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IONIC SOLVATION IN WATER + CO-SOLVENT MIXTURES. PART 20. THE 'NEUTRAL' COMPONENT OF FREE ENERGIES OF TRANSFER OF SINGLE IONS FROM WATER INTO MIXTURES OF WATER + HYDROXYLIC CO-SOLVENTS

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ABSTRACT

Values for the free energy of transfer of neutral inorganic and organic molecules from water into mixtures of water with a series of hydroxylic co-solvents, $\Delta G_t^\ominus(i)_n$, have been calculated from the solubilities of gaseous molecules. These are utilised to calculate the free energy of transfer of the charge alone, $\Delta G_t^\ominus(i)_e$, for some ions and $\Delta G_t^\ominus(i)_e$ is compared with the physical properties and $\Delta G_t^\ominus(i)_e$ values available for large organic cations and anions. By combining the equations of the scaled particle theory with $\Delta G_t^\ominus(i)_n$, it is possible to calculate, for low mole fractions of co-solvent, the change in the free energy of interaction of the dissolved molecule with the surrounding solvent arising from the transfer water → mixture, $\Delta G_t^{int}(i)$. For inorganic molecules, ΔG_t^{int} has small negative values, whilst higher negative values are found for larger organic molecules.

INTRODUCTION

Recently, we have attempted to assess the extent of the contribution to the free energy of transfer of single ions from water into water + ethanol mixtures arising from the transfer of the electrically neutral bulk of the ion, by calculating the free energy of transfer of a range of electrically neutral inorganic and organic molecules [1]. These calculations were then extended using the relationship of Pierotti [2] for the free energy of solution of a gaseous molecule into a solvent, eqn. (1)

$$\Delta G^\ominus = G^{cav} + G^{int} + RT\ \ln(RT/V) \qquad (1)$$

where $\Delta G^\ominus$ is the free energy for the process gas → solution, G^{cav} is the partial molar free energy of the formation of the cavity to contain the solute molecule, G^{int} is the partial molar free energy of the interaction between the solute molecule in the cavity with the surrounding solvent and V is the molar volume of the solvent. In practice, it is difficult to calculate G^{cav} with

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any certainty for a structured liquid like water or an alcohol, so we attempted to eliminate G^{cav}. If subscript w and s indicate pure water and a mixture of water + co-solvent, respectively, the free energy of transfer of the 'neutral' molecule from water into the mixture will be given by eqn. (2)

$$\Delta G_t^{\ominus}(i)_n = \Delta G_s^{\ominus} - \Delta G_w^{\ominus} = \left(G_s^{\text{cav}} - G_w^{\text{cav}}\right) + \left(G_s^{\text{int}} - G_w^{\text{int}}\right) + RT\ \ln(V_w/V_s) \tag{2}$$

For water-rich mixtures $(G_s^{\text{cav}} - G_w^{\text{cav}}) \to$ zero, so assuming conditions where $(G_s^{\text{cav}} - G_w^{\text{cav}}) = 0$, and putting $(G_s^{\text{int}} - G_w^{\text{int}}) = \Delta G_t^{\text{int}}(i)_n$, eqn. (2) can be re-arranged for water-rich conditions to

$$\Delta G_t^{\text{int}}(i)_n = \Delta G_t^{\ominus}(i)_n + RT\ \ln(V_s/V_w) \tag{3}$$

V_s/V_w can be calculated from eqn. (4)

$$\frac{V_s}{V_w} = \frac{(x_1 M_w + x_2 M_2)\,d_w}{d_s M_w} \tag{4}$$

where x_1 and x_2 are the mole fractions of water and the co-solvent, respectively, in the mixture, d is density and M_w and M_2 are the molecular weights of water and the co-solvent. $\Delta G_t^{\ominus}(i)_n$ can be calculated from the experimental gas solubilities in water and in the mixture, s, as in

$$\Delta G_t^{\ominus}(i)_n = RT\ \ln\left(s_w^{\ominus}/s_s^{\ominus}\right) \tag{5}$$

When eqns. (3)–(5) were applied to water + ethanol mixtures, it was found [1] that $\Delta G_t^{\text{int}}(i)_n$ where i is a small inorganic molecule had a small negative value which was relatively invariant with x_2 for $x_2 < 0.20$, except when i is I_2; whereas, for hydrocarbons, $\Delta G_t^{\text{int}}(i)_n$ at any particular x_2 became increasingly negative with increasing size of i and, for any particular hydrocarbon, $\Delta G_t^{\text{int}}(i)_n$ became increasingly negative with increasing x_2 for $x_2 < 0.25$. We now report the application of eqns. (3)–(5) to inorganic and organic molecules dissolved in mixtures of water with other hydroxylic co-solvents.

CALCULATION OF $\Delta G_t^{\ominus}(i)_n$ IN WATER + CO-SOLVENT MIXTURES

Values for $\Delta G_t^{\ominus}(i)_c$ on the molar scale are directly available for 4-nitroaniline [3] and 1,10-phenanthroline [4] in water + methanol mixtures, and these have been converted to the mole-fraction scale using eqn. (6)

$$\Delta G_t^{\ominus}(i) = \Delta G_t^{\ominus}(i)_c + RT\ \ln\left[\frac{18.015 d_s}{M_s d_w}\right] \tag{6}$$

where $M_s = 100/[(\text{wt.\% MeOH}/32.04) + (\text{wt.\% } H_2O/18.015)]$. Densities were interpolated from the data of Mikhail and Kimel [5]. $\Delta\mu^{\ominus}$, the difference in the standard chemical potential of argon between the liquid and vapour phases in water + methanol [6], was used in eqn. (7)

$$\Delta G_t^{\ominus}(i) = \Delta\mu_s^{\ominus} - \Delta\mu_w^{\ominus} \tag{7}$$

to calculate $\Delta G_t^{\ominus}(i)$ for $i = \mathrm{Ar}$ on the molar scale, and these are converted to the mole-fraction scale using eqn. (6). $\Delta G_t^{\ominus}(i)_m$ values on the molality scale are available [7] in water + methanol for tris(hydroxymethyl)aminomethane (THC) and these have been converted to the mole-fraction scale using eqn. (8)

$$\Delta G_t^{\ominus}(i) = \Delta G_t^{\ominus}(i)_m + RT \ln\left(\frac{18.015}{M_s}\right) \tag{8}$$

