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Effect of Polyelectrolyte Charge Density on the Adsorption and Desorption Behavior on Mica

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The XPS (ESCA) method was employed to quantitatively determine polyelectrolyte adsorption on the mica basal plane from low ionic strength solutions. Particular emphasis was given to the effect of the polyelectrolyte charge density. By combining the results obtained from XPS and surface force measurements it was possible to analyze the cation exchange at the surface that occurs as a result of polyelectrolyte adsorption. AFM-imaging was used to obtain information on the structure of the adsorbed layer when the polyelectrolyte coverage was low. Further, the desorption of preadsorbed polyelectrolyte layers by addition of inorganic salt and by addition of an anionic surfactant was investigated by XPS and some complementary surface force measurements. The results demonstrate that the lower the polyelectrolyte charge density is, the easier it is to remove the polyelectrolyte from the surface. The surfactant, which by itself does not adsorb to the mica surface, is more efficient in this respect than the inorganic salt. This observation can be rationalized by considering that the surfactant and polyelectrolyte form complexes with each other. Thus, the surfactant brings negative charges into the adsorbed layer that reduces the affinity to the surface. However, high-charge-density polyelectrolytes are removed to a very limited degree even when the surfactant concentration is above the critical micellar concentration, which is explainable by the poor solubility of the polyelectrolyte–surfactant complexes formed.

Introduction

Modification of the surface chemistry of solid substrates can be carried out in a number of ways including various forms of vacuum deposition and plasma treatment, reactions with specific molecules such as silanes on silica or thiols on gold, Langmuir–Blodgett deposition, or adsorption from solution. Of these methods, adsorption from solution is by far the simplest and is most commonly used when stabilizing or destabilizing colloidal particles. Adsorption from solution may also be used for modifying solid surfaces, e.g., to give the surfaces protein-repellent properties.[1] In such cases it is preferable to use macromolecules, particularly charged ones. The reason is that the macromolecules can anchor to the surface by several segments and introduction of charges on the polymer with opposite sign to that of the surface tends to increase its affinity to the surface. However, relying on adsorption for long-lasting surface modification also has disadvantages. For instance, the properties of the layers cannot be tailored to the same extent as when using Langmuir–Blodgett deposition or functionalized thiols on noble metal surfaces. Another drawback is that even though desorption of polymers from a surface is a slow process,[2] it is not irreversible in the thermodynamic sense. Further, addi-

tives in the solution may affect the surface–polymer affinity, giving rise to irreversible changes in the adsorbed layer or desorption.

There is a need to be able to follow how the adsorbed layer changes as a result of exposure to various additives present in the solution. Some convenient ways to follow such changes are by means of ellipsometry,[3–6] reflectometry,[7–10] or quartz crystal microbalance (QCM).[11–13] However, all these methods demand some special requirements of the substrate surface, and they do not give any chemical information. XPS (or ESCA) does provide chemical information, and quantification of the adsorbed amount is possible. For instance, the adsorbed amount of a fatty diamine on flat quartz surfaces and quartz powder has recently been quantified and the desorption process followed.[14] The XPS method has also been employed to

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Table 1. Charge Density (τ) and Molecular Weight of the Investigated Polyelectrolytes[a]

polyelectrolyte	τ (theoretical), %	τ (elemental analysis), %	τ (potentiometry), %	τ (NMR), %	MW
AM-MAPTAC-1	1	0.5	0.98		900 000
AM-MAPTAC-10	10	10	9	8.9–9.5	1 000 000
AM-MAPTAC-30	30	31	31	24.2–25.6	780 000
AM-MAPTAC-100	100	99	95		480 000

[a] Data provided by Laboratoire of Physico-Chimie Macromoleculaire, Paris.

quantify the adsorption of polyelectrolytes on cellulose.[15] In this study we employ the same method to determine adsorption isotherms of polyelectrolytes of various charge densities on mica and also to follow their desorption behavior due to addition in the bulk phase of inorganic salt (NaCl) and anionic surfactant (sodium dodecyl sulfate).

Experimental Section

Materials and Methods. The polyelectrolytes used in this investigation were random copolymers of uncharged acrylamide (AM) and positively charged [3-(2-methylpropionamido)propyl] trimethylammonium chloride (MAPTAC). By balancing the ratio MAPTAC/AM in the (radical) copolymerization process, macromolecules with different charge densities (percentage molar ratio of cationic monomers) were synthesized and kindly provided by the Laboratoire de Physico-Chimie Macromoleculaire (Paris). In Table 1 a list of the studied polyelectrolytes along with their charge densities (or cationicity, τ) and molecular weight (from viscosimetry measurements) is provided. For convenience, the polyelectrolytes are referred to as "*AM-MAPTAC*-X" where *X* is a number which indicates the respective percentage charge density (e.g., AM-MAPTAC-100 is poly(MAPTAC), with no AM units). Note that in this study both low- and high-charge-density polyelectrolytes were considered.

Potassium bromide (pro-analysis grade) from Merck was roasted for 24 h at 500 °C before use to remove organic contaminants. Commercially available sodium dodecyl sulfate (SDS) purchased from BDH Ltd was subjected to successive recrystallizations from water and ethanol and final freeze-drying. The quality of the surfactant was checked by surface tension measurements. The absence of a minimum in the surface tension isotherm was used as criteria for purity. Water used in all the experiments was first purified by a reverse osmosis unit (Milli-RO 10 Plus), which includes depth filtration, carbon adsorption, and decalcination. A Milli-Q Plus 185 unit was then used to treat the water with UV light and with a Q-PAK unit consisting of an activated carbon column, a mixed-bed ion exchanger, and an Organex cartridge with a final 0.22-μm Millipack 40 filter.

Prior to use, all glassware were left overnight in chromosulfuric acid followed by extensive rinsing with Milli-Q water. TEFZEL test tubes used in the adsorption/desorption experiments were cleaned with SDS micellar solution followed by repeated ethanol and water washings.

AFM Microscopy. Invaluable information about polymer morphology can be obtained from STM and AFM studies. In particular, AFM has become one of the most advanced methods for the examination of polymer surfaces [16] and for imaging of single polymer chains.[17−22] One of the major advantages of such techniques as compared to, e.g., electron microscopy (EM) is that imaging can be performed under near native conditions, thus eliminating sample damage and related artifacts that may be introduced when using EM.[23]

Imaging of adsorbed polymer on mica was accomplished by using a Nanoscope III MultiMode scanning probe microscope (Digital Instruments, Santa Barbara, CA). The tapping mode imaging technique was used to study the sample's topography by lightly tapping the surface with an oscillating tip. In this operation, a piezo stack, mounted under the cantilever holder, mechanically excites the cantilever's substrate normal to the surface, causing the tip to oscillate near its resonance frequency.[24] As the tip is tapped across the sample surface, it tends to be deflected due to its interaction with the surface material, but a feedback loop maintains constant tip oscillation amplitude by changing the vertical position of the sample (using a piezoelectric tube on which the sample is mounted). Maintaining constant amplitude ensures that tip−sample interactions remain constant throughout the imaging procedure. The vertical position of the scanner (*z*) at each (*x,y*) location is thus used to reveal the topographic image of the sample surface.

