Experimental report

15/09/2016

Proposal: **9-12-453**

Council: 4/2016

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 9-12-381

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Samples: Deuterated tetradecyltrimethylammonium bromide
deuterated water (D2O)
tetradecyltrimethylammonium bromide
Sulfonated Poly(phenylene sulfone)
Poly(acrylamido methyl propanesulfonate sodium salt) (PAMPS)
lupin protein isolate

Instrument	Requested days	Allocated days	From	To
FIGARO Adsorption troughs	5	4	13/07/2016 24/08/2016	16/07/2016 26/08/2016

Abstract:

The stability of foam films in polyelectrolyte/surfactant mixtures determines the efficiency of many of the product formulations we use in our everyday life including cleaning products and foodstuffs. A clear correlation between foam film stability and the surface tension of such mixtures, however, has been badly missing. Our recent work on FIGARO has related the foam film stability to the changing interfacial composition with respect to the bulk composition - one paper was published and another manuscript is in preparation. Indeed on FIGARO the interfacial composition can now be resolved with much higher precision than ever before by exploiting its 'low Q analysis' approach. Therefore now we propose to exploit this capability by extending the project to examine the effects of ionic strength on the two systems studied to date - one involving a rather flexible and the other a rather stiff polyelectrolyte - and a plant protein. These precise and efficient measurements should allow us to extend the parameter space significantly by understanding the relation between foam film stability and the bulk/interfacial compositions with respect to the ionic strength for the first time.

Report for 4-Day Experiment #9-12-453 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. 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[6].
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 (Figure 1)[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. In order to resolve the interfacial structure, NR measurements of two additional contrasts over the full Q range are necessary. These data were co-refined together with one ACMW data set (Figure 2) to resolve the locations of PE and S in the interfacial arrangement.

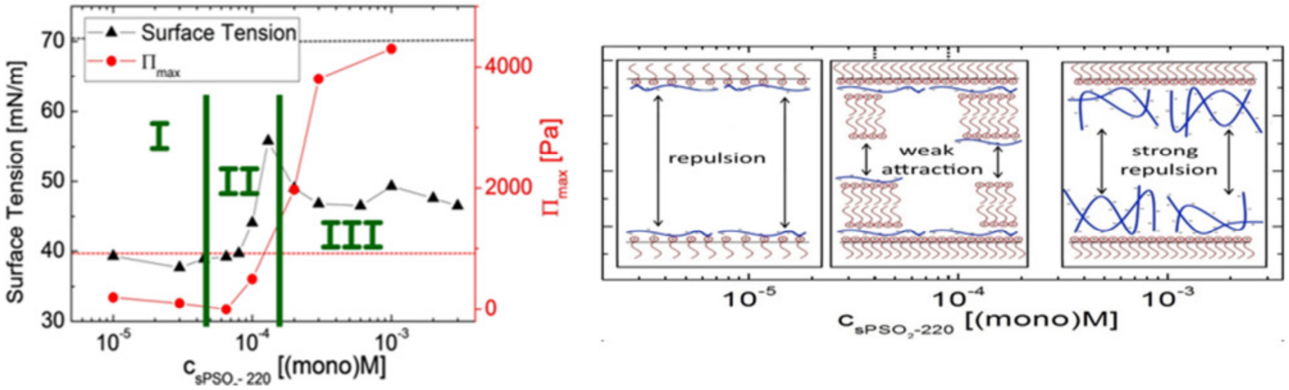

Figure 1 (left). Surface tension and maximum disjoining pressure Π$_{max}$ before film rupture of sPSO$_2$-220/C$_{14}$TAB mixtures with fixed C$_{14}$TAB concentration (10^{-4} M) and variable sPSO$_2$-220 concentration. The dashed lines correspond to the surface tension and Π$_{max}$ of pure C$_{14}$TAB at 10^{-4} M. **Figure 1 (right).** Schematic of the interfacial structures at the three concentration regimes

Out of the fits, the number of layers, length scales and charges can be resolved. With these, we were able to explain the different foam film stability of sPSO$_2$-220/C$_{14}$TAB mixtures[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 (Figure 1, right). 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].

