Eur. Phys. J. B **5**, 905–911 (1998)

THE EUROPEAN PHYSICAL JOURNAL B

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Mixed monolayers of cationic surfactants and anionic polymers at the air-water interface: Surface tension and ellipsometry studies

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Received: 16 October 1997 / Revised: 14 May 1998 / Accepted: 15 May 1998

Abstract. Equilibrium surface tension measurements have been carried out on mixed solutions of a non-surface active polyelectrolyte (polyacrylamide sulfonate) and cationic surfactants. A strong synergistic lowering of the surface tension is found in the concentration range where no appreciable complexation of surfactant and polymer occurs in the bulk solution (as seen from viscosity measurements). The surface tension decrease does not depend upon the polymer molecular weight, and there is a limited influence of the surfactant chain length. The influence of the degree of charge of the polymer is more important: for small degree of charge, the complexation is less cooperative, and the structure of the surface complex is looser.

PACS. 68.10.Cr Surface energy (surface tension, interface tension, angle of contact, etc.) – 78.66.SqComposite materials – 82.70.Gg Gels and sols

1 Introduction

Interactions between surfactants and polymers is a rapidly growing field of interest in colloid science [1]. Many practical systems for industrial applications contain mixtures of polymers and surfactants, which are widely used as thickeners in water based formulations such as paints, drilling muds, *etc.* In these applications, polyelectrolytes are of particular interest, because of the important role of polymer charges. Biological membranes are structured complexes of lipids and proteins, which are also charged polymers. Whereas there is an extensive literature on surfactant solutions on one hand, and polymer solutions on the other hand, much less is known for the mixed solutions. Polyelectrolytes solutions are less well understood than neutral polymer solutions, but recent work has allowed to improve the current knowledge [2]. These polymers form much more extended structures than neutral polymers, with effective persistence lengths much larger than those of neutral polymers. The polyelectrolyte solutions are in the semi-dilute range at very small polymer concentrations; however, the viscosity of the solutions increases less rapidly with concentration than for neutral polymers, because the polyelectrolyte chains are rod-like and less strongly entangled. The influence of the counterions is subtle: partial counterion condensation frequently occurs and the concentration of counterions is enhanced close to the polyion. When two polyelectrolytes of opposite charge are mixed, the two polyions associate, thus releasing the counterions in the solution, and increasing the entropy of the solution [3]. It was observed that the behaviour of polyelectrolyte-surfactant solutions is similar to the behaviour of polyelectrolyte-polymer solutions: no association when the surfactant or the polymer are nonionic or when the two species have the same charge, and strong association for opposite charges. The case of surfactant-polymer mixtures is however less simple, because the size and the shape of the surfactant aggregates can vary [4–9].

Polymers and surfactants also form complexes at surfaces, either solid-fluid or fluid-fluid surfaces. Complexation in bulk or at a surface are generally related [10]. Surface complexation is also important for practical applications such as colloidal stabilization, wettability, adhesion, *etc.* Only few studies have focused on surfactant-polyelectrolyte complexation at a surface [11–16]. In this work we present a study of polymer-surfactant complexation at the free surface of an aqueous solution. We have studied a model polymer for drilling muds formulations: polyacrylamide sulfonate. A first study has already been reported [17]. Here, the study is extended, and the role of different parameters is reported: surfactant chain length, polymer molecular weight, and polymer degree of charge. We have characterized the bulk complexation by viscosity

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measurements, and the surface complexation by surface tension and ellipsometry measurements.

2 Experimental section

2.1 Materials

The cationic surfactants, dodecyl and hexadecyl trimethyl ammonium bromides (DTAB and CTAB) from Aldrich (99%), were recrystallized (2 g surfactant, 10 ml ethyl acetate, 1 ml ethyl alcohol) 3 times before use. For both surfactants, no minimum in the surface tension *versus* surfactant concentration was observed. Potassium bromide (KBr) was supplied by Fluka.

