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IONIC SOLVATION IN WATER + CO-SOLVENT MIXTURES.
PART 17. THE "NEUTRAL" COMPONENT OF FREE ENERGIES OF TRANSFER OF SINGLE IONS FROM WATER INTO WATER + ETHANOL MIXTURES

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ABSTRACT

The influence of the contribution to the total free energy of transfer of an ion i $\Delta G_t^\ominus(\text{i})$ arising from the transfer of the neutral bulk of the ion $\Delta G_t^\ominus(\text{i})_n$ is assessed. Values for $\Delta G_t^\ominus(\text{i})_n$ for a range of inorganic and organic molecules, in the transfer water → water + ethanol mixtures, are calculated from the solubilities of the gaseous molecules in general, and of solid molecules in one case. $\Delta G_t^\ominus(\text{i})_n$ is then compared with $\Delta G_t^\ominus(\text{i})$ previously determined for ions. By using the basic relationship of scaled particle theory, after eliminating the contribution from the free energy of cavity formation by restricting consideration to the transfer to water-rich mixtures only, experimental values for the specific effect of changes in solvent composition on the interaction of the neutral bulk of i with the solvent are obtained. It is shown that this latter contribution to $\Delta G_t^\ominus(\text{i})$ is small for simple inorganic ions, leaving the free energy of transfer of the charge alone $\Delta G_t^\ominus(\text{i})_e$ dominant in determining $\Delta G_t^\ominus(\text{i})$. For more complex ions containing organic groups, the contribution of $\Delta G_t^\ominus(\text{i})_n$ to $\Delta G_t^\ominus(\text{i})$ begins to compare with $\Delta G_t^\ominus(\text{i})_e$, depending on the size of the organic groups.

INTRODUCTION

Several attempts have been made to assess the contribution of the "neutral" and "electrostatic" components to the free energies of transfer of single ions. If $\Delta G_t^\ominus(\text{i})$ is the total free energy of transfer of an ion i, the two components, "neutral" (with subscript n) due to the ionic bulk, and "electrostatic" (with subscript e) arising from the charge on the ion, arise as follows

$$\Delta G_t^\ominus(\text{i}) = \Delta G_t^\ominus(\text{i})_n + \Delta G_t^\ominus(\text{i})_e \qquad (1)$$

In one approach, $\Delta G_t^\ominus(\text{i})_n$ has been estimated experimentally by determining free energies of transfer of neutral molecules of similar size and similar (but not identical) chemical constitution, e.g. organometallic compounds, interpolating for mixtures from the free energy of transfer between water

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and the other pure liquid [1] or by measuring directly this free energy of transfer for the mixture [2]. The contribution $\Delta G_t^{\ominus}(\mathrm{i})_e$ is then determined using treatments resulting in inverse dependences on the radius of the species transferred or by difference between $\Delta G_t^{\ominus}(\mathrm{i})$ and $\Delta G_t^{\ominus}(\mathrm{i})_n$ [1,2]. Attempts have also been made to show that scaled particle theory [3], using a hard sphere solute in a mixture of hard sphere solvent molecules, applies to solutions in water and its mixtures with alcohols [4], even though strong reservations must exist on its direct applicability to such structured liquids.

Alternatively, $\Delta G_t^{\ominus}(\mathrm{i})_e$ has been determined for larger molecules using acid–base equilibrium constants for a positively charged acid A^+ providing a neutral conjugate base B or for a neutral acid A providing a negatively charged conjugate base B^- [5]. If the molecules are large, then the neutral member of the conjugate pair is very close in size and structure to the charged member. For the first pair

$$\Delta G_t^{\ominus}(A^+) = \Delta G_t^{\ominus}(A^+) - \Delta G_t^{\ominus}(B) = RT\ \ln(K_s/K_w) + \Delta G_t^{\ominus}(H^+) \qquad (2)$$

and for the latter pair

$$\Delta G_t^{\ominus}(B^-)_e = \Delta G_t^{\ominus}(B^-) - \Delta G_t^{\ominus}(A) = RT\ \ln(K_w/K_s) - \Delta G_t^{\ominus}(H^+) \qquad (3)$$

Attention has recently been directed [6] to estimates of $\Delta G_t^{\ominus}(\mathrm{i})_e$ made using this method for water + ethanol, because values for $\Delta G_t^{\ominus}(H^+)$ required in eqns. (2) and (3) are roughly comparable in the range of mole fraction of ethanol $x_2 \sim 0.28$–0.40 as determined by the spectrophotometric solvent sorting method [7], the TATB reference ion method which assumes $\Delta G_t^{\ominus}(Ph_4As^+) = \Delta G_t^{\ominus}(BPh_4^-)$ [8] or the TAB method with $\Delta G_t^{\ominus}$ (triisoamyl(n-Bu)N^+) = $\Delta G_t^{\ominus}(BPh_4^-)$ [8]. It was therefore thought to be instructive to calculate values for the free energies of transfer of neutral molecules in the same mixtures for comparison with these values for $\Delta G_t^{\ominus}(\mathrm{i})_e$.

