

Effect of Sodium Dodecyl Sulfate on Adsorbed Layers of Branched Polyethylene Imine

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The effect of an anionic surfactant, sodium dodecyl sulfate, SDS, on the properties of adsorbed layers of a cationic highly branched polyelectrolyte, polyethylene imine, PEI, has been investigated using surface force measurements, atomic force microscopy, and ESCA. The strategy used was to preadsorb PEI on negatively charged muscovite mica surfaces from a 20 ppm polyelectrolyte solution in 10 mM NaCl. The adsorption of PEI under these conditions gives rise to a strong recharging of the surface, i.e. after adsorption of PEI the surface carries a net positive charge. This conclusion was supported by ESCA measurements. Despite the high molecular weight of PEI (1.8×10^5 g/mol), the adsorbed layer is found to be very flat, and a repulsive double-layer force dominates at large separations. At smaller separation a strong attractive force is the main feature. Addition of SDS to a concentration of 0.01 cmc results in a nearly complete removal of the double-layer force, an increase in compressed layer thickness, and an increase in the magnitude of the adhesion force. Hence, significant SDS incorporation in the adsorbed layer occurs already at this low surfactant concentration. A recharging of the layer occurs at higher surfactant concentrations. At 0.5 cmc, the compressed thickness of the adsorbed layer is increased significantly and the adhesion between the surfaces has disappeared. We argue that each layer now is coated with an outer SDS layer oriented with the polar groups toward solution. In fact, there are striking similarities between the interfacial association between SDS and PEI and the adsorption of an ionic surfactant to an oppositely charged mineral surface. AFM imaging reveals that the adsorbed PEI layer is somewhat nonhomogeneous and contains polyelectrolyte patches. These surface features are smoothed out by addition of SDS to a concentration of 6 mM (1 cmc in 10 mM NaCl). ESCA measurements showed that exposure of the preadsorbed PEI layer to SDS concentrations around the cmc resulted in a limited desorption; about 15% of the initially adsorbed polyelectrolyte was removed after 16 h.

Introduction

Polyethyleneimine (PEI) is a polyamine with a highly branched structure.¹ The PEI-based polyelectrolytes are widely used as adhesives, dispersion stabilizers, thickeners, and flocculating agents. In these applications the function of PEI is largely determined by its interfacial properties. The adsorption of PEI on oppositely charged surfaces depends on parameters including pH and ionic strength, which can significantly change the charge density of the polymer and the surface. However, the nonelectrostatic surface affinity and the solvent quality are also of great importance. Furthermore, the branched structure and the peculiar charging properties of PEI makes the surface properties of this type of polyelectrolyte even more complex.

The interfacial properties of PEI on muscovite mica and silica surfaces have previously been investigated.^{2–4} At low pH the adsorbed PEI layer was found to be flat, whereas at high pH a more extended adsorbed layer and larger adsorbed amount was found. Notably, a strong overcompensation of the surface charge due to the adsorption of PEI was observed.

Studies on the interaction of polyethyleneimine with sodium dodecyl sulfate in aqueous solution have shown peculiar changes

in the conductivity and pH^{5,6} and revealed interesting aggregation behavior.⁷ A pH increase in moderately alkaline PEI solutions with increasing added surfactant concentration has been observed and shown to be due to the charge density regulation of PEI due to noncooperative surfactant binding.⁸

The binding of SDS to preadsorbed layers of PEI on silica has recently been investigated by ellipsometry.⁹ The adsorption of the dodecyl sulfate ions to the preadsorbed PEI layer was found to be consistent with the noncooperative binding mechanism of SDS to PEI in the bulk solution.³

Various surface force techniques have been used rather extensively during the past years for investigating association between anionic surfactants and cationic polyelectrolytes on negatively charged surfaces. When comparing these studies one has to distinguish between three cases that give vastly different results: (i) the polyelectrolyte and surfactant is first allowed to associate in bulk, and then the complex is allowed to adsorb to the surface;^{10–12} (ii) the polyelectrolyte is first allowed to adsorb in absence of surfactant, and then the surfactant is added to the solution that contains polyelectrolyte;¹³ (iii) the polyelectrolyte is preadsorbed on to the surface, and then the surfactant is added to the polyelectrolyte-free solution in contact with the polyelectrolyte-coated surface. The studies using preadsorbed polyelectrolyte layers have emphasized the effect of the polyelectrolyte charge density and surfactant concentration. For low charge density polyelectrolytes a progressive desorption with increasing surfactant concentration is found.¹⁴ For moderately

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charged polyelectrolytes strong swelling of the preadsorbed polyelectrolyte layer is the most noticeable feature,^{15,16} whereas structured polyelectrolyte–surfactant complexes have been found to form on the surface for one highly charged polyelectrolyte.¹⁷

In this investigation we use the surface force technique with the focus on the association between anionic surfactant and the highly branched polyethylene imine preadsorbed to negatively charged surfaces. This is the first time a branched polyelectrolyte is used in such a study and, as will be shown, the branched architecture of the polyelectrolyte has significant impact on the association process at the surface. The objectives of this work are thus to elucidate the association between preadsorbed PEI and SDS on a negatively charged surface and to explore the changes in surface interaction and layer structure due to surfactant addition. The polyelectrolyte alone adsorbs strongly to the surface, whereas the surfactant is nonadsorbing. The surface is thus selective for the polyelectrolyte. The pH was chosen to be 5.7. At this pH approximately 60–70% of the amine groups are protonated.³ Hence, PEI is highly charged. By comparison with results obtained with other highly charged linear polyelectrolytes, the effect of branching, as in PEI, can be evaluated. The surface force technique provides information on the surface interactions as a function of separation as well as the adsorbed layer thickness. Another method of choice was atomic force microscopy that provided information on the organization of the adsorbed layer at the surface (patch-wise or homogeneous). Finally, ESCA measurements were performed to evaluate the adsorbed amount of PEI and the eventual desorption of the polyelectrolyte due to exposure to SDS solutions.

Experimental Section

The polyethylene imine (PEI) produced by BASF AG used in this study has a molecular weight of 1.8×10^5 g/mol (obtained by static light scattering). It was supplied by Larodan Fine Chemical AB in the form of a 30 wt % aqueous solution. The pH of the PEI solution was adjusted to ca. 5.7 (at 23 °C) by addition of HCl. The PEI is a hyperbranched polyelectrolyte. The charges arise from primary, secondary, and tertiary amine groups in the ratio 1:2:1. A typical structural element is shown in Figure 1.

The anionic surfactant sodium dodecyl sulfate (SDS), with > 99% purity, was obtained from BDH and used without further purification. The sodium chloride, with >99.5% purity, was obtained from Merck and used as received. The water used was first pretreated with a Milli-RO 10 Plus system and further purified with a Milli-Q PLUS 185 system. When used in the surface force apparatus, it was deaerated for at least 1 h using a water jet pump. All glassware was cleaned by Hellmanex solutions for 24 h. It was then rinsed with purified water and finally blow-dried with nitrogen gas.

