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Counterions in layer-by-layer films—Influence of the drying process

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Abstract

The amount of counterions, measured by means of X-ray photoelectron spectroscopy (XPS), in layer-by-layer (LbL) films of poly(allylamine hydrochloride) (PAH) and poly(styrene sulfonate) (PSS), prepared from solutions with various NaCl concentrations, is shown to be greatly influenced by the film drying process: a smaller amount of counterions is observed in films dried after adsorption of each layer, when compared with films that were never dried during the film preparation. This is attributed to the formation of NaCl nanocrystals during the drying process which dissolve when the film is again immersed in the next polyelectrolyte solution. The presence of bonded water molecules was confirmed in wet films indicating that the counterions near the ionic groups are immersed in a water network. The number of counterions is dependent on the amount of salt in polyelectrolyte solutions in such a way that for a concentration of 0.2 M the relative amount of counterions attains saturation for both dried and wet samples, indicating that the process which leads the aggregation of counterions near of the ionic groups is not influenced by the drying process. Moreover, it is proven for wet samples that the increase in salt concentration leads to a decrease in the number of PAH ionized groups as predicted by the Muthukumar theory [J. Chem. Phys. 120 (2004) 9343] accounting for the counterion condensation on flexible polyelectrolytes.

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1. Introduction

The layer-by-layer (LbL) technique has received significant attention over the last years mainly due to the possible large-scale fabrication of low cost molecular heterostructures for organic-based electronic and photonic devices [1–5] and sensors [6,7]. Since film formation is based on the alternate adsorption from aqueous solutions of oppositely charged polyelectrolytes onto solid substrates, it involves rather complex processes and phenomena that are still not understood. One of these phenomena concerns the presence of counterions in the LbL films as a result of complete or partial replacement of counterions by oppositely charged polyelectrolytes. Results in the literature are contradictory. In LbL films of poly(acrylic acid)/poly(allylamine hydrochloride) (PAA/PAH) [8] and poly(butyl viologen) dibromide (PBV)/poly(styrene sulfonate) (PSS) [9] no counterions were found, in contrast to films of PSS/poly(diallyldimethylammonium chloride) (PDADMA) [10,11]. Although preliminary experiments failed to detect counterions [12] in films of PAH/PSS, the presence of counterions in those films has already been reported [13–15]. Recently, it was shown that counterions are incorporated in PAH/PSS LbL films with its amount tending to constant values as the ionic strength is increased [16]. The presence of counterions in these films was explained as a result of condensation of counterions and water molecules near polyelectrolyte ionic groups leading to an increase in the effective size of the polyelectrolyte ionic group and accounting for the increase in film thickness with ionic strength up to a constant value [16,17]. As a result, a region rich in counterions and water molecules is created between opposite polyelectrolyte ionic groups, like in an ionic network [16]. This is corroborated by the well-known presence of water molecules in LbL films [18–20] and by the thickness decrease when the samples are dried [18,21]. Although in 1994 Decher et al. [22] showed that the drying influences the film structure, there have been few studies of the drying effects. For example, Halthur et al. [23]
studied the stability of LbL films of poly(l-glutamic acid) (PGA) and poly(l-lysine) (PLL) taking into account the drying effect on thickness and refractive index and concluded that the intermediate drying and measurement in air does not affect the contribution for layer buildup. Moreover, upon drying the PGA/PLL LbL films thickness collapsed by as much as 70%, without any irreversible changes in the layer structure. Chen et al. [24] studied LbL films of diphenylamine-4-diazonium-formaldehyde resin (DR) and 2-nitro-N-methyl-4-diazonium-formaldehyde resin (NDR) and other polyelectrolytes and concluded that the samples dried after adsorption of each layer had higher adsorbed amounts than samples prepared without drying and showed that drying makes the films flatter and rather hydrophobic. It was also observed that drying at every step of adsorption increased the thickness of adsorbed films due to enhanced surface roughness of PAH/PSS LbL films [25]. De Souza et al. [26] noted that drying affects the film build-up and morphology, with LbL films dried under room conditions displaying a more homogeneous surface (lower roughness) and higher adsorbed amounts when compared with films dried under vacuum or by nitrogen flow. The lower roughness was attributed to lower solvent evaporation rates for samples dried in air. An increased ionic strength was also shown to lead to rougher surfaces [27]. Recently, Patel et al. [28] verified that the net growth of an enzyme layer increases when the drying step is omitted. Drying of enzymes layers reduces the activity of the assembly to some extent. With such conflicting evidence for the role of drying, one decided to investigate the effect from drying on the contents of counterions in PAH/PSS films LbL prepared from solutions having different ionic strengths. This article shows that the amount of counterions is influenced by the drying process and the presence of counterions in the LbL films changes the PAH degree of ionization.

