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IONIC SOLVATION IN WATER + CO-SOLVENT MIXTURES. PART 8. TOTAL FREE ENERGIES OF TRANSFER AND FREE ENERGIES OF TRANSFER WITH THE "NEUTRAL" COMPONENT REMOVED OF SINGLE IONS FROM WATER INTO WATER + ACETONE

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ABSTRACT

The acid dissociation constants of a wide range of acids in water+acetone mixtures have been combined with values for the free energy of transfer of the proton, $\Delta G_t^0(H^+)$ to calculate values for the free energy of transfer of ions which derive only from the charge on the ion, $\Delta G_t^0(i)_e$ As the values of $\Delta G_t^0(H^+)$ have been revised, revised values for the total free energies of transfer of cations and anions, $\Delta G_t^0(M^+)$ and $\Delta G_t^0(X^-)$, are given New data for $\Delta G_t^0(MX_n)$ is also split into values for $\Delta G_t^0(M^{n+})$ (where $n = 1$ and 2) and $\Delta G_t^0(X^-)$. These free energies of transfer, both total and those deriving from the charge alone, are compared with similar free energies in other mixtures water+co-solvent Values for $\Delta G_t^0(i)_e$ do not conform to a Born-type relationship and show the importance of structural effects in the solvent even when only the transfer of the charge is involved

INTRODUCTION

Some free energies of transfer for single ions from water into water + acetone have been presented previously [1], but as new data for the free energy of transfer of salts, $\Delta G_t^0(MX_n)$, and of acids, $\Delta G_t^0(HX)$, including data for MX_n and HX not previously considered, have since become available, and as the values for $\Delta G_t^0(H^+)$ have been refined, these are discussed again before proceeding to the calculation of proton affinities in water + acetone by the method used previously for water + methanol [2].

$\Delta G_t^0(M^+)$ AND $\Delta G_t^0(X^-)$ IN WATER+ACETONE

Values for the free energy of transfer of acids, $\Delta G_t^0(HX)$, available from data on electrode potentials in water and in mixtures of water with co-solvents are used to derive values for $\Delta G_t^0(X^-)$ by calculating values for $\Delta G_t^0(H^+)$. These values for $\Delta G_t^0(X^-)$ can then be used with values for $\Delta G_t^0(MX_n)$ to derive values for the free energies of transfer of cations, $\Delta G_t^0(\mathrm{M}^{n+})$. This has been done for co-solvents methanol [1,3], acetone [1], isopropanol [1], glycerol [1], ethylene glycol [4], *t*-butanol [5], dioxan [6] and dimethylsulphoxide [7].

$\Delta G_t^0(\mathrm{H}^+)$ is calculated by considering the transfer of the charged sphere containing the tetrahedral structure $\mathrm{H_3^+O(H_2O)_4}$ from water into the mixed solvent for which $\Delta G_t^0(\mathrm{H}^+)_e$ for the transfer of the charge is given by eqn. (1)

$$\Delta G_t^0(\mathrm{H}^+)_e = \frac{Ne^2}{6\,r_{\mathrm{H_2O}}}\left(D_s^{-1} - D_w^{-1}\right) \tag{1}$$

where $r_{\mathrm{H_2O}}$ is the radius of the water molecule, N is Avogadro's number, and D_s and D_w are the dielectric constants for the mixture and for water, respectively. Then the free energy change resulting from the solvent sorting equilibrium (2) is considered

$$\mathrm{(H_2O)_xH^+_{solv} + ROH_{solv}} \overset{K}{\rightleftharpoons} \mathrm{\{(H_2O)_{x-1}\,ROH\}H^+_{solv} + H_2O_{solv}} \tag{2}$$

where ROH is the co-solvent, $x \geqslant 5$ and K is the thermodynamic equilibrium constant. This free energy change is given by (3)

$$\Delta G_t^0(\mathrm{RO^+H_{2solv}}) = -RT\ln K \tag{3}$$

For the addition of a small concentration of *p*-nitroaniline B the following equilibria are set up

$$\mathrm{B_{solv} + (H_2O)_xH^+_{solv}} \overset{K_1}{\rightleftharpoons} \mathrm{BH^+_{solv} + H_2O_{solv}} \tag{4}$$

$$\mathrm{B_{solv} + \{(H_2O)_{x-1}ROH\}H^+_{solv}} \overset{K_2}{\rightleftharpoons} \mathrm{BH^+_{solv} + ROH_{solv}} \tag{5}$$

where K_1 and K_2 are also thermodynamic equilibrium constants. For equilibria (2), (4) and (5), eqn. (6) can be derived,

$$\frac{cc_\mathrm{R}}{c_\mathrm{R} - c} = \frac{K_2F_2}{K_1F_1}\cdot\frac{w_\mathrm{R}c_0}{a}\cdot\frac{c_\mathrm{R}}{c_0 - c_\mathrm{R}} + \frac{c_0w_\mathrm{R}}{K_1F_1a} \tag{6}$$

where a = the total [ROH], c_0 = the total added concentration of *p*-nitroaniline, c_R and c are $[\mathrm{B_{solv}}]$ with and without ROH present, $w_\mathrm{R} = [\mathrm{H_2O}]$ in the presence of ROH, $F_1 = f_\mathrm{B}f_\mathrm{p}/f_{\mathrm{BH^+}}f_{\mathrm{H_2O}}$ and $F_2 = f_\mathrm{B}f_{\mathrm{R\overset{+}{O}H_2}}/f_{\mathrm{BH^+}}f_{\mathrm{ROH}}$ where f is activity coefficient → 1 as [ion] → 0 and [ROH] → 0. The assumption needed in the derivation of eqn. (6), $(K_1F_1'/w) = (K_1F_1/w_\mathrm{R})$ has been shown [1–9] to hold, where $F_1' = F_1$ and $w = w_\mathrm{R}$ in the absence of ROH. For a wide range of ROH, linear plots of $cc_\mathrm{R}/(c_\mathrm{R} - c)$ against $c_\mathrm{R}/(c_0 - c_\mathrm{R})$ have been obtained [1–9]. If $K_c = [\{\mathrm{(H_2O)_{x-1}ROH\}\underset{+}{H^+}}]/[\mathrm{(H_2O)_xH^+}][\mathrm{H^+}]$ and $F_c = f_{\mathrm{R\overset{+}{O}H_2}}f_{\mathrm{H_2O}}/f_\mathrm{p}f_{\mathrm{ROH}}$, where f is defined as above, $\mathrm{R\overset{+}{O}H_2} = \mathrm{\{(H_2O)_{x-1}ROH\}H^+_{solv}}$ and $\mathrm{P = (H_2O)_xH^+_{solv}}$, then eqns. (7)–(10) follow