The ratios of the solubilities of oxygen in water and in the mixtures at 25 ° C [8] have been converted to $\Delta G_t^{\ominus}(O_2)_c$ values via eqn. (5) and then converted to the mole-fraction scale using eqn. (6). The solubilities of carbon dioxide in water + methanol are available [9] for a range of temperatures and the values at 25 ° C were found by graphical interpolation. These produce $\Delta G_t^{\ominus}(CO_2)$ values directly on the mole-fraction scale from eqn. (5). All these values for $\Delta G_t^{\ominus}(i)_n$ on the mole-fraction scale are collected in Table 1.

The ratios of the solubilities of oxygen in water + propan-1-ol at 25 ° C [8] have been converted to $\Delta G_t^{\ominus}(O_2)_c$ values using eqn. (5), and eqn. (6) was then used to produce $\Delta G_t^{\ominus}(O_2)$ on the mole-fraction scale: the densities were interpolated from the data of Mikhail and Kimel [10] and of Chu and Thompson [11], and $M_s = 100/[(\text{wt.\% 1-PrOH}/60.11) + (\text{wt.\% H}_2\text{O}/18.015)]$. For water + propan-2-ol mixtures, $\Delta G_t^{\ominus}(i)_c$ is directly available [3] for 4-nitroaniline and the solubilities of benzene have been measured [12]. The former have been converted to the mole-fraction scale using eqn. (6) and densities interpolated from the data of Chu and Thompson [11], and the latter, after $\Delta G_t^{\ominus}(C_6H_6)_m$ was produced from eqn. (5), was converted to the mole-fraction scale using eqn. (8). These values for $\Delta G_t^{\ominus}(i)_n$ are given in Table 1.

For H_2 and He in water + *t*-butyl alcohol, the $\Delta\mu_m^{\ominus}$ values on the molality scale at 25 ° C have been interpolated graphically from the variation of $\Delta\mu_m^{\ominus}$ with temperature [13] at each concentration of *t*-butyl alcohol. $\Delta G_t^{\ominus}(i)_m$ calculated from eqn. (7) is then converted to $\Delta G_t^{\ominus}(i)$ on the mole-fraction scale using eqn. (8) with $M_s = 100/[\text{wt.\% } t\text{-BuOH}/74.12 + (\text{wt.\% H}_2\text{O}/18.015)]$. For O_2 [14] and Ar [15], similar graphical interpolations of the temperature variation at each concentration of *t*-butyl alcohol were performed to derive log $s^{\ominus}$ at 25 ° C. These were substituted into eqn. (5) to produce $\Delta G_t^{\ominus}(i)_m$ on the molality scale which was converted to the mole-fraction scale via eqn. (8). The mole-fraction solubilities [9] of CO_2 in water + *t*-butyl alcohol at 25 ° C were interpolated graphically from the variation with temperature for each concentration of *t*-butyl alcohol and then used in eqn. (5) to produce $\Delta G_t^{\ominus}(i)_n$. $\Delta G_t^{\ominus}(i)_c$ values on the molar

TABLE 1

Variation in $-\Delta G_t^{\ominus}(i)_n$ (kJ mol^{-1}) with solvent composition for the transfer of neutral species from water into water + co-solvent at 25 °C

Co-solvent		Molecule transferred								
wt.%	Mole fraction	O_2	CO_2	Phen [a]	Ar	4-NA [b]	THC [c]	C_6H_6	H_2	He
Water + methanol										
0.80	0.0045	0.050	–	–	–	–	–	–	–	–
1.60	0.0091	0.085	–	–	–	–	–	–	–	–
2.40	0.0136	0.123	–	–	–	–	–	–	–	–
3.60	0.0200	–	0.077	–	–	–	–	–	–	–
4.00	0.0229	0.173	–	–	–	–	–	–	–	–
4.04	0.0231	–	–	0.460	–	–	–	–	–	–
6.10	0.0352	0.266	–	–	–	–	–	–	–	–
8.00	0.0466	0.327	–	–	–	–	–	–	–	–
8.15	0.0475	–	–	0.93	–	–	–	–	–	–
8.56	0.050	–	–	–	0.427	–	–	–	–	–
10.00	0.059	–	–	–	–	0.82	−0.203	–	–	–
10.20	0.060	0.385	–	–	–	–	–	–	–	–
12.20	0.073	0.550	–	–	–	–	–	–	–	–
12.46	0.074	–	–	1.49	–	–	–	–	–	–
16.41	0.099	–	–	1.85	–	–	–	–	–	–
16.50	0.100	–	–	–	0.79	–	–	–	–	–
20.00	0.123	–	–	–	–	2.41	−0.424	–	–	–
20.02	0.125	–	0.413	–	–	–	–	–	–	–
20.77	0.129	–	–	2.32	–	–	–	–	–	–
23.89	0.150	–	–	–	1.00	–	–	–	–	–
30.00	0.194	–	–	–	–	3.65	−0.68	–	–	–
30.78	0.200	–	–	–	1.27	–	–	–	–	–
35.50	0.240	–	1.06	–	–	–	–	–	–	–
37.22	0.250	–	–	–	1.56	–	–	–	–	–
40.00	0.272	–	–	–	–	–	−0.97	–	–	–
43.25	0.300	–	–	–	1.99	–	–	–	–	–
48.92	0.350	–	–	–	2.40	–	–	–	–	–
50.00	0.360	–	–	–	–	7.2	−1.35	–	–	–
54.25	0.400	–	–	–	2.80	–	–	–	–	–
59.27	0.450	–	–	–	3.24	–	–	–	–	–
65.50	0.515	–	2.87	–	–	–	–	–	–	–
Water + propan-1-ol										
0.80	0.0024	0.044	–	–	–	–	–	–	–	–
1.60	0.0049	0.072	–	–	–	–	–	–	–	–
2.40	0.0073	0.096	–	–	–	–	–	–	–	–
4.00	0.0123	0.158	–	–	–	–	–	–	–	–
6.10	0.0191	0.186	–	–	–	–	–	–	–	–
8.00	0.0254	0.228	–	–	–	–	–	–	–	–
10.20	0.0329	0.258	–	–	–	–	–	–	–	–
12.20	0.0400	0.293	–	–	–	–	–	–	–	–
Water + propan-2-ol										
1.94	0.0059	–	–	–	–	–	–	0.148	–	–
4.21	0.0130	–	–	–	–	–	–	0.304	–	–
8.21	0.0261	–	–	–	–	–	–	0.79	–	–

