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Ionic Solvation in Water + Cosolvent Mixtures

Part 9.—Free Energies of Transfer of Single Ions from Water into Water + Ethanol Mixtures

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Values for the free energy of transfer of the proton $\Delta G_t^\circ(H^+)$ have been determined experimentally using spectrophotometric measurements on *p*-nitroaniline in water + ethanol employing the method previously used for other cosolvents mixed with water. Values for $\Delta G_t^\circ(i)$ for other individual ions, i = anion X^-, have been determined by combining these values for $\Delta G_t^\circ(H^+)$ with values for $\Delta G_t^\circ(HX)$ calculated from electrochemical data. These values for $\Delta G_t^\circ(X^-)$ are subsequently used with values for $\Delta G_t^\circ(MX)$ and $\Delta G_t^\circ(MX_2)$ derived from electrochemical and solubility data to provide values for $\Delta G_t^\circ(M^+)$ and $\Delta G_t^\circ(M^{2+})$. $\Delta G_t^\circ(X^-)$ and $\Delta G_t^\circ(X^{2-})$ for anions where $\Delta G_t^\circ(HX)$ and $\Delta G_t^\circ(H_2X)$ are not available are calculated from $\Delta G_t^\circ(MX)$ and $\Delta G_t^\circ(M_2X)$ obtained from solubility measurements and the above values for ΔG_t°(cation).

The free energy of transfer of single ions from water into water + cosolvent mixtures have been determined using a range of cosolvents each with a range of concentrations. The cosolvents investigated include methanol,[1,2] isopropyl alcohol,[2] t-butyl alcohol,[3] ethylene glycol,[4] glycerol,[2] acetone,[2,5] dioxane[6] and dimethylsulphoxide.[7] The method used involves first calculating the free energy of transfer of the proton $\Delta G_t^\circ(H^+)$ and separating the latter into two processes: $\Delta G_t^\circ(H^+)_e$ is the free energy of transfer of the aqua-proton from water into the mixture and $\Delta G(R\overset{+}{O}H_2)$ is the free energy for rearrangement of solvent molecules in the mixed solvent which results from the intrusion of the aqua-proton. The relationship is represented as:

$$\Delta G_t^\circ(H^+) = \Delta G_t^\circ(H^+)_e + \Delta G(R\overset{+}{O}H_2) \qquad (1)$$

where $\Delta G_t^\circ(H^+)_e < \Delta G(R\overset{+}{O}H_2)$ and the former is always[1-7] $< 10\%$ of the latter for cosolvent concentrations not exceeding 30 wt %.

The details of this method have recently been critically reviewed.[8] $\Delta G_t^\circ(H^+)_e$ for the transfer of the spherical aqua-proton on the molar scale is given by[8]

$$\Delta G_t^\circ(H^+)_e = \frac{Ne^2}{6r_{H_2O}}(D_s^{-1} - D_w^{-1}) \qquad (2)$$

where e is the electronic charge, N is Avogadro's number, r_{H_2O} is the radius of the water molecule and D_s and D_w are the dielectric constants of the mixture and of pure water, respectively. After the transfer, the solvent molecules rearrange themselves and

$\Delta G(\mathrm{R\overset{+}{O}H_2})$ is derived by treatment of all these changes subsequent to the transfer as the solvent-sorting equilibrium:

$$(\mathrm{H_2O})_x\mathrm{H^+_{solv}} + \mathrm{ROH_{solv}} \rightleftharpoons \{(\mathrm{H_2O})_{x-1}\mathrm{ROH}\}\mathrm{H^+_{solv}} + \mathrm{H_2O_{solv}}$$

where $x \geqslant 5$ to include solvent movements outside the immediate contact solvation sphere of $\mathrm{H_3^+O}$.[8, 9] $\Delta G(\mathrm{R\overset{+}{O}H_2})$ is given[8] on the molar scale by

$$\Delta G(\mathrm{R\overset{+}{O}H_2}) = -[\mathrm{R\overset{+}{O}H_2}]\,\boldsymbol{RT}\ln\,(K_c[\mathrm{H_2O}]\,F_c) \tag{3}$$

where $[\mathrm{R\overset{+}{O}H_2}] = \{(\mathrm{H_2O})_{x-1}\mathrm{ROH}\}\mathrm{H^+_{solv}}$ and the activity-coefficient ratio $F_c = y_{\mathrm{R\overset{+}{O}H_2}}y_{\mathrm{H_2O}}/y_{\mathrm{P}}y_{\mathrm{ROH}}$. As the concentrations of all species are varying, the standard state for all species i treated as solutes in the mixture is $[i] = 1$ mol dm^{-3} and $y_i = 1.0$ with $y_i \rightarrow 1$ as $[i] \rightarrow 0$.[8] Using eqn (1)–(3) and correcting to the mole-fraction scale,[8] the total free energy of transfer on the mole-fraction scale is given by[8]

$$\Delta G_t^\circ(\mathrm{H^+}) = \frac{Ne^2}{6r_{\mathrm{H_2O}}}(D_s^{-1} - D_w^{-1}) - [\mathrm{R\overset{+}{O}H_2}]\,\boldsymbol{RT}\ln\,\{K_c[\mathrm{H_2O}]\,F_c\} + \boldsymbol{RT}\ln\frac{d_s M_w}{d_w M_s} \tag{4}$$

where d_s and d_w are the densities of the mixture and of pure water, respectively, and M_s and M_w are the molecular weights of the mixture and pure water, respectively[8] The last term on the right-hand side of eqn (4) only begins to make a significant contribution to $\Delta G_t^\circ(\mathrm{H^+})$ when the concentration of cosolvent exceeds 30 wt %.[8]

K_c is determined spectrophotometrically by adding a minute concentration of *p*-nitroaniline (B), when the following equilibria become involved:

$$\mathrm{B_{solv}} + \mathrm{P_{solv}} \overset{K_1}{\rightleftharpoons} \mathrm{BH^+_{solv}} + \mathrm{H_2O_{solv}} \tag{5}$$

$$\mathrm{B_{solv}} + \mathrm{ROH_{2solv}} \overset{K_2}{\rightleftharpoons} \mathrm{BH^+_{solv}} + \mathrm{ROH_{solv}}. \tag{6}$$

