Experimental report

18/01/2018

Proposal: **9-12-462** **Council:** 4/2016

Title: Adsorption of polyelectrolyte - surfactant mixtures at the fluid interfaces

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: Poly(diallyl-dimethyl-ammonium chloride)
h & d sodium cocoyl methyl taurate
h & d sodium laureth sulfate
h & d sodium cocoamidopropylbetaine

Instrument	Requested days	Allocated days	From	To
FIGARO Overflowing cylinder	5	4	04/11/2016	07/11/2016
			27/02/2017	28/02/2017

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 and an Overflowing Cylinder. 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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Adsorption of polyelectrolyte - surfactant mixtures at the fluid interfaces

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Scientific Background

The understanding of the interaction of polyelectrolyte – surfactant mixtures with fluid interfaces has undergone a spectacular development in the last year due to its recognized importance for many scientific and technological fields. This has fostered an extensive research to shed light on the physico-chemical bases governing the formation of interfacial layers in such systems. Despite many works have been carried out for the understanding of the complex physico-chemical behaviour of this type of systems, many aspects still remains not well understood, especially when concentrated systems are considered, thus further work is required to provide a comprehensive explanation of their complex behaviour. The combination of tensiometric techniques with others that provide structural and morphological information on the organization of the material at the interface can help on the understanding of the complex interfacial behaviour of polyelectrolyte-surfactant mixtures. One of the open questions is related to the differences existing between diluted and concentrated mixtures, and the effect of the bulk aggregation on their interfacial behaviour. This is due to the relevance of concentrated systems on most technological application involving this type of systems. The appearance of surface tension fluctuations which are different to the surface tension peaks found for diluted systems is probably one of the most outstanding differences found for concentrated systems. Furthermore, the interfacial composition is strongly correlated to bulk aggregation in concentrated systems. Therefore, the combination of surface tension measurements and neutron reflectivity provides important insights on the complex physico-chemical behaviour of these systems.

Experimental Part

Mixtures formed by a polycation, poly(diallyldimethylammonium chloride) (PDADMAC) and anionic surfactant sodium N-lauroyl-N-methyltaurate (SLMT) 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 deuterated SLMT 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 SLMT surface excesses (Γ_S) in 10 mixtures of PDADMAC and SLMT 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 the two different isotopic contrasts in the whole Q-range. The use of two isotopic constant was necessary because ACMW is most sensitive to the amount of surfactant and D_2O is most sensitive to the amount of polyelectrolyte.

It is worth mentioning that the analysis of the experimental data required the splitting of the surfactant in three layers (see Figure 1). This approach is not common but in the here studied systems was used to provide a physical representative model of the experimental data. This constrain arrives from the molecular structure of the SLMT.

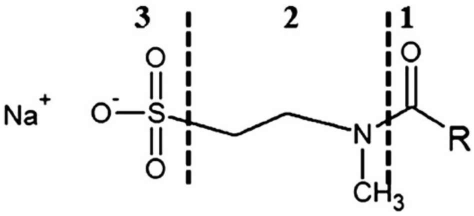

Figure 1. Molecular structure or SLMT with R corresponding to an alkyl chain of 11 carbon atoms. The vertical lines show how the molecule needed to be split up into different layers for the analysis of neutron reflectometry data.

The main novelty of the present study relies in the use of solutions including polymer concentrations several times higher than those commonly studied. This leads to important differences in the bulk aggregation phenomena and consequently to the interfacial behavior of these systems.

Results

Figure 2 shows for the sake of example two reflectivity curves over the whole accessible Q-range obtained at two different isotopic contrasts and the corresponding fitting obtained using a three-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 D_2O).

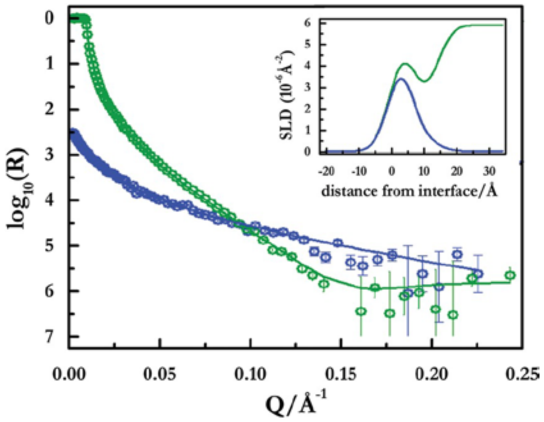

Figure 2. Representative reflectivity profiles for PDADMAC–SLMT mixtures (SLMT concentration $3 \cdot 10^{-6}$ g/g) obtained using two different isotopic contrasts: deuterated surfactant in ACMW (blue) and in D_2O (green). The lines represent the fitting of the results to the models. The inset the SLD dependence on the distance from the interface for the curves in the main figure.