2. Experimental

The LbL films were prepared from aqueous solutions of poly(allylamine hydrochloride) (PAH) (average \( M_w = 50,000–65,000 \text{ g/mol} \)) and poly(styrene sulfonate) (PSS) (\( M_w = 70,000 \text{ g/mol} \)) with concentrations of \( 10^{-2} \text{ M} \) and with different sodium chloride concentrations. The polyelectrolyte concentrations were based on the molecular weight of the repeat unit. The chemicals purchased from Aldrich, have their concentrations were based on the molecular weight of the repeating unit. The chemicals, purchased from Aldrich, have their concentrations were based on the molecular weight of the repeating unit. The chemicals, purchased from Aldrich, have their concentrations were based on the molecular weight of the repeating unit.

Pure water with a resistivity of 18 MΩ cm, supplied by a Millipore system (Milli-Q, Millipore GmbH), was used to prepare all aqueous solutions. For XPS measurements, 8-bilayer LbL films (PAH/PSS)_8 were adsorbed onto 10 × 20 mm² substrates obtained from aluminum foils. The adsorption time for each layer was 10 min. The substrates were washed with pure water and dried with a nitrogen flow. In order to maintain the PAH electrically charged, solutions were obtained from pure water resulting in a pH of about 5. The films were prepared by washing the film with pure water after adsorption of each layer. Some samples were dried leaving the samples at room conditions after each layer adsorption for a few minutes (dried samples) and other samples were not dried between the adsorption of each layer (wet samples). Drying at room conditions was chosen in face of the results obtained by de Souza et al. [26], who reported more homogeneous surfaces and higher adsorbed amounts in LbL films dried at room conditions comparatively to those dried with a nitrogen flux.

To investigate the presence of counterions the samples were analyzed in an X-ray photoelectron spectrometer XSAM800 (Kratos) operating in the fixed analyzer transmission (FAT) mode [29], with a pass energy of 10 eV, a power of 130 W and the non-monochromatized Mg Kα X-ray (\( h\nu = 1253.7 \text{ eV} \)). All the samples were analyzed on the central part of the sample, i.e., over a \( 1 \times 3 \text{ mm}^2 \) spot area at an angle of \( 0° \) relative to the normal to the sample surface using the High Magnification condition. At least 2 specimens were analyzed for each preparation condition. The spectra were recorded with a Sun SPARC Station 4 with Vision software (Kratos) using a step of 0.1 eV. The X-ray source satellites were subtracted, Shirley background and pseudo-Voigt profiles (Gaussian and Lorentzian products) were fitted to each region using a non-linear least-squares algorithm. No charge compensation (flood-gun) was used. Binding energies (BE) were corrected by using aliphatic C 1s BE equal to 285.0 eV [30]. For quantification purposes, sensitivity factors were 0.66 for O 1s, 0.25 for C 1s, 0.42 for N 1s, 0.54 for S 2p, 2.3 for Na 1s, 0.73 for Cl 2p and 0.21 for Al 2s as described elsewhere [16]. As a remark, it is worth to mention here that the main source of error in quantification of a given XPS spectrum comes from the baseline definition. This error depends on the number of counts in the peak, \( N' \) (relative error \( \approx 1/\sqrt{N} \)) and is displayed in all figures as error bars.

The UV–visible absorbance spectra of dried and wet (PAH/PSS)_8 LbL films prepared onto hydrophilized BK7 optical glass substrates were measured using a Shimadzu UV-2101PC spectrophotometer.

3. Results and discussion

3.1. Dependence of counterions with salt concentration

The XPS spectra revealed the presence of carbon (C), sulfur (S), oxygen (O), nitrogen (N), sodium (Na) and chloride (Cl) and allowed the evaluation of atomic percentages. In this work, square brackets with the element symbol in between refer to the calculated atomic percentage. The values obtained for wet samples, for different salt concentrations, have already been

![Polypelectrolyte molecular structures: (a) poly(allylamine hydrochloride) (PAH), (b) poly(styrene sulfonate) (PSS).](image)

Fig. 1. Polypelectrolyte molecular structures: (a) poly(allylamine hydrochloride) (PAH), (b) poly(styrene sulfonate) (PSS).
reported [16], while the percentages for dried samples were determined in this work and are listed in Table 1.