The polyanion (synthesized by SNF Floerger) is a statistical copolymer composed of neutral monomers of acrylamide (AM) and charged monomers of acrylamido methyl propane sulfonate (AMPS). The polymer chemical structure has been characterized by titration *via* a bromidation reaction for the amide function and potentiometric titration for the sulfonate. The molecular weight and polydispersity of the polymer were measured by size exclusion chromatography (SEC) coupled with multiangle light scattering. Two different molecular weights were studied, $M_w = 2.2 \times 10^6$ and $M_w = 4 \times 10^5$. For $M_w = 2.2 \times 10^6$, two degrees of charge were investigated: $f = 25$ mol% and 10 mol% (f is the fraction of charged monomers; the number of charged monomers per macromolecule is $x = fN$, where N is the total number of monomers). The characteristics of the three polymer samples studied are summarized in Table 1. To eliminate any traces of surfactant molecules and low molecular weight impurities, the polymer solutions were passed through an ultrafiltration unit with a 20 000 cut-off membrane. Final concentrations were determined using a total carbon analyzer Shimatzu TOC 5050. After this purification, the polymer displays no surface activity at concentrations below 2000 ppm. Pure water was taken from a Millipore Milli-Q system. Polymer-surfactant mixtures were obtained by mixing pure surfactant and pure polymer solutions.

2.2 Surface tension measurement

Experiments were performed at room temperature 20±1 °C. Measurements were carried out in a Teflon trough (6 cm diameter) housed in a Plexiglas box with an opening for the tensiometer. The surface tension was measured with an open frame version of the Wilhelmy plate (to avoid the wetting problems of the classical plate [18]). The rectangular (20 mm × 10 mm) open frame, made from a 0.19 mm diameter platinum wire, was attached to a force transducer (HBM Q11) mounted on a motor allowing it to be drawn away from the surface at a controlled constant rate.

For mixed solutions at low concentrations of surfactant and polyelectrolyte, the approach to the equilibrium could take more than 3 hours and we did not find any reliable method to get the equilibrium surface tension of such a system by extrapolation to infinite time. Thus, it was assumed *arbitrarily* that equilibrium had been reached when the surface tension variation was less than 0.01 mN/m over 10 minutes.

The reproducibility, including long equilibration time and/or contamination effects, was 0.5 mN/m for mixed solutions. Surface tensions measured on polymer-free solutions of surfactants were in good agreement with the literature values.

2.3 Viscosity measurement

Relative viscosities of polymer solutions and mixed polymer-surfactant solutions were measured using a low shear viscosimeter (Contraves 30) which has a coaxial cylindrical geometry. The shear thinning behaviour of the polymer has been characterized and all subsequent measurements have been done at low shear rates, below $0.5\ \mathrm{s}^{-1}$.

2.4 Ellipsometry

Ellipsometric angles were measured by means of a PLASMOS (SD 2300) rotating-analyzer ellipsometer. Measurements on free surface of water, ethanol and cyclohexane were in good agreement with the values given in reference [19]. In our experiments, two sets of measurements are performed, one on pure water (reference $\psi_0,\ \Delta_0$), the second on the solution ($\psi_d,\ \Delta_d$). The thickness d and the refractive index n_d of the adsorbed layer are then deduced from the ellipsometric angles variations $\delta\psi = \psi_d - \psi_0$ and $\delta\Delta = \Delta_d - \Delta_0$. Assuming flat and homogeneous layers, the ellipsometric equations are inverted according to reference [20]. For the layers studied here, the thicknesses are very small and $\delta\psi$ is of the order of the experimental accuracy. It is then important to check the consistency of the values of d and n_d determined by this way, with those obtained from a different analysis based on $\delta\Delta$ and the determinations of area per molecules from the Gibbs equation (see Ref. [17] for details).

3 Results and discussion

We have worked with polymer/surfactant solutions of fixed polymer concentration and varying surfactant concentration. We have thus studied the changes induced by the presence of fixed amount of polymer in the surfactant solutions.

