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ABSTRACT:

Polyelectrolyte multilayers and layer-by-layer assemblies are susceptible to structural changes in response to ionic environment. By altering the salt type and ionic strength, structural changes can be induced by disruption of intrinsically bound ion pairs within the multilayer network via electrostatic screening. Notably, high salt concentrations have been used for the purposes of salt-annealing and self-healing of LbL assemblies with KBr, in particular, yielding a remarkably rapid response. However, to date, the structural and swelling effects of various monovalent ion species on the behavior of LbL assemblies remain unclear, including a quantitative view of ion content in the LbL assembly and thickness changes over a wide concentration window. Here, we investigate the effects of various concentrations of KBr (0 to 1.6 M) on the swelling and deswelling of LbL assemblies formed from poly(diallyldimethylammonium) polycation (PDADMA) and poly(styrenesulfonate) polyanion (PSS) in 0.5 M NaCl using quartz-crystal microbalance with dissipation (QCM-D) monitoring as compared to KCl, NaBr, and NaCl. The ion content after salt exchange is quantified using neutron activation analysis (NAA). Our results demonstrate that Br⁻ ions have a much greater effect on the structure of as-prepared thin films than Cl⁻ at ionic strengths above assembly conditions, which is possibly caused by the more chaotropic nature of Br⁻. It is also found that the anion in general dominates the swelling response as compared to the cation because of the excess PDADMA in the multilayer. Four response regimes are identified that
delineate swelling due to electrostatic repulsion, slight contraction, swelling due to doping, and film destruction as ionic strength increases. This understanding is critical if such materials are to be used in applications requiring submersion in chemically dynamic environments such as sensors, coatings on biomedical implants, and filtration membranes.

**Introduction**

Layer-by-layer (LbL) assembly of complementary polyelectrolytes is a versatile method capable of producing thin films and modified surfaces of tunable properties.\(^1\)-\(^9\) These may be used for applications including sensors, smart coatings, microelectronics, self-healing materials, nanofiltration membranes, and biological applications such as tissue engineering.\(^10\)-\(^18\) Therefore, it is important to understand how these thin films respond to external stimuli, such as salt, if they are to be deployed in aqueous conditions of varying salt type or concentration.

Thin film polyelectrolyte multilayers (PEMs) prepared using LbL assembly have been described as polyelectrolyte complexes (PECs) that are sequentially deposited on and bound to a substrate in a kinetically trapped state. The structure and properties of LbL films formed from strong polyelectrolytes are determined largely by the ionic strength and by the counterion species in the assembly environment. However, LbL film structure and properties are also sensitive to changes in the post-assembly conditions. Generally, it has been shown that increasing salt concentration disrupts ion pair crosslinks, even up to the point of disassembling the LbL film.\(^19\)-\(^21\) To date, there are many studies that discuss the impact of counterion identity and concentration on the assembly growth and structure of LbL films,\(^5\), \(^22\)-\(^26\) while the post-assembly responsive properties of completed PEMs to changes in ionic environments remains less explored.

For a given LbL assembly, changes in ionic strength and ion type may induce swelling to varying degrees. Salomäki *et al.* explored the effects of monovalent ions on the post-assembly swelling behavior of LbL assemblies formed from poly(diallyldimethylammonium) (PDADMA) and
poly(4-styrenesulfonate) (PSS) assembled in the presence of 0.1 M NaF and 0.1 M NaBr.\textsuperscript{27} It was reported that the effect of specific anions on the swelling behavior of the films followed a trend in the anion hydration entropies. LbL films assembled in the presence of Br\textsuperscript{−} exhibited a higher degree of swelling than those assembled in the presence in F\textsuperscript{−} anions when exposed to various ionic species along the Hofmeister series at equal ionic strengths. This behavior was attributed to the variance in internal film structure (\textit{i.e.} coiled vs. extended chain conformation upon deposition) based on the assembly ionic conditions as well as the relative hydration levels of the various incoming anions after assembly. It was concluded that the post-assembly swelling of the film with regard to anion type mirrored the Hofmeister series. Zan \textit{et al.} reported that the extent of uptake of additional polyelectrolyte by completed PDADMA/PSS thin films exhibited a clear dependence on the polyelectrolyte molecular weight, the counteranions’ position along the Hofmeister series, and the ionic strength of the polyelectrolyte bathing solution. They found that the greatest degree of swelling and polyion uptake was associated with Br\textsuperscript{−} ions, which most effectively disrupted intrinsic binding sites within the LbL film.\textsuperscript{28-29} Ghostine \textit{et al.} reported that the PDADMA/PSS system had a higher doping constant for Br\textsuperscript{−} than for Cl\textsuperscript{−}.\textsuperscript{30} This is odd, however, considering that previous rankings of the halide anions place Cl\textsuperscript{−} and Br\textsuperscript{−} close or next to each other in terms of their net effect on LbL film properties along the Hofmeister series. Typically, Cl\textsuperscript{−} is regarded as a “null point” in the series. These results point to the strong response of LbL assemblies to Br\textsuperscript{−}, as compared to other monovalent anions, although the reason for this is not well understood. However, a recent theoretical study on ion condensation\textsuperscript{31} showed little difference in the behavior of Cl\textsuperscript{−} and Br\textsuperscript{−} ions around isolated PDADMA chains suggesting that the ion specificity could be related to complexation.

