Experimental report

06/03/2016

Proposal:	**9-12-380**	**Council:**	10/2014
Title:	Interfacial structures of linear-dendritic co-polymer/surfactant mixtures		
Research area:	Soft condensed matter		

This proposal is a new proposal

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Samples: PEO-PL linear-dendritic polymers

Instrument	Requested days	Allocated days	From	To
FIGARO Adsorption troughs	4	3	29/06/2015	30/06/2015
			27/07/2015	29/07/2015

Abstract:

Linear-dendritic polymers possess a unique macromolecular architecture, combining the steric hindrance tuneable by tailoring the dendritic block and the entanglement of the linear block. As part of a UK EPSRC Case Award jointly funded by Proctor & Gamble (P&G), here we propose the first comprehensive NR study of interface structures resulting from the interactions between an anionic surfactant (SDS) and a linear-dendritic system comprising amphiphilic PEO-lysine co-polymer at the air-water interface. The unique experimental setup suited for such air-water interfacial structural characterisation at FIGARO will be used. By correlating polymer molecular architecture, molecular weight, and surfactant concentration with its interfacial structure, we will gain a fundamental understanding of the interactions involved, which underpin their untapped potential in a vast array of applications where thin film stability facilitated by polymer-surfactant mixtures plays a critical role.

Interfacial structures of comb co-polymer/surfactant mixtures

Aim of experiment

The aim of the experiment was to study the interactions of a surfactant and a comb co-polymer system comprising of anionic SDS and a neutral amphiphilic PEG-PVAc based comb (centipede) co-polymer. Unprecedented structural and compositional information of these novel polymer systems were investigated, and these will be invaluable to unlocking their potential in facilitating thin film stability in foaming and detergency applications. A series of complementary characterisation was performed prior to the experiment (surface tension measurements), as well as XRR study performed at I07 Diamond (UK).

Experimental

Polymer A was freeze-dried prior to the use. SDS (both hSDS and dSDS) were recrystallised from ethanol prior to the experiment. Air contrast matched water (ACMW) was prepared as 8.9 wt% D_2O in H_2O. We have used four different contrasts for SDS samples: a) hSDS in ACMW, b) hSDS in D_2O (this contrast was used as we have not observed any aggregate formation), c) dSDS in ACMW, and d) dSDS in D_2O. There was no deuterated Pol A, therefore the same contrasts were used for the mixed polymer/surfactant systems. 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. Five concentrations of SDS (all 4 contrasts) were measured in combination with 2 concentrations of Pol A. In addition, 3 concentrations of Pol A were also measured.

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 SDS and Pol A. The thickness, solvation and roughness were fitted using Motofit package in IGOR Pro.

Results

Fitting of pure systems

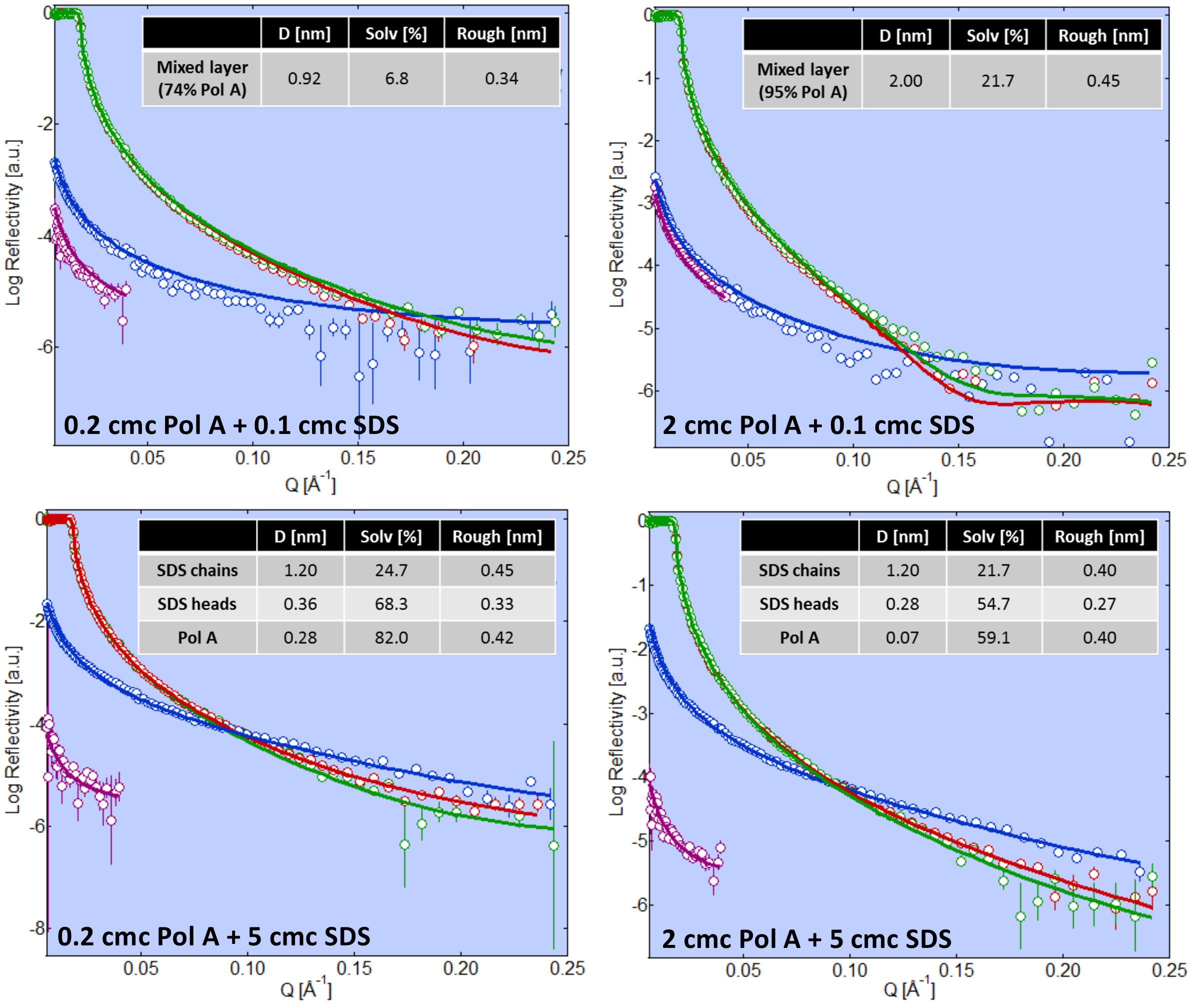
Initially, pure polymer or surfactant systems were fitted, in order to obtain a fitted SLD value, as well as the thickness and solvent penetration of the layers formed from the single component systems. The polymer data was fitted using a 1 layer model with homogenous SLD, as the PVAc grafts are considered not to be long enough to occupy a separate layer at the interface. Contrary to this, the SDS molecule can be split into two separate layers: the hydrocarbon chain (SLD depends on hSDS or dSDS) and the ionic head group (same SLD for both hSDS and dSDS). The two concentrations of pure SDS fitted (0.1 and 1.2 cmc) were both best described with the two layer model.

