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IONIC SOLVATION IN WATER + CO-SOLVENT MIXTURES. PART 19. FREE ENERGIES OF TRANSFER OF SINGLE IONS FROM WATER INTO MIXTURES OF WATER WITH POLYHYDROXY COMPOUNDS: AN EXAMINATION OF THE ASSUMPTIONS USED IN DETERMINING $\Delta G_t^{\ominus}(i)$

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ABSTRACT

The assumptions underlying the spectrophotometric solvent-sorting method for determining $\Delta G_t^{\ominus}(i)$ for individual ions from water into water-rich water + co-solvent mixtures have been critically examined. Additions of the hydrophilic co-solvents glucose, mannitol, sorbitol and inositol to water support the original view, derived from the effect of additions of glycerol, that the main assumption holds at least for $x_2 \leq 0.25$ and for some with $x_2 \leq 0.35$. Errors in criticisms of this method are specified and the extent of the applicability of the TATB method for producing $\Delta G_t^{\ominus}(i)$ is examined.

Free energies of transfer for H^+, Cl^-, Na^+, K^+ and OH^- have been calculated from $E^{\ominus}$ data and vapour pressures for these hydrophilic co-solvents where available. These are compared with values obtained using additions of hydrophobic alcohols and aprotic co-solvents.

INTRODUCTION

Following the determination of the free energy of transfer of the proton, $\Delta G_t^{\ominus}(H^+)$, between water and water-rich mixtures of water with hydrophobic co-solvents such as primary [1–3], secondary [3,4] and tertiary alcohols [3,5], we have now applied the spectrophotometric solvent-sorting method to the more hydrophilic co-solvents, glucose, mannitol, sorbitol and inositol, as a continuation of the determination of $\Delta G_t^{\ominus}(H^+)$ for ethane-1,2-diol [3,6] or glycerol [3,4] mixed with water. In particular, measurements in water + glycerol mixtures have been used to support an assumption used in the method of determination [7]. As the extent of the composition range to which this assumption can be applied in mixed solvents has recently been

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questioned [8], it was thought desirable to extend these measurements to include mixtures of water with other polyhydroxy compounds. In order to specify the implications of this assumption more precisely, the principles of the method used will first be re-examined as concisely as possible; in the course of this, criticisms [9,10] of the standard states used will also be examined.

OUTLINE OF THE METHOD FOR DETERMINING $\Delta G_t^\ominus(H^+)$

The transfer is divided into four processes: (i) the making of a hole in the mixture $n(H_2O) + n(ROH)$ to accommodate the aqua-proton, $H_{aq}^+ = H^+(H_2O)_5$; (ii) the transfer of the spherical aqua-proton from water into the specified mixture, $n(H_2^+O) + n(ROH)$; (iii) the collapse of the hole in pure water left by the departure of H_{aq}^+; and (iv) the rearrangement in the specified mixture after (ii), according to

$$\left(H_{aq}^+\right)_s + ROH_s \rightleftharpoons \left(R\overset{+}{O}H_2\right)_s + H_2O_s \tag{1}$$

where (H_{aq}^+) is enlarged to $H^+(H_2O)_x$ with $x \geqslant 5$ and $(R\overset{+}{O}H_2) = \{(H_2O)_{x-1}ROH\}H^+$. The free energy change for (i) is given by

$$\Delta G(\text{Born}) = \frac{Ne^2}{6r_{H_2O}}\left(D_s^{-1} - D_w^{-1}\right) \tag{2}$$

and for (iv) by

$$\Delta G_2 = -\left[R\overset{+}{O}H_2\right] RT \ln K_c [H_2O]_s F_c \tag{3}$$

where D is the dielectric constant, r_{H_2O} is the radius of an H_2O molecule, the subscripts w and s indicate pure water and the specified mixture, respectively, $K_c = [R\overset{+}{O}H_2]/[ROH][H_{aq}^+]$, $[H_2O]_s$ (w_R in earlier publications) is the molar concentration of water in the specified mixture, $F_c = y(R\overset{+}{O}H_2)_s y(H_2O)_s / y(ROH)_s y(P)_s$ with $P = H_{aq}^+$, where the standard states for $R\overset{+}{O}H_2$ and H_{aq}^+ are defined as $y_s = 1.0$ and $[i] = 1.0$ with $y_s \rightarrow 1.0$ as $\Sigma[i] \rightarrow 0$ in the mixture, and for $y(H_2O)_s$ and $y(ROH)_s$, $y_s \rightarrow 1.0$ as $\Sigma[i] \rightarrow 0$ in the mixture $n(H_2O) + n(ROH)$ (these will be discussed again below). Provided that the mole fraction x_{ROH} of ROH in $n(H_2O) + n(ROH)$ is low enough for $\Delta G(\text{i}) = \Delta G(\text{iii})$, $\Delta G_t^\ominus(H^+)$ on the mole fraction scale is now given by

$$\Delta G_t^\ominus(H^+) = \Delta G(\text{Born}) + \Delta G_2 + RT \ln\left(d_s M_{H_2O}/d_w M_s\right) \tag{4}$$

where d is density and M is molecular weight with $M_s = 100/\{(\text{wt.\%ROH}/M_{ROH}) + (\text{wt.\%H}_2\text{O}/M_{H_2O})\}$.

DETERMINATION OF K_c AND F_c

Equilibrium (1) is examined by adding a trace concentration c_0 of 4-nitroaniline to the specified mixture $n(H_2O) + n(ROH)$ containing HCl, when equilibria (5) and (6) are set up

$$B_s + P_s \overset{K_{1s}}{\rightleftharpoons} BH_s^+ + H_2O_s \tag{5}$$

$$B_s + \left(R\overset{+}{O}H\right)_s \overset{K_{2s}}{\rightleftharpoons} BH_s^+ + ROH_s \tag{6}$$

where

$$K_{1s} = \frac{[BH^+]_s[H_2O]_s}{[B]_s[P]_s} \frac{y(BH^+)_s y(H_2O)_s}{y(B)_s y(P)_s}$$

and

$$K_{2s} = \frac{[BH^+]_s[ROH]_s}{[B]_s\left[R\overset{+}{O}H_2\right]_s} \frac{y(BH^+)_s y(ROH)_s}{y(B)_s y\left(R\overset{+}{O}H_2\right)_s}$$

As above, the standard states are all defined in the mixture: those for BH^+, B, H_{aq}^+ and $R\overset{+}{O}H_2$ are all defined as $y_s = 1.0$ and $[i] = 1.00$ mol dm^{-3} with $y_s \to 1.0$ as $\Sigma[i] \to 0$; for ROH and H_2O, $y_s \to 1.0$ as $\Sigma[i] \to 0$ in the mixture, with the standard chemical potentials in $n(H_2O) + n(ROH)$ defined by

$$\mu^{\ominus}(H_2O)_s = \left(\frac{\partial G}{\partial n(H_2O)}\right)_{T,P,n(H_2O)+n(ROH),\Sigma[i]=0}$$

$$\mu^{\ominus}(ROH)_s = \left(\frac{\partial G}{\partial n ROH}\right)_{T,P,n(H_2O)+n(ROH),\Sigma[i]=0}$$

These standard chemical potentials in the mixtures are related to the two standard chemical potentials in the individual pure liquids, $\mu^{\ominus}(H_2O)_{H_2O}$ and $\mu^{\ominus}(ROH)_{ROH}$ via eqns. (7) and (8)

$$\mu^{\ominus}(H_2O)_s = \mu^{\ominus}(H_2O)_{H_2O} + RT \ln x_{H_2O} f_{H_2O} \tag{7}$$

$$\mu^{\ominus}(ROH)_s = \mu^{\ominus}(ROH)_{ROH} = RT \ln x_{ROH} f_{ROH} \tag{8}$$

where $f = 1.0$ for the pure liquid, H_2O or ROH, and x is the mole fraction.

