Experimental report

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Proposal:	**9-12-567**	**Council:**	4/2019
Title:	Interfacial adsorption of polymer-zwitterionic surfactant at liquid/vapor interfaces		
Research area:	Chemistry		

This proposal is a new proposal

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Samples:
D_2O
KCl
Poly(diallyldimethylammonium chloride) solution
deuterated cocobetaine

Instrument	Requested days	Allocated days	From	To
FIGARO Adsorption troughs	4	3	21/02/2020	24/02/2020

Abstract:

The interfacial behavior of polyelectrolyte - surfactant mixtures presents non conventional features that are associated with the appearance of non-equilibrium arrested states. This leads to the formation of different kind of aggregates that affect both the equilibrium interfacial composition and the dynamic of incorporation of material to the interface. The scientific and technological interest of such systems includes many fields from drug delivery platform fabrication to functional food and cosmetic formulations. The use of neutron reflectometry is known to help solve the complex behavior of these polymer-surfactant mixtures - both the equilibrium and dynamic ones. In the present proposal we examine mixtures under more industrially-relevant conditions both in adsorption troughs. The structure at the static air/water interface will give insight in our previous observations on the surface tension and rheology. The interfacial composition at both the static and dynamic air/water interface will then be compared to help elaborate the real properties of these systems by understanding the dynamics of incorporation of material to the interface.

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Interfacial adsorption of polymer-zwitterionic surfactant at liquid/vapor interfaces

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Scientific Background

The study of the adsorption of mixtures formed by polyelectrolytes and oppositely charged surfactants at the water/vapour interface has undergone a spectacular development in the last year due to the recognized interest of these systems in different scientific and technological fields, e.g. cosmetics, drug delivery, food science. However, different international regulations have suggested the progressive substitution of the charged surfactants for zwitterionic or non-ionic ones. This makes it necessary of extensive research works to shed light on the physico-chemical bases governing the formation of interfacial layers in systems involving such surfactants. The combination of tensiometric techniques with others that give access to structural and morphological information on the organization of the material at the interface, such as the neutron reflectometry, may help on the understanding of the complex interfacial behaviour of polyelectrolyte-surfactant mixtures. One of the open questions is related to the interfacial composition, especially knowing that previous studies on mixtures of polyelectrolyte and oppositely charged surfactants have shown that the interfacial composition resembles that of the complexes formed in solution. The understanding of this aspect in polyelectrolyte-zwitterionic surfactant mixtures is especially important because on the basis of surface tension and rheological measurements it should be expected a rather difficult behaviour, and a surfactant-like behaviour of the mixtures at the interface would be probably found, even though the formation of polyelectrolyte-surfactant complexes similar to those formed in mixtures of oppositely charged compounds were found in solution. Therefore, the elucidation of the interfacial composition is necessary to obtain a comprehensive description of the behaviour of these mixtures, which impact in their future applications. This makes it mandatory to understand the possible correlations existing between the bulk aggregation and the interfacial behaviour of the mixtures.

Experimental Part

Mixtures formed by a polycation, poly(diallyldimethylammonium chloride) (PDADMAC) at a fixed concentration of 0.05 g/L and two different zwitterionic surfactants, CB1 and CB2 (see Figure 1) at the water/vapor interface were studied by neutron reflectometry using the time-of-flight horizontal reflectometer FIGARO at the Institut Laue-Langevin (ILL, Grenoble, France). For this study, measurements of mixtures of PDADMAC with the deuterated and the hydrogenated surfactants were carried out using pure D_2O and in air contrast matched water (ACMW) as solvent, and the data were analyzed following two different approaches:

1. Direct measurements of the surfactant surface excesses (Γ_S) in 10 mixtures of PDADMAC and the two deuterated surfactants in ACMW were obtained by the analysis of the scattering excess in the low-Q range.
2. Structural analysis was performed applying consistent physical model to data obtained in four different isotopic contrasts in the whole Q-range. The use of different isotopic contrast was required because experiments in ACMW are most sensitive to the amount of surfactant, whereas those performed in D_2O are more sensitive to the amount of polyelectrolyte.

