Experimental report

04/02/2016

Proposal:	**9-12-381**	**Council:**	10/2014
Title:	Understanding the properties of mixtures of rigid polyelectrolytes and surfactants at the air-water interface		
Research area:	Soft condensed matter		

This proposal is a new proposal

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Local contacts:	Richard CAMPBELL

Samples:
deuterated water (D2O)
tetradecyltrimethylammonium bromide
Sulfonated Poly(phenylene sulfone)
tetradecyltrimethylammonium bromide (deuterated)

Instrument	Requested days	Allocated days	From	To
FIGARO Adsorption troughs	3	3	24/07/2015	27/07/2015

Abstract:

The surface properties of polyelectrolyte (PE)/surfactant mixtures play an important role in the performance and stability of lots of colloidal dispersions in common consumer products (e.g. foams and emulsions). The interfacial composition and structure of flexible PE/surfactant mixtures have been investigated extensively over the years using neutron reflectivity (NR) measurements. We have recently completed a study on the relation between the interfacial composition and the foaming properties of a mixture involving a very flexible PE, PAMPS/C14TAB. Insight into the complex correlations was gained, but the influence of the polymer chain conformation on the surface properties and foam stability is not yet clear. Thus, we propose to build on the findings of the former studies by investigating the interfacial composition and structure of a rigid PE/surfactant mixture on FIGARO. The system is question is sulphonated poly(phenylene sulfone) (S220)/C14TAB mixtures: S220 is stiffer than in PAMPS but it has the same headgroup. We have complementary data on the system already, but the correlations with the interfacial composition are missing.

Report for 3-Day Experiment #9-12-381 on FIGARO:

Understanding the properties of mixtures of rigid polyelectrolytes and surfactants at the air-water interface

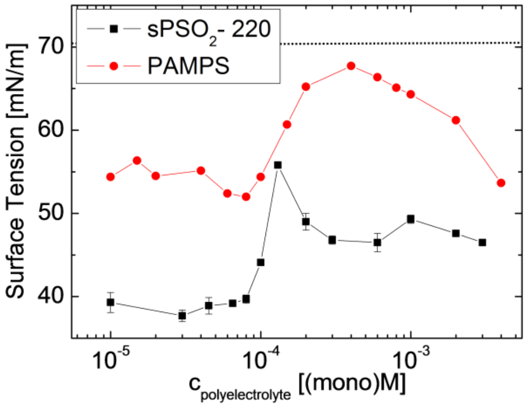
Scientific Background

Polyelectrolyte (PE)/surfactant mixtures and their surface properties play an important role in colloidal dispersions (foams, emulsions) e.g. for cosmetics, cleaning products and in food technology[1]. In former studies we used a model system of a flexible polyanion, poly(acrylamidomethyl propanesulfonate) sodium salt (PAMPS) and a cationic surfactant, tetradecyl trimethyl ammonium bromide ($C_{14}TAB$)[2]. A strong non-monotonic behavior in both the surface tension and surface elasticity with increasing polyanion concentration (at a fixed low surfactant concentration) was observed. However, the results of the surface measurements did not directly coincide with the foam film stability[2]. This lack of clarity was solved using neutron reflectometry (NR) experiments on FIGARO which showed surfactant depletion, at certain polyanion concentrations, which were used to rationalize the foam film instability[3].

However, for foam films it is not fundamentally clear to what extent the adsorbed amount or surface charge of material (related to the hydrophobic/hydrophilic balance) or the electrostatic interaction between two opposing macroscopic surfaces in the thin film (related to the charge ratio in the complex) play a role in stabilisation. A reason for this lack of clarity might be the polyanion chain conformation. Therefore, it was proposed to carry out comparable studies on $C_{14}TAB$/rigid polyanion mixtures. So far, only very few studies have been carried out, which determined the film properties of PE/surfactant mixtures using a PE with a rigid backbone[4], but no correlation with surface properties has been investigated.

Preliminary Investigations

The rigid PE we chose is sulfonated poly(phenylenesulfone) ($sPSO_2$-S220), which is a relatively new synthetic PE. It is of high scientific interest as it shows high thermal, thermooxidative and hydrolytic stabilities[5]. In this work it is a model system for similar synthetic rigid polyelectrolytes. In comparison to the former studied PAMPS it is stiffer, but it has the same charged group, i.e. a sulfonate group.



