Specific ζ-Potential Response of Layer-by-Layer Coated Colloidal Particles Triggered by Polyelectrolyte Ion Interactions

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The ζ-potential of PSS/PAH and PSS/PDADMAC coated silica particles was studied in the presence of ClO_4^- and $H_2PO_4^-$ salts. In the presence of ClO_4^-, layer-by-layer (LbL) coated silica particles with PDADMAC as the top layer show a reversal in the surface charge with increasing salt concentration but remain positive in phosphate solutions. LbL particles with PAH as the top layer become, however, negative in the presence of $H_2PO_4^-$ but retain their positive charge in the presence of ClO_4^-. Charge reversal was explained by specific interaction of ClO_4^- ions with the quaternary amine groups and of $H_2PO_4^-$ with the primary amines through hydrogen bonding. Atomic force microscopy (AFM) and quartz crystal microbalance with dissipation (QCM-D) were employed to study the corresponding layer stability on planar surfaces.

Introduction

Polyelectrolyte multilayers fabricated by the "layer-by-layer (LbL) technique" represent an easy and powerful tool for surface modification and nanoscale device fabrication.[1−3] The LbL technique is based on the alternative assembly of oppositely charged polyelectrolytes onto planar charged surfaces and charged colloidal particles. The resulting thin polymer film has a thickness of the order of nanometers.[2−4] Thickness and composition of the LbL films can be controlled with nanoscale precision. Multicompartmentation and multifunction can be endowed as well with various substances such as nanoparticles,[5] lipids,[6] proteins, and DNA into or onto the multilayers or by replacing selected polyelectrolyte layers. Examples of LbL applications are drug loading into multilayer microcapsules,[7,8] incorporation of cell growth factors into 3D scaffolds for tissue engineering,[9,10] and fabrication of hybrid optical devices,[11] and so forth.

Despite significant ongoing research on these films and the ease of their fabrication, there are still open questions related to the stability of the film and the build-up mechanisms. LbL films constitute a special case of polymer complexation, where the complexes are formed stepwise on a support. The top layer is always charged. This is brought about by charge overcompensation, and it is the prerequisite for the formation of the next layer.[12] The strength of the complex formation in the multilayer is, in analogy to complex formation in solution, related to the nature and density of charge of the polymer constituents; that is, these can be weak or strong polyelectrolytes, which are either fully or partially charged depending on the case of weak polyelectrolytes on the assembly conditions. Furthermore, chemical features associated with particular macromolecular building blocks may impose additional topological constraints for the organization of the chains into the macromolecular assembly. Among the many combinations of polycations and polyanions employed for LbL architectures, the following polyelectrolyte pairs have been widely used: poly(allyl amine hydrochloride) (PAH)/poly(styrene sulfonate) (PSS) and poly(diallyl dimethyl ammonium chloride) (PDADMAC/PSS.[13] The PAH/PSS pair shows a higher mechanical modulus with a stronger affinity between the positively and negatively charged polyelectrolyte than PDADMAC/PSS, which on the other hand has a much higher swelling capability.[14] PAH is a weak polymer with primary amines in the monomers, whose charge can be varied with the pH. On the other hand, PDADMAC is a strong polyelectrolyte with quaternary amines and its intrinsic charge does not depend on variations of pH.

The interaction of the polyelectrolyte pairs forming the multilayers can be tuned by the presence of salts. It has been, for example, demonstrated that polyelectrolyte layers can be degraded and finally removed in high ionic strength NaCl solutions.[15] Salts may have additional effects besides weakening the multilayer structure, such as creating a more hydrophobic

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environment in the layer as it is the case with $LiClO_4$,[16] which has a pronounced influence on the water content in the multilayer. Another interesting example is the assembly of LbL multilayers in the presence of counterions, following the Hofmeister series of ion affinity.[17] In this case, it was observed that film formation may not occur or be significantly reduced if the affinity of the counterions to the monomers is strong, which is the case for PDADMAC with ClO_4^-.[17−19] The Hofmeister series classifies ions according to their capability to stabilize or precipitate proteins, which is related to the effects of those ions on the structure of the solvent. Ions, such as citrate, sulfate, phosphate, and Al^{3+}, can be classified as "structure maker" or cosmotropes. They stabilize proteins or hydrophobic aggregates and reduce the solubility of hydrophobic species. Conversely, other ions are classified as "disorder maker" or chaotropes when they unfold proteins, destabilize hydrophobic aggregates, and increase the solubility of hydrophobic species, for example, I^-, NO_3^-, NH_4^+, and ClO_4^-.[19]

