)chemists, surface chemists and computational biologists. (T. Nylander, V. Alfredsson) (<http://biocontrol.tau.ac.il/>)

## **NANO GROWTH**

This EPSRC (UK) funded project studies the fundamental aspects of crystal growth in nanoporous materials. It involves the application of a powerful set of complementary techniques to the study of crystal growth of open-framework materials comprising: atomic force microscopy, high resolution transmission and scanning electron microscopies, in-situ NMR with enhanced data processing, X-ray diffraction and mass spectrometry. A substantially better understanding of the synthesis process is likely to yield important economic benefits, for example, better process control, increased efficiency in reagent usage, improved reproducibility and the capacity to modify or tailor products for specific applications. (V. Alfredsson)  
(<http://www.ucl.ac.uk/nanogrowth/index.htm>)

## **NordForsk Network**

### **Nordic Milk Science Initiatives, 2008-2011 (NordicMilk Network)**

Research within dairy science has a long tradition in the Nordic and Baltic countries and the level of the research has been on high international standard. Recent research has revealed in cow's milk many protective components and their derivatives displaying a range of bioactivities. The research has been focused on product and process development directly related to the traditional use of the milk raw material. This also involves health and nutritional aspects as well as linking the genetic variants of the milk components to the product quality. This project joins multidisciplinary research groups from five Nordic countries and two Baltic countries who are working on milk compounds related to health and technological aspects. This project will join high know-how in chemical, analytical, technological, structural, in vitro studies and human clinical studies related to milk compounds. (Tommy Nylander)  
[https://portal.mtt.fi/portal/page/portal/www\\_en/Projects/Nordicmilk](https://portal.mtt.fi/portal/page/portal/www_en/Projects/Nordicmilk)

## **The division of surface chemistry of the Swedish Chemical Society**

The Division of Surface Chemistry of the Swedish Chemical Society was founded in 2001 to promote contacts between chemists interested in surface and colloid chemistry. The main activity of the Division is to organize the Annual Surface and Colloid Symposium in Lund. The aim of the 8th Symposium was to highlight the role of surface and colloid science for the synthesis and processing of advanced polymeric and inorganic materials. Four main topics were covered, namely, polymers and organic coatings, materials from renewable resources, porous materials and nanoparticles.

## Strategic Research Areas at Lund University

nmC@LU is a interdisciplinary research environment in nanoscience. One focus of the multi-disciplinary Nanometer Structure Consortium at Lund University (<http://nano.lth.se>) is on materials science and synthesis. Viveka Alfredsson, Tommy Nylander, Ulf Olsson are associated with this programme. Multipark is a translational programme that ranges from pre-clinical research to studies on the life situation of patients with Parkinson's disease ([www.med.lu.se/multipark](http://www.med.lu.se/multipark)). Emma Sparr is associated partner in this programme, participating in sub-project dealing with biophysical studies of protein-membrane interactions.

## CONFERENCES, TRAVELS AND SEMINARS

Lennart Piculell held an invited lecture at AkzoNobel, Brewster, NY, USA. He also gave a lecture at the "13th IACIS and the 83rd ACS Colloid & Surface Science", Columbia university, NYC. He presented a poster at "the 23rd ECIS" in Antalya, Turkey. At an event at Procter & Gamble, Cincinnati, USA in October he was an invited external expert.

Olle Söderman gave an oral presentation at the "Material Research Society Fall Meeting 09" in Boston, USA. He also gave an invited talk at the "83rd ACS Colloid and Surface Science Symposium" in New York, USA.

Gerd Olofsson gave an oral presentation at the "COST D 36 meeting" in Maribor, Slovenia, and visited University of Maribor and University of Ljubljana.