THE CALCULATION OF $\Delta G_t^{\ominus}(\mathrm{i})_n$ IN WATER + ETHANOL MIXTURES

$\Delta G_t^{\ominus}(\mathrm{i})_n$ can be calculated from the solubilities of the gaseous solute under standard conditions in water ($s_w^{\ominus}$) and in the mixture ($s_s^{\ominus}$) using

$$\Delta G_t^{\ominus}(\mathrm{i})_n = RT\ \ln\left(s_w^{\ominus}/s_s^{\ominus}\right) + C \qquad (4)$$

As $\Delta G_t^{\ominus}(\mathrm{i})_n$ is required on the mole fraction scale, the value for C depends on the units used for $s^{\ominus}$. If $s^{\ominus}$ is on the molar scale, $C = RT\ \ln(18.015\ d_s/M_s\ d_w)$, where d is density and $M_s = 100/[(\text{wt\% co-solvent}/46.07) + (\text{wt\% } H_2O/18.015)]$, and if $s^{\ominus}$ is on the molality scale, $C = RT\ \ln(18.015/M_s)$. Alternatively, if $\Delta\mu^{\ominus}$ is the difference between the standard chemical potential of i between the liquid and vapour phases in either water (w) or the mixture (s)

$$\Delta G_t^{\ominus}(\mathrm{i})_n = \Delta\mu_s^{\ominus} - \Delta\mu_w^{\ominus} + C \qquad (5)$$

with corrections C used as appropriate to the scale used for $\mu^{\ominus}$.

For the hydrocarbon molecules both methods were used. For methane and ethane, tabulated values [9] of $\Delta\mu^{\ominus}$ at 25 °C on the molar scale were inserted into eqn. (5) with the calculated values for C using the interpolated densities for water + ethanol mixtures [10]. For butane, propane, cyclopropane, 2-methylpropane, 2,2-dimethylpropane and propene, values for log $s^{\ominus}$ (cm^3 kg^{-1}) are available [11] for a range of temperatures. For each solute at each solvent composition, log $s^{\ominus}$ was plotted against T (K) and the value of log $s^{\ominus}$ was interpolated for 278.15 K. These were substituted into eqn. (4) and corrected from the molality scale to the mole fraction scale. The values for $\Delta G_t^{\ominus}(i)_n$ so obtained are collected in Table 1.

Data are available for two inert gases. For argon, plots of log $s^{\ominus}$ (cm^3 kg^{-1}) against composition are available [12] for a range of temperatures, and values of log $s^{\ominus}$ were read from these for suitable values of x_2. These were then plotted against T (°C) for each composition and the values for log $s^{\ominus}$ interpolated at 25 °C were inserted into eqn. (4) together with $C = RT \ln(18.015/M_s)$. Values for $\Delta\mu^{\ominus}(Ar)$ on the molar scale are available [13], from which $\Delta G_t^{\ominus}(Ar)$ was calculated using eqn. (5) with $C = RT \ln(18.015\ d_s/M_s\ d_w)$. For helium the same procedure was followed for the graphs available of $\Delta\mu^{\ominus}$ (on the mole fraction scale) versus x_2 [14] for a range of temperatures, and the graphically interpolated $\Delta\mu^{\ominus}$ at 25 °C was inserted into eqn. (5) with $C = 0$.

For polyatomic inorganic molecules, three sets of data are available for O_2, with one each for CO_2, H_2 and I_2 (using the solid in the latter case). For molecular oxygen, one set of data [15] gives the ratio of the solubilities in various water + ethanol compositions relative to that in pure water, from which $\Delta G_t^{\ominus}(O_2)$ on the molar scale can be derived and converted to the mole fraction scale. Another set provides plots of log $s^{\ominus}$ (cm^3 kg^{-1}) against T (°C) for a range of compositions [16]. From these plots at each composition, the value of log $s^{\ominus}$ at 25 °C was interpolated and substituted into eqn. (4) with $C = RT \ln(18.015/M_s)$. Ostwald coefficients are also known at 25 °C for molecular oxygen dissolved in water + ethanol mixtures [17]. $\Delta G_t^{\ominus}(O_2)$ on the molar scale was calculated from these values and converted to the mole fraction scale. The data for $\Delta\mu^{\ominus}$ for H_2 were treated in the same way as for helium above. Cargill and MacPhee [18] provide solubility data for CO_2 in water + ethanol on the mole fraction scale from which $\Delta G_t^{\ominus}(CO_2)$ was calculated using eqn. (4) with $C = 0$. Solubilities in g per 100 g of solution for molecular iodine [19] in water + ethanol were first converted to molalities and then to $\Delta G_t^{\ominus}(I_2)$ using eqn. (4) with $C = RT \ln(18.015/M_s)$. Solubilities for CO in water + ethanol mixtures were interpolated for various compositions using the relationship and data provided by Dake and Chaudhari [20]. $\Delta G_t^{\ominus}(CO)$ was then calculated on the mole fraction scale using $C = RT \ln(18.015\ d_s/M_s\ d_w)$ in eqn. (4).

