

Surface Rheology and Foam Stability of Mixed Surfactant–Polyelectrolyte Solutions[†]

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We have studied the surface rheology of mixed solutions of anionic polyelectrolytes and cationic surfactants. Surface elasticity and viscosity exhibit a maximum at a surfactant concentration much smaller than that for solutions of the pure surfactant. Foaming and foam stability were found to depend on these coefficients, although a systematic relation is difficult to establish. Still more surprisingly, the behavior of foams and foam films is very different in these systems.

1. Introduction

The Interaction between polymers and surfactants in solution is a growing field of interest.¹ The case of polyelectrolytes is interesting as the polymer charges play an important role still far from being fully elucidated, even in the absence of surfactant.² Furthermore, polyelectrolytes being in general water soluble, they are found in many industrial and biological processes, frequently associated with neutral or charged surfactants. The case of mixed solutions of polymers and surfactants of opposite charges is specially interesting; it can lead to the precipitation of the polymer–surfactant complex in the form of concentrated liquid-crystalline phases.³ Lamellar phases have recently received a lot of attention for the case of DNA, where it was found that the polymer is confined between the surfactant bilayers and forms organized substructures.⁴ Similar associations occur at the surface of the solution, where the surfactant monolayer is complexed with the polymer adsorbed in a flat configuration.⁵ This mixed surface layer is thicker than the pure surfactant monolayer and should in principle enhance the resistance of the surface to stretching or shear and thus stabilize the foams.⁶ The aim of the present work is to investigate the surface rheological properties of the mixed solutions as well as their foaming properties and to correlate the two sets of information. Earlier studies of the thin films made from these solutions will also be

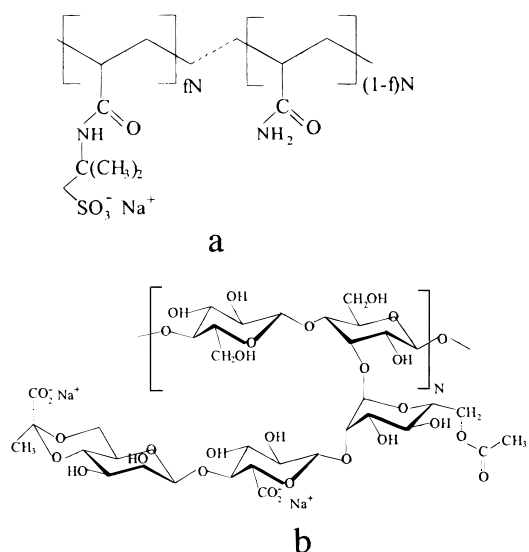


Figure 1. Molecular structures of (a) PAMPS and (b) xanthan.

compared with the foaming properties.⁷ Two different polyelectrolytes, with very different backbone rigidities, have been selected in order to check for the influence of this property on the behavior of the mixed layers.

2. Materials and Methods

2.1. Systems. We have studied different mixed surfactant–polyelectrolyte aqueous solutions. The surfactant chosen is dodecyltrimethylammonium bromide (C₁₂TAB), a cationic surfactant. It was obtained from Aldrich (purity 99%) and recrystallized three times before use.

Two different anionic polyelectrolytes have been selected (Figure 1):

(a) An anionic statistical copolymer of neutral monomers of acrylamide and charged monomers of acrylamidomethyl propanesulfonate (PAMPS). Copolymers with two different amounts of the charged monomer, namely, 10% and 25% were used, these amounts corresponding to the number fraction of the ionized monomer. The polymers were obtained from SNF Floerger, dissolved in deionized water (Millipore Milli-QSystem) and purified with an ultrafiltration unit with a 20 000 Da cutoff membrane. The weight-averaged molecular weights of the polymers, as measured by size exclusion chromatography (SEC) coupled with multiangle light scattering, are 10⁵ g/mol for the

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two samples. We refer to these polymers as PAMPS 10% and PAMPS 25%.

(b) Xanthan, an anionic polysaccharide. Xanthan is an extracellular polysaccharide produced by fermentation of a microorganism *Xanthomonas Campestris*. Its primary structure, as shown in Figure 1b, consists of a linear 1–4 linked D-glucan chain substituted on every glucose residue by a trisaccharide side chain. The polymer has been obtained from IDF and thoroughly purified using microfiltration at low flow rate through decreasing sizes Micropore filters and ultrafiltration with a molecular cutoff of 20 000 Da. Weight-average molecular weight M_w of the sample is around 11×10^6 g/mol.