TABLE 1 (continued)

Co-solvent		Molecule transferred								
wt.%	Mole fraction	O_2	CO_2	Phen[a]	Ar	4-NA[b]	THC[c]	C_6H_6	H_2	He
Water + propan-2-ol										
10.02	0.0323	–	–	–	–	1.03	–	–	–	–
14.62	0.0488	–	–	–	–	–	–	1.54	–	–
17.94	0.062	–	–	–	–	–	–	1.92	–	–
20.02	0.070	–	–	–	–	3.28	–	–	–	–
24.90	0.090	–	–	–	–	–	–	3.95	–	–
30.02	0.113	–	–	–	–	6.3	–	–	–	–
31.88	0.123	–	–	–	–	–	–	6.9	–	–
42.93	0.184	–	–	–	–	–	–	10.1	–	–
45.48	0.200	–	–	–	–	9.1	–	–	–	–
50.02	0.231	–	–	–	–	9.6	–	–	–	–
51.58	0.242	–	–	–	–	–	–	11.7	–	–
Water + *t*-butyl alcohol										
9.54	0.025	0.169	–	–	0.64	–	–	–	–	–
10.00	0.263	–	–	–	–	1.13	–	–	–	–
10.60	0.028	–	−0.088	–	–	–	–	–	–	–
17.80	0.050	0.273	–	–	0.50	–	–	–	0.61	0.68
20.00	0.057	–	–	–	–	4.07	–	–	–	–
25.01	0.075	0.69	–	–	1.01	–	–	–	–	–
30.00	0.094	–	–	–	–	6.9	–	–	–	–
31.37	0.100	1.53	–	–	1.81	–	–	–	1.59	1.71
33.71	0.110	–	0.58	–	–	–	–	–	–	–
37.02	0.125	2.16	–	–	–	–	–	–	–	–
42.10	0.150	–	–	–	–	9.0	–	–	–	–
50.00	0.196	–	–	–	–	9.7	–	–	–	–
50.70	0.200	3.88	2.01	–	3.97	–	–	–	4.02	3.10
63.81	0.300	5.2	–	–	5.4	–	–	–	–	–
73.28	0.400	–	–	–	–	–	–	–	6.8	–
Water + ethane-1,2-diol										
10.00	0.0312	–	–	–	–	0.88	−0.163	–	–	–
30.00	0.111	–	–	–	–	2.63	−0.410	–	–	–
50.00	0.225	–	–	–	–	5.03	−0.63	–	–	–
Water + glycerol										
1.31	0.0026	0.091	–	–	–	–	–	–	–	–
2.52	0.0050	0.119	–	–	–	–	–	–	–	–
3.74	0.0075	0.173	–	–	–	–	–	–	–	–
6.16	0.0127	0.267	–	–	–	–	–	–	–	–
9.18	0.0194	0.392	–	–	–	–	–	–	–	–
10.00	0.0211	–	–	–	–	−0.35	–	–	–	–
12.21	0.0265	0.52	–	–	–	–	–	–	–	–
15.23	0.0340	0.66	–	–	–	–	–	–	–	–
18.26	0.0417	0.79	–	–	–	–	–	–	–	–
30.00	0.077	–	–	–	–	1.26	–	–	–	–
50.00	0.162	–	–	–	–	3.32	–	–	–	–

[a] 1,10-Phenanthroline.
[b] 4-Nitroaniline.
[c] Tris(hydroxymethyl)aminomethane.

scale for i = 4-nitroaniline [3] were converted to $\Delta G_t^{\ominus}(i)_n$ on the mole-fraction scale using eqn. (6) and the densities interpolated from the data of Kentämaa, Tommila and Martti [16]. These $\Delta G_t^{\ominus}(i)_n$ values on the mole-fraction scale are collected in Table 1.

Solubilities are available for oxygen, 4-nitroaniline and tris(hydroxymethyl)aminomethane in mixtures of water with polyhydroxy co-solvents. $\Delta G_t^{\ominus}(i)_n$ values for i = 4-nitroaniline on the mole-fraction scale are available for water + ethane-1,2-diol [17] and for water + glycerol [18], and for i = THC in the former mixtures [17]. The ratio of the solubilities of oxygen on the molar scale in water and in water + glycerol [8] have been used in eqns. (5) and (6) with densities interpolated from the data of Ernst, Watkins and Ruwe [19] and $M_s = 100/[(\text{wt.\% glycerol}/92.1) + (\text{wt.\% H}_2\text{O}/18.015)]$, to produce $\Delta G_t^{\ominus}(O_2)_n$ values on the mole-fraction scale. These latter values are given in Table 1 and the above values are included for comparison.