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 as shown Figure 3.

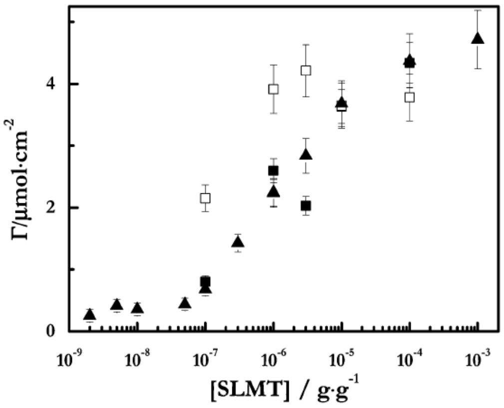

Figure 3. Dependences on the SLMT concentration of surface excesses obtained for PDADMAC (□) and SLMT (■) using structural analysis and the surface excesses obtained from the analysis of the reflectivity profile in the low-Q range for SLMT (▲).

The surface excesses obtained for the surfactant using both approaches present a good agreement within the combined error bars, showing a monotonic increase with the surfactant concentration. The dependence of the surface excess of PDADMAC at the interface on the surfactant concentration reveals an interesting trend that was not found previously for most diluted systems. At low surfactant concentration, the structural analysis evidence the existence of a large excess of polymer segments at the interface, becoming the surface excess of monomer unit almost three times that of the surfactant. However, at the highest surfactant concentration the surface excesses of polymer and surfactant become similar, and even an inversion of the trend is found with the surface excess of the surfactant exceeding that of the PDADMAC. 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. Thus, the interfacial composition mirrors the composition of the bulk. For the lowest surfactant concentration, a large excess of polyelectrolyte was found at the interface which is rationalized considering the low amount of surfactant remaining free in solution (less than 1%) and the formation of bulk complexes with a high number of monomers in relation to the number of surfactant molecules. It is worth mentioning that the complexes are undercompensated in the entire surfactant concentration range. Thus, the results found at the highest surfactant concentrations evidence the important role of small amounts of free surfactant in determining the interfacial properties of the system. Therefore, the neutron reflectometry experiments have pointed out that for concentrated mixtures a transition from complex adsorption to synergetic co-adsorption of complex and free surfactant is a plausible physical scenario describing the experimental results.

Conclusions

The study of the adsorption at fluid interfaces of mixtures of polyelectrolytes and oppositely charged surfactants with compositions close to that used in commercial formulations has pointed out strong differences in relation to previous studies on more dilute systems. The main source of such differences is associated with the existence of a low amount of free surfactant in the solutions. Therefore, the adsorption of the complexes formed in the bulk present a more relevant role than in dilute systems in which a synergistic co-adsorption of complexes and free surfactant provides a better description of the physical scenario.

Diffusion of the results

The results obtained in this proposal have been published in the following articles:

- S. Llamas, L. Fernández-Peña, A. Akanno, E. Guzmán, V. Ortega, F. Ortega, A.G. Csaky, R.A. Campbell, Ramón G. Rubio, Towards understanding the behavior of polyelectrolyte–surfactant mixtures at the water/vapor interface closer to technologically-relevant conditions. Phys. Chem. Chem. Phys. 20 (2018) 2018, 1395-1407. DOI: 10.1039/c7cp05528e.
- S. Llamas, E. Guzmán, A. Akanno, L. Fernández-Peña, F. Ortega, R.A. Campbell, R.Miller, R.G. Rubio, Study of the Liquid / Vapor Interfacial Properties of Concentrated Polyelectrolyte – Surfactant Mixtures Using Surface Tensiometry and Neutron Reflectometry: Equilibrium, Adsorption Kinetics and Dilational Rheology, J. Phys. Chem. C submitted.