Björn Lindman gave plenary lectures at the "Conference on Advanced Polysaccharide Based Materials" in Turku, Finland, at the "3rd Asian Conference on Colloid and Interface Science" in Jeju, Korea and workshops on polysaccharides in Nottingham, England and in Jena, Germany. He gave keynote or invited lectures at the "13th IACIS and the 83rd ACS Colloid & Surface Science", Columbia university, NYC, the COST Chemistry Workshop on "Structure-performance relationships at the surface of functional materials", Benahavis, Spain, and the "nano09 workshop" in Braga, Portugal. He also gave a talk at the COST workshop on "Biopolymer based surfactants – stabilisation and functionalisation of particles and surfaces" in Maribor, Slovenia. He attended the "Molecular Frontiers Conference" in Stockholm, the "Neutrons in Biology Conference" in Lund, the "3rd Iberian Meeting on Colloid and Interface Science (RICI III)" in Granada, Spain and the "23th Conference of the European Colloid and Interface Society (ECIS)" in Antalya, Turkey, where he also organized and chaired a workshop. During the year Björn Lindman visited a number of universities and other research centers and in most cases he presented a lecture. The institutions visited included: University of Rome "Tor Vergata"; Universidade Federal de Rio Norte, Natal, Brazil; University of Nottingham, UK; Åbo Akademi University, Finland; the International Iberian Nanotechnology Institute, Braga, Portugal; Universidade Beira Interior, Covilha, Portugal; University of Maribor, Slovenia; InnovNano Research Center, Aljustrel, Portugal; Akzo Nobel Research Center, New York; Henkel Research Center, Düsseldorf; Beiersdorf, Research Center, Hamburg; Karl-Franzens-Universität Graz, Austria; Cognis Research Center, Düsseldorf, Germany; Wella Research Center, Darmstadt, Germany, Greenwich University, U.K.; Akzo Nobel Surface Chemistry, Stenungsund, Sweden; Korea Advanced Institute of Science and Technology, Daedeok Science Town, Daejeon, South Korea; Columbia University, New York; GlaxoSmithKline Research Center, Weybridge, UK. Björn Lindman also visited national research councils in conjunction with reviewing research proposals. Björn

Lindman was visiting professor at the Department of Chemistry, Coimbra University, Portugal.

Viveka Alfredsson gave an oral presentation at “SCANDEM-2009” in Reykjavik, Iceland. She held an invited lecture at the “International Workshop on Synthesis and Characterization of mesoporous materials” in Shanghai, China. At the “Korea-Sweden workshop on nanoporous materials”, at KAIST in Daejeon, Korea, she held a oral presentation. Viveka Alfredsson participated in the Meeting in Ludwigshafen with BASF, the final meeting with Post Doc project of Hao Wang, and in the Neutron Scattering experiments at ILL in Grenoble, France. She also participated in Neutron Scattering experiments at Paul Scherrer Institut in Villigen, Switzerland and in the “Workshop on Porous Crystals from basic to potential application” in Stockholm. She gave an oral presentation at Berzeliusdagarna, Stockholm, 30-31 January (popular scientific) entitled ”Naturens vägar till ordning – att skapa ordnade material”.

Tommy Nylander gave invited talks at the Department of Physics, Technical University, Munich, Germany; Institute of Bioengineering and Nanotechnology, A-Star, Singapore; University of Cagliari, Cagliari, Italy; University of Florence, Florence, Italy; ISIS Bilayer 2009, Cosenors House, Abingdon. He gave talks at Biophysical Society Meeting in Boston, USA; International Conference on Neutron Scattering, Knoxville, USA; International Conference on Neutron and X-ray Scattering 2009 (ICNX 2009), Kuala Lumpur, Malaysia. He also gave a poster presentation at European Colloid and Interface Society in Antalya, Turkey. Tommy Nylander participated in the Meeting in Ludwigshafen with BASF, the final meeting with Post Doc project of Hao Wang, and in Neutron Scattering experiments at ILL in Grenoble, France.

Ulf Olsson gave invited talks at the “Annual meeting of the German Physical Society” in Dresden, Germany; at the “ESF Exploratory workshop: Frontiers in European Research on Liquid Crystals” in Bandol, France; at the “LUXC workshop” in Lund, at the “Association in Solution II” in Tomar, Portugal and at the “MAX-lab User Meeting” in Lund. He also participated in the following meetings: the “6th Nordic Workshop on Scattering from Soft Matter” in Aarhus, the “8th Annual Surface and Colloid Symposium” in Lund and the “ECIS 2009” in Antalya. He visited Yeditepe University and the University of Reading where he also gave talks.