COMPARISON OF $\Delta G_t^{\ominus}(i)_n$, $\Delta G_t^{\ominus}(i)_e$ AND $\Delta G_t^{\text{int}}(i)_n$

The free energy of transfer of a single ion i is generally regarded as being composed of two separate free energies

$$\Delta G_t^{\ominus}(i) = \Delta G_t^{\ominus}(i)_n + \Delta G_t^{\ominus}(i)_e \tag{9}$$

where $\Delta G_t^{\ominus}(i)_e$ is the free energy of transfer of the charge on the ion and $\Delta G_t^{\ominus}(i)_n$ is the free energy of transfer of the electrically neutral bulk of the ion. It has often been assumed that $\Delta G_t^{\ominus}(i)_n$ will be given by the free energy of transfer of a 'neutral' molecule of the same size as the ion, yet a proviso must be included that the 'neutral' molecule is as nearly as possible chemically related to the ion [20]. Of the molecules listed in Table 1, Ar closely resembles K^+ and Cl^-, and He closely resembles Li^+. Figure 1 shows a comparison for water + methanol mixtures of $\Delta G_t^{\ominus}(Ar)_n$ with $\Delta G_t^{\ominus}(K^+)$ and $\Delta G_t^{\ominus}(Cl^-)$ derived using the spectrophotometric solvent-sorting method [21,22] and using the TATB/TPTB method [23] which assumes

$$\Delta G_t^{\ominus}(Ph_4As^+) = \Delta G_t^{\ominus}(Ph_4P^+) = \Delta G_t^{\ominus}(BPh_4^-) \tag{10}$$

As these latter values are on the molar scale, they were first converted to the mole-fraction scale using eqn. (6). A similar comparison is also made for water + *t*-butyl alcohol in Fig. 2, but at present $\Delta G_t^{\ominus}(K^+)$ and $\Delta G_t^{\ominus}(Cl^-)$ values are only available for the spectrophotometric solvent-sorting method [22,24]. For this latter mixture, Fig. 2 shows the comparison of $\Delta G_t^{\ominus}(He)$ and $\Delta G_t^{\ominus}(Li^+)$ values obtained using the same method [22,24]. Although $\Delta G_t^{\ominus}(K^+)$ and $\Delta G_t^{\ominus}(Cl^-)$ values in water + methanol from the two methods differ (the TATB/TPTB method tends to reduce the spread of $\Delta G_t^{\ominus}(i)$ with varying i [1]), they are all positive, in contrast with the negative $\Delta G_t^{\ominus}(Ar)$.

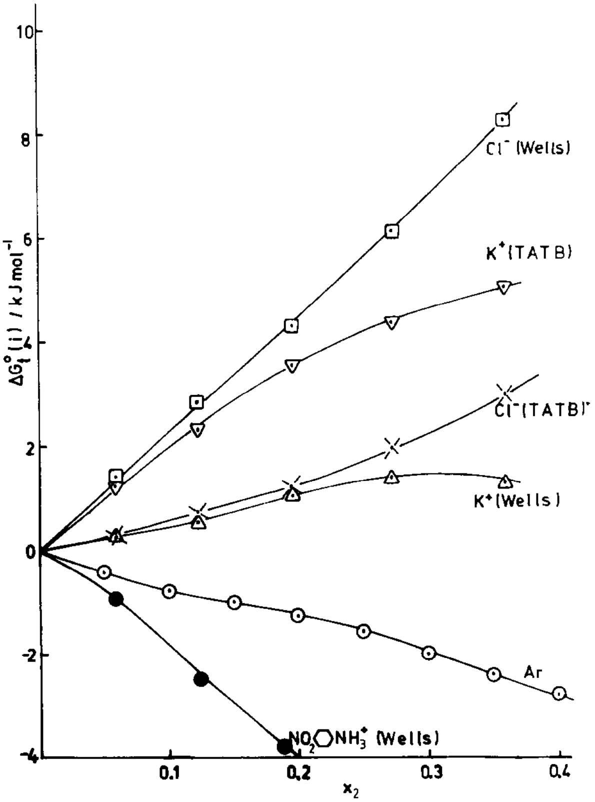

Fig. 1. $\Delta G_t^{\ominus}(i)$ in water + methanol: comparison of $\Delta G_t^{\ominus}(K^+)$ and $\Delta G_t^{\ominus}(Cl^-)$ with $\Delta G_t^{\ominus}(Ar)$, and the variation of $\Delta G_t^{\ominus}$(4-nitroanilinium) with mole fraction of methanol x_2 at 25 °C.

Figure 3 shows that $\Delta G_t^{\ominus}(K^+)_e$ and $\Delta G_t^{\ominus}(Cl^-)_e$ values obtained using eqns. (11) and (12)

$$\Delta G_t^{\ominus}(K^+)_e = \Delta G_t^{\ominus}(K^+) - \Delta G_t^{\ominus}(Ar) \tag{11}$$

$$\Delta G_t^{\ominus}(Cl^-)_e = \Delta G_t^{\ominus}(Cl^-) - \Delta G_t^{\ominus}(Ar) \tag{12}$$

are positive, although some small inaccuracies may arise in eqns. (11) and (12) due to the slight size differences. These positive values from eqns. (11) and (12) are in accord with the expectation from the simple Born approach for the transfer of either a positive or a negative charge from water to water + methanol treated as a dielectric continua: yet this accord does not extend to equal values for $\Delta G_t^{\ominus}(K^+)_e$ and $\Delta G_t^{\ominus}(Cl^-)_e$ expected from this simple approach for two ions of approximately the same size. Moreover, Fig. 3 shows that this observed accord does not extend to water + *t*-butyl alcohol mixtures with $x_2 \leq 0.15$ which possess a greater degree of structure formation than water + methanol mixtures [25]. Although $\Delta G_t^{\ominus}(Ar)$ is still negative in water + *t*-butyl alcohol, $\Delta G_t^{\ominus}(K^+)$ is more negative for $x_2 \leq 0.15$,

