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The effect of surfactants on adsorbed layers of a cationic polyelectrolyte

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Abstract: A comparative study of the influence of anionic (sodium dodecyl sulfate, SDS), cationic (tetradecyltrimethylammonium bromide, TTAB) and non-ionic (penta-ethyleneglycol mono n-dodecyl ether, $C_{12}E_5$) surfactants on the structure and composition of adsorbed layers of cationic hydrophobically modified hydroxyethylcellulose (Quatrisoft LM 200) on hydrophilic surfaces (mica and silica) was carried out using surface force apparatus and *in situ* null ellipsometry. It is shown that a complex interplay of electrostatic, hydrophobic, and steric effects govern polymer/surfactant/surface interactions and that the effect of surfactant addition strongly depends on its nature and concentration.

Both anionic and non-ionic surfactants exhibit aggregation on the polymer hydrophobes. SDS has the most profound influence on Quatrisoft interfacial behavior due to the changes in electrostatics accompanying formation of the polymer/surfactant complex. In the case of $C_{12}E_5$, large surfactant clusters bound to the polymer affect the macromolecules' conformation in the adsorbed layer via steric effects. In contrast to SDS and $C_{12}E_5$, no evidence of interaction between the polycation and a like-charged surfactant, TTAB, was obtained. At the same time, TTAB adsorbs on the surface in competition with the polyelectrolyte. This results in partial displacement of the latter and its looser attachment to the surface.

Key words: Adsorption – polymer–surfactant interactions – ellipsometry – surface forces

Introduction

A proper understanding of interfacial behavior of polymer–surfactant mixtures is not only a matter of academic interest, but is becoming the barest necessity, due to the increasing number of technological applications in which polymers are used along with surfactants to control bulk characteristics (mostly rheological) of media and surface-related properties such as stability of dispersions, wettability, and adhesion.

To purposely use the various effects brought about by polymer–surfactant, polymer–surface and surfactant–surface interactions, one has to unravel the detailed molecular mechanisms which govern these interactions. The complexity of the system (surface-polymer-surfactant-medium) as well as the diversity in the molecular nature and individual properties of the components make the task far from trivial. At the present stage, collection of reliable and comprehensive experimental information concerning the behavior of various polymer–surfactant mixtures at interfaces is needed to improve our understanding of these systems and to serve as a base for future theoretical developments.

The polymer chosen for study here – cationic hydrophobically modified hydroxyethylcellulose Quatrisoft LM 200 – belongs to the class of hydrophobe-modified (HM) polyelectrolytes. Their unique rheological behavior (being "associative thickeners", they exhibit shear-thinning properties), especially in the presence of surfactants [1], and their strong tendency to adsorb on oppositely charged surfaces, makes them attractive for many industrial applications. Being hydrophobically modified, the polymer is expected to affect surfactant self-assembly via hydrophobic interactions, the strength of the effect being dependent on the type of surfactant. These polymer–surfactant interactions may have an influence on the state of the adsorbed polymer layers. At the same time, surfactants can affect the adsorbed layer via competitive adsorption, provided their affinity to the surface is high enough to enable their competition with the polyelectrolyte for the surface sites.

In our previous paper [2], we discussed the influence of an anionic surfactant on Quatrisoft adsorbed layers studied by the surface force apparatus (SFA) and in situ null ellipsometry. These techniques proved to be useful in obtaining information on the structure and composition of adsorbed polymer layers.

In the present study, we compare the effects of anionic (sodium dodecylsulfate, SDS), cationic (tetradecyltrimethylammonium bromide, TTAB) and non-ionic (pentaethyleneglycol mono n-dodecyl ether, $C_{12}E_5$) surfactants on interfacial behavior of HM cationic polyelectrolyte Quatrisoft LM 200.

Experimental

Materials and chemicals

The water used in this study was purified by the following consecutive steps: distillation, percolation through a Millipore Water System and final double distillation in an all-Pyrex apparatus. The mica used in our SFA experiments was best quality, optically clear muscovite green mica, obtained from Mica Supplies Ltd. (England). Si/SiO_2 plates for ellipsometry were prepared and cleaned as described elsewhere [3]. Sodium dodecyl sulfate (specially pure, from BDH) was further purified by triple recrystallization from pure water. Penta-ethyleneglycol mono n-dodecyl ether ($C_{12}E_5$) was purchased from Nikko Chemicals (Japan) and was used as supplied. Tetradecyltrimethylammonium bromide (TTAB) was obtained from Fluka and recrystallized from the acetone/ethanol mixture (30:1 v/v). Quatrisoft LM 200 was obtained from Union Carbide Chemicals and Plastics Co., Inc. It was purified by extensive dialysis and freeze-dried. The polymer is a N, N-dimethyl-N-dodecylammonium derivative of hydroxyethylcellulose with molecular weight of approximately 100 000 [4].

Surface force measurements

The forces between mica surfaces bearing adsorbed layers were measured using a Mark IV surface force apparatus [5]. The technique allows an accurate determination of the force, $F(D)$, acting between two mica sheets, mounted in the apparatus in a crossed cylinder configuration, as a function of surface separation D [6]. The measured forces were scaled with the mean local radius of curvature R of the curved mica sheets.

At the beginning of each experiment mica surfaces were brought into contact in air and then in water to verify the absence of debris and other types of surface contamination. The contact position as measured in water, was used throughout subsequent experiments as a zero distance reference. An aliquot of concentrated polymer solution was then injected into the apparatus with a syringe to obtain a final polymer concentration of 34 ppm. The interaction forces between polymer layers were also measured in the presence of added surfactants. The systems were allowed to equilibrate for 12–24 h until no change of the force profile with time could be detected. Force measurements were conducted both on approach (compression) and separation (decompression), the separation was changed at a rate of 0.47 nm/s and at least two reproducible runs were recorded for each system composition. All measurements were performed at 22 °C in a thermostated room.