The probe used in the experiments consisted of 125 μm-length, single-beam cantilever and a tip (5−10 nm nominal radius of curvature) as an integrated assembly of single-crystal silicon produced by etching techniques (TappingMode etched silicon probe model TESP). The nominal spring constant and resonance frequency are reported by the manufacturer to be 20−100 N/m and 290−346 kHz, respectively.

Before imaging, the mica substrate was cut and gently pressed onto a sticky tab on a 15-mm diameter metal disk that was then attached to a magnetic sample holder located on top of the piezoelectric scanner (Model AS-12V "E" vertical MultiMode SPM scanner with 10 μm × 10 μm scan size and 2.5 μm vertical range). Since some of the studied polymers tend to swell in aqueous systems, [25] AFM imaging in air (or nitrogen) is a better choice than imaging under water. The use of ambient conditions (RH > 30%) however, may introduce a layer of adsorbed water molecules on the sample surface that gives rise to extra capillary forces between the tip and the sample and thus interferes with the AFM experiment.[26,27] To avoid this problem, a constant relative humidity nitrogen stream, supplied through a humidity generator (Model RH-100, VTI Corporation), was flowed continuously through the sample chamber. The temperature and relative humidity were set in all cases at 20 °C and close to 0%, respectively.

Substrate Preparations for Adsorption Experiments. Muscovite mica from Reliance Co. (NY) was used as substrate in all the experiments. Pieces of the mica were cleaved several times on both sides in a laminar flow cabinet until an adequate thickness was obtained. All the employed tools were previously cleaned, and protective clothing and gloves were worn to minimize contamination on the high-energy mica surfaces.

Adsorption and Desorption Experiments. Aqueous solutions of the polyelectrolyte at different concentrations (5−500 μg/mL) were prepared by dilution of a ca. 2000 μg/mL polyelectrolyte stock solution (with 0.1 mM KBr background electrolyte). The substrates (freshly cleaved mica pieces) of 5 × 1 cm size

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were immersed in the respective polyelectrolyte solution contained in TEFZEL test tubes for an equilibration time of 18–24 h. In the next step, the sample was withdrawn and the excess solution eliminated by a nitrogen jet. To study the desorption of the polyelectrolyte by NaCl or SDS, some of the samples (without any drying) were immersed in new TEFZEL test tubes containing the appropriate solution and left for another 18–24 h. Before withdrawing the samples, the test tube was immersed in a large beaker of water to avoid possible Langmuir–Blodgett deposition of polyelectrolyte–surfactant aggregates. The samples were finally dried with a nitrogen jet and cut to about 2×1 cm prior to XPS analysis.

X-ray Spectrometer. The X-ray photoelectron spectrometer (Kratos Analytical, AXIS-HS) utilized an Al Kα X-ray (1486.6 eV) source with a hemispherical analyzer. A relatively large sample area was irradiated by X-rays from a dual anode, and the electrostatic lens was used to collect the photoelectrons (the analyzed area is relatively large, of the order of 1 cm^2). Due to the large analyzed area and the close proximity between sample and the dual anode, the signal intensities (or raw areas) in this operational mode are enhanced. A more detailed account on the experimental technique and the procedure followed for calculating the amount of adsorbed polyelectrolytes on mica can be found in ref 15. Briefly, the method takes advantage of known surface properties of muscovite mica. The adsorbed amount is calculated by comparing the signal intensities for potassium (either K2s or K2p) from the mica substrate with that from the nitrogen (N1s) signal from the adsorbed polyelectrolyte. It is estimated that the accuracy in the evaluation of the adsorbed amount by XPS is about 10% between measurements.

Surface Force Measurements. The interferometric surface force apparatus (Mark II) was used to determine the forces acting between polyelectrolyte-coated mica surfaces. This instrument has been described in detail in numerous publications, see, e.g., refs 28,29.

Results and Discussion

AFM Imaging. Figures 1a-d show tapping mode AFM images of adsorbed copolymers of AM and MAPTAC on mica after adsorption at a polymer concentration of 0.1 μg/mL. This concentration, together with the large volume-to-specific area ratio used in the adsorption experiments, was chosen so as to avoid surface saturation and allow imaging of "individual" polymer chains adsorbed on the mica surface.

It is interesting to note that as the polyelectrolyte charge density is reduced it becomes more difficult to image the adsorbed polymer. This is in part due to the fact that low-charge-density polyelectrolytes tend to adsorb less strongly and in a more loose conformation on oppositely charged surface as compared to high-charge-density ones.

From large area scans (not shown) it was observed that the AM-MAPTAC-100 copolymer adsorbs uniformly (regularly) on the mica surface. As the polyelectrolyte charge density is reduced it is observed that the number density of adsorbed molecules increases and some "aggregates" (or "patches") of polymer molecules are formed. The increase in the adsorbed amount for polymers of lower cationicity is explained by the fact that in such cases more polymer units are needed to compensate the mica lattice surface charge (2.1×10^{18} negative charges/m^2 according to Güven[30]). This observation is corroborated by XPS quantitative measurements on similar systems (see following sections).

The section profiles shown in Figures 2a and 2b indicate an apparent chain thickness of ca. 0.2–0.7 nm, consistent with a very flat adsorbed layer. Furthermore, it is noticed

that the AM-MAPTAC-1 copolymer has a smaller "roughness" (ca. 0.2 nm) compared to that of AM-MAPTAC-100 (ca. 0.5–0.7 nm). This observation is consistent with a "bulkier" AM-MAPTAC-100 as anticipated from the molecular structure of this polymer. The reported values for polymer thickness, however, can only be taken as approximate since under the present conditions molecular resolution is limited by tip broadening. It should be noted that tip-broadening effects preclude the determination of the width of the polyelectrolyte chain. The AFM images did not provide any information about the thickness of the adsorbed layer at higher surface coverage due to that the tip could not reach or "contact" the mica surface. However, the surface force apparatus was used for studying the mean thickness of the adsorbed layers under these conditions. In air a value of less than one nm was obtained for AM-MAPTAC-100, increasing to more than 2 nm for the low-charge-density polyelectrolytes. In aqueous solutions the layer thickness for the low-charge-density polyelectrolytes is appreciably larger due to significant swelling. Finally, it should be mentioned that a comparison between AFM and SFA results is not straightforward since in the first case an estimate of the adsorbed layer roughness is obtained while the actual adsorbed layer thickness is measured with the SFA.