$$K_cF_c^{-1} = c_0/(\text{slope})a \tag{7}$$

$$\Delta G_t^0\left(\mathrm{R\overset{+}{O}H_2}\right) = -RT\ln\{K_cF_cw_\mathrm{R}\} = -RT\ln\left\{\frac{w_\mathrm{R}c_0F_c^2}{(\text{slope})a}\right\} \tag{8}$$

$$\Delta G_t^0(H^+) = \Delta G_t^0(H^+)_e + \Delta G\left(R\overset{+}{O}H_2\right) \tag{9}$$

$$\Delta G\left(R\overset{+}{O}H_2\right) = \left[R\overset{+}{O}H_2\right] \Delta G_t^0\left(R\overset{+}{O}H_2\right) \tag{10}$$

As $[R\overset{+}{O}H_2]$ can be obtained from K_c [1–9], values for $\Delta G[R\overset{+}{O}H_2]$ can be derived from the slopes for the linear plots of $cc_R/(c_R - c)$ against $c_R/(c_o - c_R)$ provided $F_c = 1.0$: it has been shown [1–9] that, as expected for such a symmetrical term, this assumption is correct. Values for $\Delta G(R\overset{+}{O}H_2)$ for water + acetone have been derived earlier [1] for such linear plots, but the earlier values for $\Delta G_t^0(H^+)_e$ are incorrect as the values for D_s used for water + acetone [10] deviate markedly from two other sets of data for D_s [11,12] which are themselves in mutual agreement. Hence, the values for $\Delta G_t^0(H^+)_e$ have been re-calculated using D_s interpolated from the joint data of Albright and of Graffunder and Heymann. The new values for $\Delta G_t^0(H^+)$ derived using these new $\Delta G_t^0(H^+)_e$ and the previous values for $\Delta G(R\overset{+}{O}H_2)$ are given in Table 1.

The values for $\Delta G_t^0(Cl^-)$ derived previously [1] from the values for $\Delta G_t^0(HCl)$ calculated from the E^0 data then available [13] have been corrected using these revised values for $\Delta G_t^0(H^+)$. Also, the data of Smits et al. [14] for $\Delta G_t^0(HCl)_c$ on the molar scale published since the previous analysis [1], after conversion to the mole fraction scale via eqn. (11)

$$\Delta G_t^0(HX) = \Delta G_t^0(HX)_c + 11.41 \log(18.016\, d_s/M_s d_w) \text{ kJ mole}^{-1} \tag{11}$$

have been combined with $\Delta G_t^0(H^+)$ to give $\Delta G_t^0(Cl^-)$: $M_s = 100/\{(\text{wt.\% acetone}/58.08) + (\text{wt.\% water}/18.016)\}$; d_w and d_s are the densities of pure water and the mixture, respectively, found by interpolation of the data of Kurtz et al. [15]. The resulting values for $\Delta G_t^0(Cl^-)$ are given in Table 1 and the average values are plotted in Fig. 1.

From bromide ions, new data [16] are available for $\Delta G_t^0(HBr)$ using the cell (12)

$$\text{Pd, } H_2\,|\,\text{HBr, water + acetone}\,|\,\text{AgBr–Ag} \tag{12}$$

and these have been combined with $\Delta G_t^0(H^+)$ to give $\Delta G_t^0(HBr)$. The values for $\Delta G_t^0(Br^-)$ derived previously [1] using the E^0 data of Bax et al. [13] have been corrected for the new values of $\Delta G_t^0(H^+)$. $\Delta G_t^0(Br^-)$ values are collected in Table 1 and plotted against solvent composition in Fig. 1. For $\Delta G_t^0(I^-)$, the calculations based on $\Delta G_t^0(HI)$ derived from the E^0 data of Bax et al. [13] have been corrected for the new values of $\Delta G_t^0(H^+)$ and the new values appear in Table 1 and Fig. 1.

Similarly, the new values for $\Delta G_t^0(i)$ for $i = Ph_4B^-$, ClO_4^-, K^+, Rb^+, Cs^+, $(CH_3)_4N^+$, $(n\text{-}Pr)_4N^+$, $(n\text{-}Bu)_4N^+$ and the ferrocinium ion (Fic^+) based on a combination of the data of these latter authors with the new values for $\Delta G_t^0(H^+)$ are also included in Table 1. However, some of these latter values for $\Delta G_t^0(i)$ can now be supplemented by new values based on additional experimental data in the literature. That for Rb^+ is considerably expanded by the use of values of $\Delta G_t^0(RbCl)_c$ of Smits

TABLE I

Values of $\Delta G_t^0(i)$ (kJ mole $^{-1}$) in water + acetone at 25°C

Wt % Acetone	Mole fraction acetone	H^+	$K^{+\,a}$	Rb^+	$Cs^{+\,a}$	Ag^+	$Zn^{2+\,f}$	Me_4N^+	n-Pr_4N^+	n-Bu_4N^+
3.79	0.0121	−1.20								
4.91	0.0158									−1.86 [g]
5.00	0.160	−1.61		−1.77 [b]				−1.53 [g]		
5.00	0.160									
7.30	0.0238	−2.31								
7.94	0.0261									−3.04 [g]
9.64	0.0320					−1.71 [c]				
10.00	0.0333	−3.13		−2.32 [b]				−3.07 [g]		
10.00	0.0333									
10.00	0.0333									
10.60	0.0355	−3.28								
11.96	0.0405									−4.48 [g]
13.6	0.0466	−4.02								
15.00	0.0519			−3.16 [b]				−4.39 [g]		
16.00	0.0558	−4.75								
16.50	0.0578	−4.91								
16.56	0.0580					−3.16 [e]				
19.80	0.0711					−4.18 [c]				−7.1 [g]
20.00	0.0720	−5.8	−3.44	−3.38 [a]	−3.76	−4.42 [d]		−4.63 [a]	−6.9	−8.6 [a]
20.00	0.0720			−4.02 [b]				−5.9 [g]		
20.00	0.0720									
20.00	0.0720									
21.60	0.0787	−6.2								
25.00	0.0937	−6.9		−4.66 [b]						