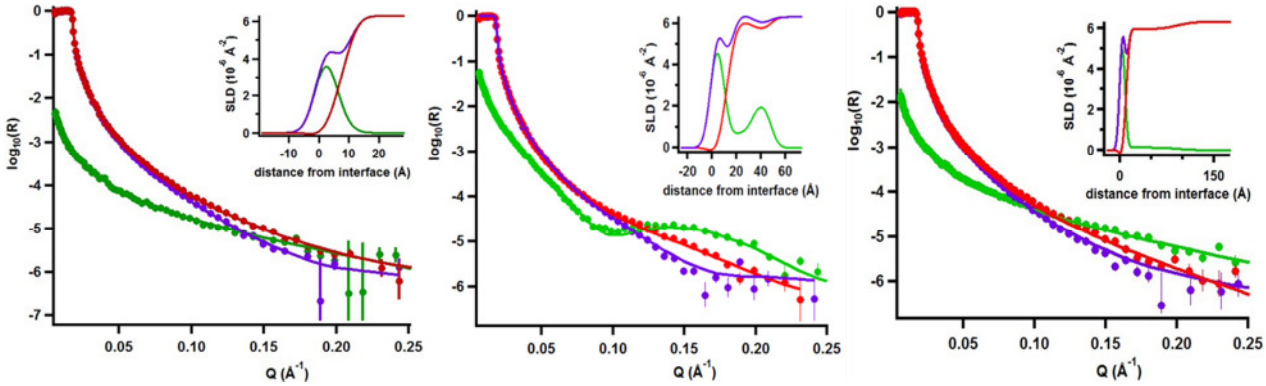

Figure 2. Neutron reflectivity profiles for the three contrasts: hydrogenous $sPSO_2$-220 ($hsPSO_2$-220) + deuterated $C_{14}TAB$ ($dC_{14}TAB$) in D_2O, $hsPSO_2$-220 + hydrogenous $C_{14}TAB$ ($hC_{14}TAB$) in D_2O and $hsPSO_2$-220 + $dC_{14}TAB$ in ACMW. The bulk surfactant concentration is fixed at a concentration of 10^{-4} M .The solid lines correspond to model fits. **left**: $c_{sPSO_2\text{-}220} = 1 \times 10^{-5}$ (mono)M. **middle** $c_{sPSO_2\text{-}220} = 8 \times 10^{-5}$ (mono)M **right:** $c_{sPSO_2\text{-}220} = 3 \times 10^{-3}$ (mono)M.

Recent Results

The interfacial composition and structure of the adsorbed layer was measured 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 (LiBr for $sPSO_2$-220 and NaBr for PSS, considering the different counterions of the polyelectrolytes). 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: $hsPSO_2$-220 + $dC_{14}TAB$ in ACMW and $hsPSO_2$-220 + 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. We started with a low salt concentration of 10^{-4} M. Details to the data analysis for the interfacial composition can be found in the experimental report #9-12-381.

The resulting surface excesses showed only minor changes compared to the results without salt. Unfortunately, a following increase to a salt concentration of 10^{-3} M, led to the same result, which meant that the full aims of this experiment were not completed. Positively however, a salt concentration of 10^{-2} M showed a significant effect (Figure 3).

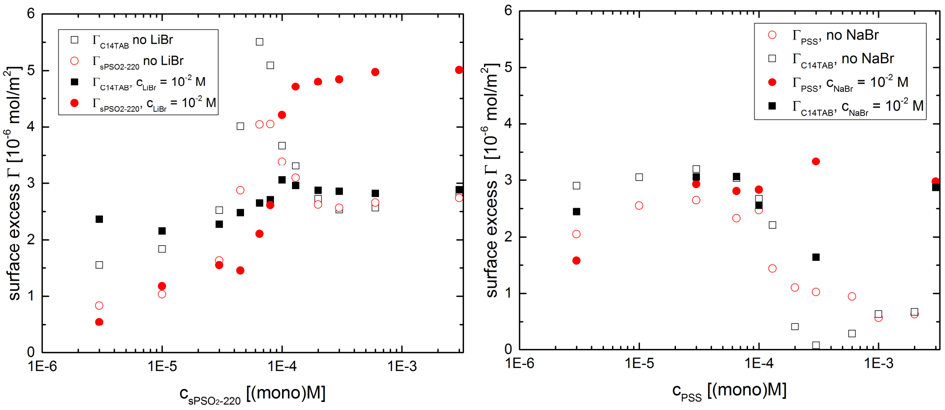

Figure 3. Surface excesses for $sPSO_2$-220/$C_{14}TAB$ mixtures (**left**) and PSS/$C_{14}TAB$ mixtures (**right**) derived from the NR measurements. The closed symbols correspond to the current results and a LiBr concentration of 10^{-2} M. The open symbols correspond to former results of the systems without LiBr (data from exp. # 9-12-381).

For both compounds, at low $sPSO_2$-220 concentrations, the surface excesses are similar to those without salt. But the former observed peak in surface excess for $C_{14}TAB$ is only weakly pronounced for a LiBr concentration of 10^{-2} M. At high $sPSO_2$-220 concentrations the surface excesses of $C_{14}TAB$ is again similar to those without salt. For $sPSO_2$-220, the peak in surface excess is vanished; instead the surface excess increases with increasing $sPSO_2$-220 concentration until a plateau at around 5×10^{-6} mol/m^2 is reached.

Contrary to the other salt concentrations (0, 10^{-4} and 10^{-3} M), at 10^{-2} M there is a higher amount of sPSO$_2$-220 present at the surface than C$_{14}$TAB for high sPSO$_2$-220 concentrations.

