Experimental Report

14/10/2014

Proposal:	**TEST-2326**	**Council:**	10/2012
Title:	Polymer/surfactant mixtures		

This proposal is a new proposal

Researh Area:

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Experimental Team: FAUSER Heiko

Local Contact: CAMPBELL Richard

Samples: Poly (2-Acrylamido-2-Methylpropane sulfonic acid)
tetradecyl trimethyl ammonium bromide

Instrument	Req. Days	All. Days	From	To
FIGARO	1	1	06/08/2013	07/08/2013

Abstract:

Final Report for FIGARO Experiments #9-12-279 & TEST-2326

Summary

Two FIGARO experiments were carried out in this project: #9-12-279 (3 days) in October 2011 and the follow-up TEST-2326 (1 day) in August 2013. The work concerned elucidation of the interfacial composition of the polyelectrolyte/surfactant mixture poly(acrylamidomethylpropane sulfonate sodium salt)/tetradecyltrimethylammonium bromide (PAMPS/C_{14}TAB) and its relation to previous data on the foam film properties. A low bulk surfactant concentration was used so that the samples did not precipitate. The interfacial composition was determined using three different methods: full-Q neutron reflectometry (NR) analysis, low-Q NR analysis and combined NR/ellipsometry analysis. It was the first time the three methods had been used in parallel to optimize the precision of the analysis. We rationalized a peak in surface tension in terms of the changing surface composition related to changes in the ionic strength at high bulk polyelectrolyte concentrations. The comparison between the determined surface excess with the zeta potential and foam stability elaborated on a previous hypothesis that the stability of electrostatically stabilized CBFs arises not only from the properties surface layer but also from an additional contribution of the polyelectrolyte in the film bulk. This work was submitted for publication in *J. Phys. Chem. B* on 23rd September 2014 in a manuscript titled "Surface Adsorption of Oppositely Charged C_{14}TAB-PAMPS Mixtures at the Air/Water Interface and the Impact on Foam Film Stability" and at the time of writing is under peer review.

Introduction

Oppositely charged polyelectrolyte/surfactant mixtures exhibit rich phase behavior which has been extensively studied. The interfacial properties however are much less understood. Nevertheless, it is crucial to know the adsorption behavior of these mixtures in order to understand the foaming properties of these systems. Surface tension and elasticity measurements are the main tools to characterize the surface layer. However, these measurements are sometimes not sufficient to explain, for example, the stability of a foam film lamella. Furthermore, such techniques provide no information about structure and composition of the adsorbed layer. The interactions and are mainly driven by the gain in entropy due to the release of counterions. This leads to the formation of complexes which can be very hydrophobic, depending on the polyelectrolyte/surfactant ratio. Therefore, the ratio of the polyelectrolyte/surfactant mixtures can be used as a tool to control the adsorption of the aggregates at the film interfaces and related with the foam film stability.

A recent foam film study of oppositely charged polyelectrolyte/surfactant mixtures has shown that the foam film stability strongly depends on the net charge of the formed polyelectrolyte/surfactant complexes [*J. Phys Chem B*, **2009**, *113*, 7986]. With decreasing charge, the foam film stability (represented by the maximum surface pressure on a thin film balance, π_{max}) is reduced until the isoelectric point (IEP) is reached (cf. Fig. 1A). At this point, the charges of the polyelectrolyte are all compensated and the foam films can no longer be stabilized by electrostatic repulsion of the interfaces. When the polyelectrolyte concentration is further increased, the foam film stability rises again. However, the surface tension and elasticity data give no evidence for a charge reversal at the air/water interface. On the contrary, they indicate a depletion of complexes from the interface above the IEP indicated by a rise in the surface tension (Fig. 1B). At higher polyelectrolyte concentrations a decrease in surface tension is observed, while the film stability further increases. The stabilization mechanism therefore was unclear and motivated the current experiments on FIGARO.