Xanthan has a rigid backbone, whereas PAMPS is more flexible, their intrinsic persistence length being respectively 5 nm (for xanthan in pure water)⁸ and 1 nm². In the presence of salt, xanthan takes a double helix configuration that is much more rigid, the persistence length being 140 nm.⁸

2.2. Surface Viscoelasticity. The surface rheological properties have been investigated using excited capillary waves. In this way, the surface compression elasticity and viscosity are measured in the frequency range $\omega = 100$ –1000 Hz.⁹ The Gibbs elasticity is given by

$$\epsilon = A \frac{\partial \gamma}{\partial A} \quad (1)$$

where γ is the surface tension of the solution and A the surface area. This elasticity is the compression elasticity for an insoluble monolayer. Here the mixed layer is in equilibrium with surfactant and polymer dissolved in bulk water. When the surface is compressed, dissolution can occur. This leads to dissipation and to a viscoelastic behavior conveniently described by a complex number

$$\epsilon(\omega) = \epsilon_r(\omega) + i\epsilon_i(\omega) = \epsilon_r(\omega) + i\omega\kappa(\omega) \quad (2)$$

where ϵ_r is the elastic modulus, equal to the Gibbs elasticity at high frequency (when the monolayer does not have time to dissolve) and κ is the compression surface viscosity.¹⁰ Surface viscoelasticity measurements were carried out using a capillary wave setup. The system is described in detail elsewhere.⁹ The surface of the liquid is subjected to transverse (capillary) waves. The values of wavelength and decay coefficient of the waves are determined. The viscoelastic coefficients are subsequently calculated by using the dispersion equation and the surface tension, which is measured independently by the Wilhelmy plate method using an open rectangular frame. All experiments were carried out at room temperature (23 ± 1 °C).

It should be stressed here that the coefficients measured with this method are not pure compression coefficients but the sum of the compression and shear coefficients. However, the shear coefficients are generally very small compared to the compression coefficients in soluble monolayers.¹¹

2.3. Foam Formation and Stability Studies. Foam formation was studied using a vertical column consisting of a long (50 cm) glass tube (diameter 3 cm) with a fritted glass filter at the bottom (Figure 2). Nitrogen from a gas cylinder is blown through the filter and the solution located above. The flow rate is measured using a flowmeter. For a given gas flow rate, the height of the foam column in stationary conditions is taken as a measure of the foamability. To estimate the foam stability, we have measured the time (T_f) taken by the foam to decay to half the original height after the gas flow is stopped. These results, though qualitative in character, allow comparison of the foamability and foam stability of the different solutions.

3. Results

All our experiments were carried out with solutions of fixed polymer concentration and varied surfactant con-

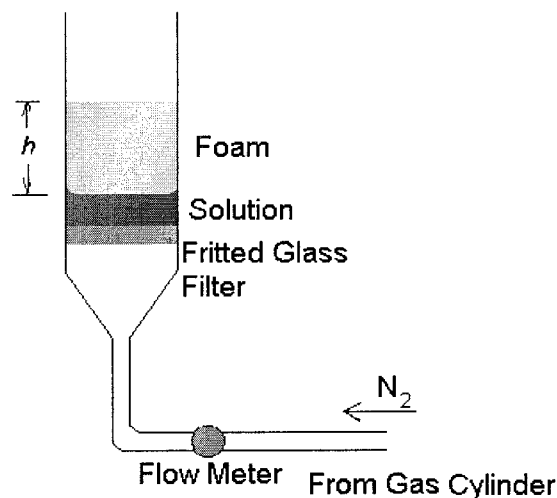


Figure 2. Schematic diagram of the foam column. The foam height is denoted by h .