Ingemar Wadsö gave a key lecture at the 15th International Conference on Biological Calorimetry in Pécs, Hungary.

Karin Schillén did poster presentations and an oral presentation at XXIII European Colloid and Interface Society Conference, Antalya, Turkey and poster presentations at the 9th Annual Surface and Colloid Symposium Dynamics, Steady State and Arrest, Lund, Sweden. She gave an invited seminar at the Department of Chemistry, University of Rome (La Sapienza), Rome, Italy, December 2009.

Håkan Wennerström participated in the “Workshop on Porous Crystals from basic to potential application” in Stockholm. He gave a invited lecture at “Gordon Tiddy – A Lifetime in Formulation”, Manchester.

Emma Sparr gave invited lectures at the “International Colloid and Surface Science Symposium / ACS Colloid Science” in New York, USA; at the “9th Annual Surface and Colloid Symposium” in Lund, Sweden; at the “Biocontrol workshop” in Odense, Denmark and at the “Scanco conference” in Malmö, Sweden. She presented posters at the “Biophysical Society Annual Meeting” in Boston, USA and at “Neutrons in Biology” in Lund, Sweden.

Daniel Topgaard gave a poster presentation at the Biophysical Society 53rd

Annual Meeting in Boston, USA. He also gave an oral presentation at the EUROMAR Magnetic Resonance Conference in Gothenburg, Sweden and held an invited talk at the 9th Annual Surface and Colloid Symposium in Lund, Sweden.

Çelen Çağrı Cenker did poster presentations at “Neutrons in Biology” in Lund Sweden, “ECIS” in Antalya Turkey and on the “Surface and Colloid Symposium” in Lund Sweden.

Luis Pegado gave an oral presentation at “the 9th Meeting of the Physical Chemistry Section of the Portuguese Chemical Society” in Aveiro, Portugal. He also gave oral presentations at the “Association in Solution II: Structure, Function and Performance” in Tomar, Portugal and at the “23rd Conference of the European Colloid and Interface Society” in Antalya, Turkey.

Jonas Carlstedt presented a poster at the “DNA and Chromosomes: 5th International Summer School” in Cargèse, Corsica, France. He also gave an oral presentation at the “12th European student colloid conference (ESC)” in Almería, Spain.

Alexandra Machado presented a poster at the conference “Association in Solution II. Structure, Function & Performance” that took place in Tomar, Portugal. She presented two posters at the “American Association of Pharmaceutical Scientists (AAPS) Meeting” in Los Angeles, USA, and also did one poster presentation at the “9th Annual Surface and Colloid Symposium. Dynamics, Steady State and Arrest” in Lund.

Joakim Balogh gave an oral presentation at the “3rd Iberian Meeting of Colloids and Interfaces RICIII” and a Poster presentation at “2009 ECIS conference” in Antalya, Turkey.

Fátima Costa Balogh gave oral presentations at the “3rd Iberian Meeting of Colloids and Interfaces RICIII” and at the “1st SPCAL meeting” in Lisbon, Portugal as well as a poster presentation at the “2009 ECIS” conference in Antalya, Turkey.

Bruno F.B. Silva presented a poster at the “23rd Conference of the European Colloid and Interface Society” in Antalya, Turkey.

Ingrid Åslund presented posters at “EUROMAR2009” in Gothenburg, Sweden; at “Diffusion Fundamentals III” in Athens, Greece and at the “9th Annual Surface and Colloid Symposium” in Lund, Sweden.

Johanna Bailey Jönsson, Malin Christensen, Lennart Piculell and Ola J. Karlsson presented a poster at the “IPCG Conference: Polymer Colloids, Il Ciocco” being held in Italy.

Joakim Stenhammar gave a poster presentation at the “International Workshop on Multiscale Materials Modeling” in Berlin, Germany. He also held oral presentations at the “12th European Student Conference of the European Colloid and Interface Society” in Almería, Spain and at the “3rd Annual Symposium of the Division of Theoretical Chemistry of the Swedish Chemical Society - Materials Oriented Modeling - Catalysis and Interactions” in Stockholm, Sweden.

