Interaction between sodium poly(styrene sulfonate) and dodecyltrimethylammonium bromide at the air/water interface

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The results of dynamic surface elasticity measurements in mixed aqueous solutions of sodium poly(styrene sulfonate) (PSS) and dodecyltrimethylammonium bromide (DTAB) are inconsistent with the model of Goddard *et al.* proposing complex formation in the surface layer and show that hydrophobic segment/segment and segment/surfactant tail interactions should be taken into account.

The interactions between polyelectrolytes and oppositely charged surfactants in aqueous solutions have been intensively studied.[1–4] Although the surface properties of these systems can be of practical importance, the studies have focused mainly on the properties of the bulk phase.[1–3,5] Only surface tension was measured rather frequently as a function of surfactant concentration at a constant polyelectrolyte content.[1–4] These studies gave evidence for the formation of complexes with high surface activity in the surface layer. Goddard *et al.* proposed a simple model for the surface structure of dilute polyelectrolyte/surfactant solutions.[1–3] The surfactant ions form a monolayer at the liquid surface and attract electrostatically charged macromolecules. The charged groups of the polymer play the role of counterions. Note that, although this picture seems rather natural, it cannot be examined by means of surface tension measurements only.

More elaborated methods of surface chemistry have been applied to polyelectrolyte/surfactant solutions only recently.[6–12] Although the number of experimental techniques is large, most of them were applied only to one or two particular systems. For example, among adsorbed films of anionic polyelectrolytes and cationic surfactants, only the system of poly(styrene sulfonate)/alkyltrimethylammonium bromides (PSS/ATAB) was studied by neutron reflectivity.[8] The dynamic surface elasticity was measured only for solutions of polyacrylamide sulfonate and ATAB by the capillary wave[10,11] and oscillating bubble methods.[9]

In this work, we applied another technique, the oscillating barrier method, to adsorbed films of PSS/dodecyltrimethylammonium bromide (PSS/DTAB). The aim was to study the range of low surfactant concentrations where other experimental techniques indicated a relatively simple surface structure and

where the model of Goddard *et al.* allowed conclusions on the surface dilational viscoelasticity. The interpretation of surface rheological data for PSS/DTAB films can be facilitated in comparison with other systems. Indeed, apart from the X-ray technique,[6] PSS/DTAB films have been recently investigated in detail by neutron reflectivity[8] and ellipsometry.[12] Moreover, the surface viscoelasticity of adsorbed PSS films has been studied by the same methods in broad frequency and concentration ranges.[13]

The experimental setup and the experimental procedures were described in detail elsewhere.[13,14] A moving barrier induced low frequency oscillations of the liquid surface area in a Langmuir PTFE trough. The corresponding surface tension oscillations
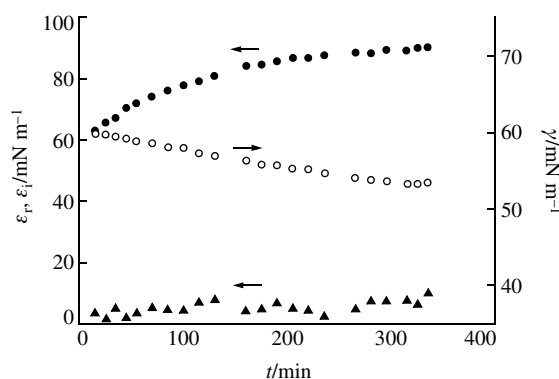

Figure 1 Kinetics of the dynamic surface tension (open circles), the real (closed circles) and imaginary (closed triangles) parts of the dynamic surface elasticity of PSS/DTAB solutions at $c_p = 0.05$ wt.% and $c_s = 0.15$ mM.

were measured by the Wilhelmy plate method. For small perturbations, linear relations describe the system, and the surface tension perturbation is proportional to the area change. In this case, the dilational dynamic surface elasticity, which is a proportionality factor, does not depend on the perturbation amplitude. If the surface film is viscoelastic, the oscillations of surface tension and surface area proceed out of phase and the surface elasticity proves to be a complex quantity: $\varepsilon = \varepsilon_r + i\varepsilon_i$. PSS with a molecular mass of 70000 (Aldrich) was used. DTAB (Aldrich) was purified by double recrystallization from an ethyl acetate/ethanol mixture. Fresh twice-distilled water was used for the preparation of the solutions.

All the measurements were performed at two PSS concentrations, $c_p = 0.01$ and $c_p = 0.05$ wt.%, and various concentrations of DTAB c_s. Figure 1 shows the dependence of the dynamic surface tension and dynamic surface elasticity on the surface age t at a frequency of 0.14 Hz. The rate of equilibration increases with DTAB concentration only in the range of very dilute solutions ($c_s \leq 0.2$ mM). At $c_s > 1$ mM, the relaxation times of surface tension and surface elasticity are not shorter than 20 min. This behaviour indicates that the adsorption kinetics in the test system is not controlled by diffusion from the bulk phase to the surface. This conclusion is corroborated by calculations of the characteristic diffusion time τ_D according to the relation[15]

$$\tau_D = \frac{1}{D}\left(\frac{\Gamma}{c}\right)^2, \tag{1}$$

where Γ is the adsorbed amount, D is the diffusion coefficient in the bulk phase, and $c = c_p$ or $c = c_s$.