3.1 Role of the surfactant

Mixed solutions of DTAB and AMPS show a synergistic lowering of surface tension at very low surfactant concentrations. As seen in Figure 1, the surface tension curve exhibits two break points: the first one, known as the critical aggregation concentration (CAC), corresponds to the

Table 1. Characteristics of the polymer samples studied. The gyration radii have been measured in 0.1 M of $LiNO_3$.

polymer sample (notation)	degree of charge f	molecular weight M_w (g/M)	average gyration radii R_g^0 (nm)	polydispersity M_W/M_n	average degree of polymerization N	average number of charges per chain
C25M0.4	25%	4×10^5	39	1.6	3620	905
C25M2.2	25%	2.2×10^6	87	1.7	19910	4980
C10M2.2	10%	2.2×10^6	83	2.1	25350	2535

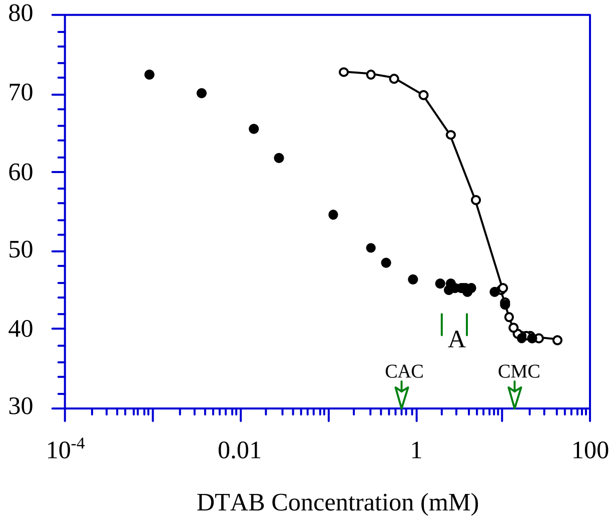

Fig. 1. Effect of the AMPS copolymer on DTAB surface tension: (open circles) DTAB; (closed circles) DTAB + 750 ppm of C25M2.2 (6.8 mM of monomers). The range of surfactant concentrations noted "A" corresponds to turbid mixed solutions.

beginning of the formation of a significant number of polymer/surfactant complexes in the bulk. The second one corresponds to the critical micellar concentration (CMC) of the polymer-free solutions. The surface tension does not change if the polymer concentration is decreased down to very small values (below 10 ppm): this can be explained by remarking that the complex formation at the surface is a cooperative phenomenon where the surfactant counterions are replaced by the polymer charged units, and both the surfactant and polymer counterions are released in the bulk solution. One can thus show that the surface tension variation with polymer and surfactant concentrations (c_p and c_s respectively) is given by [12–17]:

$$d\gamma = -kT\Gamma_s d\ \ln\ (c_s c_p^{1/x}) \qquad (1)$$

where Γ_s is the surface excess surfactant concentration, x the number of charges carried by one polymer chain, k the Boltzmann constant and T the absolute temperature. If we use this equation for the data of Figure 1, we find that around the CAC:

$$A_s = 1/\Gamma_s \sim 78 \pm 5\ \text{Å}^2.$$

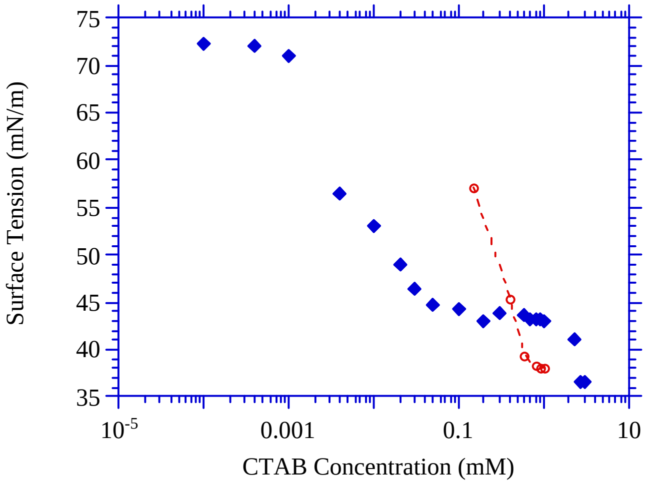

Fig. 2. Effect of the AMPS copolymer on CTAB surface tension: (open circles) CTAB; (closed diamonds) CTAB + 750 ppm of C25M2.2 (6.8 mM of monomers).

