Experimental report

29/10/2018

Proposal:	**9-12-487**	**Council:**	10/2016
Title:	Effect of ionic strength on the relation between foam film stability and interfacial composition of polyelectrolyte/surfactant mixtures		
Research area:	Chemistry		

This proposal is a continuation of 9-12-453

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Local contacts:	Richard CAMPBELL

Samples: Deuterated tetradecyltrimethylammonium bromide
Poly(styrene Sulfonate)
deuterated water (D2O)
tetradecyltrimethylammonium bromide

Instrument	Requested days	Allocated days	From	To
FIGARO Adsorption troughs	2	2	08/02/2017	10/02/2017

Abstract:

The stability of foam films in polyelectrolyte/surfactant mixtures determines the efficiency of many of the product formulations we use in our everyday lives including detergents and some foodstuffs. A clear correlation between foam film stability and the surface properties of such mixtures, however, has been missing. Our work on FIGARO has allowed us to relate foam film stability to the changing interfacial composition with respect to the bulk composition - one paper has been published. Recently, we found that not only the interfacial composition but the interfacial structure, and in particular repulsion due to the charge and length scale of the molecules facing the film bulk, to be crucial for foam film stability. Now we have started to extend the project to examine the effect of ionic strength. We have found a strong influence on the interfacial composition and structure with 10^-2 M of inert electrolyte: an extended mixed structure that results in unstable films disappeared. However, we need 2 more days of beam time to complete the study we have started in order to publish a further paper on the effects of ionic strength with respect to the rigidity of the polyelectrolyte.

Report for 2-Day Experiment #9-12-487 on FIGARO:

Effect of ionic strength on the relation between foam film stability and interfacial composition of polyelectrolyte/surfactant mixtures

Scientific Background

Mixtures of polyelectrolytes (PE) and surfactant (S) and their surface properties play an important role in colloidal dispersions (foams, emulsions) e.g. for cosmetics, cleaning products and in food technology[1]. To gain fundamental knowledge about these mixtures, we have used model systems of several polyanions with different hydrophobicity (rather hydrophilic PAMPS vs. more hydrophobic PSS) or with different backbone stiffness (flexible PAMPS vs. rigid $sPSO_2$-220) and the cationic surfactant, tetradecyl trimethyl ammonium bromide ($C_{14}TAB$) in several studies[2,3,4]. For these systems a strong non-monotonic behaviour in the surface tension and the surface elasticity with increasing polyanion concentration (at low fixed surfactant concentration) could be shown[2,3,4]. However, the surface measurements did not coincide with foam film stability. To solve this lack of clarity, NR experiments on FIGARO were carried out to resolve the interfacial composition. For PAMPS/$C_{14}TAB$, these results were used to rationalize the foam film instability[5]. For $sPSO_2$-220/$C_{14}TAB$, a significantly higher surface excess of PE/S complexes was measured, consistent with the lower surface tension[6]. Furthermore, it was revealed that the most stable film is not measured for the strongest adsorption of $sPSO_2$-220/$C_{14}TAB$ complexes but for the highest total ionic strength[4].

To further increase our fundamental knowledge of foam film stability, we chose to investigate an extra variable: the ionic strength. It was chosen because it is well known that the ionic strength plays a major role in the properties of oppositely charged PE/S mixtures[7], and in foam film stabilization[8].

Previous Results

We investigated mixtures of the rigid $sPSO_2$-220 and $C_{14}TAB$. The foam film stability could not be explained in terms of the surface tension[4]. Using NR with two different contrasts of the adsorbed material both in air contrast matched water (ACMW) and benefitting from the high flux at FIGARO, we could resolve the interfacial composition, i.e. the surface excesses of $C_{14}TAB$ and $sPSO_2$-220, respectively (see experimental report #9-12-381). However, it was shown that the results on the interfacial composition were not sufficient to explain the foam film stability. Instead, we found the interfacial structure to be crucial for the explanation[6]. At low $sPSO_2$-220 concentration, the NR experiment revealed a compact structure of a $C_{14}TAB$ monolayer and underneath a $sPSO_2$-220 layer, so that equal charged $sPSO_2$-220 layer facing the film bulk and leading to repulsion and quite stable films. At intermediate $sPSO_2$-220 concentration, there is an extended structure of $C_{14}TAB$ bilayers and mixed $sPSO_2$-220/$C_{14}TAB$ layers facing the film bulk. This leads to a decrease in repulsion or even to weak attraction between the two surfaces and this results in very unstable foam films. For the high $sPSO_2$-220 concentration, also an extended structure was found but containing a $C_{14}TAB$ monolayer and a swollen $sPSO_2$-220 layer of ~ 8 nm. So, repulsion of the negatively charged $sSPO_2$-220 layer occurs and additionally the length scale is sufficient to stabilize in the Common Black Film regime of 20 – 30 nm. This yields in the most stable foam films[6].