On the basis of this significant change in surface excess due to a salt concentration of 10^{-2} M, we further investigated the structure of the adsorbed layer for this condition. Therefore, the following two contrasts were necessary: hsPSO$_2$-220 + dC$_{14}$TAB in D$_2$O and hsPSO$_2$-220 + hC$_{14}$TAB (hC$_{14}$TAB) in D$_2$O (additional to the already mentioned contrast: hsPSO$_2$-220 + dC$_{14}$TAB in ACMW). Since low Q measurement are insensitive to the structure, this measurements were carried out over the full Q range (0.01 – 0.25 Å^{-1}) (Figure 4).

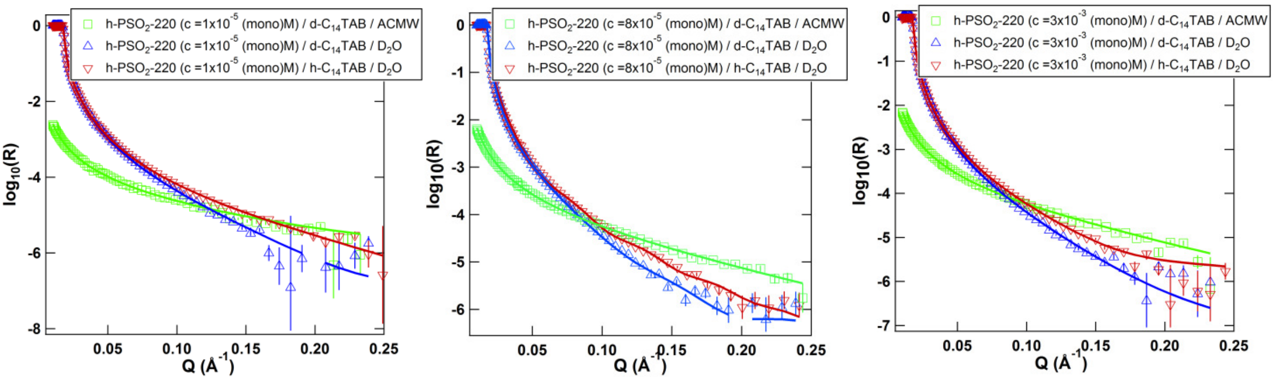

Figure 4. Neutron reflectivity profiles for the three contrasts: hsPSO$_2$-220 + dC$_{14}$TAB in D$_2$O, hsPSO$_2$-220 + hC$_{14}$TAB in D$_2$O and hsPSO$_2$-220 + dC$_{14}$TAB in ACMW. The bulk surfactant concentration is fixed at a concentration of 10^{-4} M and the bulk LiBr concentration is fixed at a concentration of 10^{-2} M. The solid lines correspond to model fits. **left**: $c_{sPSO_2\text{-}220} = 1 \times 10^{-5}$ (mono)M. **middle** $c_{sPSO_2\text{-}220} = 8 \times 10^{-5}$ (mono)M **right:** $c_{sPSO_2\text{-}220} = 3 \times 10^{-3}$ (mono)M.

Comparing the reflectivity profiles to those without salt (Figure 2) reveals, especially for intermediate PE concentration, significant and interesting changes due to the elevated ionic strength. The Keissing fringe in the data involving S + dC$_{14}$TAB in ACMW vanished, indicating a reduction in the complexity of the interfacial structure of the adsorbed layer. Indeed the structural fits are still being developed. Nevertheless, the data clearly show the significant influence of the increased ionic strength on the interfacial structure.

After discovering the remarkable influence of the high salt concentration on the interfacial composition and structure, we further investigated the second system: PSS/C$_{14}$TAB-mixture. We succeeded to measure six different PSS concentrations, each in two contrasts to resolve the interfacial composition (Figure 4, right). At low and intermediate PSS concentrations the surface excesses are quite similar to the data without salt, but at high PSS concentrations, the decrease in surface excesses for PSS is vanished.The data show an equally surprising influence of the salt as for sPSO$_2$-220. However the data are not complete as we ran out of time to complete the experiment. More importantly, the data for the structure are still missing.

Summary

We used FIGARO to investigate mixtures of the rigid sPSO$_2$-220 and C$_{14}$TAB with different salt concentration. Unexpectedly, we found nearly no influence for salt concentrations of 10^{-4} and 10^{-3}. In contrast, we found significant changes in both the interfacial composition and structure for a salt concentration of 10^{-2} M. We have already started to expand the NR measurements to mixture of the more flexible PSS and C$_{14}$TAB for the high salt concentration. Those results will be correlated to the on-going measurements of foam film stability of the mixtures. To complete the compositional and structural measurements on PSS/C$_{14}$TAB for publication, we would need to continue our work on FIGARO. This would allow us to increase our fundamental knowledge about foam film stability and reveal the influence of the ionic strength for different systems while publishing third FIGARO paper in this project.

References

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