Adsorption of Cationic Polyelectrolytes on Mica. Figure 3 shows the nitrogen number density as, determined by XPS, for AM-MAPTAC-1 on mica in aqueous 0.1 mM KBr solution. The corresponding adsorbed amount was determined from following ref 15 considering the structure and the charge density of the polyelectrolyte and the nitrogen surface number density (see Figure 4, open circles).

As expected, the adsorption isotherm of AM-MAPTAC-1 on mica is of high affinity type and saturation is reached at a rather low polyelectrolyte concentration. The plateau or saturation value is ca. 2.5 mg/m^2, the same as obtained on silica using ellipsometric measurements.[25] This supports the hypothesis that steric interactions between adsorbed chains is the limiting factor for the adsorbed amount at this low polymer cationicity.

The adsorption isotherms for AM-MAPTAC polyelectrolytes with increasing charge density (10, 30, and 100%, respectively) on the muscovite mica basal plane are also shown in Figure 4. In all cases the adsorption took place in aqueous 0.1 mM KBr solution. It is evident that the plateau adsorbed amount is reduced as the polyelectrolyte cationicity is increased as expected for an adsorption process that is mainly electrostatically driven. As the polymer linear charge density is increased, less polyelectrolyte is needed to neutralize the substrate surface charge. The data obtained for AM-MAPTAC-100 agree well with what previously has been found for a structurally similar polyelectrolyte.[31] Since XPS does not provide information on the polymer configuration at the solid–liquid interface, complementary techniques such as surface force and ellipsometry are valuable in order to obtain a better understanding of the adsorption process. As will be demonstrated by the surface force data presented below, an increase in the polyelectrolyte cationicity results in a thinner and more flat configuration on the surface when it is in equilibrium with the polyelectrolyte solution.

The effect of the polyelectrolyte charge density on the plateau adsorption on mica is summarized in Figure 5. For copolymers of AM-MAPTAC the cationic groups are most strongly adsorbed on the negatively charged mica

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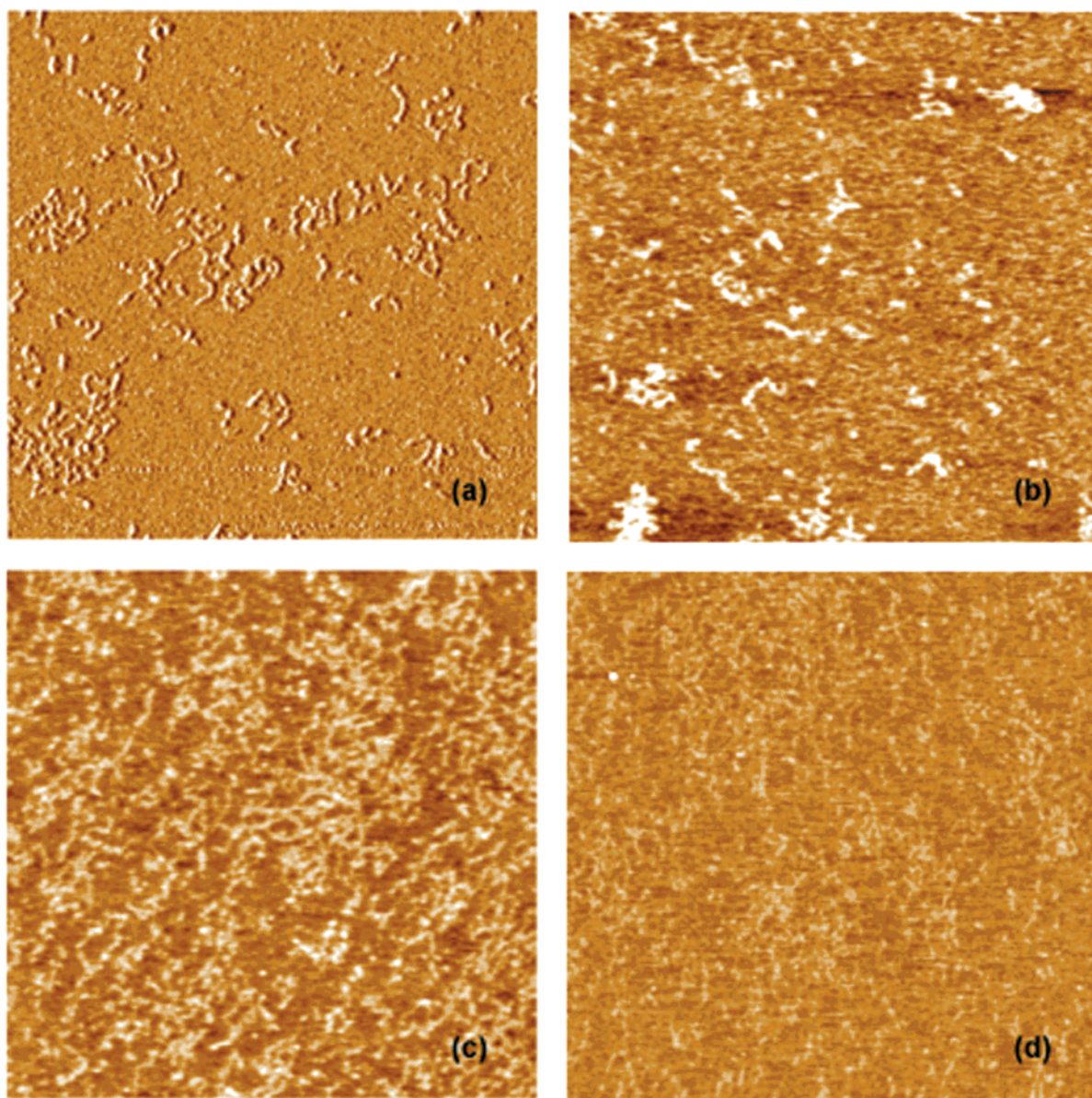
Figure 1. Tapping mode image (0%RH) of adsorbed polyelectrolyte on mica after equilibrium adsorption in 0.1 μg/mL bulk polymer concentration (scan range 1 × 1 μm²): (a) AM-MAPTAC-100; (b) AM-MAPTAC-30; (c) AM-MAPTAC-10; (d) AM-MAPTAC-1.

surface. Other studies[32,33] have found that the adsorption energy of uncharged acrylamide on negatively charged Na-montmorillonite and silica surfaces is small, and it was demonstrated that for a given polyelectrolyte molecular weight the plateau adsorption is very small at low (close to zero) charge densities. The adsorption was then found to increase with the charge density until a maximum in the adsorbed amount (at ca. 1% charge density) was found. At higher charge densities the adsorbed amount decreases again. These findings are in qualitative agreement with theoretical predictions[34–36] for an electrostatically driven adsorption process. The data presented here are consistent with previous findings in that it is sufficient with having one percent of the segments charged to obtain a strong adsorption, and in that the adsorbed amount decreases with increasing cationicity. It should be pointed out that molecular weight differences among the various polymers considered in this study have a negligible effect on the adsorbed amount. This remark is supported by observations made in similar systems by Tanaka et al.[37] who found that the adsorbed amount is nearly independent of the polymer chain length for cationic polyacrylamides adsorbed on PS-latex particles (except for cases of ultrahigh molecular weight polymers).