Exposure to aqueous solutions of high salt concentration has also been used as a means of salt-annealing LbL thin films. Ghostine \textit{et al.} previously reported on the effects of salt-annealing on the surface roughness of LbL assemblies.\textsuperscript{32} PDADMA/PSS multilayers soaked in NaCl solutions
at ionic strengths $\geq 1.0$ M for 20 h showed significant reduction in surface roughness, which was attributed to the softening and restructuring of the plasticized network. Similarly, Fares et al. studied the effects of repeated salt annealing as a means to achieve stoichiometrically balanced LbL assemblies.\textsuperscript{33} By repeatedly immersing the films in 2.0 M NaCl solution followed by 10 mMol PSS in 1.0 M NaCl solution, excess PDADMA underwent an extrinsic-intrinsic conversion as PSS was absorbed into the multilayer. This was achieved by swelling of the network and added mobility induced by the 2.0 M NaCl immersion step, allowing for more free diffusion of excess PDADMA to the surface to interact with the incoming PSS in the second step. The result was a nearly complete intrinsic network with a more uniform structure and a smoother surface.

On the other hand, recent studies have utilized various divalent counterions or NaCl at varying ionic strengths to elicit structural responses from LbL assemblies.\textsuperscript{34-37} Wei et al. reported that PSS-capped PDADMA/PSS multilayers assembled at 0.5 M NaNO\textsubscript{3} could be physically cross-linked upon doping with divalent nitrate salts at low concentration (0.01 M).\textsuperscript{38} The cross-linking caused the films to contract due to ion bridges formed between polyelectrolyte charge sites. Similarly, Reid et al. explored the reversible swelling behavior and thermal properties of PDADMA/PSS multilayers capped with PDADMA in response to exposure to various divalent ion solutions across a range of ionic strengths.\textsuperscript{39} The responsive behavior was divided into two regimes. The first was characterized by swelling induced by electrostatic repulsion at low salt concentrations, and the second was described by swelling resulting from excessive doping at elevated salt concentrations. LbL assemblies exposed to CaCl\textsubscript{2} and MgCl\textsubscript{2} exhibited linear changes in thickness in high-salt concentration regime with respect to increasing salt concentration, whereas those exposed to NaSO\textsubscript{4} showed no clear trend.

Here, we explore the responsive swelling and deswelling behavior and the compositional changes of PDADMA/PSS LbL assemblies upon exposure to monovalent salts (KBr, NaBr, NaCl, and KCl) across a broad range of concentrations to understand the underlying reasons for KBr’s
influence. The PDADMA/PSS system was selected because it represents a model system of strong polyelectrolytes whose properties have been extensively studied. KBr was selected as the primary focus of this study because previous studies have shown that Br\textsuperscript{-} ions have a significant effect on the structure and properties of PDADMA/PSS thin films and complexes. NaCl, NaBr, and KCl were selected as a means to compare against other ion combinations, and NaCl was of special interest because of its widespread use in the practice of salt annealing LbL thin films. The primary tool used to explore the response during ion exchange was quartz-crystal microbalance with dissipation (QCM-D) monitoring, which yields changes in the film’s hydrated thickness and mass. Free standing LbL films were also analyzed using \textsuperscript{1}H NMR and neutron activation analysis (NAA) in order to understand film composition and to quantify changes in ion content. These results are discussed in the broader context of how and why LbL films respond to different ion species and salt concentrations.

Experimental Section

Materials. Poly(diallyldimethylammonium chloride) (PDADMA, $M_w = 200,000−350,000$ g/mol, 20 wt % solution), poly(styrenesulfonate sodium salt) (PSS, $M_w = 500,000$ g/mol), and linear polyethyleneimine (LPEI, $M_w = 25,000$ g/mol) were purchased from Sigma-Aldrich, Scientific Polymer Products, and Polysciences, Inc., respectively. Sodium chloride (NaCl), sodium bromide (NaBr), potassium chloride (KCl), and potassium bromide (KBr) were all purchased from Sigma-Aldrich. Teflon sheet and quartz crystals were used as substrates and were purchased from McMaster-Carr and Q-Sense, respectively.

Preparation of Free-Standing LbL Films. Free-standing LbL films were fabricated on Teflon substrates using an automated HMS slide stainer (Carl Zeiss, Inc.). PDADMA and PSS were first dissolved in Milli-Q water at 1 mg/mL concentration and ionic strength of 0.5 M NaCl. The Teflon substrates were cleaned prior to use by sonication in ethanol (15 min) followed by rinsing twice
thoroughly with Milli-Q water. The assembly sequence for the LbL films was carried out by immersing the substrates in PDADMA solution for 15 min, followed by three rinses for 2, 1, and 1 min in Milli-Q water (0.5 M NaCl). This same sequence was repeated for the deposition of PSS. Films were completed after 140 layer pairs (or cycles), and any excess salt was removed from the surface of the films by a final rinse in pure Milli-Q water (no salt) for 3 s. After rinsing, the films were allowed to dry under ambient conditions in a hood overnight followed by drying under vacuum at 115°C for 3 h. The completed films are denoted as (PDADMA/PSS)$_n$, where $n$ represents the number of layer pairs.

**Proton Nuclear Magnetic Resonance Spectroscopy.** Proton nuclear magnetic resonance (\textsuperscript{1}H NMR) spectroscopy (500 MHz proton frequency, Varian Inova 500 spectrometer) was used to determine the composition of PDADMA/PSS free-standing films prepared by LbL assembly. Sample preparation was carried out as follows: approximately 10 mg of dried (PDADMA/PSS)$_{140}$ LbL film was dissolved in 0.75 mL of deuterium oxide (D$_2$O) solution with 2.5 M KBr. The mole percent of the polyelectrolyte components was calculated by comparing the relationship between the aromatic peaks associated with PSS and the aliphatic peaks associated with PDADMA as described in previous reports.\textsuperscript{40-41}

**Neutron Activation Analysis (NAA) of Free-Standing LbL Films.** Free-standing LbL films of PDADMA and PSS were assembled as previously described. After completion, an ion exchange was performed by immersing the films into a solution containing the desired concentration of KBr for 1 h followed by a final 3 s rinse in Milli-Q water. The films were then dried under ambient conditions overnight and then under vacuum at 115°C for 3 h.

