Specific Anion Effect in Swelling of Polyelectrolyte Multilayers

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ABSTRACT: The well-known strong polyelectrolytes poly(diallyldimethylammonium) cation (PDADMA) and poly(4-styrenesulfonate) anion (PSS) form multilayers (PEMs) where formally the small counterions do not participate in any way. Previously, we have shown that by replacing the conventional chloride as the counteranion of PDADMA by other small anions occupying different positions in the Hofmeister series the resulting PEMs had widely different thicknesses in the dry state [*Langmuir* 2004, *20,*3679] and widely different stiffnesses in the wet state [*Macromolecules* 2004, *37,*9585]. In this work we show that even more striking differences are observed in the swelling behavior when comparing PSS/PDADMA multilayers made in the presence of fluoride or bromide. PSS/PDADMA-F shows nearly no swelling at different concentrations of NaF whereas PSS/PDADMA-Br shows strong swelling, especially at low concentrations of NaBr. The similar difference appears also when using the solutions of NaF, HCOONa, $NaBrO_3$, NaCl, $NaClO_3$, $NaNO_3$, and NaBr as swelling agents. Again swelling of PSS/PDADMA-F is negligible but PSS/PDADMA-Br swells, the extent of swelling having some correlation with the hydration entropy of anion; i.e., the more negative is the entropy, the stronger is swelling.

Introduction

Polyelectrolyte multilayers (PEMs) can be sequentially adsorbed on a charged surface, thus tailoring the surface with high precision in a nanometer scale.[1] Polyelectrolyte multilayer films are potentially suitable for many applications including drug delivery,[2] chemical sensors,[3] functional membranes,[4] and light-emitting diodes.[5] Even though the polyelectrolyte multilayers are nowadays well-studied systems,[6] still rather simple polyelectrolyte multilayer structures may possess characteristic properties that have remained more or less unexplored. From a point of view of possible future applications, it is crucial to understand the behavior of the film in contact with solution, including information on swelling and mechanical changes caused by different solutions.

Small ions have been known to participate strongly in the polyelectrolyte multilayer formation.[7] Small ions do not only determine the buildup rate but also have also a central role in the formation of the internal structure of a multilayer. The main function of small ions is the charge compensation of a polyelectrolyte which can take place both in the solution and in the multilayer phase. In addition to the big role of counterions, there are several short-range interactions affecting the deposition and structure of the multilayer,[8] for example, type of electrolyte,[7,9] polymer charge density,[10,11] pH,[12] deposition time,[7] quality of the solvent,[7,13] polymer contour length,[14] and temperature of the solution.[15,16]

The internal structure of the multilayer film has a key role in the swelling behavior. The zone model of the polyelectrolyte multilayers describes adequately the structure by charge compensation inside the multilayer.[17] In a typical case, a polyelectrolyte multilayer made of strong polyelectrolytes, the bulk of the film (zone II), contains polyions having intrinsic charge compensation. On the other hand, the film−solution interface (zone III) contains polyions with partial extrinsic charge compensation. The final structure of a multilayer film is assumed to consist mostly of 1:1 complexes of polyelectrolytes,[7,18,19] although there are also reported exceptions.[20,21] The presence of counterions inside the multilayer film has been discussed widely. Small counterions are claimed to be removed during the washing period, leading to a locally neutral polyelectrolyte complex.[22,23] Nevertheless, it has also been shown that the multilayer contains both polyions and small ions,[24−26] and also ca. 30% of the charged sites on polyions may be bound by oppositely charged fluorescent probes.[27]

The swelling of polyelectrolyte multilayer films has been induced by increasing the ionic strength of the solution.[28,29] The increase of salt concentration has been attributed to partial breaking of bonds between the oppositely charged polyions in the bulk of the film (zone II). As a consequence, the counterions and water of hydration will swell the film. The bond breaking can also lead to a complete destruction of the film in a sufficiently high ionic strength.[30] At the same time the increased ionic strength has been shown to smooth the film surface,[28] which refers to a partial reorganization of the bonds between the oppositely charged polyions. The surface of the film is "liquefied", and the bonds are reorganized so that the structure tends to a global energy minimum. The swelling that is dependent on the last deposited layer has been also observed.[31−35] The effect can be attributed to the zone III, usually predominated by the last adsorbed polyelectrolyte. The hydrophilicity and the ion penetration properties of the last deposited layer may dictate the properties of the whole film. The variation in the outer layer may end up in a sequential swelling−deswelling cycle in the adsorption process. Swelling depending on the outer layer has been detected equally well in case of weak and strong polyelectrolytes. Multilayer films with a combination of weak and strong polyelectrolytes and the films with only weak polyelectrolytes show significant swelling that depends on pH of the solution or the humidity of the environment.[36−39]

