**Supplementary Information:** Quantification of Water-Ion Pair Interactions in Polyelectrolyte Multilayers Using a Quartz Crystal Microbalance Method

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Experimental section

Modeling of QCM-D Data

All QCM-D data obtained were analyzed using the QTools modeling software by Biolin Scientific. The changes in frequency and dissipation of the third, fifth, seventh and ninth overtones recorded over the time of the experiment were modeled using the viscoelastic model (Equation 1). All parameters except the fluid viscosity were set in accordance with previous work by O’Neal et al. Parveen et al. show that the changing fluid properties, density, and viscosity of the varying concentrations of NaCl solution used would influence the QCM-D modelling results.\(^1,2\) Similarly, as a wide range of salt solutions are used for our experiments, the full data set was broken down in sections shown in Table S1 and modelled separately for a truly accurate measure of our system. Additionally, the extended viscoelastic model was chosen due to the lower \(\chi^2\) values provided compared to the regular viscoelastic model.\(^3\) All experiments were carried out in triplicate and the reported values for changes in thickness are averages of the three experiments per data point. The error bars were produced using the standard deviation. Changes in frequency and dissipation are described as follows:

\[
\Delta f \approx - \frac{1}{2 \pi \rho_0 d_0} \left\{ \frac{\eta_2}{\delta_2} + d_1 \rho_1 \omega - 2 d_4 \left( \frac{\eta_2}{\delta_2} \right)^2 \frac{\eta_2 \omega^2}{\mu_1^2 + \omega^2 \eta_1^2} \right\} \quad \text{Equation S1}
\]

\[
\Delta D \approx \frac{1}{2 \pi \rho_0 d_0} \left\{ \frac{\eta_2}{\delta_2} + 2 d_1 \left( \frac{\eta_2}{\delta_2} \right)^2 \frac{\eta_2 \omega^2}{\mu_1^2 + \omega^2 \eta_1^2} \right\} \quad \text{Equation S2}
\]
where \( f \) is the resonance frequency, \( \varrho \) is the density, \( \mu \) is the elastic modulus, \( \eta \) is the viscosity, \( d \) is the thickness and \( \delta = \frac{2\eta}{\varrho \omega} \). The subscripts 0, 1, and 2 correspond to the quartz crystal, adsorbed film, and flowing fluid, respectively.

**Proton Nuclear Magnetic Resonance (1H NMR) Spectroscopy**

Proton nuclear magnetic resonance (1H NMR) spectroscopy (500 MHz proton frequency, Varian Inova 500 spectrometer) was used to determine the composition of free-standing PSS/PDADMA PEMs. Approximately 10 mg of dried free-standing films were dissolved in 0.75 ml of deuterium oxide (D\(_2\)O) solution with 2.5 M KBr. The polyelectrolyte composition was then calculated by comparing the relationship between the aromatic peaks associated with PSS and the aliphatic peaks associated with PDADMA.

**X-ray Photoelectron Spectroscopy (XPS)**

X-ray photoelectron spectroscopy (XPS) was performed using an Omicron ESCA Probe with Mg K\( \alpha \) radiation (\( h\nu = 1253.6 \) eV). Survey scans were performed with steps of 1.0 eV and 50 ms dwell time within a range of 10 - 1100 eV. High resolution scans were performed with steps of 0.05 eV and 500 ms dwell time. All spectra were calibrated using the C 1s peak for carbon atoms (284.8 eV). The XPS was carried out on the coated SiO\(_2\) sensors directly. Sulfur/Nitrogen (S/N) ratios were calculated from atomic percentages (%) of elements.

**Profilometry**

The PEM-coated crystal was dried first using a stream of nitrogen and dried next under ambient conditions for 24 hours. To ensure all moisture was eliminated, the PEM was further dried for 3
hours at 115 °C in a vacuum oven. A small scratch was made on the film, and the dry thickness was immediately measured using a KLA Tencor D-500 profilometer.

