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hexaethylene glycol monododecyl ether and poly-(dimethyldialyl ammonium chloride)

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The structure and composition of surfactant–polymer mixtures of sodium dodecyl sulphate, hexaethylene glycol monododecyl ether and poly-(dimethyldialyl ammonium chloride) adsorbed at the air–water interface

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Abstract. Specular neutron reflection has been used to investigate the composition and structure of the surfactant–polymer mixture of sodium dodecyl sulphate (SDS) and hexaethylene glycol monododecyl ether ($C_{12}E_6$), and the cationic polymer poly-(dimethyldialyl ammonium chloride) (dmdaac), at the air–water interface. In particular, the effects of surfactant and polymer concentration are investigated. The addition of the cationic polymer results in an interface more rich in SDS. The variation of surfactant composition with polymer and surfactant concentration shows a complex behaviour, which is related indirectly to the bulk solution phase behaviour. The amount of polymer at the interface increases with increasing polymer concentration, but decreases with increasing surfactant concentration at a fixed solution polymer concentration. At a polymer concentration ~ 100 ppm there is a marked change in the structure of the adsorbed polymer layer: the thickness of the absorbed layer increases from ~ 20 Å to ~ 30 Å. In contrast the thickness of the absorbed layer, when only the surfactant is visible at the interface, shows no significant change with increasing polymer concentration.

1. Introduction

Polymers in aqueous surfactant solutions are extensively used in many important technological applications, as viscosity modifiers, stabilizers and deposition aids. Systems of neutral polymers with an anionic surfactant, and of a charged polymer with a single surfactant of opposite charge have been extensively studied and well documented [1, 2]. Most technological applications, however, involve the use of surfactant mixtures, and the bulk and interfacial properties of mixed surfactant–polymer complexes have also attracted much interest [3, 4]. Such complex mixtures are less well understood, and this is particularly true of the interfacial properties. Recent studies [5] have shown that the bulk behaviour, as revealed through measurements such as surface tension, are not necessarily correlated with the interfacial properties. Adsorption at the air–water interface involves a balance between complex formation in bulk and at the interface, and also in a modification of surfactant monomer concentration adsorbed at the interface. A variety of different techniques have been used to study polymer–surfactant complexes [6, 7], but none give a complete picture of adsorption at interfaces. The

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interpretation of conventional methods, such as surface tension, is complicated by the formation of complexes in bulk and at interfaces, and the resulting variation in surfactant activity renders the Gibbs equation difficult to apply. Furthermore such techniques provide no direct structural information.

In recent years a number of new techniques, which offer considerable potential in this area, have emerged [7, 8]. We have demonstrated that one of these, neutron reflectivity, is a powerful method for determining adsorbed amounts of surfactants at interfaces [9], especially for multi-component mixtures [10, 11], and for obtaining detailed surface structure [12]. Of particular relevance to this paper is the use of neutron reflectivity [5, 13, 14] and the complementing x-ray reflectivity [15] to study the adsorption of polymer–surfactant mixtures at the air–water interface. We have previously reported the preliminary use of neutron reflectivity to study the adsorption of the mixed surfactants of sodium dodecyl sulphate (SDS) and hexaethylene glycol monododecyl ether ($C_{12}E_6$) at the air–water interface, in the presence of the cationic co-polymer, poly-(dimethyldialyl ammonium chloride (dmdaac)–acrylamide) and the cationic homo-polymer dimethyldialyl ammonium chloride. The anionic-nonionic surfactant mixture of SDS/$C_{12}E_6$ has been extensively studied in the absence of the polymer [11]. Its adsorption at the air–water interface has been characterized over a broad concentration and composition range, and was shown to be broadly consistent with the predictions of regular solution theory (RST) [16]. We have demonstrated, in the results published earlier [13], that the addition of the cationic polymer produces a surface more rich in the anionic surfactant, SDS, and that the polymer–surfactant interaction is primarily with the cationic dmdaac block of the co-polymer. This is confirmed in recent measurements which show that the co-polymer and dmdaac homo-polymer behave in a similar way.

In this paper we report the effect of surfactant and polymer concentration on the adsorption of SDS/$C_{12}E_6$ and the cationic homo-polymer, poly-dmdaac, at the air–water interface. The effect of surfactant and polymer concentration on the surface composition (both of surfactant and polymer) and on the structure of the adsorbed layer will be considered.

2. Experimental details

2.1. Neutron reflectivity

The specular reflection of neutrons provides information about inhomogeneities normal to an interface or surface, and the technique is described in detail elsewhere [8]. The basis of a neutron reflectivity experiment is that the variation in specular reflection with Q (the wave vector transfer normal to the surface, and defined as $Q = (4\pi/\lambda)\sin\theta$ where λ is the neutron wavelength and θ the grazing angle of incidence) is simply related to the composition or density profile in a direction normal to the interface. In the kinematic or Born approximation [17] it is just related to the square of the Fourier transform of the scattering length density profile, $\rho(z)$,

$$R(Q) = \frac{16\pi^2}{Q^2}\left|\int \rho(z)e^{-iQz}dz\right|^2 \tag{1}$$

where $\rho(z) = \sum_i n_i(z)b_i$, $n_i(z)$ is the number density of the ith nucleus and b_i its scattering length.

The key to the use of the technique for the study of surfactant adsorption is the ability to manipulate the scattering length density or neutron refractive index profile (where the neutron refractive index is defined as $n = 1 - \lambda^2\rho(z)/2\pi$) at the interface using hydrogen, H/deuterium, D, isotopic substitution (where H and D have vastly different scattering powers for neutrons).

The specular neutron reflectivity measurements were made on the SURF reflectometer [18] at the ISIS pulsed neutron source at the Rutherford Appleton Laboratory, UK. The

measurements were made using a single detector at a fixed angle, θ, of $1.5°$, using neutron wavelengths, λ, in the range 0.5 to 6.8 Å to provide a Q range of 0.048 to 0.5 Å^{-1}. The reflectivity at high Q ($Q > 0.2$ Å^{-1}) is dominated by sample dependent background. This arises primarily from incoherent scattering from the bulk solution, and is constant in Q. The background is determined from the reflectivity in the limit of high Q, and has been subtracted from the data before any subsequent analysis. This has been shown to be a valid procedure providing there is no pronounced off-specular or small angle scattering from the bulk solution, and this has been verified here by making off-specular measurements (either side of the specular reflection). The absolute reflectivities were calibrated with respect to D$_2$O [19].

