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Complexation of Cationic Surfactant and Anionic Polymer at the Air−Water Interface

Atef Asnacios,[*,†] Dominique Langevin,[†] and Jean-François Argillier[‡]

Centre de Recherche Paul Pascal, Avenue Albert Schweitzer, 33600 Pessac, France, and
Institut Français du Pétrole, 1 et 4 avenue du Bois-Préau, 92506 Rueil,
Malmaison Cedex, France

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ABSTRACT: Equilibrium surface tension measurements have been carried out on solutions of a non-surface-active anionic polyelectrolyte (poly(acrylamide sulfonate)) mixed with various surfactants. While the surface tension does not change when the polymer is added to nonionic and anionic surfactant solutions, a strong synergistic lowering of the surface tension is found with cationic surfactants. In the latter case, we also find that the surface tension is practically independent of the amount of polymer over the range of concentrations studied. Assuming that the polymer stretches out at the interface to form a neutral complex with the surfactant, this behavior can be explained by the classical Gibbs adsorption equation. Furthermore, ellipsometry measurements on these solutions are consistent with our adsorption model.

Introduction

The study of interactions between surfactants and polymers is a rapidly growing field of interest in colloid science.[1] Indeed, many practical systems for industrial applications contain mixtures of polymers and surfactants. These mixtures are widely used as thickeners in water-based formulations such as paints, drilling muds, etc. Moreover, in biology, membranes are beautiful examples of architectures where lipids (surfactants) and proteins (polymers) form important structured complexes. Whereas there is an extensive literature on surfactant solutions on one hand and polymer solutions on the other hand, less is known for the mixed polymer−surfactant systems. It has recently been suggested that polymer-surfactant solutions are similar to polymer−polymer solutions.[2] If 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. It is also observed that the behavior of polyelectrolyte−surfactant solutions is similar in that no association for neutral or similarly charged surfactants occurs, yet there is a strong association for oppositely charged surfactant−polymer combinations.[2] However, surfactant−polymer mixtures are more complicated because the surfactant aggregates (i.e. micelles, bilayers, etc.) must also be considered.[3−6]

In this work, our objective is to study the polymer−surfactant interaction at the air−water interface. These interactions are important to many practical applications such as colloidal stabilization, wettability, and adhesion. While complexation in the bulk is generally related,[7] only few studies have focused on surfactant−polyelectrolyte interactions at a surface.[8−11] Therefore, our work is centered around poly(acrylamide sulfonate) (a model anionic polyelectrolyte for drilling muds) in combination with a variety of common surfactants. First, the bulk polymer−surfactant interactions are characterized by viscosity measurements. We then use a combination of surface tension and ellipsometry measurements to probe the surface complexes at the air−water interface.

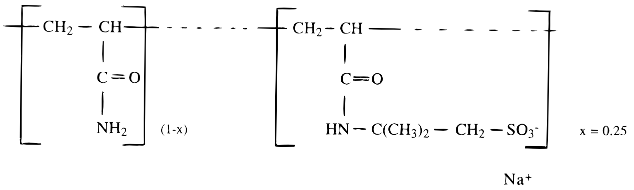

Figure 1. AM/AMPS copolymer structure.

Experimental Section

Materials. Nonionic surfactant penta(ethylene glycol) mono-*n*-decyl ether ($C_{10}E_5$) from Nikko (Nikkol BD-5SY) and anionic surfactant dioctyl sulfosuccinate (AOT) from Sigma (99%) were used as received. Cationic surfactant, dodecyltrimethylammonium bromide (C_{12}TAB) from Aldrich (99%), was recrystallized (2 g of C_{12}TAB:10 mL of ethyl acetate:1 mL of ethyl alcohol) three times before use. For all three surfactants, no minimum in the surface tension versus surfactant concentration was observed. Potassium bromide (KBr) was supplied by Fluka.

The polyanion is a statistical copolymer of acrylamide (AM) and acrylamidomethylpropanesulfonate (AMPS) synthesized by SNF Floerger. The sample used is composed of 75 mol % of neutral AM and 25 mol % of charged AMPS monomers. The structure of the polymer is shown in Figure 1. The polymer's 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, which gave $M_w = 2.8 \times 10^6$ and $M_w/M_n = 1.5$. In 1 g/L NaCl, the average radius of a polymer chain is $R_w = 110$ nm. 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 cutoff membrane. Final concentrations were determined using a Shimatzu TOC 5050 total carbon analyzer. After this purification, the polymer displayed no surface activity at concentrations below 2000 ppm (see Figure 2). Pure water was taken from a Millipore Milli-Q system. Polymer−surfactant mixtures were obtained by mixing pure surfactant and pure polymer solutions.