Figs. 2a and 2b show the plots of [Na]/[S] and [Cl]/[N] percentage ratios, respectively, as a function of the salt concentration in the polyelectrolyte solution for both types of samples. These ratios were chosen because Na⁺ and Cl⁻ are the counterions for PSS and PAH polyelectrolytes, respectively. For samples that were not dried the [Na]/[S] and [Cl]/[N] relative percentages increased till a salt concentration of 0.3 M and reached average plateaus of 0.8 and 0.5, respectively, while for dried samples, the same relative percentages of counterions attained values of 0.08 and 0.03, respectively, for the same salt concentration. The obtained values for dried samples indicate that the charge compensation results from polyelectrolyte/polyelectrolyte interactions the so-called intrinsic charge compensation. However, two main questions arise when the obtained values for the wet samples are taken into account: What makes the polymer cohesion when the Na/S ratio is near the unity? How PSS groups with PAH groups are bound? The extrinsic charge compensation due to small ions must play here an interesting role. In addition one might wonder why the drying process is leading to a decrease in these ratios in an order of magnitude? The presence of counterions in LbL films has been attributed to condensation of counterions, the Manning counterion condensation [31], and water molecules near polyelectrolyte ionic groups. This 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 it is well known, the film thickness is influenced by polymer conformation which depends on charge compensation and salt concentration. It must be remarked here that both type of films were prepared from solutions with polyelectrolyte molecules that were completely charged, i.e., with a degree of charge close to unity.

These data show that the conditions of film formation have a significant importance in the presence of counterions in the films. For both type of samples the amount of counterions increases non-monotonically, revealing both the same behavior with the salt concentration. However the amount of counterions for the dried samples is one order of magnitude lower. In addition, one can conclude that the process which is leading to the aggregation of the counterions with the ionic groups depends of an initial salt concentration of about 0.3 M, above which the number of counterions in the PAH/PSS LbL films tends to a saturation value. As the results are similar, curves present the same general behavior, for both types of samples the involved process should be the same. Consequently, the drying is only affecting the amount of counterions and does not influence the process of

Table 1
Element composition in percentage, obtained from XPS spectra taken at 0° of incidence, of (PAH/PSS)₈ films prepared with different salt concentrations (SC) and rinsed with ultra-pure water and dried after each layer adsorption.

<table>
<thead>
<tr>
<th>SC (M)</th>
<th>C (%)</th>
<th>O (%)</th>
<th>N⁺ (%)</th>
<th>[−NH₃⁺] (%)</th>
<th>S (%)</th>
<th>Cl (%)</th>
<th>Na (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>72.7±0.7</td>
<td>17.5±0.2</td>
<td>5.2±0.3</td>
<td>4.9±0.3</td>
<td>4.1±0.2</td>
<td>0.12±0.02</td>
<td>0.13±0.03</td>
</tr>
<tr>
<td>0.30</td>
<td>72.3±0.7</td>
<td>16.6±0.2</td>
<td>5.9±0.3</td>
<td>4.7±0.3</td>
<td>4.1±0.2</td>
<td>0.18±0.04</td>
<td>0.43±0.09</td>
</tr>
<tr>
<td>0.35</td>
<td>72.1±0.7</td>
<td>18.7±0.2</td>
<td>4.1±0.2</td>
<td>3.8±0.2</td>
<td>3.9±0.2</td>
<td>0.16±0.03</td>
<td>0.86±0.1</td>
</tr>
<tr>
<td>0.40</td>
<td>72.9±0.7</td>
<td>17.3±0.2</td>
<td>5.0±0.3</td>
<td>4.6±0.3</td>
<td>4.1±0.2</td>
<td>0.11±0.02</td>
<td>0.51±0.02</td>
</tr>
<tr>
<td>0.45</td>
<td>70.5±0.7</td>
<td>18.5±0.2</td>
<td>5.6±0.3</td>
<td>4.3±0.2</td>
<td>4.7±0.2</td>
<td>0.17±0.03</td>
<td>0.29±0.06</td>
</tr>
<tr>
<td>0.5</td>
<td>71.1±0.7</td>
<td>18.4±0.2</td>
<td>5.6±0.3</td>
<td>5.4±0.3</td>
<td>4.5±0.2</td>
<td>0.15±0.03</td>
<td>0.27±0.05</td>
</tr>
</tbody>
</table>

a Total atomic percentage of nitrogen.

