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Molecular Mechanisms Controlling the Self-Assembly Process of Polyelectrolyte Multilayers

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ABSTRACT: The distance dependent interaction between polyelectrolyte-covered mica surfaces in aqueous solution was investigated with the surface forces apparatus. We find the following: (i) The surface charge changes sign, when an oppositely charged polyelectrolyte from a concentrated polyelectrolyte solution is adsorbed. (ii) Tails and loops of the adsorbed polyions dangle into the bulk phase, inducing a small steric force. If polycations and poyanions are adsorbed on top of each other, a strong short range attractive force is seen due to ion-pair formation after crossing a large repulsive electrostatic/steric barrier. (iii) Obviously, after polyelectrolyte adsorption, there are still nonoccupied binding places (point charges) on the substrate. We show that these adsorption properties regulate the build-up of polyelectrolyte multilayers: Ion pairs between oppositely charged polyion segments and the substrate are formed, until the surface charge is inversed. The electrostatic barrier limits the adsorbed amount, guarantees the equal thickness of consecutively adsorbed layers, and furthermore causes a strong adsorption hysteresis, which leads to conveniently stable polyelectrolyte multilayers in various environmental conditions.

Introduction

Polyelectrolyte multilayers formed by the alternating adsorption of polycations and polyanions have been recently introduced as a simple and powerful method for surface modification.[1] With these charged linear chain molecules, various biocompatible surfaces have been prepared.[2] Also, the polyelectrolyte multilayers are interesting from a materials engineering point of view, since films consisting of functionalized synthetic polymers can be conducting[3] or electroluminescent[4] (the latter after an elimination reaction). Already in the first publication it has been demonstrated that the amount of adsorbed polycation (respective polyanion) is reproducible for each successive adsorption step.[1]

Intuitively, for the preparation of polyelectrolyte multilayers the change of surface charge due to adsorption of oppositely charged polyelectrolyte (charge overcompensation) is essential. Otherwise one could not add as many polycation/polyanion layers as one wishes. Polyelectrolyte desorption during the washing after each adsorption step would be most inconvenient, but luckily the adsorbed layer remains on the surface when the solid is immersed into clean water, a behavior which can be described from a thermodynamic point of view as an adsorption hysteresis. Less obvious is the role of surface heterogeneity and the binding mechanism; here formation of ion pairs due to local electrostatic attraction as discussed in the Theoretical Background is most likely. Further open questions are how tight the polyelectrolytes are bound to the surface, how far loops and tails extend into the water, and how they influence the multilayer build-up.

The order of the multilayer perpendicular to the surface has been investigated with neutron and X-ray reflection.[5] It has been shown that no short range order exists between adjacent polycation/polyanion bilayers; i.e., there is no Bragg peak when every polyanion is deuterated. Obviously, the positively and negatively charged chains mingle. However, a superlattice structure could be detected, indicating long range order between every fourth or every sixth layer (i.e., with every second or every third polyanion layer deuterated). Layer thickness and interpenetration depend very little on the molecular weight of the polyelectrolytes, if they are adsorbed from a salt-free solution.

In this paper, we shall concentrate on polyelectrolyte adsorption at the solid/fluid interface and how this self-assembly process controls the adsorbed amount of polyelectrolyte and the internal structure of a polyelectrolyte multilayer.

Polyelectrolyte adsorption from a concentrated polyelectrolyte solution onto an oppositely charged surface is expected to change the surface charge. To show this charge overcompensation, the interaction between different surfaces, i.e., clean mica and polycation-covered mica and polycation- and polyanion/polycation-covered mica is investigated in the surface forces apparatus (SFA). To find out how far tails and loops extend into the bulk phase after adsorption, identical surfaces consisting of polycation monolayers or polyanion/polycation bilayers, respectively, are studied. To probe the stability of the chain conformation, the surfaces are dried and investigated in polyelectrolyte-free solution, yet no effect of the surface treatment was found. We observe a subtle interplay of electrostatic repulsion, steric interaction due to dangling tails and loops, as well as a strong short-range attractive force, the latter only when the surfaces are covered with polyelectrolyte bilayers. An amazing property of this attractive interaction is its independence of ionic strength, a feature indicative for the formation of localized ion pairs between oppositely charged polyions. From the range of the attractive "ion-pair force" we shall conclude that after adsorption of polyanions onto a polycation-covered surface both positively and negatively charged polyions coexist on the surface and even dangle into the bulk phase. To demonstrate the dominant role of ion-pair formation on the build-up of polyelectrolyte multilayers

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and to investigate the role of chain conformation and entropy, we adsorb various polycations on polycation-terminated polyelectrolyte multilayers.

Theoretical Background

The simplest adsorption theory of polyelectrolytes may be called the ion-exchange model:[6] due to entropy the adsorbed polyelectrolyte successfully competes with small monovalent ions and neutralizes the surface charges. This view is qualitatively correct, even if chain configurations are taken into account,[7,8] as well as monovalent counterions, which lead to charge regulation and potential screening of both the surface and the polyion. Experimentally the ion-exchange model has been qualitatively verified, higher charged surfaces adsorb more oppositely charged polyelectrolyte, and also a variation of the polyion charge by varying the pH can be explained.

However, there are some features which cannot be understood in the framework of the simple ion-exchange theory: Certain polycations adsorb on net positively charged TiO_2,[9] where positive and negative point charges coexist. A polycation being very close to such a heterogeneous surface sees both attractive negative and repulsive positive charges and forms ion pairs with the negative charges. This behavior is supported by theoretical studies.[10,11]

Another feature unpredicted by the simple ion-exchange theory is the experimentally found charge overcompensation occurring on polyelectrolyte adsorption.[12,13] In this surface forces work, the surfaces are immersed into solutions of oppositely charged polyelectrolyte. With increasing polyelectrolyte concentration, the adsorption increases, too, until saturation occurs. Accordingly, the surface charge decreases, changes sign, and increases again. Poly(styrenesulfonate) covered surfaces[12] (the same polyanion used in the experiments shown below) never showed an attractive force. In the system studied by Claesson's group,[13] an attractive force occurred which was attributed to bridging forces—no indication of hydrophobicity was found. Then, as theoretic models[8] got more elaboarate, a slight charge overcompensation was explained in terms of a balance in entropic and electrostatic energy. Yet careful adsorption studies of random copolymers with charged and neutral monomers onto latex particles with fixed surface charge show an even more complicated picture.[14] The minimum overcompensation occurred in the case when the average distance between the charges on the chains and those on the surface matched. Again, this behavior is suggestive of the formation of ion pairs. In such a case, a mean-field description assuming a smeared surface charge[8] is bound to fail. Therefore, it was concluded that "it is not the net surface charge which determines the adsorption, but rather the possibility to form ion pairs between polymer and surface groups."[6] Ion pairs are defined as contacting molecular groups of opposite charge; the electrostatic binding energy is very weak, $\approx kT$.[15] The polyelectrolyte sticks to the surface since there are many of these bonds, not because these bonds are strong.