For a DTAB solution with a concentration of 2CMC, the area per molecule as calculated with the Gibbs equation for charged monolayers $d\gamma = -2kT\Gamma_s d\ln c_s$ is $A_s \sim 48$ Å^2, *i.e.* significantly smaller.

We have tried to study the surface tension variation with polymer concentration below 75 ppm. Unfortunately, the equilibration times are extremely long (several days) and it is very difficult to get reproducible results. We can only say that the saturation regime (closed circles of Fig. 1) is reached around 30 ppm [21].

Figure 2 shows the surface tension of mixed polymer-surfactant solutions in the case of CTAB. This surfactant has the same polar head than DTAB, his tail lenght is longer by 4 CH_2 groups. The general aspect of the curves of Figures 1 and 2 is similar. The same synergistic lowering of the surface tension at low surfactant concentrations is observed. The surface tension plateau after the CAC is 2 mN/m smaller for CTAB. As the CMC, the CAC decreases with increasing surfactant chain length. To be rigorous, we should note that the second break point in Figure 2 is not a CMC but rather a Krafft point, at the temperature of our measurements. The main difference between the two surfactants is that the CAC plateau stops before the CMC for DTAB and after for CTAB. In other words, the surface tension of the C25M2.2-DTAB mixtures is always smaller than that of the pure DTAB

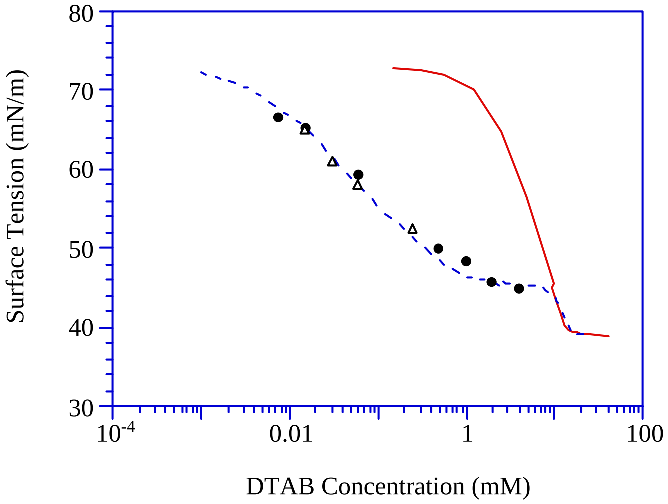

Fig. 3. Influence of the polyelectrolyte molecular weight on the AMPS-DTAB interaction: comparison of the effect of C25M2.2 and C25M0.4 on DTAB surface tension, (full line) DTAB; (dotted line) DTAB + 750 ppm of C25M2.2 (6.8 mM of monomers); (closed circles) DTAB + 750 ppm of C25M0.4 (6.8 mM of monomers); (open triangles) DTAB + 75 ppm of C25M0.4 (0.68 mM of monomers).