Let us now turn to some results obtained from surface force measurements. The substrate surface is muscovite mica, and this surface carries a layer of cationic polyelectrolytes. The data shown in Figure 6 are obtained for cationic polyelectrolytes with different charge densities under conditions where no long-range double-layer force is observed. The adsorption took place from a dilute electrolyte solution (0.1 mM KBr concentration or lower) and the polyelectrolyte concentration was 20 μg/mL for AM-MAPTAC-100,[38] 20 μg/mL for AM-MAPTAC-30,[39] 10 ppm for AM-CMA-10 (structurally similar to AM-MAPTAC-10),[40] and 50 ppm for AM-MAPTAC-1.[25] We note that

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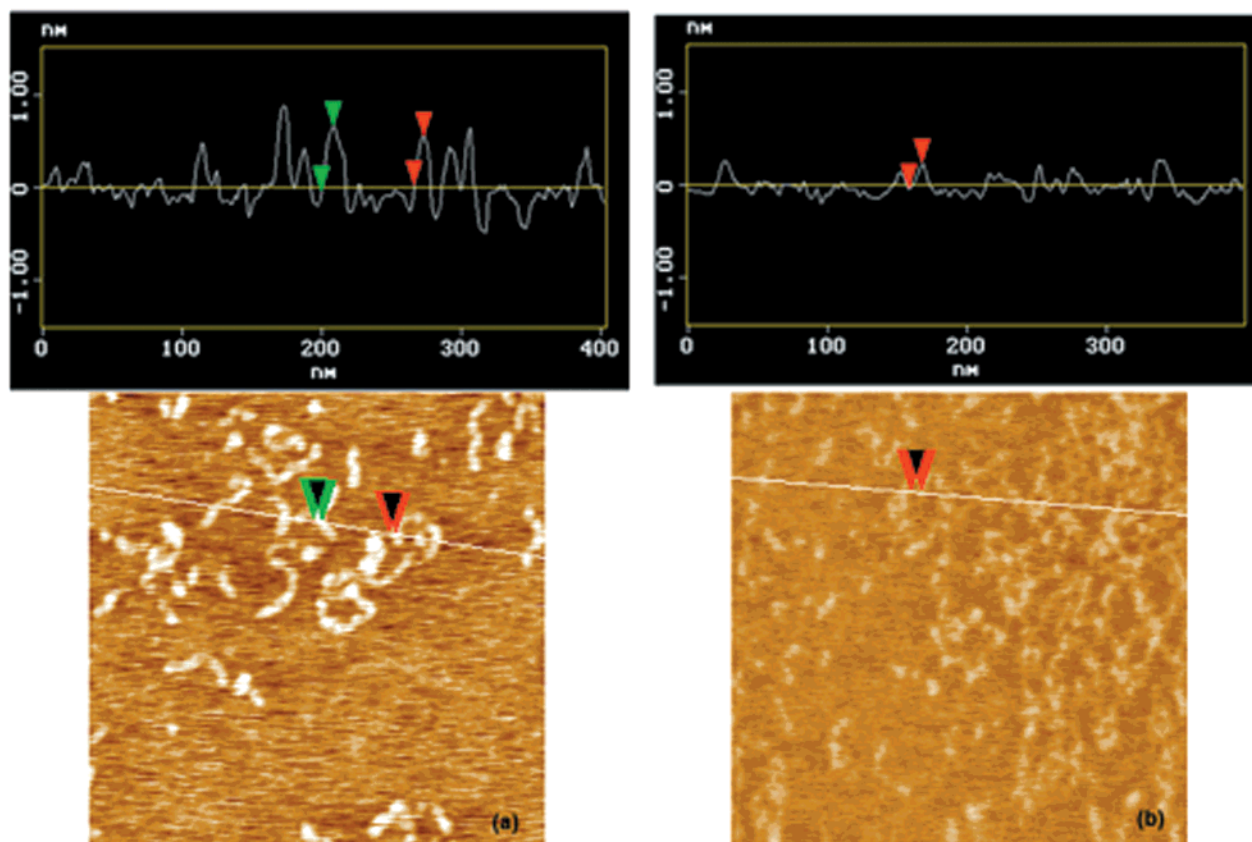
Figure 2. Tapping mode image (0%RH) of adsorbed polyelectrolyte on mica after equilibrium adsorption in 0.1 μg/mL bulk polymer concentration (scan range 400 × 400 nm^2): (a) AM-MAPTAC-100; (b) AM-MAPTAC-1. A line profile is also included on top of each image. For AM-MAPTAC-100 vertical distances of 0.53 and 0.68 nm are indicated (red and green arrows). For AM-MAPTAC-1 a vertical distance of 0.224 nm is indicated.
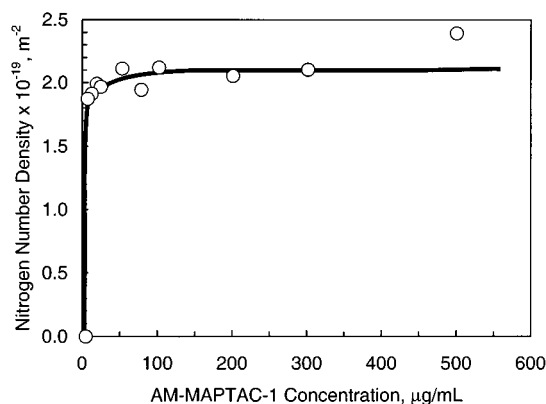

Figure 3. Nitrogen number density of AM-MAPTAC-1 adsorbed on mica from 0.1 mM KBr aqueous solution as determined by XPS.

Figure 4. Adsorption isotherms for AM-MAPTAC-1 (○), AM-MAPTAC-10 (□), AM-MAPTAC-30 (◇), and AM-MAPTAC-100 (■) on mica from aqueous 0.1 mM KBr solution determined by XPS. An additional curve for AM-MAPTAC-30 (●) from data in ref 39 is also included.

the long-range forces are similar when AM-MAPTAC-100 and AM-MAPTAC-30 are used. For instance, hardly any long-range repulsion is observed, and a bridging attraction dominates at distances below 10−15 nm. The position of the attractive minimum is located at a separation of about 1 nm for the 100% charged polyelectrolyte and at about 3−4 nm for the 30% charged one. No further compression of the adsorbed layer occurs under
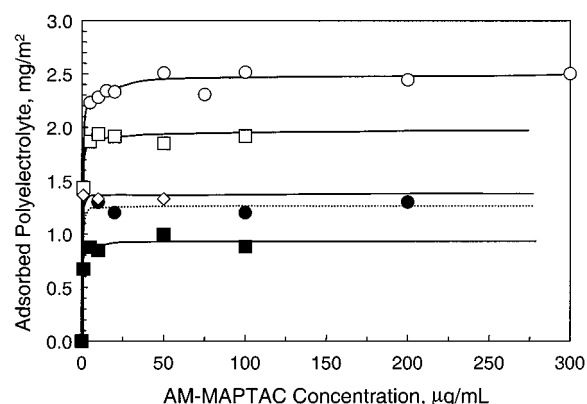
a high load. The magnitude of the pull-off force needed to separate the polyelectrolyte-coated surfaces is between 70 and 300 mN/m for the 100% charged case and between 2 and 5 mN/m for the 30% charged case. Thus, the layer thickness increases and the maximum attractive force decreases with decreasing charge density of the polyelectrolyte.