Films were then analyzed \textit{via} instrumental NAA using a comparator method, in which the calibrators and the unknown samples were irradiated using a 1 MW TRIGA reactor and the gamma-ray emissions were counted under identical conditions. Due to the strong signal associated with Br$^-$, two different sets of experimental parameters were employed to obtain data for Br$^-$ and
Cl\(^{-}\) (set 1) as well as Na\(^{+}\) and K\(^{+}\) (set 2). A more detailed experimental explanation can be found in the Supporting Information. In summary, calibrator solutions were weighed and heat-sealed in acid-washed 2/5-dram polyethylene irradiation vials. The LbL films samples were transferred into pre-weighed irradiation vials inside a dry-nitrogen glove box in order to prevent water uptake prior to the analysis. The closed sample vials were then weighed in ambient conditions and heat sealed prior to irradiation. Gamma-ray emission spectrometry was performed using a high-purity Ge gamma-ray detector (Ortec). Data analysis was performed using NAA software from Canberra Industries. The values for ion content reported in Table 1 are averages of three separate experimental repeats per data point.

**Quartz-Crystal Microbalance with Dissipation (QCM-D) Monitoring.** QCM-D data was collected using a Q-Sense E4 instrument. LbL films were assembled on SiO\(_2\) coated AT-cut quartz crystals with a resonant frequency of 4.95 MHz. The quartz crystals were cleaned by plasma treatment using an O\(_2\)-plasma etcher for 15 minutes followed by immersion in 2 vol % sodium dodecyl sulfate in water for 10 minutes, rinsing with Milli-Q water, drying with nitrogen, and a final O\(_2\)-plasma treatment for 15 minutes. The temperature for all QCM-D experiments was held at 25°C. The flow rate for all solutions was kept constant at about 115 µL/min. A baseline for each measurement was established by flowing Milli-Q water (pH 4.5) over the quartz crystal for approximately 45 min. An anchor layer of LPEI (pH 4.5) was then deposited onto the crystal for 15 min in order to enhance the surface charge and accelerate early growth of the LbL film, followed by a 5 min rinse in Milli-Q water (pH 4.5).\(^{39}\) The LPEI layer has been shown to skew the LbL stoichiometry towards having excess PDADMA.\(^{42}\) Deposition of the LbL film was carried out by alternating the flow of 0.1 mg/mL PSS (0.5 M NaCl) and 0.1 mg/mL PDADMA (0.5 M NaCl) for 15 min each. After each polyelectrolyte deposition, the system was rinsed for 5 min with Milli-Q water (0.5 M NaCl). All films in this study were capped or terminated with PDADMA, and the total number of layer pairs was either six or seven, depending on the concentration of the exchange
salt. Immediately following the final rinse, the films were exposed to either KBr, KCl, NaCl or NaBr at various concentrations and the system was allowed to equilibrate for up to 3 hours. Films produced using QCM-D are denoted as LPEI/(PSS/PDADMA)$_m$, where $m$ is the number of layer pairs.

**Modeling of QCM-D Data.** Changes in frequency and dissipation from each QCM-D experiment were analyzed using QTools modeling software (Biolin Scientific). Specifically, the extended viscoelastic model was used to fit the third, fifth, seventh, and ninth overtones, and the value used for material density ($L_1$) and fluid density was fixed at 1050 kg/m$^3$, (see Supporting Information and Table S1). It is acknowledged that the fluid density of various salt solutions differs as concentration increases or decreases. However, altering the value of fluid density in the modeling parameters did not yield significant changes in the reported data trends, and the fixed value proved to be sufficient for the present study (see Figures S1 and S2). This allowed all results to be collected in a consistent fashion. Additionally, the extended viscoelastic model was chosen due to the lower $\chi^2$ values provided compared to the regular viscoelastic model.$^{39}$ Reported values for changes in thickness and dissipation are averages of at least three experiments per data point, and the error bars were produced using the standard deviation.

**Results and Discussion**

**Composition of PDADMA/PSS Free-Standing LbL Assemblies.** It is important to first gain a clear understanding of PDADMA/PSS LbL film composition in order to more accurately comment on the salt exchange behavior discussed later. To do this, $^1$H NMR was employed to determine the PSS:PDADMA molar ratio (by repeat unit) within free-standing (PDADMA/PSS)$_{140}$ LbL films assembled at 0.5 M NaCl and, in turn, the mol % PSS. Previous $^1$H NMR studies on the PDADMA/PSS system indicate that the PSS:PDADMA ratio can be easily determined via a relationship between the aromatic peaks of the PSS chains and the aliphatic peaks associated with
both PSS and PDADMA.\textsuperscript{41} The mol % PSS was determined to be 35-36 mol % indicating a substantial excess of PDADMA within the PDADMA/PSS LbL films. This result is consistent with previous reports for the PDADMA/PSS polyelectrolyte system.\textsuperscript{5,25,33,42}