Ellipsometry

An automated Rudolph Research thin-film null ellipsometer, type 43603-200E, was used in this study. A detailed description of our experimental set-up can be found elsewhere [7]. The optical characteristics of the substrate (Si/SiO_2 plates) were determined at the beginning of each experiment by ellipsometric measurements in two ambient media as discussed in [7]. Then, a certain amount of polymer was injected into the cuvette, which originally contained 5 ml H_2O, and the ellipsometric angles Ψ and Δ were recorded continuously until an equilibrium was reached. Then, the system composition was changed either by addition of a desired amount of surfactant or by pumping (at 20 ml/min) preheated pure water through the cuvette (rinsing). All measurements were conducted at the wavelength $\lambda = 401.5$ nm and the angle of incidence $\phi = 67.2°$ in a thermostated cuvette at 25 ± 0.1 °C under continuous stirring by a magnetic stirrer at about 300 rpm.

The results of Ψ and Δ measurements were interpreted within the framework of an optical four-layer (silicon-silica-adsorbed film-medium) model, assuming isotropic media and planar interfaces. The mean refractive index n_f and the average thickness d_f of the adsorbed layer were calculated using a numerical procedure described in [3]. The adsorbed amount (Γ) was calculated from n_f and d_f according to [8] using $dn/dc = 0.152$ cm^3/g, as measured in polymer solutions.

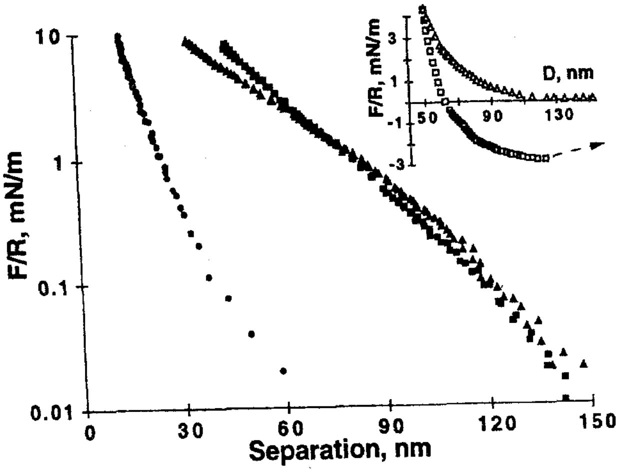

Fig. 1. Force vs. distance profiles between Quatrisoft layers measured in water (circles) and in the presence of $4 \cdot 10^{-5}$ M (squares) and $2 \cdot 10^{-3}$ M (triangles) SDS. The main chart shows the forces measured on approach, while the insert presents those recorded on separation. The arrow indicates a slow jump apart from a deep force minimum observed in Quatrisoft/$4 \cdot 10^{-5}$ M SDS system

Results

Surface forces

Figure 1 shows the force-distance profiles measured after equilibration of mica surfaces with a 34 ppm aqueous solution of Quatrisoft, both alone and also in the presence of SDS. In the pure polymer case the measurable repulsive force extends to a separation of about 60 nm. Upon compression the repulsion rises gradually and reaches $F/R = 10$ mN/m at separation of about 14 nm. Both the decay and the magnitude of the force indicate a nonelectrostatic nature to the repulsion. Under large applied load the adsorbed layer of Quatrisoft can be compressed down to 8.5 nm but cannot be squeezed out. A shallow ($F/R = -150$ μN/m) but distinctive and reproducible minimum was observed on separation (see the insert of Fig. 2). This attractive minimum can be attributed to the bridging induced by compression and interpenetration of adsorbed layers. Upon addition of $4 \cdot 10^{-5}$ M SDS to the system, the force profile changes dramatically. On approach, the onset of a monotonically increasing repulsion was observed when the surfaces were some 145 nm from water contact, i.e., at separations substantially larger than in the pure polymer case (60 nm). With an applied force of about 10 mN/m, a separation $D = 43$ nm was reached, and under strong compression the polymer/surfactant layers could be squeezed down to 18 nm. Thus, addition of small amounts of anionic surfactant considerably changes both the extent and compressibility of the adsorbed layers. The latter can result from an increase in the amount of material in the gap and/or in the strength of intralayer repulsive interactions. In another experiment the polymer adsorption was followed by addition of SDS, to a final concentration of $2 \cdot 10^{-3}$ M. The force–distance profile measured after equilibration is also shown in Fig. 1. On first inspection, the force appears to be rather similar to that measured in the presence of $4 \cdot 10^{-5}$ M SDS, at least with respect to the onset of repulsion. However, a number of differences is evident. A less steep increase in repulsion at distances below 100 nm results in a shorter separation attained at $F/R = 10$ mN/m, namely, 31 nm, compared to 43 nm in the previous case. Further compression led to a 12 nm-thick bilayer, again thinner than at $4 \cdot 10^{-5}$ M SDS. Furthermore, the force profiles measured on separation displayed qualitatively different patterns at these two SDS concentrations. This is illustrated in the insert of Fig. 1, where the decompression profiles obtained at $4 \cdot 10^{-5}$ M and $2 \cdot 10^{-3}$ M SDS are compared. A deep attractive minimum ($F/R = -2.8$ mN/m at $D = 130$ nm), indicative of a strong affinity between the adsorbed layers, was observed in the

