Counterions in Poly(allylamine hydrochloride) and Poly(styrene sulfonate) Layer-by-Layer Films

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The amount of counterions in layer-by-layer (LBL) films of poly(allylamine hydrochloride) (PAH) and poly(styrene sulfonate) (PSS) has been determined with X-ray photoelectron spectroscopy (XPS) for films prepared from solutions with various NaCl concentrations. Sodium and chloride counterions are present in LBL films produced from salt solutions, which are located at the surface and in the bulk of the films. The percentage of bulk counterions increases with the ionic strength of the polyelectrolyte before reaching a constant value. The bulk sodium/sulfur percentage ratios tend to 0.8 for samples washed with pure water and for samples washed with NaCl aqueous solutions, while the bulk chlorine/nitrogen percentage ratios tend to 0.5 for the same samples. The ratio between the percentages of polyelectrolyte ionic groups lies close to unity for all samples, indicating that counterions do not contribute to charge compensation in the polyelectrolyte during the adsorption process. The presence of counterions in LBL films is explained by Manning condensation near the polyelectrolyte ionic groups, leading to inter-polyelectrolyte ionic bondings via ionic networks. It is believed that condensation leads to the formation of NaCl crystallites in these LBL films, which was confirmed by X-ray diffraction measurements.

Introduction

The alternate adsorption from solution of oppositely charged polyelectrolytes, that is, the layer-by-layer (LBL) technique, is promising for the fabrication of functional molecular heterostructures in electronic and photonic devices. Since LBL films are obtained from adsorption processes at a solid/liquid interface, adsorption parameters such as solution concentration, molecular weight, temperature, time, pH, and ionic strength affect film buildup and structure. Ionic strength, in particular, plays an important role in the adsorbed layer thickness by altering the polyelectrolyte conformation in solution and consequently at the solid surface. In addition, adsorption is believed to take place when polyelectrolyte ionic groups bind to oppositely charged ionic groups of already adsorbed polyelectrolyte. As a consequence, polyelectrolyte counterions are expected to be replaced by the ionic groups of the opposite polyelectrolyte and stay in solution. However, reported experimental results are still contradictory concerning the role of salt and counterions in the formation of polyelectrolyte multilayers. For example, Schmitt et al. estimated an incorporation of 0.5–0.8 counterions per monomer unit, Fery et al. showed that salt concentration influences the structure of poly(acrylic acid)/poly(allylamine hydrochloride) LBL films, Laurensen did not detect salt ions in films of poly(butyl vinylidene-dibromide(PBV)/PSS washed with water after each adsorption step, and Sukhorukov et al. showed that sodium and chloride ions do penetrate into poly(allylamine hydrochloride)/poly(styrene sulfonate) LBL films reversibly. Recently, Riegler and Esser showed that LBL films must contain small counterions for charge compensation, since the polyelectrolyte charge stoichiometry is not exactly 1:1, which supports the experimental results of Schmitt et al. and Fery et al.

Concerning the interactions accounting for polyelectrolyte adsorption, ionic and secondary interactions such as hydrogen bonding and hydrophobic interactions have been reported. A classification of the various types of LBL films in terms of the mechanisms responsible for adsorption was proposed by Oliveira et al. Hydrogen bonds play an important role in both the stability and the adsorption of LBL films, particularly when protonated groups are present. Molecules with hydrogen-bonding capability easily adsorb by this, but hydrogen bonds may...
also contribute to the adsorption of polyelectrolytes via the formation of water molecule networks.\(^{17}\) In addition, counterions may be involved in those networks if present as that of the polyelectrolyte solution, after each adsorption layer.

The layer-by-layer films were prepared from aqueous solutions of poly(allylamine hydrochloride) (PAH) and poly(styrene sulfonate) (PSS) and, unless otherwise stated, were not rinsed with pure water. Both, type I and II samples were dried after the completion of each layer.