Nikolay Oskolkov did a poster presentation at the 9th Annual Surface and Colloid Symposium “Surface and Colloid Science for Advanced Materials” in Lund, Sweden.

Sebastian Björklund gave an oral presentation at the “Skin and Formulation 3rd symposium and Skin Forum 10th Annual Meeting” in Versailles, France. He also gave an oral presentation at “OMM mini-symposium” on diffusive transport in Lund.

Anna Carnerup gave an oral presentation at “SCANDEM-2009” being held in Reykjavik, Iceland.

Juanfang Ruan gave an oral presentation at "SCANDEM-2009", Reykjavik, Iceland. She also held an invited lecture at the "International Workshop on Synthesis and Characterization of mesoporous materials" in Shanghai, China.

Tomas Kjellman presented a poster at the "International Workshop on Synthesis and Characterization of mesoporous materials" in Shanghai, China and participated in the "Workshop on Porous Crystals from basic to potential application" in Stockholm.

Nina Reichhardt presented a poster at the "9th Annual Surface and Colloid Symposium" being held in Lund. She also held a oral presentation at the "Korea-Sweden workshop on nanoporous materials" at KAIST in Daejeon, Korea. She participated in Neutron Scattering experiments at Paul Scherrer Institut in Villigen, Switzerland.

Salome Santos held oral presentations at the "National Meeting of Physical Chemistry" in Portugal and at the "Association in Solution II" in Portugal. She held two poster presentations at the "ECIS" in Turkey.

Dan Lundberg participated in Neutron Scattering experiments at ILL in Grenoble, France.

Peter Linton participated in the "Workshop on Porous Crystals from basic to potential application" in Stockholm.

John Janiak presented a poster at Sixth Nordic Workshop on Scattering from Soft Matter, University of Aarhus Denmark and gave a oral presentation at European Student Colloid Conference, Spain.

Guiseppa Lazzara presented a poster at 9th Annual Surface and Colloid Symposium Dynamics, Steady State and Arrest, Lund, Sweden. He also gave an invited seminar at Technische Universität Berlin Stranski-Laboratorium für Physikalische Chemie und Theoretische Chemie Institut für Chemie, Berlin, Germany.

Agnieszka Nowacka, held an oral presentation at the "12th European Student Conference of the European Colloid and Interface Society" in Almeria, Spain and presented a poster at the 9th Annual Surface and Colloid Symposium "Surface and Colloid Science for Advanced Materials" in Lund, Sweden.

## **EXTERNAL PROFESSIONAL ACTIVITIES**

Ingemar Wadsö served on the International Scientific Committee for the "15th International Conference on Biological Calorimetry" in Pécs, Hungary.

Lennart Piculell is a section editor for the Polyelectrolytes section of "Current Opinion in Colloid and Interface Science", a member of the editorial board of "Soft Matter", and a member of the international organizing committee of the biannual "International Polyelectrolyte Symposia". He is a member of the board of the Department of Chemistry at Lund University and the Chairman of the Division of Surface Chemistry of the Swedish Chemical Society. He was also chairing the program committee and the local organizing committee of the annual three-day "9th Annual Surface and Colloid Science Symposium", organized by Division of Surface Chemistry and Physical Chemistry, that took place in November in Lund, with 100 registered participants. He is a member of the program committee for "Formula VI", an international conference to be held in Stockholm 2010. He is the director of the Linnaeus center OMM. He served in 2009 as an external examiner of the PhD thesis of Diana Costa at the University of Coimbra, Portugal, and as faculty opponent at the PhD defense of Anna Hillerström at Karlstad University. He was also a member of the grading committee at the thesis defense of Christian Johansson, Uppsala University.

Olle Söderman served as a member of the grading committee at the thesis defense

of Bruno da Silva, University of Porto.

