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Supporting Information for the Manuscript "Effects of Hofmeister series of sodium salts on the solvent properties of water"

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S1.1 Solvatochromic studies

All salt solutions were prepared in deionized water. The solvatochromic probes 4-nitroanisole, 4-nitrophenol, and Reichardt's carboxylate-substituted betaine dye were used to measure the dipolarity/polarizability π^*, HBA basicity β, and HBD acidity α of the media in the osmolytes solutions. Aqueous solutions (ca. 10 mM) of each solvatochromic dye were prepared and 5-15 µL of each was added separately to a total volume of 500 µL of the salt solution. A strong base was added to the samples (~5 µL of 1 M NaOH to 500 µL of the salt solution) containing Reichardt's carboxylate-substituted betaine dye to ensure a basic pH. A strong acid (~10 µL of 1 M HCl to 500 µL of the solution) was added to the samples containing 4-nitrophenol in order to eliminate charge-transfer UV/Vis absorption bands of the phenolate anion that were observed in some solutions. The respective blank solutions without dye were prepared separately. The samples were mixed thoroughly in a vortex mixer and the UV/Vis absorption spectra of each solution were acquired. To check the reproducibility, possible aggregation and specific interactions effects, the position of the band maximum in each sample was measured in five separate aliquots. The effects of adding 2 M NaOH on the position of the band maximum of Reichardt's carboxylate-substituted betaine dye in each salt solution and 2 M NaOH on the position of the band maximum of 4-nitrophenol in each salt solution were checked in separate experiments and found to be negligible within the experimental error limits. A UV-VIS microplate reader spectrophotometer SpectraMax Plus384 (Molecular Devices, Sunnyvale, CA, USA) with a bandwidth of 2.0 nm, data interval of 1 nm, and high resolution scan (~0.5 nm/s) was used for acquisition of the UV–Vis molecular absorbance data. The absorption spectra of the probes were determined over the spectral range from 240 to 600 nm in each solution. Pure salt solutions containing no dye (blank) were scanned first to establish a baseline. The wavelength of maximum absorbance in each solution was determined as described previously[S1], using the PeakFit software package (Systat Software Inc., San Jose, CA, USA), and averaged. The standard deviation for the measured maximum absorption wavelength was ≤0.4 nm for all dyes in all solutions examined.

The behavior of the probes (4-nitrophenol, and Reichardt's carboxylated betaine dye) in several solvents (water, n-hexane, methanol) was tested in the presence and absence of HCl (for 4-nitrophenol) and NaOH (for the betaine dye) at different concentrations of the probes, acid or base, and the maximum shifts of the probes were compared to reference values found in the literature and were within the experimental errors in all cases (data not shown).

The results of these solvatochromic studies were used to calculate π^*, β, and α as described by Marcus[S2].

Determination of the solvent dipolarity/polarizability π^*. Values of parameter π^* were determined from the wave numbers ($\tilde{\upsilon}_1$ in 1000 cm^{-1} = 1 kK) of the longest-wavelength absorption band of 4-nitroanisole using relationship (1):

$$\pi^* = 0.427 \bullet (34.12 - \tilde{\upsilon}_1) \qquad (1)$$

Determination of the solvent hydrogen-bond acceptor (HBA) basicity β. Values of parameter β were determined from the wave numbers ($\tilde{\upsilon}_2$ in 1000 cm^{-1} = 1 kK) of the longest-wavelength absorption band of the 4-nitrophenol using relationship (2):

$$\beta = 0.346 \bullet (35.045 - \tilde{\upsilon}_2) - 0.57 \bullet \pi^* \qquad (2)$$

Determination of the solvent hydrogen-bond donor (HBD) acidity α. Values of parameter α were determined from the longest-wavelength Vis absorption band of Reichardt's standard betaine dye no. 30 using relationship (3):

$$\alpha = 0.0649 \cdot E_T(30) - 2.03 - 0.72 \cdot \pi^* \tag{3}$$

The $E_T(30)$ values (in kcal/mol) are based on the negatively solvatochromic standard pyridinium *N*-phenolate betaine dye no. 30 (Reichardt's dye) as probe. They are obtained directly from the wavelength (λ in nm) of the Vis absorption band of the corresponding carboxylate-substituted betaine dye, according to equation (4)[S3]:

$$E_T(30) = (1/0.932) \cdot [(28591/\lambda) - 3.335] \tag{4}$$

Table S1. Solvent dipolarity/polarizability (π^*) of water in aqueous solutions of indicated salts at different concentrations

