Final Report - KM1: 116629

Tuning the interfacial properties of fluid interfaces by strongly interacting polyelectrolytes and surfactants: the role of equilibrium and non-equilibrium features

Background

The bulk and interfacial properties of macromolecule / surfactant mixtures determine the performance of countless household, cosmetic, food and medical products. Traditionally the properties of these systems were discussed assuming that they reach equilibrium on the timescale of the measurements. However in the first decade of this century it was demonstrated that the bulk properties of the oppositely charged polyelectrolyte / surfactant (PE/S) mixtures are often dominated by the formation of non-equilibrium aggregates that can persist for weeks, months or years in these systems.[1,2] Despite of these bulk results the interfacial properties of the PE/S mixtures were still discussed assuming the equilibrium of the system. Based on the characteristics of the surface tension isotherms and the structure of the interfacial layer J.Penfold and R.Thomas suggested that two types of PE/S mixtures exist (Type 1 vs. Type 2) and the different characteristics of these systems can be interpreted in terms equilibrium solubility of the PE/S complexes.[3] This approach was challenged by the PI of this project (Dr. Imre Varga) and his main collaborator (Dr. Richard Campbell). Before the start of the current project we could successfully demonstrate that the formation of bulk non-equilibrium aggregates can indeed have a pronounced effect on the interfacial properties of the PE/S systems. On the one hand the depletion (e.g. slow settling) of the bulk aggregates from the aqueous phase can lead to the appearance a phenomenon called the ‘surface tension cliff edge peak’ in the surface tension isotherms of specific PE/S systems (indirect effect).[4,5] On the other hand the transport of the bulk aggregates to the interface and their spreading can provide an alternative mechanism to the formation of the self-assembled adsorption layer formation.[6] Based on these results we defined three main area of research in our project. The achieved results are summarized below.

Work Package 1: General characteristics of the interfacial properties of PE/S systems

In this work package we aimed at developing a unifying general physical description of the behavior of oppositely charged polyelectrolyte/surfactant mixtures at the air/water interface in terms of equilibrium vs. non-equilibrium extremes. We focused on two specific systems, namely the poly(diallyldimethylammonium chloride)/sodium dodecyl sulfate (pdadmac/SDS) mixtures with added NaCl and the poly(sodium styrenesulfonate)/dodecyltrimethylammonium bromide (NaPSS/DTAB) system, which represents the two ’school examples’ of the Type1 and Type 2 PE/S systems defined by Thomas & Penfold. We carried out systematic investigation in two characteristic surfactant concentration range using a variety of bulk and surface techniques: in the surfactant concentration range of the associative phase separation (where close to charge neutral P/S complexes form that lack colloid stability) and at low level of surfactant binding where the formation of equilibrium PE/S complexes can be expected. Similarities in the general behavior are observed for all the investigated PE/S systems.

In the surfactant concentration range of the associative phase separation, following the slow precipitation of aggregates in the equilibrium two-phase region, which can take several days or even weeks, depletion of surface-active material can result in a surface tension peak. The limiting time scale in the equilibration of the samples is discussed in terms of a balance between those of aggregate growth and settling. Bulk aggregates may spontaneously dissociate and spread material in the form of a kinetically-trapped film if they interact with the interface, and a low surface tension then results out of equilibrium conditions. These interactions can occur prior to bulk equilibration while there remains a suspension of aggregates that can diffuse to the interface, and following bulk equilibration for certain systems if the settled precipitate is disturbed. Two clear differences in the behavior of the systems are the position in the isotherm of the surface tension peak and the time it takes to evolve (Fig.1). These features can be both rationalized in terms of the nature of the bulk binding interactions. However, the general interfacial properties of the investigated systems were found identical in the range of the associative phase separation regardless if they were claimed Type 1 or Type 2 previously.