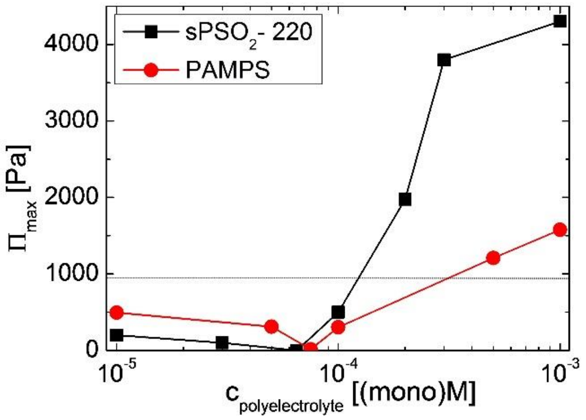


Figure 1 (left). Surface tension of $sPSO_2$-220/$C_{14}TAB$ solutions with fixed $C_{14}TAB$ concentration (10^{-4} M) and variable $sPSO_2$-220 concentration. For comparison the surface tension of the respective PAMPS/ $C_{14}TAB$ mixtures is added[3]. The dashed line corresponds to the surface tension of pure $C_{14}TAB$ at 10^{-4} M.

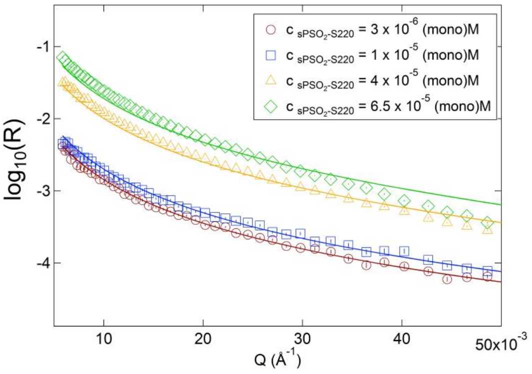
Figure 2 (right). The maximum disjoining pressure Π_{max} before film rupture versus respective polyelectrolyte concentration for $sPSO_2$-220/$C_{14}TAB$ films in comparison to PAMPS/ $C_{14}TAB$ films [3].The dashed line corresponds to the stability of a pure $C_{14}TAB$ film at 10^{-4} M.

We conducted surface tension and foam film stability experiments to get an insight into the surface adoption and foam film stability of $sPSO_2$-S220/$C_{14}TAB$ mixtures. In all experiments the surfactant concentration was kept constant at 10^{-4} M and the polyelectrolyte concentration was varied. It can be seen that in comparison to PAMPS/C_{14}TAB the surface tension for $sPSO_2$-S220/C_{14}TAB mixtures is strongly reduced, indicating a stronger synergistic effect. Also the foam film stability is significantly higher for $sPSO_2$-S220/C_{14}TAB mixtures. To get a better understanding of the reasons for enhanced adsorption and better film stability for $sPSO_2$-S220/C_{14}TAB, we conducted NR experiments using FIGARO.

FIGARO Results

The interfacial composition of the layers was measured using NR on FIGARO. The solutions were contained in Teflon troughs with a volume of 45 ml. The high flux of the instrument combined with the TOF analysis allowed us to resolve the interfacial composition of sets of 6 samples in less than eight hours each allowing for equilibration. This approach consists of measuring the reflectivity profile only at low Q using just two contrasts: hydrogenous $sPSO_2$-220 + deuterated C_{14}TAB (d C_{14}TAB) in air contrast match water (ACMW) and hydrogenous $sPSO_2$-220 + contrast match C_{14}TAB (cm C_{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 is a convolution of the amount of material and its scattering properties.

Examples of the data from the 2 contrasts can be seen in Figure 3 and 4.



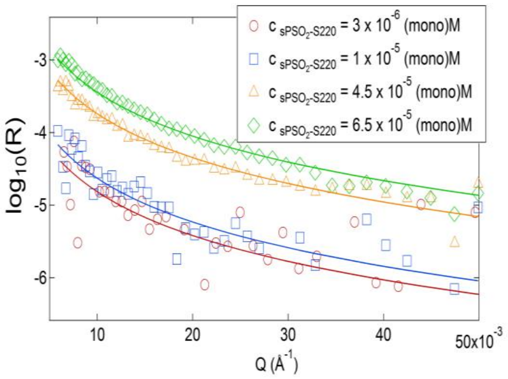


Figure 3 (left). Neutron reflectivity profiles for solutions prepared from $sPSO_2$-220 and dC_{14}TAB in ACMW. The bulk dC_{14}TAB concentration for the mixtures is fixed at a concentration of 10^{-4} M. In this contrast, the reflectivity is dominated by the dC_{14}TAB. The solid lines correspond to model fits. **Figure 4 (right).** Neutron reflectivity profiles for solutions prepared from $sPSO_2$-220 and cmC_{14}TAB in ACMW. This contrast is sensitive only to $sPSO_2$-220 at the interface. The solid lines correspond to model fits.