K_1 and K_2 are the thermodynamic equilibria for the standard states defined as above. If $F_1 = y_{\mathrm{B}}y_{\mathrm{P}}/y_{\mathrm{BH^+}}y_{\mathrm{H_2O}}$ and $F_2 = y_{\mathrm{B}}y_{\mathrm{ROH_2}}/y_{\mathrm{BH^+}}y_{\mathrm{ROH}}$, we can obtain[8]

$$\frac{CC_{\mathrm{R}}}{(C_{\mathrm{R}}-C)} = \frac{K_2F_2}{K_1F_1}\,\frac{C_0[\mathrm{H_2O}]}{[\mathrm{ROH}]_{\mathrm{T}}}\,\frac{C_{\mathrm{R}}}{C-C_{\mathrm{R}}} + \frac{[\mathrm{H_2O}]\,C_0}{K_1F_1[\mathrm{ROH}]_{\mathrm{T}}} \tag{7}$$

where $[\mathrm{ROH}]_{\mathrm{T}}$ and C_0 are the total added concentrations of cosolvent and B, respectively, C and C_{R} are the concentrations of B without added ROH and with ROH for the same C_0 and the same total mineral acid concentration $[\mathrm{H^+}]_{\mathrm{T}}$. At constant temperature, with constant C_0 and $[\mathrm{ROH}]_{\mathrm{T}}$, plots of $CC_{\mathrm{R}}/(C_{\mathrm{R}}-C)$ against $C_{\mathrm{R}}/(C_0-C_{\mathrm{R}})$ for varying $[\mathrm{H^+}]_{\mathrm{T}}$ at constant ionic strength are always linear,[1–8] $K_c F_c^{-1} = C_0/(\mathrm{slope})\,[\mathrm{ROH}]_{\mathrm{T}}$, where the slopes are derived from the linear plots of eqn (7) and F_c is shown to be unity.[8] At low mole fractions of cosolvent, x_2, $[\mathrm{H_2O}] = 55.345-[\mathrm{ROH}]_{\mathrm{T}}$ can be used in eqn (4), but at higher x_2, $[\mathrm{H_2O}]$ is more accurately[8] given by $(1000d_s-[\mathrm{ROH}]_{\mathrm{T}}M_{\mathrm{ROH}})/M_w$, where M_{ROH} is the molecular weight of pure ROH. All values for $\Delta G_t^\circ(\mathrm{H^+})$ in water+cosolvent mixtures have been calculated[8] using the latter values for $[\mathrm{H_2O}]$ in eqn (4): $\Delta G_t^\circ(i)$ values have been calculated[8] for all cosolvents[1–7] using these $\Delta G_t^\circ(\mathrm{H^+})$ values with up-dated electro-

Table 1. Values for K_c(dm^3 mol^{-1}) calculated from K_2F_2 and of $K_cF_c^{-1}$ (dm^3 mol^{-1}) derived from the slopes at ionic strength = 1.00 mol dm^3 and at 25 °C

total added acidity/ mol dm^{-3}	concentration of ethanol (wt %)						
	4.00	8.08	16.51	25.31	34.52	44.16	54.26
0.10	0.18	0.23	0.37	0.75	0.98	1.5	3.4
0.16	0.18	0.23	0.35	0.77	1.2	1.4	0.8
0.20	0.18	0.23	0.35	0.79	2.3	2.2	1.0
0.40	0.17	0.23	0.36	0.89	53	—	4.6
0.80	0.17	0.21	0.36	1.2	—	—	—
K_2F_2	92	73	46	23	14.0	10.5	10.2
$K_cF_c^{-1}$ from slope	0.173 ±0.002	0.217 ±0.002	0.339 ±0.005	0.66 ±0.01	1.10 ±0.02	1.46 +0.03	1.51 ±0.03

chemical and solubility data for salts and new pK_w data. $[R\overset{+}{O}H_2]$ in eqn (4) is derived from:

$$[ROH_2] = 0.5\{A-(A^2-4[ROH]_T)^{\frac{1}{2}}\} \tag{8}$$

$$A = ([ROH]_T+1+K_c^{-1}) \tag{9}$$

where $[R\overset{+}{O}H_{2,\,solv}]+[P_{solv}] = 1$.

EXPERIMENTAL

MATERIALS

p-Nitroaniline was purified as described previously.[10] Water was distilled once in an all-glass still and AnalaR ethanol, HCl and NaCl were used.

PROCEDURE

All mixtures were made up by mixing known volumes of solution. The contractions of the solutions on mixing were determined to allow an accurate estimation of the molar concentrations. Concentrations of the unprotonated *p*-nitroaniline (B) were determined spectrophotometrically at 383 nm[10] using the thermostatted-cell compartment of a Unicam SP500 series 2 spectrophotometer.

RESULTS AND DISCUSSION

DETERMINATION OF $\Delta G_t^\circ(H^+)$ IN WATER + ETHANOL

Plots of $CC_R/(C_R-C)$ against $C_R/(C_0-C_R)$ were found to be linear in 5, 10, 20, 30, 40, 50 and 60% v/v ethanol, using measurements at each acidity quoted in table 1 as found previously with other cosolvents.[1-9] Ionic strength was maintained at 1.00 mol dm^{-3} by adding NaCl to supplement the HCl.[9] Values for $K_cF_c^{-1}$ determined from the slopes are given in table 1. Intercepts for these plots were calculated using $C_0/K_1'F_1'[ROH]_T$ where $K_1' = [BH^+]y'_{BH^+}/[B][P]y'_By'_P$ determined in water[8-10] for the equilibrium

$$B_{aq}+P \overset{K_1'}{\rightleftharpoons} BH^+_{aq} \tag{10}$$

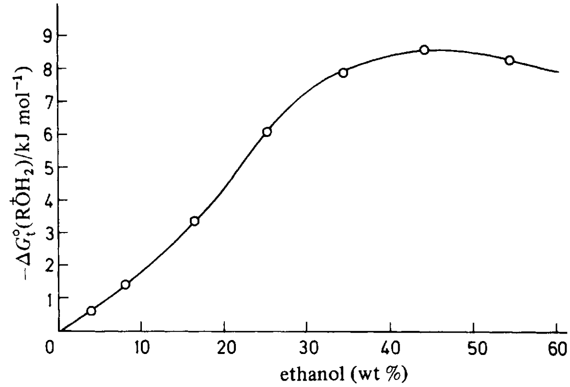

Fig. 1. Plot of $\Delta G(\mathrm{R}\overset{+}{\mathrm{O}}\mathrm{H}_2)$ in water+ethanol mixtures at 25 °C.

