Experimental report

15/09/2016

Proposal:	**9-12-410**	**Council:**	4/2015

Title: Interfacial structures of graft co-polymer/surfactant mixtures

Research area: Soft condensed matter

This proposal is a new proposal

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Samples:
PEG-PVAc comb polymer
d-C12E5

Instrument	Requested days	Allocated days	From	To
FIGARO	3	3	09/12/2015	12/12/2015

Abstract:

Understanding the adsorption behaviour of polymer/surfactant mixtures at the air-water interface is of fundamental importance and has direct relevance to a variety of practical applications, e.g. consumer goods products, and paper and oil industries. In recent years, studies using surface-sensitive experimental techniques such as X-ray and neutron reflectivity have considerably advanced our understanding on interfacial behaviours of polymer/surfactant mixtures.

In this proposal, the focus is on two neutral comb co-polymers with a hydrophilic PEG backbone and a varying length and density of hydrophobic PVAc grafts, particularly when they are with a non-ionic surfactant C12E5 (bearing similar molecular structure to the PEG backbone). We are motivated by their conjectured effective roles in stabilizing foams and removing grease in P&G household products. Comb co-polymers can be thought of as a very sparsely grafted polymer brushes, and therefore, some interesting interfacial properties are expected following their self-assembly with surfactant at the air-water interface.

Interfacial structures of graft 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 non-ionic $C_{12}E_5$ 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 our previous NR experiment investigating the polymer/SDS mixtures (experiment number 9-12-380).

Experimental

We have used four different contrasts for $C_{12}E_5$ samples: a) h $C_{12}E_5$ in ACMW, b) h $C_{12}E_5$ in D_2O (this contrast was used as we have not observed any aggregate formation), c) d $C_{12}E_5$ in ACMW, and d) d $C_{12}E_5$ in D_2O. There was no deuterated Pol A, therefore the same contrasts were used for the mixed polymer/surfactant systems. All data was recorded at room temperature.

The data was reduced and normalised against the background measurements of ACMW and D_2O.

Five concentrations of $C_{12}E_5$ (all 4 contrasts) were measured in combination with 2 concentrations of Pol A. In addition, 2 concentrations of pure $C_{12}E_5$ were also measured.

The surface excess was calculated from the data acquired in ACMW, both for $C_{12}E_5$ and Pol A. The thickness, solvation and roughness was fitted using Motofit package in IGOR Pro.

Results

Fitting of pure systems

The reduced data was plotted and fitted using Igor Pro (Motofit package).

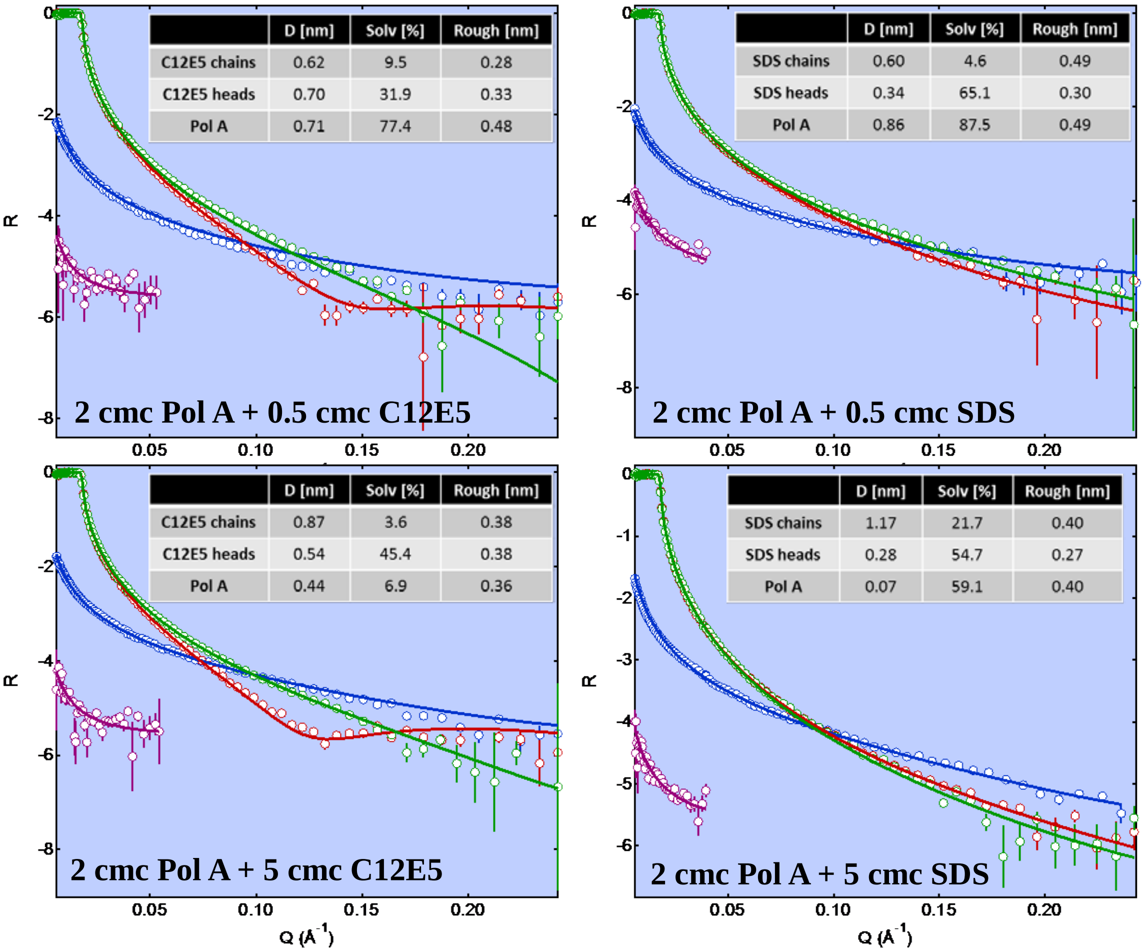
The polymer data was fitted using a 1 layer model with homogenous SLD, as the PVAc grafts are considered not to be long enough to occupy a separate layer at the interface. Contrary to this, the $C_{12}E_5$ molecule can be split into two separate layers: the hydrocarbon chain (SLD depends on h $C_{12}E_5$ or d $C_{12}E_5$) and the PEG-based head group (same SLD for both h $C_{12}E_5$ and d $C_{12}E_5$).