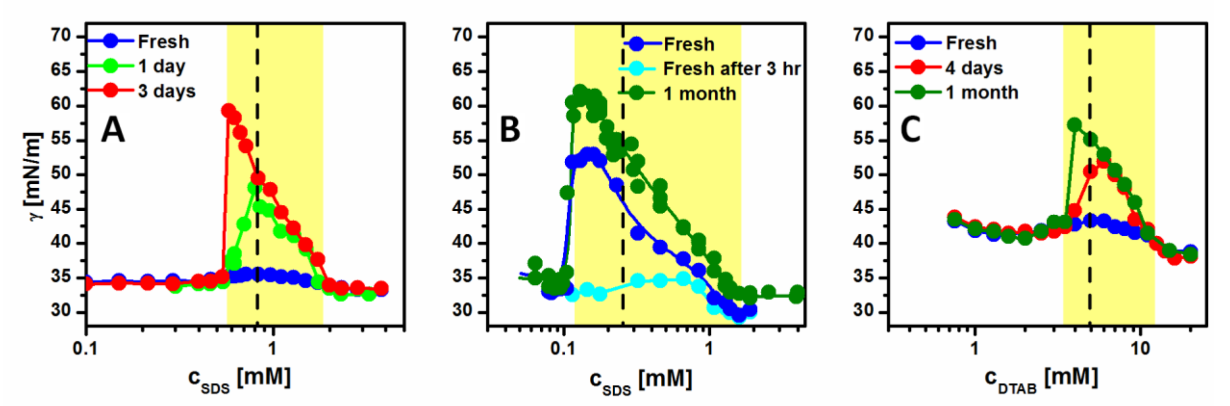
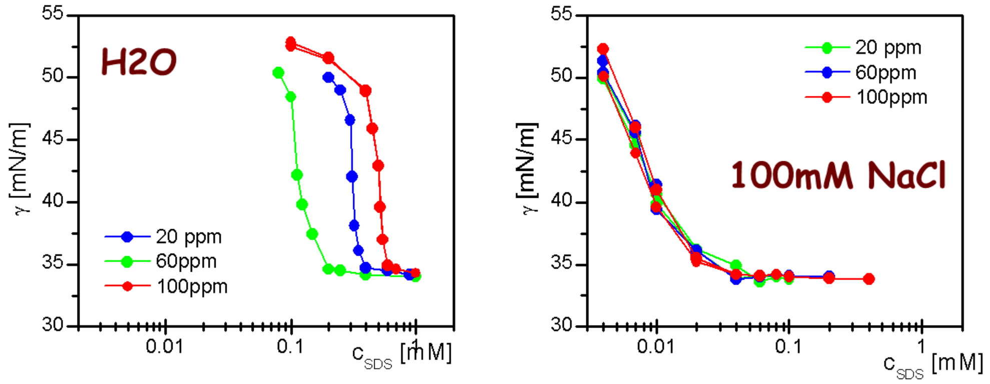


Fig. 1. Surface tension of freshly mixed and aged samples of (A) 100 and (B) 10 ppm Pdadmac/SDS in 0.1 M NaCl and (C) 100 ppm NaPSS/DTAB in pure water.

Imre Varga, Richard A. Campbell:
General Physical Description of the Behavior of Oppositely Charged Polyelectrolyte/Surfactant Mixtures at the Air/Water Interface,
Langmuir, **2017**, *33*, 5915–5924.
Independent citations at ACS: 41.

Next we investigated the surface tension isotherms of the pdadmac/SDS and the NaPSS/DTAB systems in the low surfactant concentration range where the PE/S mixtures form a one phase equilibrium system under appropriate sample preparation and treatment to avoid the formation of trapped non-equilibrium aggregates. Previously it has been claimed that in this surfactant concentration range Type 1 and Type 2 PE/S systems show a profoundly different surface tension isotherms. Namely, while the surface tension isotherms of Type 1 systems (e.g. NaPSS/DTAB) show a steeply decreasing step with increasing surfactant concentration and this step shifts to larger surfactant concentrations with increasing polyelectrolyte concentration, in the case of Type 2 systems (e.g. pdadmac/SDS) the surface tension isotherms are independent of the polyelectrolyte concentration and exhibit a less steep decrease with increasing surfactant concentration. However, based on thermodynamic considerations we hypothesized that the observed differences of the surface tension isotherms are related to the presence of the inert electrolyte in the investigated pdadmac/SDS system and its absence in the case of NaPSS/DTAB system. To confirm this prediction we measured the surface tension isotherms of both systems at three different polyelectrolyte concentrations in pure water and in 100 mM NaCl. The experimental surface tension isotherms clearly confirmed our prediction showing polyelectrolyte concentration dependent surface tension isotherms in pure water and polyelectrolyte concentration independent ones in 100 mM NaCl (Fig.2).

Pdadmac/SDS surface tension isotherms



NaPSS/DTAB surface tension isotherms

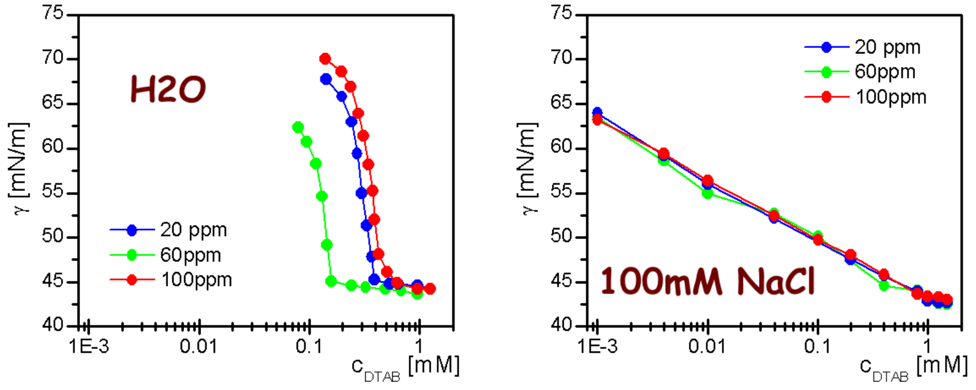


Fig. 2. Surface tension isothems of the 100 ppm Pdadmac/SDS and the100 ppm NaPSS/DTAB sytems in pure water (left) and in 100 mM NaCl (rigth).