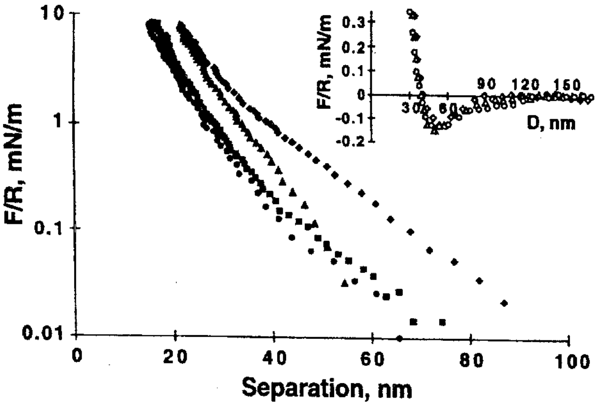

Fig. 2. Force vs. distance profiles between Quatrisoft layers adsorbed on mica measured in water (circles) and in the presence of 10^{-4} M (squares) and 10^{-3} M (triangles) and 10^{-2} M (diamonds) $C_{12}E_5$. The insert shows a shallow attractive minimum observed on separation in all cases

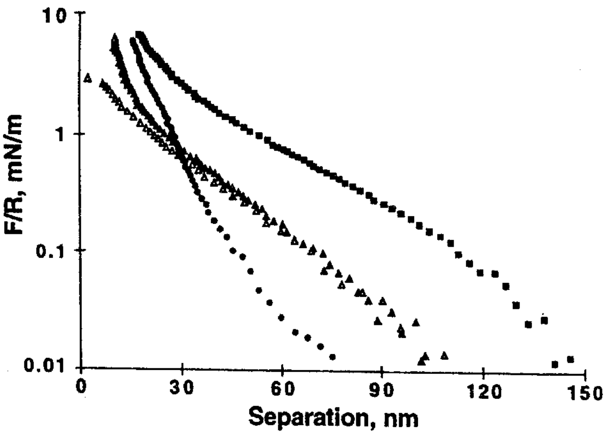

Fig. 3. Force vs. distance profiles between Quatrisoft layers adsorbed on mica measured in water (circles) and in the presence of $1.5 \cdot 10^{-3}$ M (squares) and $6 \cdot 10^{-3}$ M (triangles) TTAB. After measurements in $6 \cdot 10^{-3}$ M TTAB the box was drained and refilled with pure water. The force curve measured shortly afterwards is shown by open triangles. The surfaces jumped from separation of about 7 nm into a deep adhesive minimum (the pulloff force $F/R = 170$ mN/m) at $D = 2.7$ nm. No force minima were detected on separation at high TTAB concentrations

presence of $4 \cdot 10^{-5}$ M SDS, while at $c_{SDS} = 2 \cdot 10^{-3}$ M the measured interaction was purely repulsive and retraced the compression curve. Thus, although exhibiting the same range of repulsive interaction, the polymer/surfactant layers formed at low and high SDS concentrations are clearly different.

Force measurements in systems containing non-ionic surfactant revealed that, unlike SDS, $C_{12}E_5$ does not cause dramatic changes in either the range or the magnitude of interaction between Quatrisoft adlayers. The results are shown in Fig. 2. At $c_{C_{12}E_5} = 10^{-4}$ M addition of the surfactant causes only a slight increase in the force magnitude. When the surfactant concentration was raised to 10^{-3} M a clearly stronger repulsion was observed at separations below 50 nm. This feature apparently indicates a higher material density in the adsorbed layer. Further increase in surfactant concentration, namely, up to 10^{-2} M, led to an expansion of the adsorbed layer (the repulsive force was detected at a separation of about 90 nm) which was not accompanied by any visible change in the thickness of the compressed layers. Moreover, when the polymer/surfactant mixture was drained from the box and replaced with pure water, the measured compression profile (not shown for clarity) lay slightly below the initial polymer compression curve. A looser attachment of the polymer to the surface and even its partial (however, not substantial) desorption are possibly responsible for the features observed at the highest $C_{12}E_5$ concentration studied. It is of note that even at high $C_{12}E_5$ concentrations, an attractive minimum, similar to that measured in the absence of surfactant, was observed (see the insert of Fig. 2). This implies that the bridging, which is the most plausible cause of the above minima, is not affected by the non-ionic surfactant.

In the next experiment the effect of a cationic surfactant (TTAB) on the interaction forces acting between Quatrisoft-covered mica surfaces was addressed. Figure 3 shows the results. At a surfactant concentration of $1.5 \cdot 10^{-3}$ M, i.e., about half the CMC ($3.5 \cdot 10^{-3}$ M), a substantial increase of the interaction range, relative to the surfactant-free case, was observed. The repulsive interaction sets in at a separation of 145 nm. The middle part of the force curve ($D = 30$–110 nm) appears to be linear on a semi-logarithmic scale, but its decay length of 28 nm is well above the value expected for electrostatic interaction at this ionic strength (7.9 nm). Thus, the measured force can be attributed to the compression of the adsorbed polymer layers. The fact that, at high applied loads, a separation which is close to that in the pure polymer case can be reached, implies that none of the factors determining the layer compressibility (the adsorbed amount of the polymer, the macromolecules stiffness, the intralayer electrostatic interactions) are appreciably affected by addition of TTAB. Thus, the observed increase in the force range is most probably due to formation of larger loops and tails than in the absence of surfactant.