Turbidity Measurements. The turbidity of mixed polyelectrolyte–surfactant solutions was determined employing a HACH Ratio Turbidimeter. In these measurements the surfactant stock solution prepared in 10 mM NaCl was first diluted with 10 mM NaCl to the appropriate concentration. After this a small amount (0.5 mL) of polyelectrolyte in 10 mM NaCl was rapidly added from a 1000 ppm stock solution at pH 5.7. The final polyelectrolyte concentration was 20 ppm in each sample. The mixtures of PEI–SDS were blended by carefully turning the beakers up and down several times, avoiding bubble formation.

Electrophoretic Mobility Measurements. The electrophoretic mobility of complexes formed between PEI and SDS

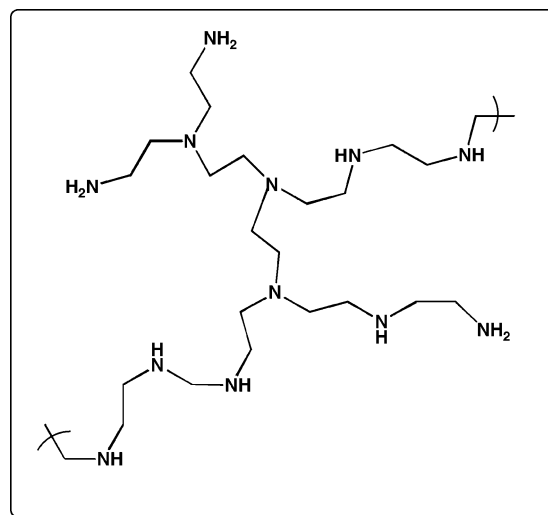


Figure 1. Typical structural element of a hyperbranched PEI with the primary, secondary, and tertiary amine group ratio 1:2:1. The degree of protonation at pH 5.7 is 60–70%.

was measured using a Zetasizer 2000, Malvern Instruments England, employing the standard electrophoresis cell ZET5104. The instrument was calibrated using Malvern Zeta Potential Transfer Standard (code MRK403-02) prior to use.

ESCA. The adsorbed amount of PEI on mica surfaces was determined by means of a Kratos AXIS-HS X-ray photoelectron spectrometer (ESCA also called XPS) equipped with a hemispherical analyzer. Photoelectron emission was induced by non-monochromatic X-rays (Al K α , 1486.6 eV) emitted from a dual anode. Electrostatic lenses were used to collect the photoelectrons that were emitted normal to the surface plane. The quantification was carried out as described previously¹⁸ using the sensitivity factors for K2p and N1s provided by Kratos. The samples used for XPS analysis were prepared in the following way. Freshly cleaved mica pieces were immersed in 10-mL beakers containing 20 ppm PEI and 10 mM NaCl for 40 min. Next the beakers with the surfaces were immersed in 2.5 L of 10 mM NaCl and withdrawn from this solution. The effect of SDS on the adsorbed PEI layer was tested by immersing the PEI-coated surfaces in 10-mL beakers containing 10 mM NaCl and SDS at different concentrations. This desorption step was allowed to proceed for 1 h, except for the 2 cmc SDS sample that was soaked in SDS for 16 h, before the beakers were immersed in 2.5 L of water for 10 min. The surfaces were withdrawn from water and dried by a nitrogen jet. All surface preparation steps were carried out inside a dust-free laminar flow cabinet.

Surface Force Measurements. The forces acting between muscovite mica surfaces coated with polyelectrolyte or polyelectrolyte–surfactant aggregates were studied with a surface force apparatus, SFA, using the Mark IV¹⁹ model. The technique is described in detail in refs 20 and 21. The results of the surface force measurements are plotted as force normalized by the geometric mean radius, F/R , as a function of surface separation, D . The distance resolution is about 2 Å, and the F/R detection limit about 1×10^{-5} N/m. We note that the force normalized by radius for the crossed cylinder geometry used in the experiments is related to the free energy of interaction per unit area (G_f) between flat surfaces ($F/R = 2\pi G_f$). This relation is valid when the radius of the surfaces (~ 2 cm in our experimental setup) is much larger than the range of the measured forces, and when the surfaces do not deform. The force measuring

system is unstable once the slope of the force, dF/dD , exceeds the spring constant. When this occurs, a “jump” to the next mechanically stable region of the force curve takes place.

Some measurements were carried out by placing a 60- μ L droplet of an aqueous solution containing 20 ppm PEI and 10 mM NaCl between the surfaces. In other cases the surfaces were immersed in an aqueous 10 mM NaCl and 20 ppm PEI solution outside the surface force apparatus for 30 min and then rinsed in polyelectrolyte-free 10 mM NaCl for 10 min. The surfaces were then immediately mounted in the surface force apparatus that was filled directly with 10 mM NaCl. The pH of the solutions was 5.7.

Atomic Force Microscopy. The principles of atomic force microscopy (AFM) have been described in detail by Binnig et al.²² In our study we used a Nanoscope III, Digital Instruments, Santa Barbara CA. In brief, a very sharp tip, attached on a weak cantilever spring is scanned across the surface. When no force is acting between the tip and the surface, the cantilever remains undeflected. When the tip and the surface are in close proximity to each other, a force acts on the tip, thus forcing the cantilever to deflect. A laser beam is shone on the backside of the cantilever and reflected to a split photodiode that is employed to detect the bending of the spring. The AFM images of polyethylene imine or polyethylene imine–SDS adsorption layers on a mica surface were obtained in contact mode in the liquid, using silicone cantilevers CSC21/Cr-Au/50 (Ultrasharp Cantilevers & Gratings, Russia). We used cantilevers with typical spring constants of 0.12 N/m. In the contact mode the tip is moved across the surface in a raster pattern. At the same time the sample height is regulated in response to the force acting between the sample and the tip. With perfectly selected gains the deflection of the tip is kept constant, and a true topographical height image is obtained (ignoring tip broadening effects). We used a dual screen mode and captured both height and deflection data simultaneously. The height image maps the sample vertical position, whereas the deflection image maps the tip deflection. Both images contain information about the surface features. The adsorbed layers were imaged using a very weak force. The force acting between the sample and the tip during imaging was due to the electrostatic double-layer repulsion. Hence, there was no direct contact between the tip and the sample, which minimized the risk of damaging the adsorbed layers while dragging the tip over the surface. The images were obtained at a scanning speed of 5 Hz. The fluid cell is made of glass and constructed so that it can be sealed with the help of a rubber ring positioned in a groove. Thus, a small liquid volume (0.1 mL) can be injected into the cell, and if needed, the liquid can be easily exchanged. The adsorption of polyethylene imine was accomplished simply by introducing a 20 ppm aqueous solution in 10 mM NaCl into the fluid cell and allowing the tip and the freshly cleaved substrate, mica, to equilibrate with this solution for 30 min. After this the polyelectrolyte solution was replaced by a polyelectrolyte-free 10 mM NaCl solution, and then the adsorbed layer was imaged. The images in the presence of SDS were obtained after subsequently introducing the appropriate SDS concentration, 1 cmc in 10mM NaCl, into the measuring cell.