A further reduction in polyelectrolyte charge density to 10% of the segments results in a further increase in adsorbed layer thickness and a decrease in the magnitude of the pull-off force. A bridging attraction is still present in the distance range 10−20 nm whereas a steep steric force is present at smaller separation.[40] However, even if

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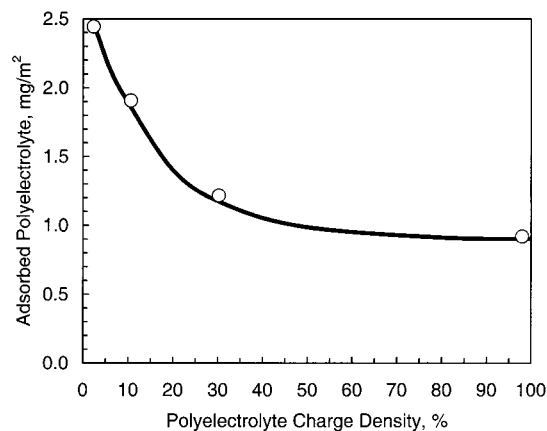(40) Kjellin, U. R. M.; Claesson, P. M.; Audebert, R. *J. Colloid Interface Sci.* **1997**, *190*, 476.

Figure 5. Plateau adsorbed amount for copolymers of AM-MAPTAC of different charge densities on mica as substrate.
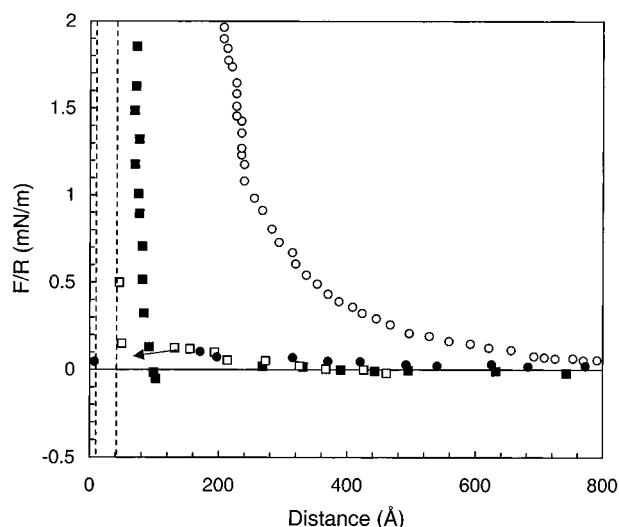
Figure 6. Force normalized by radius as a function of surface separation between mica surfaces precoated with various polyelectrolytes. The forces were measured across an aqueous 0.1 mM KBr solution. The polyelectrolytes were PCMA (●), AM-MAPTAC-30 (□), AM-CMA-10 (■), and AM-MAPTAC-1 (○). The arrow indicates an inward jump and the vertical lines the layer thickness for PCMA (left line), and for AM-MAPTAC-30 (right line).

Figure 7. Illustration of the configuration at the interface of adsorbed polyelectrolytes with low (a) and high charge density (b) (the circles with a + sign represent MAPTAC charged units).

Figure 8. Degree of charge compensation upon polyelectrolyte adsorption on mica: number of charged nitrogen atoms in the adsorbed layer per unit mica lattice charge for polyelectrolytes of various charge densities.

the steric force is steep it is clear that the adsorbed layer, unlike the ones formed by the more highly charged polyelectrolytes, is somewhat compressible. For AM-MAPTAC-1 no bridging attraction is observed. [25] Instead, a long-range steric force is the dominating feature. Clearly, the layer thickness, layer compressibility, and range of the steric/bridging force decreases with polyelectrolyte charge density, whereas the magnitude of the pull-off force increases. These trends are also predicted from Monte Carlo simulations. [38]

From the surface force and XPS results we can thus conclude that the decrease in the plateau value of the adsorption for cationicities between 1 and 100% is accompanied by a successively more flat adsorbed layer structure for surfaces in contact with low ionic strength aqueous solutions. Thus for the most highly charged polyelectrolyte the majority of segments are adsorbed directly to the surface. As the charge density is decreased, more and longer loops are formed as a consequence of the preferential adsorption of the charged segments. Figure 7 depicts how the polyelectrolyte configuration at the interface varies with the charge density of the polyelectrolyte.
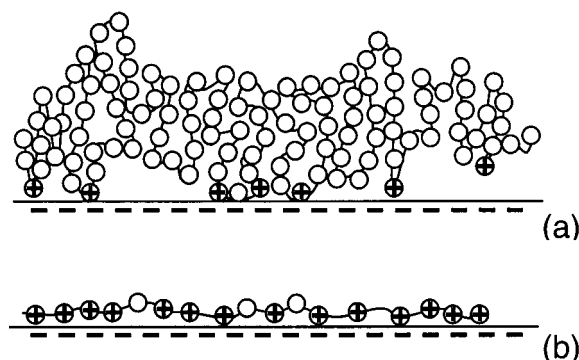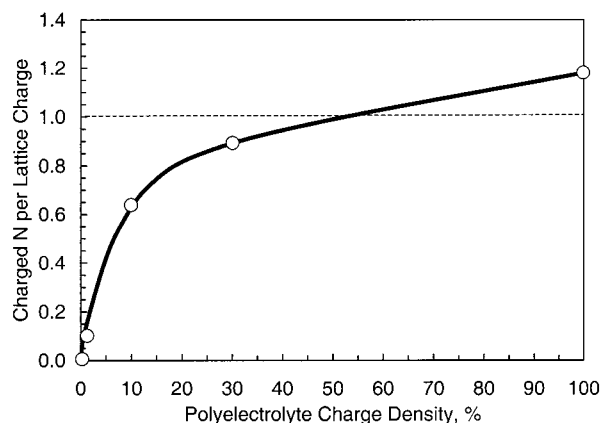
An interesting issue is to what extent the substrate charge is compensated (or neutralized) upon adsorption of polyelectrolytes with different cationicities. The degree of charge compensation upon adsorption can be estimated from the ratio of the number density of charged nitrogen atoms (from the adsorbed polyelectrolyte at the interface) and the mica surface lattice charge (2.1×10^{18} negative sites/m^2). Figure 8 shows how this ratio depends on the polyelectrolyte charge density. For low-charge-density polyelectrolytes the system is undercompensated (e.g., only ca. 10% of the surface charges are neutralized by an adsorbed polyelectrolyte with $\tau = 1\%$). This is so despite the fact that for this polyelectrolyte the adsorbed amount is the largest. Clearly, in this case the adsorbed amount is limited by the steric interactions between adsorbed chains rather than by charge compensation. As the polyelectrolyte charge density increases the degree of charge compensation due to the adsorption process increases. The mica surface charge is fully compensated when polyelectrolytes of ca. 30–40% charge density are adsorbed. Further increase of the polyelectrolyte charge density produces some overcompensation of charge (i.e., a recharging of the system) at high enough polyelectrolyte concentrations. This has also been confirmed by surface force measurements. [31]