In order to facilitate a general and predictive description of the surface tension isotherms of PE/S systems, we developed a thermodynamic framework. In this model the PE/S complex was treated as a small system that contains the polyelectrolyte coil, surfactant ions and the necessary amount of polyelectrolyte counterions to neutralize the small system. This PE/S complex is in equilibrium with the aqueous solution of free surfactant and an inert electrolyte. In this bulk equilibrium two binding mechanism of the surfactant is taken into account: an ion exchange equilibrium (monomer binding) and the binding of the surfactant ions in the form closed micelle-like surfactant aggregates (cooperative binding). To describe the surface tension isotherms it was assumed that the surface active bulk components (the PE/S complex, and the surfactant) form a uniform interfacial layer resulting in an interfacial composition different from the composition of the (PE/S complex). Using this physical model the following general form could be derived for the Gibbs equation describing the surface tension isotherm of any PE/S system:

$$-d\sigma = \Gamma_S \left[\frac{1+y}{N} dG_{PS}^0 + \left\{ 1 - (1+y)\frac{n}{N} \right\} RT(dlna_S - dlna_X) \right]$$

Where Γ_S is the surfactant surface excess, N is the number of monomer units in the polyelectrolyte chain, y is the ratio of the monomer units neutralized by an inert counterion and by a surfactant ion in the adsorption layer, G_{PS} is the standard Gibbs free energy of the P/S small system, which varies with increasing surfactant binding and finally a_S and a_X denote the bulk activity of the surfactant ions and the counterions, respectively. In the presence of a large concentration of an inert electrolyte and below the critical aggregation concentration of the surfactant (cac) this expression reduces to the simple expression derived earlier by Langevine:[7]

$$-d\sigma = \Gamma_S RT dlnx_S$$

Unfortunately, the above expression remains an empty formalism until a reliable predictive polyelectrolyte/surfactant binding model is developed, which is currently missing in the literature. To overcome this limitation, we decided to determine the surfactant binding data (surfactant binding isotherms) experimentally and try to use those data and the above expression to predict the surface tension isotherms of the investigated systems. However, good quality surfactant binding data barely exist in the literature due to the extreme difficulties related to its measurement. These difficulties originate from the fact that due to the strong interaction of the oppositely charged surfactant and polyelectrolyte, surfactant binding often sets on in the micromolar surfactant concentration range and the measurement of such low free surfactant concentrations in the presence of the P/S complexes is rather challenging. Typically this is done by surfactant selective electrodes. However, due to the extreme surface activity of the P/S mixtures usually not only the surfactant adsorbs on the electrode surface but the P/S complexes as well, which shifts the normal potential of the electrode making the measured potentials and the derived binding data questionable. As an alternative we developed two different approaches to determine surfactant binding isotherms.

In the first case the dynamic surface tension curve of P/S mixtures were measured using a high molecular weight polyelectrolyte. Since in such a case the characteristic diffusion time of the surfactant and the P/S complex to the interface can be significantly different, at the beginning of the dynamic surface tension curve a steady state surface tension can be measured that is characteristic for the free surfactant concentration of the mixture, while after sufficiently long equilibration the surface tension value characteristic for the PE/S mixture is reached (Fig.3).

The main advantage of this method is that it allows binding measurement using a few hundred microliter P/S mixtures. At the same time it requires the application of a high molecular weight polymers and the lower limit of the accessible surfactant concentration range is limited to the surfactant concentration where the surface tension of the pure surfactant is decreased by at least a few mN/m compared to the solvent.

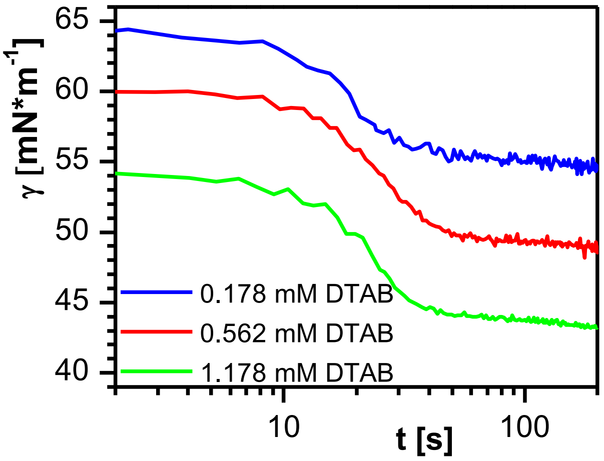


Fig. 3. Dynamic surface tension curves measured for a few 470 kDa poly(sodium acrylate)/DTAB mixtures.

Bence Fehér, Imre Varga:
Application of Dynamic Surface Tension Measurements for the Characterization of the Bulk Interaction of Polyelectrolyte/Surfactant Mixtures,
Langmuir, In preparation.