Although the influence of ionic strength on swelling has been a subject in several articles, one aspect which has not been adequately covered in previous reports is the specific effects of monovalent ions on swelling. This paper is an attempt to study these effects and as a model polyelectrolyte we have taken poly(diallyldimethylammonium) (PDADMA) cation. This is a quaternary ammonium compound which should have no specific interaction, e.g., by hydrogen bonding, with small counteranions. Poly(4-styrenesulfonate) (PSS) was chosen as the anionic polyelectrolyte.

Anions (and cations) are often arranged in a sequence called Hofmeister series. Originally observed as the order of efficiency in coagulating egg white, the sequence is now considered as manifesting the effects of ion hydration. There is no unambigu-

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ous physical or chemical parameter which gives the order of ions in the sequence fitting to every possible application, but ions are still divided into two groups: cosmotropic ions or water-structure-makers and chaotropic ions or water-structure-breakers. Of the simple halide ions, fluoride is cosmotropic and bromide and iodide chaotropic. Chloride is a borderline case between these two groups. As representatives of these two groups we have taken fluoride and bromide used as counteranions for PDADMA when making the multilayers with PSS. We have previously shown the profound influence on the shear modulus[25] and layer thickness[9] when changing the counterion from bromide to fluoride in the growth process. These measurements were mainly done during the layer-by-layer fabrication of the multilayers. A natural question arises: what happens if a ready-made multilayer is brought into contact with solutions containing the same or different anions as during their preparation? Is it possible that PSS/PDADMA-F changes to PSS/PDADMA-Br when contacting with bromide solution or vice versa? What happens if the multilayer is in contact with a solution containing a foreign anion? These are the questions to which we hoped to find answers in this work using a quartz crystal resonator (QCR) as our analytical tool.

Experimental Section

Materials. Poly(sodium 4-styrenesulfonate) (PSS, 70 kDa, from Aldrich) and 2-mercaptoethanesulfonic acid, sodium salt (MESA, from Aldrich), were used as received. Poly(diallyldimethylammonium chloride (PDADMA, 100−200 kDa, from Aldrich) was dialyzed against electrolyte solutions using a membrane with a nominal M_w cutoff of 3500 ("SnakeSkin" dialysis tubing, Pierce Biotechnology, Inc.), in order to exchange the counteranions. The 2% (w/w) water solution of PDADMA (150 mL) was dialyzed twice against 5 L of 0.1 M electrolyte solution containing NaBr or NaF. Dialysis was carried out in a continuous-flow system for 48 h. After that the polymer was dialyzed against water to remove the excess of electrolyte. Polymer content was determined by evaporating a known portion of solution and drying to constant weight by first evaporating the excess of water in a rotary evaporator and then heating up to 110 °C for 24 h, which was enough to reach a plateau in mass decrease.

The degree of sulfonation of PSS was found to be ca. 80% by using photometric titration of cetyltrimethylammonium bromide with toluidine blue as a metachromatic indicator.[40]

Multilayer Preparation for Quartz Crystal Analysis. The polished quartz crystals with gold plating (10 MHz, International Crystal Manufacturer, Oklahoma, or Lap-Tech, Inc., South Bowmanville, Ontario) were rinsed with water and dried. The crystals were cleaned in oxygen and hydrogen plasma before use.[41] The MESA primer layer was deposited at the gold surface of the crystal in order to obtain a negative ionic charge on the surface (a droplet of 1 mM water solution of MESA for 1 h on the gold surface of the crystal). After that, the crystal was mounted in a flow cell.

The multilayer films were made by using an automated multilayer deposition system consisting of a flow cell and a computer-controlled peristaltic pump with a multiposition valve for switching between the coating and the rinsing solutions. The general deposition sequence was as follows: Sequentially, a 1.5 mL portion of 10 mM (referring to monomer concentrations) solution of PDADMA or PSS (in 0.1 M aqueous solution NaBr or NaF) was injected into the cell and allowed to adsorb for 15 min. The crystal was then rinsed for 5 min with 20 mL of corresponding 0.1 M electrolyte solution. The ionic strength of solution inside the cell was kept constant during the whole deposition process to ensure that there were no swelling and deswelling of the film. The solutions were deaerated before use by bubbling helium for 30 min.