For the UV–visible spectrophotometric and X-ray measurements, PAH/PSS LBL films were similarly prepared onto hydrophilized glass. The glass hydrophilization was obtained by keeping the glass substrates for 30 min in an etching solution, or a piranha solution, comprised of hydrogen peroxide and sulfuric acid (3:1). Note that care must be taken in preparing and handling this solution, as the reaction is exothermic and the solution is highly corrosive.

The X-ray photoelectron spectrometer was an XSM800 (Kratos) operated in the fixed analyzer transmission (FAT) mode, with a pass energy of 10 eV and non-monochromatized Mg K\(\alpha\) X-radiation (\(h\nu = 1253.7\) eV). A power of 130 W was used. Samples were analyzed in an ultrahigh vacuum (UHV) chamber (\(10^{-10}\) Pa) at room temperature, using a glancing angle of incidence of (PAH/PSS)\(_8\) samples prepared with different NaCl salt concentrations and rinsed with ultrapure water, Type I and II samples.

XPS Measurements. To investigate the presence of counterions in LBL films, the XPS spectra were measured for (PAH/PSS)\(_8\) films prepared with different NaCl salt concentrations at different angles of incidence. Type I films were washed with ultrapure water, and type II films were washed with a salt solution with the same concentration as that of the polyelectrolyte solution and, unless otherwise stated, were not rinsed with pure water. Both, type I and II samples were dried after the completion of each layer.

Table 1. Element Compositions in Percentages, Obtained from XPS Spectra Taken at 0° Incidence, of (PAH/PSS)\(_8\) Films Prepared with Different Salt Concentrations and Rinsed with Ultrapure Water, Type I Samples

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<tr>
<td>0</td>
<td>58.5 ± 0.5</td>
<td>29.4 ± 0.3</td>
<td>1.9 ± 0.1</td>
<td>1.01 ± 0.05</td>
<td>0.98 ± 0.05</td>
<td>0</td>
<td>0</td>
<td>9.1 ± 0.5</td>
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<tr>
<td>0.05</td>
<td>71.8 ± 0.7</td>
<td>17.6 ± 0.2</td>
<td>5.5 ± 0.3</td>
<td>5.1 ± 0.3</td>
<td>4.1 ± 0.2</td>
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<td>0.15</td>
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<tr>
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<td>16.6 ± 0.2</td>
<td>4.6 ± 0.2</td>
<td>3.8 ± 0.2</td>
<td>4.0 ± 0.2</td>
<td>1.1 ± 0.1</td>
<td>2.1 ± 0.1</td>
<td>0.38 ± 0.02</td>
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<tr>
<td>0.3</td>
<td>67.2 ± 0.7</td>
<td>19.9 ± 0.2</td>
<td>3.2 ± 0.2</td>
<td>2.9 ± 0.2</td>
<td>4.1 ± 0.2</td>
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<td>4.2 ± 0.2</td>
<td>0.46 ± 0.09</td>
<td>2.8 ± 0.6</td>
<td>0.97 ± 0.05</td>
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<td>34.4 ± 0.3</td>
<td>2.5 ± 0.2</td>
<td>2.0 ± 0.2</td>
<td>3.3 ± 0.2</td>
<td>1.8 ± 0.2</td>
<td>2.5 ± 0.3</td>
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<tr>
<td>0.5</td>
<td>67.8 ± 0.7</td>
<td>19.6 ± 0.2</td>
<td>3.3 ± 0.3</td>
<td>2.7 ± 0.3</td>
<td>4.0 ± 0.2</td>
<td>0.92 ± 0.2</td>
<td>3.9 ± 0.7</td>
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Figure 1. Polyelectrolyte molecular structures: (a) poly(allylamine hydrochloride) (PAH); (b) poly(styrene sulfonate) (PSS).