Fitting of mixed polymer/surfactant systems

Two different models were 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) 3 layer model: top layer composed of $C_{12}E_5$ 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 $C_{12}E_5$ (0.05 cmc and 0.1 cmc $C_{12}E_5$ with both concentrations of Pol A). At any higher concentration of $C_{12}E_5$, 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).



	D [nm]	Solv [%]	Rough [nm]
C12E5 chains	0.62	9.5	0.28
C12E5 heads	0.70	31.9	0.33
Pol A	0.71	77.4	0.48

	D [nm]	Solv [%]	Rough [nm]
SDS chains	0.60	4.6	0.49
SDS heads	0.34	65.1	0.30
Pol A	0.86	87.5	0.49

	D [nm]	Solv [%]	Rough [nm]
C12E5 chains	0.87	3.6	0.38
C12E5 heads	0.54	45.4	0.38
Pol A	0.44	6.9	0.36

	D [nm]	Solv [%]	Rough [nm]
SDS chains	1.17	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 d-surfactant in D_2O, b) green h-surfactant in D_2O, c) blue d-surfactant in ACMW, and d) purple represents h-surfactant in ACMW. The polymer used in all samples was hydrogenated.

Surface excess

Surface excess calculations from data obtained in ACMW is plotted in Figure 2 versus the $C_{12}E_5$ 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 $C_{12}E_5$ at two concentrations with an exponential fit between these two points (dark brown).

The surface excess of $C_{12}E_5$ in mixtures with Pol A (0.2 cmc Pol A mixtures represented by a green line, and 2 cmc Pol A mixtures represented by dark green) suggest the surface excess of $C_{12}E_5$ is dependent on the polymer concentration only at lower concentrations of $C_{12}E_5$. It is interesting to note that the surface excess reaches the same values as for the pure surfactant system, at concentrations of 0.5 cmc of $C_{12}E_5$ and above. This is a different behaviour to the one we have observed previously in systems with SDS, suggesting that our polymer is interacting much less with $C_{12}E_5$ compared to the anionic SDS, or that $C_{12}E_5$ is more effective at depleting the air-water interface of the polymer, and possibly forming mixed micelles in the bulk. The surface excess of the polymer decreases proportionally to the increasing $C_{12}E_5$ concentration, suggesting that the polymer is depleted from the surface by the surfactant. Increasing the concentration of the $C_{12}E_5$ leads to decrease of surface excess of the polymer, until reaching a plateau at ~ 0.5 cmc of the surfactant, the onset of this plateau is observed much earlier compared to the systems with SDS.