All these values calculated for $\Delta G_t^{\ominus}(i)_n$ on the mole fraction scale are collected in Table 1. Also included for comparison are the values of the free

TABLE 1

Variation in $-\Delta G_t^{\ominus}(\mathrm{i})_n$ for the transfer of neutral species from water into water + ethanol mixtures at 25 ° C

Mole fraction EtOH x_2	Molecule transferred							
	CO	H_2	He	Ar	O_2	I_2	CO_2	CH_4
0.0031	–	–	–	–	0.027 [a]	–	–	–
0.0063	–	–	–	–	0.077 [a]	–	–	–
0.0095	–	–	–	–	0.101 [a]	–	–	–
0.0149	–	–	–	–	–	0.384	–	–
0.0160	–	–	–	–	0.158 [a]	–	–	–
0.020	–	–	–	–	0.216 [c]	–	–	0.276
0.025	–	–	–	0.266 [e]	0.223 [a]	–	–	–
0.025	–	–	–	0.244 [d]	0.152 [b]	–	0.378	–
0.027	–	–	–	–	0.256 [c]	–	–	–
0.030	–	–	–	–	–	–	–	0.383
0.033	–	–	–	–	0.271 [a]	0.87	–	–
0.040	0.52	–	–	–	–	–	–	–
0.0425	–	–	–	–	0.324 [a]	–	–	–
0.045	–	–	–	–	–	–	–	0.490
0.050	–	–	–	0.483 [e]	0.352 [b]	–	–	–
0.050	–	–	–	0.402 [d]	–	–	–	–
0.052	–	–	–	–	0.371 [a]	1.33	0.378	–
0.053	–	–	–	–	0.364 [c]	1.35	–	–
0.060	–	–	–	–	–	–	–	0.59
0.062	–	–	–	–	–	–	–	–
0.069	0.89	–	–	–	–	–	–	–
0.071	–	–	–	–	–	1.85	–	–
0.075	–	–	–	0.53 [c]	0.440 [b]	–	–	–
0.075	–	–	–	0.53 [d]	–	–	–	–
0.090	–	–	–	–	0.51 [c]	–	–	0.82
0.094	–	–	–	–	–	2.65	–	–
0.096	–	–	–	–	0.53 [c]	–	–	–
0.098	–	–	–	–	–	–	–	–
0.100	–	0.59	–	0.70 [e]	–	–	0.445	–
0.100	–	–	0.41	0.64 [d]	0.485 [b]	–	–	–
0.106	–	–	–	–	0.56 [c]	3.00	–	–
0.120	1.49	–	–	–	–	3.77	–	1.11
0.125	–	–	–	0.84 [e]	0.65 [b]	4.06	–	–
0.125	–	–	–	0.80 [d]	0.76 [c]	–	–	–
0.129	–	–	–	–	–	4.39	–	–
0.145	–	–	–	–	–	5.1	–	–
0.148	–	–	–	–	–	5.4	–	–
0.150	–	–	–	1.01 [d]	–	–	–	1.50
0.155	–	–	–	–	–	5.7	–	–
0.159	1.94	–	–	–	–	–	–	–
0.168	–	–	–	–	–	–	–	–
0.172	–	–	–	–	–	6.4	–	–
0.175	–	–	–	1.29 [d]	–	–	–	–
0.185	–	–	–	–	–	7.0	–	–

C_2H_6	C_3H_8	C_4H_{10}	Cyclo- C_3H_6	2-Me- C_3H_7	2,2-diMe- C_3H_6	Propene	NO_2  NH_2
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
0.364	0.373	0.339	–	–	–	–	–
–	–	–	–	0.70	0.73	–	–
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
0.52	–	–	–	–	–	–	–
–	–	–	0.480	–	–	0.469	–
–	0.72	0.81	–	–	–	–	–
–	–	–	–	–	–	–	0.84
0.65	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
0.86	–	–	–	–	–	–	–
–	–	–	–	1.26	1.44	–	–
–	1.18	1.46	–	–	–	–	–
–	–	–	0.97	–	–	0.86	–
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
1.24	–	–	1.19	–	–	1.12	2.34
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
–	1.61	2.10	–	–	–	–	–
–	–	–	–	1.75	2.19	–	–
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
1.76	2.18	2.93	1.67	–	–	–	–
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
–	–	–	–	2.94	3.67	–	–
–	–	–	–	–	–	–	4.56
–	–	–	2.52	–	–	2.57	–
2.47	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
3.58	–	4.75	–	–	–	–	–
–	–	–	–	5.3	6.7	–	–
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
–	–	–	2.79	–	–	3.71	–