We started to investigate the effect of ionic strength on this system by adding inert salts to the mixtures. Starting from low concentrations (10^{-4}, 10^{-3} M LiBr, we choose LiBr as it is the combination of the two counterions of $C_{14}TAB$ and $sPSO_2$-220), the resulting surface excesses showed only minor changes compared to the results without salt. Positively however, a salt concentration of 10^{-2} M showed significant effects (Fig. 1).

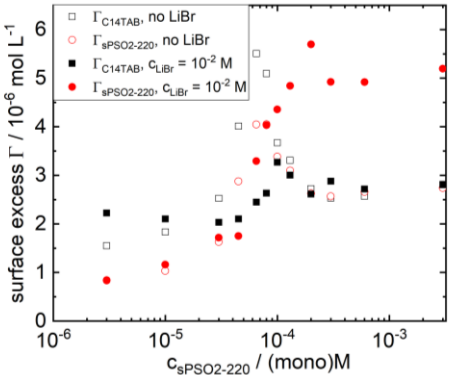

Figure 1. Surface excesses for $sPSO_2$-220/$C_{14}TAB$ mixtures derived from the NR measurements. The closed symbols correspond to a LiBr concentration of 10^{-2} M (data from exp. # 9-12-453). The open symbols correspond to former results of the systems without LiBr (data from exp. # 9-12-381).

At low $sPSO_2$-220 concentration, the surface excesses of PE and S are similar to those without salt, but at intermediate $sPSO_2$-220 concentration, the peak in the surface excesses disappears. At high $sPSO_2$-220 concentration, the surface excess of $sPSO_2$-220 is elevated, and here we may infer the presence of polyelectrolyte loops stabilized by charge screening from the small ions.

Comparing the results of the structural analysis, we found a remarkably changes due to the elevated ionic strength for the intermediate $sPSO_2$-S220 concentration (see Figure 2). The Keissing fringe in the data involving $sSPO_2$-220 + $dC_{14}TAB$ in ACMW vanished, indicating a resolving of the bilayer structure, which we relate to more efficient charge screen of the near-surface monolayer.

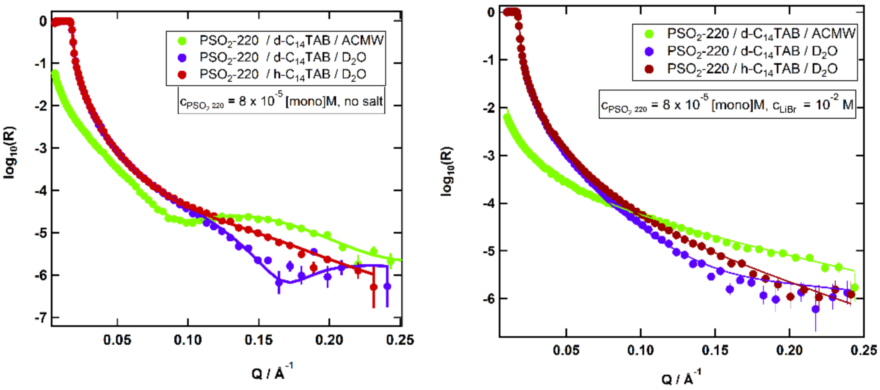

Figure 2. Neutron reflectivity profiles for three contrasts: $sPSO_2$-220 + $dC_{14}TAB$ in D_2O, $sPSO_2$-220 + $hC_{14}TAB$ in D_2O and $sPSO_2$-220 + $dC_{14}TAB$ in ACMW. The bulk surfactant concentration is fixed at a concentration of 10^{-4} M and the polyelectrolyte concentration is 8 x 10^{-5} (mono)M. The solid lines correspond to model fits. **left**: without added LiBr (data from exp. # 9-12-381) **right:** c_{LiBr} = 10^{-2} M (data from exp # 9-12-453).