Calculated Force Curves. Force curves were calculated in the DLVO framework. The double-layer force was calculated using the nonlinear Poisson–Boltzmann approximation and the known ionic strength of the solution. The double-layer potential was used as a fitting parameter. It will be referred to as the apparent double-layer potential in recognition of the approximate nature of the Poisson–Boltzmann theory. The van der Waals

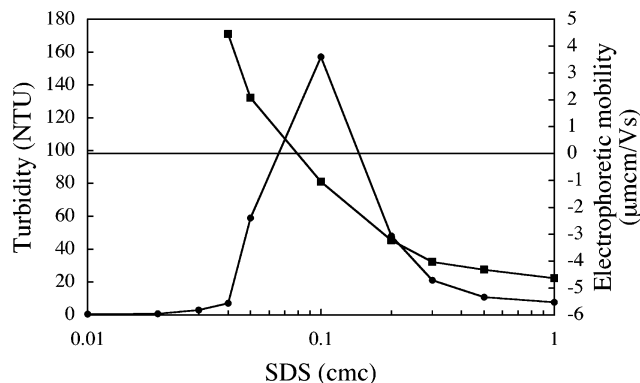


Figure 2. Turbidity of a 20 ppm PEI solution in 10 mM NaCl containing various amounts of SDS immediately after mixing (●). Electrophoretic mobility of the complexes formed in the turbid solutions (■).

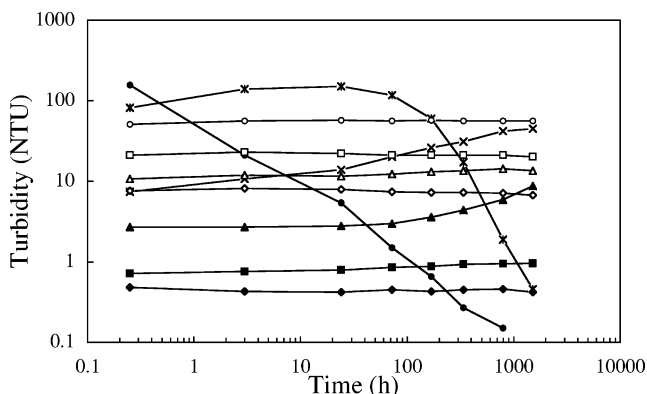


Figure 3. Evolution of turbidity of PEI–SDS mixtures in time. The PEI concentration was fixed at 20 ppm. The SDS concentrations are 0.01 (◆), 0.02 (■), 0.03 (▲), 0.04 (×), 0.05 (*), 0.1 (●), 0.2 (○), 0.3 (□), 0.5 (Δ), 1 (◇) cmc SDS.

force was calculated using a nonretarded Hamaker constant of 2×10^{-20} (J). Both the double-layer force and the van der Waals force were assumed to originate from the position of the compressed adsorbed layer.

Results

Turbidity. To get a rough idea of the association between PEI and SDS in bulk solution, the turbidity of the polyelectrolyte–surfactant mixture was determined as a function of SDS concentration. The PEI concentration in 10 mM NaCl was fixed to 20 ppm, and the pH was around 5.7. We note that 1 cmc SDS in 10 mM NaCl is 6 mM.²³ The results obtained immediately after mixing the solutions are shown in Figure 2.

The turbidity is low at concentrations below 0.02 cmc SDS. It reaches a maximum between 0.05 and 0.1 cmc and decreases again at higher SDS concentrations. We note that at low SDS concentrations and below 0.05 cmc the mobility of the complexes formed is positive, i.e. the complexes contain an excess of PEI. At SDS concentrations at and above 0.1 cmc the mobility is negative, demonstrating that the complexes formed contains excess SDS. The general features reported in Figure 2 are similar to these reported for other cationic polyelectrolyte–SDS complexes.¹¹ When the turbidity is measured as a function of time, see Figure 3, we notice that stable values are obtained up to an SDS concentration of 0.02 cmc. At 0.03 and 0.04 cmc SDS a slow increase in turbidity with time is noticed, indicating slow flocculation and growth of the aggregates. At the SDS concentration of 0.05 cmc the turbidity first increases and then decreases with time, whereas at 0.1 cmc

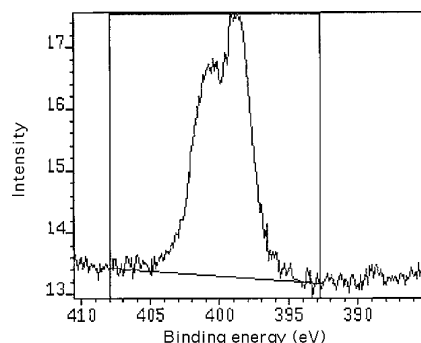


Figure 4. A typical ESCA detail spectrum of the N1s peak. This particular spectrum was obtained for a preadsorbed PEI layer that was not exposed to SDS.

TABLE 1: Total Amount of Nitrogen Atoms and the Percentage of Charged Nitrogen Atoms in PEI Layers on Mica after Exposure to 10 mM NaCl Containing Different SDS Concentrations

SDS (cmc)	number N atoms/cm ² * 10 ⁻¹⁴	charged N (%)
0	7.5	46
0.01	7.2	54
0.1	6.8	57
0.5	6.2	57
2	6.5	67

SDS the turbidity decreases significantly with time due to sedimentation. At higher SDS concentrations stable turbidity values are observed, indicating the formation of colloiddally stable complexes. There is thus a clear correlation between a high electrophoretic mobility and stable turbidity values, which emphasizes the importance of electrostatic double-layer forces for the stability of the complexes formed. Similar results have previously been reported under slightly different conditions.⁸

ESCA. A typical ESCA spectrum for the N1s peak emanating from the adsorbed polyelectrolyte is shown in Figure 4.

The peak is clearly a doublet, where the peak at higher binding energies corresponds to charged ammonium groups and the one at lower binding energies corresponds to that of uncharged amine groups. By curve fitting the relative amounts of charged and uncharged nitrogen in the layer can be evaluated. The results are shown in Table 1.

Clearly, the fraction of charged nitrogen increases with SDS concentration from 46% in the absence of SDS to 67% after exposure to a 2 cmc SDS solution. We note that the number of nitrogen atoms and also the number of charged ammonium groups greatly exceed the mica lattice charge ($2.1 \times 10^{14} \text{ cm}^{-2}$), demonstrating that adsorption of PEI results in charge reversal. This result is strikingly different from what is found for adsorption of linear polyelectrolytes on mica where the number of polyelectrolyte charges in the adsorbed layer most often is found to be equal or less to the mica lattice charge.¹⁸ We also note that the ESCA analysis was carried out in high vacuum, which means that the substrate with its adsorbed polyelectrolyte and other associated ionic species has to be electroneutral. Hence, the fact that an excess of charged ammonium groups, over the mica lattice charge, is observed shows that counterions, chloride and dodecyl sulfate, have to be incorporated in the dried layer despite the rinsing step employed. The desorption of the polyelectrolyte due to exposure to SDS solutions is relatively small, reaching about 15% at an SDS concentration corresponding to twice the cmc.