To overcome the limitation of the above method we developed another approach for the binding isotherm measurement. In this case dialysis equilibrium was established between a small volume (~ 1ml) of polyelectrolyte free surfactant solution and a large volume of P/S mixture. The concentration of the separated equilibrium surfactant solution (the free surfactant concentration in the PE/S mixture) was determined by utilizing that the mixtures of oppositely charged surfactants show an extreme surface activity. Thus, a well-defined amount of oppositely charged surfactant was added to the equilibrium surfactant solution and the surface tension of the mixture was measured. The equilibrium surfactant concentration was determined by using a calibration curve. This method allowed the determination of the free surfactant concentration from a few micromolar surfactant concentration and polyelectrolytes with a few kDa can be characterized by using suitable dialysis membrane. Using this method we could determine the surfactant binding isotherm for both the padadmac/SDS and the NaPSS/DTAB systems in 100 mM NaCl (Fig.4).

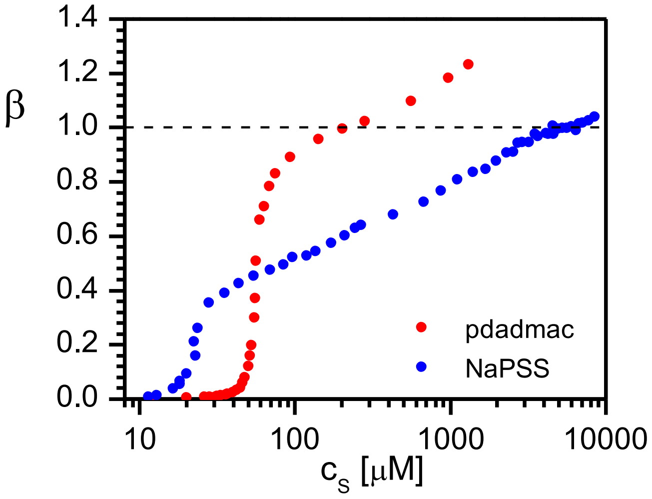


Fig. 4. The surfactant binding isotherms determined for the NaPSS/DTAB. And pdadmac/SDS mixtures in 100 mM NaCl

Róbert Szőke, Richard Campbell, Imre Varga:
A Novel Surface Tension Measurement Based Method to Determine the Binding Isotherms of Polyelectrolyte/Surfactant mixtures,
Langmuir, In preparation.

Finally, we utilized the experimentally determined binding data for the prediction of the surface tension isotherms both in the NaPSS/DTAB and the pdadmac/SDS system using the previously derived thermodynamic framework and a simple molecular interaction model. The calculations are currently in progress and the publication of the results is anticipated for the first half of 2022.

Imre Varga:
Prediction of the Surface Tension Isotherms of Polyelectrolyte/Surfactant Mixtures from the Experimentally Determined Bulk Binding Data: A General Thermodynamic Framework and its Application for Specific Systems
Physical Chemistry Letters, Planned for 2022.

The measured binding isotherms suggests that a major difference between the NaPSS/DTAB and the pdadmac/SDS system is that the initial steep binding regime extends to a much higher level of surfactant binding in the case of the pdadmac/SDS system and as a consequence the stoichiometric complexes form at more than an order of magnitude smaller equilibrium surfactant concentration. In addition while the stoichiometric pdadmac/SDS precipitate is a powder like material, the stoichiometric NaPSS/DTAB forms a gluey, highly viscous coacervate phase. Though, this may imply that structural differences between the two types of PE/S complexes govern these differences, structural data of the NaPSS/DTAB system is practically unavailable in the literature. Thus, we performed a SAXS investigation to monitor how the structure of the NaPSS/DTAB complexes evolves with increasing surfactant binding. Our investigations shows that at the cac small spherical surfactant aggregates start to bind in the polyelectrolyte coil, which goes on until all NaPSS chains incorporate a surfactant aggregate. This happens at ~35% surfactant binding when the steep binding regime changes to a linear regime. In the linear regime with increasing binding the shape of the polymer bound surfactant associate does not change but remains spherical, while the surfactant aggregation number continuously increases. We also found that the stoichiometric precipitate preserve the same structural elements and the spherical surfactant aggregates form a hexagonal closed packed structure as revealed by the observed Bragg peaks.

Bence Fehér, Attila Bóta, András Wacha, Jan Skov Pedersen, Imre Varga:
The evolution of equilibrium NaPSS / DTAB supramolecular structure in dilute aqueous solution with increasing surfactant binding,
Langmuir, Submitted.

Work Package 2: Delivery of macromolecules to surfaces by utilizing the aggregate spreading mechanism

In this work package first we developed a new methodology to prepare loaded polyelectrolyte/surfactant films at the air/water interface by exploiting Marangoni spreading resulting from the dynamic dissociation of hydrophobic neutral aggregates dispensed from an ***aqueous*** dispersion of NaPSS/DTAB. The developed method resulted in the interfacial confinement of more than one third of the macromolecules in the system even though they were not even surface-active without the surfactant. The interfacial stoichiometry of the films was resolved during measurements of surface pressure isotherms in situ in a Langmuir trough for the first time using a newly developed neutron reflectometry method. The interfacial coverage is determined by the minimum surface area reached when the films were compressed beyond a single complete surface layer. The films exhibited linear ripples on a length scale of hundreds of micrometers during the squeezing out of material, after which they behaved as perfectly insoluble membranes with consistent stoichiometric charge binding (Fig.5).