A marked decrease in both the range and the magnitude of the repulsive interaction was observed when the TTAB concentration was increased to $6 \cdot 10^{-3}$ M. The decay length of the force again indicates a predominantly non-electrostatic origin to the interaction. Although the force onset occurs at a larger separation (c.a. 105 nm) than in the pure polymer case, the fact that the profiles cross over at high applied loads points unequivocally to a partial desorption of the polymer at this surfactant concentration. The sharp upturn in the force at separations below 20 nm is another remarkable feature of the interaction measured at $c_{\text{TTAB}} = 6 \cdot 10^{-3}$ M.

It is well established that cationic surfactants adsorbing onto mica form highly charged bilayers at bulk concentrations close to the CMC [9, 10]. The electrostatic repulsion between such bilayers superimposed on a relatively weak steric component may substantially enhance the repulsion at short surface separations. In order to verify this supposition, the solution was drained from the box and replaced with pure water so that the surfactant bulk concentration was decreased by factor of 100, i.e., down to $6 \cdot 10^{-5}$ M. The force profile measured after thermal equilibration shows that the long-range interaction (beyond 20 nm) remains essentially unchanged, meaning that both the polymer conformation and adsorbed amount were not altered by the dilution. This fact implies that the cationic surfactant does not adsorb on the polymer chains, since otherwise its desorption would have resulted in a decrease of the charge of the chains, and, consequently, have led to changes in their conformation (i.e., the range of interaction) and the layer compressibility (i.e., the force decay). At the same time, at short separations the system exhibits a qualitatively different behavior. Thus, the repulsive force was found to be markedly reduced and the surfaces jumped from a separation of about 7 nm into a deep adhesive minimum (the pull-off force $F/R = 170$ mN/m) located 2.7 nm out from water contact. This finding supports the idea that the interaction observed at separations below 20 nm in $6 \cdot 10^{-3}$ M TTAB solution is strongly influenced by repulsion between the surfactant bilayers formed on the mica surfaces. Indeed, according to [9], dilution leads to desorption of the second surfactant layer, reduction of the effective surface charge, and an inward shift of the plane of its origin. All of the above cause a decrease in both the range and the magnitude of the electrostatic interaction. This enables attraction to take over at short separations and the surfaces attain a contact characterized by a high adhesion value due to hydrophobic interaction between the surfactant layers. Note that both the contact separation and adhesion observed in our experiment are in good accord with those found for dodecyl ammonium chloride [10] and CTAB [9] layers. A strict comparison, however, is hardly justified since, in addition to surfactant, a certain amount of polymer is coadsorbed on the surfaces in our system.

Interpretation of the experimental observations has, so far, been based on analysis of qualitative features and on semiquantitative comparison of the thicknesses and compressibilities of adsorbed layers at different solution compositions. A lack of quantitative information regarding adsorption of both the polymer and surfactants at the interface renders the interpretation rather speculative and does not allow a clear understanding of the molecular mechanisms by which the surfactants influence properties of the polymer adsorbed layers. In the following section, we present the results of an ellipsometric study of the polymer/surfactant layers on a SiO_2 surface. We will show that these results provide the required complementary information.

Ellipsometric results

The adsorbed amount Γ is the quantity most commonly extracted from ellipsometric measurements. This is due to the fact that, unlike n_f and d_f, Γ is relatively insensitive to the model chosen for the substrate as well as to the small accidental errors in ellipsometric angle determination. A Γ value of (1.6 ± 0.2) mg/m^2 was obtained for Quatrisoft adsorption on different wafers. This value was not affected by the removal of polymer from the water phase (rinsing) which indicates a (quasi)irreversibility of the polycation adsorption

Table 1. Ellipsometrically measured values of adsorbed amount (Γ), average layer thickness (d_f) and mean refractive index (n_f) of Quatrisoft layer adsorbed onto SiO_2 surface from 34 ppm polymer solution in water and the effect of surfactants on characteristics of the layer. Surfactants were introduced into the system after completion of Quatrisoft adsorption

	At equilibrium:			After rinsing:		
	Γ, mg/m^2	d_f, nm	n_f	Γ, mg/m^2	d_f, nm	n_f
Quatrisoft	1.6	7	1.375	1.6	7	1.375
+ SDS	CMC = $8.3 \cdot 10^{-3}$ M					
$2 \cdot 10^{-5}$ M	2.5	14	1.369	2.1	10	1.374
$4 \cdot 10^{-5}$ M	4.0	36.5	1.359	2.8	23	1.361
$1 \cdot 10^{-4}$ M	2.8	25	1.359	2.3	17	1.363
$2 \cdot 10^{-4}$ M	2.1	15	1.363	1.9	12	1.366
$5 \cdot 10^{-4}$ M	1.8	13	1.363	1.7	8	1.374
$2 \cdot 10^{-3}$ M	1.8*	57	1.347	1.5	7.5	1.372
$9 \cdot 10^{-3}$ M	0.2*	62	1.343	–	–	–
+ $C_{12}E_5$	CMC = $6.5 \cdot 10^{-5}$ M					
$5 \cdot 10^{-5}$ M	1.7	7	1.379	1.6	7	1.375
$2 \cdot 10^{-4}$ M	2.5	7	1.396	1.6	7	1.375
$5 \cdot 10^{-4}$ M	3.2	11	1.386	1.6	7	1.375
$2 \cdot 10^{-3}$ M	3.8	19	1.373	1.6	7	1.375
10^{-2} M	3.9	23	1.368	1.3	6	1.376
+ TTAB	CMC = $3.5 \cdot 10^{-3}$ M					
$1.5 \cdot 10^{-3}$ M	1.7	8.5	1.373	1.3	5	1.382
$6 \cdot 10^{-3}$ M	1.7	7	1.380	0.7	3	1.377

on the SiO_2 surface. This feature will be recalled in the following discussion.