The crystal parameters were measured as described in detail in our previous publication using a prototype crystal analyzer with impedance detection. The principle of operation of the instrument has been published earlier.[42] The flow cell was placed in a container in a thermostat bath with a steady air flow in order to achieve the accurate thermal stability needed in the quartz crystal measurements. The cell temperature was kept constant during the measurement (25 ± 0.03 °C). The whole deposition and measurement system was controlled by a computer program written with the National Instrument's LabVIEW general instrumentation utility.

In this work the results from the QCR measurements are expressed as the complex surface acoustic impedance and given in the units of rayl (1 rayl = 1 kg m^{-2} s^{-1}). This is a more natural and mathematically consistent way to express these measurements than the customary relative frequency change and dissipation.[42,43] If needed, the real and imaginary parts of surface acoustic impedance can be easily transformed to dissipation and relative frequency change.[40]

Results and Discussion

Measurements on a Quartz Crystal Resonator. The multilayers studied in this work are rather thick; for instance, the PSS/PDADMA-F multilayer was composed of 200 layers and PSS/PDADMA-Br of 60 layers. For thin films it is customary to use the classical Sauerbrey equation in simple mass measurements. This approximate equation tells essentially that the relative decrease in the mechanical resonance frequency is equal to the relative increase in the mass of the resonator in the effective oscillating area. For thick layers this method of mass measurement is often considered liable to errors, such as caused by the viscoelasticity of the layer, bad contact, or slippage at the resonator−film interface or simply a layer too thick for the Sauerbrey approximation. Fortunately, as we have previously shown, the errors are generally smaller than usually thought.[43] As long as the thickness is reasonably far from the acoustic resonance of the film, the imaginary part of the surface acoustic impedance grows linearly with the areal mass density of the film, quite irrespective of the viscoelasticity. This means that if we observe a linear increase of the imaginary part of the surface acoustic impedance (or decrease in the relative resonance frequency) as a function of the layer number from the beginning of the LbL process, we can rely in most cases on the calculated areal mass density in the linear range. If the layer material is very "soft", i.e., its shear modulus is low, it might be necessary to use the medium-corrected form of the Sauerbrey equation:[44]

$$\Delta\zeta'' = \omega\Delta m\left(1 - \frac{\omega\rho_l\eta_l}{\rho_f}\,\mathrm{Im}\,J\right)$$

where $\Delta\zeta''$ is the change in the imaginary part of the surface acoustic impedance, ω is the angular frequency ($=2\pi f$), Δm is the change in the areal mass density of the film, ρ_l and η_l are the density and viscosity of the solution, respectively, and $\rho_f$is the density of the film. The correction term is proportional to the imaginary part of the shear compliance J. In the case of PSS/PDADMA-F the shear modulus[25] is $G = 6.0 + j5.5$ MPa, giving Im $J = 8.3 \times 10^{-8}$ kg^{-1} m s^2. Assuming the film density of 1200 kg m^{-3}, the correction amounts to ca. 0.4%; i.e. it is negligible in the present context. The shear modulus of PSS/PDADMA-Br is many times higher, meaning that the medium correction is still smaller. Sometimes the interfacial slippage is considered as a source of error when dealing with thick layers. As a matter of fact, slippage on a quartz crystal resonator at the film−liquid contact can be observed in some special cases of hydrophobic−hydrophilic interfaces with a dramatic influence on the mass measurements.[45] The incipient interfacial slippage either at the resonator−film interface or the film−liquid interface should be observed as irregularities in the growth curves during the LbL process. However, the graphs were smooth and linear (Figure 1).

Swelling Induced by Ionic Strength. The swelling event is rather difficult to study with very thin multilayers, where the

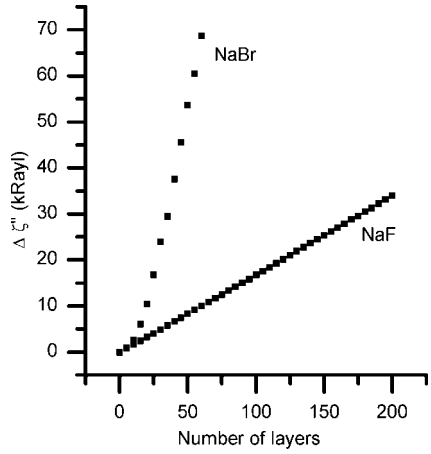

Figure 1. Buildup of PSS/PDADMA multilayers in 0.1 M NaBr and NaF. The imaginary part of the surface acoustic impedance of every fifth layer is plotted as a function of the layer number.