where K_1' is the thermodynamic equilibrium constant with the standard states defined as above and y_i' is the activity coefficient in water ($F_1' = y_B' y_P' / y_{BH^+}'$).

Values from K_c can also be calculated from the equation

$$K_c = \frac{[\mathrm{R}\overset{+}{\mathrm{O}}\mathrm{H}_2]}{([\mathrm{H}^+]_T - [\mathrm{R}\overset{+}{\mathrm{O}}\mathrm{H}_2])([\mathrm{ROH}]_T - [\mathrm{R}\overset{+}{\mathrm{O}}\mathrm{H}_2])} \tag{11}$$

using[1-10] the value of $K_2 F_2$ calculated from the slope and intercept (derived as described above) for the linear plots representing eqn (7). These values are also included in table 1, showing the invariance of K_c with varying $[\mathrm{H}^+]_T$ except possibly at the higher mole fractions of ethanol because of the very low values for ($[\mathrm{H}^+]_T - [\mathrm{R}\overset{+}{\mathrm{O}}\mathrm{H}_2]$) used in eqn (11): this erratic behaviour at high $[\mathrm{ROH}]_T$ has been experienced[1-10] with all the cosolvents. The agreement between $K_c F_c^{-1}$ from the slope and K_c from eqn (11) shows that $F_c = 1.0$ using ethanol, as found with all the other cosolvents.[1-10] This, together with the linearity of the plots representing eqn (7), supports the correctness of the assumption $K_1' F_1' = K_1 F_1/[\mathrm{H_2O}]$ made in the derivation of eqn (7),[8] as found with all other cosolvents.[1-10]

Values of $\Delta G_t^\circ(\mathrm{H}^+)$ were calculated using eqn (1), (2) and (4). Values for $\Delta G(\mathrm{R}\overset{+}{\mathrm{O}}\mathrm{H}_2)$ were found from the experimental data for $K_c F_c^{-1}$ ($F_c = 1.0$), $[\mathrm{H_2O}] = (1000\, d_s - [\mathrm{ROH}]_T M_{\mathrm{ROH}})/M_w$ and $[\mathrm{R}\overset{+}{\mathrm{O}}\mathrm{H}_2]$ derived using eqn (8) and (9) at the concentrations of ROH used for the spectrophotometric measurements. Values for $\Delta G(\mathrm{R}\overset{+}{\mathrm{O}}\mathrm{H}_2)$ are plotted against wt % ethanol in fig. 1. Values for $\Delta G(\mathrm{R}\overset{+}{\mathrm{O}}\mathrm{H}_2)$ were then interpolated from fig. 1 for concentrations of ethanol where $\Delta G_t^\circ(\mathrm{H}^+)$ was required and values for $\Delta G_t^\circ(\mathrm{H}^+)_e$ computed[8] using eqn (2). Values for the dielectric constants were interpolated graphically using the data of Åkerlöf,[11] Wyman,[12] Graffunder and Heymann,[13] Martin and Brown[14] and Hall and Phillips,[15] which are all in good agreement. Values for the density were those of Bates.[16] The resulting values for $\Delta G_t^\circ(\mathrm{H}^+)$ are given in table 3.

ΔG_t°(anion) IN WATER + ETHANOL

A wide range of electrochemical data exist from which $\Delta G_t^\circ(HCl)$ can be calculated. For the cell[17-20]

$$\mathrm{Pt, H_2|HCl, EtOH+H_2O|AgCl, Ag} \qquad (12)$$

$\Delta G_t^\circ(HCl)$ can be calculated directly on the mole-fraction scale using

$$\Delta G_t^\circ(\mathrm{HCl}) = 96.5(E_w^\circ - E_s^\circ)\ \mathrm{kJ\ mol^{-1}} \qquad (13)$$

and the E° values, where subscripts w and s represent water and water + ethanol, respectively. From other E° values for cell (12),[21-25] $\Delta G_t^\circ(HCl)_m$ on the molality scale can be derived and converted to $\Delta G_t^\circ(HCl)$ on the mole-fraction scale using

$$\Delta G_t^\circ(\mathrm{HCl}) = \Delta G_t^\circ(\mathrm{HCl})_m + 11.41\ \log_{10}\left(\frac{18.016}{M_s}\right)\ \mathrm{kJ\ mol^{-1}} \qquad (14)$$

where $M_s = 100/\{(\mathrm{wt\%\ EtOH}/46.07) + (\mathrm{wt\%\ H_2O}/18.016)\}$. In addition, E° data for the cell[26]

$$\mathrm{Pt, H_2|HCl, EtOH+H_2O|Hg_2Cl_2, Hg} \qquad (15)$$

exist, from which $\Delta G_t^\circ(HCl)$ can be calculated directly using eqn (13). E° data on the molar scale for the cell[27]

$$\mathrm{glass|HCl, EtOH+H_2O|AgCl, Ag} \qquad (16)$$

produce $\Delta G_t^\circ(HCl)_c$ on the molar scale from eqn (13) which can be converted to the mole-fraction scale using

$$\Delta G_t^\circ(\mathrm{HCl}) = \Delta G_t^\circ(\mathrm{HCl})_c + 11.41\ \log_{10}\left(\frac{18.016 d_s}{M_s d_w}\right)\ \mathrm{kJ\ mol^{-1}}. \qquad (17)$$

Valus for $\Delta G_t^\circ(H^+)$ for the appropriate composition of $H_2O + EtOH$ can then be used with $\Delta G_t^\circ(HCl)$ to produce values for $\Delta G_t^\circ(Cl^-)$ *via*

$$\Delta G_t^\circ(\mathrm{Cl^-}) = \Delta G_t^\circ(\mathrm{HCl}) - \Delta G_t^\circ(\mathrm{H^+}). \qquad (18)$$

The resultant values are given in table 2: good mutual agreement is obtained and a smooth curve can be drawn using all the data for $\Delta G_t^\circ(Cl^-)$ in table 2.