Fig. 2. (a) [Na]/[S] and (b) [Cl]/[N] ratios determined from XPS data as a function of salt concentration. Solid and empty circles correspond to wet and dried samples, respectively.
counterions aggregation near of the ionic groups. As a remark, both dried and wet films were prepared from polyelectrolyte solutions in the same conditions during the adsorption of each layer. The explanation for the decrease of the number of counterions when the samples are dried can be accounted by the remotion of the salt after drying as will be discussed in the next section.

3.2. Role of water molecules

During the measurement of the XPS spectra both types of samples are submitted to high vacuum for several hours. Consequently water molecules present that are not bounded in both types of samples will be removed for both type of samples. However, the bonded water molecules will be not removed since the remotion of water molecules from the surfaces of high or ultrahigh vacuum chambers is a hard task due to water vapor high sticking coefficient [32]. This signifies that water molecules are expected to be present in both types of samples, fact which is confirmed by the presence of oxygen peaks in the XPS data and by the salt concentration independence behavior of the [O]/[C] atomic percentage ratios for dried and wet samples, with values of 0.25 ± 0.01 and 0.28 ± 0.01, respectively. Oxygen atoms are associated with both sulfur groups and water molecules. The higher [O]/[C] percentage ratio values obtained for wet indicates that wet samples have slightly higher oxygen molecules amount. However, the presence of water molecules in the LbL films could be confirmed from the oxygen (O 1s) XPS spectra. The O 1s XPS spectra obtained at 0° of incidence for wet and dried samples, prepared with 0.4 M of NaCl salt concentration, are shown in Figs. 3a and 3b, respectively.

At the O 1s core level binding energies region, both samples exhibit three components centered at 531.9 ± 0.2, 533.0 ± 0.2 and 534.2 ± 0.2 eV. The first one is assignable to the oxygen in the sulfonic group [33], and the third one to water entrapped in the polymeric film [34]. The second one may be associated oxygen in the sulfonic group bound to isolated water molecules. In fact, it is known that hydrogen bonding increases the binding energy of the element sharing its lone pair with the hydrogen [35]. The approximate ratio of 2 between the second and third components areas suggests that each water molecule binds to two sulfonate oxygen atoms. For wet samples both the second and the third components increase and a fourth component centered at 535.9 ± 0.2 eV appears corresponding to water molecules aggregates entrapped in the film. The increase in the O 1s binding energy is due to the sharing of the lone pairs with the hydrogen of other water molecules. For water in ice, for instance, a binding energy of 537.1 eV was measured [36]. Moreover, the current data is consistent with the following mechanism for the decrease of the number of counterions in dried samples. Water molecules and counterions are surrounding the polyelectrolyte molecules in an ionic network. Drying leads to a decrease in the number of water molecules, in such a way that the ionic network is broken and NaCl nanocrystals tend to be formed. When the LbL film is again immersed in the next polyelectrolyte solution the nanocrystals are easily dissolved and consequently part of the sodium and chloride ions are removed from the LbL film.

It is worth to mention at this point that films dried with a nitrogen flux present lower amounts of sodium and chloride, as revealed by the obtained [Na]/[S] and [Cl]/[N] ratios values, which are smaller or close of those obtained for dried films at room conditions. For comparison, a trial sample was prepared from a 0.3 M salt concentration solution, in which each layer was dried with a nitrogen flux. In this sample, the obtained [Na]/[S] and [Cl]/[N] ratios attained values of 0.057 and 0.065, respectively. This indicates that the drying process is affecting significantly the amount of counterions retained in the film and also explains the dispersion found in the counterions ratios values shown in the graph of Fig. 2a, namely for the 0.3 M salt concentration where a maximum of [Na]/[S] was observed. However, the relative amounts are of the same order of magnitude comparatively with the ones found in films dried at room conditions. The presence of sodium and chloride ions even when the films are dried with nitrogen can be explained by the difficulty in the remotion of the water molecules that strongly are bond to the polyelectrolyte in networks.