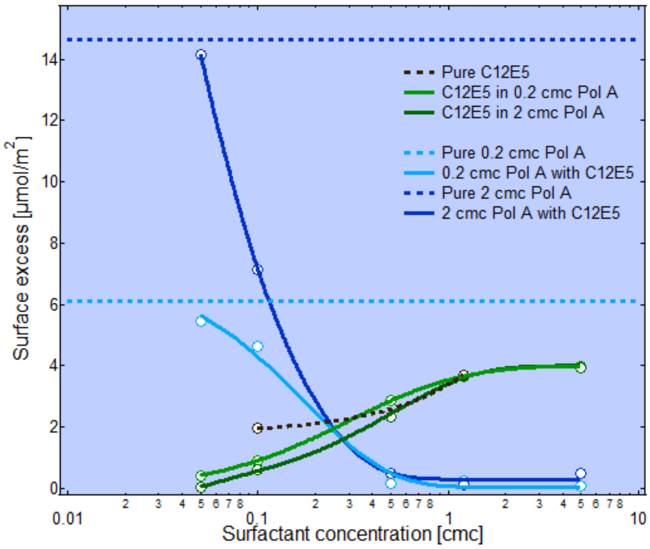


Figure 2 The calculated surface excess versus $C_{12}E_5$ concentration of mixed Pol A + $C_{12}E_5$ systems. The dashed lines represent calculated values of pure systems (dark brown for $C_{12}E_5$, pale blue for 0.2 cmc Pol A, dark blue for 2 cmc Pol A). The solid lines represent double exponential fit for the $C_{12}E_5$ data (pale green for $C_{12}E_5$ in 0.2 cmc Pol A, and dark green for $C_{12}E_5$ in 2 cmc Pol A), and for the Pol A data (pale blue for mixtures of $C_{12}E_5$ in 0.2 cmc Pol A, and dark blue for mixtures of $C_{12}E_5$ in 2 cmc Pol A).

Conclusions

In general, the thickness of polymer layer decreases with increasing concentration of $C_{12}E_5$, as expected due to the polymer being depleted from the interface by $C_{12}E_5$.

			1st layer			2nd layer			3rd layer			
Pol A [cmc]	C12E5 [cmc]	model	d [Å]	solv [%]	rough [Å]	d [Å]	solv [%]	rough [Å]	d [Å]	solv [%]	rough [Å]	χ^2
0.2	-	1 layer	10.426	23.706	4.7687							
2	-	1 layer	26.919	21.824	4.1878							
-	0.1	-	-	-	-	-	-	-	-	-	-	-
-	1.2	2 layer	8.1983	6.7669	2.5518	10.782	19.636	4.7902				0.0338388
0.2	0.05	1 layer (75% Pol)	14.054	22.814	4.6795							0.0301433
0.2	0.1	1 layer (60% Pol)	14.491	18.922	4.9612							0.0207812
0.2	0.5	3 layer	7.1452	20.464	3.9232	5.949	7.5758	3.3974	3.642	67.753	2.926	0.0294166
0.2	1.2	3 layer	9.3959	18.27	4.7675	4.7481	10.96	4.3068	5.8606	61.563	3.5875	0.00992002
0.2	5	3 layer	9.8201	11.952	3.9942	4.6953	9.3775	4.03	4.2367	44.626	2.7982	0.0132415
2	0.05	1 layer (100% Pol)	23.475	17.883	2.6054							0.0377105
2	0.1	1 layer (95% Pol)	22.289	15.566	2.5882							0.0447206
2	0.5	3 layer	6.2238	9.4799	2.7686	7.0228	31.93	3.2919	7.0948	77.441	4.8482	0.0282292
2	1.2	3 layer	9.6838	15.78	4.4947	4.5393	15.528	3.6491	4.0029	40.179	2.7586	0.0143515
2	5	3 layer	8.7112	3.5593	3.8219	5.3982	45.43	3.7901	4.3612	6.934	3.6061	0.0155775

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 $C_{12}E_5$ depletes the interface of Pol A and forms a monolayer. Compared to our data obtained for the same polymer with SDS, the non-ionic $C_{12}E_5$ seems to be more effective at depleting the interface of the polymer. The polymer then forms a layer underneath the $C_{12}E_5$, where the head groups of $C_{12}E_5$ can interact with the polymer.

The general behaviour is comparable to the one observed for polymer/SDS mixed system, however there is a clear difference in the concentrations at which the onset of this is observed. This could prove crucial for our further investigation of the foaming properties of these mixed systems, as well as bulk studies in order to investigate formation of mixed micelles in the bulk.