Supplementary Materials

Specific Ion Effects on Interfacial Water Structure near Macromolecules

Xin Chen, Tinglu Yang, Sho Kataoka, and Paul S. Cremer*

Department of Chemistry, Texas A&M University, College Station, TX 77843

May 29, 2007

E-mail: cremer@mail.chem.tamu.edu

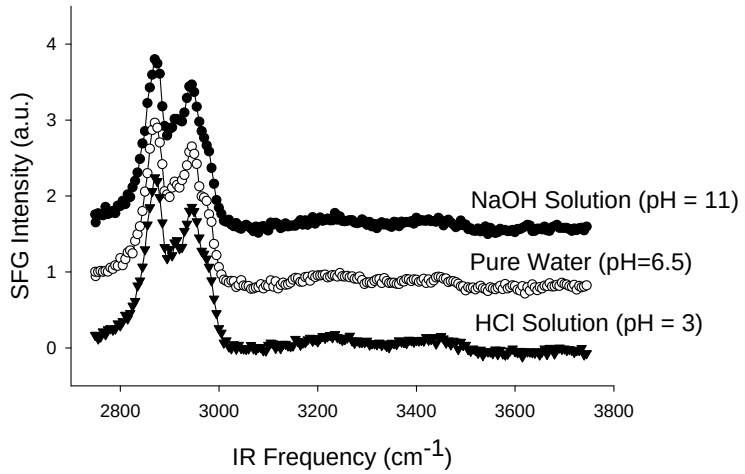

Figure S1. VSFS spectra of the air/PNIPAM/aqueous interface as a function of pH. The acidic and basic solutions were prepared by adding HCl and NaOH, respectively, with no additional salts. The spectrum of pure water is the same as the one in Figure 2b. The spectra are offset for clarity.

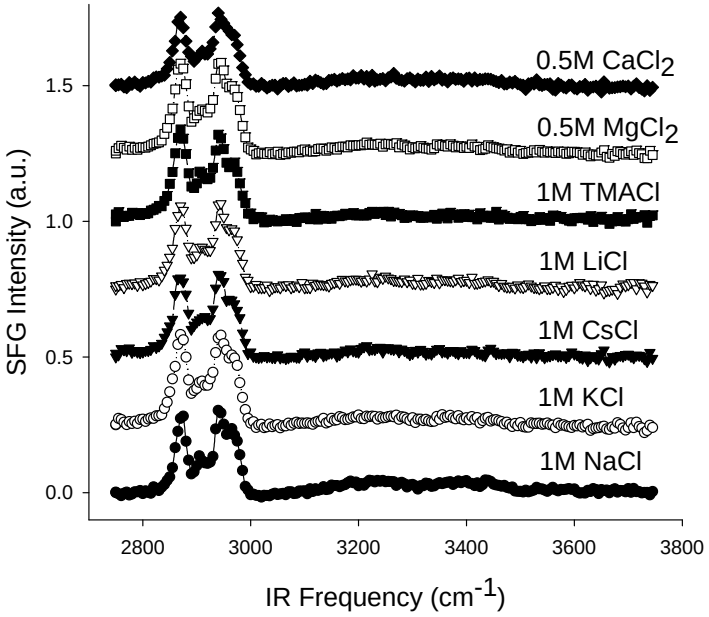

Figure S2. VSFS spectra of the air/PNIPAM/Aqueous interface as a function of cation identity. All experiments were conducted with 1 M Cl^-. This dictated using lower molar concentrations of $MgCl_2$ and $CaCl_2$. Other choices such as keeping the cation concentration or the ionic strength constant would, of course, have been possible. However, these were judged to be less desirable because changes in Cl^- concentration have a non-negligible effect on the water structure (Figure 4a). It would have also been possible to use F^- or SO_4^{2-} salts; however, many of these salts have only limited solubility in aqueous solution. The spectra are offset to avoid crowding

Table S1. Oscillator Strengths of Water Peaks as well as Relative Surface Potential Values for Air/PNIPAM/Aqueous Systems with 1 M Salt (~0.8 M for NaF and Na_2SO_4)

		NaSCN	$NaClO_4$	NaI	$NaNO_3$	NaBr	NaCl	NaF	Na_2SO_4
Oscillator Strength (a.u.)	3200 cm^{-1}	0.58	0.52	0.48	0.32	0.30	0.23	0.14	0.14
	3400 cm^{-1}	0.35	0.31	0.30	0.22	0.24	0.22	0.15	0.15
ΔSurface Potential (mV)		-69 (±8)	-58 (±12)	-60 (±23)	-22 (±10)	-33 (±15)	-8 (±12)	13 (±19)	4 (±17)

Table S2. Relative Surface Potential Values of the Air/PNIPAM/Aqueous System with Varying Concentrations of NaSCN and $NaClO_4$ in the Subphase. (unit: mV)

	0.01M	0.03M	0.1M	0.3M	0.6M	1M	1.5M	2M
NaSCN	-16 (±18)	-35 (±15)	-54 (±13)	-66 (±12)	-60 (±12)	-69 (±9)	-60 (±13)	-66 (±11)
$NaClO_4$	-24 (±13)	-36 (±18)	-51 (±12)	-68 (±18)	-59 (±14)	-58 (±12)	-58 (±16)	-47 (±9)