For a deuterated surfactant a null reflecting water (NRW) (92 mole % H$_2$O–8 mole % D$_2$O has a scattering length of zero, that is, the refractive index of air), the reflectivity arises only from the adsorbed layer at the interface. This reflected signal can be analysed in terms of the adsorbed amount at the interface and the thickness of the adsorbed layer. The most direct procedure for determining the surface concentration of surfactant is to assume that it is in the form of a single layer of homogeneous composition. The measured reflectivity can then be fitted by comparing it with a profile calculated using the optical matrix method for this simple structural model [20]. The parameters obtained for such a fit are the scattering length density, ρ, and the thickness, τ, of the layer. The area per molecule is then

$$A = \sum b_i / \rho\tau \tag{2}$$

where $\sum b_i$ is the scattering length of the adsorbed surfactant molecule. This has been shown to be an appropriate method for surfactants. The sources of error (arising from errors in the measurements due to calibration, background subtraction, or because the model is too simple) have been discussed in detail elsewhere, and give rise to an error of typically ± 2 Å^2 at an area per molecule of 50 Å^2 [9]. The simplest model, a single layer of homogeneous thickness, describes the data with sufficient accuracy. The data are not measured to sufficiently high Q for models with different functional forms (for example, a layer with a Gaussian distribution of scattering length density) or for the inclusion of interfacial roughness to be required. It has been shown that although the value of the layer thickness, τ, will be sensitive to the choice of model, the adsorbed amount depends on the product $\rho\tau$ and so is largely independent of the detailed model [9].

It is straightforward to extend this approach to the determination of the surface composition of a multi-component mixture [21]. By selective deuteration of each component in turn the surface excess of each component can be determined. For example, for a binary mixture equation (2) becomes,

$$\rho = \sum b_1 / A_1\tau + \sum b_2 / A_2\tau \tag{3}$$

where b_i, A_i are the scattering lengths and areas/molecules of each of the components in the binary mixture. Making three different reflectivity measurements, with both surfactants deuterated and with either of the two surfactants deuterated, provides a self-consistent estimate of the surface composition.

In the evaluation of the adsorbed amounts of the SDS and C$_{12}$E$_6$ at the interface it is assumed that for the polymer/surfactant mixtures discussed here, the polymer has a scattering length sufficiently close to zero and that its contribution is negligible. We have been unable to synthesize the deuterium labelled poly-dmdaac polymer, and cannot get an estimate of the amount of polymer at the interface by a direct extension of equation (3). However, the amount of polymer at the interface can be estimated indirectly by making the measurements in a different way. For measurements with both surfactants deuterated in a D$_2$O subphase, any deviation from the reflectivity of pure D$_2$O (the deuterated surfactants are here closely matched to the D$_2$O) arises from the polymer at the interface, and simple modelling can be

used to estimate its amount and its spatial extent at the interface. Analysing such reflectivity data as a single layer of uniform composition will give a layer thickness τ and a scattering length density ρ. The difference between the measured and scattering length density, ρ, and that of D_2O, ρ_{D_2O}, is assumed to be due to the presence of polymer such that

$$\rho = (1 - \phi_p)\rho_{D_2O} \qquad (4)$$

where ϕ_p is the polymer volume fraction in the layer.

The protonated surfactants were obtained from Nikkol ($C_{12}E_6$) and BDH (SDS). The deuterated SDS (d-SDS, $CD_3(CD_2)_{11}SO_4Na$) and deuterated $C_{12}E_6$ (both alkyl chain deuterated, d-C_{12}h-E_6, $CD_3(CD_2)_{11}(OCH_2CH_2)OH$ and fully deuterated, d-C_{12}d-E_6, $CD_3(CD_2)_{11}(OCD_2CD_2)OH$), were synthesized and purified by methods previously described [20], by Thomas's group at Oxford. The chemical purity of the surfactants was assessed by surface tension measurements and thin layer chromatography (TLC). The cationic polymer, poly-dmdaac was synthesized at Oxford and its molecular weight was 100 K. Deuterium oxide (D_2O) was supplied by Fluorochem and high purity water (Elga Ultrapure) was used throughout. The glassware and PTFE troughs used for the neutron measurements were cleaned using alkaline detergent (Decon 90), followed by copious washing in high purity water.

The neutron reflectivity measurements were made from the surfactant–polymer mixtures of SDS–$C_{12}E_6$ with poly-dmdaac in 0.1M NaCl solution at a temperature of 25 °C at the air–solution interface. The measurements were made predominantly in NRW using d-SDS/h-$C_{12}E_6$, h-SDS/d-C_{12}h-E_6 and d-SDS/d-C_{12}h-E_6. Measurements to estimate the amount of polymer at the interface were made using D_2O and d-SDS/d-C_{12}d-E_6. Measurements were made for a 40/60 mole % mixture of SDS/$C_{12}E_6$ at solution concentrations of 6.25×10^{-4} M, 1.25×10^{-3} M and 2.5×10^{-3} M in NRW and with added polymer concentrations from 0 to 500 ppm. Additional measurements were made at a surface concentration of 1.25×10^{-3} M at surfactant compositions of 20/80 and 60/40 with added polymer concentrations in the 0 to 500 ppm range in both NRW and D_2O. At a polymer concentration of 50 ppm measurements were made at a surfactant concentration 10^{-3} M, and a range of SDS/$C_{12}E_6$ solution compositions from 10/90 to 60/40.

2.2. Solution phase behaviour

The mixed surfactant and polymer layer adsorbed at the air–water interface is in equilibrium with a bulk solution which exhibits a complex phase behaviour. In order to correlate the surface adsorption with the bulk phase it is important to have a knowledge of the bulk phase behaviour. The bulk phase behaviour has been measured as a function of SDS/$C_{12}E_6$ composition and polymer concentration for three different surfactant concentrations (2.5×10^{-3} M, 1.25×10^{-3} M, 6.25×10^{-4} M). The phase diagram measurements were made by visual inspection of solutions prepared in H_2O. In figure 1 we show one of those bulk phase diagrams measured at a surfactant concentration of 1.25×10^{-3} M. At the lowest concentration there is a region in which the solution is cloudy, and at higher SDS compositions visible aggregates are present. The line of charge equalization between the cationic polymer and surfactant (dashed line in the figure) encompasses both regions in the phase diagram. At the two higher surfactant concentrations an additional phase containing precipitates is observed, for SDS mole fractions of < 0.50. Furthermore, with increasing surfactant concentration these distinct regions in the phase diagram extend to much higher polymer concentrations. None of these bulk phases exist for SDS mole fractions of < 0.20. Similar phase diagrams are obtained at the other two surfactant concentrations, and the different regions of aggregation occur at different polymer concentrations.
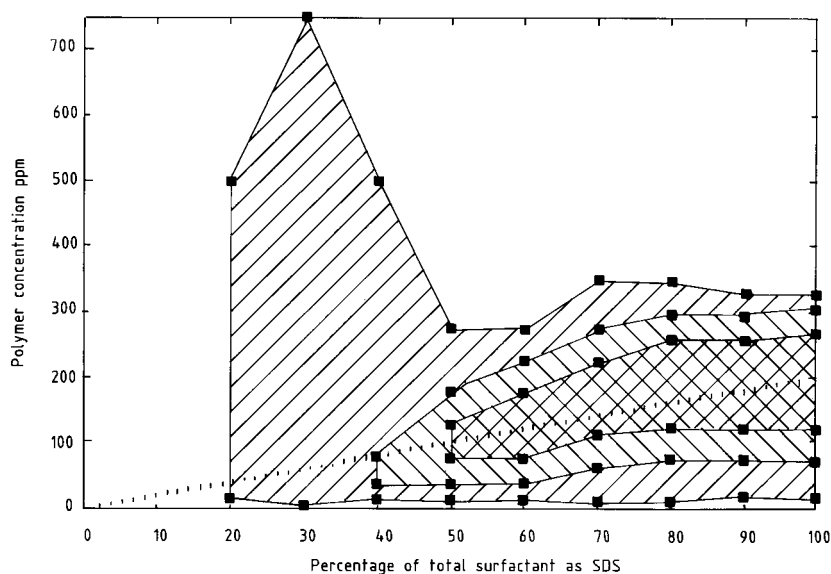
Figure 1. Phase diagram for 1.25×10^{-3} M SDS/$C_{12}E_6$/poly-dmdaac/0.1 M NaCl: (///) cloudy (\\\) visible aggregates, (XXX) precipitates. The dashed line is the line of charge equalization between the polymer and surfactant.