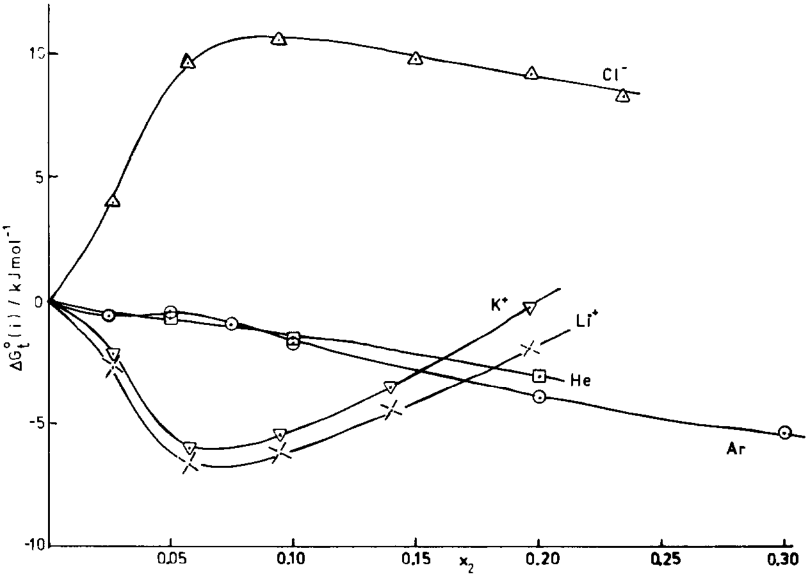

Fig. 2. Comparison of $\Delta G_t^{\ominus}(K^+)$ and $\Delta G_t^{\ominus}(Cl^-)$ with $\Delta G_t^{\ominus}(Ar)$, and of $\Delta G_t^{\ominus}(Li^+)$ with $\Delta G_t^{\ominus}(He)$ with varying mole fractions of *t*-butyl alcohol x_2 in mixtures with water at 25 °C.

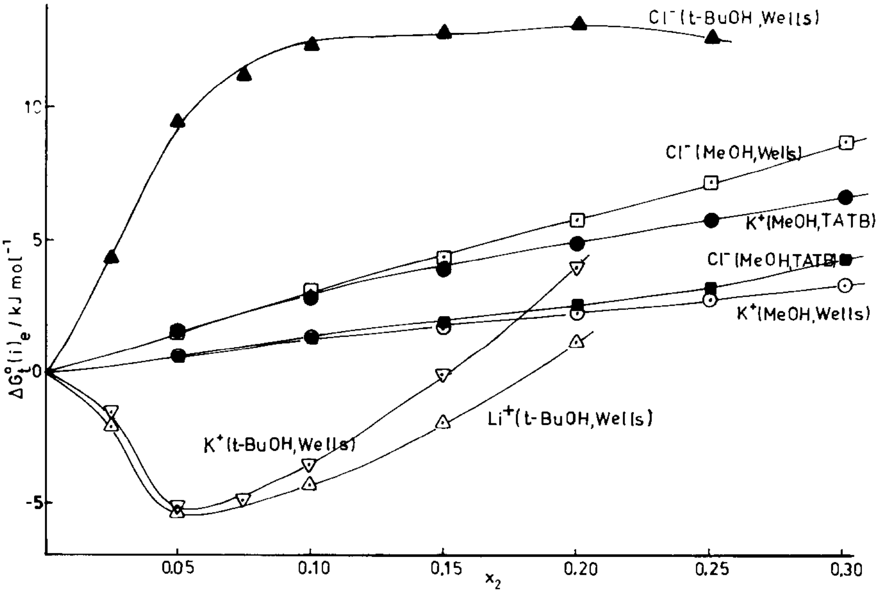

Fig. 3. Variation at 25 °C of $\Delta G_t^{\ominus}(K^+)_e$ and $\Delta G_t^{\ominus}(Cl^-)_e$ with mole fraction of methanol and *t*-butyl alcohol x_2 in mixtures with water, and the variation of $\Delta G_t^{\ominus}(Li^+)_e$ in water + *t*-butyl alcohol mixtures.

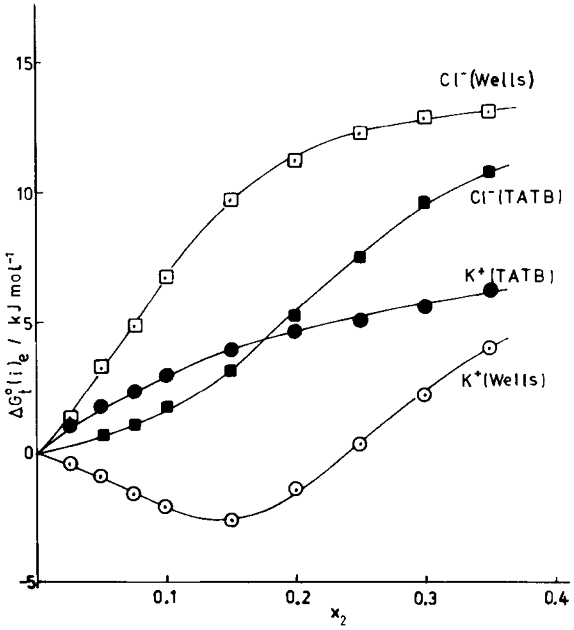

Fig. 4. Variation of $\Delta G_t^{\ominus}(K^+)_e$ and $\Delta G_t^{\ominus}(Cl^-)_e$ with mole fraction of ethanol x_2 in mixtures with water at 25 °C.