If $c_w = [B]$ in water only for a particular [HCl] and $c_s = [B]$ in $n(H_2O) + n(ROH)$ (previously written as c and c_R respectively) with the same [HCl], where [B] is determined spectrophotometrically at 383 nm [7,11], it is found that plots of $c_w c_s/(c_s - c_w)$ against $c_s/(c_0 - c_s)$ for varying [HCl] in the same mixture, $n(H_2O) + n(ROH)$, are linear. Within the accuracy obtainable for the intercepts, the latter equals $c_0[H_2O]_w/K_{1w}F_{1w}$ relating to the equilibrium

$$B_w + P_w \overset{K_{1w}}{\rightleftharpoons} BH_w^+ + H_2O_w \tag{9}$$

in pure water, with

$$K_{1w} = \frac{[BH^+]_w[H_2O]_w}{[B]_w[P]_w} \frac{y(BH^+)_w y(H_2O)_w}{y(B)_w y(P)_w}$$

and

$$F_{1w} = \frac{y(B)_w y(P)_w}{y(BH^+)_w y(H_2O)_w}$$

where now the standard states for B, BH^+ and P are defined by $y_w = 1.0$ and $[i]_w = 1.0$ with $y(i)_w \rightarrow 1.0$ as $\Sigma[i] \rightarrow 0$, and for H_2O, $y(H_2O)_w \rightarrow 1.0$ as $\Sigma[i] \rightarrow 0$.

Using the above equations, one can deduce [7,11] eqn. (10) to apply to the linear plots

$$\frac{c_w c_s}{c_s - c_w} = \frac{K_{2s}F_{2s}}{K_{1s}F_{1s}} \frac{[H_2O]_s c_0}{[ROH]_T} \frac{c_s}{c_0 - c_s} + \frac{c_0[H_2O]_s}{K_{1s}F_{1s}[ROH]_T} \tag{10}$$

where $[ROH]_T$ is the total molar concentration of ROH in the specified mixture $n(H_2O) + n(ROH)$ and

$$F_{1s} = \frac{y(B)_s y(P)_s}{y(BH^+)_s y(H_2O)_s}$$

with

$$F_{2s} = \frac{y(B)_s y\left(\overset{+}{R}OH_2\right)_s}{y(BH^+)_s y(ROH)_s}$$

In deducing eqn. (10), the following assumption is made

$$\frac{K_{1s}F_{1s}}{[H_2O]_s} = \frac{K_{1w}F_{1w}}{[H_2O]_w} \tag{11}$$

justified by the observed linearity of the plots. This reduces to

$$\frac{[BH^+]_w}{[B]_w[P]_w} = \frac{[BH^+]_s}{[B]_s[P]_s} \tag{12}$$

and does not require the assumption F_{1s} (or F_{1w}) = 1.0, as suggested by Blandamer et al., [9], or $[H_2O]_w/[H_2O]_s \doteq 1.0$, as suggested by Marcus [8].

$$\frac{F_{1s}}{F_{1w}} = \frac{y(B)_s y(BH^+)_w}{y(BH^+)_s y(B)_w} \frac{y(P)_s y(H_2O)_w}{y(H_2O)_s y(P)_w} \tag{13}$$

The first term on the right-hand side of eqn. (13) is related to the activity coefficient product in the Hammett H_0 function which has been shown [12] to be equal to unity for a wide range of water activities when $(B)_s$ and $(BH^+)_s$ are structurally related to $(B)_w$ and $(BH^+)_w$, e.g. differing substituted primary anilines; therefore it is safe to conclude that, with the same aniline, as here, it must be equal to unity. Likewise, the symmetrical second term on the right-hand side of eqn. (13) would also be expected to be unity. These assumptions will hold for a reasonable range of x_{ROH} in water-rich conditions, $x_{\mathrm{ROH}} \lesssim 0.3–0.5$, and probably wider, rather than over a very limited range as suggested by Marcus [8]. This conclusion that $F_{1\mathrm{s}}/F_{1\mathrm{w}} = 1.0$ combined with eqns. (11) and (12) leads to

$$\frac{K_{1\mathrm{w}}}{K_{1\mathrm{s}}} = \frac{K'_{1\mathrm{w}}}{K'_{1\mathrm{s}}} \quad \text{or} \quad \frac{K_{1\mathrm{w}}}{K'_{1\mathrm{w}}} = \frac{K_{1\mathrm{s}}}{K'_{1\mathrm{s}}} \tag{14}$$

where $K'_1 = [\mathrm{BH^+}][\mathrm{H_2O}]/[\mathrm{B}][\mathrm{P}]$. As a consequence of eqn. (14), if $K'_{2\mathrm{s}} = [\mathrm{BH^+}]_\mathrm{s}[\mathrm{ROH}]_\mathrm{s}/[\mathrm{B}]_\mathrm{s}[\mathrm{R\overset{+}{O}H_2}]_\mathrm{s}$, it is reasonable for variations of the closely related equilibria (5) and (6) in any particular mixture $n(\mathrm{H_2O}) + n(\mathrm{ROH})$ to assume that eqn. (15) holds

$$\frac{K_{1\mathrm{s}}}{K'_{1\mathrm{s}}} = \frac{K_{2\mathrm{s}}}{K'_{2\mathrm{s}}} \quad \text{or} \quad \frac{K_{1\mathrm{s}}}{K_{2\mathrm{s}}} = \frac{K'_{1\mathrm{s}}}{K'_{2\mathrm{s}}} \tag{15}$$

The slopes of the linear plots of $c_\mathrm{w}c_\mathrm{s}/(c_0 - c_\mathrm{s})$ are given by

$$(\text{slope}) = \frac{F_\mathrm{c}c_0}{K_\mathrm{c}[\mathrm{ROH}]_\mathrm{T}} \tag{16}$$

from which $K_\mathrm{c}F_\mathrm{c}^{-1}$ can be calculated. As, for any specified mixture $n(\mathrm{H_2O}) + n(\mathrm{ROH})$, $K_\mathrm{c}F_\mathrm{c}^{-1}$ from eqn. (16) is found equal to K_c derived from

$$K_\mathrm{c} = \frac{\left[\mathrm{R\overset{+}{O}H_2}\right]}{\left([\mathrm{H^+}]_\mathrm{T} - \left[\mathrm{R\overset{+}{O}H_2}\right]\right)\left([\mathrm{ROH}]_\mathrm{T} - \left[\mathrm{R\overset{+}{O}H_2}\right]\right)} \tag{17}$$

where subscript T indicates the total added concentration of any species and K_c is found to be invariant with [HCl] for that mixture $n(\mathrm{H_2O}) + n(\mathrm{ROH})$, it is concluded that $F_\mathrm{c} = 1.0$.