25.51	0.0960	−7.0				−5.2[c]				
26.20	0.0992	−7.2								
26.37	0.100						−14.7			
30.00	0.117	−8.0		−5.1[b]				−9.1[g]		−10.5[g]
30.00	0.117									
30.20	0.118	−8.1								
33.20	0.133	−8.7								
33.20	0.133									
33.90	0.139	−8.9								
34.43	0.140					−5.5[c]				
34.61	0.141	−9.0				−8.1[c]				
35.00	0.143	−9.1		−5.7[b]						
37.10	0.155	−9.5								
40.00	0.171	−10.1	−5.6	−6.0[a]	−6.4	−7.1[d]			−15.9	−13.8[g]
40.00	0.171			−6.2[b]				−12.9[g]		
40.00	0.171									
40.00	0.171									
40.10	0.172	−10.1								
42.08	0.184					−7.5[c]				
42.80	0.188	−10.6								
44.32	0.198					−9.4[c]				
45.00	0.202	−11.0	−6.5[b]							
45.30	0.204	−11.1								
47.50	0.219	−11.5								
49.60	0.234	−11.9								
50.00	0.237	−12.0	−7.6[b]							
50.00	0.237									
50.06	0.237									−17.1[g]
54.15	0.268					−4.8[c]				
58.01	0.300						−30.4			
58.01	0.300						−16.4			

TABLE 1 (continued)

Wt.% acetone	Mole fraction	n-C$_{10}$H$_{14}$^{g} Me$_3$N^{+}	Pic^{-}	Cl^{-}	Br^{-}	I$^{-\,d}$	ClO$_4^{-\,d}$	Ph$_4$B$^{-\,d}$	OH$^{-\,j}$
	acetone								
3.79	0.0121								2.11
4.91	0.0158								
5.00	0.160	−2.33		1.78^{a}					
5.00	0.160			1.76^{b}					
7.30	0.0238								3.91
7.94	0.0261								
9.64	0.0320								
10.00	0.0333	−4.69		3.42^{a}	2.99				
10.00	0.0333			3.49^{a}					
10.00	0.0333			3.37^{b}					
10.60	0.0355								5.5
11.96	0.0405								
13.6	0.0466								6.8
15.00	0.0519	−6.8							
16.00	0.0558			5.2^{a}					
16.50	0.0578								8.1
16.56	0.0580								
19.80	0.0711								
20.00	0.0720	−8.8	−6.4	6.4^{a}		3.94	2.50	−3.70	
20.00	0.0720			6.5^{a}					
20.00	0.0720			6.4^{a}					
20.00	0.0720			6.4^{b}					
21.60	0.0787								10.2
25.00	0.0937			7.8^{b}					
25.51	0.0960								
26.20	0.0992								11.8
26.37	0.100								

30 00	0 117	−13 1		9 4 [a]	7 8				
30 00	0 117			9 3 [h]					
30 20	0.118								13 3
33 20	0 133			10 1 [a]					
33 20	0 133								
33 90	0 139								14 6
34 43	0 140								
34 61	0 141								
35 00	0 143			10 6 [h]					
37 10	0 155								15 8
40 00	0.171	−17 5	−9 7	12 0 [a]		6 7	3 8	−10.9	
40 00	0 171			12 0 [a]					
40 00	0 171			12 0 [a]					
40 00	0 171			11 8 [h]					
40 10	0 172								16 9
42 08	0 184								
42.80	0 188								17.9
44.32	0 198								
45 00	0 202			13 2 [h]					
45 30	0 204								18 7
47.50	0 219								19 5
49 60	0 234								20 3
50 00	0 237			14 7 [h]	12 4				
50 00	0 237			14 9 [a]					
50 06	0 237								
54 15	0 268								
58 01	0 300								
58.01	0 300								

Attribution of original E^0, solubility or K_{ip} data [a] ref 13, [b] ref 17, [c] ref 22, [d] ref 21, [e] ref 20, [f] ref 19., [g] ref 18, [h] ref 14, [i] ref 16, [j] ref 23

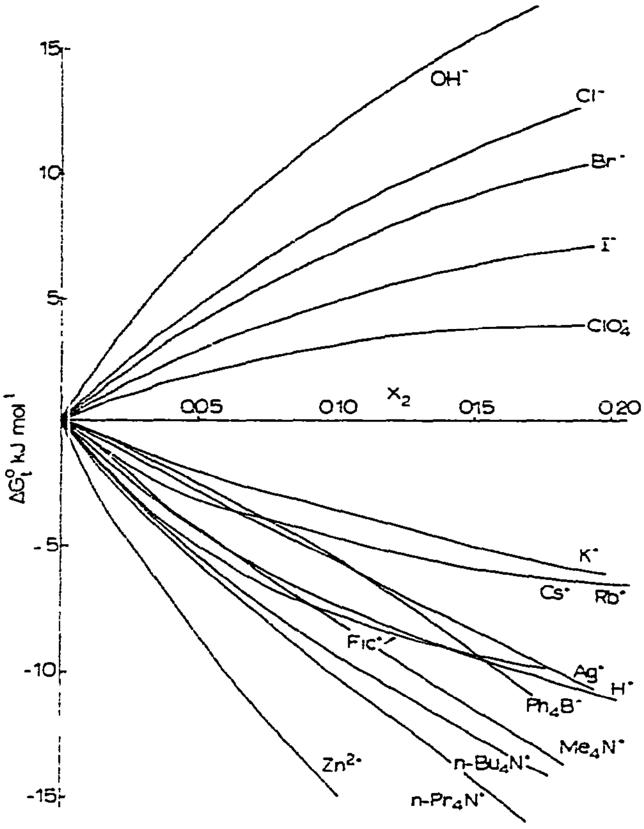

Fig 1 Plots of $\Delta G_t^0(M^{n+})$ and $\Delta G_t^0(X^-)$ at 25°C against mole fraction of acetone x_2

et al. [17] derived from cell (13)

$$\begin{array}{l|l|l} \text{ion selective} & \text{RbCl, water + acetone} & \text{AgCl–Ag} \\ \text{glass electrode} & & \end{array} \qquad (13)$$