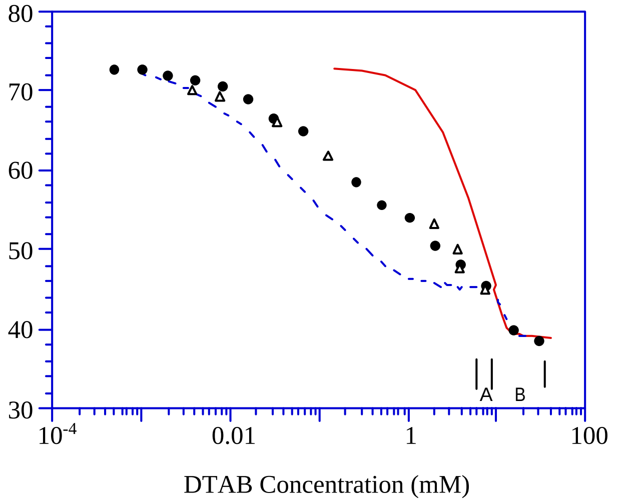

Fig. 4. Influence of the degree of charge of polyelectrolyte on the AMPS-DTAB interaction: comparison of the effect of C25M2.2 and C10M2.2 on DTAB surface tension, (full line) DTAB; (dotted line) DTAB + 750 ppm of C25M2.2 (6.8 mM of monomers); (closed circles) DTAB + 750 ppm of C10M2.2 (8.6 mM of monomers); (open triangles) DTAB + 75 ppm of C10M2.2 (0.86 mM of monomers). The area noted "A" corresponds to surfactant concentrations where the mixed solutions remain turbid for months, while the area "B" corresponds to concentrations where the solutions become clear after about a day.

solutions, while the curve for C25M2.2+CTAB and that for CTAB alone cross-over around 0.5 mM of surfactant. The behavior of CTAB is however the most frequent in polymer- surfactants solutions [1]. In this case, at surfactant concentrations higher than the CMC, the addition of polyelectrolyte induces an increase of the surface tension. This phenomenon can be explained by the association of polymer and surfactant in the bulk: if the bulk surfactant concentration is not sufficient, additional surfactant can be removed from the surface. In fact, it is interesting to note that 750 ppm of C25M2.2 polyelectrolyte correspond to 1.7 mM of charged monomers. This concentration is lower than the CMC of DTAB, but higher than that of CTAB. Thus one can say that when the surfactant concentration equals the CMC in C25M2.2-CTAB mixtures, all the charged sites of the polyelectrolytes are not bound to surfactant molecules so the CTAB is still associating with the polymer in the bulk: it is worth noting that the CAC plateau of the CTAB-C25M2.2 system stops at about 2 mM of surfactant.

3.2 Influence of the polymer molecular weight

Figure 3 shows that the polymer molecular weight does not have any measurable influence on the surface tension. Two molecular weights have been used, 2.2×10^6 and 4×10^5 g/mol. For the smallest molecular weight (C25M0.4), it has been checked that, as for the largest one (C25M2.2), the surface tension of the surfactant-free solution was that of pure water, *i.e.* that the polymer alone is not surface active. The surface tension curves of the surfactant-polyelectrolyte mixtures are not dependent on the polymer concentration either. Equation (1) shows that the area per surfactant remains the same around CAC (≈ 80 Å^2). According to the adsorption model recalled above, each surfactant being complexed by a charged monomer, the area per monomer is therefore the same, since the degree of charge of the two polymers is the same.

A similar behavior has been reported in reference [12] for mixed solutions of sodium dodecyl sulfate and poly L-lysine hydrobromide, although the surface tension plateau above the CAC is higher for the largest molecular weights, an effect not observed here.

3.3 Influence of the degree of charge of the polymer

Figure 4 shows the surface tensions for polymers with different degrees of charge: $f = 10$ (C10M2.2) and 25 mol% (C25M2.2). For a given surfactant concentration, the surface tension change increases with the degree of charge. Again, the surface tension does not depend on polymer concentration (down to 75 ppm). For the smallest degree of charge, the CAC is no longer well defined. One rather observes an inflexion point around 1 mM of DTAB, afterwhich the solutions become turbid.