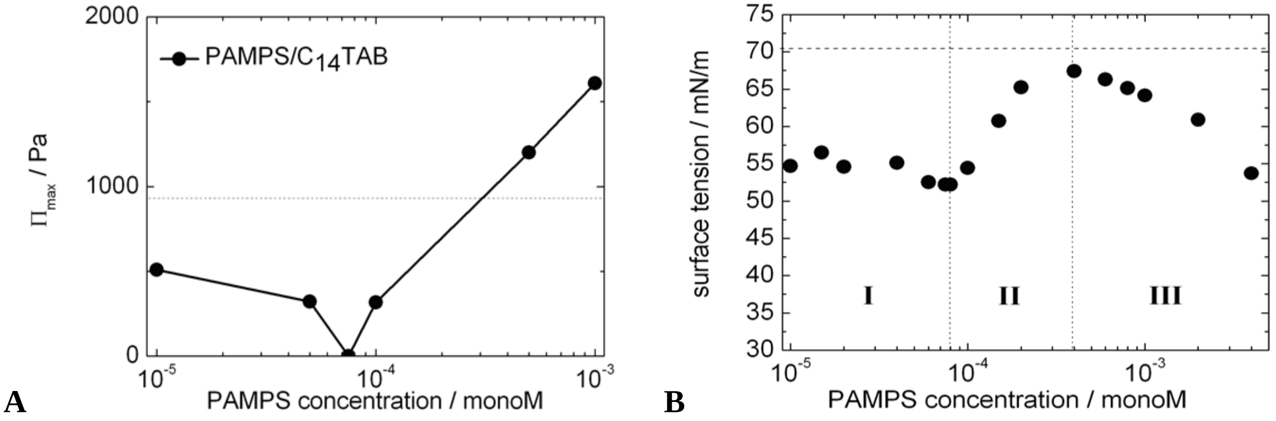

***Fig. 1:* *(A)* Maximum stability of foam films at different polyelectrolyte/surfactant mixtures with a bulk C_{14}TAB concentration fixed at 10^{-4} mol/l; π_{max}: highest pressure that can be applied before the film ruptures. *(B)* Surface tension of the corresponding polyelectrolyte/surfactant solutions.**

Results

Freshly mixed PAMPS/C_{14}TAB mixtures were measured in different isotopic contrasts using NR on FIGARO. For example, NR data from mixtures of PAMPS with dC_{14}TAB in ACMW are shown in Fig. 2A. In this case the contribution of the solvent to the specular reflection is negligible and that of the polyelectrolyte is small, so the signal arises mainly from scattering by the deuterated surfactant in the monolayer. The data indicate a minimum in the surfactant surface excess at the isoelectric point, i.e., 10^{-4} (mono)mol/l. NR data from mixtures of PAMPS with cmC_{14}TAB in ACMW are shown in Fig. 2B. In this case the contributions of the solvent and surfactant to the specular reflection are negligible and the signal arises mainly from scattering by the polyelectrolyte in the monolayer. Interestingly, a maximum in the polyelectrolyte surface excess coincides with the isoelectric point.

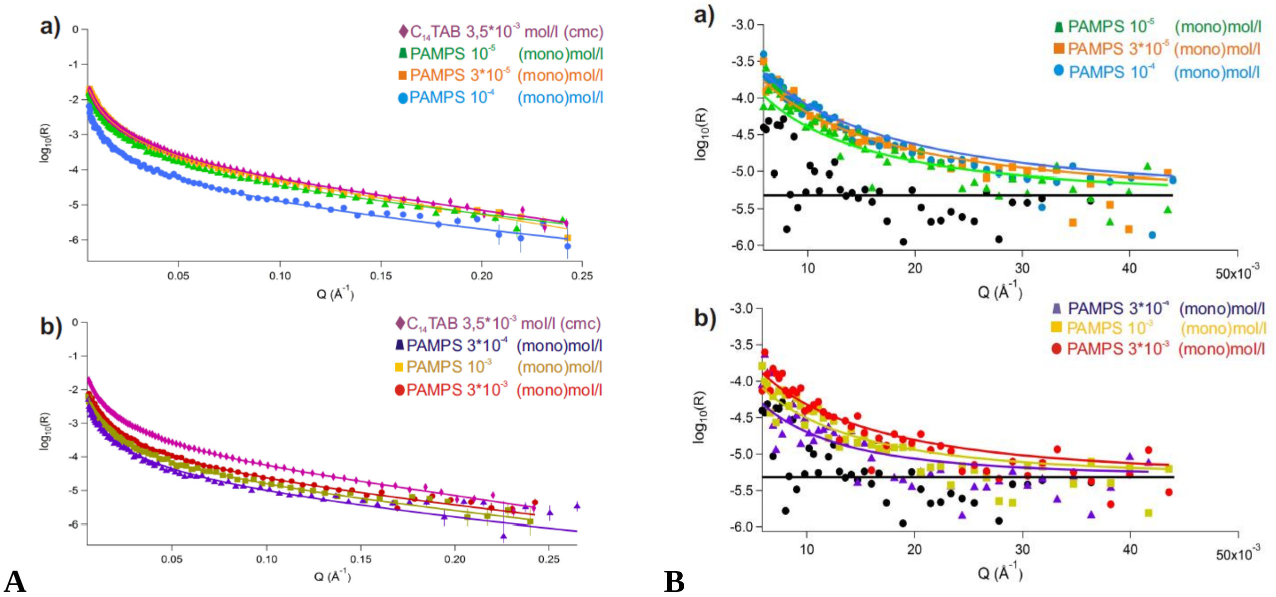

Fig. 2: *Neutron reflectivity profiles for solutions prepared from hPAMPS and **(A)** dC14TAB and in ACMW and **(B)** cmC_{14}TAB in ACMW. The bulk surfactant concentration for the mixtures was fixed at 10^{-4} mol/l. The reflectivity is dominated by the surfactant in contrast A and the polyelectrolyte in contrast B. The solid lines correspond to model fits.*