Björn Lindman was on the Advisory or Editorial Boards of “Advances in Colloid and Interface Science”, “Current Opinion in Colloid & Interface Science”, “Fine Chemicals”, “Colloid & Polymer Science”, “The open Physical Chemistry Journal” and “Journal of Dispersion Science and Technology”. Björn Lindman is a member of The Royal Swedish Academy of Engineering Sciences, of The Royal Swedish Academy of Sciences and of The Royal Physiographic Society in Lund, and honorary corresponding member of Romaniae Scientiarum Societas. During the year he was elected foreign member of the Academia das Ciências de Lisboa, the Portuguese Academy of Sciences. He is cofounder and honorary member of the European Colloid & Interface Society (ECIS). For the period 2006-2009 Björn Lindman was President of the International Association of Colloid and Interface Scientists (IACIS). He was also evaluator of research and training networks and research programs for the European Commission as well as evaluator of research programs for the Norwegian and Italian Research Councils, and Lundbeckfonden, Denmark. He was external examiner for the PhD thesis defence of Bruno Medronho, Coimbra University, Portugal and in thesis committee for Diana Costa at the same university.

Viveka Alfredsson was a faculty opponent for Malin Sörensen, KTH, Stockholm. She was a member of the PhD thesis Committee of Chuanbo Gao, Stockholm University and Alessandra Mosca, Luleå Technical University. She served partly as Vice head of the Division of Physical Chemistry.

Karin Schillén was an external examiner for PhD thesis of Telma Costa, Department of Chemistry, University of Coimbra, Portugal, January 2009. She was a Deputy Member of the PhD thesis grading committee of Niklas Källrot, Physical Chemistry. She was also a Member of the board of the undergraduate studies in chemistry at the Department of Chemistry, LU. Furthermore, Karin Schillén is the head teacher in Physical Chemistry with the responsibility of organizing the teaching given by the members of the Division of Physical Chemistry.

Håkan Wennerström is member of The Royal Swedish Academy of Sciences and The Royal Swedish Academy of Engineering Sciences; member of the Nobel Committee for Chemistry.

Ulf Olsson served on the PhD thesis committees for Peiter Saveyn University of Gent, Elena Blanco University of Santiago de Compostela, Youlia Michina, LIONS, CEA, Saclay, Bruno Silva, University of Porto, and Bruno Medronho, University of Coimbra. He was working (10% of full time) for the Science Faculty on the preparation of the faculty activities for the large scale infrastructures MAX IV and ESS. He also served on an expert committee reviewing a project within the Millennium Program of Institute Laue Langevin (ILL).

Tommy Nylander served as thesis examiner for the PhD thesis of Xiao Juan Gong, University of Sydney, Sydney, Australia, and Jesper Hedin, Chalmers University of Technology, Gothenburg, Sweden. He was member of the evaluation panel for beam time applications at Institute Laue Langevin, Grenoble, France; NIST Centre for Neutron Research, Gaithersburg, USA and ISIS, Rutherford Appleton Laboratory, Oxfordshire, UK. In addition he was evaluator of research proposals for BBSRC – Biotechnology and Biological Sciences Research Council and MIUR - Ministero dell'Istruzione, dell'Università e della Ricerca, Italy. Tommy Nylander is a member of the Scientific Advisory Group and The Stakeholders Group of European Spallation Source – Scandinavia.

Emma Sparr served on PhD thesis committee for Per Wessman, Physical Chemistry, Uppsala University.



## COURSES AND TEACHING

Members of the division of Physical Chemistry are involved in a number of undergraduate courses and a number of our graduate students serve as teaching assistants on all courses given by the division. Johan Reimer has the main part of his position within the undergraduate education, where he among other things administrates the first-year chemistry courses.

The first year of chemistry studies at the Chemical Center consists of four 5-week chemistry courses (which are given both during the fall and the spring semesters) and one 10-week course in physical chemistry. In the first basic chemistry course during the spring semester, Viveka Alfredsson, Emma Sparr, Johan Reimer and Per Linse were involved in lectures and leading exercises and question hours, whereas Viveka Alfredsson, Daniel Topgaard and Johan Reimer gave the course during the fall semester. The topic of the first-year physical chemistry course is thermodynamics and quantum mechanics and it is based on the textbook of P. W. Atkins and J. De Paula "Atkins' Physical Chemistry". Karin Schillén is the main teacher for this course and gave the lectures in thermodynamics. Joakim Stenhammar led the corresponding exercise sessions.