After quantifying the ratio of polyelectrolyte species, the counterion content in the LbL films was explored. Free-standing LbL films were immersed in Milli-Q water for 3 s to remove excess salt from the surface, ion exchanged with KBr at various concentrations, and analyzed using NAA. High activity of the selected ion species within the LbL films allowed for quantification of their content with an average error of 10% or less. Average weight percent values for the species of interest can be found in Table 1. Analysis on as-completed films (un-exchanged) revealed that Cl\textsuperscript{-} comprised nearly 3 wt % of the film, whereas Na comprised less than 0.3 wt %. This is likely due to the excess of PDADMA known to be present in PDADMA/PSS LbL film, which leaves fewer uncompensated PSS charge sites available to pair with small counterions such as Na\textsuperscript{+}.\textsuperscript{33,43} After exchange with KBr, the observed values for Na\textsuperscript{+} and Cl\textsuperscript{-} were extremely low (<0.01 wt% for Na\textsuperscript{+} and <0.1 wt% for Cl\textsuperscript{-}) compared to values prior to ion exchange (0.28 wt% for Na\textsuperscript{+} and 2.9 wt% for Cl\textsuperscript{-}). Regardless of the KBr exchange concentration, the amount of Br\textsuperscript{-} ions present in the film reached an average value of 6-8 wt %. This implies that nearly all available excess PDADMA charge sites are compensated with Br\textsuperscript{-} ions upon exchange. The NAA data also indicates a successful exchange of K\textsuperscript{+} with Na\textsuperscript{+} even at the low exchange concentration of 0.01 M KBr, which was well below the assembly concentration (0.5 M NaCl). At KBr concentrations above 0.5 M, there was a slight increase in the amount of K\textsuperscript{+} ions within the film. However, countercation species comprised less than 1 wt % of the films before and after the exchange such that the effect was not as dramatic as the Cl\textsuperscript{-}/Br\textsuperscript{-} exchange.

Table 1. Counter ion wt% within free-standing (PDADMA/PSS)\textsubscript{140} films after ion exchange with KBr.\textsuperscript{a}
<table>
<thead>
<tr>
<th>[KBr] Exchange</th>
<th>Br (wt %)</th>
<th>Cl (wt %)</th>
<th>K (wt %)</th>
<th>Na (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-Exchanged</td>
<td>ND</td>
<td>2.9</td>
<td>ND</td>
<td>0.28</td>
</tr>
<tr>
<td>0.01 M</td>
<td>6.5</td>
<td>0.023</td>
<td>0.0028</td>
<td>ND</td>
</tr>
<tr>
<td>0.25 M</td>
<td>6.8</td>
<td>0.065</td>
<td>0.35</td>
<td>0.0097</td>
</tr>
<tr>
<td>0.5 M</td>
<td>7.5</td>
<td>0.017</td>
<td>0.18</td>
<td>0.0025</td>
</tr>
<tr>
<td>0.75 M</td>
<td>7.8</td>
<td>0.075</td>
<td>0.89</td>
<td>0.0085</td>
</tr>
<tr>
<td>1.0 M</td>
<td>7.6</td>
<td>0.039</td>
<td>0.52</td>
<td>0.00058</td>
</tr>
<tr>
<td>1.25 M</td>
<td>7.4</td>
<td>0.095</td>
<td>0.92</td>
<td>0.0067</td>
</tr>
</tbody>
</table>

Data was obtained with an average error of 10% or less and reported values are averages of three samples per data point. ND = Not detectable.

These results demonstrate that the LbL film prefers to uptake K⁺ and release Na⁺ and prefers to uptake Br⁻ and release Cl⁻. This may be attributed to the more chaotropic nature of K⁺ and Br⁻ ions, which tend to be larger, more polarizable, and have a higher (more positive) energy of hydration. This could make K⁺ and Br⁻ ions less hindered in their diffusion through the film matrix by water structure networks and more efficient at screening. Combining the NAA results with the mol % PSS obtained by ¹H NMR and by assuming charge neutrality of the overall LbL film, we were able to estimate a $K_a$ value for KBr according to:

$$K_a = \frac{a_{KBr}^2}{(y^+)(y^-)}$$

where $y^+$ is the ratio of Br⁻ to PDADMA, $y^-$ is the ratio of K⁺ to PSS within the LbL film, and $a_{KBr}$ is the activity of KBr at a given ionic strength. This represents the tendency of a particular salt to dope the LbL film and disrupt intrinsic ion pairs, with lower values of $K_a$ indicating that doping is more favored. From averaging the results for 0.25 M to 1.25 M in Table 1, $K_a$ for KBr was $2.53 \pm 0.76$. This is similar to the value of 2.42 reported by Schlenoff for PDADMA/PSS polyelectrolyte complexes. The reported $K_a$ value for NaCl is 3.33, which suggests that KBr is...
more favorable to doping the LbL film in comparison to NaCl. However, it should be noted that our experimental error places our $K_a$ for KBr close to this reported value for NaCl.

The relatively low amount of cation species in the film after exchange with KBr at the low concentration of 0.01 M could be evidence that during the exchange process there is a minor extrinsic-to-intrinsic conversion of some PSS charge sites. At this low exchange KBr concentration, there are fewer $K^+$ ions available to maintain extrinsic binding sites as compared to the assembly conditions. As PSS chains become intrinsically compensated, the associated Na$^+$ counterions are released and expelled from the film. Simultaneously, the excess extrinsically compensated PDADMA chains in the film bulk may diffuse throughout the outer, more loosely packed region of the LbL film near the surface-liquid interface. This would result in a greater excess of positive charge at the surface of the film, thereby excluding additional $K^+$ ions from entering during ion exchange.