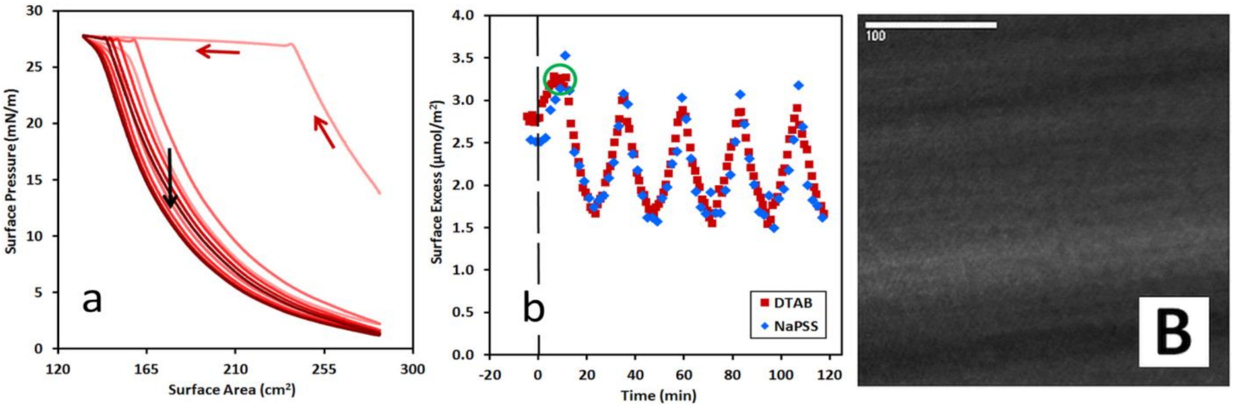


Fig. 5. a) Surface pressure vs. area isotherms of 5 compression/expansioncycles of NaPSS/DTAB films spread from neutral aggregates. ; b) Stoichiometry of NaPSS/DTAB spread films derived in situ. Full compression and expansion are marked respectively by maxima and minima. B) BAM images of NaPSS/DTAB films spread from neutral aggregates at full compression.

Richard A. Campbell, Andrea Tummino, Boris A. Noskov, Imre Varga:
Polyelectrolyte/surfactant films spread from neutral aggregates,
Soft Matter. **2016**, *12*, 5304-5312.
Independent citations at ACS: 20.

As a next step we investigated how the aggregate charge/structure and the subphase ionic strength affected our methodology to prepare loaded polyelectrolyte/surfactant films from self-assembled liquid crystalline aggregates by their fast dissociation and Marangoni spreading. In this case first we used the same NaPSS/DTAB system as before (strong polyelectrolyte) We showed that films spread on water from aggregates of low/negative charge have 1:1 charge binding and can be compressed only to a monolayer, beyond which material is lost to the bulk. For films spread from compact aggregates of positive charge, however, extended structures of the two components are created upon spreading or upon compression of the film beyond a monolayer. We applied ellipsometry, Brewster angle microscopy and neutron reflectometry as well as we measured surface pressure isotherms, which allowed us to reason that formation of extended structures is activated by aggregates embedded in the film. When spreading was performed on 0.1 M NaCl subphase upon film compression the extended structures of both components were only transient due to the presence of high concentration of small ions that could stabilize loops of the polyelectrolyte. Analogy of the controlled formation of extended structures in fluid monolayers was made to reservoir dynamics in lung surfactant.

A. Tummino, J. Toscano, F. Sebastiani, B.A. Noskov, I. Varga, R.A. Campbell:
Effects of Aggregate Charge and Subphase Ionic Strength on the Properties of Spread Polyelectrolyte/Surfactant Films at the Air/Water Interface under Static and Dynamic Conditions,
Langmuir **2018**, *34*, 2312-2323.
Independent citations at RSC: 21.

Next we used a weak polyelectrolyte, polyethylenimine, and investigated the effect of subphase pH on the film formation by spreading the PEI/SDS dispersions both on pH=4 and 10 subphase. In this case rich interfacial characteristics could be observed depending on the subphase pH and ionic strength. However, the film formation remained general phenomena. When water was used as subphase the formed films were fully elastic on repeated compression/expansion cycles, material was not lost towards the bulk phase regardless of the pH of the subphase. At the same time when a 100 mM NaCl was used as subphase on compression small loss of surfactant could be observed from cycle to cycle while the amount surface bound PEI remained constant.

A. Tummino, M.W.A. Skoda, R.A. Campbell, I.Varga.
Control of spread films of PEI/SDS at the air/water interface: aggregate charge versus pH effects.
Langmuir. In preparation.