E° values for cell (12) with Cl^- replaced by Br^-[28, 29] and I^-[30] have been used with eqn (13) to produce $\Delta G_t^\circ(HBr)$ and $\Delta G_t^\circ(HI)$ directly on the mole-fraction scale, and E° values for this cell on the molarity scale [24, 31] have been used with eqn (13) and (14) to give $\Delta G_t^\circ(HBr)$ and $\Delta G_t^\circ(HI)$ on the mole-fraction scale. Similarly, E° for cell (15) with Cl^- replaced by Br^-[32] on the molality scale has been used with eqn (13) and (14) to produce $\Delta G_t^\circ(HBr)$ on the mole-fraction scale. $\Delta G_t^\circ(HCNS)$ has been calculated from E° values on the mole-fraction scale for the cell:

$$\mathrm{Ag, AgCNS|KCNS|\,|KCl|AgCl, Ag} \qquad (19)$$

where allowance has been made for the liquid-junction potential.[33] Values[24] for $\Delta G_t^\circ(HClO_4)$ and $\Delta G_t^\circ(HBPh_4)$ on the molality scale have been converted to the mole-fraction scale using eqn (14). All these values for $\Delta G_t^\circ(HX)$ on the mole fraction scale have been used with the appropriate values for $\Delta G_t^\circ(H^+)$ to give values for $\Delta G_t^\circ(X^-)$ using equations of the type of eqn (18): these values for $\Delta G_t^\circ(X^-)$, where $X^- = Br^-, I^-, CNS^-, ClO_4^-$ and BPh_4^-, are collected in table 2.

Values for $\Delta G_t^\circ(KBPh_4)$ on the molality scale have been derived from solubility data[34] using

$$\Delta G_t^\circ(\mathrm{KBPh_4}) = 2.303\boldsymbol{R}T(\mathrm{p}K_s - \mathrm{p}K_w) \qquad (20)$$

Table 2. Values of $\Delta G_t^\circ(X^-)$ and $\Delta G_t^\circ(X^{2-})$ (kJ mol^{-1}) in water+ethanol mixtures at 25 °C (for references see end of table 3)

ethanol										
wt %	mole fraction	Cl^-	Br^-	I^-	SCN^-	OH^-	ClO_4^-	$ReCl_6^{2-}$	Pic^-	BPh_4^-
3.73	0.0151	—	—	—	—	1.02	—	—	—	—
5.00	0.0202	1.03^j	—	—	—	—	—	—	—	—
7.27	0.0298	—	—	—	—	2.00	—	—	—	—
10.0	0.0417	2.27^c	1.76^m	1.56^o	1.40	—	—	—	1.68	−0.55^p
10.0	0.0417	2.18^b	1.82^n	—	—	—	—	—	—	—
10.0	0.0417	2.24^g	—	—	—	—	—	—	—	—
10.0	0.0417	2.25^h	—	—	—	—	—	—	—	—
10.0	0.0417	2.26^i	—	—	—	—	—	—	—	—
10.0	0.0417	2.22^j	—	—	—	—	—	—	—	—
10.0	0.0417	2.24^k	—	—	—	—	—	—	—	—
10.5	0.0439	—	—	—	—	2.89	—	—	—	—
13.5	0.058	—	—	—	—	3.83	—	—	—	—
15.0	0.065	3.61^j	—	—	—	—	—	—	—	—
16.4	0.071	—	—	—	—	4.85	—	—	—	—
20.0	0.089	5.3^c	4.74^l	4.03^o	3.81	—	—	10.2	3.31	−1.60^p
20.0	0.089	5.2^d	4.50^m	—	—	—	—	—	—	—
20.0	0.089	5.3^g	4.49^n	—	—	—	—	—	—	—
20.0	0.089	5.3^h	—	—	—	—	—	—	—	—
20.0	0.089	5.3^i	—	—	—	—	—	—	—	—
20.0	0.089	5.3^j	—	—	—	—	—	—	—	—
20.0	0.089	5.3^k	—	—	—	—	—	—	—	—
20.5	0.092	—	—	—	—	—	—	—	3.44	—
21.5	0.097	—	—	—	—	6.7	—	—	—	—
25.0	0.115	6.9^j	—	—	—	—	—	—	—	—
26.2	0.122	—	—	—	—	8.4	—	—	—	—
30.0	0.144	8.3^c	7.3^e	6.4^e	—	—	6.4	—	3.94	−4.12^e
30.0	0.144	8.3^e	7.1^m	6.0^o	—	—	—	—	—	−4.10^p
30.0	0.144	8.3^g	7.1^n	—	—	—	—	—	—	—