3.3. Polyelectrolyte adsorbed amount

From the XPS experimental data, Fig. 4, one can also see that the [S]/[N] atomic ratios increase with salt concentration for both dried and wet samples up to saturation. These saturation values are about 1.25 and 0.75 for wet and dried samples, respectively.
A higher saturation value for the wet samples could be explained by an increase in the number of sulfur groups or by a decrease in the number of nitrogen groups in wet samples, in comparison to the dried samples. Plotting the \([S]/[C]\) percentage ratio versus the salt concentration for both types of samples, as shown in Fig. 5a, it can be seen that \([S]/[C]\) ratio is independent of the salt concentration and the relative amount of sulfonic groups is similar in both types of samples.

From Fig. 5b, one notes that the \([N]/[C]\) percentage ratio is independent of salt concentration for dried samples and decreases with the salt concentration for wet samples. However, at small salt concentrations this ratio is similar for both types of samples. Basically, it can be concluded that for wet samples the relative amount of nitrogen groups is smaller at higher salt concentrations.

The above results are concerned with the relative amount of sulfur and nitrogen atoms. In order to infer about the absolute amounts of nitrogen and sulfur, the UV–visible spectra, shown in Fig. 6, was measured, in the region where only PSS benzenic ring is absorbing, of wet and dried PAH/PSS LbL films with the same number of bilayers. These spectra showed that dried PAH/PSS LbL films had higher absorption relatively to wet PAH/PSS LbL films, allowing conclude that more PSS molecules are being adsorbed and effectively more sulfur atoms are present in dried LbL films than in wet ones. The adsorbed number of nitrogen groups is also higher for dried samples, since \([S]/[N]\) is higher for wet samples at high salt concentrations. Moreover, these results suggest that when the samples are dried more adsorption sites become available for the adsorption of the next polyelectrolyte. This is similar to the results of poly(o-methoxylanine) (POMA) adsorbed onto POMA/poly(vinylsulfonic acid sodium salt) (PVS) LbL films and glass substrates [37] and for polyaniline (PANI-EB) and poly(p-phenylene vinylene) precursor adsorbed onto glass and quartz substrates [38,39]. This behavior is also in accordance with results of Refs. [25] and [40], where the adsorbed amount of POMA varied with the drying process. Although the adsorbed amount has been seen to increase with roughness as revealed in POMA films [41], Ferreira et al. [42,43] observed smaller roughness values in PAH/PAZO LbL films dried with a nitrogen flux than the ones observed in wet films, being the adsorbed amount behavior with the initial surface roughness for both dry and wet films similar to that obtained for POMA films. Moreover, a higher number of “globular like structures” was observed in wet PAH/PAZO films than in dried films. These results are suggesting that molecular aggregation or coalescence is occurring in dried films. In addition, water contact angles of 39.7 ± 0.5° and 35 ± 1° were measured, respectively, for wet and dried (PAH/PSS)\(_8\) LbL films. These values are also indicating that wet films present higher roughness than the dried ones.
Fig. 6. UV–visible absorbance spectra of wet and dried (PAH/PSS)$_8$ LbL films prepared from a 0.3 M salt concentration. The films were deposited onto glass. Solid and empty circles correspond to wet and dried samples, respectively.

as it can be expected from the contact angle dependence with roughness [44]. Since roughness is smaller for the dried samples, one would expect less adsorbed amount, in such a way that the higher adsorbed amounts achieved for the dried films has been accounted. A possible explanation for the increase of adsorbed amount in dried samples is the increase of hydrophobic short-range interactions between apolar segments of both adsorbing and already adsorbed polyelectrolytes as a result the decrease in the number of water molecules in the surroundings of the polyelectrolytes apolar regions.