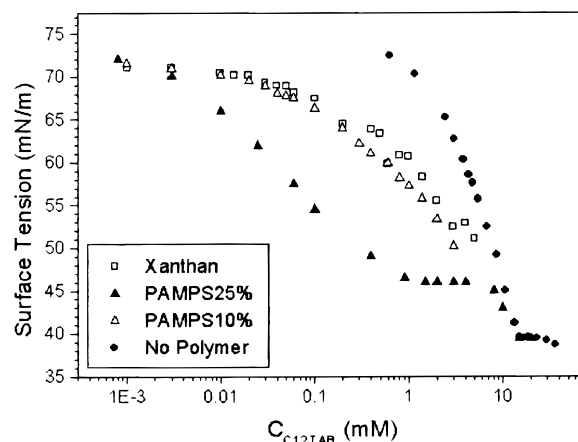


Figure 3. Surface tension as a function of C_{12TAB} concentrations: (closed circles) pure C_{12TAB} solution; (open squares) mixed xanthan– C_{12TAB} solution; (closed triangles) mixed PAMPS 25%– C_{12TAB} solution; (open triangles) mixed PAMPS 10%– C_{12TAB} solution.

centrations (c_s). The surface tensions of the solutions are plotted in Figure 3 as a function of surfactant concentration. It was shown earlier that provided the polymer concentration is not too small, the surface tension and the layer thickness are independent of the polymer concentration.^{5,12} A thermodynamic adsorption model based on the exchange of the surfactant counterions by the polymer ions at the surface allows an explanation of this behavior. Here, the polymer concentration was kept at 0.114 g/L, i.e., 114 parts per million (ppm).

The results of the viscoelasticity measurements for the surfactant–polymer mixed systems are shown in Figures 4–7. The results for solutions with only C_{12TAB} are also given (Figure 8). At low surfactant concentrations, the values of the real and imaginary parts of the viscoelastic moduli are small, and sometimes ϵ_i has a negative value. Negative values of the modulus were reported earlier.¹³ They are not physically absurd, because the surface quantities are excess quantities and a negative ϵ_i only means that the damping of the surface waves is smaller than on the pure substrate. However, up to now, no satisfactory explanation for this surprising

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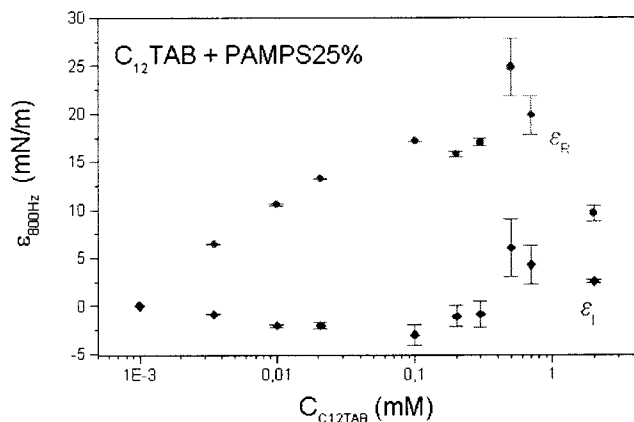


Figure 4. Surface viscoelasticity as a function of surfactant concentration for $C_{12}TAB$ solutions with PAMPS 25%.

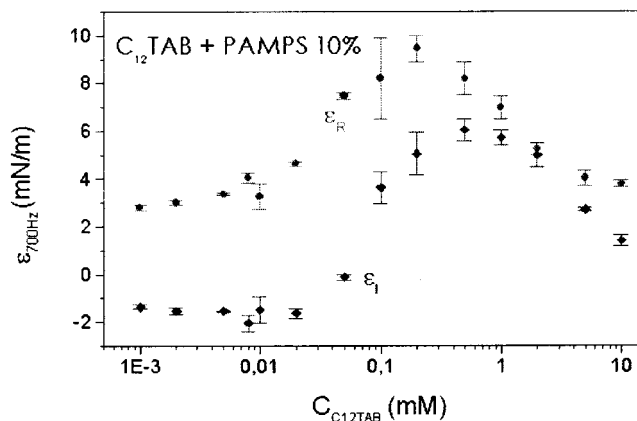


Figure 5. Surface viscoelasticity as a function of surfactant concentration for $C_{12}TAB$ solutions with PAMPS 10%.