In this Article, we address the electrophoretic behavior and stability of polyelectrolyte multilayers in the presence of ions, which have a specific interaction either with PDADMAC or with PAH. We were interested in knowing if this specific interaction in addition to electrostatic ionic strength based effects may lead to specific properties of the LbL film. We observed that PDADMAC and PAH are affected quite differently by various ions and interesting effects can be identified at the extremes of the Hofmeister series. In the work presented here, we focused on studying the ζ-potential of both PAH/PSS and PDADMAC/PSS coated submicrometer silica particles in response to a variety of salts. In parallel, layer stability and topography have been studied with quartz crystal microbalance with dissipation (QCM-D) and atomic force microscopy (AFM) on planar surfaces.
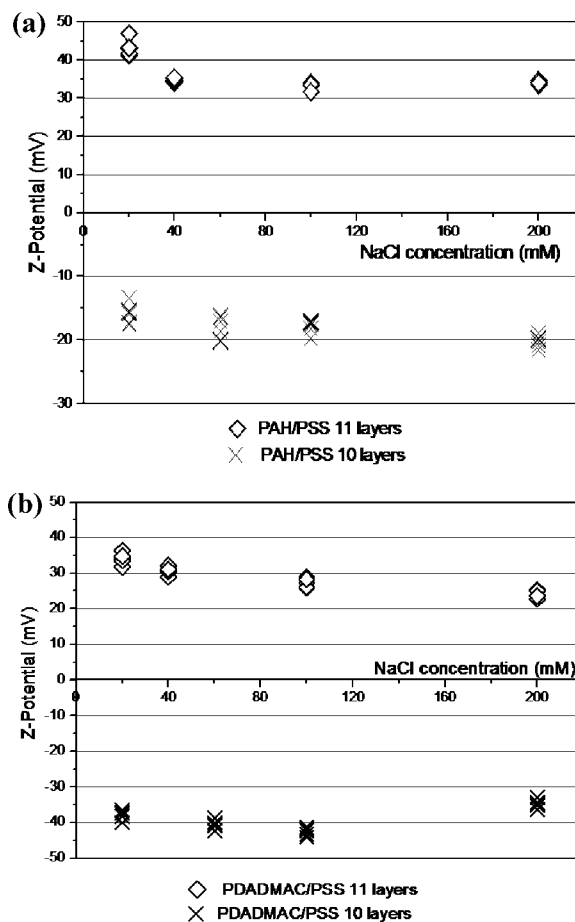
Materials and Methods

Materials. Silica particles, Ø 400 nm, were purchased from Kisker, Germany. Polyelectrolytes PSS, PAH, and PDADMAC were purchased from Aldrich. $LiClO_4$ was purchased from Fluka, and NaCl and KH_2PO_4 were from Aldrich.

Layer by Layer Assembly. For the LbL coating of the silica particles, these were suspended in 1 mg/mL polyelectrolyte and 0.5 mol/L NaCl solution. After each layer deposition, the samples were centrifuged, the supernatant was removed, and the particles were redispersed in water. The centrifugation and washing with water were repeated three times before addition of the next polyelectrolyte layer.

ζ-Potential. The ζ-potential of LbL coated silica nanoparticles was measured with a NanoSizer (MALVERN Nano-ZS, U.K.) instrument. LbL assembly on the colloids was first traced by measuring the changes in ζ-potential after each layer deposition. All the ζ-potential measurements were performed at 25 °C and with a cell drive voltage of 30 V, using a monomodal analysis model. Measurements were performed at constant pH value of 5.2.

QCM-D. An E4 quartz crystal microbalance with dissipation (QCM-D) from Q-Sense, Göteborg, Sweden, was employed for the characterization of planar multilayers. QSX 301 gold coated quartz crystals (5 MHz) from Q-Sense were used as substrates and coated in situ in the chamber with PAH/PSS and PDADMAC/PSS films of 5, 6, 10, and 11 layers.

For the QCM-D experiments, LbL assembly was performed by filling the QCM-D chamber with a polyelectrolyte solution, 1 mg/mL in 0.5 M NaCl. The deposition is traced by changes in the

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Figure 1. (a) ζ-Potential of PAH/PSS multilayered silica particles in the presence of NaCl as a function of the ionic strength for silica particles with 10 layers of PAH/PSS (with PSS as the outermost layer) and silica particles coated with 11 layers of PAH/PSS (with PAH as the outermost layer). (b) ζ-Potential of PDADMAC/PSS multilayered silica particles in the presence of NaCl as a function of the ionic strength for silica particles coated with 10 layers of PDADMAC/PSS (with PSS as the outermost layer) and 11 layers of PDADMAC/PSS (with PDADMAC as the outermost layer).

frequency of the quartz crystal. When the frequency reaches a constant value, the volume of the chamber is replaced with water, which is allowed to flow until a constant value of frequency is reached again. The procedure is repeated for the desired number of layers to be assembled.

AFM. A JPK Nanowizard II atomic force microscope (JPK Instruments AG, Germany) was used to image the multilayers. AFM measurements were performed in NaCl and $LiClO_4$ solutions in contact mode using a NP-S10 (Veeco) cantilever with a spring constant of 0.12 N/m.

Results

Figure 1 displays the ζ-potential as a function of ionic strength for LbL coated silica particles for different surface charge and layer composition. PAH/PSS and PDADMAC/PSS covered particles with either positive or negative outermost layers were compared.

It is noticeable from the data in Figure 1 that the ζ-potential shows a rather weak dependence on ionic strength when the concentration of NaCl varies from 20 to 200 mM. Theoretically, a 3-fold decrease is expected, because $\zeta \sim I^{-1/2}$. Contrarily, the value of the ζ-potential remains almost constant for a wide range of concentrations of NaCl, around 30 mV for PAH/PSS multilayers (PAH as the outermost layer) and −15 to −20 for the PAH/PSS multilayers (PSS as the outermost layer). In a

similar fashion, the PDADMAC/PSS coated particles show a ζ-potential of +30 and −40 mV for multilayers presenting PDADMAC and PSS as the outermost layer, respectively. We assume that this surprising behavior is due to the polymer based soft and charged nature of the LbL film, which permits the reorganization of the polymer molecules in response to the increase of the ionic strength.[21,22] The surface behaves more like a surface with constant potential rather than with constant charge. There are various possibilities of how this apparent charge regulation can be achieved. For example, if PAH is the top layer, increasing ionic strength results in a decrease in the pH near the layer surface. This should result in an increase of the protonation of PAH, and the surface charge should increase. However, the observed range of ζ-potential changes seems much too small to account for a substantial change in protonation. The pH cannot influence the degree of charge of PDADMAC or PSS around neutral or weakly acidic conditions. Therefore, we believe a more general mechanism than the change of the state of dissociation/protonation is at work.