making $\Delta G_t^{\ominus}(K^+)_e$ from eqn. (11) also negative, whilst $\Delta G_t^{\ominus}(Cl^-)_e$ remains positive. Similarly, for water + *t*-butyl alcohol, $\Delta G_t^{\ominus}(He)$ is negative, with $\Delta G_t^{\ominus}(Li^+)$ more negative for $x_2 \leq 0.15$, making $\Delta G_t^{\ominus}(Li^+)_e$ negative. This result for small i^+ and i^- ions in water + *t*-butyl alcohol, with $\Delta G_t^{\ominus}(i^+)_e$ being negative at low x_2, tending towards positive values at higher x_2, and with $\Delta G_t^{\ominus}(i^-)_e$ being positive, is in agreement with the results for $\Delta G_t^{\ominus}(i^+)_e$ and $\Delta G_t^{\ominus}(i^-)_e$ with larger organic i^+ and i^- ions in these mixtures [26]. Like the small positive values in Fig. 3 for $\Delta G_t^{\ominus}(K^+)_e$ in water + methanol, $\Delta G_t^{\ominus}(i^+)_e$ for larger organic cations i^+ can be slightly positive or about zero at low x_2 [20], whereas $\Delta G_t^{\ominus}(i^-)_e$ values for larger organic anions i^- are positive [20], like $\Delta G_t^{\ominus}(Cl^-)_e$ in Fig. 3. It is interesting, therefore, to apply eqns. (11) and (12) to the data for $\Delta G_t^{\ominus}(K^+)$, $\Delta G_t^{\ominus}(Cl^-)$ and $\Delta G_t^{\ominus}(Ar)$ in water + ethanol. Figure 4 shows the results of this calculation using the data for $\Delta G_t^{\ominus}(K^+)$ and $\Delta G_t^{\ominus}(Cl^-)$ from the spectrophotometric solvent-sorting method [27] and from the TATB/TPTB method [28]; the same values [1] for $\Delta G_t^{\ominus}(Ar)$ were used in both cases. Although $\Delta G_t^{\ominus}(K^+)_e$(TATB) is positive, $\Delta G_t^{\ominus}(K^+)_e$ from the solvent-sorting method is first negative at low x_2, becoming positive at higher x_2, as in Fig. 3 for water + *t*-butyl alcohol and like $\Delta G_t^{\ominus}(i^+)$ for larger organic cations i^+ in water + ethanol [20]. $\Delta G_t^{\ominus}(K^+)_e$(TATB) remains positive at low x_2, but the TATB/TPTB method which uses the assumption in eqn. (10), contracts [1,20] the overall spread of $\Delta G_t^{\ominus}(i)$ values from that found using the solvent-sorting method [27,28].

$\Delta G_t^{\ominus}(\mathrm{Cl}^-)_e$ values calculated using either method are positive, in conformity with the results for larger organic anions i^- [20]. The minimum values at low x_2 found for $\Delta G_t^{\ominus}(\mathrm{K}^+)_e$ using the solvent-sorting method in water + ethanol and water + *t*-butyl alcohol, combined with the absence of such a minimum for water + methanol, occur in the same order of x_2 as the solvent compositions where rapid structural changes occur in the water-rich mixtures. This is indicated by the change in mole fraction of co-solvent at the minimum and in the magnitude of the minimum in the relative partial molar volume of the alcohol, $\bar{V}_2 - V_2^{\ominus}$ [29], in the maximum in the ultrasonic absorption [30], and by the deviation of the excess enthalpy of mixing, $\Delta H_{\mathrm{mix}}^{\mathrm{E}}$, from $x_2 \simeq 0.5$ [16,31]: all these properties indicate little or no effect for methanol, some effect for ethanol and more for *t*-butyl alcohol, occurring at lower x_2 values in the series of mixtures.

As $\Delta G_t^{\ominus}(i^+)_e$ is known for i = 4-nitroaniline in water + methanol mixtures, values for $\Delta G_t^{\ominus}(i^+)$ can be computed for this solute using eqn. (9) and $\Delta G_t^{\ominus}(i)_n$ for i = 4-nitroaniline in Table 1. Figure 1 shows that this is negative, as found for other large organic cations in water + methanol [21,22].

The application of eqn. (3) in the calculation of $\Delta G_t^{\mathrm{int}}(i)_n$ depends on the assumption that $(G_s^{\mathrm{cav}} - G_w^{\mathrm{cav}}) \simeq$ zero in water-rich conditions in the mixtures. The variations with solvent composition of the relative partial molar volume of water, $\bar{V}_1 - V_1^{\ominus}$, at 25 °C in water + methanol [32], water + propan-2-ol [33], water + *t*-butyl alcohol [16] and in water + ethane-1,2-diol [34] show little deviation from zero in water-rich conditions, in contrast to the sharp changes in the relative partial molar volume of the co-solvent, $\bar{V}_2 - V_2^{\ominus}$, in the same conditions. Figure 5 shows the results of the calculation of $\bar{V}_1 - V_1^{\ominus}$ and $\bar{V}_2 - V_2^{\ominus}$ for water + propan-1-ol and water + glycerol at 25 °C. Although all the density data at 25 °C for water + propan-1-ol mixtures [11,35,36] are in good agreement, only those of Gonzalez-Salazar [36] are sufficiently extensive in water-rich conditions to be used in these calculations: the density data of Ernst, Watkins and Ruwe [19] were used in the calculations for water + glycerol mixtures. Like the other mixtures above, $\bar{V}_1 - V_1^{\ominus}$ deviates little from zero at high water content, in contrast with the variations in $\bar{V}_2 - V_2^{\ominus}$, particularly in water + propan-1-ol. This lack of change in $\bar{V}_1 - V_1^{\ominus}$ from zero in water-rich conditions, where there is little chance of the co-solvent molecules being involved in cavity formation and collapse, strongly suggests that the assumption used as a basis for eqn. (3), namely that $(G_s^{\mathrm{cav}} - G_w^{\mathrm{cav}})$ is zero, is reasonable for $x_2 < 0.2$, as has been found with water + ethanol mixtures [1].