Yet, as an estimate for the amount of adsorbed polyelectrolyte, the ion-exchange model is still rather good. For this apparent contradiction the following explanation was suggested:[6] Equilibrium adsorption is not obtained, but the polyelectrolyte molecules adsorb only until they are electrostatically repelled from the surface. If the polyelectrolyte is adsorbed from a solution of high ionic strength, one can adsorb more material onto the surface, due to the more efficient shielding of the electrostatic interaction. If the adjacent solution is subsequently diluted or the pH changed, the polyelecytrolyte does not necessarily desorb; indeed the pronounced adsorption hysteresis found in many systems is typical for kinetically hindered equilibria. The situation is somewhat reminiscent to the experimentally observed stability of charged particles, which are attracted by long range van der Waals forces but cannot aggregate due to the electrostatic barrier.[15]

Lacking a clear view of the underlying molecular processes, i.e., the distribution of the positively and negatively charged monovalent ions close to the surface and within the chain as well as chain configurations and rearrangements, we shall describe the adsorbed amount of polyelectrolyte found experimentally as "kinetically hindered". This phrase was chosen to highlight our awareness that by reduction of the activation energy more polyelectrolyte can be bound onto the surface. The activation energy is due to the electrostatic barrier between the surface and the polyion exhibiting the same sign of charge as well as by the electrostatically determined chain conformation of the polyion. If no electrostatic barrier would exist, we would obtain the (possible fictional) "true thermodynamic equilibrium". In the "true thermodynamic equilibrium" the amount of adsorbed polyelectrolyte would be a reversible function of polyelectrolyte and ion concentration in the solution and of the pH. If we approach two polyelectrolyte-covered surfaces in the SFA, we surmount the electrostatic barrier mechanically.

Materials and Methods

The positively charged poly(allylamine) hydrochloride (PAH, $M_W = 50000-60000$), the positively charged poly(L-lysine) hydrobromide (PL, $M_W = 40\,000$), and the negatively charged poly(styrenesulfonate) sodium salt (PSS, $M_W \approx 70\,000$) were obtained from Aldrich (Sternheim, Germany). The positively charged poly(2-vinylpyridine) (PVP, $M_W \leq 50\,000$) was from Bachem-Biochemika. PVP was adsorbed from a pH 2 aqueous solution; the pH was adjusted with HCl. The chemical structures of the monomer units are shown in Figure 1. The polycations were used without further purification. PSS was dialyzed.[16] For fluorescence experiments, PAH was labeled with the dye fluorescein isothiocyanate (about one in 400 monomer units).[16] Water was filtered in a Milli-Q unit; for surface forces experiments it was additionally distilled from $KMnO_4$ solution. The NaCl was from Merck; purity was above 99% (p.a. quality).

A polyelectrolyte layer on a glass, mica, or polyelectrolyte-multilayer surface was prepared by immersing the substrate in 0.01 monomol/L polyelectrolyte solution for half an hour. Then the substrate is retracted, washed in three beakers with clean water (each time one min), and eventually dried by a gentle stream of nitrogen.

Polyelectrolyte multilayers were built on clean glass or Si wafers, which were covered with a monolayer of positively charged poly(ethylenimine) from Aldrich. Poly(ethylenimine) forms extremely stable first layers, maybe because it is a branched polycation. Then PSS/PAH multilayers were formed as described above, yet the polyelectrolyte solutions contained 1 M NaCl in order to obtain thicker layers. Multilayers were built until they had a thickness that could be easily and exactly measured with X-ray reflection (see below), i.e., 13−17 nm.

The **surface force apparatus** (SFA) (Mark 4, ANUTECH, Australia) is a well-established tool for the investigation of surface interactions.[15,17] Briefly, the force is measured as a function of distance between two molecularly smooth surfaces in a crossed-cylinder configuration. The distance *D* is mea-

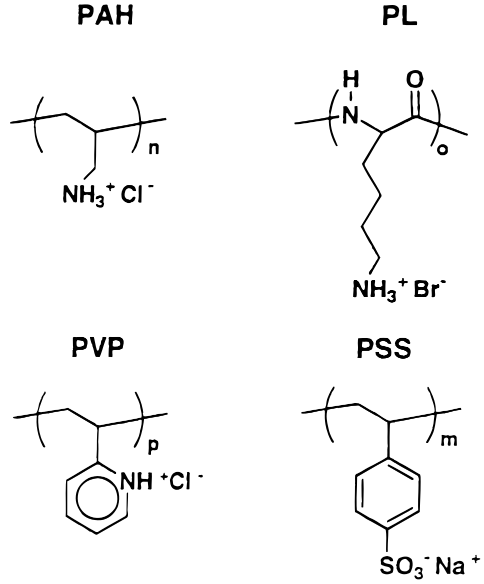

Figure 1. Chemical structures of the monomer units of the polyelectrolytes used: positively charged PAH, PL, and PVP as well as negatively charged PSS.

sured interferometrically[18] with a resolution of ≈0.2 nm. One of the surfaces is mounted on a cantilever spring of known spring constant; the force is determined from the spring deflection with a resolution of 10^{-7} N. The data are presented as the force acting between the surfaces, $F(D)$, normalized by the mean radius R of curvature of the surfaces (1−2 cm). From the normalized force the free energy of interaction per unit area between flat surfaces can be calculated:

$$F(D)/R = 2\pi G(D) \quad (1)$$

Mica is used as a solid surface, in water it is negatively charged. The polycation layers were prepared either (i) outside the SFA, then the forces were measured in a simple NaCl solution, or (ii) inside the SFA, by immersing the clean mica surfaces in a polycation solution and waiting for half an hour before starting to measure the interaction. For experiments with polyelectrolyte bilayers consisting of a polycation with a polyanion on top, the polycation layer was always prepared outside the SFA. The polyanion layer was prepared either (i) outside the SFA, then the experiments were performed in NaCl solution, or (ii) inside the SFA, then the measurements were done in solution containing both polyanion and NaCl. The data shown are the cumulative results of at least two different experiments (i.e., two different sets of mica surfaces).

Small angle X-ray (SAXS) measurements were performed with a Siemens D-500 powder diffractometer in a $\theta/2\theta$ configuration using copper Kα radiation with a wavelength of 0.154 nm, data acquisition via a DACO-MP interface connected to a personal computer. With this method the thickness of a homogeneous, smooth, nonstructured organic layer (i.e., a polyelectrolyte multilayer) on a glass substrate can be determined since refraction occurs only at the air/layer and at the layer/glass interface. Noting that the electron density of organic materials is generally below the one of glass and, furthermore, that for X-rays the electron density is directly proportional to the index of diffraction,[19] the thickness l of the layer can be determined according to

$$Q_{\min}\cdot l = (2n - 1)\pi \quad (2)$$

Here, $Q_{\min}$ is the value of the wave vector transfer Q ($Q = 4\pi/\lambda \sin(\theta)$), at which minima in the reflected intensity occur, and n is the order of these interference minima.

Fluorescence measurements were performed with a home-built setup. The angle between incident light and the fluorescence detector is 90°.

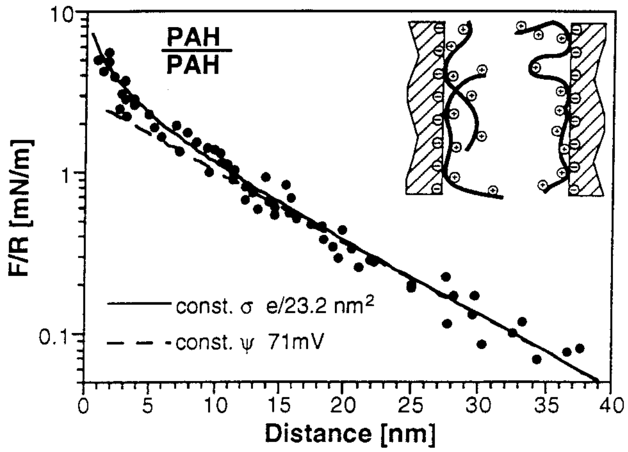

Figure 2. Normalized force between two PAH-covered mica surfaces immersed in 1 mM NaCl solution as a function of the surface separation as measured on approach. For simulations of this force curve, we assume that the force is of electrostatic origin, the plane of charge coincides with the surfaces, and charge regulation occurs as the surfaces get close. Shown are the best fits assuming constant surface potential and constant surface charge, respectively (Experimental decay length, 9.8 nm; theoretically expected Debye length in 1 mM NaCl solution, 9.6 nm). If larger compressive forces are used than those shown in the figure, the force is no longer reproducible, the polyelectrolytes are pushed out of the contact area.