Fitting of mixed polymer/surfactant systems

Three different models can be used to fit the data obtained for the mixed polymer/surfactant systems:

a) 1 completely mixed layer of polymer/surfactant complex, with the SLD calculated from ratio of the two components
b) 2 layer model: top layer composed of SDS, with a separate layer of Pol A
c) 3 layer model: top layer composed of SDS hydrocarbon chain, middle layer attributed to the SDS head groups, with the last layer occupied by Pol A

The 1 layer model (completely mixed layer of polymer/surfactant) was used for fitting the systems with the low concentrations of SDS (0.05 cmc and 0.1 cmc SDS with both concentrations of Pol A). At any higher concentration of SDS, the 3 layer model produced the best fits. A selection of the fitted data for polymer/surfactant mixtures is shown in Figure 1, as well as the fitted parameters (shown in the inset of each graph).



0.2 cmc Pol A + 0.1 cmc SDS

	D [nm]	Solv [%]	Rough [nm]
Mixed layer (74% Pol A)	0.92	6.8	0.34

2 cmc Pol A + 0.1 cmc SDS

	D [nm]	Solv [%]	Rough [nm]
Mixed layer (95% Pol A)	2.00	21.7	0.45

0.2 cmc Pol A + 5 cmc SDS

	D [nm]	Solv [%]	Rough [nm]
SDS chains	1.20	24.7	0.45
SDS heads	0.36	68.3	0.33
Pol A	0.28	82.0	0.42

2 cmc Pol A + 5 cmc SDS

	D [nm]	Solv [%]	Rough [nm]
SDS chains	1.20	21.7	0.40
SDS heads	0.28	54.7	0.27
Pol A	0.07	59.1	0.40

Figure 1 A selection of fitted data for surfactant/polymer mixed systems. The insets show the fitted parameters including the thickness (D), solvent penetration (Solv), and roughness of the layer (Rough). The data is colour coded as follows: a) red represents dSDS in D_2O, b) green hSDS in D_2O, c) blue dSDS in ACMW, and d) purple represents hSDS in ACMW.

At low concentration of SDS (0.1 cmc), the mixed polymer/surfactant layer comprises mostly of the polymer (74% for system with 0.2 cmc Pol A, and 95% for system with 2 cmc Pol A). The thickness of this layer is dependent on the polymer concentration, but the data cannot be fitted by a pure polymer layer. This suggests there is some cooperative adsorption at the interface at low surfactant concentration. At intermediate concentration of SDS (0.5 cmc), the data was fitted using a 3 layer model with the top two layers attributed to the surfactant. The fitted parameters for the surfactant layers are almost constant, however there is a clear increase in the thickness (and solvent penetration) of the polymer layer at 2 cmc Pol A, compared to the 0.2 cmc Pol A system. This suggests there is a monolayer of SDS formed at the interface (with tilted hydrocarbon chains), with the polymer forming a separate layer underneath. At high concentration of SDS (5 cmc), it is expected that a full monolayer of SDS is formed at the interface, which can be confirmed by a higher thickness of hydrocarbon chains extending to the air phase suggesting a higher density of the molecules. The polymer is therefore thought to be completely depleted from the proximity of the interface, forming a thin layer underneat the surfactant monolayer. Intriguingly, the polymer layer thickness decreases with increased polymer concentration. This could be possibly attributed to a preferential ratio of surfactant/polymer molecules at the interface forming mixed structures at the lower polymer concentrations. It is important to note the solvent penetration is significantly lower for this layer, therefore the actual polymer content might be approximately constant.