$\Delta G_t^{\mathrm{int}}(i)_n$ values have therefore been calculated for all the neutral molecules in all the solvent mixtures using eqns. (3) and (4). The densities used in eqn. (4) for mixtures of water with methanol, propan-1-ol, propan-2-ol, *t*-butyl alcohol and glycerol were interpolated as described above. Densities for mixtures of water with ethane-1,2-diol were interpolated from a plot of

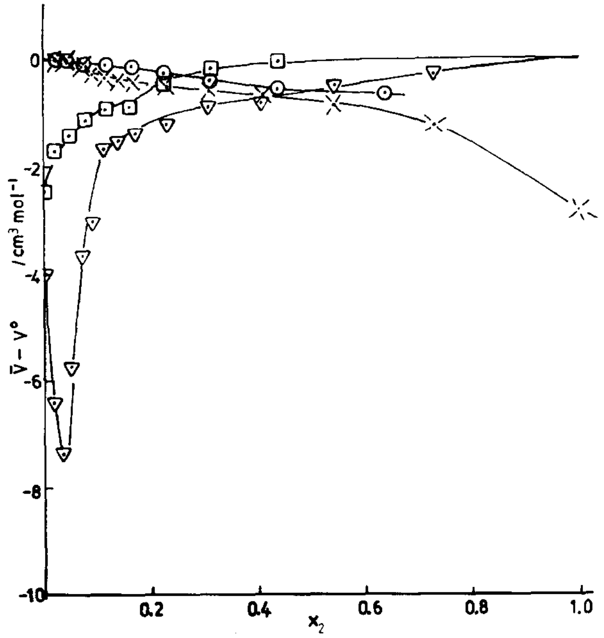

Fig. 5. Variation at 25 °C of the relative partial molar volumes of water $\bar{V}_1 - V_1^{\ominus}$ and of co-solvent $\bar{V}_2 - V_2^{\ominus}$ with mole fraction of co-solvent x_2 in mixtures with water: $\bar{V}_1 - V_1^{\ominus}$, glycerol (⊙) and propan-1-ol (×); $\bar{V}_2 - V_2^{\ominus}$, glycerol (⊡) and propan-1-ol (▽).

density versus solvent composition using data available in the literature [37]. Plots of $\Delta G_t^{\text{int}}(i)_n$ against mole fraction of co-solvent are shown in Figs. 6–9 for the various co-solvents in water-rich conditions. In Fig. 6, $\Delta G_t^{\text{int}}(i)_n$ values at low x_2 in water + methanol, with the exception of THC, display the same behaviour as found previously for water + ethanol [1]: low negative values for inorganic molecules with higher negative values, becoming higher as x_2 increases, for large organic molecules. The exception, tris(hydroxymethyl)aminomethane, has a positive $\Delta G_t^{\text{int}}(i)_n$, becoming increasingly positive as x_2 increases: no positive values were found in water + ethanol [1]. Presumably, the re-organisation of solvent molecules in the mixture caused by the three hydroxyl groups results in a de-stabilisation relative to the situation in water. Figure 8, for water + *t*-butyl alcohol, also has low negative values for inorganic molecules, with $\Delta G_t^{\text{int}}(i)_n \simeq$ zero or slightly positive for some *i*, and with higher negative values for the large organic molecule; this is similar to the situations found in water + methanol (Fig. 6) and in water + ethanol [1]. The data for the other co-solvents are much more sparse than those available for methanol, ethanol or *t*-butyl alcohol as co-solvent. Nevertheless, they give good support to the general variation found with the other co-solvents: for both propanols, glycerol and ethane-1,2-diol, negative values, becoming more negative as x_2 increases, are found for large organic molecules, with perhaps $\Delta G_t^{\text{int}}(i)_n \sim$ zero for $i =$

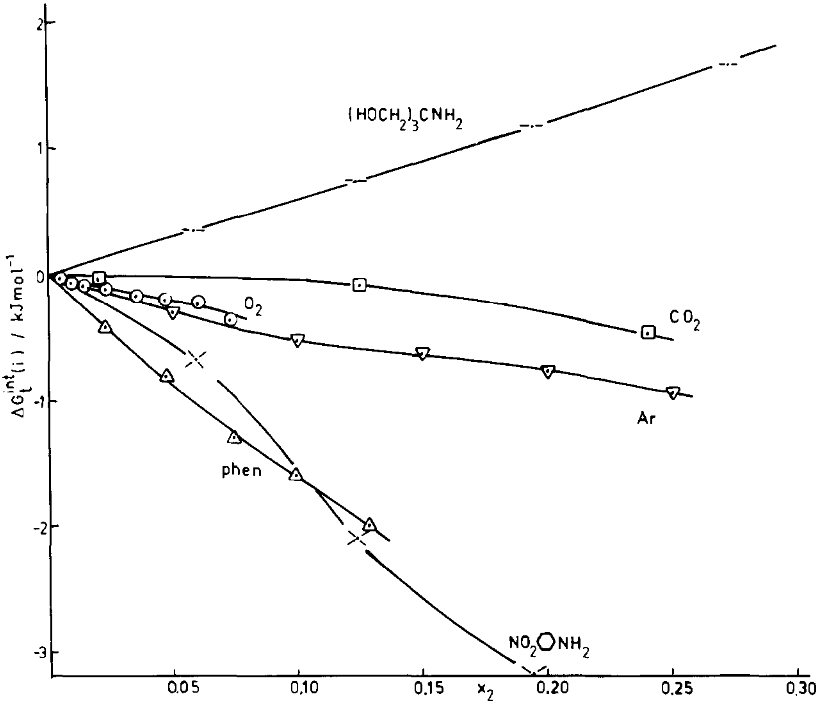

Fig. 6. Variation of $\Delta G_t^{int}(i)_n$ for inorganic and organic solutes at 25 °C with mole fraction of methanol in mixtures with water.