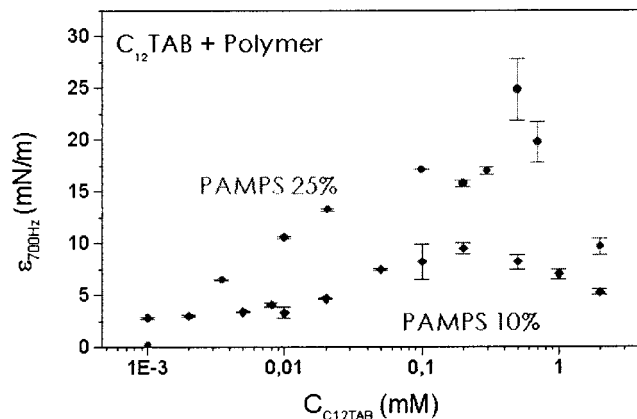


Figure 6. Surface elasticity as a function of surfactant concentration for $C_{12}TAB$ solutions with PAMPS 25% and PAMPS 10%. It is to be noted that the two curves are qualitatively similar, but the values of ϵ_r are higher for the solution with PAMPS 25%.

behavior has been found. As c_s is increased, the values of the two coefficients increase, reach a maximum, and then decrease again. This is as predicted by the Lucassen–van den Tempel (LT) model, which takes into account the dissolution in the bulk.¹⁴ As can be seen, the peak in the elasticity is at a much lower value of c_s for the surfactant polymer system, as compared to the pure surfactant system. Also, the peak value of ϵ_r is smaller for the mixed system, as compared to the surfactant system.

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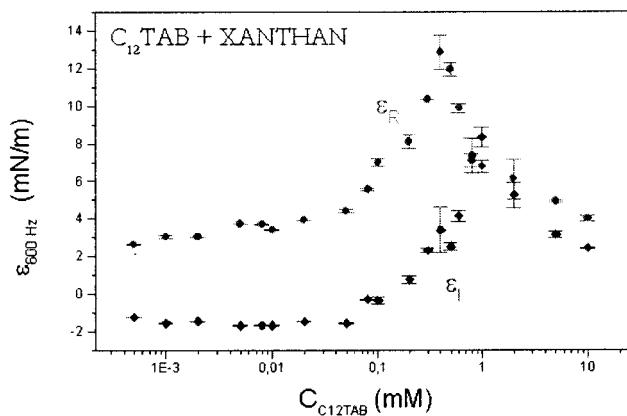


Figure 7. Surface viscoelasticity as a function of surfactant concentration for $C_{12}TAB$ solution with xanthan.

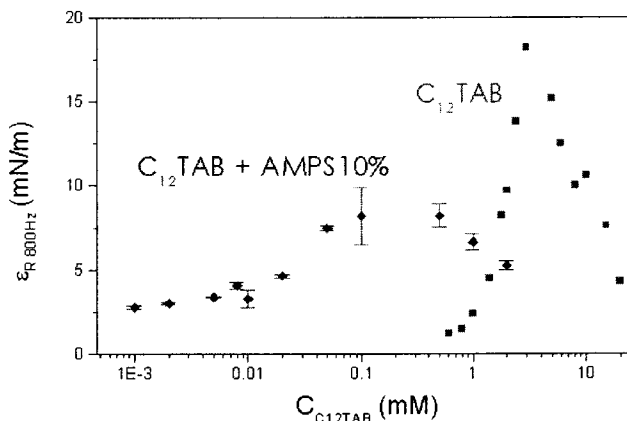


Figure 8. Surface elasticity as a function of surfactant concentration for pure $C_{12}TAB$ solutions and mixed solutions with PAMPS 10%.

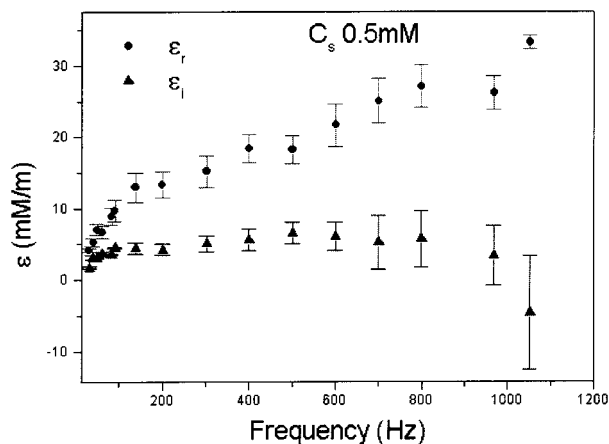


Figure 9. Surface viscoelasticity as a function of frequency for 0.5 mM $C_{12}TAB$ solutions with PAMPS 25%.