As regards higher courses, the division gives one basic and one advanced Master course in surface and colloid chemistry and another three advanced Master courses in physical chemistry. The introductory colloid and surface chemistry course is headed by Ulf Olsson and was taught by Ulf and Lennart Piculell. The advanced surface and colloid chemistry course, given during the fall semester, was taught by Emma Sparr (main teacher) along with Per Linse, Tommy Nylander, Lennart Piculell, and Håkan Wennerström. This course is based on the text book "The Colloidal Domain" by Fennell Evans and Håkan Wennerström. Two advanced Master courses were given during the spring semester by Daniel Topgaard (nuclear magnetic resonance, NMR, techniques) and Ulf Olsson, Karin Schillén and Tommy Nylander (scattering techniques). One advanced Master course in unifying concepts in nanoscience size-effects and self-assembly was given during the autumn with Tommy Nylander as main teacher.

Björn Lindman was one of the teachers in the national course on Surface Chemistry in Marstrand and at the annual course on surfactants and polymers in aqueous solution, this year given in Lisbon and he also taught courses at Coimbra University, Portugal, a course at Universidade Federal de Rio Norte, Natal, Brazil and in-house courses for industry.

Karin Schillén started to lead a PhD course on Scattering in the fall semester of 2009 based on the textbook "Neutrons, X-Ray and Light Scattering: Introduction to an Investigative Tool for Colloidal and Polymeric Systems" edited by Peter Lindner and Thomas Zemb. This course is organized as a reading course, where one chapter is discussed at a meeting every second week. Each chapter is assigned to one PhD student that acts as a chairman of the meeting.

Giuseppe Lazzara gave a course "Calorimetry: a powerful technique for a direct evaluation of the thermodynamics of self-assembling. Understanding the interactions and predicting ability" for the PhD students involved in the international graduate school on chemistry at Technische Universität Berlin Stranski-Laboratorium für Physikalische Chemie und Theoretische Chemie Institut für Chemie, Berlin, Germany.

## NEUTRONS IN BIOLOGY 2009

22-24 June 2009, Lund, Sweden

Physical Chemistry together with friends from the neutron community organised an international symposium entitled "Neutrons in Biology". As the trend towards interdisciplinarity widens for the study of biological systems, neutron scattering approaches are becoming an increasingly important part of the powerful array of techniques that are needed to study these systems in a genuinely integrated way. The Neutrons in Biology meeting a Lund University 22-24th June 2009 focused on recent progress in the application of neutron scattering to problems in biological and biomedical science. 23 Invited talks, 8 oral presentation (priority was given to young speakers and recipients of the NMI3 support) and 51 posters described recent results concerning a wide range of topics and methods, and included structural studies of proteins, nucleic acids and their complexes in solutions, lipid membranes, crystals, partially ordered systems, and at interfaces. A conscious effort was made to involve researchers whose activities currently do not exploit these methods. Therefore we also invited speakers, which normally work as physicians in the hospital and researchers from the pharmaceutical industry. The conference attracted 111 participants from all around the globe.

We would like to acknowledge the generous support from The Swedish Research Council, The Royal Swedish Academy of Sciences through its Nobel Institute of Chemistry, NMI3, ESS-Scandinavia, Lund kommun, the Skåne region, Probi AB, Chocolaterie Hovby No 9 and Akademiska Bokhandeln.

<http://www.ill.eu/news-events/events/past-events/neutrons-in-biology-2009/>

## SEMINARS

*Structure of phospholipid mixtures probed by neutron reflectometry and small angle scattering.* Hanna Wacklin (the National Deuterium Facility, Australian Nuclear Science and Technology Institution; ANSTO)

*Soft matter to silence genes: a combination of x-ray scattering and live cell work.* Cecilia Leal (University of California Santa Barbara)

*Equilibrium & Non-equilibrium Kinetics of Block Copolymer Micelles.* Reidar Lund (Donostia International Physics Center, San Sebastian, Spain)

*Specific ion binding to macro-molecules.* Mikael Lund (Theoretical Chemistry, LU)

*Synthesis of Mesoporous Silica by Co-structure Directing Method.* Shunai Che (Shanghai Jiao Tong University, China)