We calculated the effective surface charge density from the experimental values of the ζ-potential of Figure 1 applying eq 1.[22] The influence of the curvature of the particles can be neglected, since the Debye length for the lowest ionic strength is still 50 times smaller than the particle radius. In Figure 2a, the charge of PAH/PSS coated silica particles with 11 polyelectrolyte layers is presented as a function of the ionic strength.

$$\sigma(c, \zeta) = \sqrt{8kT\varepsilon\varepsilon_0 n}\sinh\left(\frac{ze_0\zeta}{2kT}\right) \qquad (1)$$

where σ is the surface charge density, ζ is the zeta potential, k is the Boltzmann constant, T is the absolute temperature, ε is the relative permittivity, ε_0 is the dielectric constant, n is the number of ions per unit volume, c is the salt concentration, e_0 is the charge of the electron, and z is the valence of the symmetric electrolyte (NaCl, $z = 1$).

A linear increase of the electrophoretically effective charge density with ionic strength is observed. The failure of the constant charge model is obvious. The best fit according to constant charge density of the particles (eq 2) is widely off the experimental ζ-potential values (Figure 2b):
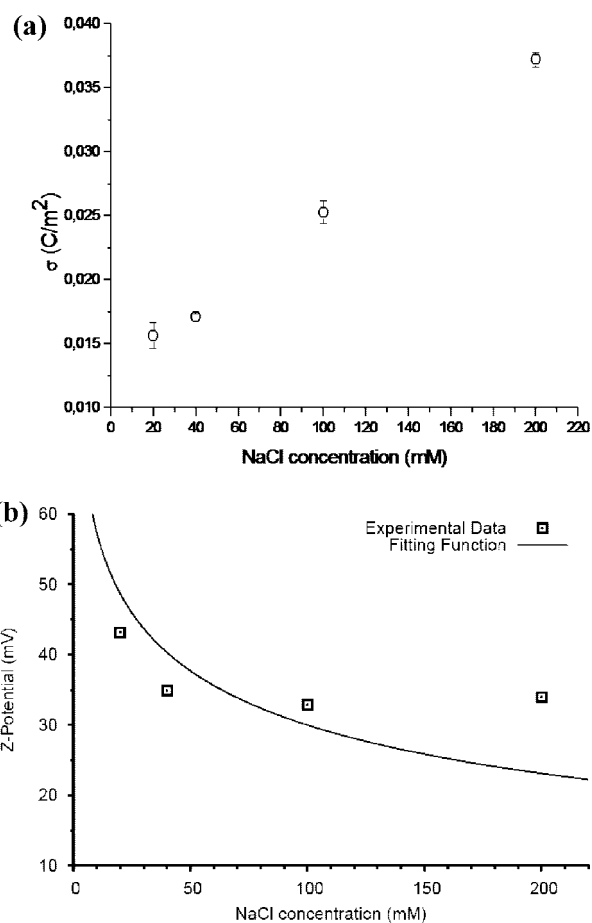
$$\zeta(c, \sigma) = \frac{2kT}{ze_0}\operatorname{asinh}\left(\frac{\sigma}{\sqrt{8kT\varepsilon\varepsilon_0 n}}\right) \qquad (2)$$

Our conclusion was that in the case of polyelectrolyte multilayers the ζ-potential as a function of ionic strength follows a much weaker trend than expected for hard and smooth surfaces with constant charge density. The mechanism leading to this interesting behavior will be subject to forthcoming detailed investigations.

In this work the data of Figures 1 and 2, which show the response of the ζ-potential with NaCl, will be regarded as the reference for purely ionic concentration induced effects. They will be compared with the specific effects of particular salts considered further below in this paper.

In Figure 3, we plotted the changes of the ζ-potential for the four multilayer coatings considered in Figure 1 but in the presence of LiClO$_4$ instead of NaCl. The salt concentrations used are the same as those for NaCl ranging from 0.02 to 0.2 mol/L.

For PSS as the outermost layer, both in combination with either PAH or PDADMAC, the behavior of the ζ-potential does