brackets containing the element symbols correspond to the calculated atomic percentages. In contrast to cast films of neat PAH and neat PSS, our data show that, for samples prepared without sodium chloride, there are no Na\(^+\) and Cl\(^-\) counterions in the LBL films. Therefore, polyelectrolyte molecules are bound via ionic attraction between the NH\(_3\)\(^+\) and SO\(_3\)\(^-\) groups of each polyelectrolyte. For the samples prepared with polyelectrolyte solutions containing salt, Na and Cl elements are present in the LBL films in a relative amount that increases with the solution salt concentration. For samples washed with a salt solution after polyelectrolyte adsorption, type II samples, the relative percentage of Na and Cl elements is higher than that for type I samples. This suggests that the washing solution prevents counterions from being removed from the film, which may even be further stabilized in the film depending on the film drying conditions. The analysis of the XPS spectra also allows one to obtain information about the adsorption process of the first PAH layer onto the aluminum substrate. The peak at 408 eV for the sample prepared without salt is associated to the \(\text{ONO}_2\) group, which means that the nitrogen group of PAH reacts with the aluminum oxide of the substrate surface.

**Degrees of Charging.** The atomic percentages of nitrogen in Tables 1 and 2 are systematically higher than those for sulfur; that is, some nitrogen groups are not ionized. The electrical charge of PAH can be estimated by calculating from the XPS spectra the percentage of nitrogen atoms associated to NH\(_2\) and NH\(_3\) groups. Two components centered at 401.0 ± 0.2 and 403.0 ± 0.2 eV could be fitted to the nitrogen region, with the only constraint imposed being the same full width at half-maximum (FWHM = 2.1 ± 0.1 eV) for both components. The [NH\(_3\)]\(^+\)/[N] values are also indicated in Tables 1 and 2 for both types of samples. For the case of the 0 M salt solution, NO\(_2\) \(\text{is present with an atomic percentage of } 0.5\%\). The fraction of electrically charged nitrogen groups, [NH\(_3\)]\(^+\)/[N], as a function of the polyelectrolyte solution salt concentration for both types of samples is plotted in Figure 2. From these plots, one can see that, at lower salt concentrations (<0.3 M), for type I samples, the fraction of electrically charged nitrogen groups is ~0.9, while, for type II samples, this fraction is ~0.7. In addition, for salt concentrations higher than 0.3 M, the fraction of electrically charged nitrogen groups tends to 0.8 for both types of samples. This latter value is consistent with the estimate by Riegler and Essler\(^8\) for PAH/PSS LBL films. The [NH\(_3\)]/S ratio values were found to be dose-to-unity, which are similar to the ones obtained by Jayanty et al.\(^{19}\) for the polyelectrolyte templated polyaniline system, although it seems that the ratio tends to decrease to 0.7 for type I samples at high salt concentrations. The deviation from 1 could only be interpreted as an increase of counterions in the films.

The sum of the total electrical charge in percentage for PAH/PSS LBL films, Q, could be estimated from the charge balance as follows:

\[
Q = a_{PAH}[N] - a_{PSS}[S] - [Na] - [Cl]
\]

where \(a_{PAH}\) and \(a_{PSS}\) are the degrees of charging for PAH and PSS, respectively, and the symbols between the square brackets correspond to the calculated atomic or electrical charge percentage of the respective elements. The degree of charging for PAH, a weak polyelectrolyte, corresponds to the [NH\(_3\)]\(^+\)/[N] ratio, while the degree of charging is equal to unity for PSS because it is fully charged. For all the samples, the total charge was as expected. The total charge is positive, which is consistent with a topmost negative layer and, consequently, with an overlayer of sodium atoms to compensate for the sulfur groups. Since XPS is more sensitive to the extreme surface in comparison to deeper layers, sodium appears with a larger signal than chloride.

**Counterion Related Percentage Ratios.** Since Na\(^+\) and Cl\(^-\) are the counterions for PSS and PAH polyelectrolytes, respectively, the plots of [Na]/[S] and [Cl]/[N] percentage ratios as a function of the polyelectrolyte solution salt concentration, shown in Figure 3, are representative of the amount of counterions in the films as the solution salt concentration is increased. The general trend is that [Na]/[S] and [Cl]/[N] increase with increasing solution salt concentration.