Results

The Interaction between two Polycation Monolayers. The distance dependent forces between two PAH-covered surfaces are shown in Figure 2, measured on approach. The distance $D = 0$ nm corresponds to contacting mica surfaces in aqueous solution. Yet, for the interaction forces, it does not matter, if the PAH layer is prepared inside or outside the SFA (after adjusting for $D = 0$ nm). Also, the electrostatically repelled polyelectrolytes in the solution do not influence the surface interaction. Obviously, no desorption occurs on washing and drying. The adsorbed layer in air is ≈0.7 nm thick and slightly hydrophobic. The chains lay flat on the surface.[16] Reimmersed into water, it hydrates again, and as we shall show later, some chains dangle into the solution.

First, let us concentrate on the force as measured on approach of the surfaces. At large separations, there is an exponentially decaying force of electrostatic nature. Allowing for charge regulation at small separations, one can even fit the whole force curve assuming only electrostatic interactions[20] (cf. Figure 2). We show numerical simulations for the two extrema: The smallest repulsive force is obtained assuming constant surface potential (causing a decrease of surface charge when the surfaces approach). The largest repulsion is obtained with constant surface charge (leading to ever-increasing surface potentials the closer the surfaces get).

Yet, not all the energy invested to compress the surfaces can be regained on separation (cf. Figure 3a). Even though the simulation in Figure 2 does look rather nice and is mathematically correct, it is physically wrong, since there is a very different force when the surfaces are separated. The smaller force needed to separate the surfaces cannot be explained by any electrostatic model based on mobile diffuse counterions. These adapt quickly to the new equilibrium configuration. However, the polyelectrolyte molecules are less mobile, and it is very likely that not all charged chains

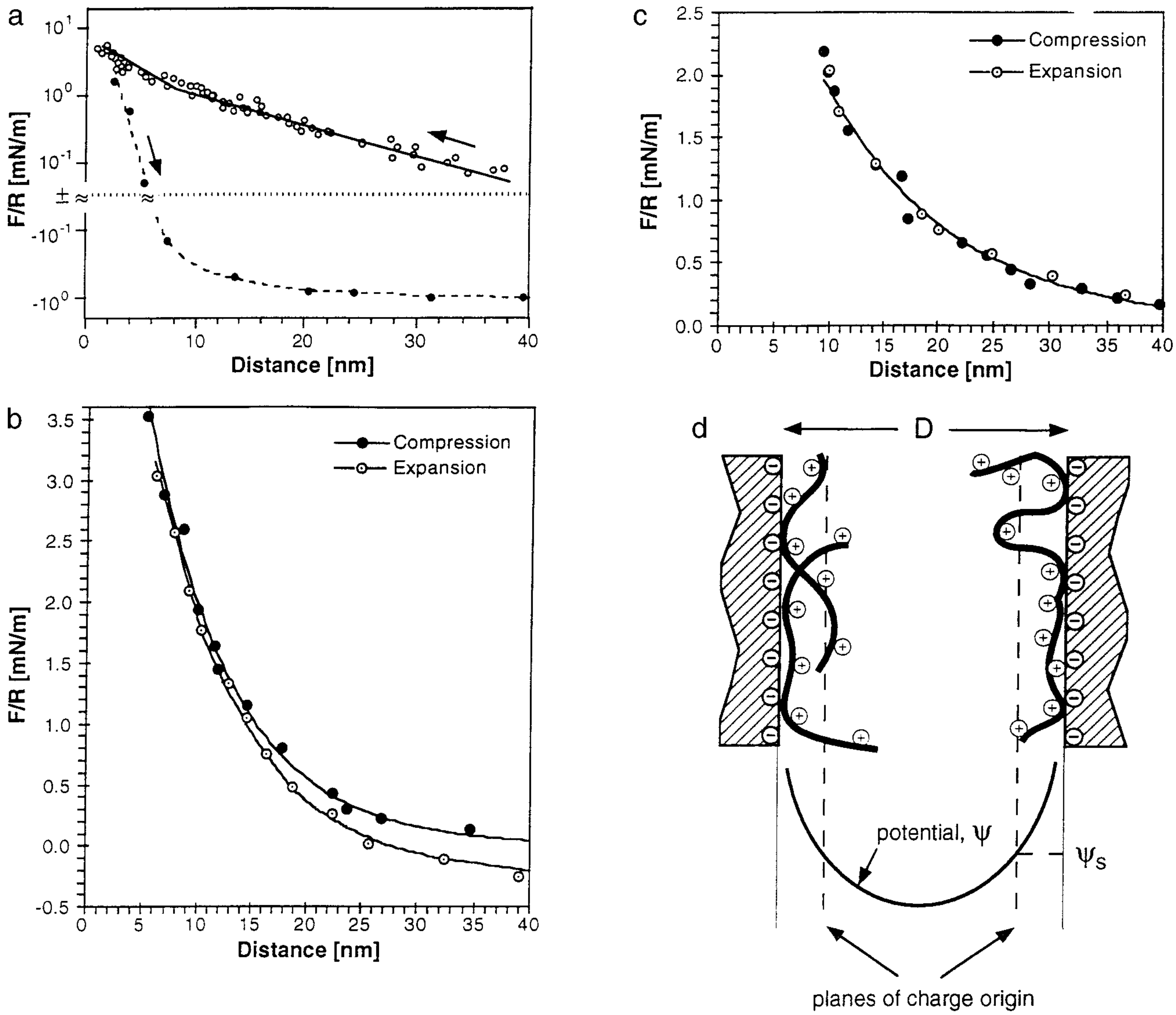

Figure 3. (a) Normalized force curve of Figure 2 as measured both on approach and on separation. A pronounced hysteresis is found, which is indicative of polyelectrolyte chain interaction. (b) and (c) Force cycles, during which the surfaces are approached up to a finite distance. (b) A hysteresis occurs when the minimum distance is 5 nm. (c) If the minimum distance is 10 nm, the forces on approach and on separation are identical, indicating that the long-range part of the force is purely electrostatic. (d) Definition of the plane of origin of the surface charge.

lie flat on the surface, but some of them dangle into the solution. To find the extension to which the chains and tails protrude into the solution, force cycles were performed, during which the surfaces were approached up to a finite distance. As parts b and c of Figure 3 demonstrate, the force cycles were reversible if the smallest surface separation is 10 nm, yet they are irreversible if the minimum separation is 5 nm. Thus, we conclude, that mobile chains extend as far as 2.5−4 nm from each surface.

The picture thus obtained is sketched in Figure 3d. Extremely close to the surface, the interaction is controlled by both entropic contributions due to chain compression and electrostatic contributions. The plane a few nanometers above the mica surface, where the chain conformation is the one of an isolated surface and beyond which entropic contributions cease, we shall call the plane of origin of surface charge. Beyond this plane the interaction is purely electrostatic.

The force necessary to compress the protruding chains appears to be very small. Since too little is known about the charge regulation occurring when the surfaces approach, it is impossible to quantify a steric force. Also, we are not sure, if we actually measure pure equilibrium forces (not very likely) or if we have viscous contributions (more likely).