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Figure 2. (a) Particle surface charge density as function of the ionic strength in NaCl calculated from the experimental ζ-potential values for silica particles coated with PAH/PSS 11 layers. (b) Comparison between experimental values of ζ-potential in NaCl (PAH/PSS 11 layers) and the theoretical potential function (constant charge model). The curve represents the "best" fit yielding a surface charge density of 0.019 C/m^2.
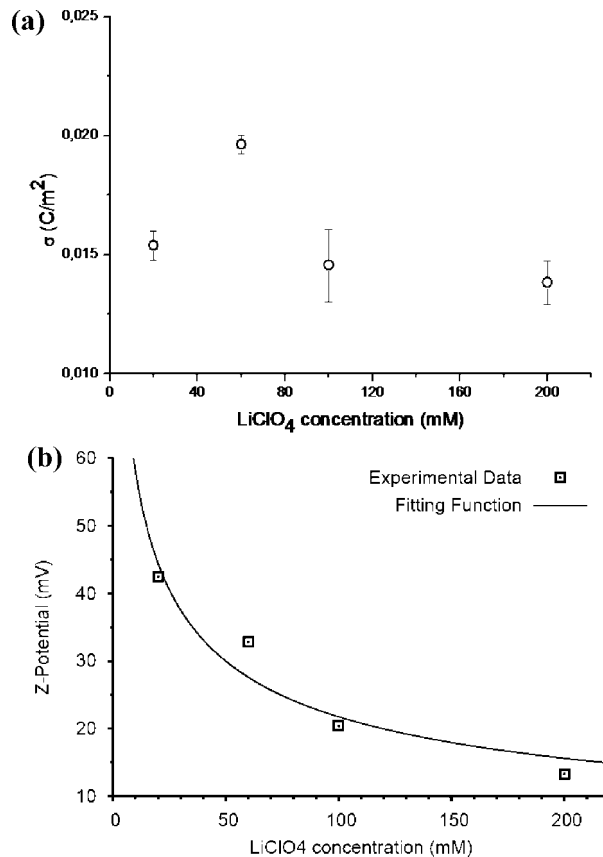
not substantially differ from that described in Figure 1 and we consider that for these films the ζ-potential behaves in LiClO$_4$ quite similar to the reference case of NaCl. The ζ-potential remains almost constant over the concentration range from 0.02 to 0.2 mol/L. For particles with PAH as the top layer, the ζ-potential curves show a different behavior from that observed in NaCl. The ζ-potential decreases more steeply with increasing salt concentration with variations of 5−10 mV between two immediate concentrations, from an initial value of + 50 mV for 0.02 mol/L LiClO$_4$ to approximately +10 mV in 0.2 mol/L LiClO$_4$. In the case of PDADMAC being the top layer, the ζ-potential shows a quite surprising behavior. At low ionic strength, the ζ-potential is slightly positive, but then the ζ-potential reverses and remains almost constant at negative values with further increase of the ionic strength. It is obvious that the interaction between the amino groups of both PAH and PDADMAC with ClO$_4^-$ is responsible for this remarkable behavior.

As Figure 4 shows, for PAH being the top layer in LiClO$_4$, the surface charge density does not show a pronounced increase with increasing ionic strength. Indeed, the ζ-potential data can be reasonably well fitted with a model of constant charge, pointing toward the absence of the above-mentioned charge density regulation behavior observed in NaCl. To understand these data and those of PDADMAC, which are even more puzzling, we have to make a few considerations.
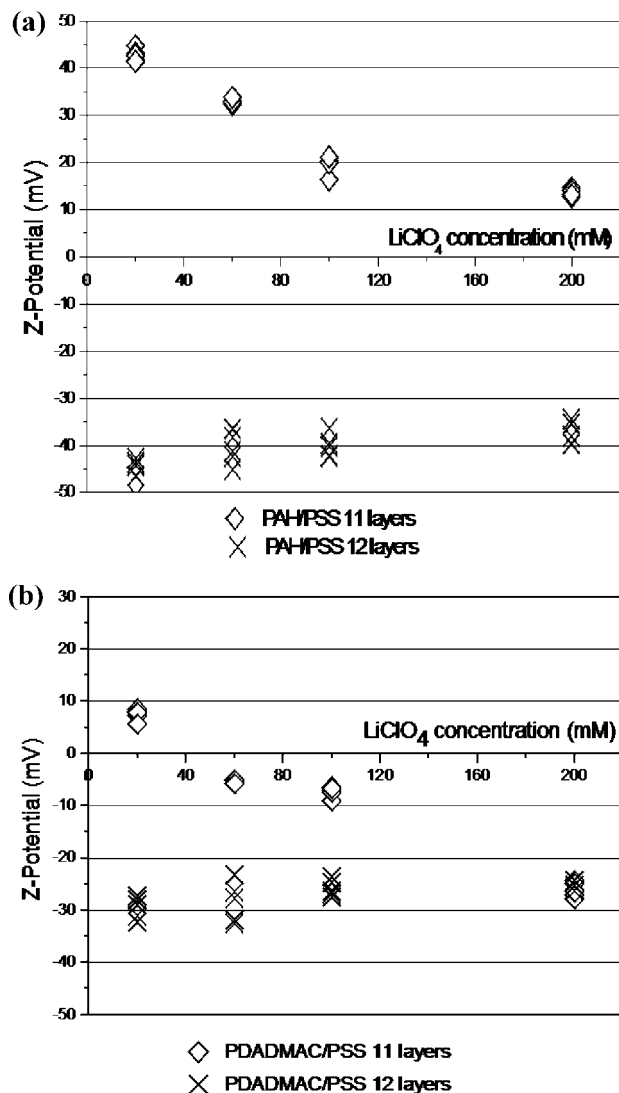
Figure 3. ζ-Potential of (a) PAH/PSS and (b) PDADMAC/PSS LbL silica particles in the presence of LiClO$_4$ as a function of the ionic strength.