A comparison of the values of ϵ_r for the solutions of PAMPS 10% and PAMPS 25% (Figure 5) shows that the shape of the curves is similar but that the values of ϵ_r are larger for PAMPS 25%. In the case of solutions with xanthan, the peak occurs at a higher value of c_s . Interestingly, here the peaks for ϵ_r and ϵ_i are shifted, whereas they are close together for the other systems, as predicted by the LT model.

In the frequency range studied, the variation of the surface viscoelastic moduli is small. This variation is illustrated in Figures 9 and 10 for PAMPS 25%.

The results from the foaming studies are shown in Figure 11. As can be seen, there is almost no foaming for

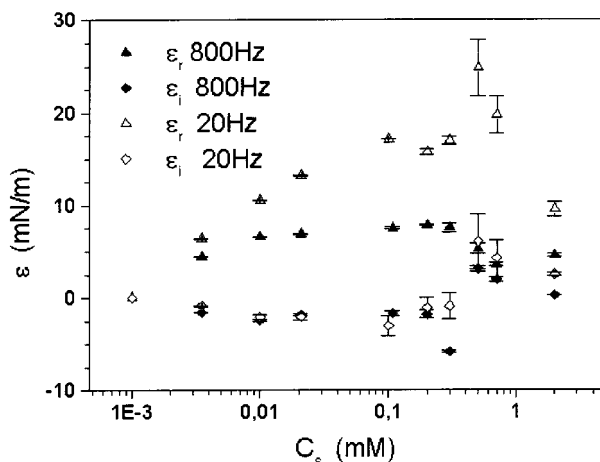


Figure 10. Surface viscoelasticity as a function of surfactant concentration for $C_{12}TAB$ solutions with PAMPS 25% at 20 and 800 Hz.

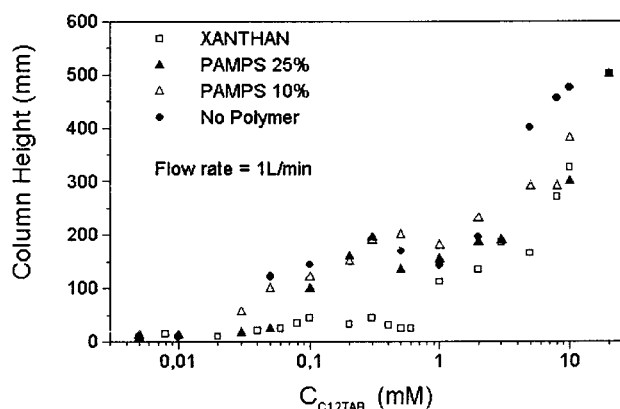


Figure 11. Foam height as a function of surfactant concentration for the different solutions, and a constant flow rate of 1 L/min of nitrogen: open squares, xanthan; closed triangles, PAMPS 25%; open triangles, PAMPS 10%; closed circles, no polymer.

surfactant concentrations c_s less than 0.01 mM. For xanthan, there is an increase in the foam height upon increasing c_s beyond 0.06 mM. The height increases with c_s up to 0.3 mM, decreases after, and then increases again very fast. Because foaming is small for these solutions, we have used a higher gas flow rate (1.5 L/min) in order to better observe the surfactant concentration variations (Figure 12). The intermediate decrease (around 0.4 mM) is reproducible, as can also be seen in Figure 11.

For PAMPS 25%, there is also an increase in foam height above 0.06 mM $C_{12}TAB$. The increase here is much larger than in the case of xanthan. This is followed by a slight decrease at around 0.5 mM, though it is not as clear as in the case of xanthan. After this, there is a rapid increase in the foam height. The behavior of PAMPS 10% is similar to that of PAMPS 25%, except that the decrease after the initial increase is even less pronounced. The same is true for the solution of $C_{12}TAB$ alone. It is interesting to note that the final increase in the foam height is almost independent of the polymer used. The values are almost identical for 20 mM surfactant for all solutions.