Surface Forces. The forces acting between mica surfaces across a solution containing 20 ppm PEI and 10 mM NaCl at pH 5.7 are displayed in Figure 5.

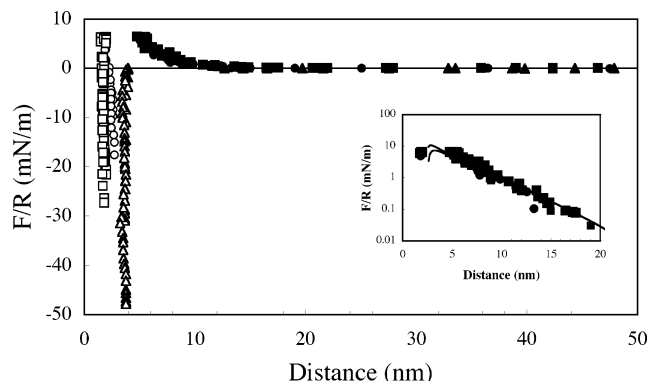


Figure 5. Force normalized by radius as a function of surface separation. The surface interactions were determined between PEI coated surfaces across 20 ppm PEI solution in 10 mM NaCl (●), in polyelectrolyte-free solution (■), and in solution containing 0.01 cmc SDS (▲). Filled symbols denote forces measured on approach, and open symbols show forces measured on separation. (Insert) The repulsive part of a force curve drawn on a logarithmic force scale. The lines represent theoretically calculated force curves using an apparent double-layer potential of 90 mV and the known ionic strength. The upper and lower lines correspond to interactions at constant charge and potential, respectively. The nonretarded Hamaker constant was set to 2×10^{-20} (J).

We note that the forces are of rather short range, reaching a measurable strength at a separation of 15–20 nm. On further compression the force increases logarithmically with a decay length of 3 nm. This is the expected decay length of a double-layer force in 10 mM NaCl, and we conclude that this is the origin of the observed repulsion. Forces calculated using DLVO theory were fitted to the experimental data using the apparent double-layer potential as a fitting parameter. From the fitting we conclude that the apparent double-layer potential is about 90 mV, which corresponds to an area per charge of 4.9 nm^2 . This excess charge is significantly lower than that determined by ESCA, which provides evidence for the incorporation of counterions, chloride in this case, in the adsorbed layer. Once the separation has decreased to about 5 nm an attractive force comes into play and the surfaces jump inward to a separation of about 2 nm. The jump-in position is located at larger distances than expected from DLVO theory, suggesting the presence of a bridging attraction. Further compression does not result in any change in surface separation. Hence, the compressed layer thickness is 1 nm per surface. On separation a strong attractive force, amounting to 10–17 mN/m is observed. The force minimum is located at a separation of 2.5–3 nm.

The interaction between mica surfaces precoated with PEI outside the measuring chamber, by allowing the polyelectrolyte to adsorb for 30 min from a 20 ppm solution in 10 mM NaCl at pH 5.7, as described in the Experimental Section, are also shown in Figure 5. These measurements were carried out across a polyelectrolyte-free 10 mM NaCl solution at pH 5.7. Thus, in this case the polyelectrolyte is present only on the surface. The measured interactions on approach are virtually identical to those measured across the 20 ppm polyelectrolyte solution. However, on separation the surfaces remain at a separation of 2 nm until they jump apart. The adhesion force is slightly higher than across the 20 ppm polyelectrolyte solution, and it is now in the range 18–27 mN/m. The difference between the two force curves displayed in Figure 5 is likely due to some limited desorption of the PEI into the polyelectrolyte-free bulk solution.

Addition of SDS to a concentration of 0.01 cmc results in significant changes in the interaction curve, Figure 5. First, the repulsive double-layer force that was present prior to addition

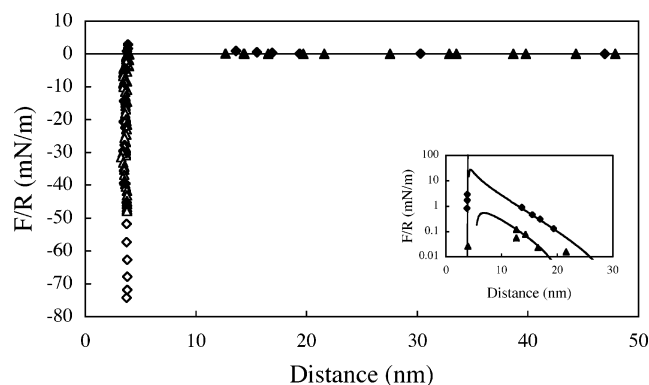


Figure 6. Force normalized by radius as a function of surface separation. The surface interactions were determined between PEI coated surfaces across 10 mM NaCl solution containing 0.01 (\blacktriangle) and 0.1 (\blacklozenge) cmc SDS. Filled symbols denote forces measured on approach, and open symbols show forces measured on separation. (Insert) The repulsive parts of the force curves drawn on a logarithmic scale. The lines correspond to theoretically calculated DLVO force curves using constant potential boundary conditions and the known ionic strength. The apparent double-layer potential at $D = 3.8$ nm was -150 mV (upper line), and ± 35 mV (lower line). The nonretarded Hamaker constant was set to 2×10^{-20} (J).

of SDS is now nearly absent; only a very weak repulsion in the distance range 16–11 nm is noticed, see Figure 6. The apparent double-layer potential was found to be ± 35 mV, corresponding to an area per charge of 19 nm^2 . This shows that the net charge of the PEI-coated mica was initially positive and that adsorption of SDS results in close to charge neutralization. We note that the ESCA results rule out desorption of PEI as the reason for the reduction in double-layer repulsion. The attractive force present at shorter separations pulls the surfaces into contact from a separation of 12–14 nm into a separation of 3.7–3.9 nm. The range of the attractive force is significantly larger than expected from DLVO theory. On separation the surfaces remain at this position until they suddenly jump apart. The magnitude of the attractive adhesion force is 30–50 mN/m, i.e. significantly larger than prior to addition of SDS. This strongly suggests that hydrophobic interactions between the tails of the surfactant that is incorporated in the layer contributes to the attraction.

A further increase in surfactant concentration to 0.1 cmc results in some further changes in the force profile, see Figure 6.