Figure 4. (a) Particle surface charge density as function of the ionic strength in LiClO$_4$ calculated from the experimental ζ-potential values for particles with PAH/PSS 11 layers (PAH is the top layer). (b) Comparison between experimental values of ζ-potential in LiClO$_4$ and the theoretical potential function calculated as the best fit from the calculated surface charge values for particles coated with PAH/PSS 11 layers. The best fit yields a surface charge density of 0.016 C/m^2.

First, we previously reported that brushes of PMETAC, a polyelectrolyte formed by monomers bearing quaternary ammonium groups, show a specific interaction with ClO$_4^-$, which results in a change of hydration state of the monomers, thus impacting the wetting properties of the brush.[23] As a consequence, the surface becomes hydrophobic when the counterions of the brush are replaced by ClO$_4^-$ species. It could thus be that the screening of the quaternary ammonium groups of PDADMAC by perchlorate could induce similar changes. ClO$_4^-$ ions are chaotropic. Their charge is distributed over a relative large volume; it does not match well with the water structure and has a pronounced affinity for nonstructured water over structured water. Quaternary amines, on the other hand, induce the formation of less structured water in their vicinity, since they cannot form hydrogen bonds with water molecules. Primary amines, however, form hydrogen bonds with water molecules and have thus a positive effect on the water structure. It is thus understandable that ClO$_4^-$ ions have a stronger affinity for the quaternary amines than for primary ones. Our explanation for the charge reversal in the case of PDADMAC is thus a strong binding of the perchlorate to the quarternary amines promoted not only by

electrostatic but also by entropic effects on the solvent. The charge of PDADMAC is thus at sufficiently large perchlorate concentrations fully compensated, and the negative ζ-potential can be attributed to the presence of some sulfonate groups in the top layer, since it is known that the layers are not completely stratified and some mixing occurs. It cannot be excluded that perchlorate may break some attachment sites between PSS and PDADMAC, thus rendering the surface more negative by changing the balance between positive and negative charges in the multilayer.

Both ClO$_4^-$ and quaternary amines are placed in an extreme of the Hofmeister series. For that reason, we decided to switch to the other extreme of the Hofmeister series and employ a kosmotropic salt, potassium phosphate, repeating the series of four samples as before: silica particles coated with PSS/PDADMAC and PSS/PAH with the polycation and the polyanion as the last layer.

In presence of KH$_2$PO$_4$, particles coated with PSS/PDADMAC multilayers presenting PDADMAC as the outermost layer always displayed positive values of ζ-potential (Figure 5b), which was almost constant over the interval of applied concentrations. Again, the colloids with PSS as the outermost layer exhibited a similar behavior as well (both with PAH and PDADMAC as layer constituents). With PAH as the topmost layer, the ζ-potential value became, however, nearly zero at about 0.02 mol/L KH$_2$PO$_4$. At higher phosphate concentrations, the ζ-potential decreased toward even negative values of about -10 mV (Figure 5a). It is known that the phosphate groups can interact with primary

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(a)

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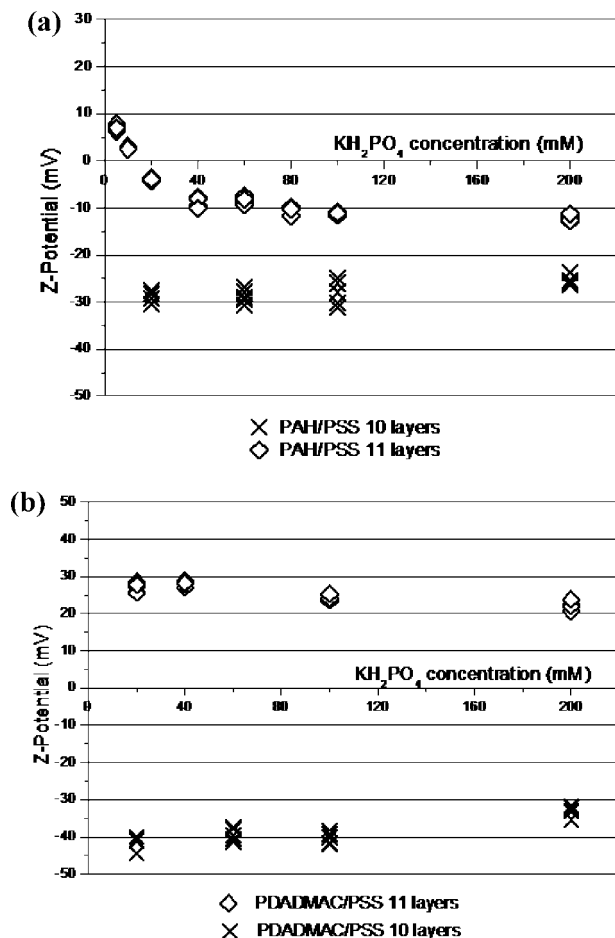
Figure 5. ζ-Potential of (a) PAH/PSS and (b) PDADMAC/PSS multilayered silica particles in the presence of of KH$_2$PO$_4$ as a function of the ionic strength.

amines through hydrogen bonding. We have recently demonstrated using IR spectroscopy this specific interaction between phosphate groups in phospholipids and the noncharged amine groups in PAH.[25−27] Conversely, hydrogen bonding interactions cannot take place with the quaternary amines. Phosphate anions thus are only able to screen the quarternary amine based surface charges as do the diffusive ion species, such as Cl$^-$.