This latter method is the one used in all applications since 1979 [2,3,13,14], assumptions (11) and $y(\mathrm{B})_\mathrm{s}y(\mathrm{BH^+})_\mathrm{w}/y(\mathrm{BH^+})_\mathrm{s}y(\mathrm{B})_\mathrm{w} = 1.0$ being completely justified experimentally with the entirely symmetrical $y(\mathrm{P})_\mathrm{s}y(\mathrm{H_2O})_\mathrm{w}/y(\mathrm{H_2O})_\mathrm{s}y(\mathrm{P})_\mathrm{w} = 1.0$ a reasonable extension of the latter, and eqns. (14) and (15) following. Prior to 1979 [1,3–7,11,15], assumption (11) was justified experimentally and it was assumed that the symmetrical $F_\mathrm{c} = y(\mathrm{ROH_2})_\mathrm{s}y(\mathrm{H_2O})_\mathrm{s}/y(\mathrm{P})_\mathrm{s}y(\mathrm{ROH})_\mathrm{s} = 1.0$. Although this is reasonable for such a symmetrical term, the above assumptions regarding terms $\pi(y)$ in eqn. (13) are more justifiable on experimental grounds and on the basis of their higher degree of symmetry. $F_\mathrm{c} = 1.0$ is also supported by the experimental observation [7] that K_c (or $K_\mathrm{c}F_\mathrm{c}^{-1}$) from the slopes of the linear plots is independent of ionic strength in the range 0.25–2.00 mol dm^{-3} and the validity of eqn. (11) over the range $x_{\mathrm{ROH}} \sim 0–0.25$ is confirmed [7] by observations with added glycerol for which $K_c \leq 0.01$ dm^3 mol^{-1}. In this paper, we investigate this further using other polyhydroxy co-solvents which are expected to have similar low values for K_c arising from the presence of the electron-attracting OH groups.

An alternative, but less satisfactory, approach would be to assume that, as $F_{1s}/F_{1w} = 1.0$, $F_{2s}/F_{1s} = 1.0$ in eqn. (10). Then, the slope $= c_0/K_c F_c[\mathrm{ROH}]_T$; but, $K_c F_c$ from the slope agrees with K_c from eqn. (17), again producing $F_c = 1.0$.

USE OF STANDARD STATES

In transferring species i from water into a mixture of water with a co-solvent, the free energy of transfer is given by

$$\Delta G_t^\ominus = \mu^\ominus(i)_s - \mu^\ominus(i)_w$$

where the standard state for $\mu^\ominus(i)_s$ is defined in the mixture and that for $\mu^\ominus(i)_w$ is defined in water. Contrary to the suggestion by Blandamer et al. [10], this is the system used by all workers in the field including the present authors [14] and Blandamer et al. [9,10].

As indicated earlier [2], the choice for equilibrium (1) by Blandamer et al. [9] as

$$(\mathrm{H}^+)_s + \mathrm{ROH}_{\mathrm{ROH}} \overset{K^*}{\rightleftharpoons} (\mathrm{ROH}_2)_s + (\mathrm{H_2O})_{\mathrm{H_2O}} \tag{18}$$

involving two separated miscible liquids is unrealistic when the free energy change for eqn. (3) is now given as [9]

$$\Delta G_2 = \left[\overset{+}{\mathrm{R}\mathrm{O}}\mathrm{H}_2\right]\left\{\mu^\ominus\left(\overset{+}{\mathrm{R}\mathrm{O}}\mathrm{H}_2\right)_s + \mu^\ominus(\mathrm{H_2O})_{\mathrm{H_2O}} - \mu^\ominus(\mathrm{H}^+_{\mathrm{aq}})_s - \mu^\ominus(\mathrm{ROH})_{\mathrm{ROH}}\right\}$$

This latter equation omits the free energy change for the transfer of H_2O from pure water into the mixture and that for ROH from pure ROH into the mixture. Thus, for our equilibrium (1) *in the mixture*

$$\Delta G_2 = \left[\overset{+}{\mathrm{R}\mathrm{O}}\mathrm{H}_2\right]\left\{\mu^\ominus\left(\overset{+}{\mathrm{R}\mathrm{O}}\mathrm{H}_2\right)_s + \mu^\ominus(\mathrm{H_2O})_s - \mu^\ominus(\mathrm{H}^+_{\mathrm{aq}})_s - \mu^\ominus(\mathrm{ROH})_s\right\} \tag{19}$$

and if eqns. (7) and (8) are substituted into this to refer the standard states of H_2O and ROH to the respective pure liquids, as suggested by Blandamer et al. [9] in eqn. (18), the true equation is

$$\Delta G_2 = \left[\overset{+}{\mathrm{R}\mathrm{O}}\mathrm{H}_2\right]\left\{\mu^\ominus(\mathrm{ROH_2})_s + \mu^\ominus(\mathrm{H_2O})_{\mathrm{H_2O}} - \mu^\ominus(\mathrm{H}^+)_s - \mu^\ominus(\mathrm{ROH})_{\mathrm{ROH}} + RT\ \ln\left(x_{\mathrm{H_2O}} f_{\mathrm{H_2O}}/x_{\mathrm{ROH}} f_{\mathrm{ROH}}\right)\right\} \tag{20}$$

Here the term $RT\ \ln(x_{\mathrm{H_2O}} f_{\mathrm{H_2O}} / x_{\mathrm{ROH}} f_{\mathrm{ROH}})$ allows for the transfer of H_2O and ROH into the mixture from their respective pure states. However, the application of an equilibrium constant $K^\star$ to eqn. (18) is spurious [2] as this equilibrium involving two separated but totally miscible liquids does not exist in a real situation.