We note that when surface forces are measured the polyelectrolyte-coated mica surface appears uncharged at a given polyelectrolyte concentration even though the XPS results clearly show that the charges of the adsorbed polyelectrolytes, for the low-charge-density cases, are not sufficient for neutralizing the mica lattice charge. The reason is that small ions, mainly H_3O^+, are also adsorbed

Table 2. The Charge Balance at the Interface between Mica and a 0.1 mM KBr Solution (σ_0 = lattice charge of mica, σ_d = net charge in the electrical double-layer, σ_p = charges of the adsorbed polyelectrolyte determined by XPS, σ_s = charges due to the presence of small ions in the adsorbed layer, $\Delta\sigma_s$ = difference between σ_s when polyelectrolyte is adsorbed with respect to the bare surface)

condition	σ_0 (C/m²)	σ_d (C/m²)	σ_p (C/m²)	σ_s (C/m²)	$\Delta\sigma_s$ (C/m²)
no polyelectrolyte	0.338	0.004	0	0.334	
AM-MAPTAC-100	0.338	0	0.388	−0.050	−0.384
AM-MAPTAC-30	0.338	0	0.296	0.041	−0.292
AM-MAPTAC-10	0.338	0	0.209	0.129	−0.205
AM-MAPTAC-1	0.338	0	0.033	0.305	−0.029

to the mica surface. The ion exchange occurring upon polyelectrolyte adsorption can be quantified by considering the charge neutralization condition:

$$\sigma_0 + \sigma_p + \sigma_s + \sigma_d = 0$$

where σ_0 = the lattice charge of mica, 0.338 C/m², σ_p = the charges of the adsorbed polyelectrolytes determined by XPS, σ_s = the charges due to the presence of small ions in the adsorbed layer, and σ_d = the net charge in the electrical double-layer, which is close to zero after polyelectrolyte adsorption as demonstrated by the data in Figure 6.

From the measured double-layer force before adding the polyelectrolyte it is possible to determine the effective mica surface charge. In 0.1 mM KBr one typically obtains a value of 0.004 C/m². The difference between the mica lattice charge and the effective charge is due to small ions accumulated next to the surface. Table 2 summarizes the ion exchange that occurs on the mica surface as a result of the polyelectrolyte adsorption. The table also includes $\Delta\sigma_s$ that is the difference between σ_s when polyelectrolyte is adsorbed with respect to the bare surface.

Clearly, in all cases adsorption of the cationic polyelectrolyte results in desorption of small cations from the mica surface, i.e., the entropy gain upon release of counterions is the main driving force for adsorption. This phenomenon is more important as the charge density of the polyelectrolyte is increased. The results agree with the experimental observations of Wang and Audebert[41] and theoretical calculations based on the SCF theory.[42,43] Further, in the case of AM-MAPTAC-100 some negatively charged ions (counterions to the polyelectrolyte) are incorporated in the adsorbed layer. This is a result of the recharging of the surface. Similar analyses of the ion exchange occurring at the solid−liquid interface due to protein adsorption have been carried out by Norde and Lyklema[44,45] and by Blomberg et al.[46]

Desorption of Preadsorbed Polyelectrolyte in NaCl Solutions. The effect of the ionic strength on the adsorption behavior of polyelectrolytes cannot be easily anticipated since it depends on the relative importance of electrostatic and nonelectrostatic interactions between the polymer and the surface.[6,36,47,48] Pelton,[49] Tanaka et al.,

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(46) Blomberg, E.; Claesson, P. M.; Fröberg, J. C. *Biomaterials* **1998**, 371.
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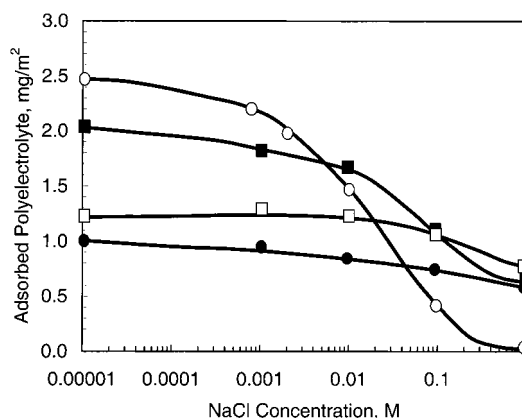
Figure 9. Desorption isotherms for copolymers of AM-MAPTAC on mica in NaCl solutions with different ionic strengths. The corresponding systems are AM-MAPTAC-1 (○), AM-MAPTAC-10 (■), AM-MAPTAC-30 (□), and AM-MAPTAC-100 (●).

[37,50] and Ödberg[51] have considered the desorption of cationic polyacrylamides by electrolytes and other species when the polymer is adsorbed on cellulosic fibers or polystyrene latex particles. In such cases the effects of the heterogeneity in the adsorbed conformation and the complex topography of the surface play an important role. When only electrostatic forces are important, the adsorbed amount decreases with increasing salt concentration. However, when also nonelectrostatic forces influence the adsorption process, the adsorbed amount may go through a maximum with increasing ionic strength. The adsorption and desorption processes are, as described by van de Steeg et al.,[42] a subtle balance of forces.

The theoretical modeling of polyelectrolyte adsorption is quite advanced,[48,52] and detailed theoretical predictions about the structure of the adsorbed layer under various conditions are available. For instance, Shubin and Linse[6] found that the adsorbed amount for AM-MAPTAC-3.4 on silica was roughly constant at 2.2−2.3 mg/m² when the salt concentration was below 10^{-2}−10^{-3} M. At higher ionic strengths the adsorbed amount decreased. The ellipsometric layer thickness increased smoothly with increasing salt concentration, in good agreement with theoretical predictions.