The repulsion on approach has increased, and it is now clearly detectable in the distance range 25–12 nm. The slope of the force curve is consistent with the expected decay length of a double-layer force. The apparent double-layer potential was found to be -150 mV, corresponding to an area per charge of 1.5 nm^2 . Thus, a strong recharging has clearly occurred. From a separation of 12 nm an attraction pulls the surfaces into a separation of about 4 nm. The range of the attraction is significantly longer than expected from DLVO theory. The adhesion measured on separation from this position is higher than at the lower surfactant concentration and amounts to 75–85 mN/m. Hence, hydrophobic interactions between the tails of the SDS molecules gives a larger contribution to the attraction as compared to those at lower surfactant concentrations.

The interaction profile across a 0.5 cmc SDS solution in 10 mM NaCl is significantly different as compared to interactions at lower surfactant concentrations, see Figure 7.

A strong repulsion is experienced once the surface separation has decreased to below 25 nm. The repulsion increases logarithmically with decreasing surface separation down to a separation of 11–12 nm. The decay length of the repulsive force

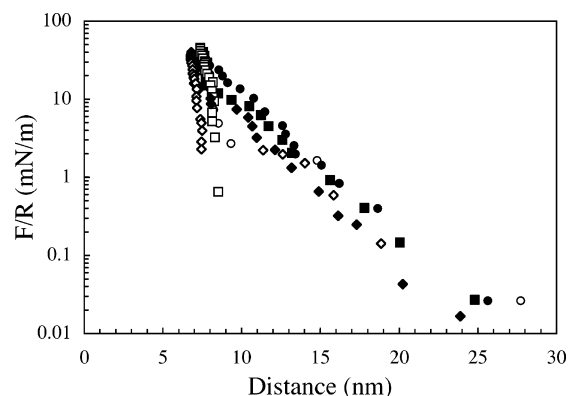


Figure 7. Force normalized by radius as a function of surface separation between mica surfaces precoated with PEI in 10 mM NaCl at pH 5.7. Forces measured on approach are represented by filled symbols and forces measured on separation by unfilled symbols. The forces during the first measurement in 0.5 cmc SDS (3×10^{-3} M) solution (\bullet), and the forces measured during the subsequent measurement (\blacksquare). The forces measured across a 2 cmc (1.2×10^{-2} M) SDS solution (\blacklozenge).

is close to, but slightly larger than, the expected decay length of a double-layer force at the given ionic strength (13 mM). Thus, we conclude that this repulsion is due to the electrostatic double-layer force between slightly swollen polyelectrolyte layers. The slightly larger decay length than expected is suggested to be caused by a change in the conformation of the adsorbed polyelectrolytes during compression that results in an inward shift of the plane of charge.²⁴ Once a separation of 12–11 nm has been reached and the layers are further compressed, the slope of the curve decreases, indicating a significant compaction of the layer due to the applied force. Once the surfaces have reached a separation of 8 nm, the force becomes very steep. Thus, the compressed layer thickness has increased significantly as compared to that at lower surfactant concentrations, indicating formation of an outer SDS layer that is sufficiently densely packed to withstand a significant compressive force. On separation the surfaces stay at a separation of 8–9 nm until they move apart. No adhesion or a very weak adhesion is observed upon separation. In the previous, lower SDS concentrations the forces measured during the first and subsequent approaches were identical. However, this is not the case when the SDS concentration is 0.5 cmc. On a subsequent approach the double-layer force is the same as during the first approach. However, the reformation of the adsorbed layer that takes place once the separation has decreased to about 12 nm occurs more readily during the second measurement. Thus, the layers have not fully relaxed between measurements (15 min).

Finally, to determine if the adsorbed layer would desorb in excess SDS solution the concentration of SDS was increased to 2 cmc, and the surfaces were left undisturbed overnight. The only minor difference between the results obtained at 0.5 and 2 cmc SDS is the adsorbed layer thickness, which is thinner by 0.5 nm at the higher concentration (see Figure 7). We note that the ESCA results show no additional desorption when increasing the SDS concentration from 0.5 to 2 cmc. The change in layer thickness is thus not due to PEI desorption but rather to a structural change within the layer. We suggest that it is due to the smoothening of the layer structure as observed by AFM (see below). The interaction across the 2 cmc SDS solution is at long range dominated by an electrostatic repulsion, which has a shorter decay length than at the previous SDS concentration due to the increased ionic strength. On further compression

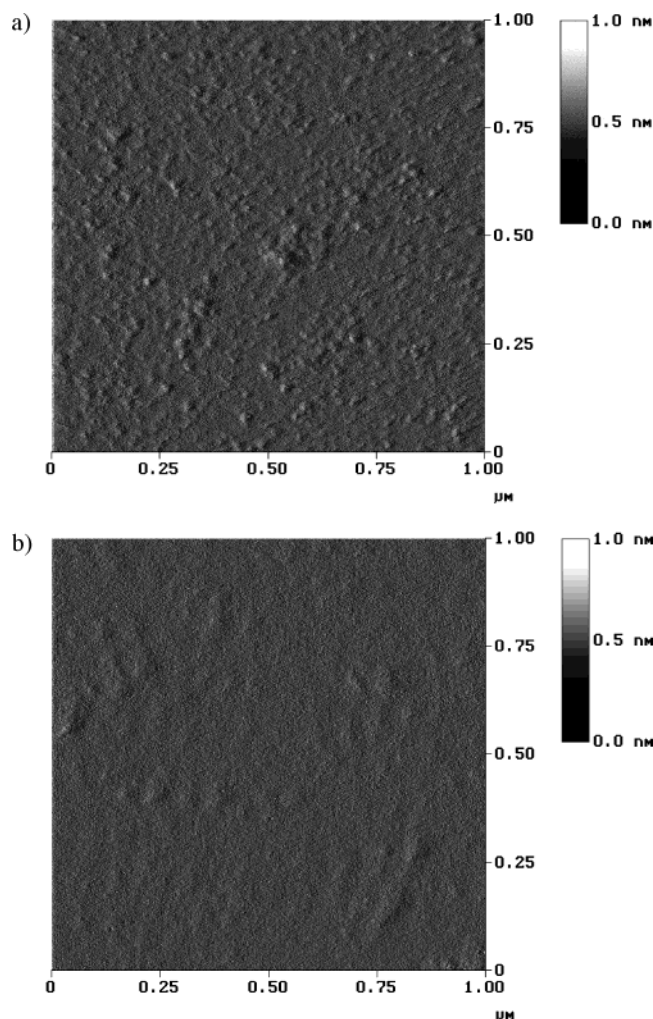


Figure 8. (a) Deflection mode AFM image of PEI adsorbed on mica from a 20 ppm solution in 10 mM NaCl for 30 min. The solution was exchanged for a polyelectrolyte-free 10 mM NaCl solution prior to imaging. (b) AFM image of the same preadsorbed PEI layer after addition of a 1 cmc (6×10^{-3} M) SDS solution in 10 mM NaCl. The scan size is $1 \times 1 \mu\text{m}$ in both images.

the adsorbed layer is forced to rearrange into a more compact structure. After the rearrangement has occurred, a very steep repulsion is encountered. No adhesion is observed upon separation from the position of the very steep repulsion at $D \approx 7$ nm. However, if a very strong compression is applied, too strong to be quantified, it is found that the separation suddenly changes from 7.1 to 3.5 nm. This demonstrates that the outer surfactant layers are removed. The hydrophobic nature of the remaining layer is confirmed by the high adhesion force, 50–55 mN/m, observed when the layers are separated from a distance of 3.5 nm.