In their eqn. (C12), Blandamer et al. [9] for $\Delta G_t^\ominus(\mathrm{H}^+)$ write

$$\Delta G_t^\ominus(\mathrm{H}^+) = \left\{\mu^\ominus(\mathrm{H}^+_{\mathrm{aq}})_{\mathrm{s}} - \mu^\ominus(\mathrm{H}^+_{\mathrm{aq}})_{\mathrm{w}}\right\} + \left[\mathrm{R\overset{+}{O}H_2}\right]\left\{\mu^\ominus\left(\mathrm{R\overset{+}{O}H_2}\right)_{\mathrm{s}} - \mu^\ominus(\mathrm{H}^+_{\mathrm{aq}})_{\mathrm{s}}\right\}$$

They correctly identify the first bracketed term on the right with our eqn. (2); but they then conclude for the solvent rearrangement in the mixture that

$$\Delta G_2 = \left[\mathrm{R\overset{+}{O}H_2}\right]\left\{\mu^\ominus(\mathrm{ROH_2})_{\mathrm{s}} - \mu^\ominus(\mathrm{H}^+_{\mathrm{aq}})_{\mathrm{s}}\right\} \tag{21}$$

and with the use of their eqn. (C7) [9]

$$\Delta G_2 = \left[\mathrm{R\overset{+}{O}H_2}\right]\left\{-RT\ \ln K^\star + \mu^\ominus(\mathrm{ROH})_{\mathrm{ROH}} - \mu^\ominus(\mathrm{H_2O})_{\mathrm{H_2O}}\right\} \tag{22}$$

which contrasts with our

$$\Delta G_2 = -\left[\mathrm{R\overset{+}{O}H_2}\right] RT\ \ln K \tag{23}$$

Apart from the inapplicability of $K^\star$ in eqn. (22) to the real situation discussed above, their equation (eqn. (21)) contrasts with the real equation (eqn. (19)) *in the mixture* using $[\mathrm{R\overset{+}{O}H_2}] \times$ the standard free energy change for equilibrium (1). With the use of the real ΔG_2 in eqn. (19), eqns. (23) and (3) follow and neither $\mu^\ominus(\mathrm{ROH})_{\mathrm{ROH}} - \mu^\ominus(\mathrm{H_2O})_{\mathrm{H_2O}}$, nor indeed $\mu^\ominus(\mathrm{ROH})_{\mathrm{s}} - \mu^\ominus(\mathrm{H_2O})_{\mathrm{s}}$, remain in eqns. (23) and (3). Their suggestion [9] that we have hidden an assumption that $\mu^\ominus(\mathrm{H_2O})_{\mathrm{H_2O}} = \mu^\ominus(\mathrm{ROH})_{\mathrm{ROH}}$ (or even $\mu^\ominus(\mathrm{ROH})_{\mathrm{s}} = \mu^\ominus(\mathrm{H_sO})_{\mathrm{s}}$) is therefore spurious. Clearly, eqn. (21) is in error compared with eqn. (19): contributions to the free energy change resulting from the removal of ROH and the appearance of H_2O in the bulk solvent mixture in process (18) are omitted from their equations [9].

Test of assumption

A test of the extent of the applicability of assumption (11) with changing solvent composition has been made using additions of glycerol [11]. Further tests are now applied using additions of other polyhydroxy compounds to water.

EXPERIMENTAL

D(+)-glucose, inositol and sorbitol were used without purification. D(+)-mannitol was recrystallized from water and dried in a vacuum desiccator. All other materials were as previously described. Absorbances at 383 nm [7,11] were measured at 25.0 °C using a Unicam SP 500 Series 2 spectrophotometer.

RESULTS AND DISCUSSION

Water + glucose mixtures

In all the earlier investigations of water + co-solvent mixtures containing HCl, NaCl and 4-nitroaniline, stable absorbances have been found at constant temperature. However, with water + glucose, such absorbances at 383 nm increased with time. This was ascribed to the interaction of glucose with 4-nitroaniline resulting in the acid-catalysed formation of a glucose anilide [16]. Therefore, the change in absorbance with time was measured for 5.0 and 40.0 wt.% glucose each with a range of [HCl] with the ionic strength maintained at 1.00 mol dm^{-3} by the addition of NaCl. These absorbances for each set of conditions were then extrapolated to zero time, the time of mixing: typical plots are shown in Fig. 1. Values for c_s obtained at zero time are compared in Table 1 with values for c_w determined in the absence of glucose and we conclude that $c_w = c_s$ for the same [HCl] with $c_0 = 1.45 \times 10^{-4}$ mol dm^{-3}.

For solutions containing only HCl, NaCl and 4-nitroaniline, equilibrium (9) operates, to which eqn. (24) applies

$$\frac{c_0 - c_w}{c_w} = \frac{K_{1w}F_{1w}}{[H_2O]_w}[H^+]_T \tag{24}$$

and from a linear plot of $(c_0 - c_w)c_w^{-1}$ against $\{H^+]_T$ in water, $K_{1w}F_{1w}/[H_2O]_w = 16.2$ dm^3 mol^{-1}. This is compared in Fig. 2 with the linear plots for $(c_0 - c_s)/c_w$ versus $[H^+]_T$ in water + glucose mixtures which yield $K_{1s}F_{1s}/[H_2O]_w = 16.8$ for 5.0 wt.% glucose and 16.3 dm^3 mol^{-1} for 40.0 wt.% glucose. The good agreement of these latter values with $K_{1w}F_{1w}/[H_2O]_w$ in water determined here and earlier [11] at an ionic strength of 1.00 mol dm^{-3} confirm the conclusion drawn from $c_w = c_s$ that $\Delta G_2 =$ zero in eqn. (4). The values for $\Delta G_t^{\ominus}(H^+)$ on the mole fraction scale calculated from eqn. (4) with $\Delta G_2 =$ zero are collected in Table 2: values for D_s were taken from the data of Malmberg and Maryott [17] and d_s was interpolated from the data of Taylor and Rowlinson [18].

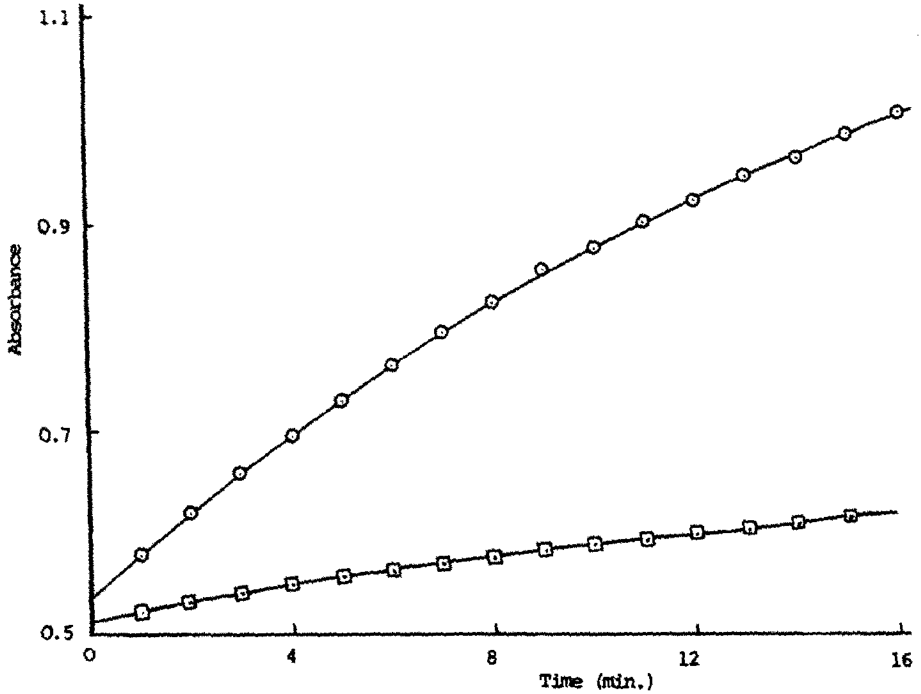

Fig. 1. Change in absorbance at 383 nm with time at 25 °C for mixtures containing 1.45×10^{-4} mol dm^{-3} 4-nitroaniline at an ionic strength of 1.00 mol dm^{-3} with: ⊙, 5.00 wt.% glucose and 0.400 mol dm^{-3} HCl; ⊡, 40.0 wt.% glucose and 0.20 mol dm^{-3} HCl.