Here we study desorption of preadsorbed polyelectrolyte layers by addition of salt. In this case only desorption may occur independent of the nature of the polymer−surface affinity. This is the case since there are no polyelectrolytes present in solution that may adsorb when the ionic strength is changed. The results are summarized in Figure 9 that shows the desorption isotherms (as determined by XPS measurements) after immersing mica sheets with preadsorbed polyelectrolytes (from 50 μg/mL polyelectrolyte solutions) in electrolyte solutions at various NaCl concentrations.

In all cases the desorption starts at rather low salt concentration (10^{-3} M to 10^{-2} M NaCl, depending on the polyelectrolyte). As the polyelectrolyte charge density is increased, higher ionic strengths are needed in order to be effective in the removal of the polyelectrolyte from the surface. The polyelectrolyte of lowest charge density (=

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(50) Tanaka, H.; Ödberg, L. In *Fundamentals of Papermaking*; Baker, C. F., Punton, V. W., Eds.; Mechanical Eng. Publ. Ltd.: London, 1989; p 453.
(51) Ödberg, L. *Nordic Pulp Paper Res. J.* **2000**, *15*, 586.
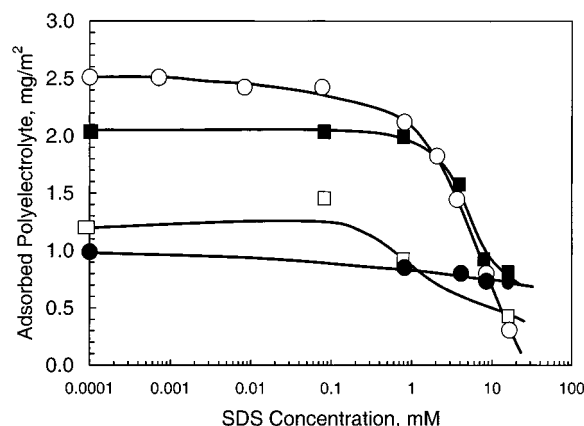(52) Böhmer, M. R.; Koopal, L. *Langmuir* **1990**, 1478.

Figure 10. Desorption isotherms for copolymers of AM-MAPTAC on mica in SDS solutions of different concentrations. The corresponding systems are AM-MAPTAC-1 (○), AM-MAPTAC-10 (■), AM-MAPTAC-30 (□), and AM-MAPTAC-100 (●).

1%) is close to completely desorbed in 1 M NaCl solution. However, for higher cationicities some polyelectrolyte still remains adsorbed on mica at the same ionic strength. The desorption is due to screening of the electrostatic interactions between the polyelectrolyte and the surface as the ionic strength of the medium is increased. Surface force measurements have demonstrated that the swelling of preadsorbed polyelectrolyte layers due to an increased ionic strength is rather limited for AM-MAPTAC-100,[38] whereas a significant swelling is observed for AM-MAPTAC-1.[25] This latter observation is consistent with the findings of Shubin et al.[6] using AM-MAPTAC-3.4 and ellipsometric measurements.

Desorption of Preadsorbed Polyelectrolyte in SDS Solutions. The desorption isotherms of preadsorbed AM-MAPTAC polyelectrolytes layers on mica due to addition of the anionic surfactant sodium dodecyl sulfate (SDS) is shown in Figure 10. It seems that hardly any desorption occurs until the SDS concentration has reached about 8 × 10⁻⁴ M (0.1 units of cmc). At higher SDS concentrations the desorption occurs more readily as the charge density of the polyelectrolyte is reduced. In particular, AM-MAPTAC-1 is largely desorbed in SDS solution at a concentration of 1.6×10^{-2} M (twice the cmc) or above.

The mechanism leading to desorption of polyelectrolyte upon addition of surfactant is somewhat different than that leading to desorption due to addition of inorganic salt. In both cases the increased ionic strength screens the electrostatic attraction between the polyelectrolyte and the surface. However, the surfactant also forms complexes with the polyelectrolyte, and it is thus incorporated in the adsorbed layer. The driving force for association is electrostatic interactions between surfactant headgroups and charged polyelectrolyte segments as well as hydrophobic interactions between the surfactant tails (which leads to their association close to the polyelectrolyte). The incorporation of negatively charged surfactants into the layer leads to a decreased affinity of the polyelectrolyte−surfactant complex to the negatively charged surface, which facilitates desorption. Hence, it is no surprise that the ionic surfactant is more efficient in removing the polyelectrolyte from the surface than the inorganic salt. Note, however, that the complexes formed by high-charge-density polyelectrolytes and oppositely charged surfactants are insoluble over a wide range of SDS concentrations,[53,54] which is one important reason
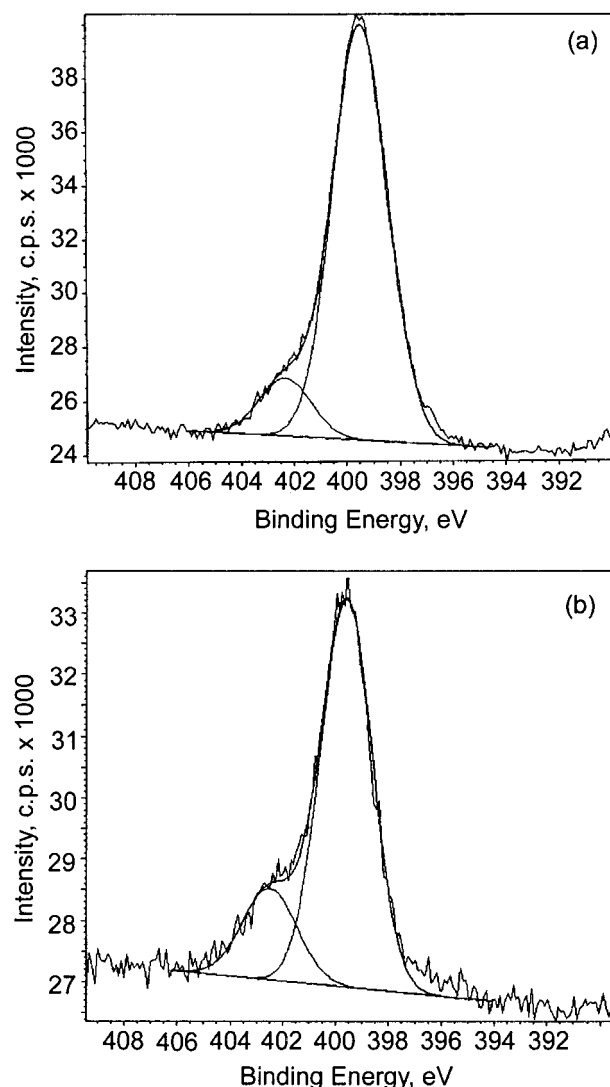

Figure 11. Detailed nitrogen 1*s* spectra for AM-MAPTAC-10 adsorbed on mica before (a) and after desorption in 16.2 mM SDS solution (b). Notice that as desorption occurs the peak corresponding to ammonium nitrogen (at a binding energy of ca. 402.5 eV) becomes more prominent as compared to the amide nitrogen peak (at a binding energy of ca. 399 eV).

for the difficulty of desorbing these polyelectrolytes by addition of SDS.