4-nitroaniline at $x_2 < 0.1$ in water + glycerol; and, although $\Delta G_t^{int}(O_2)$ is not available above $x_2 \sim 0.05$ for propan-1-ol or glycerol, only low negative values are found. Again, as in water + methanol, $\Delta G_t^{int}(i)_n$ for $i =$

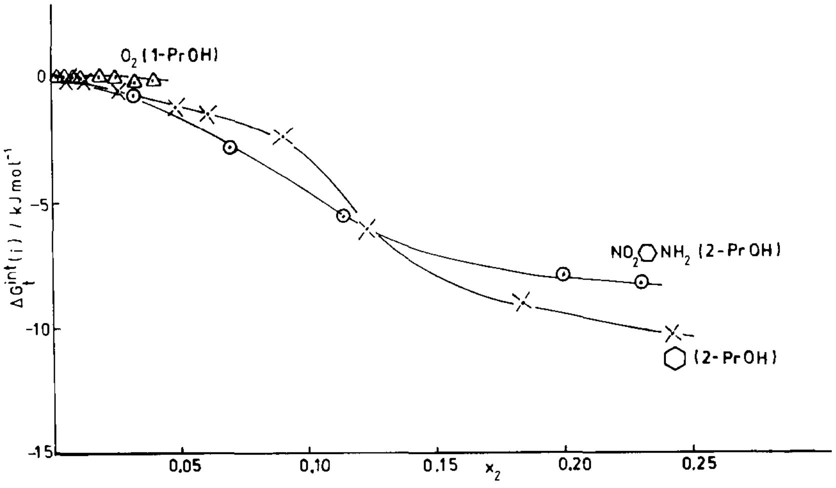

Fig. 7. Variation with mole fraction of alcohol of $\Delta G_t^{int}(i)_n$ at 25 °C for molecular oxygen in water + propan-1-ol, and for 4-nitroaniline and benzene in water + propan-2-ol.

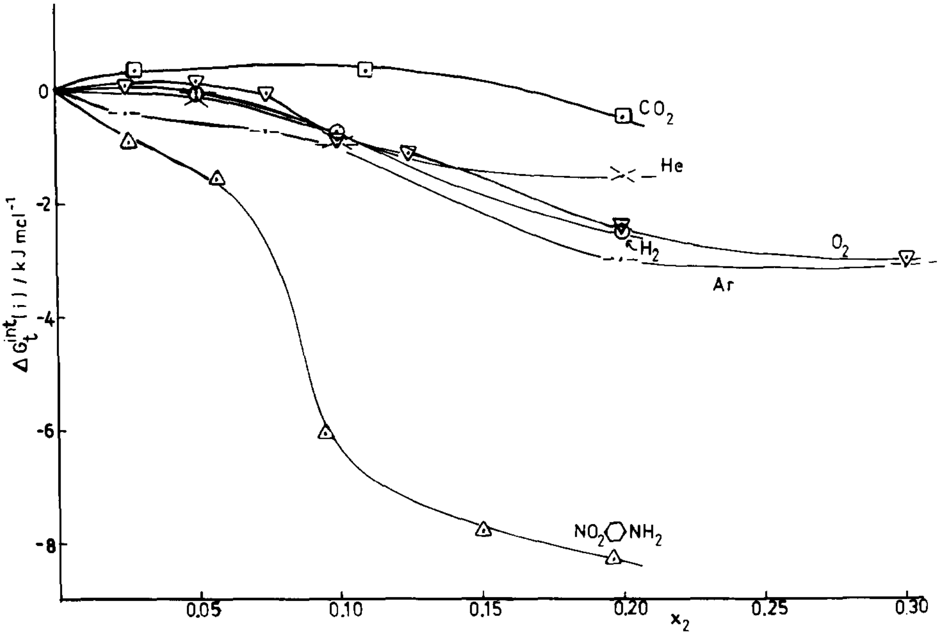

Fig. 8. Variation of $\Delta G_t^{int}(i)_n$ at 25° C for inorganic solutes and for 4-nitroaniline with mole fraction of *t*-butyl alcohol in mixtures with water.

tris(hydroxymethyl)aminomethane is positive for water + ethane-1,2-diol, presumably for the same reasons.

It is concluded, therefore, for mixtures of water with hydroxylic co-solvents

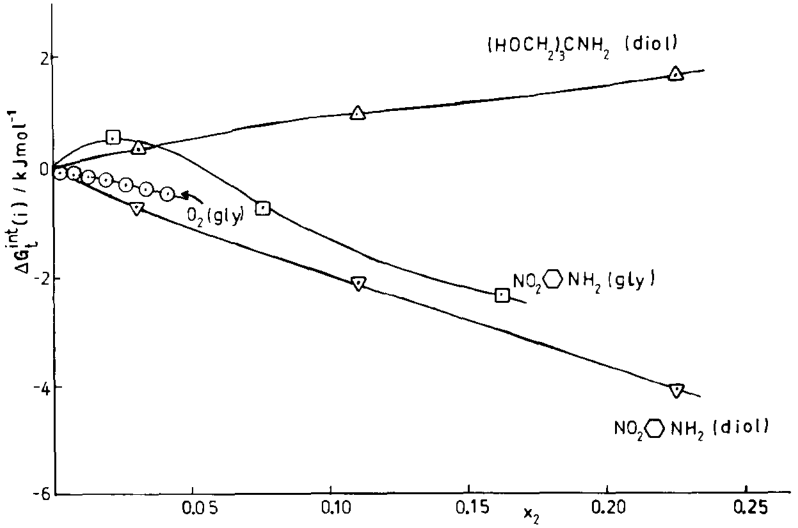

Fig. 9. Variation with mole fraction of multi-hydroxy co-solvent of $\Delta G_t^{int}(i)_n$ for molecular oxygen and 4-nitroaniline in water + glycerol, and for tris(hydroxymethyl)aminomethane in water + ethane-1,2-diol.

at low x_2, that little reorganisation of solvent is required when an inorganic molecule (excluding I_2 for water + ethanol [1]) is transferred from water and that which does occur results in a small stabilisation in the mixture. Larger organic molecules appear to involve reorganisation of solvent molecules upon transfer into the mixtures which leads to stabilisation in the mixture, with the results in water + ethanol indicating that the extent of the stabilisation increases with increasing size of the molecule transferred. The transfer of a multi-hydroxy molecule into the mixture results in a destabilisation.

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