$E^{\ominus}$ values for cell (25) [19]

$$\text{Pt,H}_2\,|\,\text{HCl,H}_2\text{O} + \text{glucose}\,|\,\text{AgCl,Ag} \tag{25}$$

were used in eqn. (26) to calculate $\Delta G_t^{\ominus}(\text{HCl})_m$

$$\Delta G_t^{\ominus}(\text{HCl}) = 96.5\left(E_w^{\ominus} - E_s^{\ominus}\right)\ \text{kJ mol}^{-1} \tag{26}$$

TABLE 1

Values for c_w (10^{-5} mol dm^{-3}) in the absence of added co-solvent and of c_s (10^{-5} mol dm^{-3}) with added co-solvents at ionic strength 1.00 mol dm^{-3} and at 25 °C

Total added [HCl] (mol dm^{-3})	c_w	c_s				
		5.00 wt.% glucose	40.0 wt.% glucose	15.0 wt.% mannitol	20.0 wt.% sorbitol	10.0 wt.% inositol
0.100	5.2	5.1	5.2	5.1	5.2	5.2
0.160	3.83	3.78	3.87	3.77	3.89	3.81
0.200	3.30	3.20	3.35	3.20	3.27	3.26
0.400	1.90	1.79	1.91	1.80	1.83	1.84
0.800	1.06	0.98	1.02	1.03	1.01	1.02

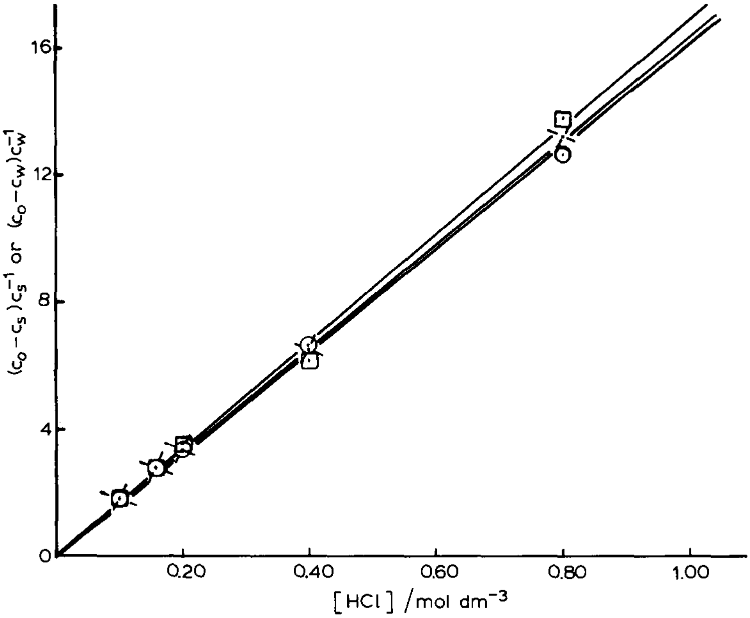

Fig. 2. Plots of $(c_0 - c_s)c_s^{-1}$ against [HCl] for 5.00 wt.% glucose (⊡) and 40.0 wt.% glucose (>·<) compared with $(c_0 = c_w)c_w^{-1}$ against [HCl] (⊙) with no added co-solvent with ionic strength = 1.00 mol dm^{-3} at 25 °C.

on the molality scale which were converted to the mole fraction scale using eqn. (27)

$$\Delta G_t^{\ominus}(\text{HCl}) = \Delta G_t^{\ominus}(\text{HCl})_m + 11.41 \log\left(\frac{18.015}{M_s}\right) \tag{27}$$

and $\Delta G_t^{\ominus}(\text{Cl}^-)$ was calculated from

$$\Delta G_t^{\ominus}(\text{Cl}^-) = \Delta G_t^{\ominus}(\text{HCl}) - \Delta G_t^{\ominus}(\text{H}^+) \tag{28}$$

using $\Delta G_t^{\ominus}(\text{H}^+)$ values in Table 2, and are also given in Table 2.

$K_{ip}^{c} = [\text{H}^+][\text{OH}^-]y_{\pm}$ values of Woolley et al. [20] on the molar scale, after conversion to the molality scale, K_{ip}^{m}, with eqn. (29)

$$\log K_{ip}^{m} = \log K_{ip}^{c} - 2 \log d_s \tag{29}$$

were used to calculate $\Delta G_t^{\ominus}(\text{H}^+)_m + \Delta G_t^{\ominus}(\text{OH}^-)_m$ from eqn. (30) [4]

$$\Delta G_t^{\ominus}(\text{H}^+)_m + \Delta G_t^{\ominus}(\text{OH}^-)_m = RT \ln\frac{\left(K_{ip}^{m}\right)_w}{\left(K_{ip}^{m}\right)_s} + RT \ln\frac{\left(a_{\text{H}_2\text{O}}^{s}\right)_m^2}{m_w m_w} \tag{30}$$

where m_w and m_s are the molalities of water in pure water and in the mixture, respectively, and for the activity of water in the mixture, $(a_{\text{H}_2\text{O}}^{s})_m = 55.509\ a_{\text{H}_2\text{O}}^{s}$(mole fraction) with $a_{\text{H}_2\text{O}}^{s}$(mole fraction) $= p_s/p_w$ using the total vapour pressures of Taylor and Rowlinson [18] with the assumption

TABLE 2

$\Delta G_t^{\ominus}(i)$ (kJ mol^{-1}) in water + co-solvent on the mole fraction scale at 25 ° C