These values were first converted to the mole fraction scale using an equation analogous to eqn. (11) and values for $\Delta G_t^0(\mathrm{Rb}^+)$ were then obtained using the new average values for $\Delta G_t^0(\mathrm{Cl}^-)$. The new values for $\Delta G_t^0(\mathrm{Br}^-)$ were combined with the ΔG_t^0 values for $(\mathrm{CH_3})_4\mathrm{NBr}$ and n-$\mathrm{Bu_4NBr}$ of Treiner et al. [18] to produce additional values for $\Delta G_t^0(\mathrm{Me_4N}^+)$ and $\Delta G_t^0(n\text{-}\mathrm{Bu_4N}^+)$. The same authors [18] also have values for $\Delta G_t^0(n\text{-}\mathrm{C_{10}H_{12}Me_3NBr})$ which were treated in the same way to produce values for $\Delta G_t^0(n\text{-}\mathrm{C_{10}H_{12}Me_3N}^+)$. New data for ΔG_t^0 for $\mathrm{Zn(ClO_4)_2}$ based on polarographic measurements [19], after first being converted from the molal scale to the mole fraction scale via eqn. (14)

$$\Delta G_t^0[\mathrm{Zn(ClO_4)_2}] = \Delta G_t^0[\mathrm{Zn(ClO_4)_2}]_m + 17.10 \log(18.016/M_s)\ \mathrm{kJ\ mole^{-1}} \qquad (14)$$

were combined with the new values for $\Delta G_t^0(\mathrm{ClO_4^-})$ to produce values for $\Delta G_t^0(\mathrm{Zn^{2+}})$: unfortunately these values of $\Delta G_t^0\{\mathrm{Zn(ClO_4)_2}\}$ depend markedly on the reference electrode employed [19] at high concentrations of acetone (Table 1).

The data for solubility products of silver salts [20] discussed previously [1] are now considered in a different manner and further data [21,22] for AgCl are included. Previously [1], the data of Barraqué et al. [20] for AgCl were used to derive values for $\Delta G_t^0(\mathrm{Ag}^+)$ which were then combined with their data for $\Delta G_t^0(\mathrm{AgBr})$ and $\Delta G_t^0(\mathrm{AgI})$ to provide values for $\Delta G_t^0(\mathrm{Br}^-)$and $\Delta G_t^0(\mathrm{I}^-)$. Now, the values for $\Delta G_t^0(\mathrm{AgX})$ for $\mathrm{X}^- = \mathrm{Cl}^-$, Br^- and I^- derived from their solubility products [20] are combined with the respective new values of $\Delta G_t^0(\mathrm{X}^-)$ for $\mathrm{X}^- = \mathrm{Cl}^-$, Br^- and I^- to give values for $\Delta G_t^0(\mathrm{Ag}^+)$. The average of all these values for $\Delta G_t^0(\mathrm{Ag}^+)$ at the concentrations of acetone used by Barraqué et al. [20] are now combined with the values for $\Delta G_t^0(\mathrm{AgSCN})$ derived from their solubility products K_s at the same concentrations of acetone to give values for $\Delta G_t^0(\mathrm{SCN}^-)$. The $\mathrm{p}K_s$ data of Morel [21] and of Anderson et al. [22] for AgCl are converted to $\Delta G_t^0(\mathrm{AgCl})_c$ using eqn. (15)

$$\Delta G_t^0(\mathrm{AgCl})_c = 2.303\ RT(\mathrm{p}K_s^w - \mathrm{p}K_s^s) \tag{15}$$

where superscripts w and s indicate pure water and the mixture, respectively. After conversion to the mole fraction scale using an equation analogous to eqn. (11), the values of $\Delta G_t^0(\mathrm{AgCl})$ are combined with the new values for $\Delta G_t^0(\mathrm{Cl}^-)$ to give values for $\Delta G_t^0(\mathrm{Ag}^+)$.

Values for $\Delta G_t^0(\mathrm{OH}^-)$ have now been calculated using the data for the equilibrium constant $K^c = a_{\mathrm{H}^+}a_{\mathrm{OH}^-}/a_w$ (where a_x is activity) on the molar scale at 25°C determined by Woolley et al. [23]. These data were first converted to ionic products $K_{ip}^c = a_{\mathrm{H}^+}a_{\mathrm{OH}^-}$ on the molar scale using values for a_w interpolated from those calculated from the vapour pressures of Taylor [24] at 25°C. These values for K_{ip}^c were converted to values K_{ip}^m on the molal scale using eqn. (16)

$$\log K_{ip}^m = \log K_{ip}^c - 2\log d_s \tag{16}$$

interpolating values for d_s as before [15]. These values for K_{ip}^m were then used to produce values for $\Delta G_t^0(\mathrm{H}^+)_m + \Delta G_t^0(\mathrm{OH}^-)_m$ with eqn. (17) [1,4,6,8]

$$\Delta G_t^0(\mathrm{H}^+)_m + \Delta G_t^0(\mathrm{OH}^-)_m = RT\left\{\frac{\ln K_{ip}^w}{K_{ip}^s} + \frac{\ln\left(a_{\mathrm{H_2O}}^s\right)^2}{m_w m_s}\right\} \tag{17}$$

where m_w and m_s are the molalities of water in pure water and in the mixture, respectively, and $a_{\mathrm{H_2O}}^s$ is the activity of water in the mixture on the molality scale derived using eqn. (18) [25]

$$a_{\mathrm{H_2O}}^s(\text{molality}) = 55.509 \times a_{\mathrm{H_2O}}^s(\text{mole fraction}) \tag{18}$$

from the interpolated values calculated above for the mole fraction scale from the data of Taylor [24]. The values of $\Delta G_t^0(\mathrm{H}^+)_m + \Delta G_t^0(\mathrm{OH}^-)_m$ were then converted to the mole fraction scale using eqn. (19)

$$\Delta G_t^0(\mathrm{HX}) = \Delta G_t^0(\mathrm{HX})_m + 11.41\log(18.016/M_s)\ \mathrm{kJ\ mole^{-1}} \tag{19}$$

and combined with values for $\Delta G_t^0(\mathrm{H}^+)$ to give $\Delta G_t^0(\mathrm{OH}^-)$.

All these values for $\Delta G_t^0(\mathrm{M}^{n+})$ and $\Delta G_t^0(\mathrm{X}^-)$ are collected in Table 1 and plotted against solvent composition in Fig. 1.