(continued)

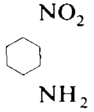
TABLE 1 (continued)

Mole fraction EtOH x_2	Molecule transferred							
	CO	H_2	He	Ar	O_2	I_2	CO_2	CH_4
	NH_2							
0.189	–	–	–	–	1.45 [c]	7.3	–	–
0.200	–	1.38	1.08	1.64 [e]	–	7.7	–	2.38
0.200	–	–	–	1.65 [d]	1.48 [b]	–	–	–
0.206	2.46	–	–	–	–	–	0.86	–
0.216	–	–	–	–	–	8.4	–	–
0.226	–	–	–	2.02 [d]	–	–	–	–
0.236	–	–	–	–	–	9.0	–	–
0.250	–	–	–	2.22 [d]	–	–	–	3.22
0.272	–	–	–	–	–	10.2	–	–
0.281	–	–	–	–	–	–	–	–
0.300	–	–	–	2.89 [e]	2.99 [b]	–	–	–
0.317	–	–	–	–	3.01 [c]	–	–	–
0.322	–	–	–	–	–	–	–	–
0.396	–	–	–	–	–	–	–	–
0.400	4.38	3.12	2.65	4.15 [e]	4.10 [b]	–	–	5.3
0.405	–	–	–	–	–	13.2	–	–
0.415	–	–	–	–	–	13.8	–	–
0.434	–	–	–	–	–	14.4	–	–
0.471	–	–	–	–	–	15.2	–	–
0.477	–	–	–	–	4.58 [c]	–	–	–
0.500	–	–	–	5.0 [e]	4.89 [b]	–	–	–
0.508	–	–	–	–	–	16.1	–	–
0.527	–	–	–	–	–	–	3.55	–
0.533	–	–	–	–	–	17.0	–	–
0.547	–	–	–	–	–	17.8	–	–
0.595	–	–	–	–	–	18.2	–	–
0.600	6.1	–	–	5.7 [e]	5.6 [b]	–	–	7.2
0.711	–	–	–	–	6.3 [c]	–	–	–
0.800	7.5	5.7	5.0	–	–	–	–	8.6
0.866	–	–	–	–	7.1 [c]	–	–	–
0.880	–	–	–	–	7.2 [c]	–	–	–
0.951	–	–	–	–	7.5 [c]	–	–	–
0.971	–	–	–	–	7.7 [c]	–	–	–
0.998	–	–	–	–	8.4 [c]	–	6.2	–

energy of transfer for 4-nitroaniline from water into water + ethanol calculated by Bose and Kundu [21] on the molar scale and converted to the mole fraction scale by adding $RT\ \ln(18.015\ d_s/M_s\ d_w)$ to these values.

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

Table 1 shows that $\Delta G_t^{\ominus}(\text{i})_n$ for all the neutral species investigated are negative in water + ethanol. This compares well with free energies of trans-

C_2H_6	C_3H_8	C_4H_{10}	Cyclo-C_3H_6	2-Me-C_3H_7	2,2-diMe-C_3H_6	Propene	NO_2  NH_2
–	–	–	–	–	–	–	–
3.86	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
–	5.5	7.2	–	–	–	–	–
–	–	–	–	7.9	9.4	–	–
–	–	–	4.59	–	–	4.76	–
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	9.0
–	8.4	10.8	–	–	–	–	–
–	–	–	–	11.1	13.2	–	–
–	–	–	6.7	–	–	7.0	–
–	10.3	12.9	–	–	–	–	–
7.9	–	–	–	–	–	–	10.5
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	11.3
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
10.1	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
11.8	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–

Solubility or $\Delta\mu^{\ominus}$ data taken from: [a] ref. 15; [b] ref. 16; [c] ref. 17; [d] ref. 13; [3] ref. 12.

fer for a variety of neutral inorganic and organic molecules from water into other pure solvents [1,2] and into mixtures of such pure solvents with water [1,2,22,23].

The inert gas molecules should provide a good neutral model for the ions either side of them in the Periodic Table possessing the same extra-nuclear electronic structure. The only match of $\Delta G_t^{\ominus}(i)_n$ with $\Delta G_t^{\ominus}(i)$ available here