**Swelling Response to KBr Solution.**

In order to understand the responsive behavior of PDADMA/PSS LbL thin films to changes in the external environment, QCM-D was employed as a tool to monitor real-time changes in film thickness, mass, and viscoelastic properties. LPEI/(PSS/PDADMA)$_6$-$7$ films were assembled from PDAC and PSS solutions at an ionic strength 0.5M NaCl onto SiO$_2$-coated quartz crystals as previously reported. The final LbL film thickness was around 140-150 nm for seven layer pair films and around 100-110 nm for six layer pair films (obtained from 10 and 5 experimental trials, respectively). Figure 1 shows representative QCM-D data for the LbL assembly and ion exchange of LPEI/(PSS/PDADMA)$_6$-$7$ films with various KBr concentrations. These reported thickness values represent the hydrated thickness as obtained from viscoelastic modeling of resonant frequency ($\Delta f$) and dissipation ($\Delta D$) changes from QCM-D experiments. Figure S1 shows a representative example of a fitted QCM-D data set. Additionally, information about the
mechanical properties can be gathered by observing changes $\Delta D$. Increases in $\Delta D$ correspond to softening of the LbL film while decreases in $\Delta D$ imply stiffening.

**Figure 1.** QCM-D data showing (a) $\Delta f_3/n$ and $\Delta D_3$ during LPEI/(PSS/PDADMA)$_7$ film assembly and subsequent exposure to 1.0 M KBr and (b) $\Delta f/n$ reflected in the various crystallographic overtones upon exposure of to 1.0 M KBr as well as data overlays of (c) $\Delta f_3/n$ and (b) corresponding $\Delta D_3$ values for LPEI/(PSS/PDADMA)$_6$-$7$ films assembled at 0.5 M NaCl and subsequently exposed to KBr solutions of varying concentrations. The caption in (c) applies to (d).

Immediately after assembly, the thin films were exposed to various concentrations of KBr under dynamic flow, and the corresponding $\Delta f$ and $\Delta D$ values were monitored throughout the ion exchange and equilibration processes (see Figure 1). From this data, the changes in hydrated thickness were estimated. Figure 2 shows changes in thickness and dissipation of the LbL films.
relative to the as-prepared, fully hydrated thickness just prior to exposure to KBr solutions. The behavior in response to altering the KBr exchange concentration can be broken down into four regimes, summarized in Scheme 1. The first regime can be described as the zero-to-near zero concentration regime, from 0 M – 0.001 M KBr. Here, the Debye length (> 10 nm) significantly exceeds the distances between the neighboring charged groups (> 1 nm) and there is an insufficient number of counterions present within the film to provide the electrostatic screening necessary to keep the film in its original compact configuration. The extrinsic charge sites associated primarily with PDADMA are left uncompensated and experience strong electrostatic repulsion from neighboring charge sites, resulting in straightening of the PE chain.\textsuperscript{50} causing the film to expand rapidly and dramatically (up to 120%). This expansion is accompanied by the uptake of additional water molecules to occupy the free volume resulting in a large increase in areal mass of the film (up to 119%). As the film rapidly expands, $\Delta D_3$ increases up to $160 \times 10^{-6}$ units, which indicates a substantial softening of the film associated with the large increase in free volume and influx of water, Figure 2b.
Figure 2. Average (a) percent change in thickness and (b) change in dissipation for LPEI/(PSS/PDADMA)$_{6-7}$ after exchange with various concentrations of KBr. Above 1.25 M KBr, the number of layer pairs was kept to six in order to ensure accurate data collection from the QCM-D due to the large degree of swelling. Reported values are averages of at least three experimental trials, and $\Delta D$ values are taken from the third crystallographic overtone. The error bars represent the standard deviation of the trials.
Scheme 1. Qualitative schematic illustrating the four regimes assigned to the swelling response of PDADMA/PSS LbL films assembled at 0.5 M NaCl and exposed to varying concentrations of KBr.

The second regime, referred to as the low concentration regime, lies in the range of exchange concentrations from 0.01M – 0.5M KBr. In this regime, the film shows slight contraction upon exposure to solutions of ionic strength lower than the assembly ionic strength of 0.5 M NaCl. This behavior may result from an adequate amount of counterions present in the incoming KBr solution that provide enough charge screening of neighboring extrinsic sites to prevent expansion from electrostatic repulsion. Under these conditions, the minor contraction of the film structure possibly gives rise to expulsion of bulk water and free, unassociated counterions. Another explanation for the LbL film contraction is that some conformational change of the polyelectrolyte chains occurs during the counterion exchange process. The slight decrease in $\Delta D_3$ in this low concentration regime implies that the film takes on a more rigid, compact configuration. The polyelectrolyte network becomes more densely packed as there exists some balance between extrinsic ion compensation and electrostatic repulsion, ultimately causing an increase in film stiffness. The
exception to this trend occurs at 0.5 M KBr where only slight changes in frequency and dissipation are observed. Here, the ionic strength of the KBr exchange solution is the same as the NaCl assembly solution, and the overall impact on the internal structure and properties of the LbL film is minimal.

The third regime is referred to as the high concentration regime 0.5 M – 1.6 M KBr. In this regime, the magnitude of the change in hydrated thickness, mass, and dissipation showed clear dependence on the KBr concentration. The reason for the observed swelling in this regime is opposite of that described in the zero-near zero concentration regime. In this case, the increased presence of counterions in the film results in a large degree of electrostatic screening and doping. The effect of the large influx of counterions is two-fold. First, the increased competition of counterions for converting intrinsic sites to extrinsic sites causes disruption of physical ion pair crosslinks. This results in an expansion of the film and an increase in free volume which yields an uptake of bulk water. Second, the influx of K⁺ and Br⁻ ions into the film is accompanied by water in the counterion hydration shell. With this expansion and influx of bulk water and hydrated counterions, the film becomes softer and more gel-like which is reflected in the large increase in dissipation in this regime (ΔD₃ up to 167 × 10⁻⁶).