Beyond the region in which clear solutions exist, a range of polymer–surfactant complexes, characterized by cloudy solutions, solutions with visible aggregates and precipitates, are in equilibrium with a dilute phase. The bulk neutron scattering is determined by these inhomogeneous phases, and the detailed nature of the bulk phase diagram has an enormous impact upon the small angle neutron scattering, SANS, from such solutions, and particularly upon the reproducibility and subsequent interpretation of the data. This is not true for the surface that is in equilibrium with that bulk phase. In this case the surface is controlled by the monomer concentration in the dilute component of the phase, and we have seen no effects of irreproducibility when assessing the neutron reflectivity data that could be associated with changes in the macroscopic phase behaviour of the solution.

3. Results and disucssion

3.1. Effect of solution surfactant composition on adsorbed layer

Measurements of the neutron reflectivity have been made at a solution concentration of 10^{-3} M in NRW, with and without 50 ppm poly-acrylamide–dmdaac co-polymer in the SDS/$C_{12}E_6$ composition range 10/90 to 60/40 (mole ratio). Measurements using d-SDS/d-$C_{12}E_6$ and h-SDS/d-$C_{12}E_6$ provide (using equation (3)) an estimate of the total amount of surfactant adsorbed, and of the surface composition of the mixed surfactants.

The sensitivity of the technique is clearly shown in figures 2(a) and (b) where the reflectivity for the two extreme solution compositions, with and without added polymer are shown for the isotopic combinations described above. The small change in the reflectivity curves for h-SDS/d-$C_{12}E_6$ compared to d-SDS/d-$C_{12}E_6$ for the 10/90 solution indicates that the surface is rich in $C_{12}E_6$. The relatively larger change in reflectivity from d-SDS/d-$C_{12}E_6$ to h-SDS/d-$C_{12}E_6$ for the 60/40 solution indicates a much smaller amount of $C_{12}E_6$ at the interface. The
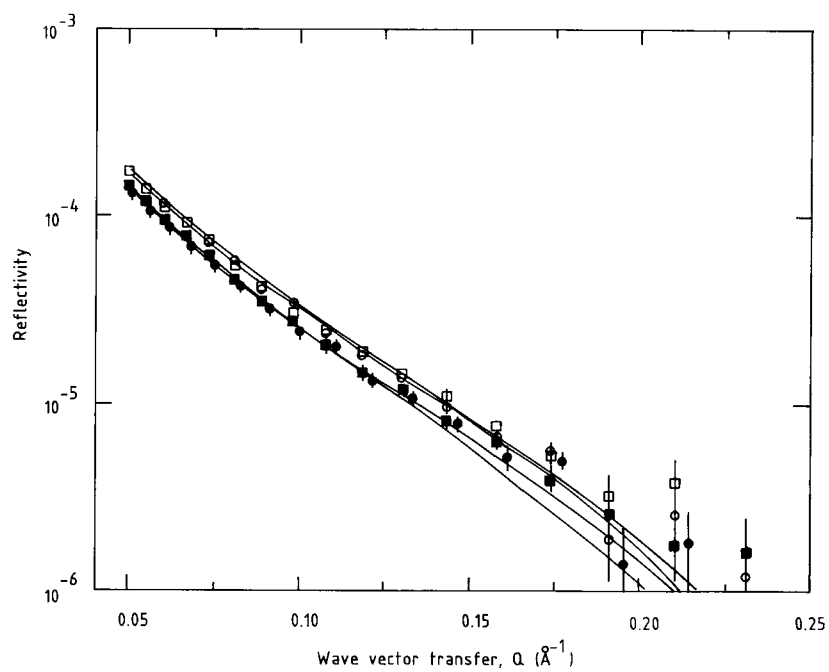
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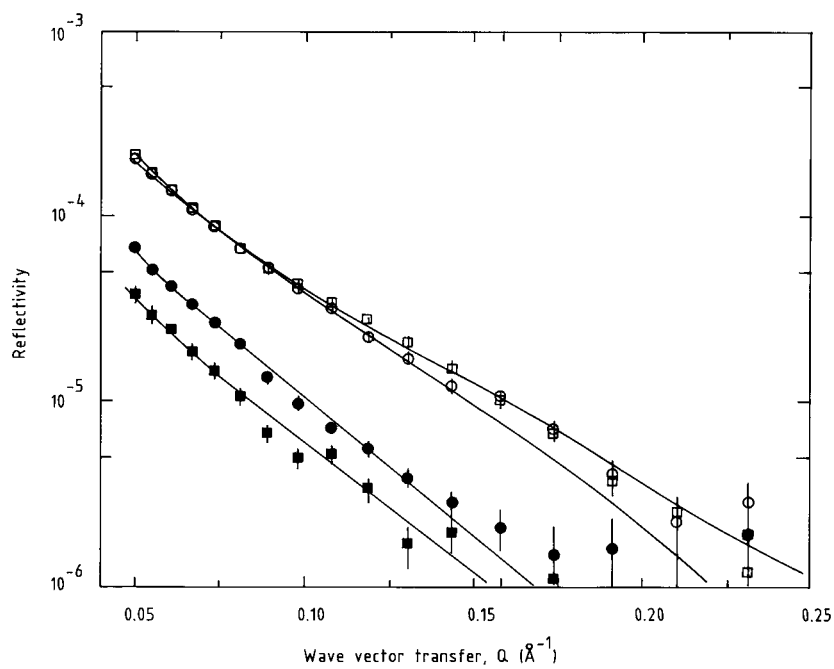
(b)

Figure 2. Neutron reflectivity for 10^{-3} M SDS/$C_{12}E_6$ in 0.1 M NaCl/NRW (a) 10/90 SDS/$C_{12}E_6$, (b) 60/40 SDS/$C_{12}E_6$; (○) d-SDS/d-$C_{12}E_6$, (□) d-SDS/d-$C_{12}E_6$, + 50 ppm co-polymer, (●) h-SDS/d-$C_{12}E_6$, and (■) h-SDS/d-$C_{12}E_6$ + 50 ppm co-polymer. The solid lines are calculations for single layers of uniform composition.