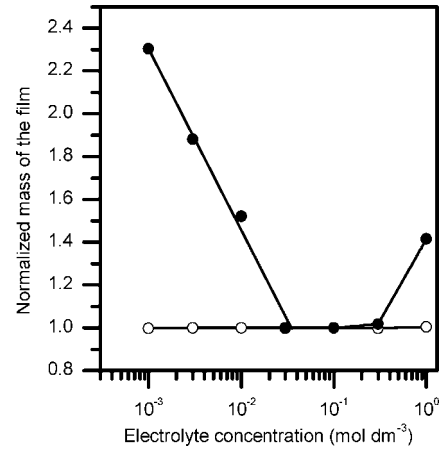

Figure 2. Mass of the PSS/PDADMA films (normalized in 0.1 M solution) vs electrolyte concentration in solution. The film deposition and the adjustment of the electrolyte concentration have been made using NaBr (solid symbols, 60 layers) and NaF (open symbols, 200 layers). The lines are a guide to the eye.

level of swelling in most cases is very low. For the measurements concerning swelling induced by ionic strength we selected two PSS/PDADMA films: a 200-layer film deposited in 0.1 M NaF (PSS/PDADMA-F) and a 60-layer film deposited in NaBr (PSS/PDADMA-Br). Both films were PSS-capped because PSS-capped films are more hydrophobic and the alterations in the solution conditions are made via anion changes in this study. Despite the lower number of layers in the films, the film deposited in NaBr has about twice the mass compared to the film deposited in NaF.

In general, the charge compensation can be treated as ion-pair formation with Bjerrum association constants described in the equilibrium eqs 1, 2, and 3. These partial reactions can be also presented in a single equilibrium equation. But in this concept the equations are kept separate in order to emphasize the individual nature of the charge compensation reactions. The association constants describe the type of charge compensation. The constants K_i, K_{ea}, and K_{ec} represent intrinsic charge compensation, extrinsic charge compensation by small anions, and extrinsic charge compensation by small cations respectively. $Pol^{+/-}$ refers to a charged monomer unit in the polymer chain, and A^- and C^+ represent small anions and cations, respectively. All the described ion-pair formation reactions can take place in the solution and in the multilayer phase.

$$Pol^+ + Pol^- \underset{K_i}{\rightleftharpoons} Pol^+Pol^- \quad (1)$$

$$Pol^+ + A^- \underset{K_{ea}}{\rightleftharpoons} Pol^+A^- \quad (2)$$

$$Pol^- + C^+ \underset{K_{ec}}{\rightleftharpoons} Pol^-C^+ \quad (3)$$

The swelling in the high ionic strength can be understood on the basis of these equilibrium equations. The increase in the ionic strength is forcing the equilibrium reactions 2 and 3 toward the products side and naturally the equilibrium 1 toward the reactant side.