For type I samples, the [Na]/[S] percentage ratio attains a constant value of ~0.8, while the [Cl]/[N] percentage ratio goes to a constant value of 0.5. These values are consistent with a practically null charge balance. The ratio results show that the Na\(^+\) and Cl\(^-\) counterion amounts are smaller than the sulfur and nitrogen amounts, respectively. Since the LBL films are temperature stable,\(^{13}\) the ionic interactions between polyelectrolytes should essentially be the same for films prepared with and without salt; that is, polyelectrolyte groups are practically all bonded to the opposite polyelectrolyte groups. As a
The lower BE component of the Na 1s region is centered at 1071.7 ± 0.1 eV for all the samples. The second component is centered at 1073.2 ± 0.6 eV for the samples prepared with salt solution. For the Cl 2p region, a similar behavior is observed: the lowest BE Cl 2p3/2 component is centered at 198.2 ± 0.1 eV, while the higher BE component is centered at 200.2 ± 0.6 eV for the samples prepared with salt solution. The first Na 1s component corresponds rather well with the BE measured for Na 1s in pristine PSS (1071.76 eV) obtained with high resolution XPS spectrometer. However, for the first Cl 2p3/2 component, a higher value is obtained than the one reported by the same authors for chlorine in pristine PAH. It seems, therefore, that interactions of chlorine ions in the LBL films are different from the ones existing in PAH.

For the second component, no assignment could be done on the basis of the literature. This fact associated with the change in BE leads us to tentatively assign it to a compound (probably NaCl) where both sodium and chlorine are present and which has an electrical conductivity different from that of the LBL film, the difference being maximum in the sample prepared from the most salt concentrated solution. The corresponding spectra are shown in Figures 4 and 5. In both spectra, the intensity of the high BE peak of the Na and Cl elements increases; that is, two kinds of bonding for Na and Cl elements can be inferred. Furthermore, when the XPS angle of incidence was increased up to 60°, the ratio between the sodium high binding energy and the total percentage of sodium increased, which means that the high BE components for Na and Cl correspond to species which are near or on the sample surface.

For type I samples, the increase in intensity of the high BE peak was not observed at high salt concentrations. In this case, ~5% of the sodium atoms can be associated with the high BE component. Hence, the washing solution plays an important role for the creation of strong interactions between Na and Cl at the sample surface, leading to other surface phenomena. In summary, for type I samples, charge compensation between opposite polyelectrolyte groups predominates, while, for type II samples, the washing causes an increase of strongly interacting counterions. Because the formation of NaCl crystallites can result from the strong inter-counterion interactions, we decided to further investigate it with X-ray diffraction, as reported below.

**X-ray Diffraction Measurements.** Since type II samples have an opaque appearance, that is, high absorption in the visible spectral range, one can attempt an explanation by suggesting the formation of NaCl crystal or crystallites at the top of the film. In looking for NaCl crystals in LBL films, X-ray diffraction spectra were measured for both types of samples. Curves A and B of Figure 6a show the X-ray diffraction spectra for a type I (PAH/PPS)h sample and a type II (PAH/PPS)b sample, respectively. Both samples were prepared with a 0.3 M salt concentration. The spectra reveal diffraction peaks, much less intense for the type I samples, as one can see from Figure 6b, for the (200) and (400) NaCl planes, indicating parallel orientation of (h00) planes to the film surface. The formation of salt crystals can account for the differences in roughness observed in LBL films obtained from different salt concentrations. The general trend is that higher salt concentrations lead to lower roughness values. This is seen in the scanning force microscope data, obtained by Fery et al., in poly(acrylic acid)/poly(allylamine) LBL films. The films prepared from 0.2 M NaCl polyelectrolyte solutions and washed with pure water showed a lower roughness than those prepared with a 0.2 M NaCl solution and washed with a 0.2 M NaCl aqueous solution.

