

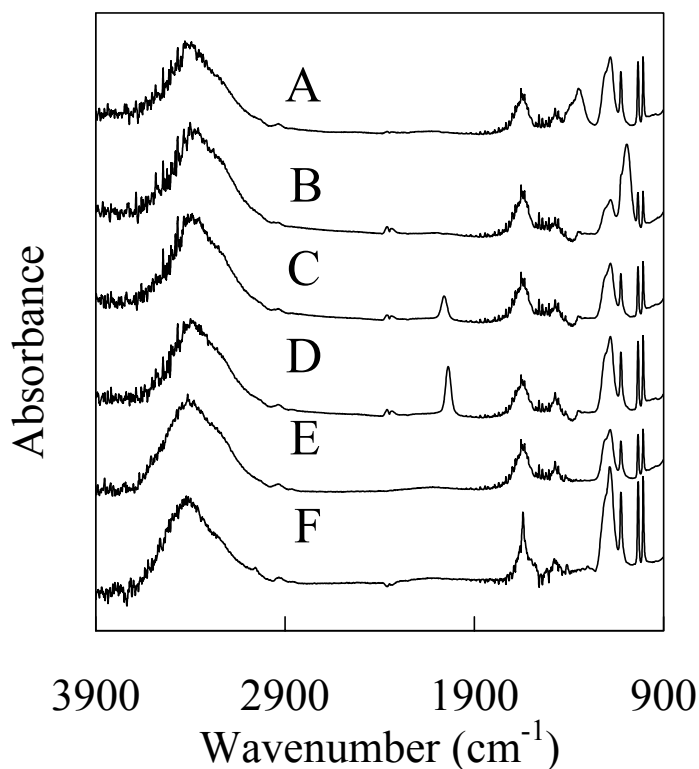
**Supporting Information**

**Hydration Contributions to Association in Polyelectrolyte Multilayers and Complexes: Visualizing Hydrophobicity**

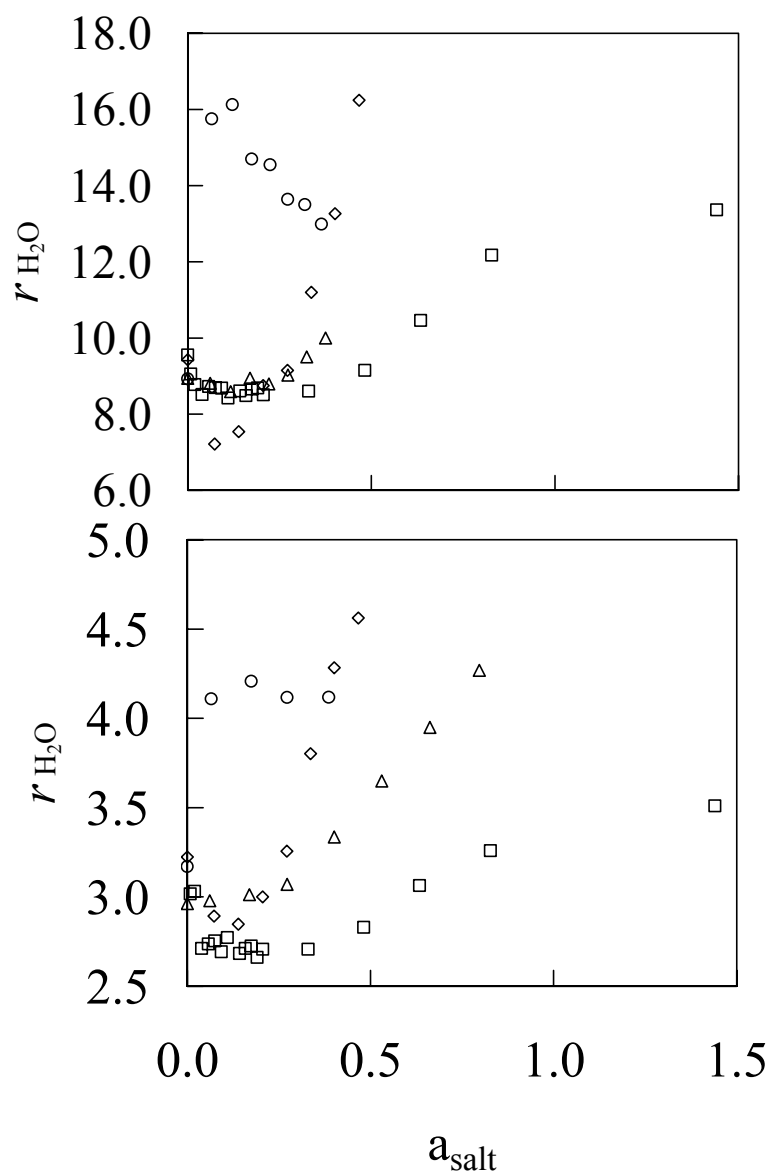
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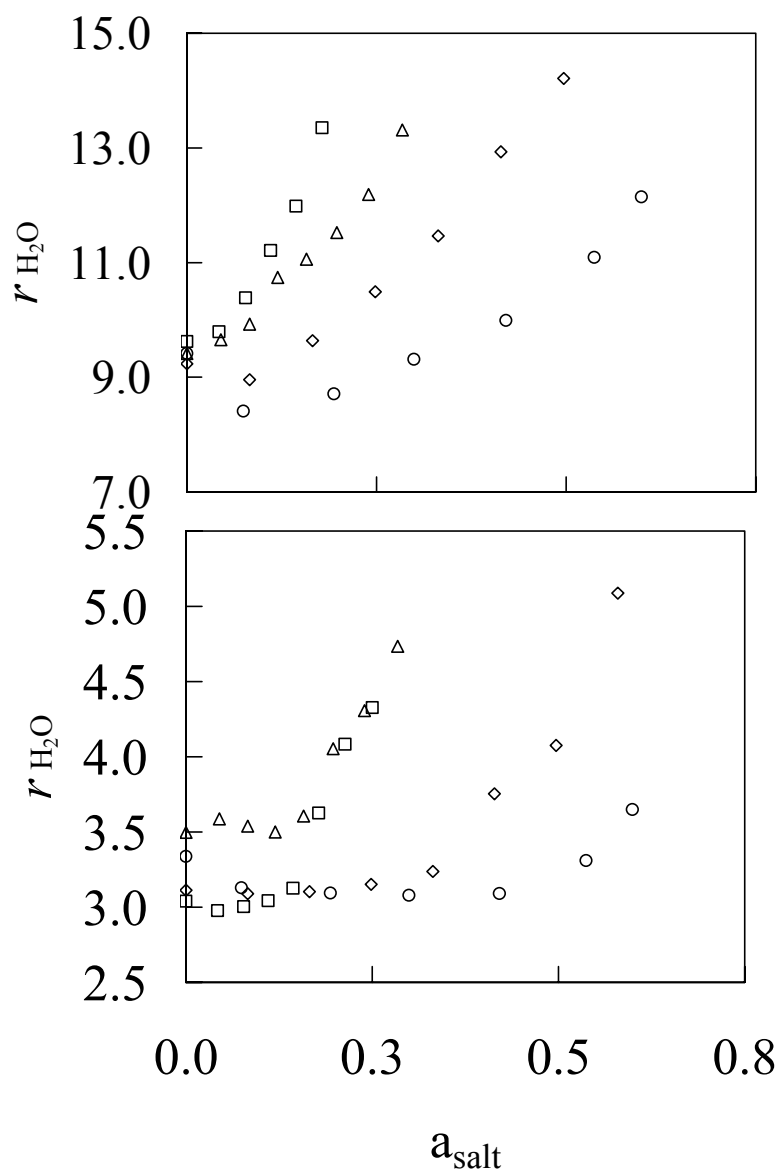
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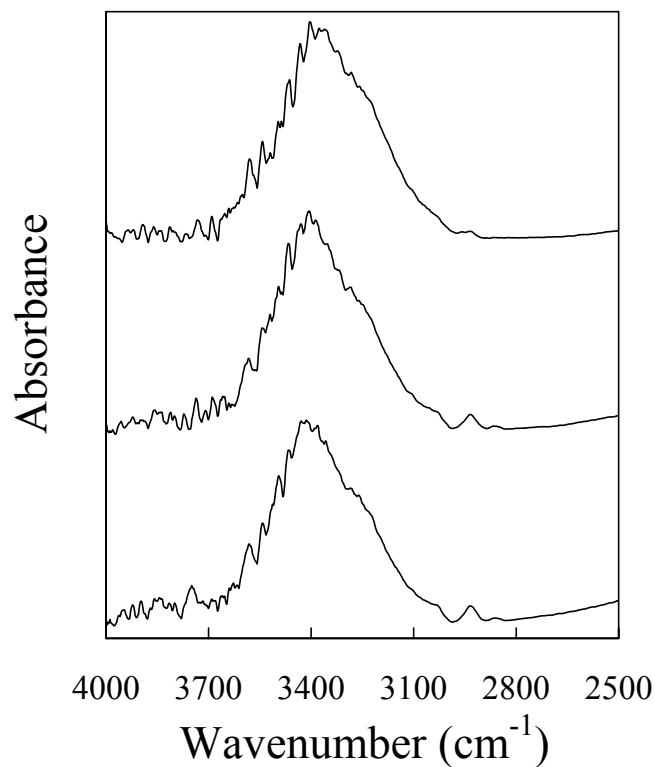
**Figure S1.** ATR-IR spectra of PDADMA/PSS doped with A,  $\text{NO}_3^-$ ; B,  $\text{ClO}_4^-$ ; C,  $\text{N}_3^-$ ; D,  $\text{SCN}^-$ ; E, undoped; F, P4VMP/PSS undoped. All spectra were recorded with 256 scans and  $4\text{ cm}^{-1}$  resolution.



**Figure S2.** Number of water molecules per ion pair,  $r$ , in PEMUs vs. solution salt concentration. PDADMA/PSS (upper panel) and P4VMP/PSS (lower panel).  $\circ$  NaF,  $\Delta$  NaBr,  $\square$  NaCl, and  $\diamond$  NaI.



**Figure S3.** Number of water molecules per ion pair vs. salt concentration for PDADMA/PSS (upper panel) and P4VMP/PSS (lower panel).  $\circ$  CsCl,  $\Delta$  CaCl<sub>2</sub>,  $\square$  MgCl<sub>2</sub>,  $\diamond$  YCl<sub>3</sub>. Notice the difference in behavior between CsCl and the multivalent ions.



**Figure S7.** IR spectra of water present in PEMU before doping with ions (bottom curve), and with NaNO<sub>3</sub> doping at 0.5M (middle curve) and with NaClO<sub>4</sub> doping at 0.3M (top curve). The dopant concentration has been chosen such that the  $y$  value for the two dopants is between 0.4 and 0.5. Films swell with water brought in by ions occupying extrinsic sites. Multilayer was built in 1.0M NaCl solution at room temperature. Spectra have been subjected to a 5 point Savitsky Golay smoothing.