30.0	0.144	8.1[j]	—	—	—	—	—	—	—	—
30.0	0.144	8.2[k]	—	—	—	—	—	—	—	—
30.1	0.144	—	—	—	—	9.3	—	—	—	—
33.7	0.166	—	—	—	—	10.2	—	—	—	—
35.0	0.174	9.0[j]	—	—	—	—	—	—	—	—
36.0	0.180	—	—	—	—	10.6	—	—	—	—
37.3	0.189	—	—	—	—	—	—	—	2.72	—
39.9	0.206	—	—	—	—	11.1	—	—	—	—
40.0	0.207	9.6[c]	8.4[l]	—	—	—	—	17.1	2.15	−9.2[p]
40.0	0.207	9.6[d]	8.3[n]	—	—	—	—	—	—	—
40.0	0.207	9.6[i]	—	—	—	—	—	—	—	—
40.0	0.207	9.6[j]	—	—	—	—	—	—	—	—
40.0	0.207	9.6[k]	—	—	—	—	—	—	—	—
42.6	0.236	—	—	—	—	11.4	—	—	—	—
45.0	0.242	9.8[j]	—	—	—	—	—	—	—	—
45.1	0.243	—	—	—	—	11.5	—	—	—	—
46.02	0.250	−9.6[o]	—	—	—	—	—	—	—	—
47.3	0.260	—	—	—	—	11.6	—	—	—	—
49.3	0.276	—	—	—	—	11.7	—	—	—	—
50.0	0.281	9.9[b]	8.6[e]	6.7[e]	—	—	5.4	—	−0.60	−13.7[e]
50.0	0.281	9.6[c]	8.1[m]	—	—	—	—	—	—	−13.8[p]
50.0	0.281	10.0[e]	8.3[n]	—	—	—	—	—	—	—
50.0	0.281	9.8[f]	—	6.2[o]	—	—	—	—	—	—
50.0	0.281	9.9[g]	—	—	—	—	—	—	—	—
50.0	0.281	9.9[j]	—	—	—	—	—	—	—	—
50.0	0.281	9.9[k]	—	—	—	—	—	—	—	—
51.0	0.289	—	—	—	—	—	—	—	−0.84	—
51.3	0.292	—	—	—	—	11.7	—	—	—	—
55.0	0.323	9.9[j]	—	—	—	—	—	—	—	—
58.8	0.358	—	—	—	—	—	—	—	−2.08	—
60.0	0.370	9.8[f]	7.9[n]	—	—	—	—	14.5	−2.27	−15.3[p]
60.0	0.370	9.9[j]	—	—	—	—	—	—	—	—
60.0	0.370	10.1[k]	—	—	—	—	—	—	—	—
65.0	0.421	9.9[j]	—	—	—	—	—	—	—	—

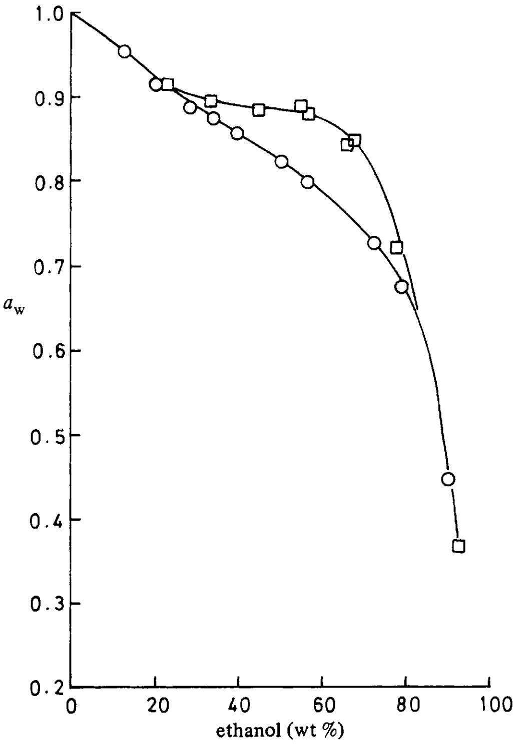

Fig. 2. Values for the activity of water at 25 °C calculated from the vapour pressure data of Dobson (○) and Dornte (□).

where pK is the negative logarithm of the solubility product. After conversion to the mole-fraction scale using eqn (14), values for $\Delta G_t^{\circ}(K^+)$, determined as described later, were used in the equation

$$\Delta G_t^{\circ}(BPh_4^-) = \Delta G_t^{\circ}(KBPh_4) - \Delta G_t^{\circ}(K^+) \qquad (21)$$

to derive further values for $\Delta G_t^{\circ}(BPh_4^-)$. A similar treatment of solubility data for potassium picrate[34] results in values for $\Delta G_t^{\circ}(Pic^-)$ on the mole-fraction scale. Similarly, solubility data[35] for Cs_2ReCl_6 have been used to derive values for $\Delta G_t^{\circ}(Cs_2ReCl_6)_c$ on the molar scale. These have been corrected to the mole-fraction scale using

$$\Delta G_t^{\circ}(Cs_2ReCl_6) = \Delta G_t^{\circ}(Cs_2ReCl_6)_c + 17.11 \log_{10}\left(\frac{18.016 d_s}{M_s d_w}\right) \text{ kJ mol}^{-1} \qquad (22)$$

and values for $\Delta G_t^{\circ}(ReCl_6^{2-})$ were derived using

$$\Delta G_t^{\circ}(ReCl_6^{2-}) = \Delta G_t^{\circ}(Cs_2ReCl_6) - 2\Delta G_t^{\circ}(Cs^+) \qquad (23)$$

with values for $\Delta G_t^{\circ}(Cs^+)$ determined as described later. These values for $\Delta G_t^{\circ}(X^-)$ or $\Delta G_t^{\circ}(X^{2-})$ derived from solubility data are collected in table 2.