addition of polymer hardly alters the reflectivity of the d-SDS/d-$C_{12}E_6$ mixture, consistent with the total amount of surfactant adsorbed at the interface being unaffected by the addition of the polymer. Furthermore the addition of polymer to the solution for the 10/90 h-SDS/d-$C_{12}E_6$ mixture also shows hardly any change in the reflectivity, indicating only a marginal effect on the surface composition, whereas the addition of the polymer to the 60/40 h-SDS/d-$C_{12}E_6$ mixture shows a significant decrease in the reflectivity, consistent with the amount of $C_{12}E_6$ at the interface decreasing and the amount of SDS increasing.
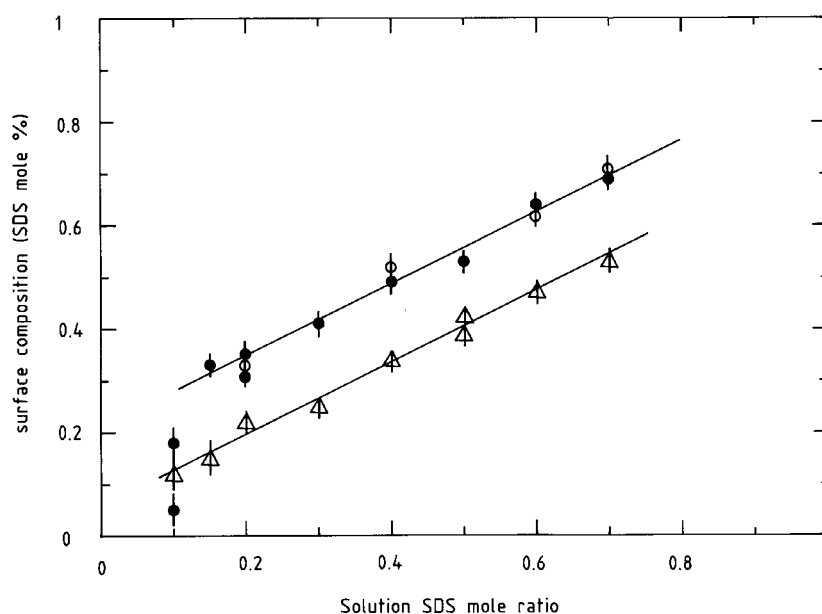

Figure 3. Surface mole ratios SDS as a function of solution composition for 10^{-3} M SDS/$C_{12}E_6$/0.1 M NaCl ($\triangle$) without polymer, ($\bullet$) with 50 ppm co-polymer and ($\circ$) 500 ppm poly-dmdaac.

The results as a function of solution composition at a fixed concentration of 10^{-3} M are summarized in figure 3, where the surface composition (in mole % of SDS) is plotted as a function of solution composition. With and without co-polymer the surface composition shows the same linear relationship with solution composition over a wide range of solution compositions. The addition of the co-polymer results in a surface more rich in the SDS. The results, with and without co-polymer, are consistent with those previously reported over a narrower range of surfactant concentrations and compositions [11, 13]. As the total amount of surfactant at the interface remains essentially constant, this also means that the amount of $C_{12}E_6$ at the interface has decreased. At low SDS mole fractions in solution (< 0.2) the amount of SDS at the interface drops markedly. Similar measurements were made for the poly-dmdaac homo-polymer (at a concentration of 500 ppm), and these results are also shown in figure 3. A similar trend with solution composition is observed, and confirms that the surfactant interaction is primarily with the charged dmdaac block and not the acrylamide. Not only are the results from the homo-polymer and co-polymer similar in trend, the effects of each polymer on the absolute adsorbed amounts of surfactant and the surface composition are very close. This arises primarily because the different polymer concentrations and molecular weights combine to produce the coincidence, rather than any universality of effect.

3.2. Effect of solution surfactant concentration on adsorbed layer

For a solution composition of 40/60 SDS/$C_{12}E_6$ neutron reflectivity measurements were made with and without 50 ppm poly-dmdaac homo-polymer in the concentration range 10^{-6} to 10^{-2} M; that is, at concentrations above and below the critical micelle concentration (CMC) of the surfactant mixture. Measurements were made for the isotopic combination h-SDS/d-$C_{12}E_6$ in NRW, and so an estimate of the amount of $C_{12}E_6$ at the interface only was obtained. The results are summarized in figure 4, where the amount of $C_{12}E_6$ at the interface is plotted as a function of surfactant concentration. $C_{12}E_6$ is the more surface-active component in the SDS/$C_{12}E_6$ mixture, and from the predictions of RST [16] and more recent theoretical predictions by Nikas *et al* [23] its adsorption at the interface should go through a maximum at the CMC. This has been previously observed by us [24] for the non-ionic mixture of $C_{12}E_3$/$C_{12}E_8$ and despite the lack of experimental points between 10^{-4} and 10^{-3} M this trend is clearly observed here for the SDS/$C_{12}E_6$ mixture. The addition of the poly-dmdaac homo-polymer has an interesting and complex effect on the $C_{12}E_6$ adsorption. Above the CMC the addition of the polymer reduces the amount of $C_{12}E_6$ at the interface, whereas below the CMC it results in an enhancement of the $C_{12}E_6$ adsorption. Furthermore, below the critical aggregation concentration (CAC) (concentration at which polymer-mixed surfactant micelle complexes start to form) the amount of $C_{12}E_6$ at the interface again increases when polymer is added.
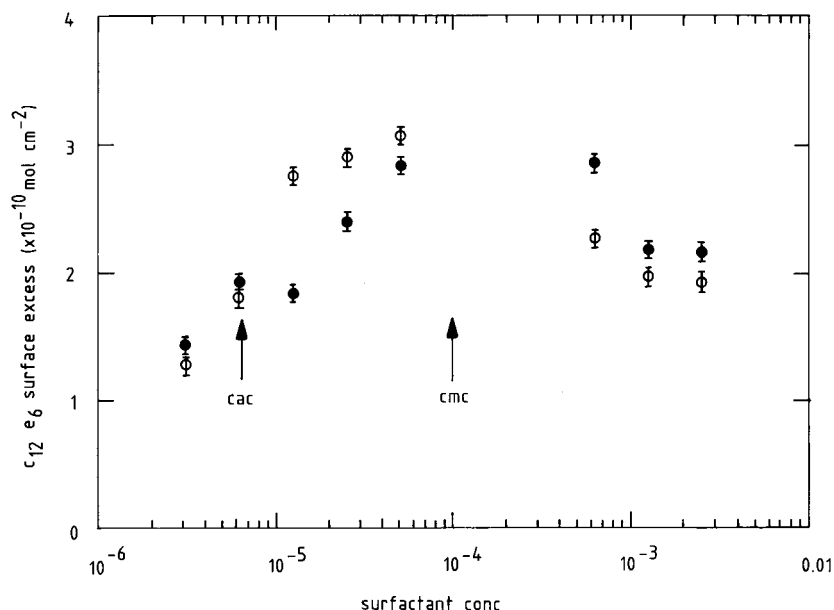
Figure 4. $C_{12}E_6$ surface excess as a function of surfactant concentration for 40/60 SDS/$C_{12}E_6$/0.1 M NaCl (●) with 50 ppm poly-dmdaac and (○) without polymer.