TABLE 2

Values for $\Delta G_t^0(B^-)_c$ (kJ mole^{-1}) for water + acetone at 25°C

B^-	ref for pK_a	Wt % acetone												
		10.0	16.12	17.8	20.0	24.45	25.0	30.0	33.11	36.4	40.0	42.12	45.9	50.0
Acetate	27		6.8			10.1			13.5			17.0		
Acetate	28			7.4						15.0			18.7	
Acetate	29	4.4			8.4			12.4			16.3			20.4
Phenylacetate	26	4.4					10.7							
o-Nitrophenylacetate	26	4.5					11.4							
m-Nitrophenylacetate	26	4.3					10.3							
p-Nitrophenylacetate	26	4.8					10.5							
o-Tolylacetate	26	4.7					11.2							
m-Tolylacetate	26	4.6					10.8							
p-Tolylacetate	26	3.8					10.9							
Benzoate	26	4.3					10.9							
Benzoate	27		7.6			11.4			15.1			19.0		
Benzoate	29	5.0			9.4			14.0			18.1			22.3
Benzoate	30				10.2			14.8			19.3			24.5
o-Nitrobenzoate	26	5.4					13.1							
o-Nitrobenzoate	30				10.6			15.6			20.9			26.5
m-Nitrobenzoate	26	4.1					10.3							

m-Nitrobenzoate	30		6.9		10.1	13.3	16.7
p-Nitrobenzoate	26	3.8		9.9			
o-Toluate	26	5.2		12.0			
m-Toluate	26	4.1		10.8			
p-Toluate	26	4.5		10.7			
o-Hydroxybenzoate	26	3.9		9.5			
o-Hydroxybenzoate	30		8.1		11.4	16.3	17.8
m-Hydroxybenzoate	26	5.1		11.3			
p-Hydroxybenzoate	26	5.2		11.1			
o-Methoxybenzoate	26	5.3		11.7			
m-Methoxybenzoate	26	4.2		10.6			
p-Methoxybenzoate	26	4.9		10.6			
o-Acetylbenzoate	26	3.6		8.7			
m-Acetylbenzoate	26	4.3		10.6			
p-Acetylbenzoate	26	4.2		10.7			
o-Fluorobenzoate	26	5.9		12.8			
m-Fluorobenzoate	26	4.0		10.7			
p-Fluorobenzoate	26	3.8		10.1			
o-Chlorobenzoate	26	5.1		12.5			
m-Chlorobenzoate	26	4.1		10.6			
p-Chlorobenzoate	26	4.2		10.5			
α-Naphthoate	26	5.2		12.3			
β-Naphthoate	26	4.7		10.8			

TABLE 3

Values of $\Delta G_t^0(A^+)_c$ (kJ mole^{-1}) for water+ acetone at 25°C

Conjugate base B for $A^+ \rightleftharpoons B + H^+$	ref. for p*K*a	Wt % acetone									
		7.96	9.3	15.6	16.0	16.12	17.3	17.8	20.0	24.45	30.0
1-Aminoethane	28							−3.2			
1-Aminopropane	28							−2.4			
2-Aminopropane	28							−3.8			
1-Aminobutane	28							−2.5			
2-aminoethanol	28								−3.2		
2-Aminoethanol	28				−2.4						
N-Methyl-2-amino-ethanol	28				−2.3						
N *N*-dimethyl-2-aminoethanol	28				−2.9						
N-Ethyl-2-aminoethanol	28				−3.4						
N *N*-Diethyl-2-amino-ethanol	28				−3.4						
N-Ethoxy-2-amino-ethanol	28				−3.4						
N *N*-Diethoxy-2-amino-ethanol	28				−3.0						
N-Ethoxy-*N*-methyl-2-aminoethanol	28				−2.9						
N-Phenyl-2-amino-ethanol	28				−3.0						

N-Phenyl-*N*-ethyl-2-aminoethanol	28				−2.1					
N-Phenyl-*N*-ethoxy-2-aminoethanol	28				−2.2					
Aniline	27					−3.3			−4.4	
Aniline	28							−3.8		
m-Nitroaniline	32		−1.7				−2.5			
o-Toluidine	31			−4.1						−5.8
p-Toluidine	31			−3.9						−5.7
N-Methylaniline	27					−2.9			−3.6	
N-Ethylaniline	27					−3.6			−4.4	
N-Isopropylaniline	27					−2.6			−3.2	
N,*N*-Dimethylaniline	27	−1.4				−2.6			−3.2	
N,*N*-Diethylaniline	27	−2.0				−3.2			−3.8	
N,*N*-Diisopropylaniline	27	−1.7				−2.8			−3.4	
p-Bromoaniline	27					−2.8			−3.5	
p-Bromo-*N*,*N*-dimethylaniline	27					−1.9			−2.2	
p-Bromo-*N*,*N*-diethylaniline	27					−2.1			−1.6	
N,*N*-Dimethyl-*p*-aminophenyl(diphenyl)carbinol	27	−1.1				−1.9			−2.1	
N,*N*-Diethyl-*p*-aminophenyl(diphenyl)carbinol	27	−0.45				−0.90			−0.67	
p-Aminophenyl(diphenyl)carbinol	27	−1.4				−2.4			−3.4	

TABLE 3 (continued)

Conjugate base B for $A^+ \rightleftharpoons B+H^+$	ref for p*K*a	30.6	33.11	33.2	36.4	38.4	40.0	42.12	45.9	50.0
1-Aminoethane	28				−4.7				−5.3	
1-Aminopropane	28				−3.9				−4.1	
2-Aminopropane	28				−5.8				−6.2	
1-Aminobutane	28				−3.7				−3.8	
2-Aminoethanol	28						−8.8			
2-Aminoethanol	28			−4.6						
N-Methyl-2-amino-ethanol	28			−6.0						
N *N*-Dimethyl-2-aminoethanol	28			−5.9						
N-Ethyl-2-aminoethanol	28			−6.7						
N *N*-Diethyl-2-amino-ethanol	28			−5.9						
N-ethoxy-2-amino-ethanol	28			−7.5						
N *N*-Diethoxy-2-amino-ethanol	28			−6.7						
N-Ethoxy-*N*-methyl-2-aminoethanol	28			−5.8						
N-Phenyl-2-amino-ethanol	28			−4.9						
N-Phenyl-*N*-ethyl-2-aminoethanol	28			−2.9						