Our investigations made on the spread films of NaPSS/DTAB and PEI/SDS dispersions clearly showed that the formation of extended structures at fluid interfaces of these synthetic mixtures can be nucleated by PE/S nanoparticles present in the interface during surface area compression. This advance surpassed decades of observations about the formation of different interfacial structures in related systems without a clear understanding of why. This inspired us to move towards more biocompatible systems in the hope to develop a physicochemical characterization of the ability of nanoparticles required to nucleate lipid reservoirs in model lung surfactant mixtures, and to exploit this new understanding. As a first step in this direction we started to investigate the film formation using poly-(L-lysine) hydrobromide (PLL), sodium dodecyl sulfate dispersions. In line with our previous investigations undercharged (positive), stoichiometric (neutral) and overcharged (negative) PLL/SDS aggregates were used in these investigations. In this case in addition to the previously applied surface pressure, ellipsometry, BAM and dynamic film composition measurements we also determined the structure of the film at full compression. The structural analysis showed the presence of a bilayer reservoir below the PLL/SDS monolayer and ~20% reservoir coverage of the surface was observed at maximum compression. Control measurements have also shown that the bilayer reservoir disappeared when the film was extended below the monolayer coverage.

J. Carrascosa Tejedor, A. Tummino, A. Santamaria, I. Varga, M. Jayne Lawrence, R.A. Campbell, A. Maestro.
Moving towards biocompatible spread polyelectrolyte/surfactant films: poly-l-lysine and sodium dodecyl sulfate.
J. Colloid Interface Sci. In preparation.

J. Carrascosa Tejedor, A. Tummino, A. Santamaria, I. Varga, A. Maestro, M. Jayne Lawrence, R.A. Campbell.
First elucidation of reservoir coverage of a polyelectrolyte/surfactant mixture during film compression/expansion dynamics.
Soft Matter. In preparation.

Since the size distribution and internal structure of the PE/S aggregates play a fundamental role in determining the characteristics of the spread PE/S films we also investigated how the aggregate formation during the sample preparation could be tuned. First, we compared two sample preparation protocols in the NaPSS/DTAB/NaCl system: in one case the samples were prepared by the rapid mixing of dilute NaPSS/NaCl and DTAB/NaCl solutions, while in the other case the samples were prepared by hundredfold dilution of concentrated NaPSS/DTAB/NaCl solutions in water. Next the effect of polyelectrolyte and salt concentration gradients were investigated in the pdadmac/SDS system. Both studies revealed large non-equilibrium effects, which can alter the phase-separation concentration range as well as the composition, morphology, and visual appearance of the prepared samples, clearly implying that sample preparation can be used to control aggregate characteristics and to modulate the efficiency of spread film formation.

K. Bali, Zs. Varga, A. Kardos, I. Varga, T. Gilányi, A. Domján, A. Wacha, A. Bóta, J. Mihály, R. Mészáros:
Effect of Dilution on the Nonequilibrium Polyelectrolyte/Surfactant Association,
Langmuir, **2018**, *34*, 14652-14660. .
Independent citations at ACS: 11.

K. Bali, Zs. Varga, A. Kardos, R. Mészáros:
Impact of local inhomogeneities on the complexation between poly(diallyldimethylammoniumchloride) and sodium dodecyl sulfate,
Colloids and Surfaces A: Physicochem. Eng. Aspects, **2019**, *574*, 21-28. .
Independent citations at Science Direct: 7.

Work Package 3: Exploitation of our understanding of the interfacial properties of PE/S systems developed at the air/water

In this work package we wanted to investigate if our understanding of the interfacial properties of the PE/S systems developed at the air solution interface could be generalized for other fluid interfaces and if the components of the PE/S mixtures could be replaced with other components to get either adsorbed or spread films at the interfaces. In this respect we turned our attention to liquid foam films, which may form from PE/S mixtures, however the variation of their stability with varying composition of the PE/S mixture remained a mystery despite the large number of studies that tried to interpret foam stability in terms of macroscopic properties such as the surface tension, elasticity, potential and composition, but for which no robust correlations have been established. For the first time we could show that a correlation can be established between the foam film stability of an oppositely charged PE/S mixture, varied through changes in its bulk composition, and the structures present at the air/water interface. The manifestation of electrostatic or steric stabilization in thin foam films is related to the spatial distributions of molecules interacting from opposing air/water interfaces. We found that maximum foam film stability could be achieved when the monolayer bound polyelectrolyte chains adopt an extended conformation. This concept can be broadened to other colloidal dispersions of high impact for technical, environmental and life science applications.

M. Uhlig, O. Löhmann, S. Vargas Ruiz, I. Varga, R. von Klitzing, R.A. Campbell:
New structural approach to understand the foam film stability of oppositely charged polyelectrolyte/surfactant mixtures,
Chemical Communications **2020**, *56*, 952-955.
Independent citations at RSC: 8.