**Counterions Location.** To find where NaCl crystals are being formed, an angle resolved XPS analysis was performed for the Na and Cl regions. The data revealed that the Na and Cl less oxidized forms decrease at higher angles, indicating that part of the counterions are at the...
sample surface. By fitting the Na spectra data into two or three peaks and those of Cl into two doublets (four peaks), Na and Cl can be classified into two classes, respectively, for high and low energies and their percentages can be computed. The low energy classes, Na\_BE and Cl\_BE, are also listed in Table 2. These two classes can only be explained if one takes into account that the percentage of Na and Cl ions for the lowest energies corresponds to the counterion bonds to the polyelectrolytes, the bulk counterions, while the highest energy peaks correspond to the inter-counterions. These inter-counterion bonds could account for the presence of NaCl salt at the film surface.

To further confirm if the Na and Cl ions are at the type II film surface, some samples were washed with ultrapure water and then the XPS was performed. The [Na]/[S] and [Cl]/[N] ratios for the type I sample washed with ultrapure water are close to the values obtained for the type I sample. This means that sodium and chloride have been removed from the samples. Nevertheless, the [Na]/[S] and [Cl]/[N] ratios are still higher for the type I washed samples than for the type I samples, which indicates that some ions have not been removed by the washing. This conclusion was also supported by the values of the [Na]/[C] and [Cl]/[C] ratios.

Figure 7 shows the [Na]/[S] and [Cl]/[N] percentage ratios for type II samples, considering the total initial percentage of these elements and the percentage of Na and Cl elements bonded with smaller energies. The inter-counterion bond could account for the presence of NaCl salt at the film surface.

Figure 7. Percentage ratios vs the NaCl concentration in the polyelectrolyte solutions for type II samples. [Na]/[S] and [Cl]/[N], solid and open circles, respectively, are the percentage ratios that consider the total initial percentage of these elements, and [Na\_BE]/[S] and [Cl\_BE]/[N], solid and open inverted triangles, respectively, are the percentage ratios that consider the percentage of Na and Cl elements bonded with smaller energies.

To confirm if the Na and Cl ions are at the type II film surface, some samples were washed with ultrapure water and then the XPS was performed. The [Na]/[S] and [Cl]/[N] ratios for the type I sample washed with ultrapure water are close to the values obtained for the type I sample. This means that sodium and chloride have been removed from the samples. Nevertheless, the [Na]/[S] and [Cl]/[N] ratios are still higher for the type I washed samples than for the type I samples, which indicates that some ions have not been removed by the washing. This conclusion was also supported by the values of the [Na]/[C] and [Cl]/[C] ratios.

Figure 7 shows the [Na]/[S] and [Cl]/[N] percentage ratios for type II samples, considering the total initial percentage of these elements and the percentage of Na and Cl elements with lower BEs, Na\_BE and Cl\_BE, respectively. The [Na\_BE]/[S] and [Cl\_BE]/[N] ratios increase with increasing polyelectrolyte salt concentration until reaching constant values. Moreover, for polyelectrolyte solutions prepared without salt, no counterions are present in the LBL film, and when increasing the solution salt concentration, the ratio between the bulk counterions and the associated polyelectrolyte ionic group is a constant.

Figure 7. X-ray diffraction spectra of PAH/PSS layer-by-layer films: curve A: (PAH/PSS)$_{16}$ type I film washed with water; curve B: (PAH/PSS)$_{8}$ type II film washed with a 0.3 M NaCl salt solution.

Figure 8. (a) Plot of the [Na]/[S] percentage ratio for type I samples (open circles) and the [Na\_BE]/[S] percentage ratio for type II samples (solid circles) determined from XPS data as a function of salt concentration; (b) plot of the [Cl]/[N] percentage ratio for type I samples (open inverted triangles) and the [Cl\_BE]/[N] percentage ratio for type II samples (solid inverted triangles) determined from XPS data as a function of salt concentration.
counterions is dependent on the number of ionic groups. The polyelectrolyte salt concentration, the data dispersion is for type II samples are plotted as a function of the bilayer and adsorbed amount per bilayer obtained by curve is in accordance with the results of the thickness general behavior, increase up to a constant value, of that ratio for type I samples is also shown in Figure 10. This ratio for type I samples is determined from XPS data as a function of salt concentration. The solid and dashed lines are only to guide the eyes.