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 a classical plate[12]). The rectangular (20 mm × 10 mm) open frame, made

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[†] Centre de Recherche Paul Pascal.

[‡] Institut Français du Pétrole.

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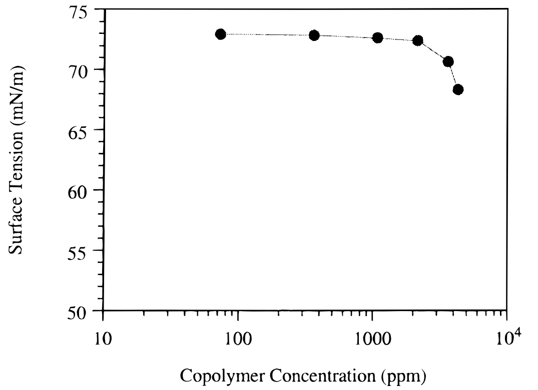

Figure 2. Surface tension vs logarithm of AM/AMPS copolymer concentration (mM) for surfactant-free solutions.

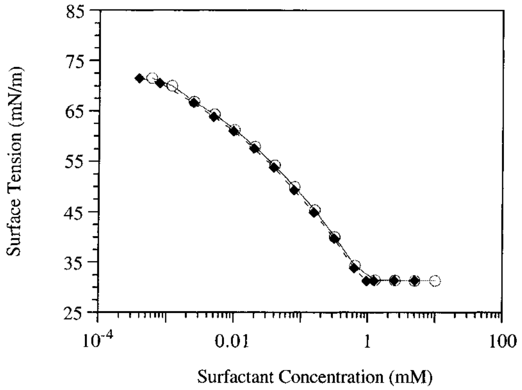

Figure 3. Effect of AM/AMPS copolymer on $C_{10}E_5$ surface tension: (○) $C_{10}E_5$; (◆) $C_{10}E_5$ + 750 ppm of AM/AMPS.

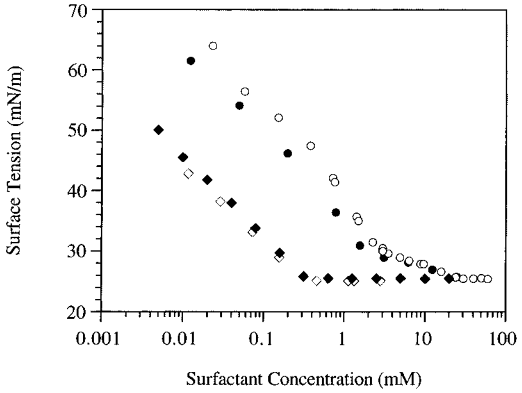

Figure 4. Effect of AM/AMPS copolymer on AOT surface tension with and without added salt in the mixed solutions: (○) AOT; (●) AOT + 750 ppm of AMPS; (◇) AOT + 0.1 M NaCl; (◆) AOT + 0.1 M NaCl + 750 ppm of AMPS.

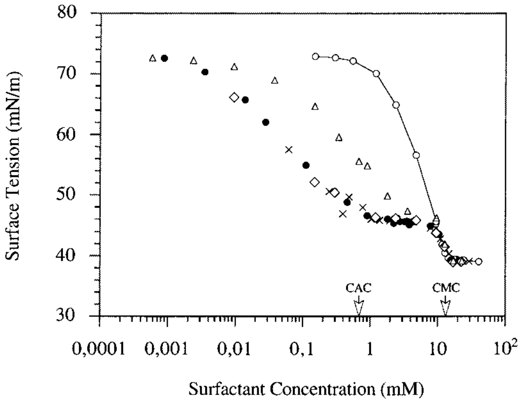

Figure 5. Effect of AM/AMPS copolymer on $C_{12}TAB$ surface tension for different polymer concentrations: (○) $C_{12}TAB$; (△) $C_{12}TAB$ + 7 ppm of AM/AMPS; (◇) $C_{12}TAB$ + 75 ppm of AM/AMPS; (×) $C_{12}TAB$ + 350 ppm of AM/AMPS; (●) $C_{12}TAB$ + 750 ppm of AM/AMPS.