[Na_2SO_4], M	π^*	[NaF], M	π^*	[CH_3COONa],M	π^*
0	1.104 ± 0.001	0	1.104 ± 0.001	0	1.104 ± 0.001
0.2	1.122 ± 0.002	0.2	1.111 ± 0.002	0.2	1.113 ± 0.002
0.4	1.137 ± 0.003	0.4	1.119 ± 0.002	0.5	1.126 ± 0.001
0.5	1.144 ± 0.003	0.5	1.122 ± 0.002	0.8	1.137 ± 0.002
		0.6	1.126 ± 0.001	1.0	1.144 ± 0.001
[NaCl], M	π^*	[NaBr], M	π^*	[NaI], M	π^*
0	1.104 ± 0.001	0	1.104 ± 0.001	0	1.104 ± 0.001
0.5	1.134 ± 0.002	0.5	1.141 ± 0.001	0.25	1.131 ± 0.002
1.0	1.158 ± 0.002	0.8	1.162 ± 0.002	0.5	1.153 ± 0.002
1.5	1.181 ± 0.002	1.0	1.176 ± 0.001	0.75	1.177 ± 0.001
		1.5	1.210 ± 0.002		
[NaSCN][a], M	π^*	[$NaClO_4$], M	π^*		
0	1.091 ± 0.003	0	1.104 ± 0.001		
0.486	1.141 ± 0.001	0.5	1.135 ± 0.003		
0.95	1.186 ± 0.001	1.0	1.167 ± 0.002		
1.394	1.226 ± 0.002	1.25	1.182 ± 0.002		
1.819	1.264 ± 0.001	1.5	1.198 ± 0.002		
2.229	1.296 ± 0.003	2.0	1.229 ± 0.001		
2.623	1.333 ± 0.007				

[a] Data from [S4].

Table S2. Solvent hydrogen bond acceptor basicity (β) of water in aqueous solutions of salts at the concentrations indicated

[Na_2SO_4], M	β	[NaF], M	β	[CH_3COONa],M	β
0	0.596 ± 0.002	0	0.596 ± 0.002	0	0.596 ± 0.002
0.2	0.609 ± 0.002	0.2	0.612 ± 0.003	0.2	0.610 ± 0.003
0.4	0.620 ± 0.003	0.4	0.629 ± 0.003	0.5	0.624 ± 0.002
0.5	0.625 ± 0.003	0.5	0.637 ± 0.003	0.8	0.640 ± 0.002
		0.6	0.645 ± 0.002	1.0	0.651 ± 0.002
[NaCl], M	β	[NaBr], M	β	[NaI], M	β
0	0.596 ± 0.002	0	0.596 ± 0.002	0	0.596 ± 0.002
0.5	0.594 ± 0.002	0.5	0.594 ± 0.002	0.25	0.597 ± 0.003
1.0	0.592 ± 0.002	0.8	0.593 ± 0.001	0.5	0.598 ± 0.002
1.5	0.590 ± 0.004	1.0	0.593 ± 0.004	0.75	0.599 ± 0.003
		1.5	0.591 ± 0.002		
[NaSCN][a], M	β	[$NaClO_4$], M	β		
0	0.599 ± 0.003	0	0.596 ± 0.002		
0.486	0.602 ± 0.001	0.5	0.597 ± 0.003		
0.95	0.605 ± 0.001	1.0	0.598 ± 0.002		
1.394	0.607 ± 0.002	1.25	0.598 ± 0.001		
1.819	0.609 ± 0.001	1.5	0.599 ± 0.003		
2.229	0.611 ± 0.001	2.0	0.599 ± 0.002		
2.623	0.614 ± 0.002				

[a] Data from [S4].

Table S3. Solvent hydrogen bond donor acidity (α) of water in aqueous solutions of salts at the concentrations indicated

[Na_2SO_4], M	α	[NaF], M	α	[CH_3COONa],M	α
0	1.233 ± 0.002	0	1.233 ± 0.002	0	1.233 ± 0.002
0.2	1.203 ± 0.004	0.2	1.219 ± 0.009	0.2	1.221 ± 0.002
0.4	1.194 ± 0.008	0.4	1.213 ± 0.003	0.5	1.214 ± 0.005
0.5	1.184 ± 0.007	0.5	1.211 ± 0.003	0.8	1.210 ± 0.009
		0.6	1.209 ± 0.012	1.0	1.207 ± 0.012
[NaCl], M	α	[NaBr], M	α	[NaI], M	α
0	1.233 ± 0.002	0	1.233 ± 0.002	0	1.233 ± 0.002
0.5	1.218 ± 0.003	0.5	1.222 ± 0.004	0.25	1.232 ± 0.002
1.0	1.210 ± 0.008	0.8	1.219 ± 0.007	0.5	1.229 ± 0.002
1.5	1.205 ± 0.009	1.0	1.217 ± 0.008	0.75	1.225 ± 0.003
		1.5	1.214 ± 0.009		
[NaSCN][a], M	α	[$NaClO_4$],M	α		
0	1.110 ± 0.003	0	1.233 ± 0.004		
0.486	1.101 ± 0.001	0.5	1.240 ± 0.003		
0.95	1.075 ± 0.001	1.0	1.238 ± 0.004		
1.394	1.035 ± 0.002	1.25	1.234 ± 0.003		
1.819	1.016 ± 0.001	1.5	1.229 ± 0.005		
2.229	0.999 ± 0.001	2.0	1.218 ± 0.006		
2.623	0.981 ± 0.002				

[a] Data from [S4].

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