The adsorbed amounts of PSS and DTAB were determined by neutron reflectivity.[8] The corresponding diffusion coefficients were published.[9,16] The estimates according to relation (1) show that for the both substances τ_D is less than 5 s at $c > 0.2$ mM. Therefore, the experimental characteristic times of the surface equilibration exceed the estimates by several orders of magnitude.

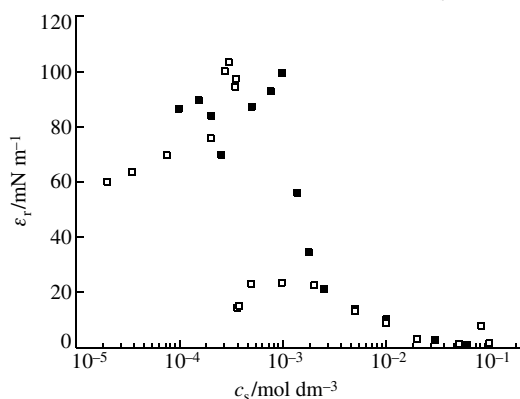Figure 2 shows the dependence of ε_r on c_s at two PSS

Figure 2 Real part of the dynamic surface elasticity *vs.* DTAB concentration at $c_p = 0.01$ wt.% (open squares) and $c_p = 0.05$ wt.% (closed squares).

concentrations at a frequency of 0.14 Hz. The large scatter of experimental points at low concentrations ($c_s < 0.3$ mM) is probably connected with large deviations from the equilibrium. In this concentration range, the surface elasticity was measured about 5 h after the surface creation while the equilibration takes a longer time. The surface elasticity is high (> 60 mN m^{-1}) at low concentrations and drops abruptly at $c_s \approx 0.3$ mM ($c_p = 0.01$ wt.%) and $c_s \approx 1$ mM ($c_p = 0.05$ wt.%) by almost one order of magnitude, thus indicating strong changes in the surface structure. At a further concentration increase, the dynamic surface elasticity decreases slowly approaching zero at $c_s > 0.02$ mol dm^{-3}.

These results can be connected with the findings of Monteux *et al*. (for $c_p = 0.05$ wt.%), who observed an abrupt increase in the ellipsometric signal with increasing DTAB concentration at $c_s \approx 1$ mM.[12] This peculiarity was explained by microgel formation at the liquid surface. At low concentrations, the thickness of the adsorbed film is low (~ 2 nm) and the polymer chains have a flat almost two-dimensional conformation,[7,8,12] which is

characterised by a high surface elasticity. At $c_s > 1$mM ($c_p = 0.05$ wt.%), the thickness strongly increases and the film becomes highly heterogeneous.[12] The data on the dilational surface viscoelasticity show that the formation of microgel particles is not the only process in the surface layer. The surface film structure between the particles, which influences the dynamic surface properties, undergoes strong changes. The appearance of a microgel phase at the surface precedes the corresponding event in the bulk phase: at $c_s > 4$ mM (close to the point where the charges brought by PSS and DTAB are equal) the solution becomes opalescent and then turbid. At $c_p = 0.01$ wt.%, where ellipsometric data are absent, the drop in surface elasticity (Figure 2) probably has the same reason.

At relatively high surfactant concentrations ($c_s > 0.02$ M), the surface rheological data give scarce information. Other methods indicate rather complex surface structure in this concentration range, for example, micelle formation in the surface layer, as was proposed[4] and confirmed later for PSS/DTAB solutions by means neutron reflectivity.[8]

When the system approaches an equilibrium at $c_s < 0.3$ mM, the surface elasticity increases and one can expect higher values at longer surface life times. At $c_s < 0.02$ mM, the measurements are impossible because of slow equilibration. However, even a rough extrapolation to small DTAB concentrations leads to high values of the dynamic surface elasticity for very dilute solutions. Therefore, one can assume that the interaction of PSS and DTAB in the surface layer proceeds in the range of extremely low concentrations, much less than the critical aggregation concentration in the bulk phase.[6,8] Note that both components of the complex dynamic surface elasticity at low concentrations are close to the values for relatively concentrated pure PSS solutions:[13] $\varepsilon_r > 60$ mN m^{-1} and it exceeds ε_i by one order of magnitude. The adsorbed film is almost purely elastic. On the other hand, both systems are characterised by extremely slow changes in surface properties. This behaviour is different from that of the adsorbed films of non-ionic polymers[14] and surfactants of low molecular weights.[15]

The similarity between pure PSS and mixed PSS/DTAB solutions means that the mechanical surface properties of the latter system at low concentrations are determined only by the interactions between charged stretched PSS chains. DTAB has no direct influence on the surface viscoelasticity and its role consists in keeping the macromolecules in the surface layer. At first sight, these conclusions are in agreement with the model by Goddard *et al*., where the DTAB molecules interact electrostatically with the ionised groups of PSS and play the role of anchors for the polyelectrolyte chain beneath the surfactant monolayer.[1–3] If not all sulfonate groups are connected with the surfactant and the chain bears some charge, it still possesses an effective rigidity of electrostatic origin and must be stretched at the surface. Strong repulsion between neighbouring segments should lead to a high dynamic surface elasticity.