From the studied pair of films the film deposited in 0.1 M NaF represents presumably a case with an entirely intrinsic charge compensation in the bulk of the film. This is mainly because of low affinity of Na^+ and F^- ions on the studied polyelectrolytes.[7] The swelling of the film in the increased ionic strength, generated by NaF, is observed, but it is rather weak. Figure 2 shows that the mass of the 200-layer film does not practically change within 3 h at the NaF concentrations below 0.3 M, while the 1 M solution induces a small mass increase, only less than 1%, which is due to the swelling of the bulk of the film. The level of swelling is remarkably lower than observed by Schlenoff et al. when using NaCl.[28] The increase of salt concentration is forcing the equilibrium eqs 2 and 3 only slightly to the reactant side. However, the polyelectrolyte multilayer deposited in 0.1 M NaBr behaves very differently. By increasing the ionic strength to 1 M, the film will swell as expected. The increase in the mass is ~40%. The higher level of swelling can be explained by the higher affinity of bromide toward PDADMA compared to fluoride and by the different internal structure of the films.[25] Even more dramatic swelling can be obtained if the ionic strength is decreased below 0.1 M. Slow swelling process is present when the concentration is less than 0.01 M. It takes ~1.5 h to level off in 10 mM solution and 4 h in 3 mM solution. During the swelling experiments we observed that there is a certain induction time needed before swelling is observed at a low ionic strength. The time was usually over 30 min. Certain induction time has earlier been noticed in the smoothing of a multilayer in moderately high ionic strength.[28] After the induction time the film would swell and deswell without initial delay in low ionic strength. Most likely this phenomenon is related to a structural rearrangement in the surface of the film, "break-in", and it will be discussed in the later sections of this paper. It is noteworthy that the deswelling process of the film is rapid, only a couple of minutes is needed to restore the original mass, when the solution is changed back to 0.1 M NaBr. A deviation from the complete restoration of mass can be observed when 1 mM solution is used. After a long period of swelling in 1 mM solution (over 6 h) the deswelling process, which is rapid, does not return the film to the original mass, but the mass remains permanently about 10% higher. The same applies to using pure water for swelling. If the swelling is sufficiently extensive, some rearrangement presumably takes place in the swollen film. The rearrangement in the bulk of the film is most probably similar to the surface smoothing in the high ionic strength, the ionic bonds organizing to reach the local energy minimum in the partially liquefied film. The extent of swelling is actually enormous. The mass increase is approximately linear in the logarithmic concentration scale below 0.03 M (Figure 2). The mass of the film in 1 mM solution is over 2 times higher than in 0.1 M solution. Similar swelling when lowering the ionic strength has been observed in PSS/PDADMA capsules.[46] Whether the low ionic strength would eventually destroy the film was not studied. But it is certainly noted that this kind of film is stable only within a limited range of ionic strength. The

film seems to be in equilibrium in 0.1 M solution or in the solution of its fabrication, and the increase or decrease of the ionic strength would induce a change in the system.

When comparing the dramatically different swelling of PSS/PDADMA-Br and PSS/PDADMA-F, the inevitable conclusion is the vital importance of the counteranion. Previously, we have demonstrated that the multilayer deposited in NaBr contains significant amounts of counteranions,[25] and the charge compensation inside the bulk of the film is partly extrinsic after the deposition. The starting point in the multilayer in the 0.1 M NaBr solution is that the equilibrium (1) is almost fully on the products side. The equilibrium (3) is almost fully on the reactants side, but the equilibrium (2) is partly on the products side because of the high affinity of bromide to PDADMA. By decreasing the ionic strength, there are no significant changes in the equilibria (1) and (3), but the equilibrium (2) is tending toward the reactants side to compensate for the drop in the bromide concentration. However, there are no free cations in the multilayer phase to compensate for the excess charge of PDADMA formed in this apparent release of ions, and as a consequence water is forced into the membrane phase by osmosis. The swelling in low ionic strength is a consequence of a normal behavior of free polyelectrolyte in solution (the polyelectrolyte effect[47]), while the swelling in high ionic strength is attributed to the natural behavior of polyelectrolyte complexes[28] or some polyzwitterions[48] (the antipolyelectrolyte effect[47]). In the case of PSS/PDADMA-F the charge compensation is mainly intrinsic; there is only a low concentration of fluoride in the membrane, and consequently the osmotic pressure is not driving water into the film. On the other hand, when the ionic strength is increased, one would expect a reverse process to occur, i.e., removal of water and the consequent deswelling of the film. However, the affinity of counterions for the film constituents more than compensates this effect. The counterions carrying hydrate water penetrate into the film inducing swelling. In conclusion, it can be stated that the shape of the swelling curve (Figure 2) gives valuable information on the nature of the charge compensation inside the film. If the film has purely intrinsic charge compensation, the curve would resemble the film made in fluoride. The film is swelling slightly only when the ionic strength is raised. But if the film has some extrinsic compensation inside the film, the curve has a U-shape having a definite minimum and swelling when the ionic strength is increased or decreased. The same U-shape but considerably lower has been found in films prepared in sodium chloride.[26,28]