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 h, 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 min.

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.

Viscosity Measurement. Relative viscosities of polymer solutions and mixed poly−surfactant solutions were measured using a low-shear viscosimeter (Contraves 30) which has a coaxial cylindrical geometry. The shear thinning behavior of the polymer was characterized, and all subsequent measurements were done at low shear rates, below 0.5 s^{-1}.

Ellipsometry. Ellipsometric angles were measured by means of a Plasmos (SD 2300) rotating-analyzer ellipsometer. Measurements on the free surface of water, ethanol, and cyclohexane were in good agreement with the values given in ref 13.

Results

To simplify the analysis of our results, we worked with polymer−surfactant solutions of varying concentration of surfactant and fixed concentration of polymer. In other words, we have studied the changes induced by the presence of a fixed amount of AM/AMPS copolymer on surface tension isotherms of different surfactants.

Nonionic Surfactant: $C_{10}E_5$. The presence of 750 ppm of AM/AMPS does not change the surface tension isotherm of $C_{10}E_5$ (Figure 3). There appears to be no interaction between the polymer and the nonionic surfactant, and, more precisely, no evidence of a hydrophobic interaction, such as that seen by Radlinska et al. with poly(styrenesulfonate).[14]

Anionic Surfactant: AOT. In this case, a fixed concentration (750 ppm) of AM/AMPS induces a weak lowering (about 4 mN/m) of surface tension for AOT concentrations below 2 mM, which is close to the cmc of the polymer-free AOT solution (Figure 4). This lowering is probably due to a salt effect. Indeed, a 750 ppm concentration of polyelectrolyte represents 1.7 mM of SO_4^- and Na^+ ions in solution. Thus, addition of 750 ppm AM/AMPS increases the ionic strength, leading to a partial screening of electrostatic repulsion between AOT head groups which leads inevitably to better packing of the surfactant molecules at the water−air interface. Measurements made in the presence of salt excess (100 mM NaCl) confirms this explanation as they show no more difference between solutions with and without polymer (Figure 4). Moreover, as 750 ppm of AM/AMPS corresponds to a lower ionic strength than 100 mM NaCl, Figure 4 shows that the surface tension isotherm of AOT + 750 ppm AM/AMPS actually lies between those of pure AOT and AOT + 100 mM NaCl.

Cationic Surfactant: $C_{12}TAB$. Mixed solutions at 750 ppm of AM/AMPS show a synergistic lowering of surface tension at very low surfactant concentrations. As shown in Figure 5, the surface tension isotherm exhibits two plateaus beginning at two characteristic

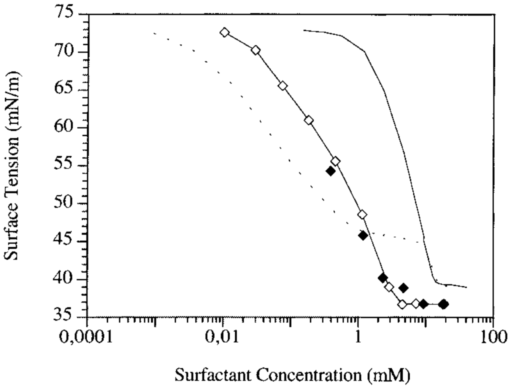

Figure 6. Comparison of the effect of AMPS copolymer on $C_{12}TAB$ surface tension with and without added salt in the mixed solutions: (—) $C_{12}TAB$; (···) $C_{12}TAB$ + 750 ppm of AMPS; (◇) $C_{12}TAB$ + 0.1 M KBr; (◆) $C_{12}TAB$ + 0.1 M KBr + 750 ppm of AMPS.

break points. The first, known as the critical aggregation concentration (cac), corresponds to the appearance of a significant amount of polymer−surfactant complexes in the *bulk*, while the second corresponds to the cmc of polymer-free $C_{12}TAB$. It is indeed interesting here to note the coincidence between the surface tension curves with and without polymer for concentrations of $C_{12}TAB$ above 9 mM.