Figure 9. Plot of the \([\text{Cl}_{\text{LBE}}/\text{N}]\) (open inverted triangles) and \([\text{Cl}_{\text{LBE}}]/[\text{NH}_3^+]\) (solid inverted triangles) percentage ratios for type I samples determined from XPS data as a function of salt concentration. The solid line is only to guide the eyes.

Figure 10. Amount of PSS adsorbed per bilayer (solid circles) and the \([\text{Al}] / [\text{C}]\) ratio (open circles) vs the solution salt concentration. The solid and dashed lines are only to guide the eyes.

washing solution at high salt concentrations. However, samples prepared with a salt concentration lower than 0.3 M and washed with water revealed lower relative amounts of counterions. Finally, it is interesting to note that, if \([\text{NH}_3^+]\) is considered instead of \([\text{N}]\), as can be seen in Figure 9, where the \([\text{Cl}_{\text{LBE}}/\text{N}]\) and \([\text{Cl}_{\text{LBE}}]/[\text{NH}_3^+]\) ratios for type II samples are plotted as a function of the polyelectrolyte salt concentration, the data dispersion is seen to decrease, which indicates that the number of counterions is dependent on the number of ionic groups.

Amount of Counterions. The buildup of the LBL films was monitored by measuring the UV-visible spectra after each bilayer had been adsorbed on a glass substrate. A linear increase with the number of bilayers was observed for the PSS absorption peak at 225 nm (not shown). The average adsorbed amount per bilayer can be calculated from the slope of these linear curves and plotted versus the polyelectrolyte solution salt concentration, as shown in Figure 10. In this case, type I samples were washed with water in order to avoid the opaque appearance. The general behavior, increase up to a constant value, of that curve is in accordance with the results of the thickness per bilayer and adsorbed amount per bilayer obtained by Ladam et al.\(^{(20)}\) for samples prepared with the same polyelectrolytes. The plot of the \([\text{Al}] / [\text{C}]\) atomic percentage ratio for type I samples is also shown in Figure 10. This plot follows a similar behavior as the one obtained for the adsorbed amount per bilayer; that is, steady values are attained for the same polyelectrolyte salt concentration. Since the adsorbed amount per bilayer becomes constant at salt concentrations higher than 0.3 M (Figure 10), the sulfur concentration per bilayer will also be constant. Consequently, the bulk sodium percentage, \([\text{Na}_{\text{LBE}}]/[\text{S}]\), tends to a constant value for the same salt concentrations, since the \([\text{Na}_{\text{LBE}}]/[\text{S}]\) ratio also attains a constant value at the same concentrations (see Figure 8a). Similar conclusions are obtained for the bulk chlorine percentage.

Discussion

According to what is accepted for the adsorption of polyelectrolytes, the increase in ionic strength with monovalent ions causes the adsorbed amount to increase up to a maximum, after which the adsorbed amount is seen to decrease to zero.\(^{(21,22)}\) The increase in the adsorbed amount is caused by a screening effect owing to the decrease in repulsion between polyelectrolyte segments, the so-called screening-enhanced adsorption effect.\(^{(21)}\) The decrease to zero after the maximum is attributed to the weakness of the polyelectrolyte to surface attraction due to ions adsorbed onto the surface, that is, the screening-reduced adsorption effect.\(^{(21)}\) For the samples analyzed in this work, only the screening-enhanced adsorption effect is expected, since the ionic strengths are not sufficiently high. The presence of sodium and chloride in the samples confirms that the screening-enhanced adsorption effect is taking place.

