Experimental report

11/09/2019

Proposal:	**9-12-541**	**Council:**	4/2018
Title:	Adsorption of polycation-zwitterionic surfactant mixtures at the water/vapor interface		
Research area:	Soft condensed matter		

This proposal is a new proposal

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Samples:	Poly(diallyl-dimethyl-ammonium chloride) h & d sodium cocoamidopropylbetaine h & d cocoylbetaine

Instrument	Requested days	Allocated days	From	To
FIGARO Adsorption troughs	4	3	19/10/2018	22/10/2018

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 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.

Experimental Report **Proposal Number:** 9-12-541

Adsorption of polycation-zwitterionic surfactant mixtures at the water/vapor interface[1]

Eduardo Guzmán (Main Proposer), Armando Maestro (Local Contact), Laura Fernández-Peña,
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Scientific Background

The interest for understanding the adsorption to fluid interfaces of solutions formed by mixtures of polyelectrolytes and surfactants has grown in recent years as result of the involvement of this type of systems in many industrial fields, e.g. cosmetics, drug delivery, food science. This has stimulated an important research activity aimed to shed light on the physico-chemical bases underlying the self-assembly in solution of complexes due to the interaction of polyelectrolyte and surfactant, and how such complexes adsorb at fluid interface. Despite the significant efforts on the understanding the complex physico-chemical behaviour of this type of systems, it still remain a lacked knowledge of several aspects related to its description, with the role of the non-equilibrium character of polyelectrolyte-surfactant systems being probably the most important. It is worth mentioning that non-equilibrium effects play even a more important role when mixtures with a high polymer concentration are considered than in the traditionally studied diluted systems. In concentrated polymer-surfactant solutions, the role of the Marangoni gradient governing the formation of kinetically-trapped complexes present an important role, triggering in most cases the physico-chemical behavior of polyelectrolyte-surfactant mixtures. It would be expected that the combination of a tensiometric characterization of polyelectrolyte-surfactant laden fluid interfaces with studied aimed to understand the organization and composition of the interfaces may help to shed light on the complex interfacial behaviour of polyelectrolyte-surfactant mixtures. Among the open questions for the understanding of the role of the bulk aggregation on the interfacial behaviour of polyelectrolyte-surfactant mixtures, the effect of the polymer concentration is accounted as the most important. This is because industrial formulations involve in most cases concentrated systems, hence the understanding of the physico-chemical behavior in systems mimicking consumer products present particular interest. It is worth mentioning that the interfacial composition is strongly correlated to bulk aggregation in concentrated systems. Therefore, the combination of surface tension measurements and neutron reflectivity may help to shed light on the complex physico-chemical behaviour of these systems.

Experimental Part

Mixtures formed by a polycation, poly(diallyldimethylammonium chloride) (PDADMAC) and the neutral dodecylpolyglucoside (DPG) at the water/vapor interface were studied by neutron reflectometry using the time-of-flight horizontal reflectometer FIGARO, using adsorption trough, at the Institut Laue-Langevin (ILL, Grenoble, France). For this study, measurements of mixtures of PDADMAC with deuterated DPG were carried out using two different 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 DPG surface excesses (Γ_S) in mixtures of PDADMAC and DPG 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

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[1] **Note:** the aim of the proposal was the study of the adsorption of mixtures formed by a polycation and zwitterionic surfactants. However, the difficulties associated with the synthetic procedure for obtaining the zwitterionic surfactants make necessary to replace the studied surfactant, and the interaction of a neutral surfactant (caprylpolyglucoside, CPG) and a polycation was studied.

necessary because ACMW is most sensitive to the amount of surfactant and D_2O is most sensitive to the amount of polyelectrolyte.

Notice that the same analysis was performed for 9 PDADMAC-DPG mixtures in which the surfactant concentration was the control variable at two different polymer concentrations.
It is worth mentioning that the analysis of the experimental data required the splitting of the surfactant in two 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.

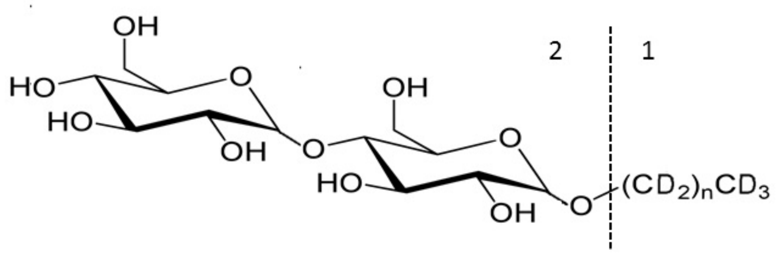

Figure 1. Molecular structure or DPG where n correspond to 11. The vertical lines show how the molecule needed to be split up into different layers for the analysis of neutron reflectometry data.

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 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 D_2O).