[Co-solvent]		Glucose			Mannitol				Sorbitol		
wt.%	Mole fraction	H^+	Cl^-	OH^-	H^+	Na^+	K^+	Cl^-	H^+	Na^+	Cl^-
3.23	0.0033	–	–	−1.70	–	–	–	–	–	–	–
5.00	0.0052	−0.027	0.182	–	−0.051	–	–	0.122	−0.037	−0.319	0.053
5.00	0.0052	–	–	–	–	–	–	0.124	–	–	–
5.17	0.0054	–	–	–	–	−0.382	−0.388	–	–	–	–
5.82	0.0061	–	–	−3.04	–	–	–	–	–	–	–
8.00	0.0086	–	–	−3.46	–	–	–	–	–	–	–
10.00	0.0110	−0.074	0.417	–	−0.108	–	–	0.240	–	–	–
10.70	0.0118	–	–	−3.83	–	–	–	–	–	–	–
11.31	0.0125	–	–	–	–	−0.84	−0.84	–	–	–	–
13.50	0.0145	–	–	−4.19	–	–	–	–	–	–	–
15.00	0.0173	−0.108	–	–	−0.166	–	–	0.366	–	–	–
15.41	0.0177	–	–	–	–	−1.15	−1.17	–	–	–	–
15.60	0.0182	–	–	−4.41	–	–	–	–	–	–	–
17.94	0.0212	–	–	–	–	–	−1.36	–	–	–	–
18.00	0.0215	–	–	−4.65	–	–	–	–	–	–	–
20.00	0.0244	−0.169	0.94	−4.84	–	–	–	–	−0.165	−1.53	0.388
23.60	0.0300	–	–	−5.1	–	–	–	–	–	–	–
30.00	0.0411	−0.225	1.47	–	–	–	–	–	–	–	–
40.00	0.063	−0.340	–	–	–	–	–	–	–	–	–
50.00	0.091	−0.464	–	–	–	–	–	–	–	–	–

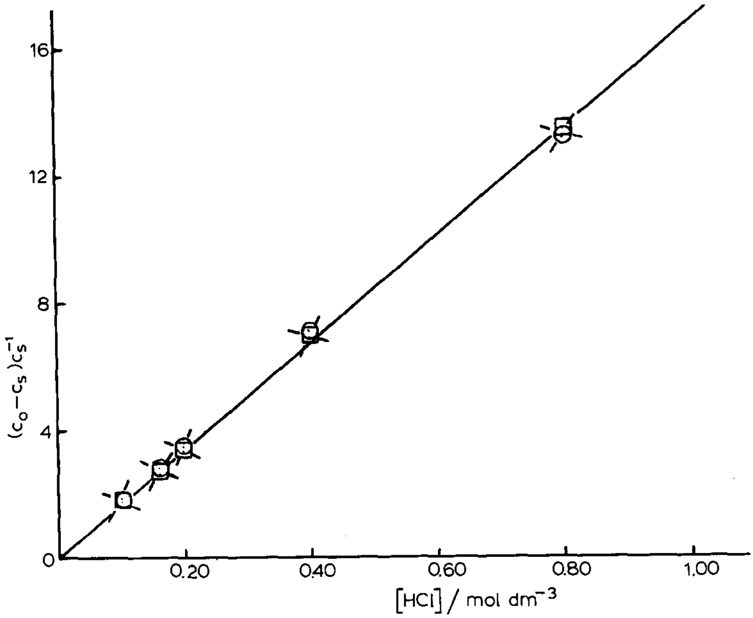

Fig. 3. Plots of $(c_0 - c_s)c_s^{-1}$ against [HCl] with an ionic strength of 1.00 mol dm^{-3} at 25 °C for 15.0 wt.% mannitol (⊙), 20.0 wt.% sorbitol (⊡) and ~10 wt.% inositol (>·<).

that the partial pressure of glucose in water + glucose is low enough to be neglected. This quantity is then converted to the mole fraction scale using an equation analogous to eqn. (27) and $\Delta G_t^{\ominus}(\mathrm{OH}^-)$, calculated from $\Delta G_t^{\ominus}(\mathrm{H}^+)$ in Table 2 and an equation analogous to eqn. (28), is given in Table 2.

Water + mannitol mixtures

Absorbances at 383 nm and 25 °C of water + mannitol mixtures containing HCl, NaCl and 4-nitroaniline were stable with time. However, Table 1 shows that $c_w = c_s$ for 15 wt.% mannitol, suggesting that $\Delta G_2 =$ zero in eqn. (4). This is confirmed by the linear plot of $(c_0 - c_s)/c_s$ versus $[\mathrm{H}^+]_\mathrm{T}$ in Fig. 3 giving $K_{1s}F_{1s}/[\mathrm{H_2O}]_s = 16.8$ dm^3 mol^{-1}. $\Delta G_t^{\ominus}(\mathrm{H}^+)$ in Table 2 for water + mannitol mixtures was calculated from eqn. (4) assuming $\Delta G_2 =$ zero with D_s interpolated from Åkerlöf's data [21] and d_s taken from Paabo and Robinson [22].

$E^{\ominus}$ values [22] for cell (25) with mannitol replacing glucose were converted to $\Delta G_t^{\ominus}(\mathrm{HCl})$ on the mole fraction scale using eqns. (26) and (27) and $\Delta G_t^{\ominus}(\mathrm{Cl}^-)$ found from eqn. (28) and $\Delta G_t^{\ominus}(\mathrm{H}^+)$ in Table 2. Activity coefficients $\gamma_\pm$ for NaCl [23] and KCl [24] in water + mannitol were converted to $\Delta G_t^{\ominus}(\mathrm{MCl})$ via eqn. (31)

$$\Delta G_t^{\ominus}(\mathrm{MCl})_\mathrm{m} = 2RT \ln \gamma_\pm \qquad (31)$$

and $\Delta G_t^{\ominus}(\mathrm{MCl})$ values on the mole fraction scale were obtained from an equation analogous to eqn. (27). $\Delta G_t^{\ominus}(\mathrm{M^+})$ was obtained using

$$\Delta G_t^{\ominus}(\mathrm{M^+}) = \Delta G_t^{\ominus}(\mathrm{MCl}) - \Delta G_t^{\ominus}(\mathrm{Cl^-}) \tag{32}$$

and the $\Delta G_t^{\ominus}(\mathrm{Cl^-})$ values in Table 2, and are also given in Table 2.

Water + sorbital mixtures

The stable absorbances of mixtures of water, sorbitol, HCl, NaCl and 4-nitroaniline at 383 nm also give $c_s = c_w$ (Table 1) and the linear plot found for $(c_0 - c_s)/c_s$ versus $[\mathrm{H^+}]_T$ in 20 wt.% sorbitol (Fig. 3) gives $K_{1s}F_{1s}/[\mathrm{H_2O}]_s = 16.8$ dm^3 mol^{-1}, confirming that $\Delta G_2 =$ zero in eqn. (4). $\Delta G_t^{\ominus}(\mathrm{H^+})$ values calculated using data for D_s and d_s taken from those of Crockford et al. [25] are given in Table 2.