Therefore, all we can really say with some confidence is that the interaction is of pure electrostatic nature at surface separations above $D = 8$ nm. If we define a plane of origin of surface charge away from the surface, this plane exhibits a small surface potential of ≈34 mV (corresponding to one electronic charge per 60.8 nm^2).

The Interaction between a Polycation Monolayer and Pure Mica. To demonstrate that indeed charge overcompensation occurs, i.e., that the PAH-covered surfaces are positively charged, the interaction between a polycation-covered surface (prepared outside the SFA) and a clean mica surface was measured (cf. Figure 4). In various experiments, one observes consistently a long-range attraction starting at $D \approx 40$ nm. Inconveniently, this attraction is too small to be quantified, yet its long range is a proof of the electrostatic nature of the attractive force. The adhesive force is rather small, indicative of a small net charge and the

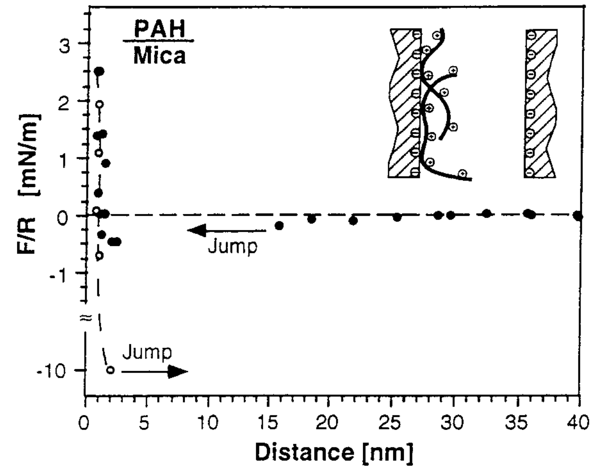

Figure 4. Normalized force between a positively charged PAH-covered surface and a negatively charged clean mica surface immersed into 1 mM NaCl solution as function of the distance. The force is unambiguously attractive for distances smaller than 25 nm, indicating the electrostatic origin of this force (spring constant, 477 N/m); however the absolute values are too small to be quantified.

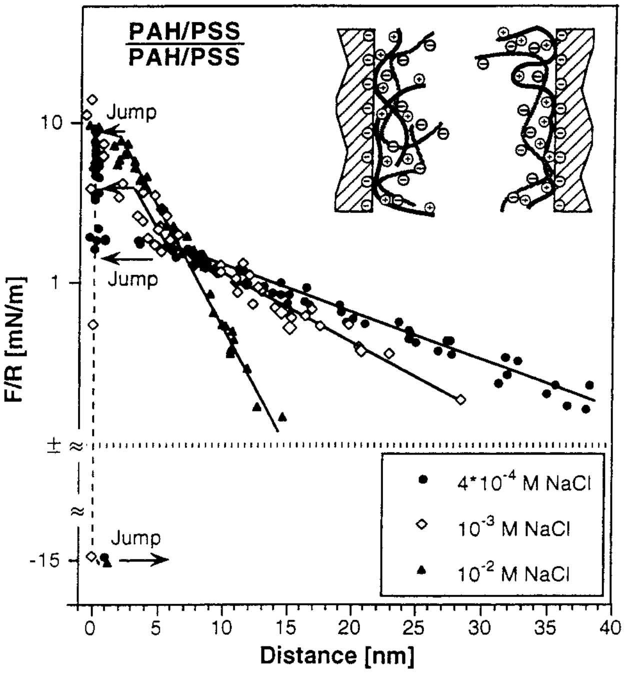

Figure 5. Normalized force between two PAH/PSS-covered mica surfaces as a function of the surface separation as measured on approach. The surfaces were immersed in salt solution of various ionic strengths as indicated. The straight lines are fits to an exponentially decaying force of electrostatic origin. The experimentally determined decay lengths are as follows: 0.4 mM, 15.3 nm (theory, 15.2 nm); 1 mM, 10 nm (theory, 9.6 nm); 10 mM, 3.0 nm (theory, 3.0 nm). Note, that the adhesion is too strong for a van der Waals force; amazingly, one obtains the same adhesion for all ionic strengths.

formation of a few ion pairs between mica and the PAH monomers.

The Interaction between two Polycation/Polyanion Bilayers. Figure 5 shows the distance dependent interaction forces between PAH/PSS bilayers immersed in aqueous solution with varying electrolyte concentration. Similar to the findings with PAH-covered surfaces, no effect of dissolved polyanion in the solution is observed. The layers deform irreversibly even under small compressive forces. Therefore the absolute thickness of the bilayers could not be determined. In Figure 5 $D = 0$ nm corresponds to the position of the adhesive minimum, which seems to be constant for all NaCl concentrations investigated (±0.25 nm).

For surface separations exceeding ≈ 7 nm, there is a long range repulsive force of electrostatic origin, which decays exponentially with the Debye length as is clearly seen on varying the NaCl concentration. At close approach, the surfaces jump into adhesive contact. With increasing NaCl concentration, one has to push with more force and to smaller separations, until the onset of the attraction. All force curves intersect at a separation of about 7 nm, a rather unusual behavior. Most surprisingly, the adhesion is independent of the NaCl concentration and is also rather large, 15 mN/m.

Superficially, the distance dependent force curve resembles the one obtained between clean mica surfaces or supported amphiphilic bilayers in water.[15,21,22] For those surfaces, the interaction is a superposition of long range repulsive electrostatic and short range attractive van der Waals forces (this concept is also known as the DLVO theory[15]). We shall try this approach, even though the adhesion is too large to be attributed to dispersion forces between organic surfaces in water (the largest adhesive force measured between extremely smooth organic surfaces was 6 mN/m[23]).

Again the electrostatic repulsion is simulated considering charge regulation of the surfaces. The potential plane is chosen to coincide with the surface planes; any chains protruding into the subphase are neglected. As Figure 6 shows, these simulations do look just as nice as the one obtained with polyelectrolyte monolayer covered surfaces (cf. Figure 2). The parameters, which describe the measurements best, are listed in Table 1. With increasing ionic strength, the surface charge increases, and the surface potential remains more or less constant. Therefore, we may claim that the whole repulsive force curve is of electrostatic origin, based on the quality of the simulation. But forewarned by the experiments with the polycation-covered surfaces, we better check if the physics makes sense. With the PAH-covered mica surfaces, we also found good simulations based on pure electrostatic forces, yet the irreversibility of approach/separation cycles was a clear indication for slowly relaxing polymer chains dangling into the subphase.

According to DLVO theory, we have an additive superposition of long-range repulsive electrostatic and short-range attractive van der Waals forces. Therefore, we perform the cross-check best at $D = 0$ nm. The attractive van der Waals forces are independent of ion concentration (in practice, they often decrease due to ion adsorption). For the repulsive electrostatic force, we determined that it increases by about an order of magnitude at $D = 0$ nm (cf. Table 1). However, we find experimentally that the adhesion remains constant. Obviously, additive superposition of an increasingly repulsive electrostatic and a constant attractive force does not lead to constant adhesion. Concluiding, superficially the experiments with polycation- or polycation/polyanion-covered surfaces suggest a DLVO-type interaction, yet close inspection leads to contradictions, and we have to consider steric forces and chain rearrangement.