Figure 5 also indicates that at low surfactant concentrations (10^{-5} M $C_{12}TAB$), surface activity of the surfactant is negligible, yet there is a substantial lowering of the surface tension when the (non-surface-active) polymer is present. This effect implies coadsorption of AM/AMPS and $C_{12}TAB$ molecules at the air−solution interface and formation of a highly surface-active polymer−surfactant complex.

To show the electrostatic nature of the interaction involved in the formation of polymer−surfactant complexes at the surface, surface tension measurements were carried out in the presence of salt. It is shown in Figure 6 that addition of 100 mM KBr suppresses the effect of the polymer on the $C_{12}TAB$ surface tension isotherm. Therefore, electrostatic attraction between AM/AMPS and $C_{12}TAB$ is evidently responsible for their strong interaction.

Moreover, Figure 6 shows that lowering of the C_{12}-TAB surface tension due to the presence of 750 ppm AM/AMPS (corresponding to 1.7 mM equivalent of salt) is stronger than that of 100 mM KBr for surfactant concentrations below the cac. Thus, the AM/AMPS effect on $C_{12}TAB$ surface tension cannot be explained by a simple salt effect below this cac.

At this point, it is interesting to note that Figure 5 also reveals the effect of bulk polymer concentration on the surface tension isotherm. Four different AM/AMPS concentrations are represented: 7 ppm (open triangles), 75 ppm (open diamonds), 350 ppm (crosses), and 750 ppm (closed circles). The data sets corresponding to the three highest concentrations follow the same behavior, and we observe no effect on the tension isotherm within this bulk polymer concentration range. The 7 ppm isotherm lies between that of polymer-free surfactant solutions and the one representing the three highest concentrations of polyelectrolyte. One can think from this observation that, at a given surface concentration below the cac, there is a polyelectrolyte concentration C_{PNa}^{exc} ($7 < C_{PNa}^{exc} < 75$ ppm) above which added macromolecules do not interact with the surfactant. This excess of uncomplexed macromolecules would then explain the fact that the surface tension is independent of the polymer concentration above 75 ppm. In fact, we shall see in the following discussion (using the Gibbs adsorption equation) that this "excess" argument cannot explain *alone* the independence of the surface tension on polymer concentrations in the range 75−750 ppm. But, to do so, we first need to get information about the polyelectrolyte−surfactant interaction in the bulk.

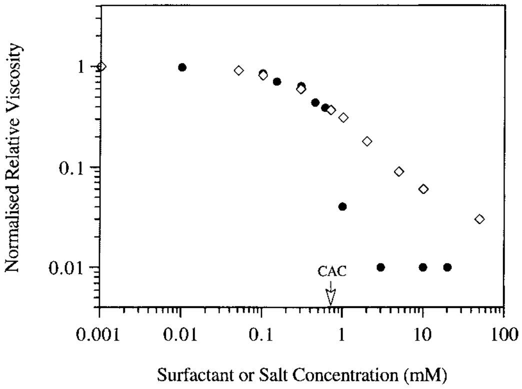

Figure 7. Comparison of the effect of $C_{12}TAB$ and salt on the relative viscosity of a 750 ppm solution of AMPS: (●) AMPS/$C_{12}TAB$; (◇) AMPS/KBr.

This additional information concerning the $C_{12}TAB$−AM/AMPS interaction in the bulk can be obtained from viscosity measurements. Thus, in Figure 7, we plot the bulk viscosity (normalized by its value for a 750 ppm AM/AMPS solution) for 750 ppm AM/AMPS−$C_{12}TAB$ and 750 ppm AM/AMPS−KBr solutions versus $C_{12}TAB$ or KBr concentration. As can be seen in Figure 7, for $C_{12}TAB$ concentrations below the cac, the decrease in viscosity with added surfactant is identical to that of added KBr. However, above the cac, $C_{12}TAB$ has a much stronger effect than KBr. In fact, slightly above the cac, the AM/AMPS−$C_{12}TAB$ mixed solutions become turbid, we observe a white precipitate, and the measured viscosities correspond to that of pure water (we actually find the same value for pure $C_{12}TAB$ solutions).