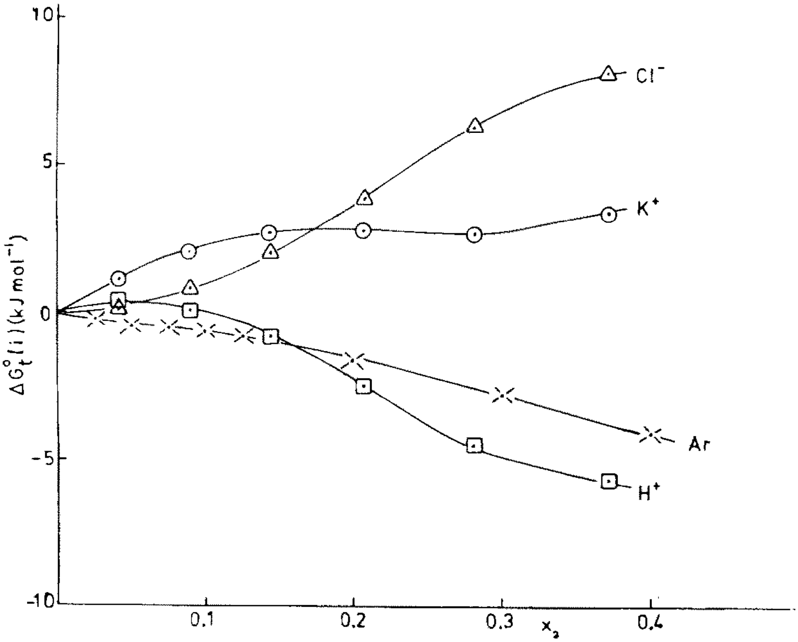


Fig. 1. Comparison at 25 °C of $\Delta G_t^\ominus(K^+)$ (⊙), $\Delta G_t^\ominus(Cl^-)$ (△) and $\Delta G_t^\ominus(H^+)$ (⊡) derived using the TATB assumption with $\Delta G_t^\ominus(Ar)$ (>·<) in water + ethanol mixtures.

for simple ions in water + ethanol is Ar for K^+ and Cl^- ions. Figure 1 shows $\Delta G_t^\ominus(K^+)$ and $\Delta G_t^\ominus(Cl^-)$, calculated from the activity coefficients derived using the TATB assumption [24] for separation into single ions and converted to the mole fraction scale, compared with the values for $\Delta G_t^\ominus(Ar)$ in Table 1. Figure 2 shows the same comparison for $\Delta G_t^\ominus(K^+)$ and $\Delta G_t^\ominus(Cl^-)$ calculated using the spectrophotometric solvent sorting method [25] for the separation of $\Delta G_t^\ominus$(salt) into values for individual ions. These comparisons show that, irrespective of the method used in separating $\Delta G_t^\ominus$(salt) into $\Delta G_t^\ominus(K^+)$ and $\Delta G_t^\ominus(Cl^-)$, the contribution of the free energy of transfer of the charge alone ($\Delta G_t^\ominus(i)_e$) as defined by eqn. (1), cannot be described as small, as suggested [2] for the transfer of other larger ions from water into a series of pure liquids and into water + acetonitrile and water + dimethylformamide mixtures. Moreover, Figs. 1 and 2 suggest that $\Delta G_t^\ominus(K^+)_e$ differs considerably from $\Delta G_t^\ominus(Cl^-)_e$. As the charges cause K^+ and Cl^- to differ slightly in size from Ar, no attempt is made to assess quantitatively the contributions of $\Delta G_t^\ominus(i)_e$ to $\Delta G_t^\ominus(i)$ in each case. However, this slight difference in size will not invalidate the above general conclusions for K^+ and Cl^-. These conclusions are similar to those derived from a direct determination of $\Delta G_t^\ominus(A^+)_e$ and $\Delta G_t^\ominus(B^-)_e$ for large organic ions using eqns. (2) and (3) [6].

In comparing $\Delta G_t^\ominus(i)_n$ for polyatomic inorganic molecules with $\Delta G_t^\ominus(i)_n$ for the monatomic inorganic molecules in Table 1, it is clear that there is no

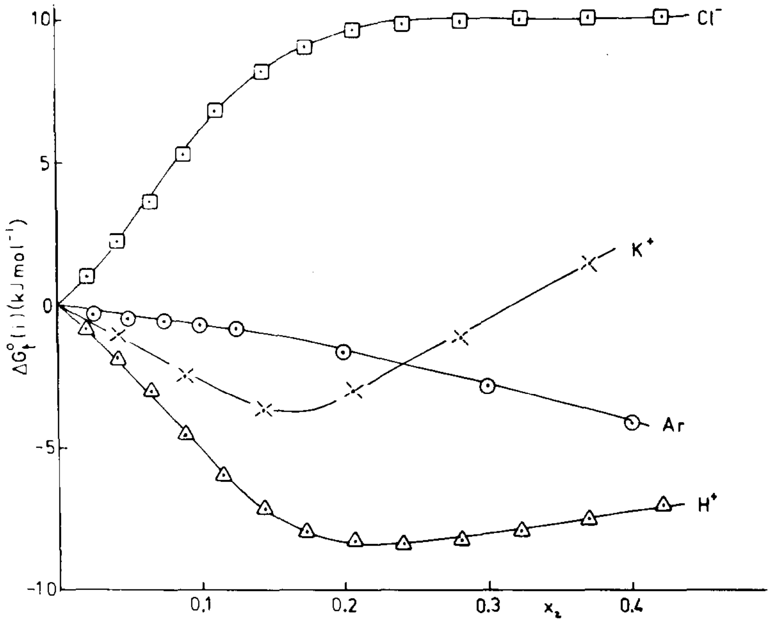


Fig. 2. Comparison at 25 °C of $\Delta G_t^\ominus(K^+)$ (>·<), $\Delta G_t^\ominus(Cl^-)$ (⊡) and $\Delta G_t^\ominus(H^+)$ (△) derived using the spectrophotometric solvent sorting method with $\Delta G_t^\ominus(Ar)$ (⊙) in water + ethanol mixtures.