Therefore, we have to think of another cause for the adhesion besides van der Waals forces. During the

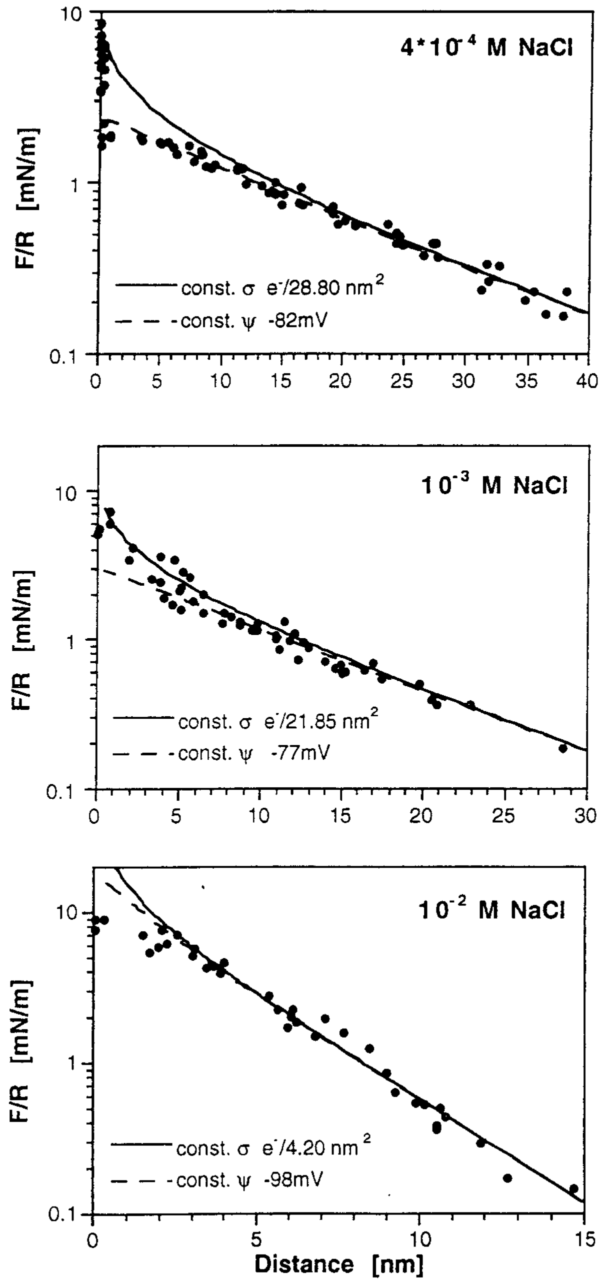

Figure 6. Normalized force between two PAH/PSS-covered mica surfaces as shown in Figure 5, together with simulations. For simulations of this force curve, we assume, that the force is of electrostatic origin, the plane of charge is assumed to coincide with the surfaces. Shown are the best fits assuming constant surface potential and constant surface charge, respectively. The Debye lengths are given in the caption to Figure 5.

Table 1. Parameters Obtained by Simulations of the Electrostatic Repulsion between two PAH/PSS Layers (cf. Figure 5) Allowing for Charge Regulation[a]

NaCl (mM)	potential ψ (mV)	surface charge (e^-/nm^{-2})	charge regulation mechanism	F/R at $D = 0$ (mN/m)
0.4	−82	−1/28.8	constant potential	1.3
1	−77	−1/21.85	inbetween	2
10	−98	−1/4.2	undetermined	10−20

[a] The potential planes are assumed to coincide with the surfaces.

adsorption of the subsequent layer, the chains mingle.[5] Therefore, the coexistence of polycations and polyanions on the surfaces is most likely. Yet mingling of the chains from apposing surfaces as a binding mechanism is not very likely; since the surfaces jump apart at once, one finds no time effects typical for steric interactions. Also, the surfaces can be brought into contact and be separated as often as one wants. Actually, the attractive force is rather reminiscent of a bridging force observed between adsorbed polymers in a bad solvent.[24] Such forces may be found if the segment−surface interaction is attractive *and* the apposing surface has unoccupied or exchangeable binding sites; in this case some polymer chains will form bridges between the two surfaces and give rise to an attractive bridging force.[15,25] The attractive segment−segment interaction is most likely the formation of ion pairs between anionic and cationic monomer units (presumably not between cationic monomer units and negatively charged mica, since we do not observe any adhesion between two PAH monolayers, yet generally we cannot exclude this mechanism, since with other polycation-covered mica surfaces such effects were found[13]). The long range of the bridging force suggests that the ion pairs are not aligned excactly in the midplane between the surfaces but are randomly distributed between the two mica/polymer interfaces. Since the observed adhesion is independent of ionic strength, monovalent ions are not involved in the segment−segment attraction.

To estimate the lateral density of the ion pairs formed between the surfaces, let us assume that the binding energy of a $(-NH_3^+) \leftrightarrow (-SO_3^-)$ pair is $1kT$ (corresponding to a binding energy of 2.48 kJ/mol).[15] If the average molecular area per bond is x nm^2, then the energy per unit area necessary to break these bonds is $E = kT/(x\ nm^2)$. According to JKR theory[26,27] we calculate this energy from the adhesion force $F/R = -1.5\pi E = -15\ mJ/m^2$. This yields one ion pair every 1.25 nm^2, a value which has to be compared with the area per segment of PSS, which varies between 0.55 and 1 nm^2 for adsorption from salt-free solution.[28,29] Therefore about 22% (i.e., $(0.55\ nm^2/1.25\ nm^1)/2 = 0.22$) to 40% of the PSS monomers of each surface do form ion pairs.

Note that the binding energy of a single ion pair is very small; the adhesive force between the surfaces is caused by the high density of junction points. Similarly, a polyelectrolyte is bound strongly to a substrate due to the cooperative effect of many ion pairs.

In this picture, the range of the attractive force is caused by polyelectrolyte chains of opposite charge bridging between the two surfaces. The range of the attractive force decreases with increasing ionic strength. Apparently, the extent to which tails and loops of opposite charge dangle into the solution decreases with increasing ionic strength. Another possible scenario is the more efficient shielding of the tails and loops by monovalent ions with increasing ionic strength.

With the density profile of the polyelectrolytes depending on the surface separation, the interaction force cannot be additive as assumed by the DLVO theory. If the surfaces are close, we expect a steric interaction, which contributes if the surfaces are 4−8 nm apart. We take the rather unusual intersection point at a separation of 7 nm as the onset of that steric repulsion. Then the planes of charge origin are away from each surface (cf. Figure 3d). The deduced surface potentials are given in Table 2; they are consistent with surfaces of constant charge of one elementary charge per 40 nm^2. The results also correspond to our electrophoresis experi-

Table 2. Parameters Obtained by Simulations of the Electrostatic Repulsion between two PAH/PSS Layers (cf. Figure 5)[a]

NaCl (mM)	potential ψ (mV)
0.4	−58.5
1	−44.7
10	−24

[a] The potential planes are assumed to be 3.5 nm away from the surface. All surface potentials listed correspond to a surface charge of one elementary charge per 40 nm^2.