*Advances in density functional theory of polymers.* Cliff Woodward (Canberra, Australia)

*Segregated polymer media. Order, disorder, and possibilities in particle synthesis.* Kristoffer Almdal (DTU Nanotech)

*MR characterization of articular cartilage.* Eveliina Lammentausta (Dept. Diagnostic Radiology, Oulu - University Hospital, Finland)

*Docent lecture: Principles of magnetic resonance imaging.* Daniel Topgaard (Physical Chemistry, LU)

*Lipid bilayer-induced secondary structure in de novo designed peptides.* Thomas Ederth (Sensor Science and Molecular Physics, Linköping)

*Self-aggregation of Lactoferrin.* Björn Persson (Theoretical Chemistry, LU)

*Nanodisks and Nuclisomes - from model membranes to targeted drug delivery.* Katarina Edwards (Div. Physical Chemistry, Uppsala University)

*Probing membrane proteins. Monitoring proton-translocation quantitatively.* Sindra Peterson Årsköld (Center for Molecular Protein Science, Lund University)

*Silk, a short story of everything!* Cedric Dicko (Pure and Applied Biochemistry, Lund; Oxford Silk group, Oxford University)

*Oligomers on the brain: the role of Abeta oligomers in Alzheimer's disease.* Dominic Walsh (UCD Conway Institute of Biomolecular and Biomedical Research, University College Dublin)

*Biophysics of Viral Infectivity - Matching Genome Length and Virus Size.* Alex Evilevitch (Center for Molecular Protein Science, LU)

*Clays - Crystal structure and macroscopic behaviour.* Thomas Fabien (Laboratoire Environnement et Minéralurgie, Vandoeuvre les Nancy)

*Are colloidal and molecular glass formation related?* Johan Mattsson (Condensed Matter Physics, Chalmers)

*Non-Equilibrium Phase Transformations at the Air-Liquid Interface.* Christoffer Åberg (Physical Chemistry, LU)

*Formation mechanism of mesoporous silica - Tailor new materials.* Peter Linton (Physical Chemistry, LU)

*The multiple chemical bond, illustrated with a number of dichromium complexes.* Björn Roos (Theoretical Chemistry, LU)

*Self-Assembly of Amyloid Peptide Fragments and Copolymers.* Ian Hamley (University of Reading)

*Interactions between nanoparticles and proteins - the size of the nanoparticles matter.* Martin Lundqvist (Biophysical chemistry, LU)

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*Determining the homogeneous length scale and the intracellular diffusion through pulsed field gradient NMR.* Ingrid Åslund (Physical Chemistry, LU)

*Single molecule spectroscopy of light emitting conjugated polymers.* Ivan Scheblykin (Chemical Physics, LU)

*Lamellae and Onions in a Nonionic Surfactant System: A Summary of 4 Years Project.* Bruno Medronho (University of Coimbra)

*Deposition at solid surfaces from associating polymer/surfactant mixtures in water.* Lennart Piculell (Physical Chemistry, LU)

*Viscoelastic Behavior of Magnetic Elastomers in a Homogeneous Magnetic Field.* Alexei R. Khokhlov (Physics Department, Moscow State University)

*Dynamics in soft matter.* Peter Holmqvist (Inst Solid State Research, Forschungszentrum Jülich)

*Dynamics of Polymer Adsorption onto Solid Surfaces in Good Solvent.* Niklas Källrot (Physical Chemistry, LU)

*Formation of mesoporous SBA-15 from a colloidal perspective.* Peter Linton (Physical Chemistry, LU)

*Lanreotide, a specific case for deciphering peptide self-assembly driving forces.* Maité Paternostre (Institute of biology technologies - CEA Saclay)

*Structure Prediction and Design of Protein Assemblies.* Ingemar André (Biochemistry, LU)

*Associating polymer-polymer and polymer-surfactant systems: phase behaviour and the influence of chemical reactions.* Salomé Santos (Physical Chemistry, LU)

*Effects on Transfection Efficiency and Physicochemical Character of a Lipid-Based Gene Delivery Formulation of the Inclusion of a Single-Tailed Amino Acid-Based Amphiphile.* Dan Lundberg (Physical Chemistry, LU) & Dept Chemistry, Univ Coimbra)

