Experimental Report

17/09/2012

Proposal: **9-10-1186** **Council:** 10/2011

Title: Examining the mechanism of multilayer formation at interfaces of polyelectrolyte/surfactant mixtures

This proposal is continuation of: 9-10-1091

Research Area: Soft condensed matter

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Samples: poly(ethylene imine)
sodium poly(styrene sulfonate)
deuterated sodium dodecyl sulfate
sodium dodecyl sulfate
deuterated dodecyl trimethylammonium bromide
dodecyl trimethylammonium bromide
deuterated hexadecyl trimethylammonium bromide
hexadecyl trimethylammonium bromide

Instrument	Req. Days	All. Days	From	To
FIGARO Adsorption troug	4	4	01/10/2012	03/10/2012
			31/10/2012	02/11/2012

Abstract:

The formation of functionalized interfaces using multilayer assemblies, such as those self-assembled at surfaces of soft matter systems, attracts considerable interest. We have recently demonstrated that interfacial multilayers in a polyelectrolyte/surfactant system can result from the transport under gravity of bulk aggregates with internal molecular order. A strong Bragg peak and off-specular scattering were observed in neutron reflectivity measurements of Pdadmac/SDS mixtures only in the phase separation region and only when creaming or sedimentation occurred in the direction of the interface. The work was carried out on FIGARO using a combination of air/liquid and solid/liquid measurements, the latter exploiting a comparison of reflection up/down configurations. As spontaneous surface self-assembly and the transport of bulk aggregates would give rise to different surface properties we need to determine if the newly-demonstrated mechanism is widespread. We propose an assessment of PEI/SDS at two different pHs and PSS/CxTABs at two different chain lengths. Our results have the potential to impact on a range of studies in soft matter and biology on FIGARO and other reflectometers.

Preliminary Report for Figaro Experiment #9-10-1186

Scientific background. The formation of functionalized interfaces using multilayer assemblies has attracted considerable recent interest both from fundamental[1] and applied[2] perspectives. The most well-known approach for the preparation of controlled surface multilayer structures is layer-by-layer deposition,[3] but it is practically laborious. In this respect the formation of self-assembled multilayers at interfaces could be an alternative. The spontaneous self-assembly of multilayers at interfaces has been reported in various systems.

The most extensive category is oppositely charged polyelectrolyte/surfactant (P/S) mixtures, such as sodium poly(styrene sulfonate) with alkyltrimethylammonium bromides (PSS/CxTAB)[4] and poly(ethylene imine)/sodium dodecyl sulfate (PEI/SDS) at high pH.[5] The studies all used neutron reflectometry (NR) where Bragg diffraction peaks in specular reflectivity profiles and off-specular scattering result from repeating structures in the plane of the interface and the plane of incidence, respectively.[6] In spite of these studies, further work is required to understand why interfacial multilayers form in some systems but not others.

Previous work on Figaro. We published a paper in the *Journal of Physical Chemistry* earlier in 2012 which showed that multilayers at interfaces of a P/S system can result from the transport under gravity of bulk aggregates with internal molecular order.[7] Measurements were done at the air/liquid interface as well as at the solid/liquid interface with different crystal orientations – a unique approach comparing reflection up and down measurements. A strong Bragg peak and clear off-specular scattering were seen in NR measurements of samples of the poly(diallyldimethylammonium chloride)/SDS (Pdadmac/SDS) system *only* in the phase separation region and *only* when creaming or sedimentation process occurs in the direction of the interface. The data were modeled quantitatively to rationalize the Bragg peak areas in different isotopic contrasts from differently orientated surfaces in terms of the rate and direction of the aggregate transport.

In contrast with this process, surface self assembly evidently gives rise to interfaces of different structure and rheological properties. It is therefore important to distinguish which mechanism is responsible for the multilayers at surfaces of a range of systems. Dedicated cells have been constructed and used to good effect in two other scheduled experiments on Figaro, #9-10-1186 and #9-13-448; see reports.

Results of Figaro experiment #9-10-1186. In following up these exciting findings on the Pdadmac/SDS system, we posed the logical next question: could there be something unique or special about this system or can we generalize our findings to our polyelectrolyte/surfactant systems? The most widely studied system in this respect is PEI/SDS, involving either polymers[4,8] or oligomers.[9] PEI is a versatile and widely studied polyelectrolyte both for investigating fundamental interactions and also for applications. The primary reason that PEI is of interest is that the polyelectrolyte charge density can be controlled by varying the solution pH; at low pH PEI has a high charge density, whilst at high pH it has a low charge density. In principle therefore, it should be possible to tune and hence examine the effects of electrostatic and hydrophobic interactions on its behavior.