Besides Γ, meaningful values of the average thickness d_f and of the mean refractive index n_f of the adsorbed film can be obtained, provided optical parameters of the substrate are properly determined. The values of d_f and n_f are model dependent and those adduced in this paper are calculated under the assumption of layer uniformity. Since the adsorbed material is, in general, distributed in some way normal to the surface, the ellipsometric averaging yields some effective d_f and n_f values which must be interpreted with caution. For highly non-uniform layers the ellipsometrically measured thickness is expected to be substantially lower than that determined via, for example, dynamic light scattering, viscosity or force measurements, i.e., by measurements of the properties sensitive to the maximal extent of the surface layer. In other words, ellipsometry "sees" the most dense part of it. Thus, for Quatrisoft on silica we measured $d_f = (7 \pm 1)$ nm, which is much lower than the layer thickness corresponding to the force onset in the SFA (c.a. 30 nm). This implies a high degree of non-uniformity of the Quatrisoft layer but does not necessarily mean poor consistency between the two results.

In Table 1, we present a summary of experimental results, illustrating the effect of addition of different surfactants on the Quatrisoft adlayer characteristics. All the values in the table refer to the plateau region and in all cases surfactants were introduced into the system after completion of the Quatrisoft adsorption. The time required to reach the plateau values ranged between 2 and 20 h depending on the system composition. The kinetics will be discussed when informative, otherwise they are beyond the scope of this study.

As can be seen from the table, in the case of SDS the adsorbed amount is a nonmonotonic function of surfactant concentration with a maximum at around $c_{SDS} = 4 \cdot 10^{-5}$ M. Up to about the CMC, Γ values exceed the one measured in the absence of SDS, which means that upon addition of surfactant more material is brought into the interfacial region. This can be SDS alone or in combination with the polymer. The fact that Γ is maximal at rather low surfactant concentrations is strong evidence that at low c_{SDS} the supplementary adsorption is dominated by the polymer.

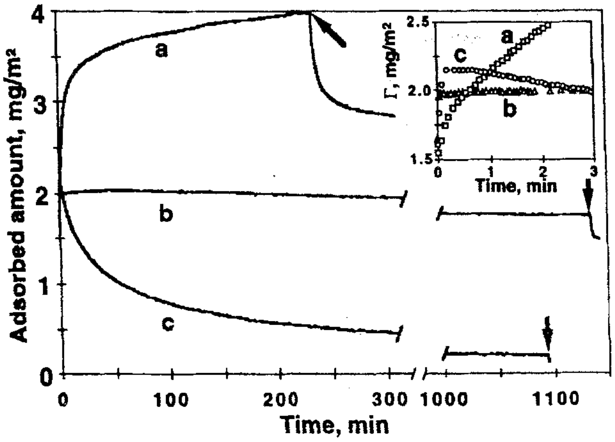

Fig. 4. Adsorbed amount vs. time dependencies measured ellipsometrically after addition (at $t = 0$) of $4 \cdot 10^{-5}$ M (curve a), $2 \cdot 10^{-3}$ M (curve b) and $9 \cdot 10^{-3}$ M (curve c) SDS to the system with a preadsorbed Quatrisoft layer ($\Gamma = 1.6$ mg/m^2). The arrows indicate the beginning of rinsing. The insert shows the changes over the first minutes in more detail

An analysis of the system behavior upon rinsing gives further support to this idea. Indeed, rinsing after addition of $2 \cdot 10^{-3}$ M SDS returns the system to its initial state, whereas at low surfactant levels, only partial removal of supplementary adsorbed material was observed. Taking into account the relative irreversibility of the polymer binding to the surface, this finding reveals that in the former case the increase in Γ upon surfactant addition is due to a reversible surfactant binding to the polymer, while in the latter one a substantial extra amount of polymer is adsorbed. The peculiarities of the kinetics of the changes induced by surfactant addition and its removal also support the above conclusion. This is illustrated in Fig. 4 which shows some examples of Γ vs. t dependencies obtained for Quatrisoft/SDS systems. Thus, at low c_{SDS}, 2–4 h were required to reach the Γ plateau after SDS addition, and about 1 h upon rinsing, while at $c_{\mathrm{SDS}} \geq 2 \cdot 10^{-3}$ M fast (within 1–2 min) changes in Γ were observed both upon surfactant addition and removal. This difference reflects a substantially longer time scale for the processes involving macromolecules. As a consequence, two clearly different regimes in Γ vs. t behavior have been observed in the case of $9 \cdot 10^{-3}$ M SDS addition. Specifically, a rapid initial increase in Γ, corresponding to the surfactant binding, is followed by a relatively slow Γ decline which can be attributed to desorption of the polymer/surfactant complex. Finally, we note that at both low and high SDS concentrations, addition of the surfactant leads to an increase in the ellipsometrically measured adlayer thickness (see Table 1), which may be due to the layer expansion and/or to the change in the density profile towards higher uniformity.

The effect of addition of nonionic surfactant on the structure and composition of the adsorbed Quatrisoft layer was clearly different. Starting from a surfactant concentration somewhat below the CMC, the adsorbed amount rises gradually and reaches saturation at $c_{\mathrm{C_{12}E_5}} \approx 10^{-3}$ M. It is notable that over this concentration range, rinsing led to a rapid decrease in Γ down to the pure polymer level. This feature, together with the observed rapid (minutes) attainment of the plateau values, clearly shows that at these $C_{12}E_5$ concentrations only the surfactant is involved in the adsorption process. For $c_{\mathrm{C_{12}E_5}} \geq 5 \cdot 10^{-3}$ M we observed a rather slow (within 1 h) decay of the initially reached Γ down to its (pseudo) equilibrium level, and the adsorption-rinsing cycle resulted in a somewhat decreased level of the adsorbed amount. These two facts indicate that, upon addition of such high $C_{12}E_5$ concentrations (two orders of magnitude above the CMC), surfactant adsorption is accompanied by detectable desorption of Quatrisoft.

