Experimental Report

18/02/2015

Proposal:	**TEST-2337**	**Council:**	4/2014
Title:	Polyelectrolyte/surfactant mechanisms		

This proposal is a new proposal
Researh Area:

Main proposer: **VARGA Imre**

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Samples:
Poly (ethylene imine)
Poly (diallyl dimethyl ammonium chloride)
Poly (sodium stryrene sulfonate)
Sodium dodecyl sulfate
Dodecyl trimethyl ammonium - bromide
$D2O$

Instrument	Req. Days	All. Days	From	To
FIGARO	3	5	19/07/2014	20/07/2014
			23/07/2014	24/07/2014
			31/08/2014	02/09/2014
			11/11/2014	12/11/2014

Abstract:

Experimental Report for TEST-2337 on FIGARO

Scientific Background

The structures created by oppositely charged polyelectrolyte/surfactant (P/S) mixtures at the air/water interface have attracted considerable attention over the years [1]. Interest in these systems arises from their common use in consumer products. Langevin described in 1996 an ion exchange model where the number of polyelectrolyte charges at the surface equals the number of surfactant charges as long as the polyelectrolyte is sufficiently flexible [2]. This model implies a compact interfacial structure as indeed it is found in some systems such as poly(diallyldimethyl-ammonium) chloride/sodium dodecyl sulfate (Pdadmac/SDS) [3]. This picture breaks down for more extended polyelectrolytes such as hyperbranched poly(amidoamine) dendrimers/SDS mixtures, which can adopt a surface trilayer structure [4]. In this case the polyelectrolyte is not sufficiently flexible to position all of its charges within the Debye length of the surfactant head groups. A reasonable understanding of the surface structures of the aforementioned mixtures therefore exists.

The focus of this proposal is the system poly(sodium styrene sulfonate)/dodecyltrimethyl-ammonium bromide (NaPSS/DTAB). Its behavior has been shown to be intermediate between that of a flexible linear polyelectrolyte and a bulky hyperbranched polyelectrolyte. For example, even though compact structures are formed in dilute samples, the presence of a surface trilayer was found in more concentrated mixtures [5]. Our recent work on FIGARO has indicated that the structures formed may be even more involved.

Preliminary Investigations

In recent years, we have worked to link the interfacial properties of oppositely charged P/S mixtures to non-equilibrium effects in the bulk. Initially we concentrated on a challenge to rationalize the surface tension behavior [e.g. 6–7] and more recently we have turned to the impact of aggregates penetrating the interfacial layer from the bulk [e.g. 8–9]. Our approach has been to place the interfacial properties into the context of the bulk phase behavior. Last year, we determined the bulk surfactant binding isotherm for DTAB on NaPSS using NMR and we carried out *test-2337* on FIGARO where we turned our attention to the surface structures created in NaPSS/DTAB mixtures. We had time to measure only 4 bulk compositions in up to 4 isotopic contrasts, but even so the range of properties surprised us. The samples involved 100 ppm, 17k NaPSS with different concentrations of DTAB according to the following table. On average the samples took 8–12 hours to equilibrate. We make observations below in relation to the panels on the following page; the axis labels are $RQ^4(Q)$ except where specified in the text below.