A closer look at regime III reveals that the percent change in thickness shows a linear dependence on the KBr concentration. Fitting the data from 0.75 M to 1.6 M KBr in this regime gives a line with the equation %Δt = 103.55C_{KBr} – 66.82 (R² = 0.99), where C_{KBr} is the concentration of the KBr solution. Reid et al. reported similar trends with respect to contraction of PDADMA/PSS LbL films exposed to CaCl₂ and MgCl₂ solutions upon reverting back to assembly conditions (0.5 M NaCl). They reported that the degree of LbL film contraction was linearly dependent on the concentration and identity of the post-assembly divalent salt solutions above 0.17 M. Film swelling in this concentration range was driven by ion doping and electrostatic screening, and film contraction upon returning to assembly conditions was dependent on both ion type and
concentration.\textsuperscript{39} It is worth noting that the changes in the film thickness in regimes II and III can be correlated with the difference between the salt concentration in the PEM (assembly concentration) and in the bulk solution. This suggests the hydrated ion flux in and out of the multilayer is dominating in the swelling response.

The final regime, referred to as the ultra-high concentration regime, deals with KBr concentrations $> 1.6$ M. It was observed that at the KBr exchange concentration of 2.0 M, the change in $\Delta f$ was quite large, indicating an immediate and substantial decrease in film thickness and mass. It was concluded that saturation of the film with counterions resulted in sufficient electrostatic screening and plasticization of the PEM structure, leading to dissolution. The data indicated that the hydrated film mass dropped from $12.4 \pm 0.45$ µg/cm$^2$ to $0.53 \pm 0.32$ µg/cm$^2$. Visual examination of the quartz crystal substrate after the experiment revealed that only a few small patches of film remained. These results are consistent with other work describing the dissolution of PEMs and PECs at salt concentrations far above their assembly ionic strengths.\textsuperscript{19,51}

A recent study by the Schlenoff group discussed the properties of PDADMA/PSS complexes fabricated using a “backwards” method in the presence of KBr at various concentrations.\textsuperscript{51} They found that the PDADMA/PSS complexes underwent distinct property changes as the concentration of the surrounding KBr increased. At low concentrations, the complexes were stable and glassy. With increasing KBr concentration, the complexes became softer and took on a more expanded configuration until the polyelectrolyte chains became so heavily doped with counterions that they formed elastic liquid coacervates and finally dissociated completely at $\sim 1.8$ M KBr, similar to our PDADMA/PSS LbL films. This shows similarities between the salt responses of complexes and multilayers.

Unfortunately, the ion content shown in Table 1 cannot be precisely correlated to the data obtained by QCM-D, and therefore to the behavior depicted in Scheme 1 for several reasons. First, the exchange process for free-standing LbL films for NAA measurements took place in a static
environment. There was no influx of new solution or removal of solution containing ions exchanged out of the film. The opposite is true of the QCM-D experiments, where the solution was constantly flowing in and out of the sample chamber. This constant addition of new ion-rich solution could be a contributing factor to the responsive behavior observed at elevated concentrations.

**Swelling Response to KBr/NaCl Solution Mixtures.**

To discern the difference between the effects of NaCl and KBr on the swelling behavior, a study was performed in which the overall ionic strength of the post-assembly ion exchange solution was held constant at 1.0 M, but the ratio of NaCl:KBr was altered. All assembly experimental parameters remained the same. In this manner, the effect of ion identity can be probed apart from ionic strength. Figure 3 shows the percent changes in thickness of LPEI/(PSS/PDADMA)$_7$ films upon exposure to NaCl/KBr solutions at varying ratios of NaCl:KBr with 1.0 M NaCl and 1.0 M KBr as controls. There is a clear dependence on the presence of KBr despite the fixed ionic strength. Directly comparing pure NaCl and KBr at 1.0 M reveals that $K^+ > Na^+$ and $Br^- > Cl^-$ with respect to impact on swelling thickness. With regard to changes in dissipation, there is very little effect on $\Delta D$ with respect to NaCl/KBr ratio. For this case, it seems that ion type strongly affects swelling thickness, but not viscoelastic properties. This suggests that film is sufficiently rigid at these conditions to prevent energy dissipation.$^{52}$

Previous studies have shown that PDADMA/PSS LbL thin films and complexes are more heavily influenced by the anionic counterion type present during assembly and that the degree of influence follows the Hofmeister series.$^{7,24,26-27,53}$ From NAA, it was observed that free standing films immersed in solutions of varying KBr concentration contained >1 wt % of the cationic counterion species while maintaining an elevated amount, 6-7 wt %, of anionic species. This is consistent with reports that $Br^-$ is known to have a greater effect on PEM structure than $Cl^-$. $^{27}$ The increase in film thickness with increasing $Br^-$ concentration is intuitive if $Br^-$ is more capable of
disrupting intrinsic ion pairs than Cl\(^-\) leading to increased plasticization from hydration water molecules throughout the bulk of the film.\(^{27,53-54}\) Additionally, the ionic radius of Br\(^-\) is slightly larger than Cl\(^-\) so the incorporation of many Br\(^-\) ions could have a collective steric effect on the film swelling. In sum, the LbL swelling effects arise from the Br\(^-\) anion’s larger ionic radius, greater polarizability and more loosely bound hydration shell, which gives rise to more disruptive interactions within the LbL network.