Another widely investigated and widespreadly used fluid interface in real life applications is the oil/water interface. Although the preparation and stability of emulsions are relatively wellunderstood, novel approaches to produce nano- and micro-capsules are still required. In this respect PE/S interfacial layers may play an important role. Controlling the structure and self-assembly of surface-active material at the oil/water interface affects both the characteristics and stability of emulsions, which has proved very challenging to understand for mixed systems in particular, where liquid crystalline aggregates can compromise the stability of emulsions. However, there is a unique but barely exploited method to stabilize emulsions with PE/S interfacial layers.[8] In this case an oil-soluble surfactant (hexadecyl amine) was used in the oil phase and the water-soluble polyelectrolyte poly(acrylic acid) in the aqueous phase to produce stable emulsions. Bulk aggregates were absent from the system, which improved emulsion stability. To further exploit this approach we investigated the surface tension isotherm at the oil/water interface with a different oil soluble surfactant (oleic acid) and with a strong (pdadamac) and a weak (PEI) water-soluble polyelectrolyte. We found that the pH of the aqueous polyelectrolyte solution had a profound effect on the surface tension isotherm even in the case of the strong polyelectrolyte. When the pH was increased from 7.0 to 9.6 the surface activity of the mixtures significantly increased and the interfacial tension dropped below 1 mN/m from ~35 mM/m in the case of pdadmac and from ~18 mN/m in the case of PEI. Interestingly the stability of the emulsions prepared from pdadmac was lower than the stability of the PEI stabilized emulsions and this was not affected significantly by the increased pH. Altogether it could be concluded that by tuning the protonation equilibrium of the adsorbed oil soluble surfactant by adjusting the aqueous pH and by varying the charge and structure of the polyelectrolyte chain the interfacial layer at the oil water interface can be controlled. However, to develop a deeper understanding, in situ structural investigations of the buried oil/water interface would be required. Unfortunately, despite of our successful beam time application at ILL due to the Covid19 pandemic we could not perform the planned structural investigations at the oil-water interface. However, due to the significance of these investigations we incorporated the continuation of this project in an NKFIH grant application (PI: Prof. R. Mészáros, Participants: I, Varga, R.A. Campbell), which was supported.

Evelyn Biró (Thesis, Supervisor: Varga Imre): ***Polielektrolit/tenzid rendszerek alkalmazása O/V emulziók stabilizálására***, Eötvös Loránd Tudományegyetem, Kémiai Intézet,, 2018

András Álmos Kovács (Thesis, Supervisor: Varga Imre): ***Bijelek előállítása polielektrolit/tenzid rendszerek felhasználásával***, Eötvös Loránd Tudományegyetem, Kémiai Intézet, 2018

In the case of protein molecules an interesting possibility to trigger the film formation of the protein is to use denaturants in the aqueous bulk phase instead of surfactant. To exploit this possibility we investigated the adsorption of lysozyme from solution at the air-water interface in the absence and in the presence of strong denaturants (urea and guanidine hydrochloride). We found that the denaturants not only results in an acceleration of adsorption and an increase of the adsorption layer thickness but it also significantly alter the adsorption layer structure due to the changes of the protein tertiary structure.

R.A. Campbell, A. Tummino, I. Varga, O.Y. Milyaeva, M.M. Krycki, S.Y. Lin, V. Laux, M. Haertlein, V.T. Forsyth, B.A. Noskov: ***Adsorption of Denaturated Lysozyme at the Air-Water Interface: Structure and Morphology***,
Langmuir **2018**, *34*, 5020-5029.
Independent citations at ACS: 8.

There is an increasing demand for the preparation of responsive nanostructures in wide range of developing applications. Responsive microgel stabilized emulsions are promising candidates for this purpose. In our grant application we proposed that pNIPAm microgel particles with a polyelectrolyte shell could be used to develop a responsive microgel interfacial layer by utilizing the PE/S interaction. This concept relied on the assumption that due to the thick polyelectrolyte shell of the core/shell microgel particles the bare microgels particles are not surface active, thus their adsorption could be tuned by controlling their interaction with the surfactant. Unfortunately, it turned out that due to the dangling outer pNIPAm chain ends that are present in the outer shell of the microgel, the microgel particles are surface active even in the absence of the surfactant, thus making our original plans obsolete. For this reason we focused on the characterization of the electrical structure of the prepared microgels and controlling their size, structure and interactions for future interfacial applications as indicated in the outlook section.

I. Varga, A. Kardos, A. Borsos, T. Gilányi:
Effect of internal charge distribution on the electrophoretic mobility of poly(N-isopropyl acrylamide) based core-shell microgel particles,
Journal of Molecular Liquids, **2020**, *302*, 111979.
Independent citations at SciDirect: 3.

A. Kardos, T. Gilányi, I. Varga:
How small can poly(N-isopropylacrylamide) nanogels be prepared by controlling the size with surfactant?,
Journal of Colloid and Interface Science, **2019**, *557*, 793–806.
Independent citations at SciDirect: 4.

I. Antoniuk, D. Kaczmarek, A. Kardos, I. Varga, C. Amiel
Supramolecular hydrogel based on pNIPAm microgels connected via host-guest interactions,
Polymers, **2018**, *10*, 566. 17.
Independent citations at Scopus: 12.