The values for $K = [H^+][OH^-]y_{\pm}^2/a_w$ for the dissociation of water[36] have been converted to the ionic product for water on the molar scale, K_{ip}^c, using the values of a_w (fig. 2) calculated from the vapour-pressure data of Dobson.[37] The vapour-pressure data of Dornte[38] were not used for this purpose: these data are absent at low wt %

ethanol and, as fig. 2 shows, a_w calculated from these vapour pressures are more irregular than those calculated using the data of Dobson and deviate markedly from the latter data at higher wt % ethanol. These ionic products for water on the molar scale were then converted to the ionic product on the molality scale, K_{ip}^{m}, using

$$pK_{ip}^{m} = pK_{ip}^{c} + 2\log_{10} d_s. \tag{24}$$

Values for $\Delta G_t^{\circ}(H^+) + \Delta G_t^{\circ}(OH^-)$ on the molality scale were calculated from these values of pK_{ip}^{m} using[1-9]

$$\Delta G_t^{\circ}(H^+)_m + \Delta G_t^{\circ}(OH^-)_m = RT\left(\ln \frac{K_{ip}^{w}}{K_{ip}^{s}}\right)_m + RT\ln\frac{(a_{H_2O}^{s})_m^2}{m_w m_s} \tag{25}$$

where m_w and m_s are the molalities of water in pure water (w) and in the mixture (s), respectively, and the activity of water in the mixture on the molality scale is derived using[1-9]

$$a_{H_2O}^{s}\,(\text{molality}) = 55.509\, a_{H_2O}^{s}\,(\text{mole fraction}) \tag{26}$$

and values for $a_{H_2O}^{s}$ interpolated from fig. 2 using Dobson's vapour pressures.[37] After correcting $\Delta G_t^{\circ}(H^+)_m + \Delta G_t^{\circ}(OH^-)_m$ to the mole-fraction scale using eqn (14), values for $\Delta G_t^{\circ}(OH^-)$ on the mole-fraction scale were calculated using the appropriate values for $\Delta G_t^{\circ}(H^+)$ and an equation analogous to eqn (18). These values are contained in table 2.

ΔG_t°(cation) IN WATER + ETHANOL

Values for $\Delta G_t^{\circ}(H^+) - \Delta G_t^{\circ}(M^+)$ on the molality scale have been recorded by Bax *et al.* for $M^+ = K^+$, Rb^+, Cs^+, Me_4N^+, $(n-Pr)_4N^+$, $(n-Bu)_4N^+$, Fic^+ and TAB^+ (where Fic^+ is the ferrocinium ion and TAB^+ is the tri-isoamylbutylammonium ion). The majority of these are based on solubility measurements,[39] but the data for Fic^+ are based on the E° measurements of Vedal.[40] $\Delta G_t^{\circ}(H^+)$ on the mole-fraction scale can be used[1-9] directly with the data to produce $\Delta G_t^{\circ}(M^+)$ on the mole-fraction scale: these values are recorded in table 3. Solubilities have also been used to produce free energies of transfer from water into water + ethanol mixtures for $TAB\cdot Pic$ and $TAB\cdot BPh_4$ on the molality scales:[34] after conversion to the mole-fraction scale using eqn (14), values for $\Delta G_t^{\circ}(TAB^+)$ have been calculated using

$$\Delta G_t^{\circ}(TAB^+) = \Delta G_t^{\circ}(TAB\cdot X) - \Delta G_t^{\circ}(X^-) \tag{27}$$

and the values for $\Delta G_t^{\circ}(Pic^-)$ and $\Delta G_t^{\circ}(BPh_4^-)$ in table 2. Solubilities[41] have also been used to provide values for $\Delta G_t^{\circ}(Ph_4As\cdot Pic)$ and $\Delta G_t^{\circ}(Ph_4P\cdot Pic)$ on the molar scale; after conversion to the mole-fraction scale using eqn (17), values for $\Delta G_t^{\circ}(Ph_4As^+)$ and $\Delta G_t^{\circ}(Ph_4P^+)$ were calculated using an equation analogous to eqn (27) with $\Delta G_t^{\circ}(Pic^-)$ from table 2. All these values for $\Delta G_t^{\circ}(M^+)$ are contained in table 3.

Some E° values have been used directly to produce free energies of salts. The cell[42]

$$\text{K(Hg)}|\text{KCl, EtOH + water}|\text{AgCl, Ag} \tag{28}$$

was used to provide $\Delta G_t^{\circ}(KCl)_m$ on the molality scale with eqn (13) and the cell[43]

$$\text{Zn(Hg)}|\text{ZnCl}_2\text{, EtOH + water}|\text{AgCl, Ag} \tag{29}$$

with eqn (13) provides values for $\Delta G_t^{\circ}(ZnCl_2)_m$ on the molality scale. $\Delta G_t^{\circ}(KCl)_m$ was corrected to the mole-fraction scale using eqn (14) and $\Delta G_t^{\circ}(ZnCl_2)_m$ using

$$\Delta G_t^{\circ}(ZnCl_2) = \Delta G_t^{\circ}(ZnCl_2)_m + 17.11\log_{10}\left(\frac{18.016}{M_s}\right)\text{kJ mol}^{-1}. \tag{30}$$

Table 3. Values of $\Delta G_t^\circ(M^+)$ and $\Delta G_t^\circ(M^{2+})$ (kJ mol^{-1}) in water+ethanol mixtures at 25 °C