Swelling Induced by Counterions. Although the effect of various counterions on the multilayer buildup has been a subject of several prior studies, the studies concerning the effect of different ions on an already made film have been sparse in number.[49,50] Anions have different binding affinities to polycations. If swelling is dependent on the ionic strength of the solution, one would expect dependence on the salt type as well. We have been using 0.1 M solutions of various electrolytes to study the effect of anions on the swelling event. For this study the films were deposited in 0.1 M NaF and 0.1 M NaBr, having 25 layers with PDADMA as the terminating layer. To characterize the binding affinities of ions, it is possible to rank the ions by their hydrodynamic radius or atom size,[49] but that is only relevant if the ions are monatomic, for example, in the halide series. The binding affinities also follow the Hofmeister series,[51] but due to the empirical nature of the series, there are no generally applicable numerical values to sort the ions into an order. We have successfully used the hydration entropy of anion[52] to characterize the binding affinity.[9] Similarly to the ionic strength induced swelling experiments, the multilayer deposited in NaF shows very little effect for changing the electrolyte solution (Figure 3). Only slight shrinking of the film

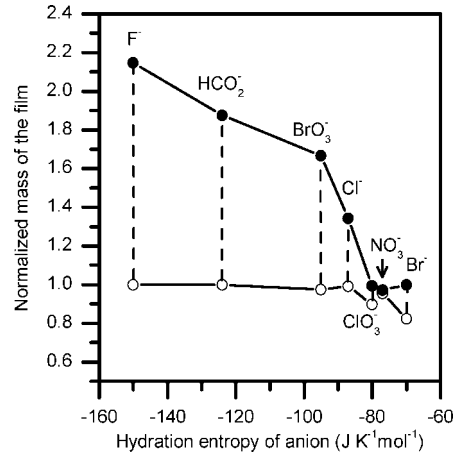

Figure 3. Mass of the PSS/PDADMA films in sodium salts of corresponding anions vs the hydration entropy of anions. The 25-layer films are deposited, and the mass is normalized in 0.1 M NaBr (solid symbols) and NaF (open symbols).

is observed when certain anions are used (ClO_3^-, NO_3^-, and Br^-), indicating very strong binding of these anions to the free charges in the film. Together with the strong binding affinity and low extent of hydration these anions would dehydrate the film. Swelling by varying the counterion but keeping the ionic strength constant can be observed by using a multilayer deposited in NaBr. Even though fluoride has the smallest atomic weight, 0.1 M NaF solution causes the largest mass increase. The swelling affinity follows the Hofmeister series of anions, and the weakest binding anion (F^-) brings along the largest amount of water into the film. The effect of fluoride is very similar to decreasing the ionic strength of the solution. The swelling time in 0.1 M NaF solution is ~1 h in the 25-layer film, but deswelling takes place within a couple of minutes, when going back to 0.1 M NaBr. The long swelling time would indicate the deformation of the morphology inside the film together with ion exchange and concurrent incorporation of water. The slow release rate of bromide has been reported also earlier.[53] Fluoride has a low affinity to PDADMA but has a large excess compared to the bromide inside the film, causing a slow exchange process. When changing back to bromide solution, bromide with high affinity to PDADMA replaces fluoride in the film very rapidly. Using anions with higher hydration entropy values than the value of bromide (I^-, SCN^-, ClO_4^-) causes permanent shrinking of the film, indicating very strong binding to PDADMA charges in the film.

Effect of the Last Deposited Layer. In the measurements concerning the swelling induced by decreasing the ionic strength, we observed the break-in time before the swelling and deswelling taking place. In those measurements we used PSS-terminated films. The break-in time of the film deposited in NaBr was estimated to be over 30 min. The break-in effect was observed with films having sufficiently high number of layers (more than 20), which may indicate that these films have a fully developed zone II. The break-in effect is demonstrated in Figure 4a. The 26-layer PSS-capped PSS/PDADMA multilayer deposited in 0.1 M NaBr is allowed to be in contact with pure water after thorough rinsing. Immediately after exposure to water the apparent mass is slightly decreased. That is mainly due to the lower density of water compared to the density of 0.1 M NaBr solution. Besides the initial decrease in mass, there are no other significant changes within the first 60 min. Then a sudden break takes place. A rapid swelling event commences, and the film swells up to 1.5 times in mass within an hour. When the solution is changed back to 0.1 M NaBr, the film reduces back to the original mass within a time span of 150 s. The swelling does

