Experimental report

21/01/2018

Proposal:	**9-12-488**	**Council:**	10/2016
Title:	Interfacial structures of comb co-polymer/cationic surfactant mixtures		
Research area:	Soft condensed matter		

This proposal is a resubmission of 9-12-452

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Samples: the two neutral comb co-polymers (termed Polymer A and B) have a hydrophilic PEG backbone (MW 6000 Da), bearing hydrophobic PVAc grafts of different amounts (total PVAc MW ~18,000 Da for A, and ~21,100 Da for B) and lengths (~11 monomer units per one
dDTAB
hDTAB

Instrument	Requested days	Allocated days	From	To
FIGARO	3	2	13/02/2017	15/02/2017

Abstract:

First of all, we would like to address directly two points from reviewers’ comments on our last submission. First, the panel queried the chemical structure of the polymers, which is now provided in Fig.1 – it is novel and not previously studied, and industrially important. We further clarify that, for this industrial collaboration (as encouraged by ILL) the results are being prepared for a manuscript for submission to Langmuir. Secondly, our previous FIGARO NR experiments on the polymers mixed with anionic and neutral surfactants showed that the interfacial structures of the complexes were different from commonly studied comb polymers (i.e. with hydrophobic or charged backbones and hydrophilic side chains). In addition, the headgroup charge played an important role in the interfacial polymer-surfactant structure. Our proposed measurements using a cationic surfactant will lead to further physical insights and form the basis of further publication. Our preliminary surface tension measurements and XRR results at Diamond (UK) point to different complex structures between the neutral polymer and differently charged surfactants (anionic SDS and cationic DTAB).

9-12-488

Interfacial structures of comb co-polymer/cationic surfactant mixtures

Aim of experiment

The aim of this experiment was to study the structures and interactions of a neutral comb co-polymer (PEG backbone with PVAc grafts) and a cationic surfactant (DTAB) at the air-water interface. We have previously studied the structures and interactions of the same comb co-polymer with a non-ionic $C_{12}E_5$ (experiment number 9-12-410) and an anionic SDS (experiment number 9-12-380) surfactants. This study therefore completes a series of measurements that allow us to directly correlate the interfacial structures of these systems with the headgroup charge and size, as well as some physical insight into different complex structures and interactions formed at the air-water interface. The interfacial structures observed differ to commonly studied comb polymers with hydrophobic backbone and hydrophilic side chains.

The structural and compositional information we were able to obtain, together with a series of complementary characterisation techniques, is critical to unlocking their potential in facilitating thin film stability in foaming and detergency applications.

Experimental

Polymer A was freeze-dried prior to the use. Both hDTAB and dDTAB (d-C_{12}h-TAB) were recrystallised from acetone:water (99:1, v:v). Air contrast matched water (ACMW) was prepared as 8.9 wt% D_2O in H_2O.

Solutions of desired concentrations of Polymer A and DTAB were prepared. We have used four different contrasts for DTAB samples: a) hDTAB in ACMW, b) hDTAB in D_2O (this contrast was used as we have not observed any aggregate formation), c) dDTAB in ACMW, and d) dDTAB in D_2O. There was no deuterated Pol A, therefore the same contrasts were used for the mixed polymer/surfactant systems.

Five concentrations of DTAB (all 4 contrasts) were measured with the higher concentration of Pol A (2 cmc). Because of time restrictions, only one contrast (hDTAB in ACMW) of the mixtures containing the lower polymer concentration (0.2 cmc) was run for five surfactant concentrations, in order to allow us to calculate the surface excess of these mixtures. In addition, 2 concentrations of pure DTAB in all four contrasts were also measured.

Approximately 40 mL was used for each measurement. The sample was carefully poured into adsorption troughs provided by FIGARO. The data was collected over time to allow for sample equilibration. All data was recorded at room temperature.
The data was reduced and normalised against the background measurements of ACMW and D_2O.

The surface excess was calculated from the data acquired in ACMW, both for DTAB and Pol A. The thickness, solvation and roughness were fitted using Motofit package in IGOR Pro.

Results

The reflectivity data was fitted using Motofit in IGOR Pro. Two models were used in this case: 1-layer model for pure polymer, pure surfactant and low concentration of DTAB with the polymer; and a 2-layer model for the mixed systems with DTAB concentration of 0.5 cmc and above. Here, we show the fitted data for the pure polymer, and 2 concentrations of pure surfactant in the top row of Fig 1; and the fitted data of mixed DTAB/Pol A systems and the calculated surface excess in the mixed systems at the bottom row.