**Classical Molecular Dynamics (MD) Simulations**

The Gromacs 5.1.2 package was used for the all-atom molecular dynamics (MD) simulations. PSS and PDADMA chains with 20 monomers neutralized by Na⁺, K⁺, Cl⁻, and Br⁻ as counterions were examined. To describe the polyelectrolytes (PEs), the OPLS-aa force field was used, with the extension for the ammonium group. For water, the explicit TIP4P water model was employed. The parameters for all the cations were taken from ref. and for chloride and bromide ions from ref. and ref., respectively. Notably, the employed force-field uses fixed point charges, i.e. is non-polarizable.

All the calculations were performed using NPT ensemble. The V-rescale thermostat with coupling constant 0.1 ps was applied at reference temperature $T=300$ K. Additionally, we used the isotropic Parrinello-Rahman barostat with the coupling constant 1 ps and reference pressure 1 bar. The long-range electrostatic interactions were calculated using the PME method. Van der Waals interactions were described using the Lennard-Jones potential with a 1.0 nm cut-off. All the bonds in the PEs and water molecules were controlled by the LINCS and SETTLE algorithms, respectively. A 2 fs time step within the leap-frog integration scheme was applied and the trajectories were written every 1 ps. First, 20 ns simulation were considered as an equilibration of the system and disregarded from the analysis. After that, a production run of 50 ns was performed. The radial distribution functions $g(r)$ were calculated using built-in Gromacs tools. Unless otherwise stated, all the distributions are calculated with respect to the central atom of the PE charge group, i.e., S in PSS and N in PDADMA.
Ab initio Molecular Dynamics (AIMD) Simulations

The (Born–Oppenheimer) *ab initio* molecular dynamics (AIMD) simulations were carried out using hybrid Gaussian and plane waves method, as implemented in the Quickstep module\(^\text{17}\) of CP2K 7.1\(^\text{18}\). The studied systems consisted of three repeat unit PE-ion pairs solvated by explicit water molecules in cubic (2.5 nm)\(^3\) simulation boxes. The initial configurations for the AIMD simulations were constructed by extracting from the final, 50 ns, configurations of the classical MD simulations three repeat units of the 20-mer PE, the counter ion closest to, or actually between, the charge groups of this PE trimer segment, and a surrounding water shell of ca. 1 nm. The missing hydrogens were added to the chain ends of the extracted trimer structures and additional water molecules were inserted in the simulation boxes. The net charges of the PSS and PDADMA systems with one counterion were \(-2e\) and \(+2e\), respectively, where \(e\) is the unit charge. The net charge was neutralized by a homogeneous background charge distribution applied automatically in CP2K.

The PBE exchange-correlation functional\(^\text{19}\) was employed in conjunction with dispersion corrections introduced by the DFT-D3(BJ) method.\(^\text{20, 21}\) The molecularly optimized double-\(\zeta\) DZVP-MOLOPT-SR-GTH basis set\(^\text{22}\) with the Goedecker–Teter–Hutter (GTH) pseudopotentials were used to all atom types.\(^\text{23-25}\) A plane wave cut-off of 600 Ry was employed with a reference grid cut-off of 50 Ry. The Kohn-Sham equations were solved by using the orbital transformation method\(^\text{26}\) with a DIIS minimizer and a FULL_SINGLE_INVERSE preconditioner. An SCF convergence criterion of \(10^{-6}\) a.u. was used. Periodic boundary conditions were applied in all directions. Prior to the AIMD simulations, the systems were geometry optimized by using the LBFGS algorithm.\(^\text{27}\) The AIMD simulations were carried out in the NVT ensemble at temperature 348.15 K maintained by the CSRV thermostat.\(^\text{12}\) The elevated temperature was used to avoid the
overstructuring of water typically induced by PBE. A time step of 1 fs was used with the Velocity-Verlet integrator. The systems were initially equilibrated for 10 ps during which strong thermostatting was implemented by using a time constant of 50 fs. After this, the thermostat time constant was increased to 100 fs and the equilibration was continued for 10–26 ps. This was followed by 60 ps production runs. The trajectories were written every 5 ps. The VMD 1.9.2 software was employed for calculating the \( g(r) \). Coordination numbers of the first solvation shells were obtained by integrating the \( g(r) \) up to the first minimum.

Visualization of both the classical MD and AIMD employ VMD software package.
Figures

**Figure S1.** Dry film thickness from profilometry for PSS/PDADMA PEMs prepared in NaCl and KBr. 6 and 4 layer-pairs for PEMs prepared in NaCl and KBr respectively.