### **Mini-symposium on Diffusive transport**

*Diffusion in Evaporating Solutions.* Alexey Kabalnov (Hewlett Packard, San Diego)

*Magnetic resonance imaging techniques for studying macroscopic molecular transport.* Daniel Topgaard (Physical Chemistry, Lund)

*Skin permeability can be regulated by the gradient in chemical potential of water.* Sebastian Björklund (Physical Chemistry, Lund)

*Diffusive mass transfer in controlled release pharmaceuticals.* Anders Axelsson (Chemical Engineering)

*Conductance of fluorescence dyes and ions across lipid membranes* Thomas Heimburg (Niels Bohr Institute, Copenhagen)

## **AWARDS**

Daniel Topgaard was elected Swedish Inventor of 2009 by SKAPA (with Karin Bryskhe and Anna Stenstam, Colloidal Resource AB).

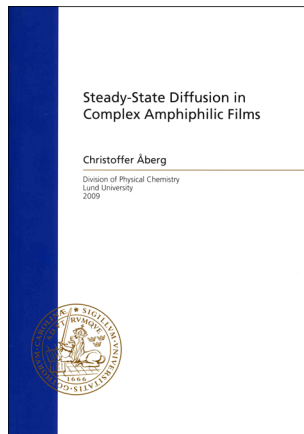
## DOCTORAL THESES

June 04, 2009

Christoffer Åberg

*Steady-State Diffusion in Complex Amphiphilic Films*

Opponent: Dr Alexey Kabalnov

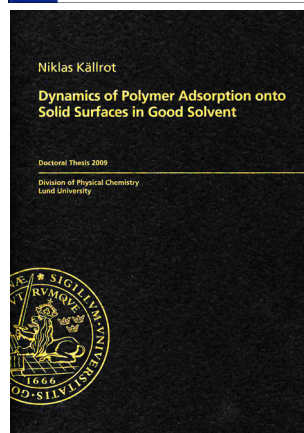
Available online: <http://www.lu.se/o.o.i.s?id=12588&postid=1390787>

November 13, 2009

Niklas Källrot

*Dynamics of Polymer Adsorption onto Solid Surfaces in Good Solvent*

Opponent: Prof. Dr. Martien Cohen Stuart

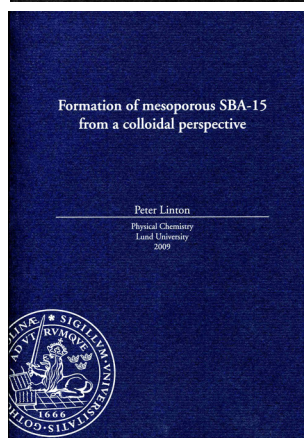
Available online: <http://www.lu.se/o.o.i.s?id=12588&postid=1494669>

November 20, 2009

Peter Linton

*Formation of mesoporous SBA-15 from a colloidal perspective*

Opponent: Prof. Daniella Goldfarb

Available online: <http://www.lu.se/o.o.i.s?id=12588&postid=1496535>

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(L) = Long term

(S) = Short term

## WELCOME TO VISITORS

Dear Visitor,

We receive many guests, who stay with us from a few hours or a day of discussions, seminars etc., to one or more years for postdocs and foreign students. Visitors are very important for us and help us to improve our level of research and education. Careful planning can significantly improve these visits. The Annual Report partly serves the purpose of introducing a person to our division prior to a call.

We hope to continue to have many visitors and here we give some information, which may be helpful for you if you plan to visit us. To arrange a visit, you may contact an appropriate member of our division. Depending on the nature of the visit different arrangements may be made. Help with accommodation can be provided by Majlis Larsson. In many cases we have found that smaller, less formal seminars, lead to better information exchange.

We recommend our visitors to fly to Kastrup Airport, Copenhagen. Then, take a train (frequency every 20 min.) from Kastrup Airport over the Öresund bridge directly to Lund railway station (takes approx. 45 min).

Visit the Kemicentrum website for further information

<http://www.kc.lu.se/english/visitors/directions>, or contact Majlis Larsson.

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