In order to better locate the onset of association in bulk, we have measured the bulk viscosity of the solutions. The results are shown in Figure 5. The effect of surfactant addition on the bulk polymer solutions is equivalent to salt addition below a concentration of about 0.7 mM. The salt screens the electrostatic repulsions that swell the polyelectrolyte molecules and reduces the dimensions

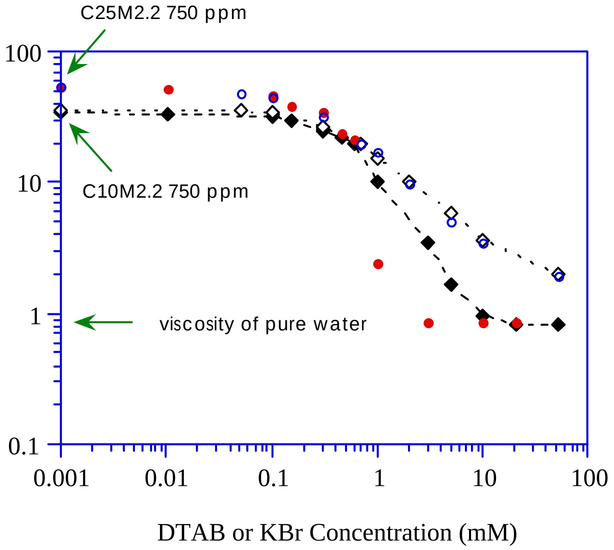

Fig. 5. Comparison of the effect of added DTAB and salt on the bulk viscosity of 750 ppm solutions of C25M2.2 and C10M2.2: (closed circles) C25M2.2/DTAB; (open circles) C25M2.2/KBr; (closed diamonds) C10M2.2/DTAB; (open diamonds) C10M2.2/KBr.

of the chains. Thus the interactions between macromolecules become weaker and the viscosity decreases.

Above 0.7 mM DTAB, the reduction of viscosity is larger with the surfactant than with the salt. This is due to the bulk complexation of polymer and surfactant and to the precipitation of the complexes: the solutions become turbid, and when all the polymer is precipitated, the solution viscosity approaches that of water. This occurs around a surfactant concentration of respectively about 2 mM and 9 mM for degrees of charge f of 25% and 10%. Clearly, the complexation occurs over a sharper concentration range for the largest degree of charge: the complexation of a surfactant molecule with a charged site of the polymer is probably favoured by the presence of a second nearby surfactant molecule. For the smallest degree of charge, the distance between charged sites is larger, and the cooperativity is thus reduced. Note that for surfactant-free solutions, above 1 mM in KBr salt concentration the electrostatic interactions are sufficiently screened, and the solutions with polymers of different degree of charge have the same viscosity.

The viscosity data tell us that there is no appreciable complexation in the bulk below 0.7 mM surfactant for $f = 10\%$. We can therefore apply equation (1) to evaluate the area per surfactant molecule at the surface in this regime. For this surfactant concentration we find:

$$A_s = 1/\Gamma_s \sim 100 \pm 5 \text{ Å}^2.$$

This area is larger than for $f = 25\%$ (78 Å^2). This is probably associated to the fact that the polymer at the surface acts as a spacer for the surfactant molecules. Indeed, each charged polymer site being complexed with a surfactant molecule, the distance between the molecules should increase if the distance between the sites increases. However, the variation in A_s is smaller than expected for a completely flat adsorption of the polymer (the area A_s should then increase by a factor 2.5). The polymer configuration near the surface is therefore certainly different, and the thickness of the polymer layer larger with the smaller degree of charge.

3.4 Ellipsometry studies

We will present now experiments done to investigate the effect of the degree of charge on the thickness of adsorbed layer. Experiments with different molecular weights have also been performed, but no differences have been observed. This is consistent with the behavior of the surface tension data.

For $f = 25\%$ and for concentrations smaller than the CAC, $\delta\psi$ is zero within instrumental accuracy (± 0.005°). This is associated to small layer thicknesses (< 100 Å). Indeed, for small δ/λ (where $\lambda = 6328$ Å is the light wavelength) [22,23]:

$$\delta\Delta \propto \left(\frac{d}{\lambda}\right) \qquad \text{and} \qquad \delta\psi \propto \left(\frac{d}{\lambda}\right)^2.$$

Thus, for $d \ll \lambda$, $\delta\psi$ is close to zero and approaches more rapidly the instrument resolution than $\delta\Delta$. The turbid solutions (around 3.6 mM) have non homogeneous interfaces. One observes two types of domains with macroscopic extensions. Certain domains are visible to the naked eye in grazing incidence. The values of $\delta\psi$ and $\delta\Delta$ show important changes from a domain to another, and are always larger than the values below the CAC or above CMC. Above CMC, $\delta\psi$ is again close to zero.