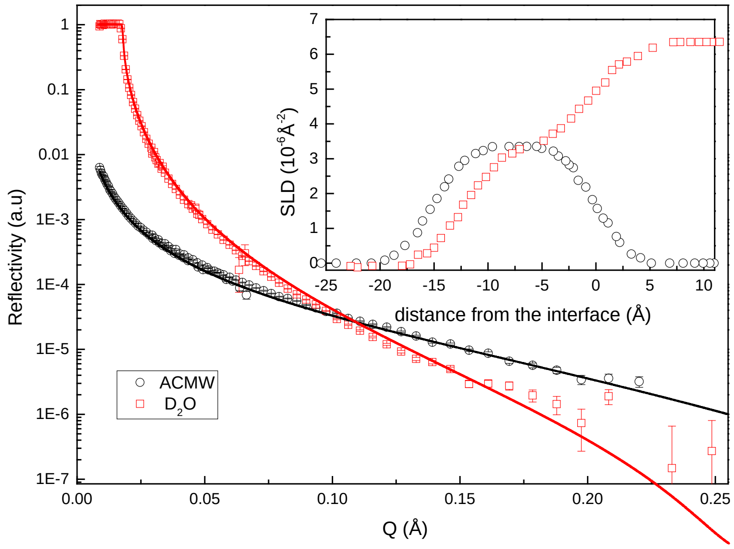

Figure 2. Representative reflectivity profiles for PDADMAC–DPG mixtures (DPG concentration 1 mM and PDADMAC concentration 0.5 wt%) obtained using two different isotopic contrasts: deuterated surfactant in ACMW (black) and in D2O (red). The lines represent the fitting of the results to the models. The 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. Figure 3 reported the surface excess obtained for some selected DPG concentrations.

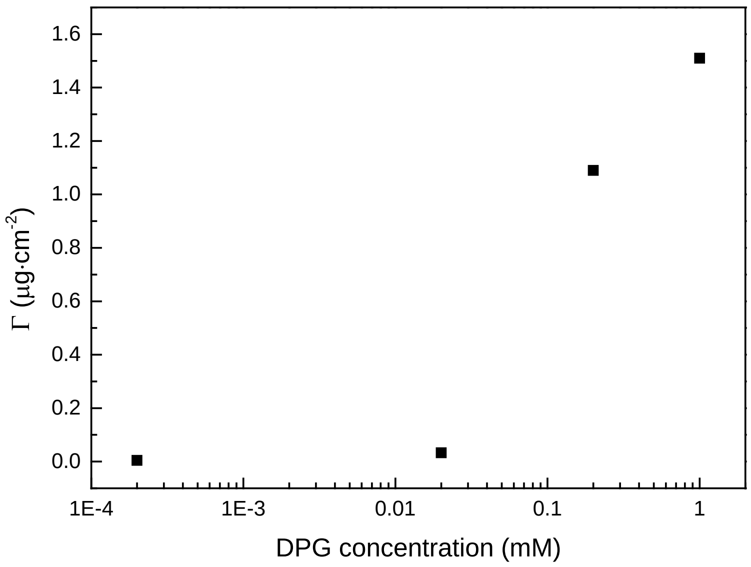

Figure 3. Dependences on the DPG concentration of the surface excesses of DPG obtained from the analysis of the reflectivity profile in the low-Q range for PDADMAC–DPG mixtures (DPG concentration 1 mM and PDADMAC concentration 0.5 wt%)

The surface excesses obtained for the surfactant using shows 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. It is worth mentioning that on the contrary to that found in mixtures of PDADMAC with an oppositely charged surfactant (experiment 9-12-462),[2] the adsorption of mixtures of PDADMAC and a neutral surfactant is relatively reduced and only when the concentration is close to that corresponding to the cmc of the surfactant, the adsorption starts to increase. The reduced adsorption found in mixtures of PDADMAC-DPG may be understood considering the reduced surface active of the formed complexes in solution, in which the hydrophilic groups of the surfactant remain exposed to the liquid phase.

Conclusions

The neutron reflectometry studies of adsorption layers of mixtures formed by a polycation and a neutral 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 which is mediated through the hydrophobic interactions between hydrophobic tails of the surfactant and the hydrophobic domains in the polymer chain. The main source of such differences is associated with the hydrophilicity in the formed complexes.

Diffusion of the results

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

-E. Guzmán, L. Fernández-Peña, A. Maestro, A.G. Csaky, R.A. Campbell, F. Ortega, R.G. Rubio. Adsorbed layers formed by polyelectrolyte-neutral surfactant mixtures: diluted and concentrated limit. In preparation (2019).

-L. Fernández-Peña, E. Guzmán, A. Maestro, S. LLamas, A.G. Csaky, R.A. Campbell, F. Ortega, R.G. Rubio. Adsorbed layers formed by a polycation and two different surfactant: effect of the surfactant nature. In preparation (2019).

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[2] E. Guzmán; A. Akanno; R.A. Campbell; L. Fernández-Peña; S. Llamas; F. Ortega; R.G. Rubio (2016). Adsorption of polyelectrolyte - surfactant mixtures at the fluid interfaces. Institut Laue-Langevin (ILL) doi:10.5291/ILL-DATA.9-12-462