Figure 5 shows how a progressive addition of the nonionic surfactant affects ellipsometric characteristics of the adsorbed layer. An analysis of the changes in ellipsometric thickness and refractivity, accompanying the adsorption process, can tell us how the adsorbed surfactant is distributed within the polymer layer. Indeed, up to about $5 \cdot 10^{-4}$ M $C_{12}E_5$ the average layer thickness remains constant, while the mean refractivity increases. This means that, although the overall density of the layer increases, its profile remains unperturbed. In other words, the surfactant adsorption does not affect the polymer conformation and its distribution replicates that of the polymer, i.e., surfactant binds uniformly or randomly along the polymer chains. At higher surfactant uptakes, a reorganization of the adsorbed layer takes place. Simultaneous increase in d_f and decrease in n_f for $c_{\mathrm{C_{12}E_5}} \geq 5 \cdot 10^{-4}$ M indicates a change of the density distribution within the adlayer towards higher uniformity. This can be

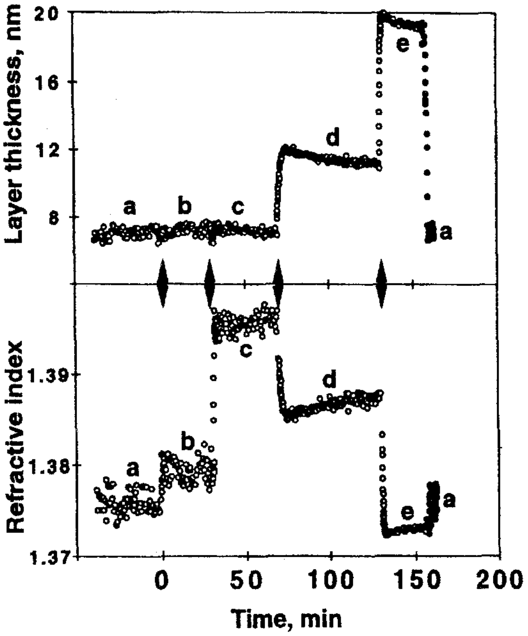

Fig. 5. The changes in ellipsometric characteristics of the Quatrisoft/surfactant layer on silica upon addition of different amounts of $C_{12}E_5$: a – none, b – $5\cdot10^{-5}$ M, c – $2\cdot10^{-4}$ M, d – $5\cdot10^{-4}$ M, e – $2\cdot10^{-3}$ M. Surfactant concentration was changed at the time moments indicated on the *t*-axis by arrows. The effect of rinsing is shown by filled points

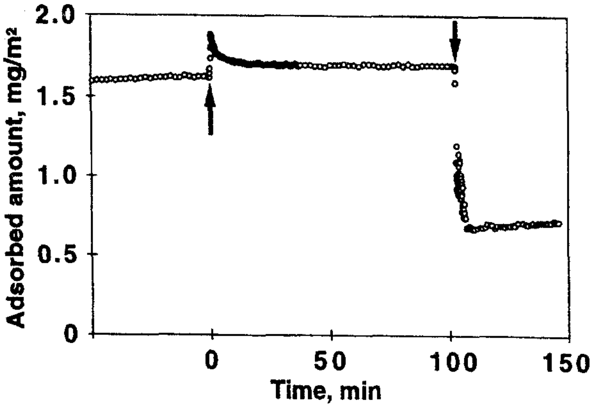

Fig. 6. The changes in ellipsometrically measured adsorbed amount upon addition of $6\cdot10^{-3}$ M TTAB (after completion of Quatrisoft adsorption) and the effect of the subsequent rinsing. The upward arrow shows the moment of surfactant injection and the downward arrow – the beginning of rinsing

due to the tendency to avoid excessive steric hindrance in the inner part of the polymer/surfactant layer. Stretching of the polymer loops and formation of bigger surfactant clusters preferentially in the outer part of the polymer layer, where the segments' density is lower, can both be considered as possible explanations for the observed changes in the optical characteristics.

In the case of cationic surfactant (TTAB) peculiar changes in the ellipsometrically measured characteristics of the adsorbed Quatrisoft layer were observed in the vicinity of the surfactant's CMC ($3.5\cdot10^{-3}$ M). Although the plateau values of Γ in the presence of surfactant are close to those measured before its addition, the change in Γ observed upon rinsing reveals that both adsorption of the surfactant in the interfacial region and desorption of the polymer take place. The details of the process kinetics, presented in Fig. 6 for $c_{\mathrm{TTAB}} = 6\cdot10^{-3}$ M, support this conclusion. Indeed, a rapid initial increase in Γ can be attributed to the surfactant adsorption which is then overcome by the polymer desorption. The subsequent rinsing leads to a quick removal of the adsorbed surfactant.