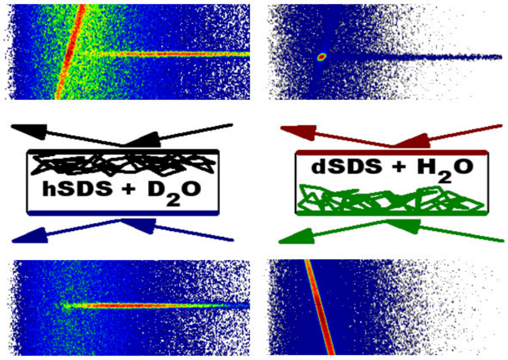
Interfacial multilayer historically has historically been observed only at its natural pH of ~ 10, and the explanation in the literature is clear: surface induced self assembly. As such we applied to the ILL see if it were possible to generalize our findings about the mechanism of interfacial multilayer formation to the PEI/SDS system, and the application was awarded 4 days on FIGARO (experiment #9-10-1186).

Experiment #9-10-1186 involved the characterization of PEI/SDS mixtures at pH 10 at the air/water interface: 6 different bulk polymer:surfactant compositions for 3 different molecular weights of polymer in only the PEI/hSDS/D_2O contrast where aggregates float upwards towards the air/water interface. The results (not shown due to space constraints) confirmed that interfacial multilayers were only seen in the phase separation region and only for the lowest molecular weight of polymer where ordered bulk aggregates are known to form.[4,8] These results were consistent with those in the literature.

Then the reflection up/down comparison was done to determine if surface self assembly could explain the interfacial multilayers (in which case both the up and down surfaces of a given sample should have the same structure) or if bulk aggregation and transport of the particles under gravity was the cause. First the experiment was carried out on using 2k PEI on hydrophilic surfaces. Figure 1 shows neutron detector images of samples with PEI/hSDS/D_2O (left) and PEI/dSDS/H_2O (right) for solid surfaces above the liquid facing down (top) and below the liquid facing up (bottom). Note that here the sample age is two weeks (the data shown were recorded after an extended equilibration period).

It is absolutely clear that the interfacial structures for the same samples with different geometries are not equivalent! PEI/hSDS/D_2O has clear off-specular scattering only on the top surface and PEI/dSDS/H_2O has clear off-specular scattering only on the bottom surface. These results demonstrate conclusively that gravity is playing a major role in the interfacial properties of the PEI/SDS system at its natural pH, even when the small polymer of just 2 kDa is involved. Moreover the results are not compatible with surface self assembly as *the* explanation for the presence of interfacial multilayers in this system.

Further visual evidence of the effects of gravity on the surfaces is given by the photo in Figure 2. Here the residues of the aggregates only on one surface for each cell can be seen. The results are consistent with the transport of aggregates in a given direction under gravity.



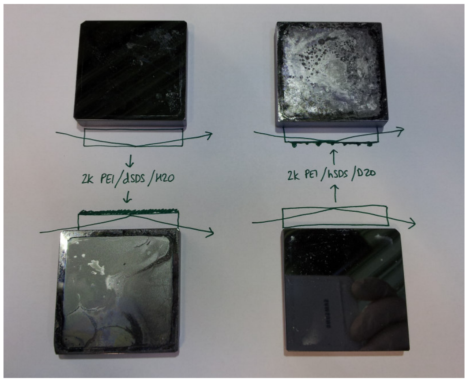
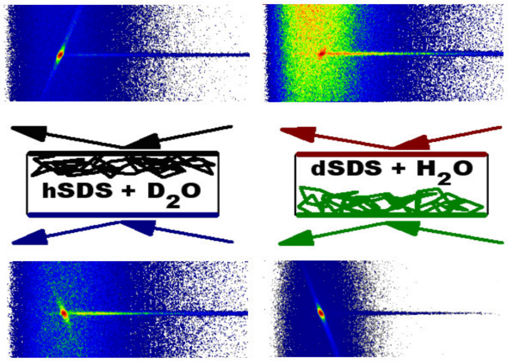
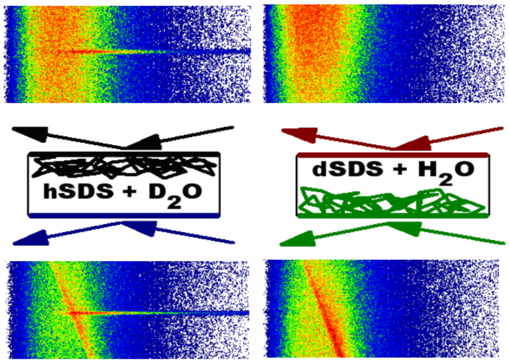