simple relationship with size. The only one which differs markedly from the others collectively is $\Delta G_t^\ominus(I_2)$ which has much greater negative values. However, a comparison of $\Delta G_t^\ominus(i)_n$ for the organic molecules in Table 1 suggests that it does become increasingly negative as the size of the hydrocarbon increases.

If one considers the process of dissolution of a gaseous solute molecule into a pure solvent in terms of two steps, i.e. the formation of a cavity in the liquid, followed by the insertion of the solute molecule into the cavity, accompanied by the interactions between the solute molecule and the molecules of the solvent, Pierotti [3] has deduced the following equation

$$\Delta G^\ominus = G^{\mathrm{cav}} + G^{\mathrm{int}} + RT\ \ln(RT/V) \qquad (6)$$

where $\Delta G^\ominus$ is the free energy of solvation, G^{cav} is the partial molar free energy of the cavity formation, G^{int} is the partial molar free energy for the interaction between the solute molecule and the solvent and V is the molar volume of the solvent. For a range of solutes in non-polar solvents [3,4,26], scaled particle theory is applied to the calculation of the terms G^{cav} and G^{int}. G^{cav} is calculated from the relationship

$$G^{\mathrm{cav}} = K_0 + K_1 r + K_2 r^2 + K_3 r^3 \qquad (7)$$

where r is the mean of the radii r_1 and r_2 of the solute and solvent molecules and $K_0 \ldots K_3$ are calculated from the physical properties of a liquid consisting of non-interacting hard spheres of radius r_2. G^{int} is calculated from the dispersion and inductive energies using the Leonard–Jones (6–12) expression involving inverse terms in powers of the radial distance of a solvent molecule from the solute molecule. Even though this produces reasonable agreement for experimental $\Delta G^{\ominus}$ with the calculated $\Delta G^{\ominus}$ [4], clearly the assumptions which apply to non-polar solvents and solutes, particularly eqn. (7), cannot apply to structured polar liquids such as pure water and its mixtures with alcohols. To avoid all the difficulties associated with modifying scaled particle theory for a complex structured liquid [27], eqn. (6) can be adapted to refer to free energies of transfer of solutes between two similarly structured liquids, effectively to eliminate G^{cav} and determine G^{int} experimentally. Thus, eqn. (8) applies to the free energy of solvation of an uncharged solute i in pure water (w)

$$\Delta G_{\text{w}}^{\ominus} = G_{\text{w}}^{\text{cav}} + G_{\text{w}}^{\text{int}} + RT\ \ln(RT/V_{\text{w}}) \tag{8}$$

and eqn. (9) to the free energy of solvation of the same solute in water + ethanol mixtures (s)

$$\Delta G_{\text{s}}^{\ominus} = G_{\text{s}}^{\text{cav}} + G_{\text{s}}^{\text{int}} + RT\ \ln(RT/V_{\text{s}}) \tag{9}$$

The free energy of transfer of i between pure water and the mixture is now given by

$$\Delta G_{\text{t}}^{\ominus}(\text{i})_{\text{n}} = \Delta G_{\text{s}}^{\ominus} - \Delta G_{\text{w}}^{\ominus} = (G_{\text{s}}^{\text{cav}} - G_{\text{w}}^{\text{cav}}) + (G_{\text{s}}^{\text{int}} - G_{\text{w}}^{\text{int}}) + RT\ \ln(V_{\text{w}}/V_{\text{s}}) \tag{10}$$

For water-rich mixtures, where the statistical chance of an ethanol molecule being involved in the cavity formation is small, we can assume that $G_{\text{s}}^{\text{cav}} - G_{\text{w}}^{\text{cav}} = 0$, as assumed for the transfer of the hydrated proton in the spectrophotometric solvent sorting method for calculating $\Delta G_{\text{t}}^{\ominus}(\text{H}^+)$ [7,25]. This assumption is supported by the relative partial molar volumes for water ($\overline{V}_1 - V_1^{\ominus}$) and for ethanol ($\overline{V}_2 - V_2^{\ominus}$) in their mixtures. In water-rich conditions, although $\overline{V}_2 - V_2^{\ominus}$ shows sharp changes with x_2, $\overline{V}_1 - V_1^{\ominus}$ shows little deviation from zero for $x_2 < 0.2$ [28], indicating that the environment of the majority of water molecules is influenced little by the presence of the ethanol molecules in these conditions. However, subsequent to the transfer, the solvent molecules surrounding the solute molecule relax to provide different solute–solvent and solvent–solvent interactions from those encountered in pure water: this is shown clearly by the NMR shifts found when xenon is transferred from water into water + ethanol [29]. The free energy associated with the relaxation is represented by $\Delta G_{\text{t}}^{\text{int}}(\text{i}) = G_{\text{s}}^{\text{int}} - G_{\text{w}}^{\text{int}}$, the difference in the interactions between the solute molecule in water and in the mixed solvent, which is now given by