The recharging of the surface for PAH coated particles due to the interaction of H$_2$PO$_4^-$ with the amine groups of PAH can be explained as follows. Upon binding of the phosphate to NH^{3+}, the charges are fully compensated, and the second OH of the phosphate groups may become deprotonated, forming a negative charge at the amino−phosphate complex. Binding may also take place to uncharged amino groups through hydrogen bonding. It may also be that there is a compensation of the charges of the PAH by the phosphate and the few PSS charges in the top layer are partially responsible for the overall negative ζ-potential.

Next, we were interested in whether these changes of the ζ-potential were reversible. A potential of 28.8 mV was originally measured for particles with PAH as the top layer in 0.1 M NaCl;

after treatment with 0.1 M phosphate and redispersion in 0.1 M NaCl, the potential showed a value of 25 mV. For PDADMAC coated particles, the potential in 0.1 NaCl was 14.8 mV; after treatment with perchlorate and resuspension in 0.1 M NaCl, the potential decreased to 5 mV. In the case of the PDADMAC coated particles, the reduction in the potential points to an irreversible change of the surface structure brought about by the interaction with perchlorate. Most likely, the top PDADMAC and PSS layer underneath got partially mixed as a result of breaking bonds between PDADMAC and PSS in the presence of perchlorate. Another possibility is that some PDADMAC had been lost.

To further explore the role of the ionic species on multilayer structures, we performed AFM measurements on the PDADMAC/PSS multilayers presenting PDADMAC as the topmost layer prior to (Figure 6a) and after treatment with ClO$_4^-$ (Figure 6b). Starting from initially small amounts of PDADMAC, the latter increased in an apparently nonlinear fashion. We observed, for example, that after depositing the 13th layer of PDADMAC the surface becomes very rough. This was correlated, as concluded from QCM-D experiments, to a remarkable increase in the amount of PDADMAC deposition. After treatment with 1 mol/L LiClO$_4$ (Figure 6b), the surface became more flat and much more homogeneous. The AFM image is very similar to the situation where PSS was the topmost layer. We concluded from these images that PDADMAC had been removed from the surface either completely or partially in 1 mol/L perchlorate. If so, this would be further evidence for the strong interaction of PDADMAC with perchlorate leading to film decomposition by replacing PSS with perchlorate.

To confirm this hypothesis, we assembled the PDADMAC/PSS multilayers in situ in a quartz microbalance with dissipation (QCM-D).[28] In Figure 7, we show the deposition of 11 polyelectrolyte layers. The increase in frequency at the 11th layer is remarkable. It corresponds to an increase of mass equivalent to the mass deposited in all the 10 previous layers taken together.

From the changes in frequency during layer deposition, it is possible to obtain quantitative information about the amount of LbL deposited polymer by employing the Sauerbrey equation.

The multilayer was then exposed to a 0.2 mol/L LiClO$_4$ solution. After flushing with water, we observed an increase in frequency values of approximately 90 Hz, which can be interpreted as a decrease in the multilayer mass (Figure 8). The last deposited layer of PDADMAC induced a 350 Hz variation in the frequency of oscillation of the crystal. Therefore, the material lost from the multilayer corresponded to almost one-fourth of a layer of PDADMAC. It is also noticeable that after the salt treatment and water washing the different overtones split. This is indicative of a vertical change in the density of the material and perhaps less densely packed last layers.

Dissipation values, which can be related to the mechanical properties of the film, decreased after LiClO$_4$ treatment. This can be understood from the loss of polymers, which is almost half of the total assembled mass. LiClO$_4$ at 0.2 mol/L was the highest concentration which was used for electrophoretic measurements. Further experiments were performed at lower ionic strength as well as at different layer thicknesses, and all these experiments confirmed a decrease in frequency albeit smaller than the corresponding increase upon formation of the respective layer. Such a change in the frequency for the PDADMAC/PSS system did not occur in the presence of phosphate. After treatment with the KH$_2$PO$_4$ salt and washing with water, the frequency always