These observations indicate that, below the cac, C_{12}-TAB is completely dissociated and behaves as a simple salt. That is, the increased ionic strength upon addition of surfactant or simple electrolyte screens the electrostatic repulsions between charged groups on the polymer backbone, leading to smaller hydrodynamic volumes and lower relative viscosities. However, at the cac, the surfactant concentration is high enough to form (in the bulk!) tightly packed polymer−surfactant complexes that eventually precipitate out of the solution to form a separate phase. This precipitation of the macromolecules may explain the coincidence between the surface tension curves with and without polymer for C_{12}-TAB concentrations above 9 mM.

To sum up, one has to keep in mind the following picture of the system. Below the cac, while there is no complexation between the polymer and the surfactant in the bulk, the two species coadsorb at the solution−air interface to form a highly surface-active complex. Above the cac, complexation occurs in bulk, the polymer molecules precipitate out, and the mixtures finally recover the surface tension and viscosity of the polymer-free surfactant solutions.

Discussion

As the viscosity measurements show, there is no significant AM/AMPS−$C_{12}TAB$ complex formation in the bulk below the cac, and we can assume that the charged species are in fully ionized state below this C_{12}TAB concentration. Therefore, we can apply the Gibbs adsorption equation to our system,

$$d\gamma = -\Gamma_{Na^+}\, d\mu_{Na^+} - \Gamma_{P^-}\, d\mu_{P^-} - \Gamma_{Br^-}\, d\mu_{Br^-} - \Gamma_{S^+}\, d\mu_{S^+} \tag{1}$$

where γ is the surface tension, the Γ's are the Gibbs surface excesses, and the μ's are the chemical potentials of the sodium (Na^+), polymer (P^-), bromide (Br^-), and dodecyltrimethylammonium (S^+) ions. Working with very low bulk concentrations, we will ignore activity corrections and express the chemical potential changes in terms of bulk concentration changes:

$$d\gamma = -kT\{\Gamma_{Na^+}\, d \ln C_{Na^+} + \Gamma_{P^-}\, d \ln C_{P^-} + \Gamma_{Br^-}\, d \ln C_{Br^-} + \Gamma_{S^+}\, d \ln C_{S^+}\} \tag{2}$$

At this stage, we can make an interesting remark on the dependence of the surface tension on the polyelectrolyte bulk concentration. As we have noticed before, the experimental results may indicate that, for a given C_{SBr} < cac and $C_{PNa} > C_{PNa}^{exc}$ ($7 < C_{PNa}^{exc} < 75$ ppm), there would be more macromolecules than needed to set the polymer−surfactant complexation at the solution surface. In other words, as one would increase the polyelectrolyte concentration from 75 to 750 ppm, there would be a constant number of complexed polymer molecules at the interface and an increasing excess amount of uncomplexed macromolecules in the bulk. However, this situation corresponding to constant Γ_{P^-} and increasing C_{P^-}, the surface tension should be dependent on the uncomplexed polyelectrolyte bulk concentration (eq 2). Thus, an excess of uncomplexed polymer molecules, although *necessary*, cannot explain *alone* the independence of the surface tension on polyanion concentrations between 75 and 750 ppm.

Now, eq 2 can be simplified. As we have assumed complete ionization in bulk, the relative changes in concentration of the separate ions are of course equal to the relative changes in concentration of the neutral salts; then

$$d\gamma = -kT\{(\Gamma_{P^-} + \Gamma_{Na^+})\, d \ln C_{PNa} + (\Gamma_{S^+} + \Gamma_{Br^-})\, d \ln C_{SBr}\} \tag{3}$$

Furthermore, if N is the degree of polymerization of AM/AMPS copolymer and x is the fraction of charged monomers, the number of charges per polymer molecule is

$$f = xN \tag{4}$$

and electroneutrality for the surface excess then gives

$$\Gamma_{Na^+} + \Gamma_{S^+} = f\Gamma_{P^-} + \Gamma_{Br^-} \tag{5}$$

At this point, we make two remarks which greatly simplify eq (5):