Interpretation of the optical thickness and the refractive index of Quatrisoft/TTAB layers is not straightforward. At first sight, these characteristics appear to be essentially unaffected by the surfactant addition, implying no change in the layer structure. But, as in the case of Γ, this conclusion is rather misleading. One can speculate that simultaneous desorption of the polymer and adsorption of TTAB on the remaining polymer chains does not affect the macromolecular conformation and results in the same density profile as in the absence of surfactant. But this is clearly inconsistent with our SFA findings and even with common sense: the charging up of the polymer chains (due to the ionic surfactant binding) and their looser attachment to the surface must lead to changes in polymer conformation. Indeed, SDS adsorption on Quatrisoft chains at $c_{\mathrm{SDS}} = 2\cdot10^{-3}$ M results in dramatic changes in both d_f and n_f (see Table 1). To all appearances, in the case of TTAB, the surfactant adsorption at the surface tends to decrease the average d_f and increase n_f, while both partial and complete desorption of polymer chains affects the characteristics in the opposite sense. The balance between the two tendencies will determine the overall ellipsometric characteristics. To refine quantitative interpretation of ellipsometric results in such a case, one should use a five-layer optical model with an additional layer corresponding to surfactant adsorbed at the surface.

Discussion

An essential background to a discussion of the interfacial behavior of polymer–surfactant mixtures is an understanding of both their behavior in bulk under different mixing ratios and their individual interaction with a surface. The properties of the individual components comprising the system under study and the general features of their pairwise interaction are rather well understood and we will refer to the acquired knowledge throughout the following discussion.

The cationic polymer (Quatrisoft), as expected, adsorbs readily on negatively charged surfaces. Like other low charged polyelectrolytes (see e.g. [11]) it adopts a rather extended conformation at the interface. The state of the adsorbed layer is, in addition to steric and entropic factors, dictated by a balance between the expansion resulting from electrostatic repulsion and contraction due to inter- and intralayer hydrophobic coupling. Strong multipoint attachment of the polycation to the surface renders the adsorption (quasi)irreversible. Indeed, no appreciable desorption was detected upon removal of the polymer from the bulk phase (rinsing) in the case of pure polymer adsorption. This effective irreversibility kinetically stabilizes (on the experimental time scale) even systems which are far away from thermodynamic equilibrium. This has to be taken into account in the interpretation of experimental results. In general, the kinetics are expected to be very different for polymer and surfactant adsorption/desorption processes so that time-resolved studies are helpful in identifying mechanisms. This was utilized in monitoring both the rate of adsorption and the effect of rinsing. The main goal of the present study has been to elucidate molecular mechanisms by which hydrophobically modified polycations and different surfactants mutually affect their interfacial behavior.

Both ionic surfactants studied are strongly hydrophilic and because of the electrostatic effects, their self-assembly into micelles is relatively unfavorable, leading to high CMCs in water. It is known, however, that in the presence of HM polymers the micelle formation occurs at much lower concentrations and surfactant self-assembly becomes less cooperative; the micelles can in this case be quite small [12]. In the case of HM polyelectrolyte the interaction will be much stronger for an oppositely charged surfactant and relatively weak for a like-charged one.

The anionic surfactant (SDS) does not adsorb on negatively charged surfaces and therefore its interaction with a polycation can only be responsible for changes in the adsorbed layer structure and composition. At low SDS concentrations the surfactant addition causes an increase in polyelectrolyte adsorption, compared to the surfactant-free case. This additional adsorption vanishes at a c_{SDS} of about one-tenth of the CMC, which means that at this surfactant concentration the solution state of the surfactant/polymer complex becomes more energetically favorable. This correlates well with the corresponding bulk behavior of such polymer/surfactant mixtures. Indeed, in bulk solution a strong attraction between oppositely charged polymer and surfactant typically leads to an associative type of phase separation with a two-phase region followed by a homogeneous solution phase formed at higher surfactant concentrations [13]. In our case the two-phase region corresponds, to all appearances, to the range of SDS concentrations where the surfactant-induced supplementary adsorption of the polymer was detected and where the adsorbed layers show high mutual affinity as revealed by the surface force measurements (a deep attractive minimum on separation).

At higher SDS concentrations ($> 10^{-3}$ M) progressive binding of surfactant molecules to the polymer results in expansion of the preadsorbed Quatrisoft layer due to the intralayer electrostatic repulsion. At the same time, the polymer/surfactant complex not only looses its ability to adsorb on the bare silica surface (adsorption from Quatrisoft/$2 \cdot 10^{-3}$ M SDS premixture results in $\Gamma = 0.2$ mg/m^2), but exhibits an increasing tendency to leave the surface. Thus, at $c_{SDS} = 2 \cdot 10^{-3}$ M only very slow Γ decline was observed (c.a. 0.01 mgm^{-2}/h), whereas at $9 \cdot 10^{-3}$ M, i.e., just above the bulk CMC, almost complete desorption of the highly charged polymer/surfactant complex occurs within 20 h.

In contrast to anionics, cationic surfactants are known to adsorb on negative surfaces in a form (individual molecules, hemimicelles, bilayers, etc.)

which depends on conditions such as surfactant nature and bulk concentration, surface charge density, and electrolyte concentration. It is recognized that for relatively long-chained (C_{12}–C_{16}) cationics, bilayer formation takes place at bulk concentrations of about 0.6–0.7 CMC [9, 10, 14], unless the surface charge density is too low. On the other hand, their association with hydrophobically-modified like-charged polymers is also feasible, provided the hydrophobic interactions are strong enough to overcome the opposing electrostatics. Although the effects are an order of magnitude weaker and observed at higher degrees of hydrophobic modification than for a pair of oppositely charged cosolutes [1], substantial viscosity increases, attributed to the interchain micellar cross-linking, were observed even for highly charged HM (3 mol % of C_{18} side groups) poly(acrylate), interacting with similarly charged surfactant (SDS) [15]. However, one should bear in mind the (generally found) lower tendency of cationics to self-assembly in polymer solutions, compared to anionic surfactants [16], and a strong dependence of the association on the hydrophobe's chain length [1].