There are two potential mechanisms by which the addition of polymer can affect the surfactant adsorption and composition at the interface. The formation of polymer-surfactant complexes in the bulk will affect the relative activities of the SDS and $C_{12}E_6$ and their monomer concentrations, and hence the surface composition. Furthermore the adsorption of polymer–surface complexes directly to the interface will alter the surface composition. Above the CMC the formation of free mixed surfactant micelles (even in the presence of polymer) will result in further changes in the SDS and $C_{12}E_6$ activities and to monomer concentrations.

The complex pattern of behaviour of surfactant adsorption with surfactant concentration can be explained by the relative contributions of these two competing effects. If we assume that at low concentrations (below the CAC) it is entropically more favourable for the polymer to interact with the surfactant at the interface than to induce micelle formation on the polymer, then polymer adsorption at the interface will result in an enhancement in the SDS adsorption, as observed. Above the CAC, but below the CMC, mixed surfactant micelles (initially more rich in SDS) form on the polymer and the SDS activity is reduced, resulting in a reduction of SDS adsorption with the further addition of surfactant. Above the CMC charge neutralization of the cationic polymer will be achieved and the SDS monomer concentration will again increase, resulting in an enhancement of the SDS adsorption at the interface.

3.3. Effect of solution polymer concentration at the adsorbed layer

The variation in surface adsorption (composition and adsorbed amounts) with polymer concentration (poly-dmdaac homo-polymer) was determined in two different sequence of measurements (for polymer concentrations up to 500 ppm), for a solution composition of 40/60 mole fraction SDS/$C_{12}E_6$ at solution concentrations of 6.25×10^{-4} M, 1.25×10^{-3} M and 2.5×10^{-3} M, and for a solution concentration of 1.25×10^{-3} M and compositions of 20/80, 40/60 and 60/40 SDS/$C_{12}E_6$. These measurements, all above the CMC, then provide an additional insight into the relative competition of the different mechanisms responsible for the surface composition in these complex mixtures. The results are summarized in figures 5 and 6, where the SDS and $C_{12}E_6$ surface excess, and surface composition (mole % of SDS) are plotted as a function of polymer concentration. In all cases the amount of SDS at the interface increases with increasing polymer concentration, to a maximum at a polymer concentration ~ 10 to 20 ppm. The amount adsorbed then reduces to a mean level in the limit of high polymer concentration which is higher than the value at low polymer concentrations. The amount of $C_{12}E_6$ at the interface shows the reverse trend, as the total amount of surfactant at the interface remains essentially constant. At a fixed composition there is little or no variation with solution concentration and each of the three concentrations measured shows very similar trends with increasing polymer concentration. At a fixed concentration, 1.25×10^{-3} M, the nature of the variation with polymer concentration is similar for each solution composition, but the features are shifted to higher polymer concentrations for the solutions more rich in SDS. The different regions of the phase diagram (see figure 1) also occur at higher polymer concentrations for the solutions richer in SDS, and to this extent the variation in the bulk behaviour is reflected by changes in the surface composition.

The evolution of adsorbed amounts of SDS and $C_{12}E_6$, and of the surface composition with polymer concentration, shown in figures 5 and 6, are consistent with the arguments presented earlier in the discussion on the extent of the data described in figure 4 regarding the variation of the adsorption of $C_{12}E_6$ with surfactant concentration in the presence of polymer (figure 4). The amount of SDS at the interface increases initially for low polymer concentrations due to the adsorption of polymer and surfactant monomers at the interface. At higher polymer concentrations the formation of SDS rich polymer–surfactant complexes results in a depletion of SDS at the interface, Above the point of charge neutralization, which occurs at low polymer concentration for solutions less rich in SDS, the amount of SDS at the interface increases again as the polymer becomes saturated with SDS. This is also accompanied by an increasing adsorption of polymer at the interface with increasing polymer concentration (see later discussion and figure 8).
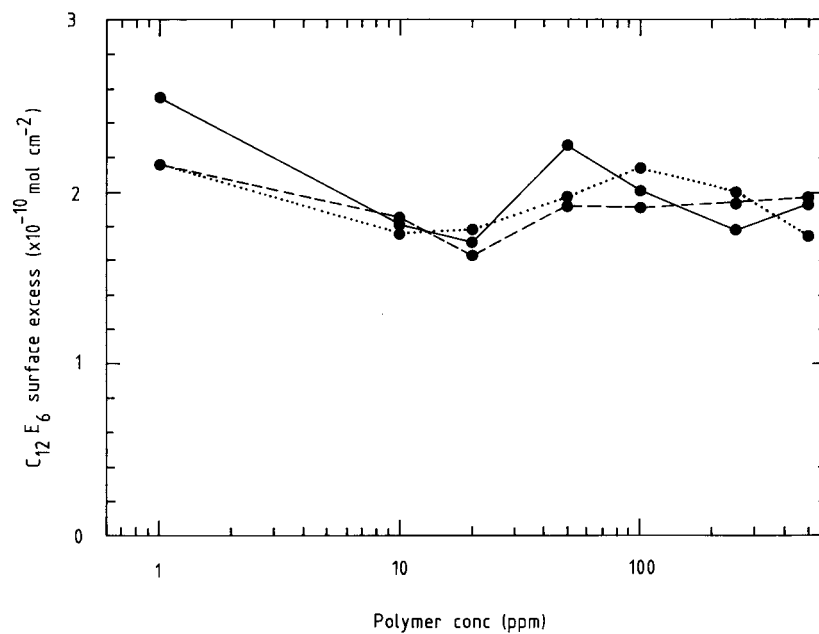
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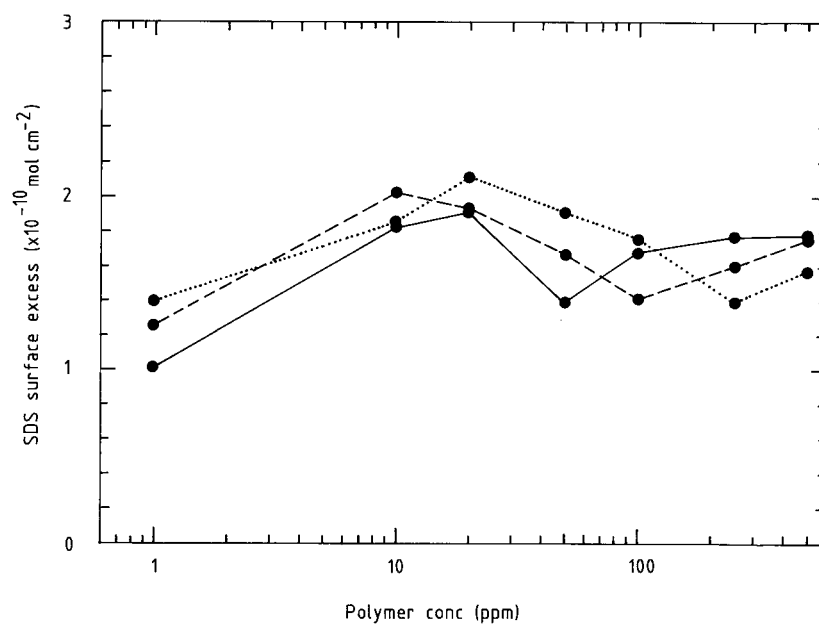
(b)