The results of foam stability are shown in Figure 13. The time of decay to half-height (T_r) is very small for c_s less than 1 mM. After that, T_r increases for all the solutions. For xanthan, the increase is slow at first, and very fast above 5 mM. In the case of PAMPS 10%, the increase occurs only above 5 mM, and it is very abrupt. PAMPS 25% shows a more uniform increase starting from

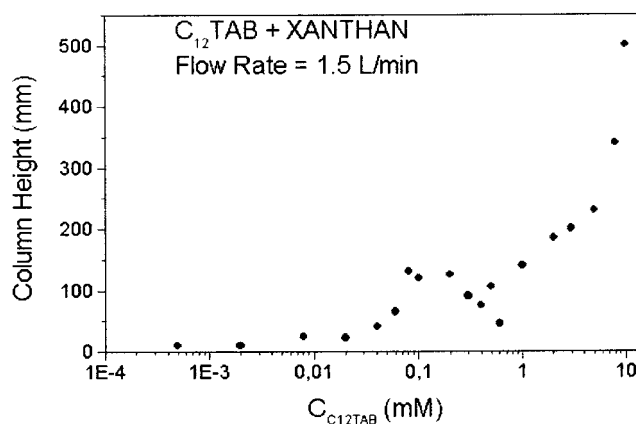


Figure 12. Foam height as a function of surfactant concentration for xanthan solution and a constant flow rate of 1.5 L/min of nitrogen.

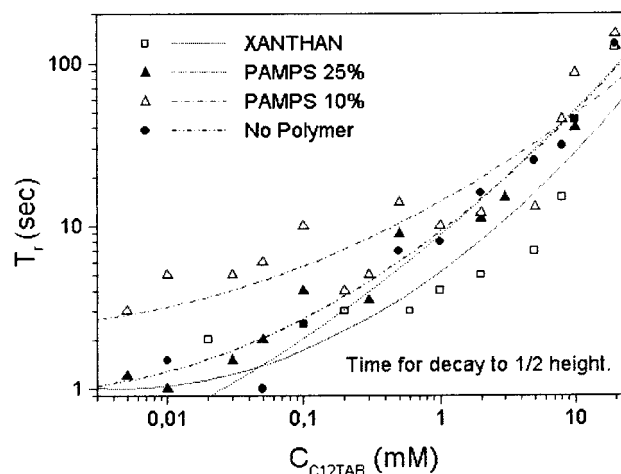


Figure 13. Foam lifetimes T_r versus surfactant concentration for the different solutions. T_r is the time taken by the foam column to drop to half its original height after the gas flow is stopped. The lines are second-order polynomial fits to the experimental points and are a guide to the eye: open squares, xanthan; closed triangles, PAMPS 25%; open triangles, PAMPS 10%; closed circles, no polymer.

0.5 mM. For the pure $C_{12}TAB$ solution, the behavior is somewhat similar to the solution with PAMPS 25%. It is to be noted that the difference in behavior between the different solutions starts decreasing after 5 mM and almost disappears at 20 mM.

Discussion

As it can be seen from Figures 4–7, there is a big change in the surface rheology of the solution upon adding the polyelectrolyte. In particular, there is a decrease in the values of c_s for the peak in ϵ_r and ϵ_i for the solutions with the polyelectrolytes. Also, the peak values of ϵ_r and ϵ_i are different depending on the polyelectrolyte used. In particular, the curves for PAMPS 10% and PAMPS 25% are similar, but the value of ϵ_r at the peak is very different. This can in principle be related to the formation of complexes by the surfactant and the polyelectrolyte at the solution–air interface. PAMPS 10% is less well coupled to the surface due to the presence of fewer charged groups and forms larger loops beneath.¹² This may be the reason for the lower elasticity of the solutions.