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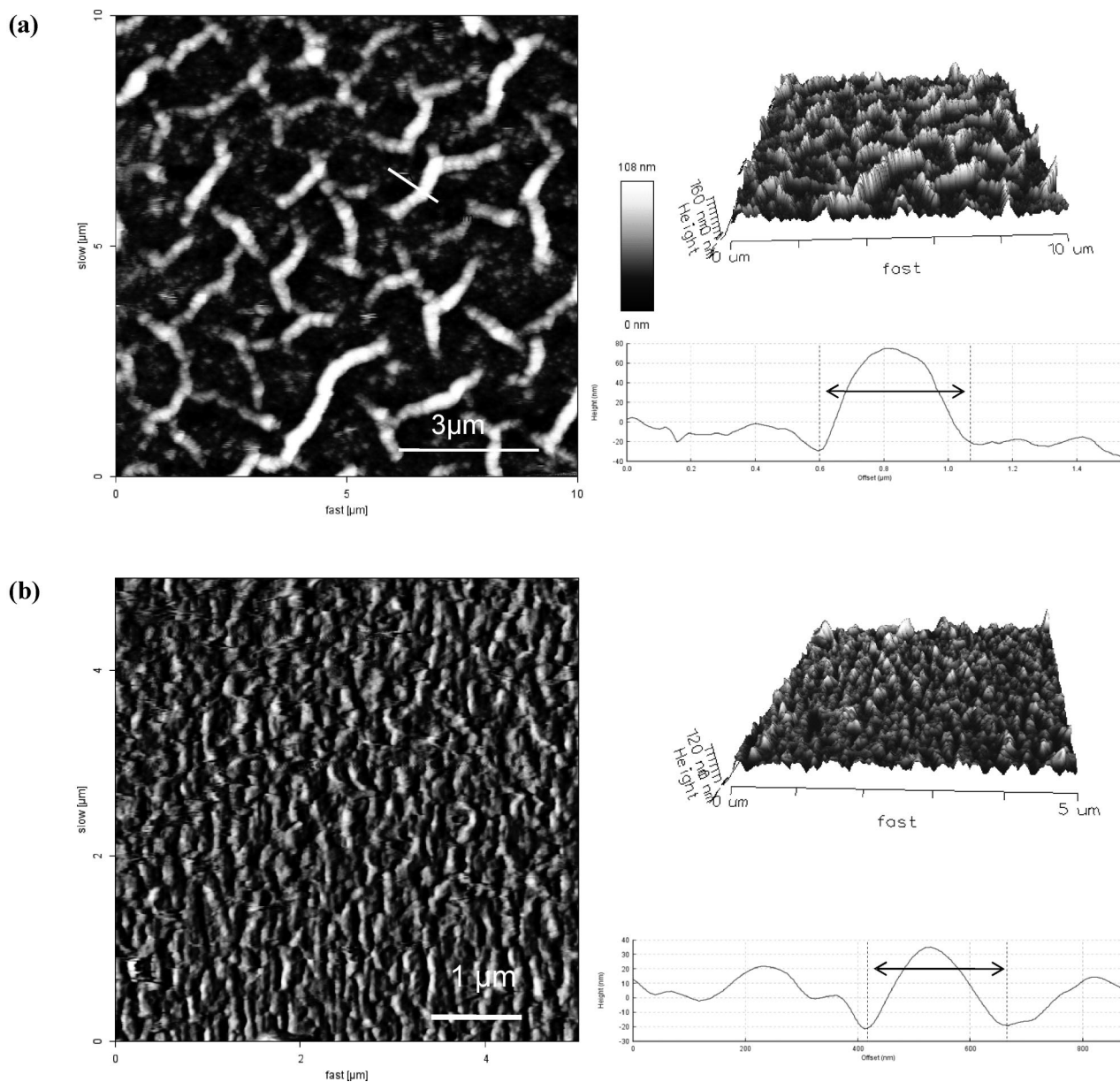
Figure 6. (a) AFM micrographs of PDADMAC/PSS 13 multilayered system before LiClO$_4$ treatment. (b) AFM micrographs of PDADMAC/PSS 13 multilayered system after LiClO$_4$ treatment.

returned to the original values, indicating the absence of any mass loss induced by phosphate.

On the contrary, QCM-D measurements on PAH/PSS multilayers presenting PAH as the topmost layer demonstrated that now a partial removal took place in the presence of phosphate ions but not with ClO$_4$$^-$. This is shown in Figure 9 displaying the changes in frequency of a PSS/PAH multilayer system consisting of 11 layers after exposure to 0.05 mol/L KH$_2$PO$_4$ and subsequent washing with water. There is a net increase in frequency toward positive values of around 9 Hz. The frequency increase on the system after the deposition of the 11th layer of PAH was approximately 15 Hz. Further increase of the phosphate concentration had no effect. At lower phosphate concentration, there was a slight frequency decrease indicating a mass increase, which is probably related to phosphate binding without desorption of PAH.

For the case of PSS terminated films, with both PDADMAC and PAH, no effects have been observed with QCM-D when exposed to either LiClO$_4$ or KH$_2$PO$_4$. This observation is in agreement with the results from the ζ-potential measurements.