The scattering excess is then converted to surface excess by solving the following linear equations:

$$(\sigma \cdot d)_1 = \mathrm{N_A}.(\Gamma_{\mathrm{surf}} \cdot b_{\mathrm{i,d-surf}} + \Gamma_{\mathrm{poly}} \cdot b_{\mathrm{i,poly}})$$

$$(\sigma \cdot d)_2 = \mathrm{N_A}.\,\Gamma_{\mathrm{poly}} \cdot b_{\mathrm{i,poly}}$$

Here the product $\sigma \cdot d$ is the fitted product of the scattering length density and layer thickness of a uniform layer at the air/water interface, b_i is the scattering length of the molecule and N_A is Avogadro's number. The results are given in Figure 5.

The strong synergistic effect of $sPSO_2$-S220/C_{14}TAB mixtures seen in surface tension measurements is in accordance with the measured surface excesses. For all mixtures the surface excess of C_{14}TAB is higher than the surface excess of pure C_{14}TAB at 10^{-4} M. The strongest surface excess of both compounds is reached slightly below the isoelectric point (IEP). Here the measured surface excess of C_{14}TAB at 10^{-4} M is even higher than the surface excess of C_{14}TAB at the cmc, indicating a very strong synergistic effect. Interestingly, it is not possible to form foam films for this mixture. The surface excess ratio surfactant/polyelectrolyte was decreasing with increasing polyelectrolyte concentration. Close to the IEP a ratio of one to one was reached, as predicted by Langevin et al[7]. At this surfactant/ polyelectrolyte ratio of 1 foam films are especially stable.

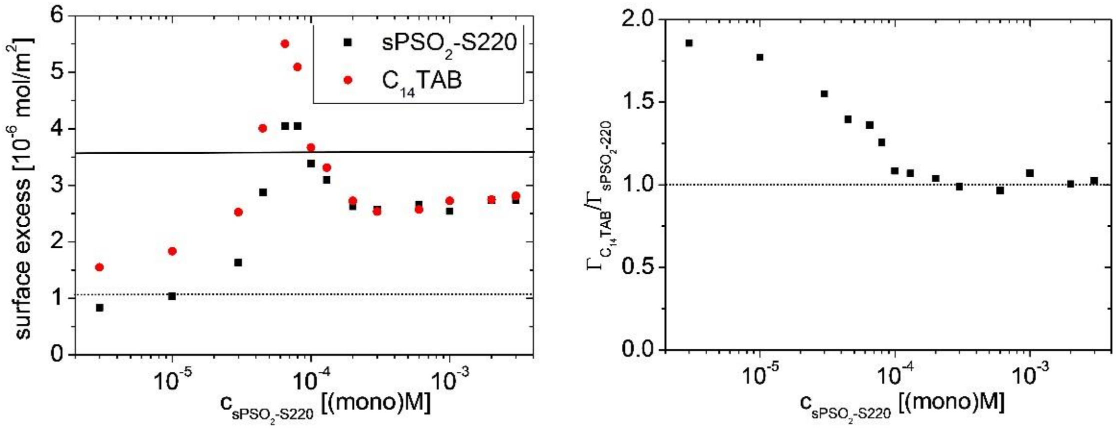


Figure 3 (left). Surface excess for the sPSO$_2$-220 / C$_{14}$TAB mixtures derived from the NR measurements. For all mixtures investigated, the concentration of C$_{14}$TAB is fixed at 10^{-4} M, while the concentration of sPSO$_2$-220 is varied. The lower dotted line corresponds to the surface excess of a pure C$_{14}$TAB solution at a concentration of 10^{-4} M. The upper solid black line correspond to the surface excess of a pure C$_{14}$TAB solution at the cmc (3.5 x 10^{-3} M). **Figure 6 (right).** The ratio of C$_{14}$TAB surface excess Γ_{C14TAB} in relation to sPSO$_2$-220 surface excess $\Gamma_{sPSO2\text{-}S220}$. The dotted line corresponds of a surface excess ratio of 1:1.

In the remaining beam time, similar experiments as for sPSO$_2$-220/C$_{14}$TAB mixtures were carried out for poly(styrene sulfonate)(PSS)/ C$_{14}$TAB mixtures. With the experimental results it was possible to explain the inability of this mixture to form stable foam films[6], as the system showed strong depletion of both surfactant and polyelectrolyte.

Summary

We used FIGARO to investigated mixtures of the rigid polyelectrolyte sPSO$_2$-S220 and C$_{14}$TAB. We found a strong synergistic adsorption of both compounds with surface excess strongly dependent on the polyelectrolyte concentration. The results are correlated to former findings about foam film stability and help to explain the increased foam film stability for sPSO$_2$-S220/C$_{14}$TAB in comparison to PAMPS/C$_{14}$TAB mixtures. Further work is now required on a range of systems to investigate other variables in addition to the rigidity of the polyelectrolyte, e.g., ionic strength from inert electrolyte and temperature. In addition to the 2015 paper in this project by Fauser et al. (ref 3), a manuscript based on the new data from FIGARO is now in an advanced stage of preparation.

References

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