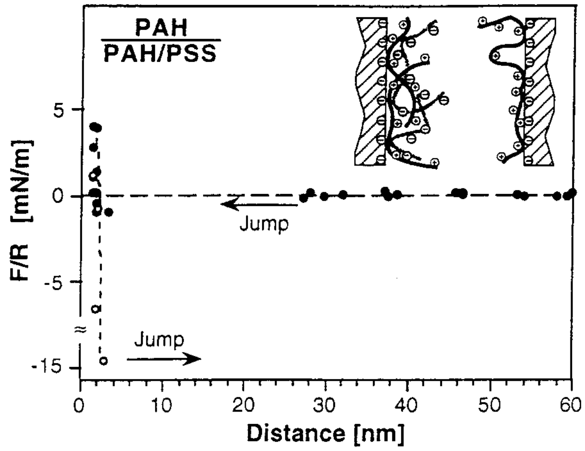

Figure 7. Normalized interaction force between a positively charged surface covered with a polyelectrolyte monolayer (PAH) and a negatively charged surface covered with a polyelectrolyte bilayer (PAH/PSS) immersed into 1 mM NaCl solution. The force is unambiguously attractive for distances smaller than 25 nm, indicating the electrostatic origin of this force; however the absolute values are too small to be quantified (spring constant, 716 N/m). Note that the adhesion is identical to the one observed between two polyelectrolyte bilayers.

ments, which exhibit constant charge behavior and similar surface potentials for PAH/PSS-covered surfaces.[30] However, it is possible that the planes of charge origin obtained by the two methods do not coincide; for electrophoresis experiments we assumed the shear plane to be the plane of charge origin.

In conclusion, we find a subtle interplay of forces with different physical origins: For large separations, electrostatic repulsion caused by the net surface charge dominates. Yet both polycation and polyanion chains dangle into the water; at close approach they lead to an additional steric repulsion. This repulsion seems to be more pronounced at high ionic strengths. Eventually, at smaller separations the segment−segment attraction between polycations and polyanions wins, and a large adhesion can be found due to the formation of ion pairs. This adhesive force is independent of the concentration of the monovalent ions in the solution, clearly demonstrating that monovalent ions are not involved in the formation of ion pairs. Yet loops and tails of isolated surfaces are surrounded by small monovalent ions whose removal is necessary for the formation of ion pairs. Therefore, the adhesive bridging force exhibits the longest range when the electrolyte strength is lowest.

The Interaction between a Polycation Monolayer and a Polycation/Polyanion Bilayer. With this asymmetric polyelectrolyte system (cf. Figure 7) one observes a long range attraction, obviously of electrostatic origin. This is clear evidence of the charge reversal of the PAH-covered mica surface caused by PSS adsorption. If we separate the surfaces and bring them again into contact, we again find the same attractive force, even if the surfaces stay in contact for 30 min. Any migration of negatively charged PSS from the PAH/PSS surface to the PAH surface would yield similar surface charges and therefore, eventually, an electrostatic repulsion. Since we do not observe any migration, we have to conclude that the polyelectrolytes in the PAH/PSS bilayer are rather effectively intertwined.

Note, that the adhesive force (15 mN/m) between a polycation monolayer and a polycation/polyanion bilayer is identical to the one between two polycation/polyanion bilayers (cf. Figure 5) and larger than the one between a polycation monolayer and a clean mica surface (10 mN/m). The quantitative agreement may be somewhat accidental; however, it nicely demonstrates that the amount of ion pairs formed between equally charged polyelectrolyte bilayers is very similar to the one between an oppositely charged PSS/PAH bilayer and a PAH monolayer.

If one assumes that the large adhesion is due to ion pairs only, then all the PSS monomers involved in ion pair formation stem from one surface, that is, 44% to 80% of the PSS monomers bind to the apposing surface (if we use the same numerical values for the area per PSS segment and the ion-pair binding energy as before). Thus, only 56% to 20% of the PSS monomers are bound to the substrate. This rough estimate is in agreement with our electrophoreses experiments there we deduced that “about $^1/_3$ of the charged groups of the top layer form ion pairs with the underneath charges”.[30]

From this, we gain some insight on a molecular scale about the conformation of an adsorbed PSS chain. Since the adhesion between the PSS/PAH bilayers is so strong, we may conclude that 50%− 70% of the positive binding places for PSS on the substrate are not occupied by PSS segments. Yet, we find charge inversion. This is due to negatively charged chains and tails, which dangle into the solution (more or less efficiently screened by monovalent ions). Thus, if we investigate well-separated surfaces, the surfaces appear as homogeneous planes of uniform negative surface charge; however, if the surfaces are close, we observe effects due to coexisting negatively and positively charged chains.

Thermodynamic Implications. On adsorption of PSS onto a PAH monolayer only a third to a half of the positive point charges are neutralized with PSS monomers. Yet, charge overcompensation has occurred; the rest of the negatively charged monomer units dangle into the subphase. “Kinetically hindered equilibrium” is obtained, and more PSS does not bind, even though binding places are still available on the substrate. We find direct evidence of these available binding places if we push PSS segments from another surface across the repulsive electrostatic barrier. Indeed, the model suggested by Cohen-Stuart[6] does describe the experiments rather well: the polyelectrolyte molecules adsorb only until they are electrostatically repelled from the surface, not until the binding places (i.e., point charges with the opposite sign) are saturated, which correspond to “true equilibrium”. Since we are far away from “true equilibrium”, it is impossible to break the few bonds by simple washing. This leads to the observed difficulty/impossiblity to remove adsobed polyelectrolytes from a surface on polyelectrolyte dilution, decrease of salt concentration, or change of pH.

It would be desirable to investigate not only polyelectrolyte bilayers but also polyelectrolyte multilayers. Yet, polyelectrolyte multilayers are very soft, a small compressive force leads already to lateral rearrangements. Typical deformations are several micrometers wide and a few nanometers high.[16] Inconveniently, polyelectrolyte rearrangements is irreversible. Already the surfaces covered with polyelectrolyte bilayers are rather soft. If they are compressed with larger forces than done in the experiments shown in Figure 5, one observes a larger adhesive force indicative of the formation of more ion pairs as well as chain intermingling. After this large adhesion is measured, chain rearrangement can be detected optically, and also the repulsive interaction is changed. In our experience forces cannot be measured reproducibly between surfaces covered with polyelectrolyte multilayers.

The ease and irreversiblity of surface rearrangements is indicative of the features prominent in the build-up of polyelectrolyte multilayers: a polyelectrolyte layer is bound by ion pairs, which exhibit a very small binding energy ($\approx 1\ kT$); therefore a single bond can be easily replaced. Usually, the amount of bound polyelectrolyte is limited by the electrostatic repulsion between the surface and the multivalent polyelectrolyte coil in solution. Yet if one brings more polyelectrolyte onto the substrate (in our case with brute force), it sticks, too, thanks to the abundance of binding sites.

It is most likely that after adsorption chain rearrangement occurs, yet it does not seem to dominate. The steric forces measure how far the chains (loops, tails) dangle into the water. In our experiments (low salt conditions with polyelectrolytes which are turned hydrophilic by charging the side groups) the chain arrangement appears to be an equilibrium property which is independent of previous surface treatment (such as drying or compression) or polyelectrolyte content in the solution. Always the same steric force is observed. Thus we obtain very clear conclusions on the adsorption hysteresis. Yet, the steric forces appear to vary for every polyelectrolyte investigated (from not detectable[13] to extremely long-ranged as observed for a polyelectrolyte with a hydrophilic backbone, polylysine[31,32]). Furthermore, one has to distinguish those adsorbed polyelectrolytes whose loops and trails collapse on first approach of the surfaces and never again relax to their original extension (as is the case for polylysine or various polycations adsorbed from high salt concentration[31–33]) from those polyelectrolytes we describe.

However, with all polyelectrolytes investigated so far, polyelectrolyte multilayers can be formed. While chain arrangement is important, it is extremely varied and dependent on the chemical nature of both polyelectrolyte and surface as well as the ionic strength of the solution. It is difficult to imagine that it leads to such a universal behavior as the build-up of the polyelectrolyte multilayer appears to be. The effect of chain arrangement seems to be more quantitative (how much is adsorbed exactly?) while the qualitative effect (is there a limit to the adsorbed amount?) is due to electrostatics.