It can be concluded that both the electrophoretic mobility experiments and the microbalance results demonstrate a similar specificity of ion polyelectrolyte interaction at the two extremes of the Hofmeister series: ClO$_4$$^-$ (chaotropic ion) strongly interacts with PDADMAC, and H$_2$PO$_4$$^-$ ions (cosmotropic ion) interact with PAH. In case of PAH being the top layer, perchlorate induced a densification of the layer, which can be inferred from the decrease of the ζ-potential with ionic strength. Such a behavior is characteristic for a hard surface, but it did not lead to the removal of the polycation from the multilayer. Therefore, we concluded that the interaction of ClO$_4$$^-$ with quaternary amines in PDADMAC is strong and specific. The driving forces are electrostatic compensation together with solvation effects due to their position in the Hofmeister series. The phosphate ions interact strongly with primary amines through hydrogen bonding. The absence of strong effects, such as layer degradation or charge reversal, does not necessarily imply that there is no specific interaction of perchlorate with primary amines. We know from previous IR measurements with PMETAC brushes that the interaction of ClO$_4$$^-$ with amines results in a restriction in the
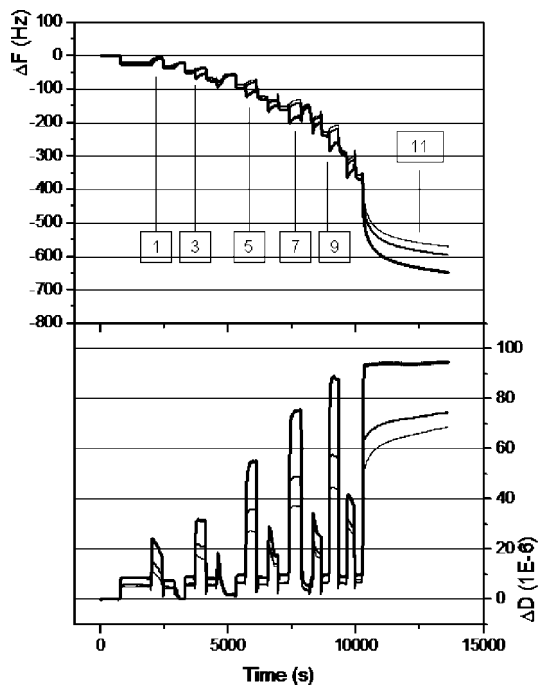
Figure 7. Changes in frequency (top) and dissipation (bottom) for the deposition of 11 polyelectrolyte layers of PDADMAC and PSS on a gold quartz crystal. The numbers in boxes in the frequency curves correspond to the assembly of PDADMAC layers.
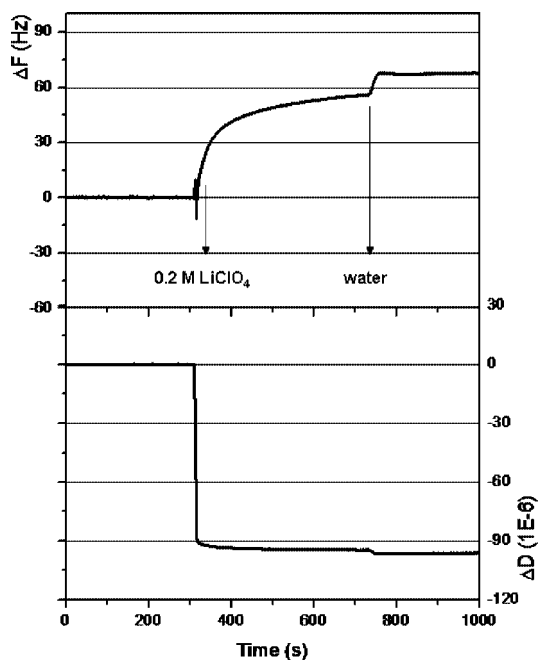
Figure 8. Changes in frequency (F3) and dissipation (D3) after LiClO₄ treatment on a multilayered system PDADMAC/PSS.

stretching mode of methylene groups close to the amine, which can be interpreted as a loss of conformational freedom. AFM data confirmed an increase in the elastic modulus for these brushes after exchange of counterions. Our interpretation is that ClO_4^- ions restrict the capacity of the PAH molecules to reorganize in the presence of salts.[22]
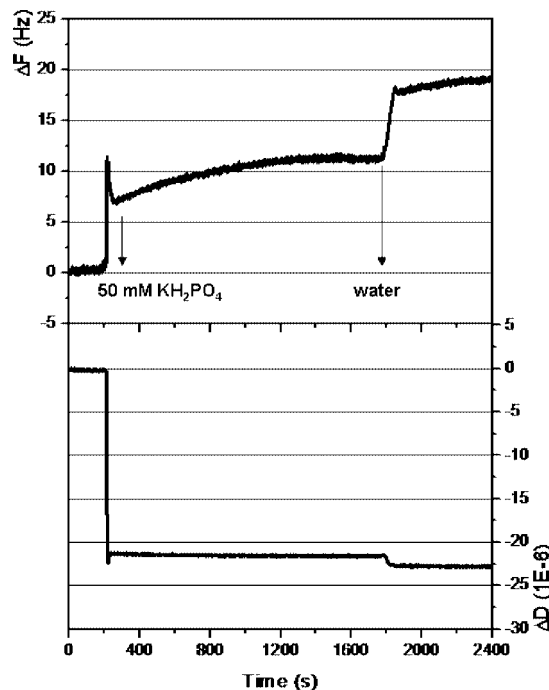
Figure 9. Frequency changes for an 11 layer PAH/PSS film after treatment with 50 mM KH_2PO_4 and washing with water.

In the cases where we have observed removal of polyelectrolytes, this process did not progress beyond the top layer. Even this layer was only partially removed. An explanation could be that the top layer has a smaller density than the intercalated polyelectrolyte layers. It can be thus more susceptible to ion binding induced effects. It is further known that there is interpenetration in LbL films and that the layers are not perfectly stratified. This interpenetration between subsequent layers may cause an extra constraint for the disassembly. The lack of a specific interaction of $H_2PO_4^-$ with the quaternary amines of PDADMAC but also their strong interaction with PAH, which we know can result from hydrogen bonding interactions, also hint that there may be hydrogen bonding between PSS and PAH. A direct confirmation of the influence of hydrogen bonding in the multilayer buildup is nevertheless missing. Further experiments are underway in this direction.

Conclusions

We demonstrated the specific interaction between ClO_4^- and PDADMAC and $H_2PO_4^-$ and PAH in LbL multilayer systems. This interaction had a pronounced influence on the ζ-potential. Charge reversal took place which was explained by the partial removal of polyelectrolytes from the top layer or charge compensation of the polyelectrolyte charge by the adsorbing ionic species. The driving forces for these interactions are ion specific. In one case (perchlorate/PDADMAC), entropic effects related to the solvent structure play a significant role. Phosphate, however, forms hydrogen bonds with primary amines.