Figure 1. Off-specular scattering measurements where detector images comprising a color map of scattering for reflection angles of ± 1.5° over a wavelength range of 1–10 Å using neutron reflectometry. Samples are PEI/SDS solutions at the solid/liquid interface for fresh hSDS/D_2O (left) and dSDS/H_2O (right) with respect to a surface above the liquid (top) or below the liquid (bottom), where [PEI] = 100 ppm; [SDS] = 1.5 mM; [NaCl] = 0.1 M. **Figure 2.** Photos of the silicon crystals after the experiment described above.

The experiment was then repeated with 2k PEI and 750k PEI on hydrophobic surfaces to mimic and compare the data more closely with those at the air/water interface; here the sample age is 48 hours. The results for the low and high molecular weight polymers are shown in Figures 3 and 4, respectively. The results from the low molecular weight samples were similar to those recorded on a hydrophilic surface (Figures 3 vs 1) with the exception that the surface structure at the top interface for PEI/hSDS/D_2O is not as strong because it takes more than 48 hours for the creaming process of the aggregates to cover the surface comprehensively. The really new results are for the high molecular weight polymer (Figure 4) where surface structure is seen for samples of both isotopic contrasts only on the lower surface. This is an important result as we may now propose a different mechanism to explain multilayer formation in the PEI/SDS system at high pH!





Figures 3 (left). Detector images recorded on Figaro for the same presentation of data as in figure 1 but for 2k PEI on hydrophobic surfaces. **Figures 4 (right).** Detector images recorded on Figaro for the same presentation of data as in figure 1 but for 750k PEI on hydrophobic surfaces.

We may conclude from these data that the accepted explanation for the lack of surface structure at the air/water interface in polymer/surfactant mixtures of high molecular weight – that the complexes formed are sufficiently disordered that there is no discernable surface structure – is at least in part incorrect. Instead it appears that in both isotopic contrasts measured the polymer/surfactant aggregates have sufficiently high density that they sink and the interfacial multilayers are only detected when the solid is below the liquid.

While the implications for free air/water interfaces remain unchanged (the surface structure is absent) we recall that air/water interfaces also exist with the air beneath the water, such as in droplets and foams. An enhanced understanding of the effects of bulk phase separation on the interfacial properties of mixed systems may therefore help to rationalize in the future surprising behavior related to droplets and foam stability where parallel measurements on a free air/water interface alone may not be as relevant as first thought.

Outlook. Having made these exciting findings, the logical next step is to investigate the effect of polyelectrolyte charge density on the interfacial multilayers for the PEI/SDS system. It is reported in the literature that there are no interfacial multilayers for PEI/SDS samples at pH 4, but in principle the bulk aggregates are better ordered. What a conundrum. We propose that bulk aggregation and gravity may explain the detection of interfacial multilayers in this system as well. We need to test the hypothesis that the interfacial multilayers are detected only when aggregates have a higher density when the interactions between the polyelectrolyte and surfactant are greater. Such a finding would cast a very different light on the accepted scientific understanding of interfacial multilayer formation in polyelectrolyte/surfactant systems as bulk aggregation and gravity would need to be considered seriously in a range of different soft matter and biophysical systems. The surface structure of PEI/SDS samples at pH 4 can only be measured with neutron reflectometry and hence a continuation proposal was submitted to Figaro in September 2012.

References.

[1] R. v. Klitzing, Phys. Chem. Chem. Phys., 2006, 8, 5012–5033; [2] Hari Singh Nalwa, Handbook of Polyelectrolytes and their Applications, Vol.1, American Scientific Publishers; 1st edition, 2002; [3] G. Decher, Science, 1997, 277, 1232–1237; [4] J. Penfold et al., Langmuir, 2005, 21, 10061–10073; [5] D. J. F. Taylor et al., Langmuir, 2002, 18, 4748–4757; [6] R. M. Richardson et al., J. Appl. Cryst., 1997, 30, 943–947; [7] R. A. Campbell et al., J Phys Chem B, 2012, 116, 7891; [8] J. Penfold et al., Langmuir, 2007, 23, 3690; [9] S. S. Halacheva et al., Langmuir, 2012, 28, 6336.