Recent Results

To continue our work on this project, we measured the interfacial composition and structures of the adsorbed layer of PSS/$C_{14}TAB$ mixtures using NR on FIGARO. The freshly prepared solutions were contained in Teflon troughs with a volume of 25 ml. The variation of ionic strength was achieved by adding the appropriate amount of inert salt (NaBr for PSS, considering the counterions of the polyelectrolyte and the surfactant). The high flux of the instrument combined the TOF analysis allowed us to resolve the interfacial composition of sets of 6 samples in less than six hours each allowing for equilibration. This approach consists of measuring the reflectivity profile only at low Q using just two contrasts: PSS + $dC_{14}TAB$ in ACMW and PSS + contrast matched $C_{14}TAB$ ($cmC_{14}TAB$) in ACMW. Measurements at low Q are insensitive to the structure of the layer and depend only on the scattering excess, which itself depends on the amount of material and its scattering properties. Details to the data analysis for the interfacial composition can be found in the experimental report #9-12-381. Due to our former finding about low added salt concentrations, we here decided only to investigate a high salt concentration (10^{-2} M NaBr). The resulting surface excesses are shown in Fig. 3 (left) together with the results without added salt.

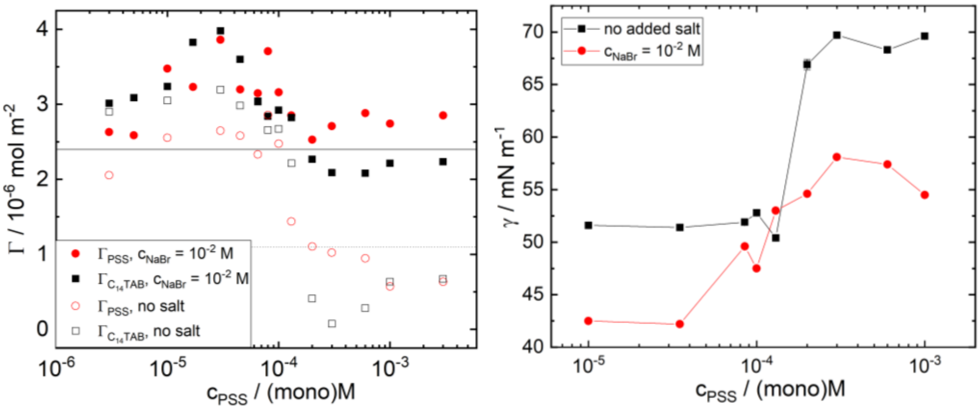

Figure 3 (left). Surface excesses for PSS/$C_{14}TAB$ mixtures derived from the NR measurements. The closed symbols correspond to a NaBr concentration of 10^{-2} M. The open symbols correspond to results of the systems without NaBr (data from exp. # 9-12-381 and the recent). The lines correspond to the surface excess of a pure $C_{14}TAB$ solution at a concentration of 10^{-4} M (dotted: no salt, solid: 10^{-2} M NaBr). **Figure 3 (right).** Surface tension of PSS/$C_{14}TAB$ mixtures with a fixed $C_{14}TAB$ concentration of 10^{-4} M, without added salt (black symbols) and with 10^{-2} M NaBr (red symbols).

As can be seen, at low bulk PSS concentrations, the surface excess of PSS and $C_{14}TAB$ have a quite high value around 3 x 10^{-6} mol/m^2. This is even higher than the surface excess of a pure $C_{14}TAB$ solution (solid black line) demonstrating the strong synergetic binding of PSS and $C_{14}TAB$ at the interface. Increasing the bulk PSS concentration slightly increases both surface excesses until a maximum at 3 x 10^{-5} monoM is reached. Further increase leads to a continuous decrease of the surface excess until at 3 x 10^{-4} monoM PSS a plateau is reached.

Here, the surface excess of C_{14}TAB is below the value of a pure C_{14}TAB solution. Compared to the data without salt, there is a similar behaviour: high surface excess at low bulk PSS concentration, a decrease at intermediate PSS concentration and a constant low excess at high PSS concentration. However, we see an influence of the salt: the surface excesses are mostly lower without salt and the decrease is quite steep. Looking at the surface tension γ of these two systems (Fig 3, right), these changes due to salt can be realised. Both systems have a low surface tension, 42 mN/m and 51 mN/m with 10^{-2} M NaBr and without, respectively at low PSS concentration. At intermediate PSS concentration, there is an increase – indicating a depletion of material from the surface. The depletion of martial can now be seen in the decrease of the surface excess. Corresponding to the different kind of decrease, a steep change in surface tension or a continuous one is found.