Atomic Force Microscopy. The deflection mode image of the preadsorbed PEI layer, formed by adsorption from a 20 ppm solution in 10 mM NaCl for 30 min and then rinsing with polyelectrolyte-free 10 mM NaCl, is seen in Figure 8a.

The adsorbed layer clearly consists of rounded flat regions of PEI of typical diameter of 20–30 nm. The forces measured between the tip and the sample (data not shown) at this stage are characterized by electrical double-layer repulsion with a decay length in agreement with the given ionic strength. The repulsion is overcome by an attractive force that at shorter separation pulls the tip into contact with the adsorbed layer. There is a strong adhesion force between the sample and the

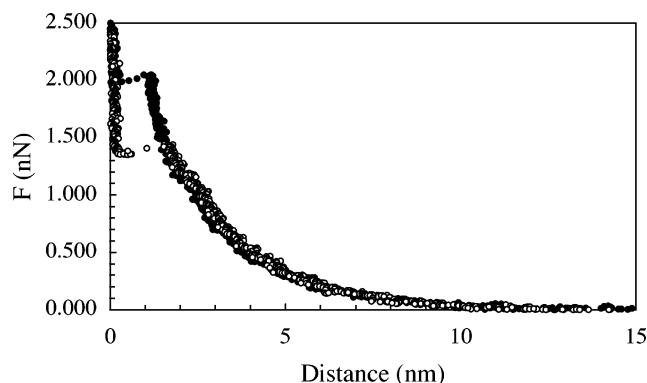


Figure 9. Force between the AFM tip and a mica surface coated with a preadsorbed PEI layer in the presence of 1 cmc (6×10^{-3} M) SDS in 10 mM NaCl. Approach (●) and separation (○).

tip on separation. The force data are qualitatively similar to those determined between two PEI-coated mica surfaces as reported in Figure 5.

Addition of SDS to a concentration of 1 cmc results in marked changes in the image. The rounded surface features are now much less pronounced, and the adsorbed layer appears significantly more homogeneous, Figure 8b. This indicates that addition of SDS weakens the bond between the surface and PEI and that this facilitates spreading of the polyelectrolyte on the surface. The notion of an SDS layer adsorbed on top of PEI is emphasized by the force curve displayed in Figure 9. We note that a repulsive double-layer force is the dominating feature at large separation. The decay length, 2.4 nm, is consistent with the ionic strength, 16 mM. A small jump of 1 nm is observed under high compression. On separation a similar small jump-out occurs at a lower force. This feature is interpreted as the removal of the outer SDS layer on compression and the readorption of this layer in the contact region during separation. At this stage there is no adhesion between the adsorbed layer and the tip.

Discussion

The Effect of Ionic Strength and Surface Nature on Adsorbed PEI Layers. The forces acting between PEI layers adsorbed on mica surfaces from a 0.1 mM salt solution have been reported in a previous publication.² It was found that PEI adsorbs in very thin layers and the compressed layer thickness was only 1.2 nm, i.e. 0.6 nm on each surface. In this study, using 10 mM NaCl as background salt, we find slightly thicker compressed layers, about 2 nm (i.e., 1 nm per surface). Thus, an increase in ionic strength results in formation of slightly more extended layers. The same trend, but more marked, has been observed for other polyelectrolytes^{25,26} and is due to screening of the electrostatic surface affinity and the repulsion between the adsorbed polyelectrolyte chains. The adhesion force in 0.1 mM salt was reported to be 135 mN/m across a 10 ppm PEI solution, decreasing to 65 and 11 mN/m when the PEI concentration was increased to 20 and 50 ppm, respectively.² This was rationalized by an increasing charge overcompensation of the mica surface charge by the adsorbing polyelectrolyte at the higher PEI concentrations. We note that Monte Carlo simulations predict a decreasing bridging attraction with increasing charge overcompensation,²⁶ which is in line with the experimental findings. In this study we find an adhesion force of about 15–25 mN/m when the PEI concentration is 20 ppm, i.e. considerably lower than at the lower salt concentration. This indicates a reduced contribution from bridging attraction at the

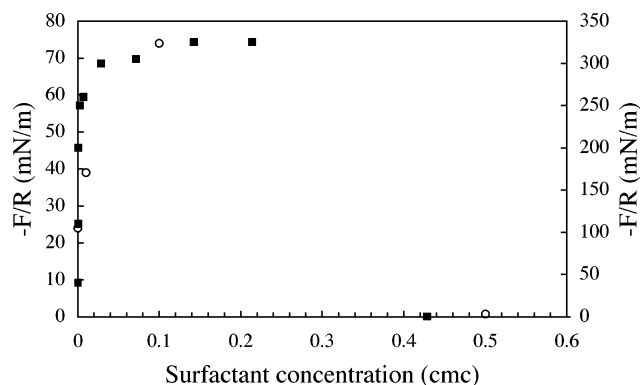


Figure 10. Adhesion force between preadsorbed PEI (○ primary axis) and DAHCl (■, secondary axis) layers as a function of surfactant concentration.

higher ionic strength. We note that the increase in layer thickness with increasing ionic strength is likely to counteract bridging.

The interactions between glass surfaces coated with PEI have also been investigated²⁷ using 0.1 mM NaCl as background salt. The adhesion force found in that study was considerably lower than that found when mica was used as substrate.² This can be rationalized by the lower charge density of glass as compared to that of mica, which makes the bridging attraction weaker. This dependence on the strength of the bridging attraction on the surface charge density of the surface has also been predicted by Monte Carlo simulations.²⁶ The adsorbed layer thickness on the glass surfaces could not be determined with the force measuring technique used by Poptoshev et al.²⁷

The ellipsometric thickness of PEI layers adsorbed on silica from a 50 ppm solution in 10 mM NaCl has been determined by Mészáros et al.⁸ They found a thickness of about 3.5 nm. This is considerably thicker than the 1 nm found for the compressed layer thickness of PEI adsorbed from a 20 ppm solution in 10 mM NaCl on mica in this study. However, they used a PEI with a considerably higher molecular weight than used in this study, 7.5×10^5 g/mol compared to 1.8×10^5 g/mol, which may be one reason for the larger layer thickness found by Mészáros et al. However, it should also be noted that the layer thickness is not a well-defined quantity, and different methods give different values. The general trend is that the hydrodynamic layer thickness > range of the steric force determined from surface force measurements > the ellipsometric thickness > the compressed layer thickness determined from force measurements. Thus, it is not surprising that the layer thickness determined by ellipsometry is larger than the compressed layer thickness measured with the surface force technique^{14,28} since compression results in a change in the segment density profile toward a more compact layer. We also note that the substrate surfaces are different in the ellipsometric and surface force measurements, which means that both the electrostatic and nonelectrostatic surface affinity is different.