Figure 6 shows the results for d and n_d after inversion of the $\delta\psi$ and $\delta\Delta$ data. Below the CAC, d is about constant and close to 70 Å (in average between 40 and 120 Å), and n_d is close to 1.37 (between 1.35 and 1.39). The domains for the turbid solutions are thicker, some are similar to the adsorbed layers before the CAC (≈ 1.37 and 200 Å), the others are thicker and denser (≈ 1.39 and 700 Å). These last domains are possibly microgels, precursors of the precipitation in the bulk. These microgels have also been observed in the foam films made from these solutions [24].

In order to check for the validity of this analysis, we have used a second type of analysis, in which we rely only on the value of $\delta\Delta$ [17]. We further assume that the composition of the layer is determined from the value of A_s, as obtained from the surface tension data and the Gibbs equation. We also use the adsorption model described previously and assume that the surface layer does not contain counterions, and that each polymer ion is complexed with a surfactant ion. For 0.7 mM DTAB, $A_s = 78 \pm 5$ Å^2, $\delta\Delta = -0.28 \pm 0.01°$ at $\Phi = 70°$, and one obtains: $n_d = 1.39 \pm 0.05$ and $d = 90 \pm 70$ Å. These results are compatible with those obtained directly from both $\delta\psi$ et $\delta\Delta$, and confirm the fact that the adsorbed layer is very thin. It is remarkable that a thickness of about 90 Å is ten times smaller than the gyration radius of the C25M2.2 molecules in a 0.1 M solution

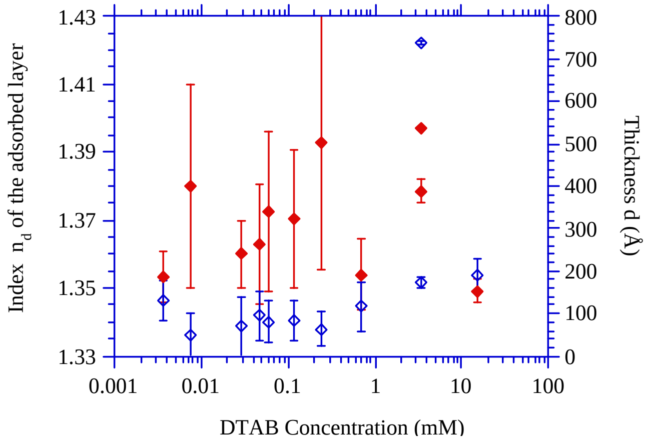

Fig. 6. The refractive indices n_d (close diamonds) and the thicknesses d (open diamonds)of the adsorbed layers determined from the $\delta\psi$ and $\delta\Delta$ values measured for a polyelectrolyte degree of charge $f = 25\%$ at $\Phi = 70°$.

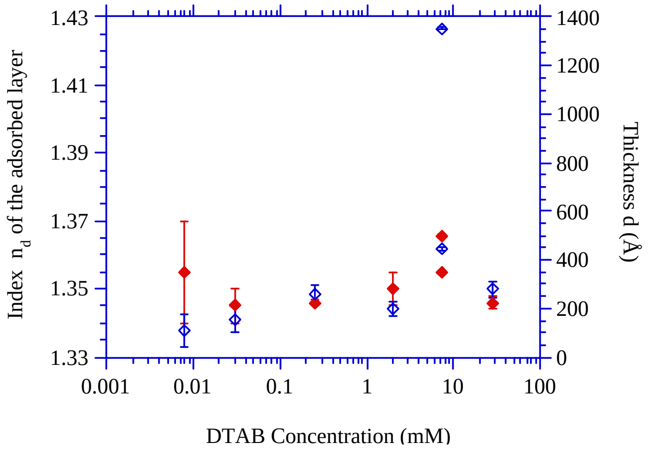

Fig. 7. The refractive indices n_d (close diamonds) and the thicknesses d (open diamonds) of the adsorbed layers determined from the $\delta\psi$ and $\delta\Delta$ values measured for a polyelectrolyte degree of charge $f = 10\%$ at $\Phi = 70°$.