N-Phenyl-*N*-ethoxy-2-aminoethanol	28			−3 6					
Aniline	27		−5.2				−5 7		
Aniline	28				−5 8			−6 3	
m-Nitroaniline	32	−3.2				−3.3			−3 5
o-Toluidine	31								
p-Toluidine	31								
N-Methylaniline	27		−4 1				−4 2		
N-Ethylaniline	27		−4 9				−5 0		
N-Isopropylaniline	27		−3.5				−3 5		
N *N*-Dimethylaniline	27		−3 3				−3.1		
N *N*-Diethylaniline	27		−3.4				−2 9		
N *N*-Diisopropylaniline	27		−3 3				−3 0		
p-Bromoaniline	27		−4 2				−4 8		
p-Bromo-*N* *N*-dimethylaniline	27		−1 8				−1.2		
p-Bromo-*N* *N*-diethylaniline	27		−0.45				+0 34		
N *N*-Dimethyl-*p*-amino phenyl(diphenyl)carbinol	27		−2 0				−2.2		
N *N*-Diethyl-*p*-aminophenyl(diphenyl)carbinol	27		−0 63				−0 57		
p-Aminophenyl(diphenyl)carbinol	27		−4 3				−5 4		

For an acid–base system (20)

$$A_{solv} \overset{K_a}{\rightleftharpoons} B_{solv} + H^+_{solv} \tag{20}$$

the change in the proton affinity of B on transferring the system from water into the mixture of water + co-solvent, ΔP_a, is given by (21) [2,6,8]

$$\Delta P_a = 5.71(pK_a^w - pK_a^s) + \Delta G_t^0(H^+) - C \text{ kJ mole}^{-1} \tag{21}$$

The magnitude of C depends on the particular scale on which the values for K_a are quoted: for the mole fraction scale, $C =$ zero; for the molality scale, $C = 5.71 \log(18.016/M_s)$; for the molar scale, $C = 5.71 \log(18.016\ d_s/M_s d_w)$ [2]. If A has a single positive charge with B electrically neutral, then ΔP_a is given by (22)

$$\Delta P_a = \Delta G_t^0(A^+) - \Delta G_t^0(B) \tag{22}$$

As B is as close an approximation as can be experimentally obtained for the bulk and structure of A, becoming closer as A and B get larger, in transferring A^+ from water into the mixture the changes in free energy produced by B will represent the changes in free energy arising from its bulk and structural aspects i.e. the electrically neutral component of the free energy change resulting from the transfer of A^+. If subscript n refers to this "neutral" component and subscript e refers to the component arising from the charge only, with $\Delta G_t^0(B) = \Delta G_t^0(A^+)_n$, then eqn. (23) follows

$$\Delta G_t^0(A^+)_e = \Delta G_t^0(A^+) - \Delta G_t^0(A^+)_n = \Delta P_a \tag{23}$$

and the values of ΔP_a are a direct measure of $\Delta G_t^0(A^+)_e$. However, if A is electrically neutral with B having a single negative charge, $\Delta G_t^0(A) = \Delta G_t^0(B^-)_n$, and eqn. (24) follows

$$\Delta G_t^0(B^-)_e = \Delta G_t^0(B^-) - \Delta G_t^0(A) = -\Delta P_a \tag{24}$$

Data for pK_a at 25°C in water + acetone are available from the work of Dippy et al. [26], Reynand [27], Douhéret et al. [28], Morel et al. [29], Singh et al. [30], Anfauvre and Comte [31] and of Ang [32]. Values for $\Delta G_t^0(B^-)_e$ calculated by combining this data with the values of $\Delta G_t^0(H^+)$ in Table 1 using eqns. (21) and (24) are given in Table 2 and values for $\Delta G_t^0(A^+)_e$ calculated in a similar manner using eqns. (21) and (23) are given in Table 3. The source of the pK_a data used is indicated in these tables.

COMPARISON OF $\Delta G_t^0(i)$ AND $\Delta G_t^0(i)_e$ IN WATER+ACETONE WITH $\Delta G_t^0(i)$ AND $\Delta G_t^0(i)_e$ IN MIXTURES OF WATER WITH OTHER CO-SOLVENTS

As with other co-solvents [1–8], in general $\Delta G_t^0(i)$ for $i =$ anion is positive and $\Delta G_t^0(i)$ for $i =$ cation is negative with acetone as co-solvent. As with methanol and dioxan [3,6], $\Delta G_t^0(Zn^{2+})$ has a greater negative value than ΔG_t^0 for the simple univalent cations and, as with all the other co-solvents [1–8], the quaternary ammonium ions have large negative values for ΔG_t^0 with acetone. The only anion which has a negative value for ΔG_t^0 is Ph_4B^-, as found also for co-solvents dioxan and dimethylsulphoxide [6–8]; in all cases the numerical value is large due to the structure forming effect of the phenyl groups. The order in ΔG_t^0 for the halides, $Cl^- > Br^- > I^-$, is the same as found with all other co-solvents [1–8], and the order $Cl^- > Br^- > I^- > ClO_4^-$ is the same as found with dioxan [6] where $\Delta G_t^0(ClO_4^-)$ is available. It is very interesting to compare $\Delta G_t^0(OH^-)$ for a range of co-solvents. For the co-solvent ethylene glycol [4,8], $\Delta G_t^0(OH^-)$ is negative and for methanol values for $\Delta G_t^0(OH^-)$ are positive but small [1,8]; in both these cases, OH^- is stabilized in the mixture relative to pure water due to the formation of alkoxide type ions. However, $\Delta G_t^0(OH^-)$ for water + acetone has larger positive values comparable with the magnitude found with the co-solvents dimethylsulphoxide [7,8] and dioxan [6,8] where no alkoxide ions are formed.

The negative values for $\Delta G_t^0(i)$ for i = cation and the absence of reasonable linearity with anything like the correct slope for plots of $\Delta G_t^0(i)$ against D_s^{-1} for i = anion shows that structural effects in the mixtures are an important factor determining $\Delta G_t^0(i)$. However, Fig. 1 shows the absence of any extrema in the variation of $\Delta G_t^0(i)$ against mole fraction, x_2, of acetone, unlike the similar plots for water + t-butanol [5,8]. This difference arises from different composition regions for the onset of structural breakdown in the mixture as represented by the extremum in the variation of ultrasonic absorption with composition: for water + t-butanol this maximum occurs at $x_2 \sim 0.1$ [33] compared with $x_2 \sim 0.4$ for water + acetone [34]. The relationship of $\Delta G_t^0(i)$ with other properties of the mixtures water + acetone has been discussed earlier [1], particularly the manner in which the sign of $\Delta G_t^0(i)$ depends on changes in the excess enthalpy and entropy of mixing of water with the co-solvent and on the structure breaking and forming capacity of i [4,8].