First, we are interested in C_{12}TAB concentrations below 9×10^{-4} M where the surfactant (without polymer) has no or weak effect on surface tension. Thus, in the case of mixed solutions (at least for $C_{PNa} > 7$ ppm), one can say that the number of "free" molecules of C_{12}TAB at the air−solution interface is negligible compared to that of surfactant molecules involved in AM/AMPS−C_{12}TAB complexes of the adsorbed layer. As the only reason for a bromide ion to be in excess at the interface is to ensure electroneutrality of a "free" surfactant molecule, one can conclude that the surface excess of the bromide ions is negligible, and we will write

$$\Gamma_{Br^-} = 0 \tag{6}$$

Furthermore, it will be assumed, as a first approximation, that all sodium counterions of an adsorbed polymer molecule have been replaced by dodecyltrimethylammonium ions (in fact, one can think that this exchange is energetically favorable for the surfactant molecules and allows an increase of the polyelectrolyte counterions' entropy). So we will neglect the sodium surface excess and write

$$\Gamma_{Na^+} = 0 \tag{7}$$

Then eq 5 becomes

$$\Gamma_{S^+} = f\Gamma_{P^-} \tag{8}$$

and a combination of eqs 3, 6, 7, and 8 gives

$$d\gamma = -kT\Gamma_{S^+}\left(d \ln C_{SBr} + \frac{1}{f}\, d \ln C_{PNa}\right) \tag{9}$$

which can be written as

$$d\gamma = -kT\Gamma_{S^+}\, d \ln(C_{SBr}(C_{PNa})^{1/f}) \tag{10}$$

From eq 10, it becomes evident that, for high values of f, the surface tension will not depend *explicitly* on variations in the polymer concentration. For our high molecular weight AM/AMPS polymer, $f \approx 6300$ and eq 10 can then be approximated by

$$d\gamma \approx -kT\Gamma_{S^+}\, d \ln C_{SBr} \tag{11}$$

Now, one sees that the only dependence of the surface tension on the polymer concentration is contained in Γ_{S^+}. In fact, $\Gamma_{S^+} = \Gamma_{S^+}(C_{SBr},C_{PNa})$ is a function of the concentrations of both polyelectrolyte and surfactant. Then, at constant amount of surfactant, Γ_{S^+} is a function of C_{PNa} only and may be constant above a characteristic polymer concentration C_{PNa}^{exc} (in our case, $7 < C_{PNa}^{exc} < 75$ ppm). Moreover, it is obvious from eq 11 that the excess uncomplexed polymer molecules (in bulk) will no longer influence the surface tension. Presumably, this explains why we do not observe a polymer concentration effect above 75 ppm in the isotherms of Figure 5. Here, it is noteworthy that assuming $\Gamma_{Na^+} \neq 0$ would lead to a different adsorption equation. In that case, eq 5 would give

$$\begin{aligned} \Gamma_{Na^+} &= \alpha f\Gamma_{P^-} \\ \Gamma_{S^+} &= (1 - \alpha)f\Gamma_{P^-} \end{aligned} \tag{12}$$

where α is the fraction of charged polyelectrolyte monomers having sodium as counterion. Equation 10 would then change into

$$d\gamma = -kT\Gamma_{S^+}\, d \ln(C_{SBr}(C_{PNa})^{1+\alpha f/(1-\alpha)f}) \tag{13}$$

Then, as soon as α represents a sizable fraction of the charged monomers, the exponent of C_{PNa} is no longer negligible when compared to unity and surface tension should be dependent on polymer concentration even in the 75−750 ppm range. This is not consistent with our experimental results and we can thus use eq 11 to interpret the surface tension isotherms.

Applying eq 11 to the best fit of the AM/AMPS 750 ppm−DTAB surface tension curve below the cac gives an area per surfactant molecule of

$$A_{S^+} = 1/\Gamma_{S^+} \approx 78\ \text{Å}^2$$

This value is much greater than the 45 Å^2 found for the saturated surface of polymer-free C_{12}TAB solutions. Likewise, using eq 8, we obtain the following area per polymer molecule:

$$A_{P^-} = fA_{S^+} \approx 5 \times 10^5\ \text{Å}^2$$

In addition to these area measurements, we also use ellipsometry to determine the adsorbed layer thickness at the air−water interface. Unfortunately, this technique does not give a direct thickness measurement; instead two "ellipsometric angles" ψ and Δ (related to intensity change and phase shift in reflected light) are measured and a model is required to obtain the adsorbed layer thickness. We analyze our data using a homogeneous and isotropic adsorbed layer model. Working at very low bulk concentrations, we consider our system as a mixed layer of surfactant, polymer, and water (with unknown refractive index n_d and layer thickness d) adsorbed between two infinite mediums, air and water.