Effect of SDS on Preadsorbed PEI Layers on Mica Surfaces in 10 mM NaCl. The association between preadsorbed PEI and SDS on negatively charged mica surfaces show many similarities to adsorption of surfactants on oppositely charged mineral surfaces, see, for example, refs 29 and 30. This is illustrated in Figure 10 that compares the magnitude of the adhesion force and Figure 11 that compares the layer thickness for the PEI–SDS system and cationic dodecylammonium chloride (DAHCl) adsorbing on negatively charged mica.

At low SDS concentration the adsorption of SDS onto the positively charged PEI-coated surface is electrostatically driven, and charge neutralization is achieved at 0.01 cmc. For com-

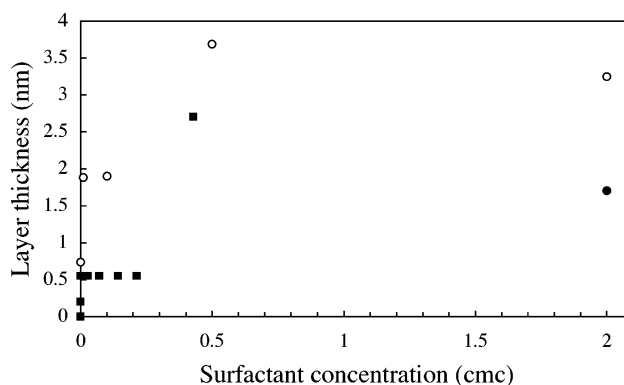


Figure 11. Increase in layer thickness for preadsorbed PEI layers on mica due to exposure to SDS (○). The solid circle represents the thickness obtained after squeezing out the outer SDS layer. The layer thickness of adsorbed DAHCl layer on mica (■) as a function of surfactant concentration.

parison, charge neutralization of mica surfaces by adsorption of dodecylammonium (DAH^+) ions occurs more readily and is achieved at a concentration of less than 0.001 cmc.³⁰ Both for dodecyl sulfate (DS^-) ions adsorbing to PEI-coated mica and dodecylammonium ions adsorbing to mica, the charge neutralization results in a more hydrophobic character of the layers and the adhesion force increases. This effect is stronger for DAHCl on mica than for SDS on PEI-coated mica. The increase in layer thickness for the PEI–SDS layer at this stage is just above 2 nm (i.e., 1 nm per surface). Further increase in SDS concentration to 0.1 cmc results in a recharging of the surface and a further increase in hydrophobic character as indicated by the increase in adhesion force. The increase in layer thickness due to incorporation of DS^- ions remains the same as at the lower surfactant concentration. These general features of an increase in adhesion force and a constant layer thickness above the charge neutralization point are also observed for DAH^+ ion adsorption to mica. It can be rationalized by a change in layer structure of the adsorbing surfactants as the surfaces are pushed together. Bilayerlike aggregates are likely to be present at large separations to minimize the interfacial tension with the solvent. However, as the surfaces are brought close together, the adsorbed layer rearranges into monolayer structures that promote interlayer interactions between the surfactant tails.

Once the SDS concentration has been increased further to 0.5 cmc, a rather complete outer layer of SDS is formed as evidenced from the large force needed to remove it from the contact zone. This results in a significant increase in compressed layer thickness by an additional 4 nm (2 nm per surface). The total increase in layer thickness by about 3.5 nm per surface is indeed consistent with bilayer structures of SDS on top of the polyelectrolyte layer. A similar formation of a bilayer structure that was stable under high compression was observed for DAH^+ ion adsorption on mica at a concentration of 0.43 cmc, but not at 0.21 cmc.³⁰ The bilayer thickness was in this case found to be 2.7 nm per surface, i.e. somewhat smaller than the thickness of the SDS bilayer formed on PEI-coated mica. In fact, the situation is slightly more complicated in the latter case since the underlying PEI layer also swells somewhat at this concentration and surfactants may partly penetrate into the polyelectrolyte layer. A further increase in SDS concentration to 2 cmc does not result in any dramatic changes in layer structure.

The picture of the interfacial association between preadsorbed PEI and SDS on mica surfaces that has emerged from this study is rather different from that obtained by the ellipsometric investigation of the association of PEI and SDS on silica.⁹ The

strong increase in layer thickness observed here was not detected in the ellipsometric study where the increase in layer thickness was found to be small, whereas the density in the adsorbed layer was increased significantly. This discrepancy needs to be analyzed somewhat. Both studies were carried out using 10 mM NaCl as background electrolyte. However, the molecular weight of PEI was larger, by a factor of 4.2, in the ellipsometric study. The adsorbed amount of PEI was also considerably smaller on silica (about 0.3 mg/m²) as compared to the adsorbed amount found in this investigation, about 0.6 mg/m². Despite this, the layer seems to be somewhat thicker on silica than on mica, even though this conclusion is not very firm since different methods have been used to evaluate the layer thickness. The AFM images presented in Figure 8b show that once SDS is added to a concentration of 6 mM the adsorbed layer on mica smoothens considerably. It seems likely that the incorporation of negatively charged DS⁻ ions in the layer facilitates spreading of the underlying PEI along the surface, but apparently the PEI–surface affinity is not decreased sufficiently to induce complete desorption (~15% desorption according to ESCA). It is very likely that the same spreading process will occur on silica. On both surfaces the association of SDS and preadsorbed PEI gives rise to two processes that occur simultaneously, spreading of the PEI layer that thins the adsorbed layer and incorporation of SDS in the layer that causes an increase in layer thickness. On mica, where the adsorbed amount of PEI is larger than on silica, the latter process is dominating, whereas on silica the effect of the two processes nearly balance each other, and the net effect is a more compact adsorbed layer.

In passing, we note that the adsorbed amount of PEI from 10 mM NaCl determined in this study is very similar to that previously found for PEI adsorbed on mica from 0.1 mM salt solutions.² In contrast, the adsorbed amount on silica increases with salt concentration. Hence, the obvious nonelectrostatic contribution to the affinity between PEI and silica is not observed for PEI adsorbing on mica.

In this context it may also be useful to recapitulate the effect of SDS on preadsorbed chitosan layers on mica.²⁵ At low ionic strength the adsorbed chitosan layer is very thin, and the association between SDS and chitosan results in adsorption of surfactant on top of the polyelectrolyte layer. On the other hand, in 30 mM salt solution the chitosan layer is significantly thicker, and in this case the incorporation of surfactant results in a significant compaction of the adsorbed layer. Furthermore, at the higher ionic strength surfactants were incorporated in the adsorbed layer more easily than at the lower ionic strength. Hence, due to the structural change of the adsorbed layer the effect of added electrolyte on the association process at the surface was found to be opposite to that in bulk solution. Hence, the interfacial association between polyelectrolytes and surfactants does not only depend on the polyelectrolyte architecture, the surfactant structure, and the nature of the solid surface but also on the structure of the initially formed polyelectrolyte layer.