When the "neutral" component of $\Delta G_t^0(i)$ is removed, $\Delta G_t^0(i)_e$, according to the Born equation, eqn. (1), ought to vary linearly with D_s^{-1}. Such plots in water + methanol for i = anion were found to be linear, but the slopes deviated markedly from those expected [2]. Moreover, values of $\Delta G_t^0(i)_e$ for cations in these mixtures were all negative [2], different in sign from that required by eqn. (1). It was therefore concluded [2] that structural factors in the mixtures also have considerable influence on $\Delta G_t^0(i)_e$ through $\Delta G_t^0(i)_{st}$ in eqn. (25)

$$\Delta G_t^0(i)_e = \Delta G_t^0(i)_{Born} + \Delta G_t^0(i)_{st} \tag{25}$$

Figures 2 and 3 show plots of $\Delta G_t^0(B^-)_e$ against D_s^{-1} for the anions in Table 2 where the data exist over a sufficiently wide range of compositions: in all these cases curves are obtained. Figures 4 and 5 show similar curves for $\Delta G_t^0(B^-)_e$ in water + dioxan [6] for the cases where the data are available over a wide range of compositions: again, curves are obtained, more pronounced than those in Figs. 2 and 3 for water + acetone. The values of D_s for water + dioxan were interpolated from the data of Critchfield et al. [35]. These curves can be compared with the plots of $\Delta G_t^0(B^-)_e$ against x_2 for B^- = carboxylate anion in water + t-butanol which show

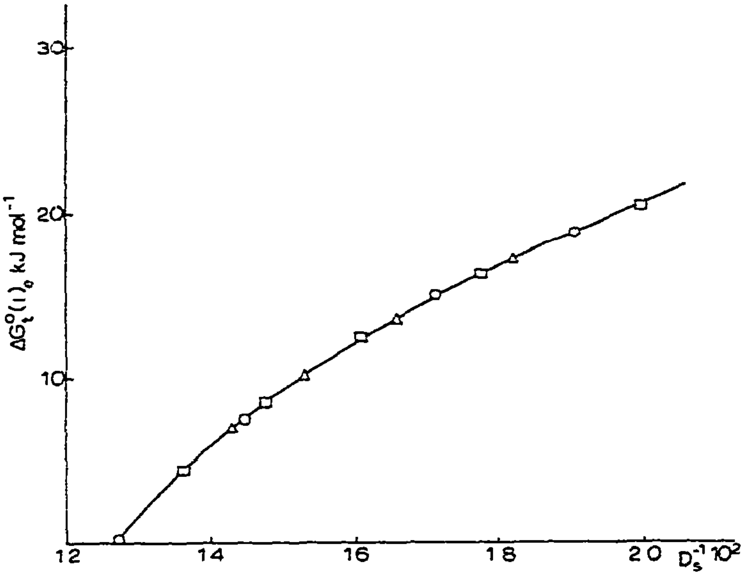

Fig 2 Plot of ΔG_t^0(acetate)$_c$ against D_s^{-1} for water+acetone at 25°C: pK_a from (○), ref 28; (□), ref 29 and (△), ref 27

[8] very sharp changes in the composition region $x_2 \sim 0.1$ where the maximum structure formation occurs for these mixtures. Thus, the linear plots for $\Delta G_t^0(B^-)_c$ against D_s^{-1} found earlier [2] in water + methanol are not found when these other co-solvents are added to water.

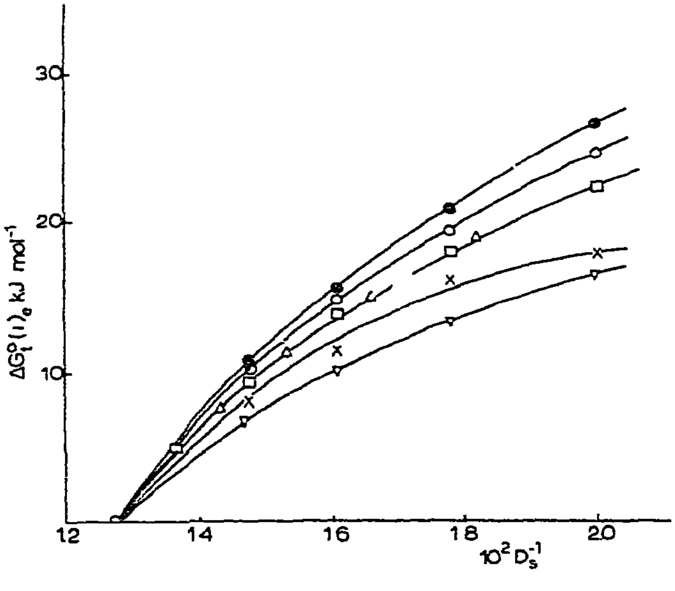

Fig 3. Plots of $\Delta G_t^0(i)_c$ against D_s^{-1} for water+acetone at 25°C for various carboxylate ions pK_a data as follows: benzoate ion: (○), ref. 30; (□), ref 29; (△), ref. 27; salicylate ion: (×), ref. 26; *o*-nitrobenzoate ion: (●), refs. 26 and 30; *m*-nitrobenzoate ion: (▽), ref. 26