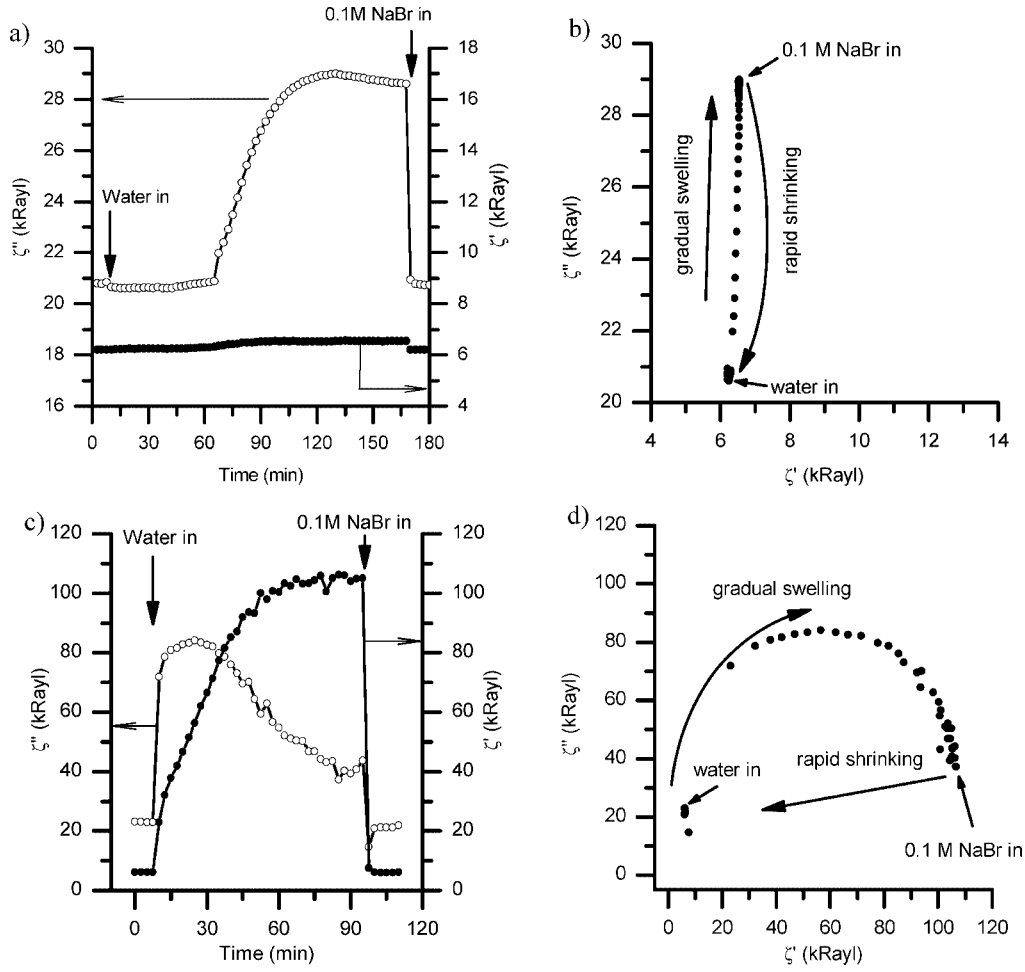

Figure 4. Surface acoustic impedance vs time (a) and complex plane representation (b) of PSS-capped 26-layer film. Surface acoustic impedance vs time (c) and complex plane representation (d) of PDADMA-capped 27-layer film. The components of complex surface acoustic impedance of the quartz crystal, ζ' and ζ'', indicate energy loss (dissipation) and mass (when Sauerbrey equation is valid), respectively.

not induce significant increase in the real part of the surface acoustic impedance, indicating very minimal additional energy losses in the oscillation. The complex plane representation in Figure 4b shows more clearly that the swelling induces only very minor changes the elastic properties of the film, justifying the use of the Sauerbrey equation. Figure 4c shows the same kind of swelling experiment with the 27-layer PDADMA-capped multilayer. After a contact with water the immediate swelling takes place. The extent of swelling is actually so high that, after some time, the $\Delta\zeta''$ is no longer proportional to the mass increase. After a local maximum there is decrease in $\Delta\zeta''$ values, as the swelling continues. The decrease in $\Delta\zeta''$ does not indicate mass lost because there is a simultaneous increase in the real part of surface acoustic impedance ($\Delta\zeta'$) as the swelling continues. In fact, the surface acoustic impedance plotted in a complex plane forms an arc (Figure 4d), which is an obvious start of a spiral. This is a direct indication that the film has reached the point of acoustic film resonance (AFR).[43] The extent of swelling shows that the film gains mass more than 4 times compared to the starting situation because the deviation in the Sauerbrey equation is always toward the lower detected mass. When the solution is changed back to 0.1 M NaBr, the film shrinks back to the original mass very rapidly.