For pure $C_{12}TAB$, the dependence of surface viscoelastic coefficients on the surfactant concentration can be explained by the LT model.¹⁴ In this model, it is assumed that upon monolayer compression, some surfactant mol-

ecules dissolve into the underlying water, to restore the equilibrium surface concentration. When the monolayer is expanded again, surfactant molecules come back to the surface, and so on. Two extreme cases are easy to understand: when the frequency of the sinusoidal compression is low, the monolayer has always time to reach equilibrium, and there is no resistance to the compression, $\epsilon_r = \epsilon_i = 0$. When the frequency is high, the monolayer has no time to respond, and it behaves as if it were insoluble, $\epsilon_i = 0$ and

$$\epsilon_r = \epsilon_0 = A \frac{\partial \gamma}{\partial A} = -\Gamma \frac{\partial \gamma}{\partial \Gamma} \quad (3)$$

where Γ is the surface concentration. In the intermediate frequency range

$$\epsilon_r = \epsilon_0 \frac{1 + \Omega}{1 + 2\Omega + 2\Omega^2} \quad (4)$$

$$\epsilon_i = \omega \kappa = \epsilon_0 \frac{\Omega}{1 + 2\Omega + 2\Omega^2} \quad (5)$$

with

$$\Omega = \left(\frac{D}{2\omega}\right)^{1/2} \frac{\partial c}{\partial \Gamma}$$

In the case of mixed layers, the exchanges between surface and bulk also occur, but they are more difficult to describe. Expressions for ϵ_r and ϵ_i have been proposed¹⁶

$$\epsilon_r = \epsilon_s \frac{1 + \Omega_s}{1 + 2\Omega_s + 2\Omega_s^2} + \epsilon_p \frac{1 + \Omega_p}{1 + 2\Omega_p + 2\Omega_p^2} \quad (6)$$

$$\epsilon_i = \omega \kappa = \epsilon_s \frac{\Omega_s}{1 + 2\Omega_s + 2\Omega_s^2} + \epsilon_p \frac{\Omega_p}{1 + 2\Omega_p + 2\Omega_p^2} \quad (7)$$

with

$$\epsilon_j = -\Gamma_j \frac{\partial \gamma}{\partial \Gamma_j}$$

and

$$\Omega_j = \left(\frac{D_j}{2\Omega}\right)^{1/2} \frac{\partial c_j}{\partial \Gamma_j}$$

Because the polymer surface concentration seems independent of the bulk polymer concentration,^{5,12} the derivative $d\Gamma/dc$ for the polymer is zero and Ω_p is infinite. This would mean that the polymer contribution to eqs 6 and 7 is negligible. However, if bulk aggregates are present, these equations are not applicable. In the case of micellar aggregates, theoretical equations have been proposed.¹⁷ These expressions are very complex, but interestingly, they allow ϵ_i/ϵ_r to be larger than 1 (not possible with eqs 4 and 5). In the case of xanthan, one observes indeed that $\epsilon_i/\epsilon_r > 1$ at some concentrations close to the maximum (Figure 7). These concentrations are above the CAC (critical aggregation concentration, at which bulk polymer–surfactants aggregates start to form in the bulk) as

evidenced from the beginning of the plateaus of the surface tension curves (Figure 2).

In view of the complexity of the equations, it is difficult to go beyond these simple arguments and to achieve a quantitative description as in the case of the pure surfactant solutions. It will be in particular difficult to explain the different variations of ϵ_r and ϵ_i with c_s for xanthan, where the two peaks are well separated. There is a small difference in the position of the two peaks for PAMPS 10%, while they are exactly at the same value of c_s for PAMPS 25%. Similarly, the frequency variation shown in Figures 9 and 10 cannot be accounted for by diffusion, much too slow at the studied concentrations.

The fact that the elasticity of the mixed layers are much larger than those of the pure surfactant layers at small c_s can nevertheless be attributed to the fact that the amount of surfactant present at the surface is greatly enhanced by the presence of the polymer.¹²

It was recognized early that foaming and foam stability are related to the surface rheological behavior.⁶ Foam properties are also generally related to the stability of the films separating the air bubbles. Qualitatively, ϵ is a measure of the ability of a film to respond to an increase in surface area. Good foamability is achieved when the bubble surfaces are rapidly covered by surfactant layers and when these bubbles do not break too quickly. Foamability and foam stability are therefore closely related. Foam stability is governed by various processes:

(a) Drainage, removal of the liquid from the space between the bubbles, and thinning of the films separating the bubbles. Surface viscoelasticity slows down (slightly) the drainage rate.¹⁸

(b) Diffusion of the gas from the small bubbles toward the larger ones (Ostwald ripening), leading to a bubble size growth with time. Gas diffusion rate decreases when the surface coverage increases¹⁹ (ϵ is closely related to Γ).