To investigate the relative roles of entropy and electrostatics in this kinetically limited adsorption process, we studied the build-up of polyelectrolyte multilayers, and tried to adsorb polycations on polycations, using both chemically identical and different polycations.

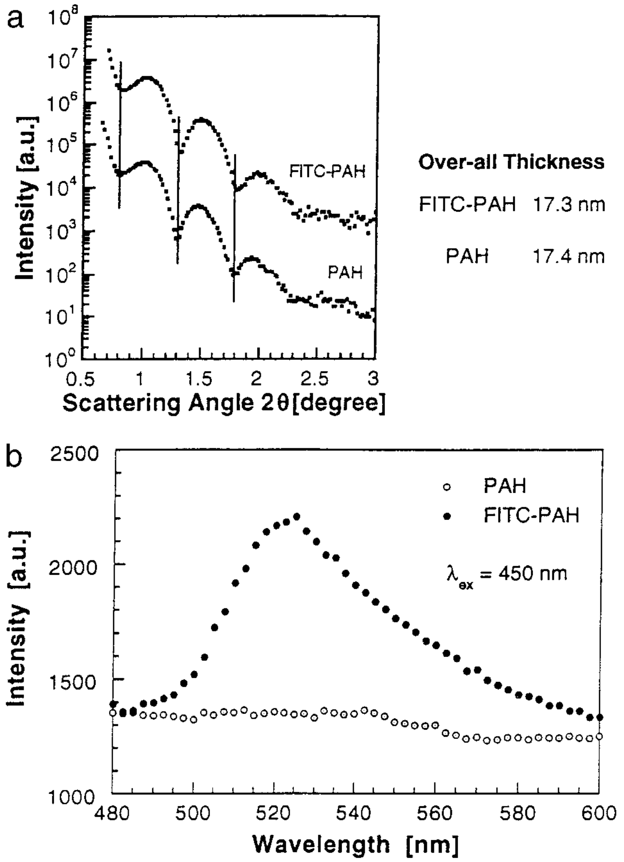

Figure 8. (a) SAXS measurements (reflected intensity as a function of scattering angle) of a PAH-terminated polyelectrolyte multilayer (top curve). Then the layer was immersed into PAH solution, this time with fluorescence-labeled FITC-PAH. As the SAXS measurement (bottom curve) shows, no thickness increase occurs. For clarity the X-ray reflectivity curves are displaced by 1 order of magnitude against each other. (b) Fluorescence measurements of the multilayer before and after its exposure to the FITC-PAH solution. Obviously, FITC-PAH has adsorbed, but since no thickness increase is observed, FITC-PAH and PAH have exchanged, demonstrating that the polyelectrolyte multilayer surfaces are in dynamic equilibrium with the polyelectrolyte solutions.

Adsorption of Polycations onto Polycation Surfaces. The strategy of the experiments is very simple: A polyelectrolyte multilayer is formed as a substrate with the polycation layer under investigation on top. The multilayer thickness is chosen to be around 15 nm, because this is a convenient range for SAXS measurements (resolution ±0.1 nm). This multilayer was built by polyelectrolyte adsorption from high concentration salt solution, since then more polyelectrolyte is adsorbed and more binding places are available.[28]

First, we need to demonstrate that the multilayer surface is indeed in dynamic equilibrium with the solution. For this we study the exchange of PAH with fluorescence-labeled PAH (which we shall abbreviate as FITC-PAH) on the multilayer surface. Such an exchange should occur since the surfaces are (i) in dynamic equilibrium and (ii) the PAH is not monodisperse; therefore slowly longer chain molecules should replace shorter chain molecules.[34]

First, the thickness of a PAH-terminated polyelectrolyte multilayer was determined by SAXS (cf. Figure 8a). Then the multilayer is immersed in solution of FITC-PAH. As Figure 8a shows, the thickness of the layer is unchanged. However, FITC-PAH got adsorbed onto the

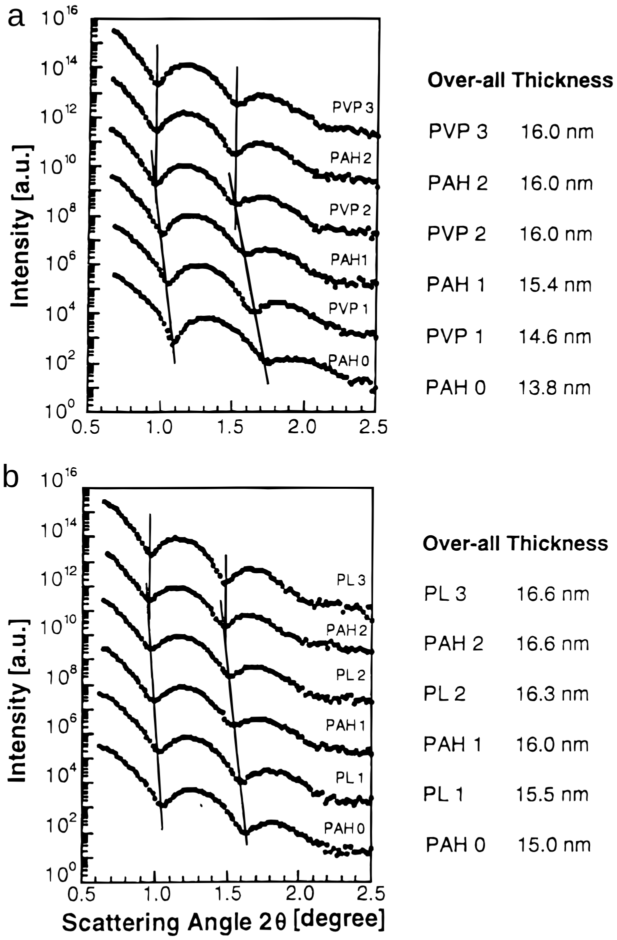

Figure 9. SAXS measurements to investigate the build-up of polyelectrolyte multilayers by the consecutive adsorption of different polycations, (a) PAH/PL and (b) PVP/PL. For both systems we find an overall thickness increase on the adsorption of the first four polycation layers, then the thickness remains constant. The thickness increase in 0.7 nm/layer for the system PAH/PVP and 0.5 nm/layer for the system PAH/PL. The overall thicknesses of the multilayers are given in the figure. For clarity the X-ray reflectivity curves are displaced by 1 order of magnitude against each other.

surface, as is demonstrated by the fluorescence increase following the immersion in the FITC-PAH solution (cf. Figure 8b). It is evident, that the top layer of a polyelectrolyte multilayer is in dynamic equilibrium with the surrounding solution.

Please note, that it is possible to disturb the dynamic equilibrium of the polyelectrolyte multilayer with the surrounding solution.[35] After a PSS-terminated multilayer was dried extremely thoroughly more PSS could be adsorbed. The drying obviously caused an irreversible reorganization of the first PSS layer.

To figure out if the electrostatic barrier to polyelectrolyte adsorption can be circumvented by entropy, we tried to build polycation/polycation multilayers, either with PAH/PVP or with PAH/PL. To exclude specific interactions (including hydrophobic interactions) between the two different polycations, we performed these experiments with PVP (poly(2-vinylpiridine)) which has a hydrophobic chain and with PL (poly(l-lysine)) whose peptide chain is extremely hydrophilic. The results are given in Figure 9. For both systems we find an overall thickness increase on the adsorption of the first four polycation layers, then the thickness remains constant. The thickness increase is 0.7 nm/layer for the PAH/PVP multilayer and 0.5 nm/layer for the PAH/PL multilayer.