Under these conditions, n_d and d can be calculated, in principle, from the changes $\delta\psi$ and $\delta\Delta$ in the measured values of ψ and Δ with and without an adsorbed layer.[15,16] Hence, two sets of measurements are performed, one on pure water and one on mixed polymer−surfactant solutions. But, we find that $\delta\psi$ is zero within experimental error, which is expected in the case of thin adsorbed layers.[17,18] Thus, we can only rely on one measurement ($\delta\Delta$) to determine the two unknowns, n_d and d.

We overcome this difficulty by two different methods:

(1) Although $\delta\psi$ cannot be measured, we know at least that it must be less than the ellipsometer resolution. Thus, we solve the ellipsometric equation (for a transparent layer between air and water[16]) using the measured $\delta\Delta$ value and simulated values of $\delta\psi$ within the experimental error.[17] In that case, we determine the "range of possible values of n_d and d" instead of the "true" (n_d,d) couple. At 20 °C and angle of incidence $\Phi = 57°$, we find for the pure water interface

$$\Delta_w = 0.18 \pm 0.04°$$

and, for AM/AMPS 750 ppm−C_{12}TAB solutions near the cac (0.7 mM C_{12}TAB),

$$\Delta_{cac} = -1.37 \pm 0.02°$$

Thus

$$\delta\Delta = \Delta_{cac} - \Delta_w = -1.55 \pm 0.02°$$

and taking $-0.001° < \delta\psi < -0.01°$ leads to

$$1.37 < n_d < 1.51 \quad \text{and} \quad 10 < d < 60\ \text{Å}$$

(2) We replace the "missing" $\delta\psi$ measurement by an available information on the adsorbed layer (in this case, A_{S^+}). First, we use the assumptions made in the surface tension discussion to estimate the adsorbed layer composition. Then the measured $\delta\Delta$ is combined with the A_{S^+} value given by eq 11 to get the thickness and refractive index of the adsorbed layer from the optical characteristics of its components (see Appendix). With $\delta\Delta = -1.55 \pm 0.02°$ and $A_{S^+} = 78 \pm 5$ Å^2, we find

$$n_d = 1.44 \pm 0.07 \text{ and } d = 30 \pm 20\ \text{Å}$$

Here, we see that the characteristic length of a polymer molecule in the plane of the interface ($2(A_{P^-}/\pi)^{1/2} \approx 800$ Å) is, at least, about 15 times its length perpendicular to this interface. This flat polymer conformation is in agreement with the assumptions used when applying the Gibbs adsorption equation. In fact, the "ion exchange" process (between nearly all sodium counterions and C_{12}TAB molecules) would be energetically favorable only if the bound molecules of surfactant were near enough to the air.

Furthermore, one can calculate from eq A.2 the water volume per adsorbed polymer−surfactant complex. For $n_d = 1.44$ we find

$$V_w \approx (1 \pm 0.8) \times 10^6\ \text{Å}^3$$

This amount corresponds to 10% water and then to a gel-like adsorbed layer. This gel structure is in agreement with the "texture" of the precipitates observed in bulk after the cac (as pointed out by Buckingham et al.,[9] complexation occurs first at the interfaces where concentrations are higher than in bulk). Moreover, we have also observed this gel behavior in foam films made from mixed polymer−surfactant solutions near the cac.[21]

Finally, as the n_d and d values found using surface tension measurements are in good agreement (within the experimental errors) with those based only on ellipsometric parameters, one can conclude that the assumptions used in our Gibbs adsorption equation analysis are probably reasonable.

Summary and Conclusion

We have shown a synergistic surface tension lowering due to coadsorption of a non-surface-active polyanion and oppositely charged surfactant ions. Relative viscosity measurements reveal 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.

We use the Gibbs adsorption equation to interpret the surprising observation that surface tension is independent of the polymer concentration in the range 75−750 ppm. This phenomenon can be explained by an "ion exchange" process where sodium counterions of an adsorbed polyelectrolyte molecule have been replaced by surfactant ions. Moreover, we see that this ion exchange process is accompanied by a relatively flat AM/AMPS conformation that allows all bound surfactant tails to be at the air−water interface. In the case of a more rigid polyelectrolyte, all charged monomers may not be simultaneously close enough to the air−solution interface, counterion exchange would not be so energetically favorable, and one would expect surface tension to be dependent on polymer concentration. We are currently clarifying this issue with a rigid polyelectrolyte.