It is worth mentioning that the analysis of the experimental data required the splitting of the surfactant molecules in two layers (see Figure 1), which is associated with the specific molecular structure of the two surfactants.

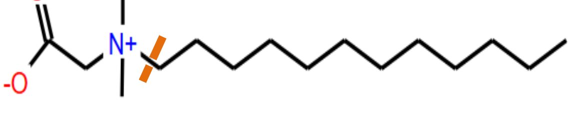
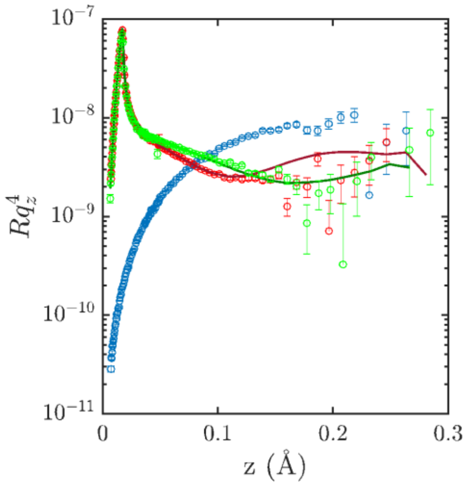


Figure 1. Molecular structure of CB1. Notice that the molecular structure of CB2 is analogous to that of CB1 with the exception that the separation between the carboxilic head and the quaternium ammonium contains two alkyl carbon. The orange line show how the molecule needed to be split up into different layers for the analysis of neutron reflectometry data.

The main novelty of the present study relies in the analysis of the effect of the separation between the two charged groups of the zwitterionic surfactants in the interfacial properties of their mixtures with a widely studies polycations.

Results

Figure 2 shows for the sake of example two reflectivity curves over the whole accessible Q-range obtained for a mixtures, with fixed polymer and surfactant concentrations, at two different isotopic contrasts and the corresponding fitting obtained using a two-layer model. The inset shows the scattering length density (SLD) profiles obtained from the analysis of the experimental scattering curves which provide information about the surface excesses of surfactant (area of the peak of the curve obtained in ACMW) and polymer (inflexion point of the curve obtained D2O).



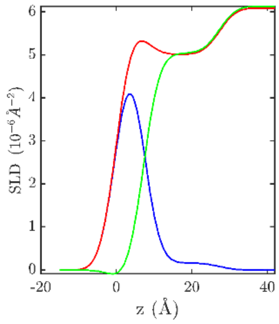


Figure 2. (left) Representative reflectivity profiles for PDADMAC–CB1 mixtures (CB1 concentration 1 mM) obtained in ACMW: deuterated surfactant (red) and hydrogenated surfactant (green), and representative profile for pure deuterated surfactant in ACMW (blue). The lines represent the fitting of the results to the models. (right) The inset the SLD dependence on the distance from the interface for the curves in the main figure.

The analysis of the experimental data have shown that even though the behavior of polyelectrolyte-surfactant mixtures considered may be considered a surfactant-like behavior in agreement with the expected from the evaluation of the surface tension ant interfacial rheology measurements. However, the existence of polymer-surfactant interactions at the interface is evident from the expansion of the size of the head group, which is associated with the electrostatic repulsion between the quaternary ammonium and the PDADMAC charges. Thus, even though the average impact of the polyelectrolyte is almost negligible when zwitterionic surfactants are considered which is the opposite behavior found for polyelectrolyte-anionic surfactant mixtures, the presence of PDADMAC modifies the intricate balance of interactions as the interface. a partial impact of the From the analysis of the experimental results following the approaches described in the experimental section it was possible to obtain the surface excesses for both polyelectrolyte and surfactant. Figure 3 reported the surface excess obtained for the two surfactant following the direct measurement approach.