From neutron reflectivity experiments we know the density profile of a PSS layer perpendicular to the layer surface. It may be roughly described as a bell curve; one PSS layer extends into the two adjacent PAH/PSS bilayers, but not further (over-all thickness about 5 layers).[28] For the multilayer the average PSS layer is rather thick since it was adsorbed from high salt conditions. Less polycation is adsorbed if the solvent contains no ions. Thus, the density profile of the top PSS layer is in our case not symmetric, the polyanion chain penetrates not two, but three consecutive polycation layers. The fact that we obtain qualitatively very similar results with two chemically very different polycations allows us to exclude any chemical specificity in the binding mechanism of the polycation onto the surface. Therefore, we have to conclude that the binding mechanism of a polycation onto a surface is the simple electrostatic attraction of positive and negative point charges, ion pairs are formed with localized PSS segments.

Another implication is the importance of entropic contributions within the adsorbed polycation layer. Even when positively charged chains and tails protrude into to water, chemically different polycations can adsorb as long as binding places can be found. Apparently the original polycation chain rearranges, when a chemically different polycation chain approaches. This result is somewhat an extension to the theory of Andelman,[10,11] who finds polyelectrolyte adsorption onto a surface of like charge, as long as ion pairs can be formed.

Discussion

Principle Model of Build-up of Polyelectrolyte Multilayers. Since all the chains are flexible and hydrated, one may imagine that the ion pairs are not confined into a plane parallel to the surface but do extend over a finite range corresponding to the thickness of the dangling chains. This behavior is suggested by the range of the bridging forces observed in the surface forces experiments as well as by the roughness found in the neutron scattering experiments.

Interpenetration of subsequently adsorbed layers is further favored by the low polyelectrolyte density which the 4 nm thick polyelectrolyte layer at the solid/liquid interface exhibits. Many holes are to be expected in an adsorbed polyelectrolyte layer, a feature which has been reported in the literature.[6]

Note that defects and roughness of the surface are of minor importance for the build-up of a polyelectrolyte multilayer consisting of polycations and polyanions, since only about half of the localized charges of the substrate are effectively used as binding places. The binding strength of an ion pair is weak, in the order of kT. The actually observed irreversible binding is due to the additive effect of many ion pairs.

The buildup of a polyelectrolyte multilayer is depicted in Figure 10. During each adsorption step, the surface charge changes sign. The electrostatic barrier limits the adsorbed amount, even if there is still an excess of binding places on the substrate. The exact value of the charge overcompensation depends on the chemical and physical details of the surface, the polyelectrolyte and the solution. On the assumption that each PSS-terminated polyelectrolyte multilayer surface is identi-

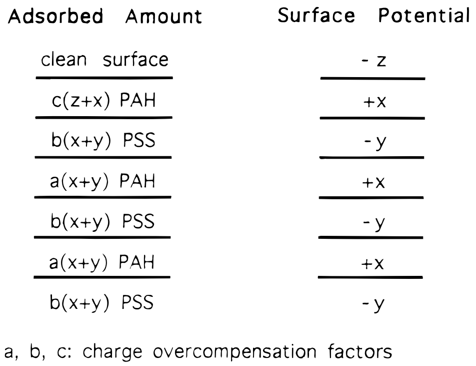

Figure 10. Schematic drawing of the principle physics occurring during the self-assembly process of polyelectrolyte multilayers: left column, adsorbed amount of polyelectrolyte; right column, surface potentials in water. During each polyelectrolyte adsorption step the surface charge changes sign, yet there is still an abundance of binding sites on the surface. On the assumption that each PSS-terminated polyelectrolyte multilayer surface is identical, each time exactly the same amount of PAH is adsorbed (or vice versa). Obviously, the first layer is different, since the clean surface exhibits another surface potential and another chemical composition. The exact value of the charge overcompensation depends on the chemical and physical details of the surface, the polyelectrolyte, and the solution.

cal, each time exactly the same amount of PAH is adsorbed (and vice versa).

A polyelectrolyte layer penetrates the two adjacent PAH/PSS bilayers;[28] therefore the assumption that only the first layer is different, and all the others are similar, is oversimplified since we neglected effects due to chain conformation and surface roughness. If one adsorbs polyelectrolytes from solutions containing about 0.1−5 mol of monovalent salt, a few layers need to be adsorbed, until the thickness increase per polycation/polyanion pair is constant.[1,29] If equilibrium is achieved, the higher the salt concentration, the more polyelectrolyte is adsorbed with each step.[28,29] Presumably, the high ion concentration in the solution causes a more coiled chain conformation. Interestingly, in neutron reflection one observes on increase of the ion concentration an increase in interfacial roughness, one PSS layer exhibits always a bell-shaped density profile extending over five layers.[28] Even the transport properties of molecules diffusing perpendicular through the polyelectrolyte multilayer are very different if the chains are coiled or flat, i.e., adsorbed from high ion concentration or from clean water.[36] Thus, for the first adsorbed layer the chain conformation is very different if adsorbed from high salt concentration, since the substrate is still smoother and chain intermingling is not yet possible; therefore a different amount of polyelectrolyte gets adsorbed. In our experiments, we adsorb from low salt concentration; these effects are less pronounced and the layer thickness is the same for each adsorption step.

Concluding, we would like to emphasize that the aim of our experiments is to clarify the universal effects leading to the build-up of polyelectrolyte multilayers: (i) The adsorbed polyelectrolyte amount is limited by the surface charge overcompensation. (ii) The binding occurs by many weak ion bonds; however, not every polyelectrolyte segment binds, there are free substrate charges which are compensated by the segments dangling into solution. (iii) The “kinetically hindered equilibrium” causes adsorption hysteresis. This is the general behavior. However, the chain conformation is affected by many influences: the specific chemical nature of the polyelectrolyte, the ion concentration in the solution, the surface roughness, specific short range chemical interactions, the previous surface treatment (how many ion pairs werde formed earlier?). These parameters determine the net charge of the polyelectrolyte coil and the change of surface potential on adsorption. Thus how much polyelectrolyte is adsorbed until charge overcompensation occurs depends on the subtle interplay of many different forces and will be subject of further investigation.

Conclusion

Direct measurements of the interaction in water were carried out between a variety of surfaces: (i) bare negatively charged mica surface and a polycation-covered surface, (ii) two polycation-covered surfaces, (iii) a polycation-covered and a polyanion/polycation-covered surface, and (iv) two polyanion/polycation-covered surfaces at different ionic strengths. Thus, some of the specific properties of polyelectrolyte adsorption as suggested theoretically[6,10,11,37] could be directly demonstrated.

For the self-assembly of an additional layer onto polyelectrolyte multilayers, one relies on the specific properties of polyelectrolyte adsorption: (i) the formation of electrostatic ion bonds between oppositely charged segments (the chemical composition of the polyelectrolyte appears to be of minor importance), (ii) the charge overcompensation of the surface, (iii) the electrostatic barrier, which kinetically limits the adsorbed amount and guarantees the equal thickness of consecutively adsorbed layers, and (iv) which furthermore provides a strong hysteresis in the adsorption isotherm leading to the convenient stability of the layers during washing.

Yet little is known about the internal structure of such an adsorbed layer and how it changes, if it is covered by more differently or equally charged layers. Yet we can circumvent the electrostatic barrier entropically and adsorb up to four layers of different polycations onto each other.

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