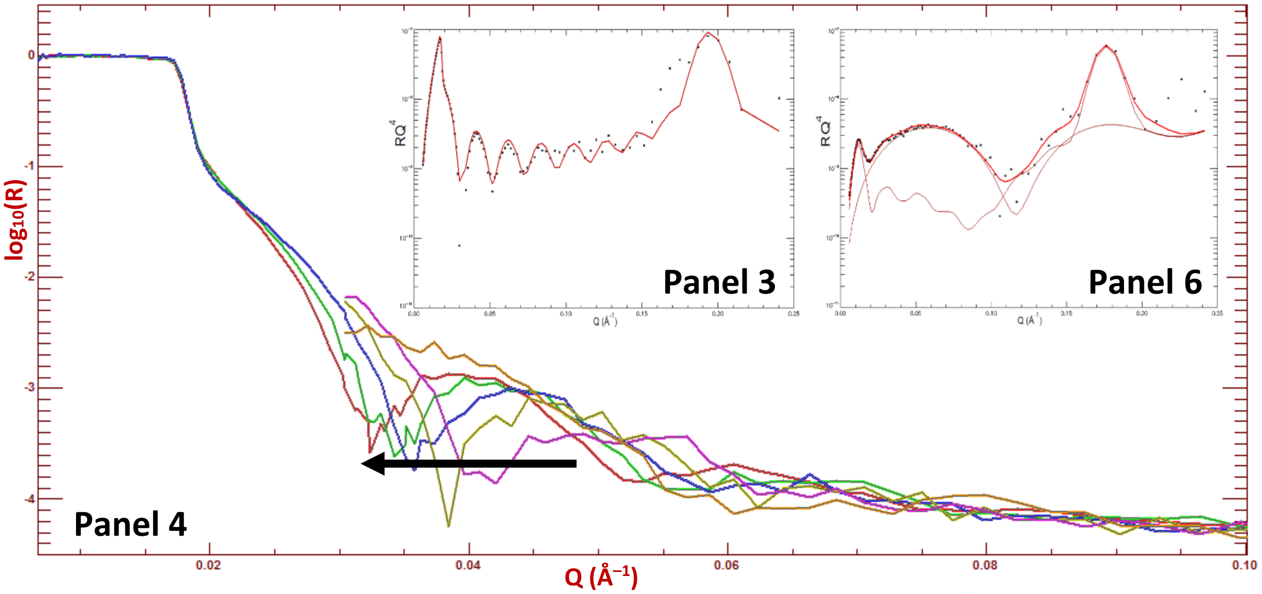
Sample	[DTAB] / mM	Equilibrium phase behavior	State of bulk aggregation
A	0.5	One-phase region	Minimal aggregates
B	1.6	One-phase region	Negative, kinetically-trapped aggregates
C	4.4	Two-phase region	Negative (swollen [10]) aggregates
D	9.0	Two-phase region	Positive (compact [10]) aggregates

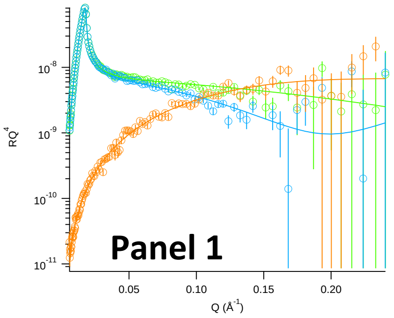
Sample A. The data from the 3 contrasts fit to a compact interfacial structure (panel 1) and there was no Bragg peak or off-specular scattering hinting at more extended structures (panel 2; axes = $2\theta(\lambda)$).

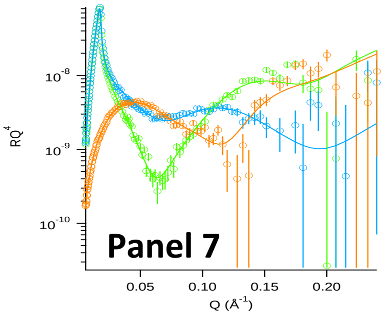
Sample B. Data from the 3 contrasts could not be co-refined indicating that buoyancy of aggregates played a role. The fit to the data in hDTAB/D_2O involved an extended multilayer structure appended to a surface monolayer (panel 3). Interestingly, we succeeded in resolving the kinetics of film formation by the progression of Keissig fringes across Q_z-space with time (black arrow in panel 4; $\log R(Q)$); the fitting is still in progress. The time scales here are: 0.75 hr (orange), 1.5 hr (pink), 2.25 hr (yellow), 3 hr (blue), 5 hr (green) and 12 hr (red). This sample took a full 12 hours to equilibrate. Curiously a double Bragg peak was observed in the data (white arrow in panel 5; axes = 2θ(λ)). To our knowledge such a feature has not previously been observed at a liquid surface. We are working on a model to fit this feature: we have initial indications that an exponential decay of a surface multilayer might work. The lack of off-specular scattering suggests that the surface is homogenous or adsorbed aggregates are smaller than the coherence length. The fit to the data in dDTAB/acmw involved a patch model with different area coverage (panel 6); faint lines mark the different structures.

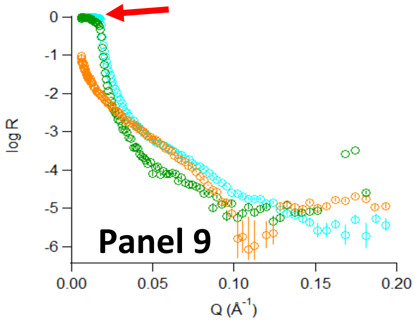
Sample C. These samples fitted to a surface trilayer like that observed in ref. [5] (panel 7). No Bragg peak or off-specular scattering hinting at extended structures was observed (panel 8; axes = 2θ(λ)).