(c) Coalescence, breakage of the film between two adjacent bubbles to form a single larger bubble. Finite elasticity values protect the films against rupture.²⁰

All three phenomena depend on the elasticity and viscosity of the surface, and high elasticities and viscosities are thus expected to stabilize the foam. Let us however point out that all the above processes occur at different time scales τ and that the surface rheological parameters to be considered are those at a frequency $\omega = 1/\tau$.

As can be seen clearly for xanthan, the foam height begins to increase on reaching the value of c_s for which the surface viscosity becomes positive. This is also true for the other polymers. Although the surface rheological behavior of the different polymers is similar, the foaming capacity is much larger with PAMPS than with xanthan. The decrease in the foam height after the initial increase corresponds to the peak in ϵ_r . This is somewhat counter-intuitive, since one would rather expect a coincidence between the peak in ϵ_r and the peak in foam height. It should be recalled however that the position of the peak in ϵ_r depends on the frequency ω : the larger the frequency, the larger the surfactant concentration at the peak. One may thus argue that the characteristic frequency of the foaming phenomenon is much less than the frequencies investigated with the capillary waves device and, in this way, correlate the intermediate foaming capacity maximum with the maximum in surface elasticity. After the local minimum in foam height, the foaming and foam

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stability of the solutions are larger. For 20 mM surfactant, there is hardly any difference between the different solutions. This could be associated to the fact that at this concentration, the surfactant monolayer is compact and there is no more penetration of the polymer in the surface layer.²¹

The foam behavior with the different polymers is noticeably different. The foam lifetime for PAMPS 10% is larger than that of PAMPS 25%, although the surface elasticity is larger for PAMPS 25%. The intermediate maxima observed in the foam height variation with surfactant concentration are not present in the foam lifetime variation. This is somewhat counterintuitive, for one expects a linear relation between the column height and T_f , which is not seen here. This suggests that something is missing in this simple model, and this needs to be investigated.

The behavior of foam films is still more different. Horizontal foam films with diameters of the order of 1–2 mm have been studied earlier with a thin film balance for the same polymer–surfactant solutions.^{7,22} The films made from the pure surfactant solutions last only a few minutes. When xanthan is added, the film breaks after a few seconds, such as, for instance, a pure water film. In the case of PAMPS, the films are much more stable; they last for hours, provided they are kept in a humidity-controlled environment. Above the precipitation concentration, their thickness is very inhomogeneous: they visibly contain small microgel domains and they become impossible to break.⁷ Surprisingly, there are no special differences on the foam behavior below and above the precipitation concentration.

There is thus little correlation between the foam stability and the film stability in this type of systems. The rapid increase in foam height and T_f values upon increasing c_s seems to indicate that the foam behavior is largely controlled by the amount of surfactant present, whereas

the foam film behavior is related more closely to the presence of the polymer. Similar observations were made recently on foams made with protein solutions.²³

Conclusions

We have studied the surface rheology of mixed solutions of anionic polyelectrolytes and cationic surfactants. We observe that the surface rheology of the solutions depends strongly on the polyelectrolyte, via the formation of complexes. Surface elasticity and viscosity exhibit a maximum at a surfactant concentration much smaller than for solutions of the pure surfactant. The foaming and foam stability depend on the surface elasticity and viscosity of the solution, though a quantitative understanding of the relationship is far from apparent. In particular, we find that while PAMPS does not affect the foaming properties much, xanthan reduces the foaming ability of the solution appreciably, although their surface elasticities are comparable. Still more surprisingly, the effect of the polymers is much less marked than on the foam films as studied in a thin film balance. This might be due to the fact that the characteristic time for foam formation (a few tens of seconds) is much shorter than that of the foam film formation in a thin film balance (a few tens of minutes). The nature of the mixed surface layers is therefore probably different in the two type of systems. Let us point out that the behavior reported here illustrates the difficulties encountered when foam behavior is inferred either from surface layer properties or from foam film properties. Further work is clearly needed to clarify these puzzling observations.

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