Comparison between Bulk and Interfacial Association. From previous studies it has been shown that the association between SDS and cationic polyelectrolyte layers that exactly balance the underlying mica surface charge (as evidenced from the absence of a double-layer force) occurs less readily than in bulk solution,¹⁷ i.e. for this situation the critical association concentration at the surface cac_s is higher than the critical association concentration in bulk solution, cac . The difference between cac_s and cac decreases with decreasing charge density of the polyelectrolyte, which is due to the more extended

structure of the adsorbed layer for polyelectrolytes with lower charge densities. It has also been shown that the value of cac_s depends on the nature of the surface.³¹

The preadsorbed PEI layer investigated in this study is different from the preadsorbed polyelectrolyte layers studied in previous investigations in one important respect: the charge of the underlying substrate is strongly overcompensated by the adsorbed PEI layer. This, of course, facilitates incorporation of oppositely charged surfactant at low surfactant concentrations due to electrostatic attraction. Thus, it is no real surprise that SDS is incorporated in the adsorbed layer already at a concentration of 0.01 cmc and that the SDS association results in charge neutralization. A further increase in SDS concentration by a factor of 10, to 0.1 cmc, results in recharging. In comparison the bulk PEI–SDS complex formed in a 20 ppm solution becomes charge neutralized at a surfactant concentration of close to 0.07 cmc, as indicated by the electrophoretic mobility measurements presented in Figure 2. The free SDS concentration during the electrophoretic mobility measurements at the charge neutralization point can be estimated from the total SDS concentration, the PEI concentration, the molecular weight of the structural unit, and the degree of protonation (about 70%) by assuming that one DS⁻ ion is associated with each protonated amine group. Thus, the free SDS concentration at the charge neutralization point is estimated to be 0.022 cmc (0.15 mM). Thus, it seems that charge neutralization of the adsorbed PEI layer occurs at a rather similar SDS concentration to, or even lower than, that needed to reach charge neutralization of the PEI–SDS complexes formed in bulk solution. Further, we note that complexes in both bulk and the adsorbed layer acquire a negative charge at 0.1 cmc SDS. A further increase in bulk surfactant concentration results in formation of an outer SDS layer with an accompanying increase in layer thickness. It has been postulated^{8,32} that the same occurs in bulk in the presence of excess SDS, i.e. the complexes should be viewed as internally charge compensated with an outer skin of SDS. The results presented in this work are in line with this hypothesis.

Effect of Polyelectrolyte Structure on Polyelectrolyte–Surfactant Complexes Adsorbed to Mica Surfaces. A considerable amount of data is now available on the effect of SDS on preadsorbed cationic polyelectrolyte layers. For very low charge density polyelectrolytes addition of SDS results primarily in desorption.³³ For moderately charged polyelectrolytes (10 and 30% of the segments being charged) addition of SDS results in considerable swelling of the adsorbed layers^{16,34} followed by some desorption when the cmc of SDS is approached.³⁵ For highly charged polyelectrolytes different effects are observed, depending on the architecture of the polymer and the ionic strength of the solvent. We note that also differences in nonelectrostatic surface affinity are likely to be important.

PCMA (poly(2-acryloxyethyl)trimethylammonium chloride) is a linear polyelectrolyte. SDS associates with preadsorbed layers of PCMA on negatively charged mica surfaces in 0.1 mM salt solution whereby structured complexes that partly dewet the surface are formed. From force measurements¹⁷ as well as SANS¹⁰ and SAXS³² data of bulk complexes it has been concluded that they consist of cylindrical SDS micelles wrapped by polyelectrolytes that are organized in a hexagonal symmetry with the structural units oriented along the surface.

The interfacial organization of chitosan–SDS complexes is different. In 0.1 mM salt solution SDS adsorbs on top of the polyelectrolyte, but no indication of an organized interfacial complex is found.²⁵ Chitosan is a linear polyelectrolyte composed of aminoglucose segments. The backbone of chitosan is

more hydrophilic and stiffer than that of PCMA, which is the likely reason for the different interfacial association pattern with SDS as compared to that with PCMA. At higher electrolyte concentrations, 30 mM, chitosan adsorbs in a more extended layer. SDS is readily incorporated in this layer, which leads to a significant compaction.²⁵

In contrast to PCMA and chitosan, PEI is a hyperbranched polyelectrolyte. The data presented in this study indicate that no thick organized PEI–SDS complexes are formed on the surface. The data rather indicate that SDS adsorbs mainly on top of the PEI layer. Thus, a composite layer is formed where PEI is located closest to the mica surface, whereas SDS is preferentially accumulated on the solution side. The disappearance of the adhesion force at high SDS concentrations indicates that sulfate groups in the outer SDS layer are oriented toward solution. This can be reconciled with an electrostatic binding of SDS to PEI followed by addition adsorption of SDS due to hydrophobic interactions resulting in bilayer structures of SDS on top of the preadsorbed PEI, which is the structure that we advocate.

Conclusions

Adsorption of cationic PEI from a 20 ppm solution in 10 mM NaCl at pH 5.7 occurs to such an extent that the mica substrate surface charge is strongly overcompensated. The adsorbed layer is thin and nonhomogeneous as evidenced by AFM and surface force measurements. The branched structure of PEI means that a large number of charges are brought down on a relatively small surface area, and high adsorption density areas can be seen in the AFM images. Addition of SDS to the polyelectrolyte-free solution outside the preadsorbed PEI layer results in association between the preadsorbed polyelectrolyte and the surfactant. Charge neutralization is already achieved at an SDS concentration of 0.01 cmc. This is accompanied by an increase in layer thickness and adhesion force. A further 10-fold increase in SDS concentration results in recharging and a further increase in adhesion force. Clearly, hydrophobic interactions between surfactant tails give a significant contribution to the attraction between the layers. A further increase in SDS concentration to 0.5 cmc results in formation of an outer SDS layer with the charged sulfate group directed toward solution which is stable under compression. As a consequence the adhesion between the layers is removed. The association between PEI and SDS at the mica surface shows strong resemblance to adsorption of an ionic surfactant to an oppositely charged mineral surface.

The interfacial association between PEI and SDS is strikingly different from that observed for other cationic polyelectrolytes and SDS. Such association processes have been reported to give rise to formation of organized self-assembled polyelectrolyte–surfactant complexes, swelling, deswelling, or desorption, depending on the charge density and architecture of the polyelectrolyte, the nature of the solid surface, the ionic strength of the solution, and the structure of the adsorbed polyelectrolyte layer prior to surfactant addition. The understanding for how these factors affect the interfacial association process is in rapid progress.

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