3.4. Influence of drying on the PAH degree of charge

Since the adsorption processes are primarily controlled by ionic interactions between the NH$_3^+$ and SO$_3^-$ ionic groups, the degree of charge must be taken into account. For the completely ionized PSS, the amount of sulfur corresponds to the number of PSS ionic groups. However, PAH is not completely ionized, as it can be inferred from the percentage values of NH$_2$ and NH$_3^+$ groups listed in Table 1. These values were obtained by fitting the XPS spectra in the nitrogen region with peaks centered at 401.0 ± 0.2 and 403.0 ± 0.2 eV, respectively, with the only constraint of the same full width at half-maximum (fwhm = 2.1 ± 0.1 eV). The plot of [NH$_3^+$]/[N] percentage ratios for both types of samples, shown in Fig. 7, reveals a fraction of electrically charged nitrogen groups, i.e. the degree of ionization, that is independent of salt concentration for dried samples, with average value of 0.94 ± 0.02. This value is near to that obtained by Petrov et al. [45], for smaller pHs, from potentiometric titration curves of (PAH/PSS)$_5$ LbL films, in which the concentration of PAH and PSS solutions was 2 mg/mL, at pH 7.0, in water, and in 0.5 M NaCl aqueous solution. The LbL films were washed in a NaCl 0.1 M solution at pH 7.0. As a remark, in the present work the PSS concentration was 1.58 mg/mL and PAH concentration was 0.93 mg/mL.

For the wet samples, the fraction of electrically charged nitrogen groups (the PAH degree of ionization) depends on the salt concentration and is similar to the one of dried samples for salt concentration below 0.3 M. For higher salt concentrations, the fraction of electrically charged nitrogen groups in the wet samples decreases with concentration down to ~0.8. Previously, it was observed that the degree of charge tends to ~0.7 when wet samples were washed with salted aqueous solutions [16].

Fig. 8 shows that the [S]/[NH$_3^+$] ratio is independent of salt concentration for the dried samples, which is consistent with a constant number of NH$_3^+$ and SO$_3^-$ groups. Since the ratio is near 0.8, the number of charged nitrogen atoms is higher than the number of sulfur atoms in the samples, in agreement with Riegler and Essler data [13] obtained for the same type of samples. For wet samples the [S]/[NH$_3^+$] ratio increases with salt concentration, consistent with a decreasing degree of charge for PAH. At high salt concentration the ratio [S]/[NH$_3^+$] tends...
to 1.6, indicating that the number of charged nitrogen groups is lower than the number of sulfonic groups.

3.5. Dependence of degree of charge with the counterions content

The degree of charging of PAH in solution has been reported to depend on the pH [45–50], as one should expect, but the present results show that the degree of charging in the LbL film also depends on the counterion amount. From the plots of degree of ionization versus relative amount of counterions, shown in graphs of Figs. 9a and 9b, one infers that for wet samples the degree of ionization decreases with increasing number of counterions. The differences in degree of charging between wet and dried samples cannot be explained by changes in pH or ionic strength, since the latter were the same for both types of sample. So, only the film preparation procedure, drying or not the samples, is responsible for the dependence of counterion contents.

These results agree with the model of Muthukumar [51] for the distribution of counterions around flexible polyelectrolytes which takes into account the compromise between the translational entropy of counterions and the electrostatic attraction of the counterions by the polymer. In fact, according to Muthukumar the polymer degree of ionization decreases with increasing concentration of added salt, when the salt counterions are chemically identical to the polyelectrolyte original counterions. Therefore, the increase in salt concentration leads to a decrease in the number of NH$_3^+$ ionized groups, as already observed in the results for the degree of ionization obtained from the [NH$_3^+$]/[N] ratio and as predicted by the Muthukumar theory [51]. Furthermore, when the charge density of the adsorbed polyelectrolyte decreases, more polyelectrolyte chains must be adsorbed in order to compensate the surface charge of the already adsorbed oppositely charged polyelectrolyte layer [52–54], as experimentally measured for these films [16,17].

4. Conclusions

It has been shown that the amount of counterions in PAH/PSS LbL films decreases by almost one order of magnitude if the film is dried under room conditions after adsorption of each layer. This is due to water removal during the drying process which allows the formation of NaCl nanocrystals, that subsequently dissolve into the solution in the adsorption of the next layer. For wet samples the increase in salt concentration leads to a decrease in the number of NH$_3^+$ ionized groups, confirming the theoretical prediction by Muthukumar [51] for the condensation of counterions on flexible polyelectrolytes. Moreover, the degree of ionization depends on the counterions present in films were prepared from the same polyelectrolytes solutions and consequently the same pH. The presence of bonded water molecules in these films is conditioned by the production process and in wet samples water aggregates molecules are entrapped in the film. The presence of bonded water molecules in wet LbL films is of extreme importance for the production of thin films with biological molecules since the presence of entrained water in the films allows the maintenance of biomolecules activity.

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