Finally, the results may also be dependent on the affinity between the polymer charged groups and the surfactant. We plan to compare the interaction between C_{12}TAB and a sulfonated or a carboxylated polymer.

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Appendix

Using the Drude approximation for thin layers,[18,19] we get

$$\frac{\delta\Delta}{4\pi} = \frac{d}{\lambda}\cos\Phi\,\tan^2\Phi\,\frac{n_a n_w^2(n_a^2 + n_w^2 - n_d^2 - n_a^2 n_w^2/n_d^2)}{(n_a^2 - n_w^2)(n_w^2 - n_a^2\tan^2\Phi)} \tag{A.1}$$

where n_a, n_w, and n_d are the refractive indexes of air, water, and adsorbed layer respectively; Φ is the angle of incidence and λ is the laser wavelength. Here we have only one equation for the two unknowns d and n_d; thus we need to establish another relation between those quantities. For this, we rely on our surface tension results.

A second independent relationship between d and n_d can be established if we again assume an adsorbed homogeneous layer composed of polyelectrolyte, surfactant, and water. We then focus our attention on a layer volume element corresponding to one polymer molecule, for which we can write

$$V_{\text{total}} = A_{P^-}d = V_{P^-} + V_{S^+} + V_w \tag{A.2}$$

$$\left(\frac{n_d^2 - 1}{n_d^2 + 2}\right)V_{\text{total}} = \left(\frac{n_{P^-}^2 - 1}{n_{P^-}^2 + 2}\right)V_{P^-} + \left(\frac{n_{S^+}^2 - 1}{n_{S^+}^2 + 2}\right)V_{S^+} + \left(\frac{n_w^2 - 1}{n_w^2 + 2}\right)V_w \tag{A.3}$$

where A_{P^-} is the area polymer molecule (taken from the Gibbs equation) and V_{P^-},n_{P^-} and V_{S^+},n_{S^+} are the volumes and refractive indexes of the polymer molecule and the f coadsorbed surfactant molecules, respectively. V_w and n_w are the volume and refractive index of water in the layer. Equation A.3 expresses the fact that the molar refractions of the species in the surface layer are additive.[20] Realizing that $V_{P^-} = M_w/(N_0\rho_{P^-})$ and $V_{S^+} = fM_{S^+}/(N_0\rho_{S^+})$ (where N_0 is Avogadro's number) and combining eqs A.2 and A.3, we can eliminate the unknown water volume and find the desired relationship between d and n_d,

$$(K_d - K_w)[N_0A_{P^-}d] = (K_{P^-} - K_w)\frac{M_w}{\rho_{P^-}} + (K_{S^+} - K_w)\frac{fM_{S^+}}{\rho_{S^+}} \tag{A.4}$$

where

$$K_\alpha = \left(\frac{n_\alpha^2 - 1}{n_\alpha^2 + 2}\right)$$

Using eqs 4 and 8, one can express eq A.4 as a function of the measured area per surfactant molecule A_{S^+}, the rate of charged monomer x, and the monomer mean weight M_{mono}:

$$(K_d - K_w)[N_0A_{S^+}d] = (K_{P^-} - K_w)\frac{M_{\text{mono}}}{x\rho_{P^-}} + (K_{S^+} - K_w)\frac{M_{S^+}}{\rho_{S^+}} \tag{A.5}$$

Now, we have two equations ((A.1) and (A.5)) for two unknowns (n_d and d) that can thus be determined from the measured $\delta\Delta$ and the calculated A_{S^+}.

References and Notes

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(17) The experimental accuracy on $\delta\psi$ is ±0.01°, while one expects $\delta\psi \approx -0.003°$ for a homogeneous layer of $d = 20$ Å and $n_d = 1.42$ at $\Phi = 57°$. In fact, if λ (=6328 Å) is the laser wavelength, $\delta\Delta \propto (d/\lambda)$ and $\delta\psi \propto (d/\lambda)^2$, so $\delta\psi$ is close to zero for thin layers ($d \ll \lambda$) and approaches more rapidly the instrument resolution than $\delta\Delta$.[15]
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