$$\Delta G_{\text{t}}^{\text{int}}(\text{i}) = \Delta G_{\text{t}}^{\ominus}(\text{i})_{\text{n}} + RT\ \ln(V_{\text{s}}/V_{\text{w}}) \tag{11}$$

Values of $\Delta G_{\text{t}}^{\ominus}(\text{i})_{\text{n}}$ determined from the experimental gas solubilities are

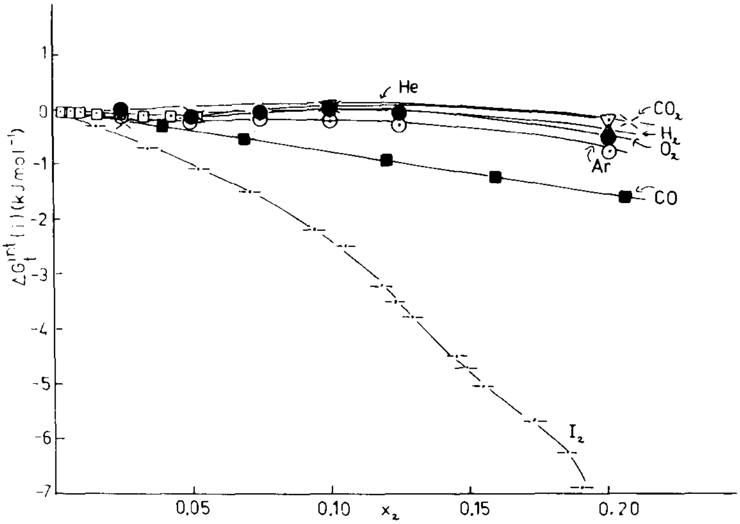


Fig. 3. Variation in $\Delta G_t^{int}(i)_n$ for inorganic solutes at 25 ° C with mole fraction of ethanol in water + ethanol mixtures.

collected in Table 1 for a series of inorganic and organic solutes in water + ethanol mixtures, and V_s/V_w can be calculated using

$$\frac{V_s}{V_w} = \frac{(x_1 M_w + x_2 M_{EtOH}) d_w}{d_s M_w} \tag{12}$$

where x_1 and x_2 are the mole fractions of water and ethanol in the mixture, respectively, M_w and M_{EtOH} are the molecular weights of water and ethanol and d_w and d_s are the densities of water and the mixture [10]. Therefore, values for $\Delta G_t^{int}(i)_n$ can be calculated for the solutes listed in Table 1.

Figure 3 shows that, for the inorganic solutes, only I_2 has appreciable negative values for $\Delta G_t^{int}(I_2)_n$: indeed $\Delta G_t^{int}(i)_n \sim 0$ for the other inorganic solutes, monatomic and polyatomic, excluding CO in water-rich water + ethanol mixtures. Values for $\Delta G_t^{\ominus}(\mathrm{Xe})_n$ are not available to compare with the NMR shifts [29]. We must conclude, then, by comparing Fig. 3 with Figs. 1 and 2 and with the variation in $\Delta G_t^{\ominus}(i)$ with x_2 for a wide range of inorganic ions in water + ethanol [25], that the free energy of transfer of the charge alone $\Delta G_t^{\ominus}(i)_e$ is the major contributor to $\Delta G_t^{\ominus}(i)$ for small inorganic ions. This is similar to the conclusion reached from the determination of $\Delta G_t^{\ominus}(i)_e$ for large organic ions in water + ethanol [6]. However, Fig. 4 showing the variation in $\Delta G_t^{int}(i)_n$ for organic solutes in water + ethanol differs from Fig. 3 in suggesting that $\Delta G_t^{int}(i)_n$ has appreciable negative values for the larger hydrocarbons with $-\Delta G_t^{int}(i)_n$ increasing with increasing size of the solute molecule. Therefore, it would appear likely that $\Delta G_t^{\ominus}(i)_n$ contributes a greater proportion to $\Delta G_t^{\ominus}(i)$ for organic ions than for inorganic ions. This must account for the observation that $\Delta G_t^{\ominus}(i)$ for