$\Delta G_t^{\ominus}(\mathrm{HCl})$ for water + sorbitol were calculated using eqns. (26) and (27) with the $E_m^{\ominus}$ data from cell (25) with sorbitol replacing glucose [25] and, thereby, $\Delta G_t^{\ominus}(\mathrm{Cl^-})$ (Table 2) from eqn. (28) and $\Delta G_t^{\ominus}(\mathrm{H^+})$. $\Delta G_t^{\ominus}(\mathrm{NaCl})_m$ can be calculated for water + sorbitol using eqn. (33) [23]

$$\frac{2\,\partial \ln \gamma_\pm}{\partial m_B} = a + bm_c + cm_c^2 + em_B \tag{33}$$

with m_B and m_c being the molalities of sorbitol and NaCl, respectively. With $a = -0.5326$ [26] and $e = +0.0134$ [26], the integrated form of eqn. (33) [23]

$$2 \ln \gamma_\pm = m_B\left(a + \tfrac{1}{2}em_B\right)$$

becomes

$$\Delta G_t^{\ominus}(\mathrm{NaCl})_m = 2\,RT \ln \gamma_\pm = RT\,m_B\left(a + \tfrac{1}{2}em_B\right)$$

$\Delta G_t^{\ominus}(\mathrm{NaCl})$ on the mole fraction scale obtained from an equation analogous to eqn. (27) then yields $\Delta G_t^{\ominus}(\mathrm{Na^+})$ (Table 2) from eqn. (32) and $\Delta G_t^{\ominus}(\mathrm{Cl^-})$.

Water + inositol mixtures

The stable absorbances for HCl + NaCl and 4-nitroaniline in 0.56 mol dm^{-3} inositol (~ 10 wt.%) (Table 1) show that $c_s = c_w$ $K_{1s}F_{1s}/[\mathrm{H_2O}]_s$ from the slope of the linear plot obtained (Fig. 3) for $(c_0 - c_s)/c_s$ versus $[\mathrm{H^+}]_T$ is 16.8 dm^3 mol^{-1}, confirming that $\Delta G_2 =$ zero for 10 wt.% inositol. $\Delta G_t^{\ominus}(\mathrm{H^+})$ has not been calculated as the D_s value for water + inositol is not available.

Comparison of K_c values

In all four cases, glucose, mannitol, sorbitol and inositol, $\Delta G_2 =$ zero as indicated by the coincidence of c_s with the value of c_w determined under the same conditions and by the linear plots of $(c_0 - c_s)/c_s$ versus $[H^+]_T$ with agreement of $K_{1s}F_{1s}/[H_2O]_s$ with $K_{1w}F_{1w}/[H_2O]_w$ found when no co-solvent is added. These observations are in agreement with those found using high concentrations of glycerol [11] and with the low concentrations used for erythritol and pentaerythritol [7]. We can conclude that hydrophilic co-solvents possessing multiple OH groups do not re-arrange preferentially with water molecules in the vicinity of an aqua-proton, $H^+(H_2O)_x$. An alternative approach has determined that K_c for these hydrophilic molecules is very small relative to K_c for the monohydric alcohols [7,11], ketones [13,15] and other co-solvent molecules [13,14], with an upper limit of $K_c \lesssim 0.01$ dm^3 mol^{-1} for the former: the electron-attracting inductive effects of the multiple OH groups considerably reduce the bascity of any particular OH group [7]. In support of this, K_c for ethane-1,2-diol is less than that for ethanol [7] but the mutual electron-attracting effect of the OH groups in glycols is reduced by placing a hydrocarbon chain between the OH groups, restoring K_c to the values found for monohydric alcohols [7]. Furthermore, for both alcohols [7] and molecules containing carbonyl groups [13,15], log K_c has a roughly linear relationship in each case with the sum of the Taft $\sigma^\star$ functions for series with similar overall structures.

Comparison of $\Delta G_t^\ominus(i)$

Figure 4 shows the variation of $\Delta G_t^\ominus(i)$ with mole fraction of co-solvent for single ions in mixtures of water with all three co-solvents. That for glucose, the co-solvent with the widest range of x_2, shows a close resemblance to the variation for H^+, Cl^- and OH^- in water + glycerol [3], with small positive values for Cl^- rising with increasing x_2, small negative values for H^+ with $\Delta G_t^\ominus(H^+)$ becoming increasingly negative with increasing x_2 and much larger negative values for OH^-. In both these cases, glycerol and glucose, the relatively large negative values for $\Delta G_t^\ominus(OH^-)$ reflect the equilibrium position for

$$OH^- + ROH \rightleftharpoons RO^- + H_2O$$

lying to the right with a protic co-solvent, as found also with ethane-1,2-diol [3,6], in contrast to the positive values found for $\Delta G_t^\ominus(OH^-)$ with aprotic co-solvents [3,13] and for protic co-solvents [1–5], where the equilibrium above lies to the left.

The variations of $\Delta G_t^\ominus(H^+)$ and $\Delta G_t^\ominus(Cl^-)$ with x_2 for mannitol and sorbitol as co-solvents follow closely that found for glucose. However, $\Delta G_t^\ominus(Na^+)$ and $\Delta G_t^\ominus(K^+)$ are negative, as is usually found at low x_2 with all co-solvents except methanol [1–5,13,14], but, in contrast to the monohydric alcohols and other co-solvents, $-\Delta G_t^\ominus(Na^+)$ or $-\Delta G_t^\ominus(K^+) > -\Delta G_t^\ominus(H^+)$. The overall variation is otherwise very similar to that found for other co-solvents, hydrophilic monohydric alcohols and protic molecules,

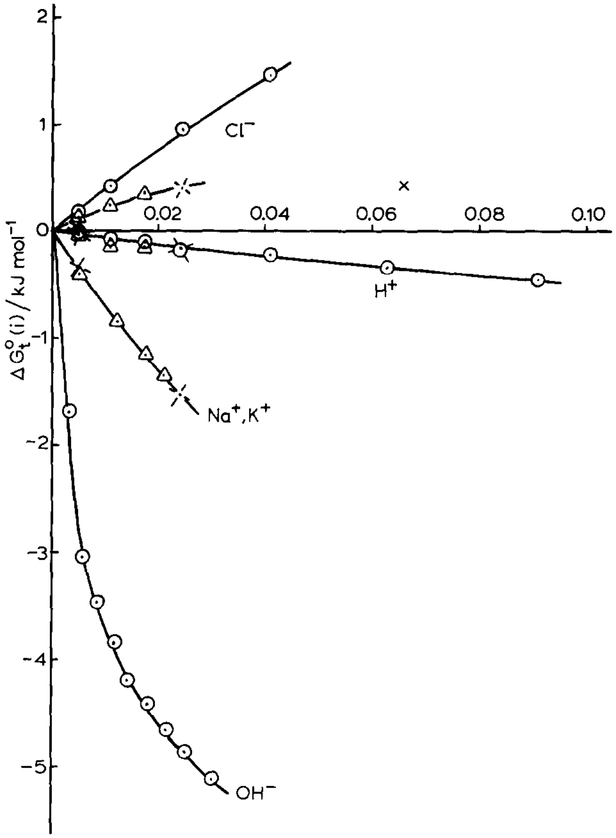

Fig. 4. Variation of $\Delta G_t^{\ominus}(i)$ for individual ions with mole fraction of co-solvent: ⊙, glucose; △, mannitol; >·< sorbitol.

with $\Delta G_t^{\ominus}$(cation) negative and $\Delta G_t^{\ominus}(Cl^-)$ positive and, for protic co-solvents, $\Delta G_t^{\ominus}(OH^-)$ negative [1–5,13,14].