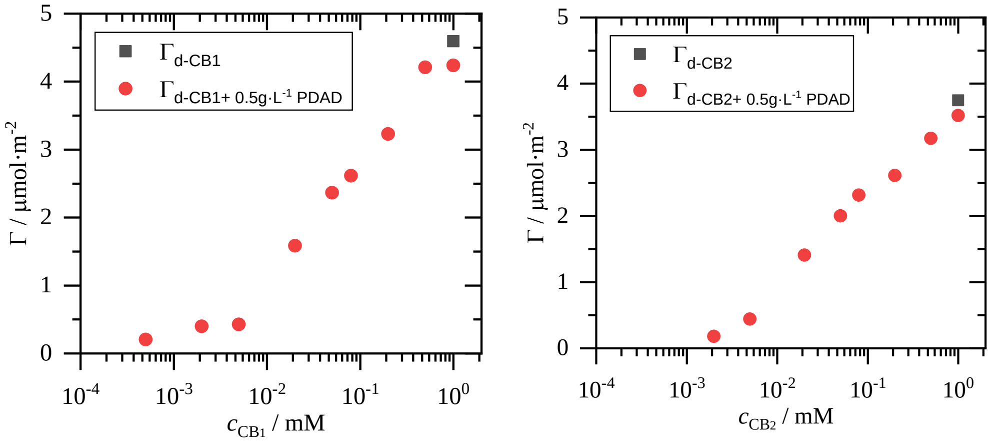


Figure 3. Dependences on the surfactant concentration of the surface excesses obtained for CB1 and CB2 for PDADMAC-surfactant mixtures (red dot) and surfactant (black squares) obtainedfrom the analysis of the reflectivity profile in the low-Q range.

The surface excesses obtained for the two surfactants present a monotonic increase with the surfactant concentration. An interpretation with physical meaning of the results requires the comparison of the interfacial excesses obtained using neutron reflectometry and the aggregation occurring in the bulk, i.e. the binding isotherm. The results evidence that the increase of the separation between the amino group and the carboxylic one on the surfactant makes it clear a worsened adsorption, i.e. for the same surfactant concentration a lower surface excess is found. This may be explained considering that the bigger length of CB2 introduces a flexibility to the surfactant, which allows its reorientation at the interface, with this being essential for an increase of the surface excess in a broad surfactant concentration range. This is not possible when CB1 is considered. For CB1, the adsorbed molecules cannot tilt at the interface, thus from the lowest surfactant concentration they adsorb directly in an orientation that is perpendicular to the interface. Furthermore, the analysis of the surface excess for mixtures and for pure surfactant evidences similar values which is again an evidence of the surfactant-like behavior of polyelectrolyte-surfactant mixtures involving zwitterionic surfactants.

Conclusions

The neutron reflectometry studies of adsorption layers of mixtures formed by a polycation and a zwitterionic surfactant has evidenced subtle differences between these mixtures and those containing a negatively charged surfactant. Such differences can be ascribed to the self-assembly phenomena occurring in solution between the polymer and the surfactant, where the electrostatic repulsion between the quaternary ammonium on the surfactant head and the PDADMAC chains can present a key role. This affects to both to the bulk and the interfacial behavior.

Diffusion of the results

The results obtained in this proposal are intended to be published in three different articles:

-L. Fernández-Peña, M. Hernández-Rivas, I. Abelenda-Nuñez, E. Guzmán, A. Maestro, S. Roscales, A.G. Csaky, F. Ortega, R.G. Rubio. Surface tension, dilational rheology and neutron reflectometry of adsorbed layers formed by polyelectrolyte-zwitterionic surfactant mixtures at the water/vapor interface. In preparation (2020).

-L. Fernández-Peña, M. Hernández-Rivas, I. Abelenda-Nuñez, E. Guzmán, A. Maestro, S. Roscales, A.G. Csaky, F. Ortega, R.G. Rubio. Adsorbed layers formed by a polycation and two zwitterionic surfactant: impact on the separation between the charged groups of the surfactant. In preparation (2019).

-L. Fernández-Peña, M. Hernández-Rivas, I. Abelenda-Nuñez, E. Guzmán, A. Maestro, R.A. Campbell, F. Ortega, R.G. Rubio. Surface tension, dilational rheology and neutron reflectometry of mixtures formed by a polycations and surfactants presenting different nature. In preparation (2020).