In both of the desorption cases considered in this investigation, i.e., when desorption is driven by addition of electrolytes or by addition of surfactants, it was noticed in the XPS spectra that as desorption proceeds the peak corresponding to ammonium nitrogen is reduced to a lesser extent as compared to the amide nitrogen peak (see Figure 11). It should be recalled that the N 1*s* signal in the form of amide groups (uncharged) appears as a peak at a binding energy of about 400 eV whereas that of ammonium groups (positively charged) is shifted toward higher binding energy.[15]

The observed behavior can be explained by the fact that each of the polyelectrolyte samples is inherently polydisperse and therefore, for a sample of a given average charge density, the less charged molecules tend to desorb first leaving the more charged ones on the surface (and thus the ammonium nitrogen peak appears more prominent for samples that have been subject to desorption).

(53) Dedinaite, A.; Claesson, P. M. *Langmuir* **2000**, 1951.

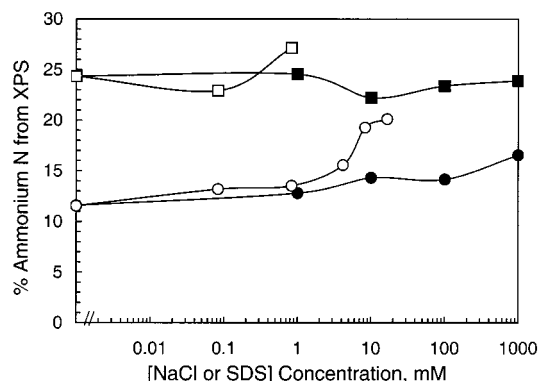(54) Dedinaite, A.; Claesson, P. M.; Bergström, M. *Langmuir* **2000**, *16*, 5257.

Figure 12. Relative percentage of ammonium nitrogen peak calculated by deconvolution of the N1s XPS signal for adsorbed layers of polyelectrolytes of 10 and 30% charge densities before and after desorption with NaCl or SDS at various concentrations. The corresponding systems are AM-MAPTAC-10 desorbed in SDS (○), AM-MAPTAC-10 desorbed in NaCl (●), AM-MAPTAC-30 desorbed in SDS (□), and AM-MAPTAC-30 desorbed in NaCl (■).

Figure 12 illustrates further this phenomenon for the polyelectrolytes of 10% and 30% charge density (the 1% and 100% charge density cases are not included since the relative strength of the ammonium nitrogen signal is too low or too high, respectively). The relative percentage of ammonium nitrogen peak was calculated by deconvolution of the N1s peaks allowing the estimation of the relative distribution of nitrogen-containing groups in the adsorbed layer as reported in Figure 12.

Surface force measurements have provided information on how the structure of the adsorbed layer is changed by addition of surfactant. For AM-MAPTAC-1 the layer thickness decreases smoothly with increasing surfactant concentration as shown in Figure 13. This is attributed to the gradual desorption of the polyelectrolyte. For AM-CMA-10[40] (structurally similar to AM-MAPTAC-10) and AM-MAPTAC-30[39] a strong swelling occurs prior to desorption. A strong swelling has also been observed for a 100% charged polyelectrolyte with structure similar to MAPTAC.[54,55] In this latter case pronounced oscillations in the force curve were observed which is indicative of the characteristic internal structure of the adsorbed layer. Much of the surface force data obtained for polyelectrolyte–surfactant systems has recently been reviewed.[56]

Conclusions

The adsorption of cationic AM-MAPTAC polyelectrolytes of different charge densities from low ionic strength solutions on negatively charged mica surfaces is of the high-affinity type. This is due to the strong electrostatic attraction between the macroion and the surface. In the case of polyelectrolytes of low charge density the adsorption is limited by steric interactions between the adsorbed
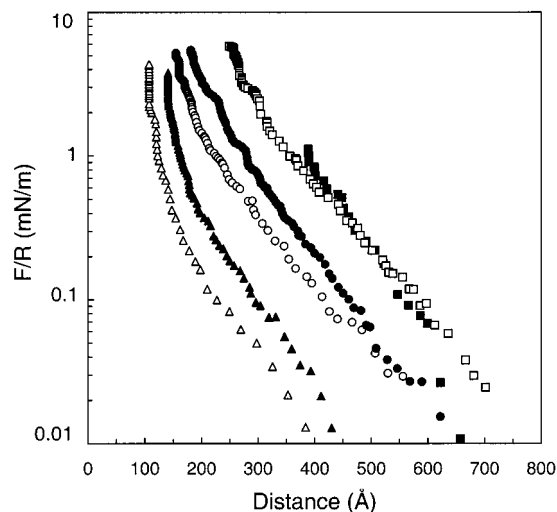
(55) Claesson, P. M.; Bergström, M.; Dedinaite, A.; Kjellin, M.; Legrand, J. F.; Grillo, I. *J. Phys. Chem. B* **2000**, *104*, 11689.
(56) Claesson, P. M.; Dedinaite, A.; Poptoshev, E. In *Physical Chemistry of Polyelectrolytes*; Radeva, T., Ed.; Marcel Dekker Inc.: New York, 2001; Vol. 99.

Figure 13. Force normalized by radius as a function of surface separation between mica surfaces precoated with AM-MAP-TAC-1. The forces were measured across an aqueous solution containing SDS at the following concentrations (relative to the cmc): no SDS (■), 0.1 cmc (□), 0.3 cmc (●), 0.75 cmc (○), 1 cmc (▲), and 2 cmc (△).

chains as evidenced from the fact that only a small fraction of the mica lattice charge is compensated when the adsorption plateau value has been reached. Overcompensation of the substrate surface charge was evidenced when the most highly charged polyelectrolyte was allowed to adsorb on mica. The polyelectrolytes adopt a flat conformation at the solid–liquid interface when the charge density is high, whereas more extended conformations dominate in the case of low-charge-density polyelectrolytes.

The exposure of mica with preadsorbed polyelectrolyte to aqueous NaCl or surfactant (SDS) solutions induces partial desorption of the polyelectrolyte, and more readily so the lower the charge density of the polyelectrolyte. In the case of NaCl addition, the desorption is due to screening of the attractive electrostatic surface–polyelectrolyte interaction. This effect also contributes to the desorption due to addition of surfactant. However, the association between polyelectrolytes and surfactants, resulting in incorporation of negative charges in the adsorbed layer, is also of prime importance for the desorption by means of surfactant addition. As a result the polyelectrolyte is more easily desorbed by addition of an anionic surfactant than by addition of inorganic salt.