Figure 5. Variation in surface composition for 40/60 SDS/$C_{12}E_6$/0.1 M NaCl as a function of polymer concentration (——) 6.25×10^{-4} M, (- - - -) 1.25×10^{-3} M and ($\cdots\cdots$) 2.5×10^{-3} M, (a) $C_{12}E_6$ excess, (b) SDS excess and (c) SDS mole fraction.
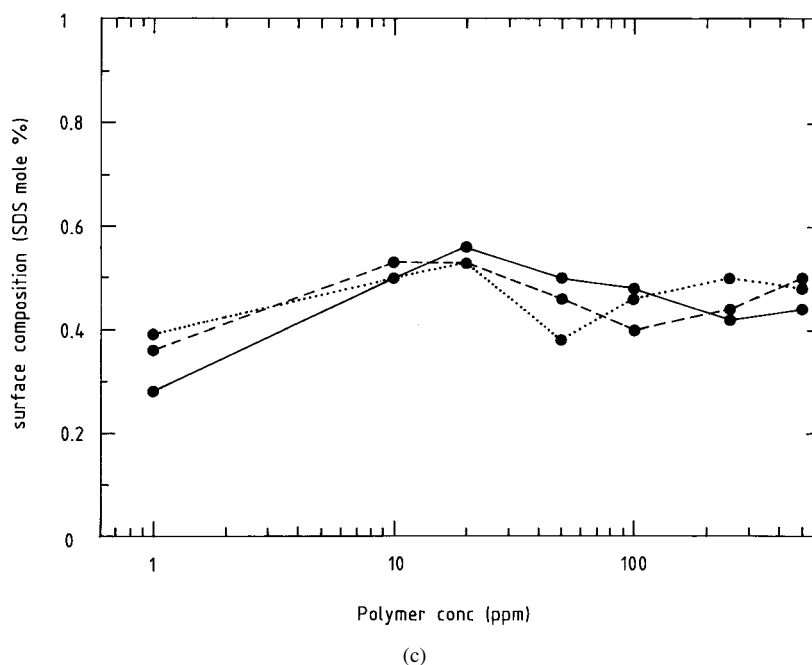
(c)

Figure 5. (Continued.)

3.4. Amount of polymer at the interface

From the measurements reported so far it has only been possible to determine the amount and composition of the mixed surfactants at the interface. For a complete understanding of the processes involved we also require a knowledge of the amount of polymer at the interface and the structure of the adsorbed layer. With deuterated polymer a straightforward extension of equation (3) would enable the amount of polymer and both surfactants at the interface to be determined. It has not proved possible to deuterate the poly-dmdaac homo-polymer nor the co-polymer; however as discussed earlier, the amount of polymer at the interface can be determined with good reliability by slightly more indirect measurements.

Measurements with both surfactants deuterated in D_2O give rise to a reflectivity close to that of pure D_2O, as the scattering length density (or refractive index) of the surfactants is close to that of D_2O. Any polymer at the interface, with a scattering length density or refractive index lower than D_2O, will result in a reduction in reflectivity, and this difference can be used to estimate the amount and the extent of the polymer at the interface. Previous reflectivity measurements of the polymer in D_2O have shown that there is no polymer at the interface in the absence of surfactant [13]. The extent of the polymer at the interface and the adsorbed amount have been calculated from a series of reflectivity measurements for 1.25×10^{-3} M 40/60 d-SDS/d-$C_{12}E_6$ in 0.1 M NaCl/D_2O for a range of polymer concentrations from 10 to 500 ppm. Figure 7 shows the reflectivity for 1.25×10^{-3} M 40/60 d-SDS/d-$C_{12}E_6$ in 0.1 M NaCl/D_2O with 50 and 250 ppm poly-dmdaac homo-polymer. The dashed line shows the reflectivity for pure D_2O. The reflectivities for 50 and 250 ppm polymer are lower than for pure D_2O and fall off more steeply with increasing Q. This is indicative of a layer at the interface with a lower scattering length density or refractive index than D_2O. The stronger Q dependence of the reflectivity for 250 ppm polymer compared to the reflectivity for 50 ppm polymer and the appearance of a weak
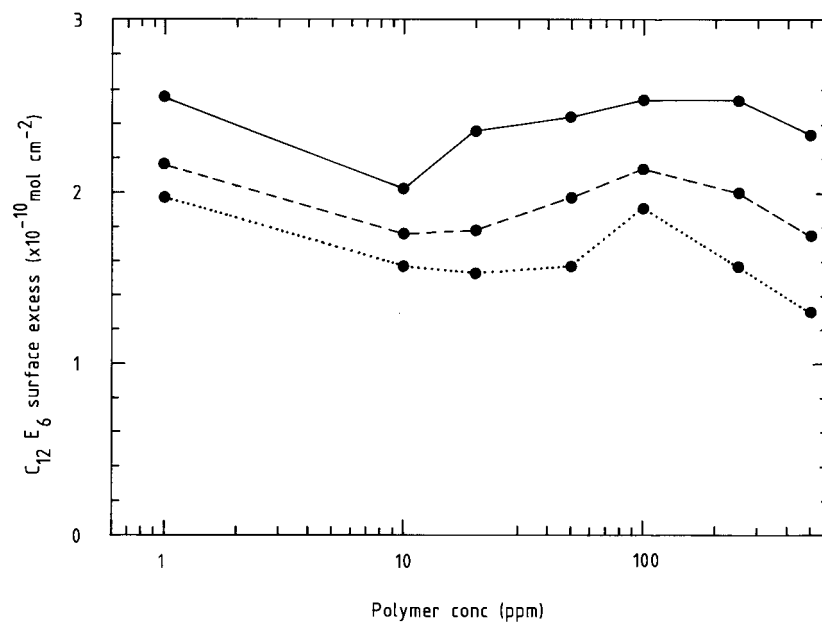
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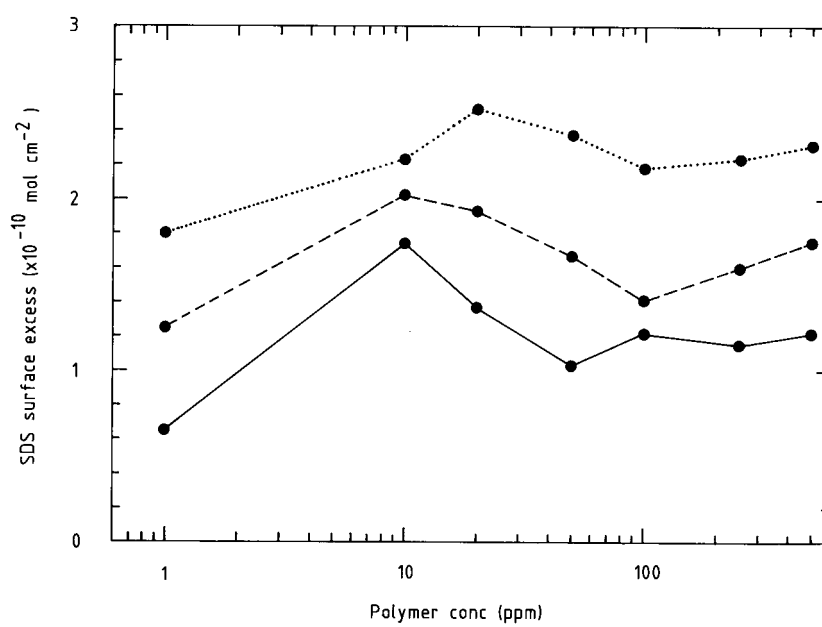
(b)