G. Li, I. Varga, A. Kardos, I. Dobryden, P.M. Claesson
Temperature-Dependent Nanomechanical Properties of Adsorbed Poly-NIPAm Microgel Particles Immersed in Water
Langmuir, **2021**, *37*, 1902-1912.
Independent citations at ACS: 2.

G. Li, I. Varga, A. Kardos, I. Dobryden, P.M. Claesson
Nanoscale Mechanical Properties of Core–Shell-like Poly-NIPAm Microgel Particles: Effect of Temperature and Cross-Linking Density
Journal Of Physical Chemistry B, **2021**, *125*, 9860-9869.

D. Kaczmarek, J.S. Diget, B. Nystrom, G. Gyulai, R. Meszaros, T. Gilanyi, I. Varga:
Response of block copolyelectrolyte complexes to addition of ionic surfactants,
Colloid Surface A, **2017**, *532*, 290-296.
Independent citations at Scopus: 8.

B Fehér, K Zhu, B Nyström, I Varga, J.S. Pedersen
Effect of temperature and ionic strength on micellar aggregates of oppositely charged thermoresponsive block copolymer polyelectrolytes
Langmuir **2019**, *35*, 13614-13623.
Independent citations at ACS: 11.

Outlook

The work started in this project resulted in many interesting results and promising further research directions. We foresee three main research directions as the direct continuation of this work. On the one hand work started at the oil/water interface will be continued in an NKFIH grant, which will focus on the preparation of controlled and responsive structures at the oil/water interface aiming at the preparation of responsive emulsions, nanocapsules, bijels and other scaffolds with buried interfacial structures using polyelectrolytes, surfactants and a wide range of nanoparticles including microgels as potential building blocks.

To develop the physicochemical background of the ability of nanoparticles required to nucleate lipid reservoirs in model lung surfactant mixtures is a challenging but important research direction. This work has already started recently under the supervision of Dr. R. Campbell. An import subfield of this research will be the application of microgels and functionalized microgels with tuned size, mechanical and interfacial properties to allow the systematic investigation of the particle characteristics in reservoir formation.

Finally with colleagues from the USA (Andrew Kim), India (Arindam Adhikari) and South Korea (Rajkumar Patel) we have reviewed the state of the art electrochemical and fluorescent sensor applications of Layered Double Hydroxides and identified potential research directions relying on the PE/S interaction assisted monolayer and film formation.

A. Kim, I. Varga, A. Adhikari, R. Patel:
Recent Advances in Layered Double Hydroxide-based Electrochemical and Optical Sensors,
Nanomaterials, *Accepted.*

References

[1] Mészáros, R.; Thompson, L.; Bos, M.; Varga, I.; Gilányi, T. Interaction of sodium dodecyl sulfate with polyethyleneimine: surfactant-induced polymer solution colloid dispersion transition. Langmuir **2003**, *19*, 609−615.

[2] Naderi, A.; Claesson, P. M.; Bergstrom, M.; Dedinaite, A. Trapped non-equilibrium states in aqueous solutions of oppositely charged polyelectrolytes and surfactants: effects of mixing protocol and salt concentration. Colloids Surf., A **2005**, *253*, 83−93.

[3] Taylor, D. J. F.; Thomas, R. K.; Penfold, J. Polymer/surfactant interactions at the air/water interface. Adv. Colloid Interface Sci. **2007**, *132*, 69−110.

[4] Campbell, R. A.; Angus-Smyth, A.; Yanez Arteta, M.; Tonigold, K.; Nylander, T.; Varga, I. New perspective on the cliff edge peak in the surface tension of oppositely charged polyelectrolyte / surfactant mixtures. J. Phys. Chem. Lett. **2010**, *1*, 3021−3026.

[5] Campbell, R. A.; Yanez Arteta, M.; Angus-Smyth, A.; Nylander, T.; Varga, I. Effects of bulk colloidal stability on adsorption layers of poly(diallyldimethylammonium chloride)/sodium dodecyl sulfate at the air−water interface studied by neutron reflectometry. J. Phys. Chem. B **2011**, *115*, 15202−15213.

[6] Campbell, R. A.; Yanez Arteta, M.; Angus-Smyth, A.; Nylander, T.; Varga, I. Direct impact of non-equilibrium aggregates on the structure and morphology of Pdadmac/SDS layers at the air/water interface. Langmuir **2014**, *30*, 8664−8674.

[7] Asnacios, A.; Langevin, D.; Argillier, J.-F. Complexation of cationic surfactant and anionic polymer at the air−water interface. Macromolecules **1996**, *29*, 7412−7417.

[8] Stamkulov, N. Sh.; Mussabekov, K. B.; Aidarova, S. B.;. Luckham, P. F Stabilisation of emulsions by using a combination of an oil soluble ionic surfactant and water soluble polyelectrolytes. I: Emulsion stabilisation and Interfacial tension measurements. Colloids Surf. A **2009**, *335*, 103.