Further, we investigate the structure of the absorbed layer for 3 PSS concentrations (1×10^{-5}, 8×10^{-5}, 3×10^{-3} monoM). Therefore, the following two contrasts were necessary: PSS + dC_{14}TAB in D_2O and PSS + hC_{14}TAB (hC_{14}TAB) in D_2O (additional to the already mentioned contrast: PSS + dC_{14}TAB in ACMW). Since low Q measurement are insensitive to the structure, these measurements were carried out over the full Q range (0.01 – 0.25 Å^{-1}). The three reflectivity curves were co-refined, assuming no structural difference due to the different contrasts while holding the resulting surface excesses constant to the values of the compositional analysis. The reflectivity curves and primary fits can be seen in Fig 4.

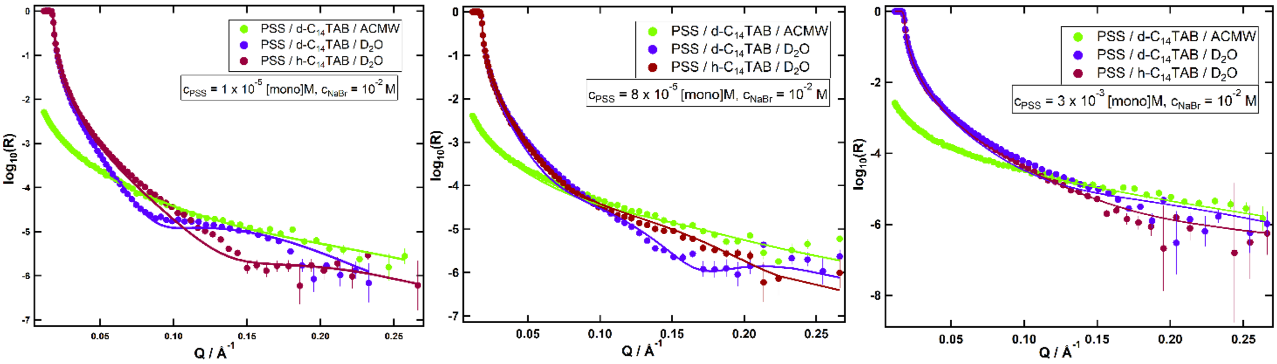

Figure 4. Neutron reflectivity profiles for the three contrasts: PSS + dC_{14}TAB in D_2O, PSS + hC_{14}TAB in D_2O and PSS + dC_{14}TAB in ACMW. The bulk surfactant concentration is fixed at a concentration of 10^{-4} M and the bulk NaBr concentration is fixed at a concentration of 10^{-2} M. The solid lines correspond to model fits.
left: $c_{PSS} = 1 \times 10^{-5}$ (mono)M. **middle** $c_{PSS} = 8 \times 10^{-5}$ (mono)M **right:** $c_{PSS} = 3 \times 10^{-3}$ (mono)M.

Although the fits are still primary, for all regimes the same structure model could be used: a monolayer of C_{14}TAB at the air/water-interface and underneath a swollen (solvent penetration < 50 %) PSS layer. So, compared to $sPSO_2$-220, we find no remarkable different structures for the three PSS regimes. Particular, no extended structure such as bilayer or vesical formation is suggested by the reflectivity data. This might be explained by the different stiffnesses of the polyelectrolytes. $sPSO_2$-220 with an intrinsic persistence length of around 20 nm[4] is much stiffer than PSS with a persistence length of around 1 nm[9]. This leads to a flat, less coiled and less swollen adsorbed polyelectrolyte layer, which might enhance the formation of bilayers[4].

Summary

We used FIGARO to investigate mixtures of the flexible PSS and C_{14}TAB with a high salt concentration (10^{-2} M NaBr). For a high PSS bulk concentration, we find a depletion of material from the surface, which correlate to the surface tension measurements. The structural measurements showed no evidence for a bilayer formation. Instead, the reflectivity curves suggest a C_{14}TAB monolayer and underneath a swollen PSS layer.

References

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