Figure 6. As figure 5 but at a concentration of 1.25×10^{-3} M and ($\cdots\cdots$) 20/80, (- - - -) 40/60, (——) 60/40.
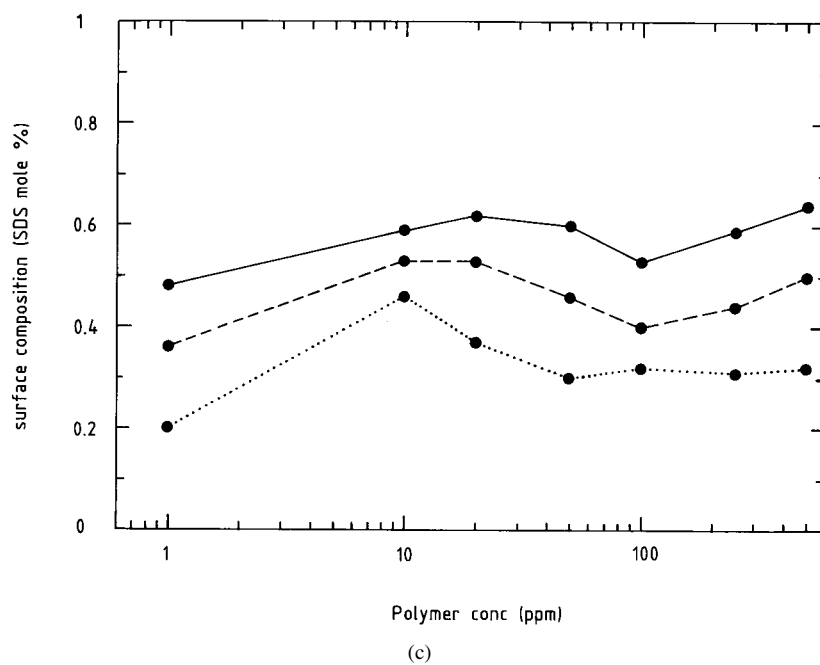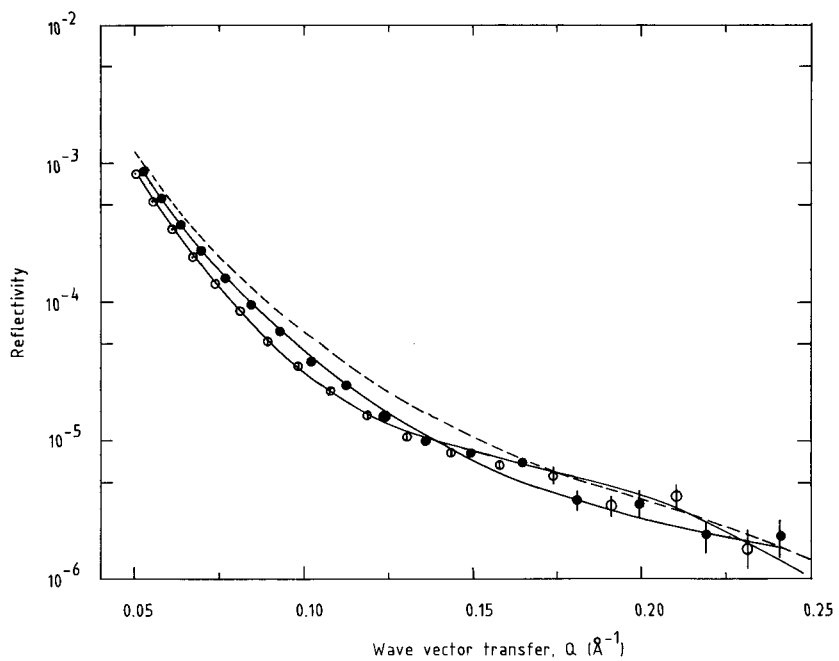
(c)

Figure 6. (Continued.)

**Figure 7.** Neutron reflectivity for 1.25×10^{-3} M 40/60 d-SDS/d-$C_{12}E_6$ in 0.1 M NaCl/D_2O: ($\bullet$) 50 ppm homo-polymer, ($\circ$) 250 ppm, the dashed line is the reflectivity for pure D_2O and the solid lines are single layer fits of uniform composition.

interference fringe at higher Q is consistent with a thicker layer. The solid lines in figure 7 are calculations for a single layer of uniform composition, as described in the experimental details.

The variation in the amount of polymer at the interface with increasing polymer concentration in solution is shown in figure 8. The amount of polymer at the interface increases from a volume fraction $\sim 11\%$ at a polymer concentration of 10 ppm to $\sim 20\%$ at 500 ppm. This contrasts with previous measurements [13] which showed that at a fixed polymer concentration, the amount of polymer at the interface decreased with increasing surfactant concentration. The earlier results [13], for 70/30 mole ratio SDS/$C_{12}E_6$ in 0.1 M NaCl/D_2O in the surfactant concentration range 10^{-4} to 10^{-2} M and for 50 ppm co-polymer, gave polymer volume fractions, ϕ_p, in the range 15 to 25%.
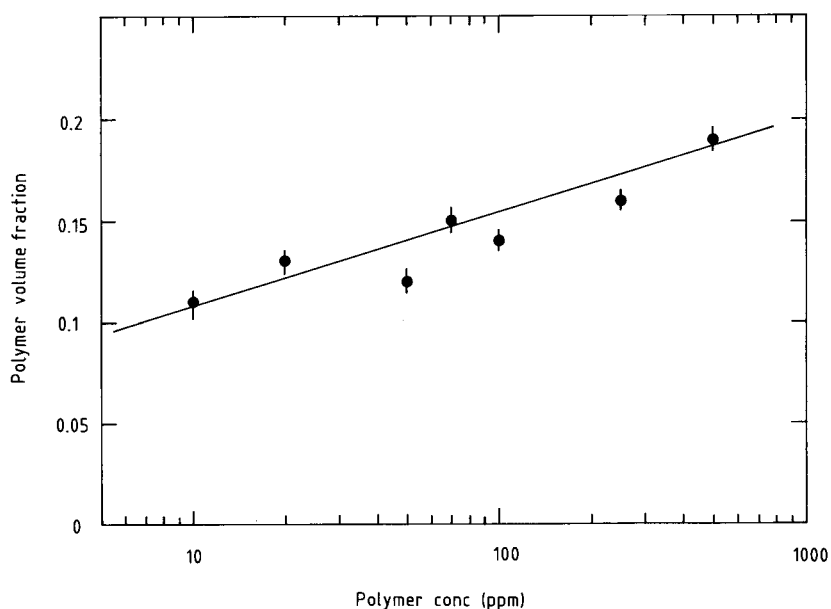

Figure 8. Polymer volume fraction at the interface for 1.25×10^{-3} M 40/60 SDS/$C_{12}E_6$/0.1 M NaCl as a function of polymer concentration.