In the present work no evidence of TTAB self-assembly on the polymer C_{12} side chains was obtained. This finding is in agreement with the absence of any visible effect of TTAB on Quatrisoft phase behavior as reported recently by Goddard and Leung [17]. At the same time, competitive adsorption of the cationic surfactant on the negative surfaces has a pronounced effect on Quatrisoft adsorbed layers. TTAB adsorption at the interface leads to a partial displacement of the adsorbed polymer and to its looser attachment to the surface. As a consequence, expansion of the adsorbed layers and their higher compressibility were revealed by surface force measurements. The absence of attraction upon surface separation in SFA experiments is in line with the above picture since the surfactant adsorption at the interface can be expected to prevent or inhibit bridge formation to a large extent. The presence of the species (TTAB molecules), competing for the surface sites, also markedly affects the kinetics of the polymer exchange with bulk solution. Thus, the same equilibrium state can be attained relatively quickly, within 30 min, independent of the way the components are added (simultaneous or consecutive). This is clearly different from the situation encountered in Quatrisoft/SDS systems, where the polymer desorption remains relatively slow even at $c_{SDS} > \mathrm{CMC}$, i.e., under conditions where the tendency of the polymer/surfactant complex to leave the interface is maximal.

Nonionic surfactants typically exhibit a strong tendency towards association at rather low concentration both in bulk [18] and at interfaces [3, 19, 20] and show cooperative self-assembly on hydrophobic groups of HM polymers [12, 21]. These features are expected to determine their effect on adsorbed layers of HM polyelectrolytes. Moreover, the surfactant chosen for the present study, $C_{12}E_5$, has a strong tendency for micellar growth with concentration [22] and this can also affect its interfacial behavior.

Our experiments show that $C_{12}E_5$ adsorbs on Quatrisoft chains starting at a concentration somewhat below the CMC, but shows no sign of adsorption on the silica surface in the presence of the polymer. This finding is in line with the observed displacement of $C_{12}E_5$ adsorbed layers by a number of cosolutes, including nonionic polymers [23], and reflects low affinity of the surfactant to the surface. At the same time, as the total $C_{12}E_5$ concentration in the system increases, the amphiphile adsorption within the polymer layer gradually approaches the saturation level, which is reached at $c_{C_{12}E_5} \approx 10^{-3}$ M. Formation of micelles on the polymer side chains at $c_{C_{12}E_5} \leq 5 \cdot 10^{-4}$ M has no effect on polymer's conformation as evidenced by both ellipsometry and force measurements (neither d_f nor the force onset distance is affected). At higher adsorbed amounts of surfactant, corresponding to the range of concentrations $5 \cdot 10^{-4}\ \mathrm{M} \leq c_{C_{12}E_5} \leq 5 \cdot 10^{-3}$ M, an increase in ellipsometrically measured layer thickness without change in the total layer extent (by SFA) can be interpreted as a consequence of an increased steric hindrance in the inner part of the adsorbed layer which causes stretching of the polymer loops and/or preferential attachment of micelles in the outer part of the layer. The surfactant binding is not accompanied by any desorption of the polymer. Moreover, adsorption from premixture shows that, even being saturated with surfactant, the Quatrisoft/$C_{12}E_5$ complex retains its ability to adsorb on the surface. However, the kinetics of adsorption is markedly slower in this case, resulting from packing problems upon adsorption. At the highest studied surfactant concentrations ($5 \cdot 10^{-3}$ M $\leq c_{C_{12}E_5} \leq 2 \cdot 10^{-2}$ M) the steric constraints within the layer, being possibly augmented by micellar growth, lead to a partial, although not substantial, desorption of the polymer and formation of longer tails which shows itself in a somewhat increased interaction range, as can be seen in Fig. 2.

Conclusion

The cationic HM polymer Quatrisoft shows a wide variety of interfacial behavior in the presence of different surfactants depending on their charge and concentration. The state of the adsorbed polymer/surfactant layer, i.e., its composition and material distribution (including conformation of macromolecules) is determined by the relative strength of pairwise interactions between the surface, polymer and surfactant. Summarizing the main findings of the present study, we can state:

1) Anionic surfactant (SDS), although not adsorbing on the surface, interacts strongly with the oppositely charged polymer and associates to hydrophobe groups on the polymer. This results, depending on surfactant concentration and, consequently, on its degree of binding, in the diversity of the effects observed. These include the enhanced polymer adsorption at low SDS concentrations, the electrostatic swelling of the adsorbed layer at intermediate ones and, finally, the desorption of the polymer/surfactant complex at $c_{SDS} \approx$ CMC. It is notable that, over a certain concentration range the polymer/surfactant interfacial behavior follows the phase separation – redissolution pattern characteristic for bulk systems.

2) Cationic surfactant (TTAB), on the contrary, does not associate with the polymer, but does adsorb on the surface. Its competition with the polycation for the surface sites leads to a partial displacement of the polymer and to its looser attachment to the surface. All this affects the extent and compressibility of the adsorbed layers.

3) Nonionic surfactant ($C_{12}E_5$) exhibits cooperative self-assembly on the hydrophobic side chains of the polymer. As the surfactant uptake by the polymer layer increases, the tendency to avoid an excessive steric hindrance in the inner part of the adsorbed layer causes certain conformational changes within the layer towards higher uniformity of material distribution and, eventually, even a minor desorption of macromolecules. On the other hand, the surfactant affinity to the surface appears to be too low to compete with the polyelectrolyte at the surface and no adsorption of $C_{12}E_5$ on silica was observed in the presence of Quatrisoft.

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