ethanol wt %	ethanol mole fraction	H^+	K^+	Rb^+	Cs^+	Zn^{2+}	Me_4N^+	Pr_4N^+	Bu_4N^+	Fic^+	TAB^+	Ph_4As^+	Ph_4P^+
5.00	0.0202	−0.81	—	−0.183^{q}	—	—	—	—	—	—	—	—	—
10.0	0.0417	−1.81	−1.02^{p}	−0.58^{q}	—	−3.54	—	—	—	—	−3.13^{p}	—	−4.65
10.0	0.0417	—	—	—	—	—	—	—	—	—	−3.17^{p}	—	—
10.2	0.0425	—	—	—	—	—	—	—	—	—	—	−4.69	—
15.0	0.065	−3.00	—	−1.10^{q}	—	—	—	—	—	—	—	—	—
19.9	0.089	—	—	—	—	—	—	—	—	—	—	—	−10.3
20.0	0.089	−4.50	−2.47^{p}	−1.83^{q}	—	−8.5	—	—	—	—	−6.9^{p}	—	—
20.0	0.089	—	—	—	—	—	—	—	—	—	−6.9^{p}	—	—
20.4	0.091	—	—	—	—	—	—	—	—	—	—	−11.0	—
25.0	0.115	−6.0	—	−2.67^{q}	—	—	—	—	—	—	—	—	—
30.0	0.144	−7.2	−3.68^{e}	−3.76^{e}	−4.37	−13.0	−6.36	−9.7	−11.4	−7.4	−11.8^{e}	—	—
30.0	0.144	—	−3.69^{p}	−3.18^{q}	—	—	—	—	—	—	−11.8^{p}	—	—
30.0	0.144	—	—	—	—	—	—	—	—	—	−11.8^{p}	—	—
30.3	0.145	—	—	—	—	—	—	—	—	—	—	−17.1	—
31.2	0.151	—	—	—	—	—	—	—	—	—	—	—	−17.2
35.0	0.174	−7.9	—	−3.14^{q}	—	—	—	—	—	—	—	—	—
39.3	0.202	—	—	—	—	—	—	—	—	—	—	—	−19.9
39.7	0.205	—	—	—	—	—	—	—	—	—	—	−20.2	—
40.0	0.207	−8.3	−3.02^{p}	−2.67^{q}	—	−13.7	—	—	—	—	−14.9^{p}	—	—
40.0	0.207	—	—	—	—	—	—	—	—	—	−15.0^{p}	—	—
45.0	0.242	−8.4	—	−1.99^{q}	—	—	—	—	—	—	—	—	—
50.0	0.281	−8.2	−1.14^{e}	−1.33^{e}	−2.13^{q}	—	−4.50	−10.9	−11.8	−7.1	−16.6^{e}	—	—
50.0	0.281	—	−1.14^{p}	−1.15^{q}	—	—	—	—	—	—	−16.5^{p}	—	—
50.0	0.281	—	—	—	—	—	—	—	—	—	−16.5^{p}	—	—
50.7	0.287	—	—	—	—	—	—	—	—	—	—	—	−20.9
50.9	0.289	—	—	—	—	—	—	—	—	—	—	−21.3	—
55.0	0.323	−8.0	—	−0.067^{q}	—	—	—	—	—	—	—	—	—
60.0	0.370	−7.5	1.33^{p}	1.13^{q}	—	—	—	—	—	—	−18.2^{p}	—	—
60.0	0.370	—	—	—	—	—	—	—	—	—	−20.8^{p}	—	—
60.9	0.379	—	—	—	—	—	—	—	—	—	—	−22.2	—
61.0	0.380	—	—	—	—	—	—	—	—	—	—	—	−21.8
65.0	—	−7.1	—	2.52^{q}	—	—	—	—	—	—	—	—	—

[a] Ref. (21); [b] ref. (18); [c] ref. (17); [d] ref. (26); [e] ref. (24); [f] ref. (23); [g] ref. (19); [h] ref. (22); [i] ref. (25); [j] ref. (27); [k] ref. (20); [l] ref. (32); [m] ref. (28); [n] ref. (29); [o] ref. (30); [p] ref. (34) and (42); [q] ref. (44).

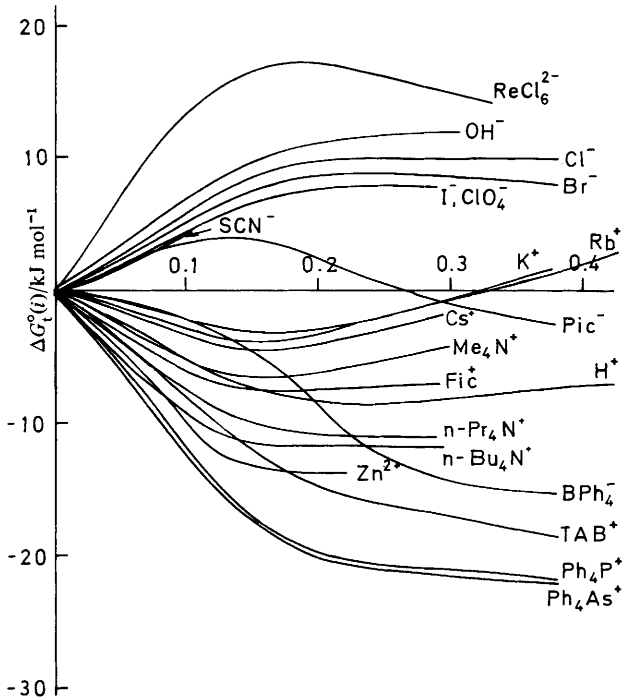

Fig. 3. Values for $\Delta G_t^\circ(i)$ for individual ions in water+ethanol mixtures at 25 °C.

$\Delta G_t^\circ(K^+)$ was then calculated using eqn (27) and the smoothed values for $\Delta G_t^\circ(Cl^-)$ in table 2 and $\Delta G_t^\circ(Zn^{2+})$ using

$$\Delta G_t^\circ(Zn^{2+}) = \Delta G_t^\circ(ZnCl_2) - 2\Delta G_t^\circ(Cl^-) \tag{31}$$

and the smoothed $\Delta G_t^\circ(Cl^-)$ values. $\Delta G_t^\circ(RbCl)_c$ on the molar scale have been calculated from the E° data for the cell[44]

$$\text{cationic glass}|RbCl, EtOH + H_2O|AgCl, Ag. \tag{32}$$

After correction to the mole-fraction scale using eqn (17), values for $\Delta G_t^\circ(Rb^+)$ were produced using an equation of the same type as eqn (27) and the smoothed $\Delta G_t^\circ(Cl^-)$ values. All these values for ΔG_t°(cation) are contained in table 3.