This simple picture, however, contradicts some other experimental findings. If it were true, only a part of sulfonate groups can be connected with DTAB. The neutron reflectivity shows that the number of surfactant molecules almost two times exceeds the number of polymer segments in the surface layer at low concentrations.[11] The excess of the free surfactant seems improbable if we take into account that the driving force for the DTAB adsorption in pure surfactant solution is negligible at $c < 1$ mM. Besides, the large number of free DTAB molecules in the surface layer leads to the fast relaxation of surface stresses, but this is not the case.

Moreover, the classical model does not explain the high surface concentrations of the complexes in extremely dilute solutions. In the bulk phase mainly the balance between the enthalpic contribution of the electrostatic interaction and the opposite contribution from the loss of translational entropy governs the formation of an ion doublet and the joining up of the counterion to a charged micelle or to a macromolecule.[17] The absolute value of the latter term increases with dilution and the equilibrium shifts to the direction of free ions. Although the complex formation in the surface layer is more complicated,

the model of Goddard *et al*. gives no idea how one can overcome this difficulty. On the other hand, if the surface layer is neutral as a whole and the electrostatic forces are the only ones in operation, the thermal motion must be responsible for the relaxation of surface stresses. Then, the above calculations of τ_D give also the estimates from above of the main relaxation times. However, the results of the oscillating barrier method indicate significantly slower relaxation at low concentrations. Probably, some other factors have to be additionally taken into consideration.

Indeed, the model of Goddard *et al*. does not take into account the high hydrophobicity of the styrene backbone chain. PSS is hydrophilic due to its sulfonate groups, but if the degree of sulfonization is not high, the polymer can form intramolecular globules in aqueous solutions and the whole structure is described by a pearl necklace.[18] The hydrophobicity of the PSS chain increases with decreasing the degree of ionization, for example, due to salt addition, and the polyelectrolyte can form two-dimensional aggregates in the surface layer.[13] The hydrophobic nature of the PSS backbone chain also displays itself at the PSS/ATAB complex formation in the bulk solution. In these systems a compact structure is formed where one PSS chain is associated with several ATAB micelles in such a way that the hydrophobic aromatic rings of the poly ion are embedded in the micellar interior.[5]

These considerations indicate that the hydrophobic nature of the PSS backbone should be taken into account in the description of the PSS/DTAB complex at the air/solution interface. One can assume that the role of ion pair formation between the surfactant cation and the sulfonate anion is mainly limited to the local neutralization of free charges at the polymer chain. Then, the hydrophobic effect leads not only to the surfactant adsorption but also to the attraction between segments of the polystyrene backbone and hydrocarbon tails of the surfactant, between the segments themselves, and, probably, between the surfactant tails. As a result, the adsorbed film contains small regions with a low effective charge and high hydrophobic interactions between the components. One can consider these regions as two-dimensional aggregates containing segments of different PSS chains (Figure 3). The charge of PSS trains between the aggregates is not completely compensated. They are rigid and strongly repulse each other as they do in the system without surfactant. The whole adsorption film is rigid due to the entanglements of different polyelectrolyte chains and strong cohesion between hydrophobic entities inside the two-dimensional aggregates. This system is characterised by a high modulus of the surface dilational elasticity. On the other hand, the entanglements between different polymer chains can lead to long relaxation times. This picture of the adsorbed film is only a little more complicated than the model by Goddard *et al*. but it is in agreement with the experimental data. Note that, recently, Babak *et al*.[19] also have taken into account the intra- and inter-macromolecular hydrophobic interactions while explaining the dilational surface viscoelasticity of adsorption layers of hydrophobically modified chitosan.

The testing of the hypothesis formulated in this study requires application of other experimental techniques. Additional information can be probably obtained by studying the frequency dependence of the surface elasticity. One can assume that, at low DTAB concentrations ($c_s < 0.3$ mmol dm^{-3}), the main characteristic frequency is low and cannot be determined by conventional experimental methods like in the case of pure PSS

adsorption films.[13] In the opposite case when $c_s \geq 0.05$ mol dm^{-3}, the adsorption film consists mainly of surfactant monomers and the characteristic frequency belongs the kilohertz range. This means that the films with low polymer content can be studied by a capillary wave technique.

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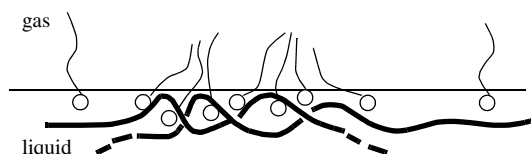19 V. G. Babak, J. Desbrieres and V. E. Tikhonov, *Colloids Surf. A*, 2005, in press.

Figure 3 Schematic diagram of aggregate formation in the surface layer at low DTAB concentrations.