## **Supplementary Information**

Fourier Transform Infrared Spectroscopy Investigation of Water Microenvironments in Polyelectrolyte Multilayers at Varying Temperatures

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Figure S1. Spectra of a bare ZnSe crystal in dry conditions.



Figure S2. OD stretch peak for low hydration measurements of a PDADMA/PSS multilayer at 35 °C. Spectra are not corrected for non-Condon effects.



**Figure S3.** Shape of OD stretch peak of PDADMA/PSS multilayer immersed in 0.25 M at 35 °C for raw FTIR spectrum and non-Condon corrected spectrum.



**Figure S4.** FTIR spectra of the fingerprint region of a PDADMA/PSS multilayer at varying salt concentrations and 40 °C. Spectra are not corrected for non-Condon effects.



**Figure S5.** Peak area and absorbance of the SO<sub>3</sub><sup>-</sup> anti-symmetric stretch peak (at 1191 cm<sup>-1</sup>) for a PDADMA/PSS multilayer as a function of the contacting solution's salt concentration at 40 °C.



**Figure S6.** Non-Condon corrected OD spectra of a single PDADMA/PSS multilayer for various salt concentrations of the contacting solution (panels a-f correspond to 0.25M-1.5M NaCl, respectively). Legend in (a) applies to all panels.



**Figure S7.** Combined deconvolutions for a PDADMA/PSS multilayer immersed in HOD solutions of different salt concentrations with arrows indicating the change in peak position as temperature increased from 35 °C to 70 °C. a) 0.25 M, b) 0.50 M, c) 0.75 M, d) 1.00 M, e) 1.25 M, and f) 1.50 M NaCl. Legend in (a) applies to all panels.



**Figure S8.** Comparison of PDADMA/PSS multilayers immersed in 5 wt%  $D_2O$  in  $H_2O$  showing the lack of interfering peaks in the OD region (2700 – 2400 cm<sup>-1</sup>). Spectra were not corrected for non-Condon effects.



**Figure S9.** FTIR spectra of the OH region (2800- 3800 cm<sup>-1</sup>) of pure water only and PDADMA/PSS multilayers immersed in water at room temperature. Spectra were not corrected for non-Condon effects.



Figure S10. FTIR spectrum of 5 wt%  $D_2O$  in  $H_2O$  solution only at 35  $^\circ C$ 

<b>Fable S1.</b> OD-peak information	for PDADMA/PSS multilayers	immersed in	n various s	alt solutions
1				

at 40 °C

40 °C										
	Bulk		Low frequency				High fr	Cumulative water		
Salt	Area	fwhm	Peak	Area	fwhm	Peak	Area	fwhm	Peak	Area
conc.			center			center			center	
[ <b>M</b> ]	[cm <sup>-1</sup> ]		[cm <sup>-1</sup> ]	[cm <sup>-1</sup> ]		[cm <sup>-1</sup> ]	[cm <sup>-1</sup> ]		[cm <sup>-1</sup> ]	[cm <sup>-1</sup> ]
0.25	1E-09	170	2509	4.6	92.0	2497.1	15.3	110.5	2556.1	19.9
0.5	1E-09	170	2509	13.0	92.6	2498.3	32.6	111.3	2562.0	45.6
0.75	1E-09	170	2509	31.5	93.0	2499.2	87.3	111.9	2568.9	118.7
1	1E-09	170	2509	30.9	93.1	2499.8	92.2	111.9	2565.7	123.1
1.25	1E-09	170	2509	24.5	93.7	2500.2	98.7	112.3	2559.6	123.2
1.5	1E-09	170	2509	31.5	94.3	2501.1	105.8	112.8	2562.4	137.3

0.25 M										
	Bulk	Low frequency High frequency						Cumulative water		
Temp	Area	fwhm	Peak center	Area	fwhm	Peak center	Area	fwhm	Peak center	Area
[°C]	[cm <sup>-1</sup> ]		[cm <sup>-1</sup> ]	[cm <sup>-1</sup> ]		[cm <sup>-1</sup> ]	[cm <sup>-1</sup> ]		[cm <sup>-1</sup> ]	[cm <sup>-1</sup> ]
35	1E-09	170	2509	31.5	92.0	2497.1	100.9	110.6	2553.7	132.4
40	1E-09	170	2509	30.8	92.0	2497.1	101.2	110.5	2556.1	132.0
45	1E-09	170	2509	29.1	92.0	2497.1	100.8	110.6	2557.4	130.0
50	1E-09	170	2509	27.7	92.0	2497.1	101.2	110.4	2559.4	129.0
55	1E-09	170	2509	27.3	92.0	2497.1	101.5	110.5	2561.3	129.0
60	1E-09	170	2509	26.4	92.0	2497.1	101.2	110.4	2562.8	127.6
65	1E-09	170	2509	25.8	92.0	2497.1	101.2	110.6	2564.5	127.1
70	1E-09	170	2509	25.1	92.0	2497.1	102.0	110.4	2566.5	127.1

 Table S2. OD-peak information for PDADMA/PSS multilayers immersed in 0.25 M NaCl at temperatures