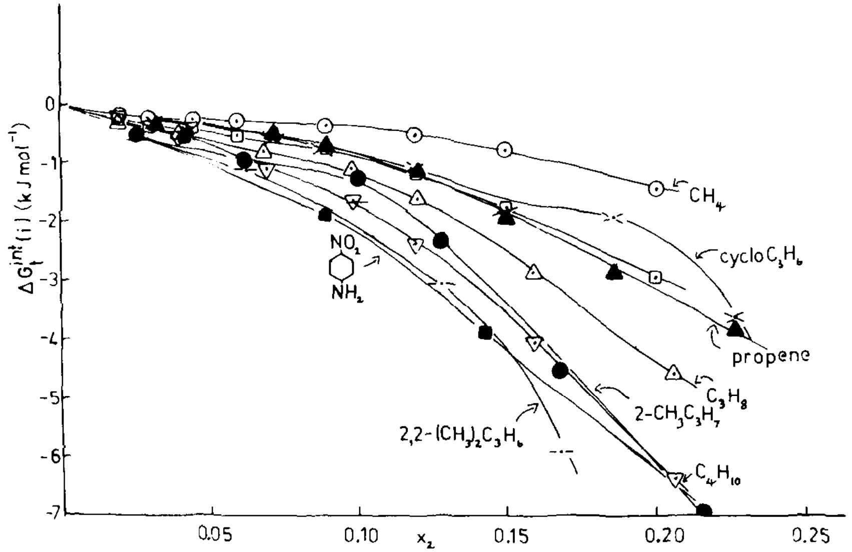


Fig. 4. Variation in $\Delta G_t^{int}(i)_n$ for organic solutes at 25 °C with mole fraction of ethanol in water + ethanol mixtures.

cations containing large organic groups have greater numerical values than simple inorganic cations bearing the same charge, with $-\Delta G_t^{\ominus}$(organic cation) $>$ $-\Delta G_t^{\ominus}$(inorganic cation). Even with the relatively small negative value found for $\Delta G_t^{\ominus}(CH_4)$ in Fig. 4, multiple CH_3 groups in an ion result in an appreciably more negative contribution of $\Delta G_t^{\ominus}(Me_4N^+)_n$ to $\Delta G_t^{\ominus}(Me_4N^+)$ [24]. The negative contribution of $\Delta G_t^{int}(i)_n$ from organic groups to $\Delta G_t^{\ominus}(i)$ for anions will depress the positive values found [6] for $\Delta G_t^{\ominus}$(organic anion)$_e$, resulting, for example, in negative $\Delta G_t^{\ominus}(BPh_4^-)$, in contrast to the positive $\Delta G_t^{\ominus}(i)$ usually found for simple inorganic anions in water + ethanol [25].

It can be concluded, therefore, that, for simple inorganic ions, the free energy of transfer of the charge alone is the major determinant of the total free energy of transfer of the ion, with only a minor contribution from $\Delta G_t^{int}(i)_n$: this produces, in general, positive $\Delta G_t^{\ominus}(i)$ for anions and negative $\Delta G_t^{\ominus}(i)$ for cations in water + ethanol [25]. For large organic ions, the contribution of $\Delta G_t^{int}(i)_n$ to $\Delta G_t^{\ominus}(i)$ increases. However, as $\Delta G_t^{\ominus}(i)_e$ is positive for large organic anions and negative for large organic cations [6], although the addition of a negative $\Delta G_t^{int}(i)_n$ will result in $\Delta G_t^{\ominus}(i) < \Delta G_t^{\ominus}(i)_e$ for both, for similarly structured anions and cations $\Delta G_t^{\ominus}$(cation) $<$ $\Delta G_t^{\ominus}$(anion). Hence, in water + ethanol, although $\Delta G_t^{\ominus}(BPh_4^-)$ is large and negative, it is not as negative as $\Delta G_t^{\ominus}(Ph_4P^+)$ or $\Delta G_t^{\ominus}(Ph_4As^+)$ which are equal [25]. Thus, in the region $x_2 \sim 0.38$, where Figs. 1 and 2 show that both methods of separation of $\Delta G_t^{\ominus}(HX)$ and $\Delta G_t^{\ominus}(MX)$ into values for individual ions result in approximately equal $\Delta G_t^{\ominus}(H^+)$, $\Delta G_t^{\ominus}(BPh_4^-) \sim -14$ kJ mol^{-1} and $\Delta G_t^{\ominus}(\mathrm{Ph_4As^+}) \sim -21$ kJ mol^{-1} [25]. As the contribution of $\Delta G_t^{\mathrm{int}}(\mathrm{i})_n$ to both ions will be approximately the same, $\Delta G_t^{\ominus}(\mathrm{BPh_4^-}) - \Delta G_t^{\ominus}(\mathrm{Ph_4As^+}) \sim 7$ kJ mol^{-1} represents the difference $\Delta G_t^{\ominus}(\mathrm{BPh_4^-})_e - \Delta G_t^{\ominus}(\mathrm{Ph_4As^+})_e$ at this composition.

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