COMPARISON OF $\Delta G_t^\circ(i)$ IN WATER+ETHANOL WITH $\Delta G_t^\circ(i)$ IN MIXTURES OF WATER WITH OTHER COSOLVENTS

In general, good agreement is obtained for values of $\Delta G_t^\circ(i)$ in water+ethanol mixtures for any particular species i over the data derived from various sources. Fig. 3 shows for low x_2 that, in general $\Delta G_t^\circ(i)$ for i = anion are all positive and for i = cation are all negative, as found with other cosolvents,[1-9] the one real exception being BPh_4^-, as found also with other cosolvents. The sequence in the anions in water+ethanol mixtures, $OH^- > Cl^- > Br^- > I^- \approx ClO_4^- \gtrsim SCN^-$, closely corresponds to the findings in other cosolvents[1-9] where the equilibrium

$$OH^- + ROH \rightleftharpoons RO^- + H_2O \tag{33}$$

lies to the left. The only difference is found with cosolvents like methanol,[1, 8] ethylene glycol[4, 8] and glycerol[2, 8], where equilibrium (33) lies to the right and OH^- moves along the series of ions depending on the extent of the stabilization of OH^- in the mixture resulting from the influence of equilibrium (33). The general observation of negative values for ΔG_t°(cation) at low x_2 shows that the effect of solvent structure on $\Delta G_t^\circ(i)$ is dominant over dielectric effects on transferring the charge from water.[9]

On the Frank–Evans[45] and Nemethy–Sheraga[46] interpretation of water structure, involving volumes of structured water on a time-average basis, organic molecules can increase or decrease the amount of structure in the liquid. The excess change in the maximum density of water resulting from the addition of alcohols shows that the latter increase the amount of structure in water:[47] the minima found in the decrease in the partial molar volume of the alcohol, $\bar{V}_2 - V_2^\circ$,[48] has been ascribed[2, 49] to the filling of the cavities between the volumes of structured water with the alkyl groups resulting in the imposition of strain and further hydrogen-bond formation within the structured volumes; the maxima for the ultrasonic absorption[50] found at the higher x_2 have been ascribed[2, 49] to the onset of structural breakdown in the water arising from this strain. Extrema in the excess enthalpy and entropy of mixing of water with the cosolvent are also associated with the formation of structure in the liquid. The extent of this strain at low x_2 of alcohol is shown by the depth of $\bar{V}_2 - V_2^\circ$ at the minimum and the point at which it is reached is indicated by the value of x_2 at the minimum. Thus isopropyl alcohol and t-butyl alcohol have deep minima in $\bar{V}_2 - V_2^\circ$ occurring at $x_2 < 0.1$,[48] whereas the depth is smaller for ethanol at $x_2 \approx 0.1$ and smaller still for methanol at $x_1 \approx 0.1$–0.15,[48] almost non-existent for ethylene glycol and non-detectable for glycerol.[48] Values for $\Delta G_t^\circ(i)$ show extrema or sharp changes at $x_2 \lesssim 0.1$ for t-butyl alcohol[3, 8] and isopropyl alcohol,[2, 8] those with methanol[1, 8] and ethylene glycol[4, 8] show some tendency for this at $x_2 \approx 0.2$–0.3 and those with glycerol[2, 8] show no tendency at x_2 up to 0.20. Ethanol shows these extrema or sharp changes in $\Delta G_t^\circ(i)$ at $x_2 \approx 0.15$. However, methanol shows no peak in the ultrasonic absorption when mixed with water,[50] but the peaks for ethanol, isopropyl alcohol and t-butyl alcohol are[50] at $x_2 \approx 0.3$, $x_2 \approx 0.15$–0.20 and $x_2 \approx 0.1$, respectively, with increasing absorption at the peak along the series, so that the broad extrema exhibited by $\Delta G_t^\circ(i)$ may reflect a combination of both effects.

It is interesting to note that, of the various cosolvents used previously, the spread of values of $\Delta G_t^\circ(i)$ over all i with varying x_2 for ethanol most closely resembles that in water+dioxane,[6,8] despite some apparent differences in the physical properties of the mixtures. Thus, water+dioxane has only a small depth for the minimum in $\bar{V}_2 - V_2^\circ$ at $x_2 \approx 0.04$[51] and only a small ultrasonic absorption,[52] and the changes in the maximum density of water with x_2 suggest[53] that the addition of small concentrations of dioxane to water breaks structure. However, the minimum in the excess enthalpy of mixing of water+dioxane,[54] the existence of which itself suggests enhanced structure formation over that existing in water, occurs at $x_2 \approx 0.15$–0.2, as it does in water+ethanol,[55] the region where the extrema in $\Delta G_t^\circ(i)$ occur in both. The maximum in the viscosity–composition curve for water+dioxane,[56] similar to those found in water+alcohols,[55, 57] also supports the formation of structure when dioxane is added to water. Water+ethanol and water+dioxane[6,8] both show $\Delta G_t^\circ(i)$ for i = an alkali metal becoming positive at $x_2 \approx 0.3$: this occurs at lower x_2 in water+t-butyl alcohol[3, 8] and at higher x_2 in water+ethylene glycol.[4, 8] In both mixtures,[6, 8] $\Delta G_t^\circ(Zn^{2+})$ is much lower than that for unipositive ions, adding support to the view[8, 58] that $\Delta G_t^\circ(i)$ becomes increasingly negative as the charge increases for ions of approximately the same size. In both mixtures,[6, 8] anions or cations with large hydrocarbon groups have large negative values arising from the large structure-forming capacity of these groups.[45, 46] Interestingly, though, values of $\Delta G_t^\circ(i)$ for BPh_4^- and TAB^+ are not equal and differ from those for Ph_4P^+ and Ph_4As^+, although the assumption of their mutual equality has been used[59] as another basis for the resolution of ΔG_t° values for salts into values for separate ions. Comparably, $\Delta G_t^\circ(Ph_4As^+)$ is also not equal to $\Delta G_t^\circ(BPh_4^-)$ in water + DMSO mixtures.[7, 8]

A new feature in water + ethanol mixtures is the high positive value for $\Delta G_t^\circ(ReCl_6^{2-})$, which contrasts with the negative value found for $\Delta G_t^\circ(ReO_4^-)$ in water + dioxane mixtures:[6, 8] presumably the high positive $\Delta G_t^\circ(ReCl_6^{2-})$ arises from the presentation of negatively charged chlorine atoms to the solvent. Ion n.m.r. studies have shown[60] that ions have a preference for water adjacent to them in water + methanol mixtures, so its seems likely that the same will apply in water + ethanol mixtures.

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