Riegler and Essler\(^{(8)}\) explained the presence of counterions in LBL films on the basis of theoretical results\(^{(23–25)}\) and by considering that the average distance between the polyelectrolyte charges is less than the Bjerrum length.\(^{(26)}\) Thus, the LBL films should contain immobilized or condensed counterions near the polyelectrolyte chains. This condensation, the so-called Manning condensation,\(^{(22,24)}\) happens also when the polyelectrolyte electrical charge is high. For PAH, the distance between the electrical charges is smaller than the Bjerrum length, and Tables 1 and 2 indicate that the electrical charge in PAH is practically constant for the same type of film regardless of the salt concentration. This corresponds to ~80% electrically charged for type I and II samples. Since stable PAH/PSS films were formed, the density of electrical charge must be above the critical charge density.\(^{(27)}\) The presence of NaCl crystallites in these films is further evidence of Manning condensation.

It is worth mentioning that the oxygen percentage for all type I and II samples is more or much more than 3 times the sulfur percentage, probably because the samples are highly hydrated. This agrees with Steitz et al.\(^{(28)}\) who estimated a water content of 40% in PAH/PSS films and with Fourier transform infrared (FTIR) results in LBL films of poly(o-methoxyaniline)(POMA)/poly(ethesulfonic acid) (PVS) that showed OH groups even though neither POMA nor PVS possesses these groups.\(^{(17)}\) Furthermore, NMR measurements in samples

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\(^{(22)}\) Hoogeveen, N. G.; Cohen-Stuart, M. A.; Fleer, G. J. J. Colloid Interface Sci. 1996, 182, 133.


\(^{(26)}\) The Bjerrum length is given by \(k_B T / e^2\), where \(e\) is the electrical charge, \(\varepsilon\) is the relative dielectric constant of the aqueous medium, and \(k_B T\) is the thermal energy.


of poly(diallyldimethylammonium chloride)/PSS showed that water molecules are less mobile and interact more with polyelectrolytes in LBL films than in polymer complexes produced with the same polyelectrolytes, a behavior that was attributed to the presence of counterions. In addition, although water molecules tend to associate more strongly with PSS, it is shown that water molecules only associate with poly(diallyldimethylammonium chloride) when this polyelectrolyte forms the outer surfaces of the film, where more small counterions are located. All these results explain the total positive charge obtained for type I and II films, once PSS is the outer layer of the LBL films. Since this anionic polyelectrolyte is highly hygroscopic, more sodium counterions are expected to be associated with these water molecules. In the absence of salt ions, the total charge is approximately null, since water molecules compensate the last PSS layer electrical charge.

Finally, condensation of counterions and water molecules near polyelectrolyte ionic groups leads to an increase in the effective polyelectrolyte ionic group size and accounts for the increase in film thickness with ionic strength up to a constant value. As a result, a region rich in counterions and water molecules is created between opposite polyelectrolyte ionic groups, like in an ionic network. These regions will give rise to the formation of NaCl nanocrystallites after film excess water is removed upon film drying. The drying process itself may affect the quantity and size of these nanocrystallites. As a remark to be made here, all films were dried by just leaving them at room conditions.

Conclusions

The present work clearly establishes that counterions are present in PAH/PSS LBL films when polyelectrolyte solutions are prepared with NaCl salt. For samples washed with water, the counterions are distributed through the film bulk, while, for samples washed with NaCl aqueous solutions, part of the counterions stay at the film surface and another part is distributed through the bulk of the LBL film. The number of bulk counterions increases with the polyelectrolyte solution salt concentration up to a constant value, which does not depend on the washing solution. The bulk sodium/sulfur percentage ratios tend to 0.8 for samples washed with pure water and for samples washed with NaCl aqueous solutions, while the bulk chlorine/nitrogen percentage ratios tend to 0.5 for the same samples. The degree of charging of PAH was estimated as 0.8 for samples washed with water and for samples washed with NaCl aqueous solutions. The ratio between the percentage of opposite polyelectrolyte ionic groups, $[\text{NH}_3^+]$/[SO$_3^-$], lies close to unity for all samples, revealing that counterions do not contribute directly to the polyelectrolyte charge compensation during the adsorption process. Counterions are located near polyelectrolyte ionic groups, which is explained by Manning condensation, leading to the formation of surface and bulk NaCl nanocrystallites during the drying process. The number and size of these nanocrystallites are possibly dependent on the drying process, which is now being further investigated.

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