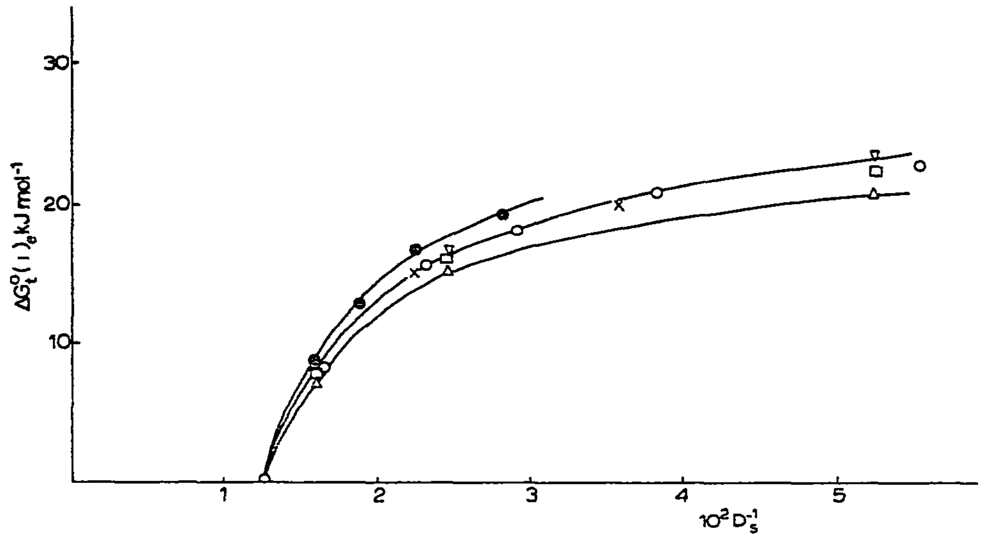

Fig 4 Plots of $\Delta G_t^0(i)_c$ against D_s^{-1} for water+dioxan at 25°C for various carboxylate ions with the pK_a-data derived as indicated in ref 6 ⊙, □ and ×, acetate, △, formate, ▽, propionate: ●, benzoate

Table 3 shows that all the values for $\Delta G_t^0(A^+)_c$ are negative in water + acetone, comparable with those found in water + methanol [2] and water + dioxan [6]. However, the values in water + acetone, like those in water + methanol [2], do not show an extremum such as found in water + dioxan [6], illustrated in Fig. 6. These negative values for $\Delta G_t^0(A^+)_e$ in water + methanol, water + acetone and water +

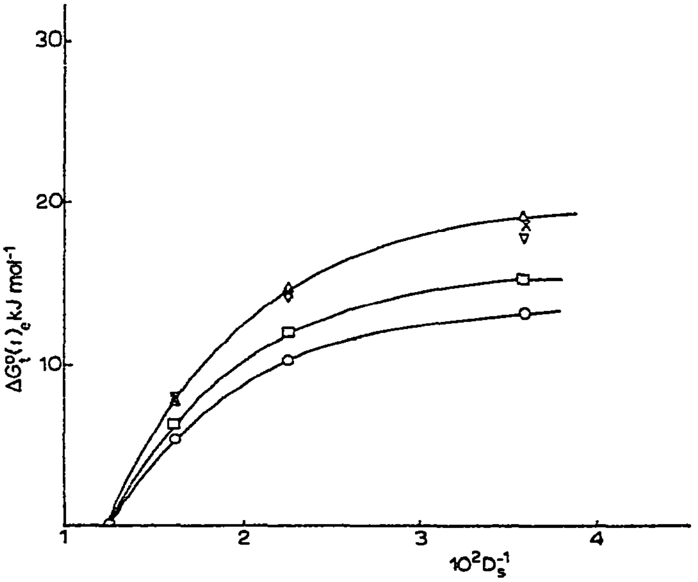

Fig 5. Plots of $\Delta G_t^0(i)_e$ against D_s^{-1} for water+dioxan at 25°C for various anions with the pK_a-data derived as indicated in ref. 6. ⊙, 2,4-dinitrophenate, □, 2,5-dinitrophenate; △, dimedone, ×, *l*-ascorbate; ▽, reductone

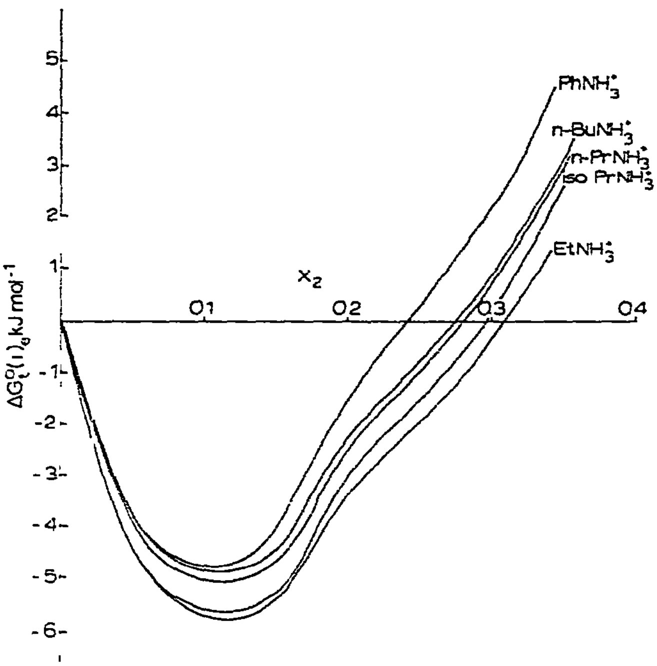

Fig 6 Plots of $\Delta G_t^0(i)_e$ in water–dioxan against mole fraction of dioxan x_2 at 25°C for alkyl- and aryl ammonium ions, with the $\mathrm{p}K_a$-data derived as indicated in ref 6

dioxan, together with the curves found for $\Delta G_t^0(\mathrm{B}^-)_e$ vs. D_s^{-1} in the last two mixtures, support the view expressed earlier [2] that $\Delta G_t^0(i)_{st}$ in eqn. (25) has a considerable influence on $\Delta G_t^0(i)_e$; in the case of $\Delta G_t^0(\mathrm{A}^+)_e$, $\Delta G_t^0(\mathrm{A}^+)_{st}$ must dominate over $\Delta G_t^0(\mathrm{A}^-)_{\mathrm{Born}}$. This conclusion does not in any way invalidate the method [1–8] used for computing $\Delta G_t^0(\mathrm{H}^+)$ outlined above, where, in eqn. (9), $\Delta G_t^0(\mathrm{H}^+)_e = \Delta G_t^0(\mathrm{H}^+)_{\mathrm{Born}}$, as expressed in eqn. (1): here the free energy change arising from the *total* structural effects, $\Delta G(\mathrm{R}\underset{+}{\mathrm{O}}\mathrm{H}_2)$, is determinated experimentally through K_c and includes both $\Delta G_t^0(\mathrm{H}^+)_{st}$ and $\Delta G_t^0(\mathrm{H}^+)_n$.

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