Surface excess

Surface excess calculations from data obtained in ACMW is plotted in Figure 2 versus the SDS concentration.

The dashed lines represent the calculated surface excess of pure Pol A (0.2 cmc pale blue, and 2 cmc dark blue), and pure SDS at two concentrations with an exponential fit between these two points (purple).

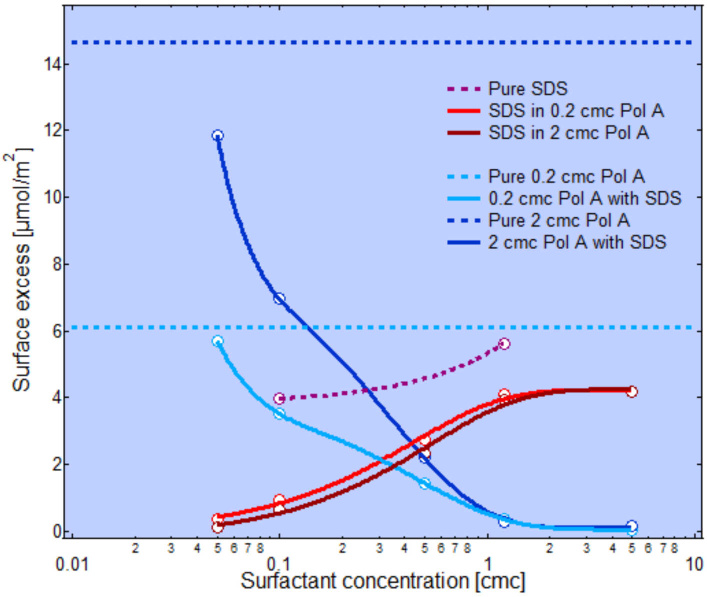


Figure 2 The calculated surface excess versus SDS concentration of mixed Pol A + SDS systems. The dashed lines represent calculated values of pure systems (purple for SDS, pale blue for 0.2 cmc Pol A, dark blue for 2 cmc Pol A). The solid lines represent exponential fit for the SDS data (pale red for SDS in 0.2 cmc Pol A, and dark red for SDS in 2 cmc Pol A), and a double exponential fit for the Pol A data (pale blue for mixtures of SDS in 0.2 cmc Pol A, and dark blue for mixtures of SDS in 2 cmc Pol A).

The surface excess of SDS in mixtures with Pol A (0.2 cmc Pol A mixtures represented by red line, and 2 cmc Pol A mixtures represented by dark red) suggest the surface excess of SDS is dependent on the polymer concentration only at lower concentrations of SDS, however it is important to note that the surface excess is much lower than for the pure surfactant system. There is also a clear plateau at concentrations above 1 cmc of the surfactant, after which the amount at the surface is constant (and below the value calculated for pure SDS). This data is in agreement with the fitted thickness values.

The surface excess of Pol A in the same set of mixtures was also evaluated (mixtures in 0.2 cmc Pol A are shown in pale blue, mixtures in 2 cmc Pol A are shown in dark blue). The surface excess of the polymer decreases proportionally to the increasing SDS concentration, suggesting that the polymer is depleted from the surface by the surfactant. This is again consistent with the fitted thickness values. At the lowest concentration of the surfactant (0.05 cmc), the surface excess of Pol A at the interface almost reaches the same value as for pure polymer at 0.2 cmc concentration. At concentration of 2 cmc of the polymer, there is a significant decrease compared to the pure polymer values, suggesting that the polymer is depleted from the interface even at a very low concentration of the surfactant. Increasing the concentration of the SDS leads to further decrease of surface excess of the polymer, until reaching a plateau at 1.2 cmc of the surfactant. This plateau value is in the order of 1×10^{-4} mol/m^2 for both the 0.2 cmc (0.058 µmol/m^2) and 2 cmc (0.162 µmol/m^2) of the polymer.

Conclusions

In general, the thickness of polymer layer decreases with increasing concentration of SDS, as expected due to the polymer being depleted from the interface by SDS. The thickness of the SDS chain increases steadily with increasing SDS concentration. The head group thickness is relatively constant for all the systems (this was constrained to be between 2 and 4 Å in the fitting parameters).

The results are in agreement with the surface tension measurements and the surface excess calculation. We can conclude there is competitive adsorption at the air-water interface in these polymer/surfactant mixed systems, where SDS seems to deplete the interface of Pol A and form a monolayer. The polymer then forms a layer underneath the SDS, where the head groups of SDS can interact with the polymer.