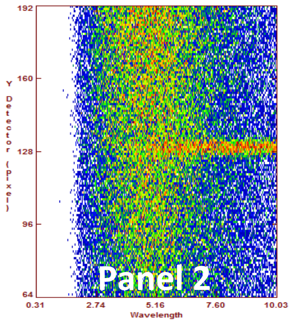
Sample D. This sample exhibited a split critical edge in the data of total reflection (red arrow in panel 9; axes = logR(Q) to emphasize modification of the critical edge), a Bragg diffraction peak and intense off-specular scattering (panel 10; axes = 2θ(λ)) – but only in the contrast with hDTAB/D_2O, which indicated that again buoyancy was significant. These data are qualitatively consistent with the unspecific penetration of compact liquid crystalline aggregates to the interface from the bulk.

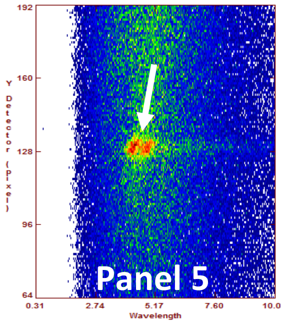


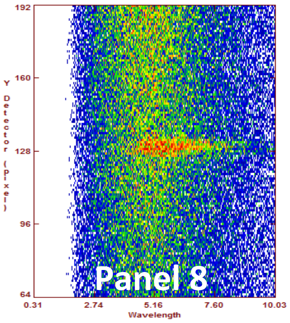


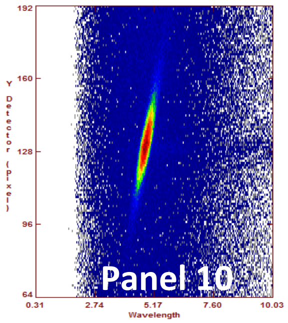












Outstanding Issues

It seems that there is a relation between the rich interfacial structures of NaPSS/DTAB mixtures and the bulk phase behavior. However, this has not been determined unambiguously due to the small number of samples measured and many interesting questions were raised. Why is there a double Bragg peak in samples with negative kinetically-trapped aggregates: are there two types of particles or is there surface rearrangement? Following the creation of macroscopic film why does the thickness arrest at several tens of nanometers, and is this an equilibrium feature that can be tuned by changes in the bulk composition or is it affected by the nature of aggregates formed during mixing which cream to the surface? Why does the sample with more aggregates of negative charge in the equilibrium two-phase region not have a Bragg peak: could it be that the aggregates break down as soon as they reach the surface and if so why is the interfacial film much thinner? For the equivalent sample with positive aggregates why is there the pronounced off-specular scattering? Is it again related to the penetration of aggregates in the surface layer and how is that if the particles have the same charge as the surfactant head groups? This initial study has raised many questions to answer.

We wish to determine if the different features observed at the 4 different bulk compositions studied to date are part of systematic changes of the interfacial structure that can be related to the adsorption properties of the species in solution or specific effects from aggregates, themselves related to equilibrium and non-equilibrium aspects of the bulk phase behavior. To do this we need to carry out a *much more* thorough study than 4 samples, and we propose this investigation for FIGARO.

A beam time proposal was submitted in February 2015 to carry out a comprehensive study on 18 bulk compositions in 3 different isotropic contrasts (dDTAB in D_2O and air contrast matched water + hDTAB in D_2O). As the samples take about 10 hours to equilibrate, and the 6-position changer can be used, we requested 4 days of beam time. These data will complement those already recorded in the bulk (mobility/UV-vis/NMR) and, allowing for some repeats, will enable us to answer some of the questions raised above and publish a comprehensive review of the factors which determine the interfacial structures in oppositely charged P/S systems.

References

[1] D. J. F. Taylor et al. *Adv. Colloid Interface Sci.* **2007**, *132*, 69; [2] A. Asnacios et al. *Macromolecules* **1996**, *29*, 7412; [3] E. Staples et al. *Langmuir* **2002**, *18*, 5147; [4] M. Yanez Arteta et al. *J. Phys. Chem. B* **2014**, *118*, 11835; [5] D. J. F. Taylor et al. *Langmuir* **2002**, *18*, 4748; [6] R. A. Campbell et al. *J. Phys. Chem. B* **2011**, *115*, 15202; [7] Á. Ábraham et al. *Langmuir* **2013**, *29*, 11554; [8] A. Angus-Smyth et al. *Soft Matter* **2013**, *9*, 6103; [9] R. A. Campbell et al. *Langmuir* **2014**, *30*, 8664; [10] K. Pojják et al. *Langmuir* **2011**, *27*, 9139.