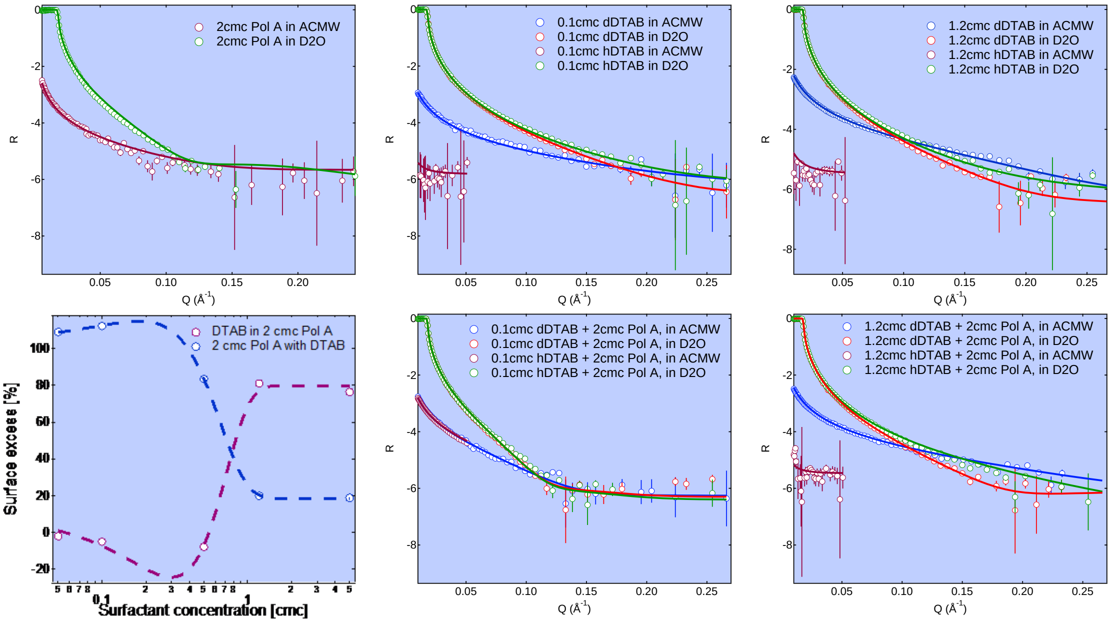

Figure 1 Reflectivity data shown for chosen concentrations of DTAB/Polymer A mixtures and pure surfactant and polymer systems, with the fits shown as solid lines. Bottom left figure shows the calculated surface excess of the polymer and DTAB with increasing DTAB concentration.

The fitted values are shown in Table 1, with clear indication of partial association between the polymer and DTAB, as well as some competition in the interface adsorption. This is further supported by the calculated surface excess of the components. It is important to note that the SLD of the polymer was used to fit the data of 0.1cmc DTAB and 2cmc Pol A, together with a much higher roughness of the backing interface, confirming no surfactant was present at the interface at this concentration of the mixed system.

Table 1. Fitted values of chosen concentrations of DTAB/Polymer A mixtures and pure surfactant and polymer systems.

	DTAB layer			Pol A layer		
	thickness [Å]	solvation [%]	roughness [Å]	thickness [Å]	solvation [%]	roughness [Å]
0.1DTAB	6.9	22.5	5.6	-	-	-
1.2DTAB	14.8	16.5	5	-	-	-
2PolA	-	-	-	26.2	20.1	5
0.1DTAB+2 Pol A	-	-	-	28.2	0.6	5.8
1.2DTAB+2Pol A	8.7	0	3.5	3.7	20	3
5DTAB+2Pol A	8.0	0	3.5	4.4	20	3

Conclusions

Our complementary surface tension measurements (Fig 2) show an indication of synergistic effect at low surfactant concentration, especially in the systems with SDS. At higher surfactant concentration, the surface tension data points towards competitive adsorption with the polymer being depleted from the air-water interface.

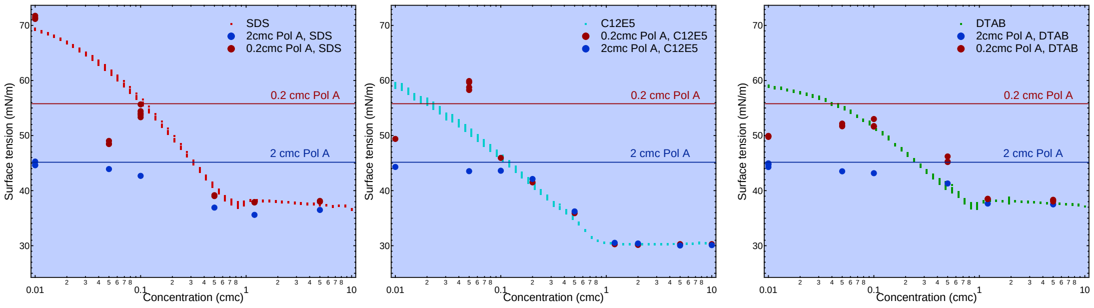

Figure 2 Surface tension data of Pol A with SDS, C12E5 and DTAB, respectively. The solid lines represent the surface tension of the pure polymer, the dashes represent the surface tension of the pure surfactant, and the solid circles represent the surface tension data of the mixed systems.

Based on the reflectivity data, a clear difference can be seen in the behaviour of the polymer/DTAB mixture compared to that of polymer/SDS and polymer/$C_{12}E_5$ mixtures. At low concentration of surfactant, the surfactant encourages polymer surface adsorption, unlike in the case of SDS and $C_{12}E_5$ where even low surfactant concentration induces competitive adsorption where the surfactant replaces the polymer. Even at a DTAB concentration above its cmc, there is a considerable amount of polymer present at the interface. This has been also observed in the fitted thickness of the respective layers. This behaviour could be rationalised by partial dissociation of the carbonyl groups in the polymer leading to a partial negative charge which then could readily associate with the cationic DTAB, forming complexes both at the interface as well as in the bulk.