![Diagram](image)

**Figure 3.** (a) Percent change in thickness and (b) absolute changes in dissipation of LPEI/(PSS/PDADMA)\(_{6-7}\) LbL thin films assembled at 0.5 M NaCl and then exposed to NaCl/KBr mixtures where the overall salt concentration was held at 1.0 M and the fraction of KBr was varied. Therefore, a mole fraction of KBr = 0 indicates that the exposure solution was 1 M NaCl. Reported
values are averages of at least three experimental repeats, and ΔD values are taken from the third crystallographic overtone. The error bars represent the standard deviation of the trials.

**Reversibility of Swelling Response**

The reversibility of the swelling response in the high concentration regime was examined by exposing LPEI/(PSS/PDADMA)$_{6-7}$ films assembled at 0.5 M NaCl to KBr solutions at 0.75 M, 1.0 M, 1.25 M, and 1.6 M, allowing them to reach equilibrium swelling behavior and then reverting to 0.5 M NaCl. Figure 4 shows film thicknesses and dissipation values just after assembly, after equilibration in the selected KBr concentration, and after re-exposure to NaCl. The results indicate that for 0.75 M, 1.0 M, and 1.25 M KBr the films return to a thickness slightly lower than their assembly thickness. This is likely due to a restructuring of the chains when returning from the expanded, swollen state to a more densely packed configuration.$^{24}$ This is consistent with the practice of “salt annealing” which is used to smooth and restructure LbL surfaces.$^{32-33}$ Representative fits of the raw QCM-D data for reversibility experiments are shown in Figure S2.

The degree of internal restructuring is directly correlated with the concentration of the KBr exchange solution in the high concentration regime. Previous studies on the effects of assembly with regard to ion type indicate that increasingly chaotropic counterions result in films with more loosely packed internal structures and roughened surfaces.$^{26}$ The effect is seen to increase in strength with increasing atomic radii and decreasing hydration shell. This is attributed to the stronger interactions of the ions with the polyelectrolyte charge sites allowing for greater electrostatic screening and coiled conformations during construction and assembly.$^{24,26-27}$ In this case, the post-assembly swelling response of LbL assemblies to increasing KBr concentration follows a similar pattern as to that seen for assembly.$^{26}$ The polyelectrolyte chains are entangled in a kinetically trapped network, and the addition of more structurally disruptive ions at ionic strengths above the assembly conditions disrupts intrinsic binding sites allowing the network to
loosen. Water enters the LbL assembly and plasticizes the network allowing for further enhanced chain mobility. As the film swells and more ions enter along with bulk water, the effects are exacerbated until a new equilibrium structure is reached. Reversion back to assembly conditions, 0.5 M NaCl in this case, results in a relaxation of the PEM structure to a more compact configuration. The average reductions in thickness for films exposed to 0.75 M, 1.0 M, and 1.25 M KBr upon reverting back to 0.5 M NaCl were 6.5 nm, 16.5 nm, and 26 nm, respectively (or 4%, 7%, and 12% of the initial state). Each of these changes in thickness were accompanied by changes in mass related to the expulsion of bulk water upon collapse of the films.

**Figure 4.** Reversible swelling response showing changes in (a) thickness and (b) dissipation after assembly at 0.5 M NaCl (post-assembly in red), exchange with KBr at various concentrations (ion
exchange in green), and reverting back to 0.5 M NaCl (reverted in blue). Reported values are averages of at least three experimental repeats, and ∆D values are taken from the third crystallographic overtone. The error bars represent the standard deviation of the trials.

For films exposed to 1.6 M KBr, the change in thickness upon reverting back to 0.5 NaCl was much larger, averaging around 50% reduction in film thickness. Such a large loss in thickness is likely not only contributed to internal restructuring of the film but also to deconstruction of the film upon reversion. To verify whether or not the films would continue to dissociate upon further switching between 1.6 M KBr and 0.5 M NaCl, this cycle was repeated three consecutive times on the same LPEI/(PSS/PDADMA)₆ film. The second, third, and fourth KBr → NaCl exchanges resulted in less than 5 nm change in thickness, which remained near 50% of the post-assembly thickness. This could be attributed to the more intimate interactions between the inner layers of the film and the SiO₂ coated crystal surface, which would yield a more densely packed network associated with the first few deposited layer pairs. This explanation is consistent with the diffusion model and the influence of substrate effects related to PEM growth reported elsewhere. The elevated packing density of the polyelectrolyte chains near the substrate makes them less influenced by changes in the ionic environment.