Stubenrauch *et al* [15] have reported similar polymer volume fractions at the interface for dodecyltrimethyl ammonium bromide (C_{12}TAB) with the anionic polyelectrolyte polystyrene sulphonate (PSS) and polyacrylamide sulphonate (PAMPS). For C_{12}TAB/PSS ϕ_p was $\sim 14\%$ and for C_{12}TAB/PAMPS $\sim 17\%$, and in both cases ϕ_p was independent of surfactant and polymer concentration.

3.5. Structure of the absorbed layer

Figure 9 shows the variation in thickness of the adsorbed surfactant layer (obtained from the measurements with deuterated surfactant in NRW) and of the polymer at the interface (from the measurements in D_2O). The extent of the polymer at the interface shows an abrupt change at a polymer concentration ~ 100 ppm, whereas the spatial extent of surfactant at the interface shows a more gradual increase. Furthermore the amount of polymer at the interface shows no such transition, and we can assume that the transition is associated with a change in conformation of the polymer and not just an increase in the adsorbed amount.
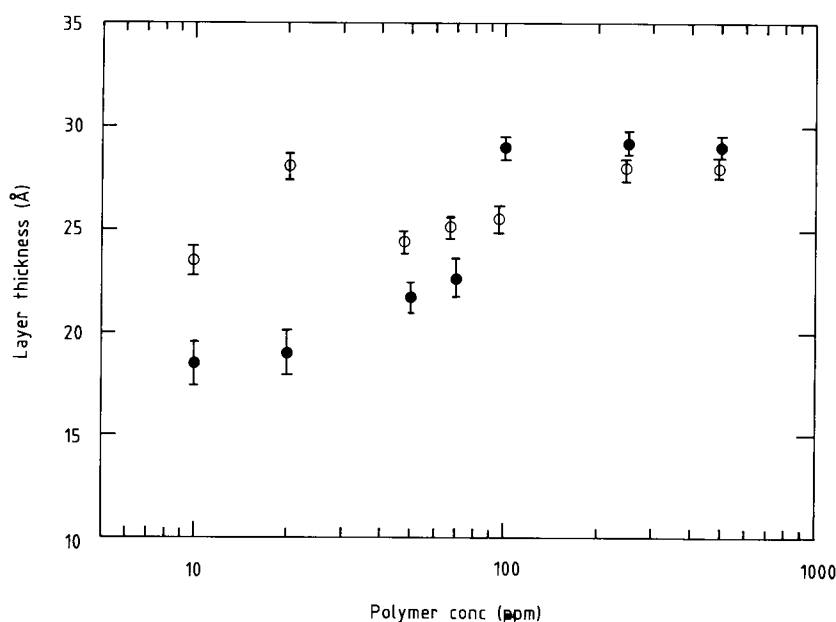
Figure 9. Variation in thickness of the (○) adsorbed surfactant layer, and (●) polymer with increasing polymer concentration for 1.25×10^{-3} M 40/60 SDS/$C_{12}E_6$/0.1 M NaCl.

The surfactant layer is in general thicker in the presence of polymer than without, and hence the polymer is altering the distribution of surfactant at the interface. The increase in the thickness of the surfactant layer with the addition of polymer is consistent with measurements on other related systems. Cooke *et al* [25] observed a modest increase in the SDS thickness in SDS/poly-ethylene oxide (PEO) mixtures from 19 to 21 Å, and from $\sim$ 19 to 20 Å for CsDS and LiDS [26]. However the addition of poly-vinyl pyrolidone (PVP) to SDS [5] resulted in no increase in the thickness of the SDS layer at the interface.

Changes in the thickness of the polymer layer at the interface, in the presence of surfactant, have also been observed. Cooke *et al* [25, 26] have observed increases in the thickness of the PEO layer at the air–water interface in the competitive adsorption of the dodecyl sulphate anionic surfactants with PEO. For SDS/PEO (PEO molecular weight $\sim$ 25 k) the PEO layer increased from 30 to 34 Å [25]. For CsDS the increase was 25 to 30 Å (for PEO molecular weight of 25 k) and 18 to 48 Å (for PEO molecular weight of 100 k), and for LiDS $\sim$ 24 to 33 Å. From x-ray reflectivity measurements Stubenrauch *et al* [15] found that the thickness of the adsorbed layer at the air–water interface for the polyelectrolyte/C_{12}TAB system was invariant with surfactant and polymer concentration; 14.5 Å for PSS/C_{12}TAB and 21 Å for PAMPS/C_{12}TAB. The polyelectrolyte/C_{12}TAB layers are more compact than either the PEO/surfactant or the poly-dmdaac SDS/$C_{12}E_6$ layers.

The changes in the poly-dmdaac conformation at the interface with increasing polymer concentration are consistent with these observations from other polymer/surfactant systems. What is particularly interesting, and not previously observed, is the abrupt nature of the transition which suggests that this coincides with a packing constraint at which the conformation of the polymer is substantially altered. This implies that there comes a point at which more polymer can only be accommodated at the interface by allowing it to extend further into solution from the interface, rather than displacing surfactant. This abrupt change

in polymer conformation at the interface occurs at a polymer concentration at which the SDS adsorption at the interface goes through a minimum. The increase in SDS at the interface beyond this polymer concentration is partially attributed to the onset of charge neutralization on the polymer in the bulk solution. Further measurements, but with a deuterium labelled polymer, will provide more detailed information about the structure of the mixed layer and this actual mechanism for this change in the conformation of the polymer.

4. Summary

Specular neutron reflection has been used to characterize the adsorption of the surfactant mixture of SDS/$C_{12}E_6$ and the cationic polymer, poly-dmdaac, at the air–water interface. The addition of the cationic polymer results in an interface more rich in SDS. The variation of the mixed surfactant composition at the interface with solution concentration and composition shows a complex behaviour which is related to the bulk phase behaviour. The amount of polymer at the interface has also been estimated. It increases with increasing polymer concentration in solution for a fixed surfactant concentration and composition, but decreases with increasing surfactant concentration at a fixed polymer concentration in solution. With increasing polymer concentration there is an abrupt change in the thickness of the polymer layer at the interface. In contrast, neither the amount of polymer at the interface, nor the extent of surfactant at the interface, show such discontinuities. The increase in thickness is attributed to a change in the polymer conformation at the interface, due to packing constraints.

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