Ellipsometry measurements were also made of the mixtures, which are shown in Fig. 3A. The three different analysis methods were then applied to determine the interfacial composition. The averaged values are shown in Fig. 3B. At the two lowest bulk polyelectrolyte concentrations there are equivalent amounts of polyelectrolyte and surfactant at the interface. This can be rationalized in terms of stoichiometric binding of anionic groups in the polyelectrolyte to the cationic head groups of surfactant in the near-surface monolayer. At the isoelectric point, the surface excess of surfactant falls dramatically while the amount of polyelectrolyte at the interface remains high. This can be attributed to the increasing negative charge of the complexes formed in the bulk. As PAMPS is not surface active alone, the interfacial polyelectrolyte structure must involves loops with a reduced degree of binding at the interface. A further increase of the bulk polyelectrolyte concentration results also in its depletion from the interfacial layer although it is still present in an excess which shows that the polyelectrolyte binding to the surfactant remains weak and loops are present.

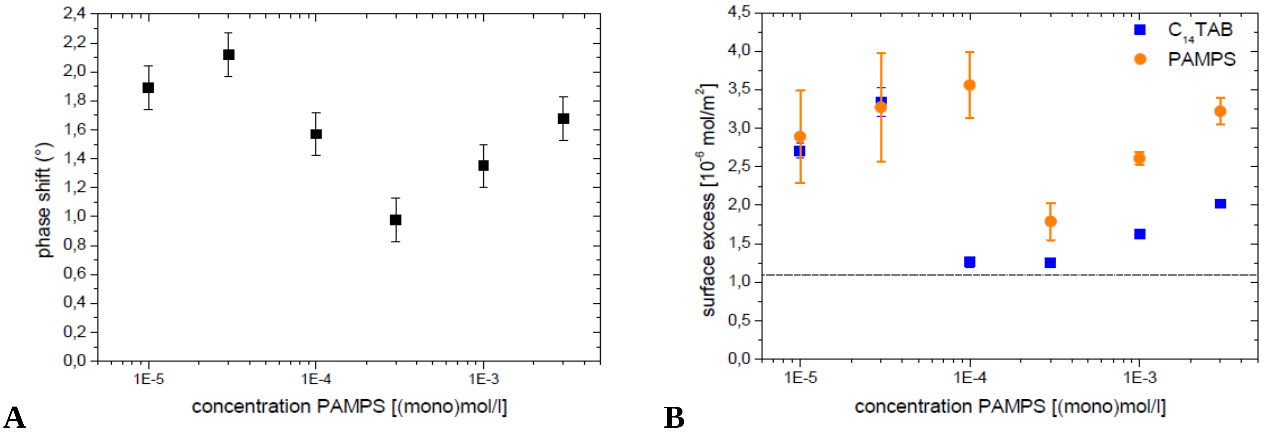

Fig. 3: ***(A)*** *Ellipsometry phase shift of PAMPS/C_{14}TAB mixtures.* ***(B)*** *Calculated surface excess values for PAMPS/C_{14}TAB mixtures which are averaged from the 3 different analysis methods. The dashed line is the surface excess of pure C_{14}TAB at a bulk concentration of 10^{-4} mol/l. The error bars correspond to deviations between the values derived from the different analysis methods.*

Discussion

Foam Film Stability – The interfacial composition (Fig. 3B) can now be set in the context of the previous foam film stability data (Fig. 1A). A key factor in the stabilization of foam films is the change in surface charge and therefore a change in the electrostatic repulsion forces due to the adsorption of polyelectrolyte. The low foam stability at low bulk polyelectrolyte concentrations coincides with the neutral adsorption layer. The higher film stability at high bulk polyelectrolyte concentrations coincides with the enhanced synergistic adsorption resulting from an increase in the ionic strength of the system. Nevertheless, the interplay between these factors in determining the stability of foam films merits further work and will motivate future beam time applications.

Surface Adsorption – The interfacial composition (Fig. 3B) can also now be set into the context of the previous surface tension measurements of (Fig. 1B). As there becomes excess bulk polyelectrolyte in region II there is a rise in the surface tension which then falls in region III. We have shown that the rise in surface tension (region II) coincides with the loss of surfactant from the interfacial layer, which is related to the increasing negative charge of the complexes in the bulk. The drop in surface tension (region III) can be attributed to the large increase in total ionic strength of the system as a result of the screening of electrostatic interactions and enhanced packing in the surface monolayer. Hence we have achieved our objective of explaining the surface tension peak for this system.