Swelling response to NaCl, KCl, and NaBr

To gain a deeper understanding of the differing effects of individual counterion species on the swelling response of LPEI/(PSS/PDADMA)ₘ LbL thin films, it was necessary to explore different combinations of monovalent ions. To this end, LPEI/(PSS/PDADMA)₆₋₇ films assembled at 0.5 M NaCl were exposed to post-assembly solutions of NaCl, KCl, and NaBr at selected concentrations to mirror those performed with KBr. Figure 5 shows the comparison of the three counterion combinations. The results indicate that NaBr and KBr had similar effects on the degree of swelling as well as comparable effects on the viscoelastic properties as shown by the magnitude of dissipation changes, which highlights the strong effect of Br⁻ ions.
In the cases of NaCl and KCl, however, the trend is quite different above and below 0.5 M ionic strength when compared with NaBr and KBr. One substantial difference was reflected in the third concentration regime. At 1.6 M NaCl and KCl, the LbL films swelled by only 19% and 22%, respectively, compared to 93% and 101% in the case of both NaBr and KBr. The ΔD₃ values at this elevated concentration were also considerably smaller for both NaCl, 13 × 10⁻⁶, and KCl, 20 × 10⁻⁶, compared to NaBr and KBr, which showed ΔD₃ values of 124 × 10⁻⁶ and 175 × 10⁻⁶, respectively. The implication of this behavior is that there is a relatively small influx of Na⁺, K⁺, and Cl⁻ counterions during the exchange process. Since there is already Cl⁻ present in the film, there is little to no significant competition for binding sites that are already formed between the extrinsic PDADMA/Cl⁻ sites or pre-formed intrinsic binding sites. Additionally, the films are capped with PDADMA, creating an excess of positive charge at the surface.⁵, 25, 39, 43 It is possible that the lack of favorable competition for binding sites combined with the excess positive surface substantially shields a large portion of the Na⁺ or K⁺ counterion species from entering the bulk of the film. Those counterions that do cross the interfacial barrier have only a weak net effect on the film properties as compared to the more disruptive, dominating Br⁻ anions.
Figure 5. Comparison of (a) percent change in thickness and (b) change in dissipation for LPEI/(PSS/PDADMA)$_{6-7}$ after exchanges with various concentrations of NaCl, KCl, KBr, and NaBr. Reported values are averages of at least three experimental repeats, and $\Delta D$ values are taken from the third crystallographic overtone. The error bars represent the standard deviation of the trials.

For the films exchanged with 0.001 M NaCl and KCl, substantial swelling and water uptake were observed as reflected in large decreases in frequency and increases in dissipation. The changes in thickness due to swelling were 115% and 124%, respectively, for NaCl and KCl. These values are comparable to that observed for films exchanged with Milli-Q water (no salt), which
swelled by 120%. Electrostatic repulsion among like charge sites causes the film to swell rapidly as the assembly counterions are leached from the film. This theory is supported by the fact that PEMs exposed to 0.001 M of both KBr and NaBr swell by 33% and 57%, respectively. The clear dependence of the anion can be seen by this trend. The ability of Br\(^-\) to dope the film at all concentrations more rapidly and efficiently than Cl\(^-\) is made clear by the large difference in swelling behavior. Above 0.1 M ionic strength, electrostatic forces are adequately screened, and the films contract slightly by about 5-10% for all salts.

Previous reports on salt mediated self-healing and annealing of polyelectrolyte multilayers and complexes have shown that by adjusting the post-assembly ionic environment, structural defects can be resolved or even totally reversed.\(^{17,33,36,56}\) The key to self-healing of PEMs is the increased mobility of chains as this allows them to diffuse across damaged regions. As we have just discussed, the type of salt, specifically the anion species, has a significant impact on the polyelectrolyte chain mobility and the structural properties of LbL assemblies. We have shown that exposure of PEMs prepared in NaCl to various KBr and NaBr concentrations above the assembly conditions results in a much larger degree of swelling and increased chain mobility compared to the same elevated concentrations of NaCl and KCl. The ability of Br\(^-\) ions to quickly and effectively dope thin films makes them a good candidate for further study in the area of self-healing thin films and coatings.

**Conclusion**

The response and salt uptake of PDADMA/PSS LbL thin films assembled in 0.5 M NaCl and exposed to various concentrations of NaCl, KCl, NaBr, and KBr was studied. Salts containing Br\(^-\) had substantially greater impact on film swelling than salts containing Cl\(^-\). This likely arose from the Br\(^-\) anion’s larger ionic radius, greater polarizability and more loosely bound hydration shell, which gave rise to more disruptive interactions with intrinsic ion pairs within the LbL
network. NAA revealed that countercationic species comprised less than 1 wt% of PDADMA/PSS free-standing films before and after ion exchange with various KBr concentrations. Conversely, counteranion species were present at much higher concentrations before and after exchange, indicating an excess of PDADMA in the PEMs. QCM-D revealed four KBr concentration regimes associated with the swelling response. At 0 M – 0.001 M KBr, swelling was dominated by electrostatic repulsion, and at 0.1 – 0.5 M KBr, slight film contraction and stiffening was observed as the ionic strength approached that of the original assembly conditions. For 0.5 – 1.6 M, swelling in the presence of KBr was reversible and accompanied by a relaxation of the film, consistent with the practice of salt annealing. In this regime, swelling was linear with KBr concentration. Finally, at 1.6 M KBr and higher, partial dissolution of LbL films was observed and was attributed to excessive electrostatic screening and disruption of intrinsic ion pairs. A comparison of post-assembly behavior in the presence of various monovalent salts verified that the anion identity was the dominating factor in the swelling response.

These findings provide insight into the response of LbL thin films in the presence of monovalent ions across a broad range of concentrations and serve to explain the mechanism of salt annealing, self-healing, and KBr’s dramatic effects on polyelectrolyte complexes and multilayers.26-27, 43, 57-58 Understanding how the structure and properties of LbL assemblies are affected by both subtle and drastic changes in ionic environment is critical for applications such as sensors, responsive coatings, and separation membranes. Future work could expand to more ion types and concentrations and include various mixtures of counterions to gain further understanding of how these thin films respond to more complex environmental changes.

ASSOCIATED CONTENT

Supporting Information. Representative raw and fitted QCM-D data, a table of the parameters used to fit QCM-D data, and details describing the NAA instrumentation and sample preparation
can be found in the Supporting Information, available online free of charge on the ACS publications website at DOI:

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Notes

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