**Figure S2.** NMR spectra of 140 layer-pairs of PSS/PDADMA free-standing films at varying assembly salt concentrations. The blue region represents peaks of the 4 aromatic hydrogens from PSS found between 5 and 9 ppm. The grey region in grey represents peaks of the 16 aliphatic hydrogens from PDAMDA found between 0 and 4.6 ppm.
Figure S3. Sample XPS survey scans showing the sulfur (S), carbon (C), nitrogen (N) and oxygen (O) peaks of PSS/PDADMA PEMs prepared in 0.25 M (Q6) and 0.5 M NaCl (Q8).

Figure S4. The total number of water molecules associated intrinsic ion pairs “i” and the hydration coefficient of PSS/PDADMA PEMs prepared at varying concentrations of a) NaCl and b) KBr.
Figure S5. Representative snapshots of a PSS (at left) and PDADMA (at right) molecules in the MD simulations. The PEs were neutralized by Na\(^+\), K\(^+\), Cl\(^-\), and Br\(^-\) ions, highlighted in the snapshots in blue, pink, orange, and red, respectively. Water molecules are omitted in the visualization for clarity. In the middle, the radial distribution functions \(g(r)\) calculated between the central atom in the PE charge group (S for PSS and N for PDADMA) and respective counterion are presented. The continuous lines correspond to the data obtained from the classical MD simulations. For comparison, the vertical dashed lines mark the corresponding peak maxima as determined from the \textit{ab initio} MD (AIMD) simulations data. In AIMD simulations, a single counterion was considered at quantum mechanical detail level.
Tables

**Table S1.** QTools modeling parameters.

|       | NaCl                                      | KBr                                      |
|-------|-------------------------------------------|------------------------------------------|
|       | Fluid properties                          | L1                                       | Fluid properties                          | L1                                       |
| Section | Density (kg/m³) | Viscosity (kg/ms) | Density (kg/m³) | Section | Density (kg/m³) | Viscosity (kg/ms) | Density (kg/m³) |
| PEM assembly | 1050 | 0.001 | 1050 | PEM assembly | 1050 | 0.001 | 1050 |
| 0 – 0.1 M  | 997.87 | 0.00091 | 1050 | 0 – 0.1 M | 1004.06 | 0.00089 | 1050 |
| 0.1 – 1.0 M | 1021.24 | 0.00097 | 1050 | 0.1 – 1.0 M | 1050.75 | 0.00087 | 1050 |
| 1.0 – 2.0 M | 1054.21 | 0.001 | 1050 |         |          |            |          |

**Table S2.** PDADMA and PSS composition of 6 (NaCl) and 4 (KBr) layer pairs of PSS/PDADMA PEMs prepared at varying concentrations of NaCl and KBr obtained from XPS.

| Assembly salt | Assembly salt concentration (M) | C (at%) | O (at%) | S (at%) | N (at%) | S/N ratio | PSS % | PDADMA % |
|---------------|---------------------------------|---------|---------|---------|---------|-----------|-------|----------|
| NaCl          | 0.25                            | 63.58   | 24.79   | 5.27    | 6.06    | 0.870     | 46.52 | 53.48    |
|               | 0.5                             | 61.11   | 26.3    | 7.23    | 5.15    | 1.405     | 58.42 | 41.58    |
|               | 0.75                            | 63.09   | 23.61   | 6.34    | 6.94    | 0.913     | 47.73 | 52.27    |
|               | 1                               | 67.42   | 19.36   | 5.28    | 7.92    | 0.666     | 39.98 | 60.02    |
| KBr           | 0.25                            | 63.47   | 24.95   | 5.18    | 6.38    | 0.813     | 44.84 | 55.16    |
|               | 0.5                             | 64.35   | 22.72   | 6.26    | 6.65    | 0.941     | 48.48 | 51.52    |
|               | 0.75                            | 60.46   | 27.92   | 7.27    | 4.33    | 1.677     | 62.64 | 37.36    |
|               | 1                               | 64.19   | 24.08   | 5.81    | 5.91    | 0.983     | 49.57 | 50.43    |
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