of $LiNO_3$ (Tab. 1). Therefore, the polymer probably lies flat at the surface, thus allowing the complexed surfactant molecules to have their hydrocarbon chains in the air. To end, even though there are large experimental uncertainties, the agreement between the two estimations of d and n_d supports the validity of the adsorption model with no low molecular weight counterions. These dense interfacial complexes with no counterions may prefigurate the structure of the bulk precipitates above the CAC.

Figure 7 shows the results obtained for $f = 10\%$.

The indices are slightly smaller than for $f = 25\%$, consistent with larger thicknesses. Below the CAC, n_d is in average close to 1.35 and d is around 200 Å (instead of 1.37 and 70 Å for $f = 25\%$). These values confirm that the adsorbed layers are thicker, as expected from the surface tension data. The turbid solutions show heterogeneous surfaces with domains similar to the layers before the CAC (≈ 1.36 and 400 Å), and others denser (≈ 1.37) and much thicker (around 1400 Å).

As before, we will estimate n_d and d from $\delta\Delta$ and A_s. For 0.25 mM DTAB, $A_{s+} = 100 \pm 5$ Å^2, $\delta\Delta = -0.43 \pm 0.01°$ at $\Phi = 70°$, and we obtain: $n_d = 1.45 \pm 0.04$ and $d = 23 \pm 8$ Å. In this case, there is no real agreement with the direct determination from the ellipsometric angles as for $f = 25\%$: here the two thicknesses differ by a factor of order 10, well above the experimental uncertainty. This might be due to the fact that the validity of the adsorption model fails when the degree of charge decreases. We have seen that the cooperativity of the adsorption and of the complexation in the bulk is less important for the less charged polymer, and it is possible that some counterions are still present in the surface layer. In the limit case $f = 0$, we expect no complexation at the surface at all, and the model would then be completely inappropriate.

Let us finally compare these thicknesses to those of polymer free solutions. For a DTAB solution with a concentration of 2CMC, one measures: $d = 10 \pm 1$ Å [25]. The thickness of the mixed layer is therefore mainly the thickness of the polymer region.

4 Summary and conclusion

We have observed a synergistic surface tension lowering due to coadsorption of a non surface active polyanion and oppositely charged surfactant ions. Viscosity measurements revealed a difference in the polyelectrolyte-surfactant interaction in the bulk and at the air/solution interface. While there is formation of a highly surface-active complex at the interface, there is no significant binding between the two species in the bulk at the very low surfactant concentrations where the synergistic effect takes place.

The effect is very similar for surfactants of different chain lengths: for longer chains, the bulk aggregation is observed at smaller surfactant concentrations (because of the larger hydrophobicity), and surfactant molecules at the surface can be eventually depleted into the bulk for complexation with the polymer. No effect of the polymer molecular weight was observed. This is as expected from the very flat configuration of the adsorbed complex. The effect of the degree of charge of the polymer is more significant. For small degrees of charge, the adsorbed layer is thicker and less dense. The polymer chains probably dangle into water in between complexation sites at the surface. The ellipsometric data also indicates that the adsorption model with no counterions present in the adsorbed layer is not completely appropriate in this case. The complexation is clearly less cooperative, in the bulk as well as at the air/water interface.

Other polyelectrolytes, with more hydrophobic character or with larger persistence lengths are currently under study to generalize these observations.

This work was supported in part by "Institut Français du Pétrole".

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