PDADMA-capped film swells more than PSS-capped film. A similar swelling event has been reported by Bruening et al.[35] They observed that when PSS/PDADMA multilayer is deposited in high ionic strength (0.5 M NaCl), there is a significant difference in swelling between the films capped by polycation or polyanion . This does not occur in the films that are deposited at a lower ionic strength (0.1 M NaCl). However, extensive swelling was observed in the films containing fewer layers than in this paper. The PSS/PDADMA system has been studied also by McCormick et al. by using NMR methods,[54] and an observation relevant to the present work was the slower dynamics of water molecules in the PSS-capped film compared with the PDADMA-capped film.

We propose that the explanation to this swelling behavior is in the multilayer film structure. The bulk of the PSS-capped film consists of PSS/PDADMA complexes in addition to Br-compensated PDADMA[25] which is liable to behave like free polyelectrolyte in low ionic strength. The surface of the newly deposited film consists of stratified PSS layer. When exposed to pure water, the expected expansion of Br- compensated PDADMA (the polyelectrolyte effect) in the bulk of the film is held up by the intact PSS layer. Several reasons can be suggested for this behavior. The capping PSS layer is rather hydrophobic.[55] Additionally, the buildup in these conditions generates very deep diffusion of polyions. Our buildup analysis revealed that the apparent penetration depth of polyions is about 88 nm,[16] while the whole film in this measurement is ~200 nm ($d = \Delta\zeta''/(\omega\rho_f)$, assuming film density of 1200 kg m^{-3}). Consequently, the thickness ratio between the bulk (zone II) and the surface (zone III) indicates that the last deposited layer is a dominant factor in controlling the interfacial properties of this film. Furthermore, this film is mechanically very stiff, resembling almost glass-like material.[25] Combining these features, we have a film with thick, stiff, and hydrophobic surface zone, where the mobility of water is diminished.[53] Apparently, for that

reason, the film structure prevents the expansion of the underlying PDADMA layer for a reasonably long time. But, once the expansion of PDADMA starts, it speeds up the breaking of the protecting PSS cap and generates a rush of water inside the film. The concurrent softening of the film also evidently accelerates the diffusion inside film, blending the material between the bulk and the surface zone. The break-in does not completely destroy the last deposited PSS layer because the deposition with PDADMA is still possible. The reason why the break-in time is not observed in PDADMA-capped films is apparently because there is no solid stratified PSS layer below the capping PDADMA layer, but instead entangled polyelectrolyte complexes, allowing rapid expansion of PDADMA chains.

Conclusions

We have used a quartz crystal resonator to receive information on the effect of anions on swelling of PSS/PDADMA multilayers. The extent of swelling induced by changes in ionic strength of the bathing solution was found to be dependent on the internal structure of the multilayer. The structure takes form at the time of deposition, and it is strongly influenced by the deposition conditions. The PSS/PDADMA multilayer deposited in the presence of fluoride exhibits very minor swelling. That is attributed to the intrinsically compensated polyion pairs and low affinity of fluoride toward PDADMA. The multilayer deposited in the presence of bromide exhibits very pronounced swelling, especially at low concentrations. At some conditions the mass gain was more than 4 times compared to the original mass. That is ascribed to the extrinsically compensated PDADMA which is liable to behave like free polyelectrolyte, and therefore it is able to expand at low ionic strength. Strong contribution of the counteranion on swelling was found also by keeping the ionic strength constant but varying the anions. The trend was basically similar to the variation of ionic strength. The multilayer containing extrinsically compensated PDADMA gave clear response to the different electrolytes. The extent of swelling in this case was found to correlate with the hydration entropy of anion. The anion with the most negative entropy value induced the strongest swelling. The seven anions tested in this work seem to follow the famous Hofmeister series in their swelling power, the structure-breaking anions causing least swelling.

In some PSS-terminated films the swelling begins after a certain induction time. The interfacial zone induced a delay of ~60 min on the expansion of extrinsically compensated PDADMA inside the film. The behavior is attributed to the hydrophobicity of the capping layer and the protracted diffusion of water, combined with considerable thickness and rigidity of the interfacial zone.

As a conclusion, when stored in NaF solution, the properties of PSS/PDADMA-Br film do not resemble the properties of PSS/PDADMA-F film. The same applies to storing in NaBr solution.

References and Notes

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