APPLICABILITY OF THE SOLVENT-SORTING METHOD AND THE TATB METHOD

The three assumptions used in the solvent-sorting method are: (a) equality of ΔG for cavity formation and collapse in water and water-rich mixtures; (b) $K_{1w}F_{1w}/[H_2O]_w = K_{1s}F_{1s}/[H_2O]_s$; and (c) $y(B)_s y(BH^+)_w / y(BH^+)_s y(B)_w = y(P)_w y(H_2O)_w / y(H_2O)_s y(P)_w = 1$. Assumption (c) has already been commented on above, concluding that evidence from Hammett's acidity function supports $y(B)_s y(BH^+)_w / y(BH^+)_s y(B)_w = 1$ and by analogy, $y(P)_s y(H_2O)_w / y(H_2O)_s y(P)_w = 1$ for a wide range of conditions. Further evidence in support of the original conclusion (b) drawn from experiments with added glycerol is presented in this paper: (b) certainly applies in the water-rich conditions, mole fraction of water $x_1 = 1$–0.75 (or mole fraction of co-solvent $x_2 \lesssim 0.25$) [11] and evidence of linear plots for $c_w c_s/(c_w - c_s)$ versus $c_s/(c_0 - c_s)$ with intercepts corresponding to $c_0[H_2O]_w/K_{1w}F_{1w}[ROH]_T$ supports (b) outside this region ($x_2 \lesssim 0.35$) for some co-solvents [1–6,13,14]. It would seem unlikely that (a) will fail significantly in this water-rich region, certainly for hydrophilic co-solvents related to water, because, as eqn. (2) for the transfer of the singly charged sphere of radius = $3_{r_{H_2O}}$ essentially applies to two unstructured continua as media, any structural adjustments will be incorporated into eqns. (1) and (3). We conclude, therefore, that this method can be applied with confidence generally up to a mole fraction of co-solvent $x_2 \sim 0.25$ and beyond, as long as the linear plots discussed above are obtained experimentally.

The TATB method now incorporates the TPTB form in which it was proposed by Grunwald et al. [27]. Thus the assumption is

$$\Delta G_t^{\ominus}(Ph_4As^+) = \Delta G_t^{\ominus}(Ph_4P^+) = \Delta G_t^{\ominus}(BPh_4^-) \tag{34}$$

Grunwald et al. [27] based their original proposition on the following observation

$$\Delta G_t^{\ominus}(Ph_4P \cdot BPh_4) = 2\ \Delta G_t^{\ominus}(Ph_4C) \tag{35}$$

found for 50 wt.% dioxane only. Since then, eqn. (34) based on eqn. (35) has been assumed by a series of authors [8–10,28–30] to have almost universal applicability to both transfers between two pure liquids and between one pure liquid and a mixture of it with a co-solvent for mole fractions $x_2 = 0$–1.0. The equivalence of eqn. (34) has also been extended to enthalpies [31,32] and entropies of transfer [32]. The assumption is that the charge on Ph_4As^+, Ph_4P^+ and BPh_4^- will be so "buried" inside the ion as to have little or no influence on the surrounding solvent with eqn. (35) applying for a similar neutral species of about the same size. However, although Grunwald et al. [27] found quite good agreement for eqn. (35) in 50 wt.% dioxane, Tables 3 and 4 show that eqn. (35) does not apply universally to such free energies calculated from the published data [28] for transfers between two pure liquids: indeed, in some cases, particularly involving alcohols, the difference between $\Delta G_t^{\ominus}(Ph_4As \cdot BPh_4)$ and $2\Delta G_t^{\ominus}(Ph_4C)$ are considerable. Kim et al. [29] have taken three solvents for which $\Delta G_t^{\ominus}(Ph_4As \cdot BPh_4) - 2\ \Delta G_t^{\ominus}(Ph_4C)$ is on the low side (approx. 35%) and found an approximate agreement between $\Delta G_t^{\ominus}(Ph_4As \cdot BPh_4)$ and $\Delta G_t^{\ominus}(Ph_4C) + \Delta G_t^{\ominus}(Ph_4Ge)$ for the transfer water → water + DMF, water + CH_3CN and water + DMSO: yet, even here, for the best agreement in water + DMSO, the difference rises from 9% at low x_2 to 35% for $x_2 = 1.0$; and for water + CH_3CN, the mean difference for $x_2 = 0$–1.0 is $28 \pm 3\%$, and for water + DMF for $x_2 = 0$–1.0 is $29 \pm 2\%$. Kim et al. [29] then ascribe the difference to electrostatic effects on the solvent molecules of the charges to be divided equally between Ph_4As^+ (or Ph_4P^+) and BPh_4^-. However, it is quite clear that this approximately $\frac{1}{3}$ difference between $\Delta G_t^{\ominus}(Ph_4As \cdot BPh_4)$ and

TABLE 3

Comparison of $\Delta G_t^\ominus(\mathrm{Ph_4As \cdot BPh_4})$ with $2\Delta G_t^\ominus(\mathrm{Ph_4C})$ at 25 °C for the transfer acetonitrile → solvent

Solvent	$\Delta G_t^\ominus(\mathrm{Ph_4As \cdot BPh_4})$ (kJ mol^{-1})	$2\Delta G_t^\ominus(\mathrm{Ph_4C})$ (kJ mol^{-1})
Nitromethane	−0.57	−2.3
Propylene carbonate	−6.9	0
Acetone	12.6	−4.6
Methanol	18.3	5.7
Ethanol	20.6	5.7
Formamide	17.1	19.4
N,*N*-Dimethylformamide	−10.9	−8.0
N,*N*-Dimethylacetamide	−10.3	−9.1
N-Methyl-2-pyrolidene	−14.3	−13.7
Dimethyl sulphoxide	−12.6	−9.1
Hexamethylphosphoramide	−12.0	−10.3

$\{\Delta G_t^\ominus(\mathrm{Ph_4C}) + \Delta G_t^\ominus(\mathrm{Ph_4Ge})\}$ or the difference between $\Delta G_t^\ominus(\mathrm{Ph_4As \cdot BPh_4})$ and $2\Delta G_t^\ominus(\mathrm{Ph_4C})$ can arise from the difference between two large opposing effects for the two ions. Even Grunwald et al. [27] admitted that about 70% of the single charge on the central atom would be transmitted to the surface of the ion. Strehlow et al. [33] have pointed out that the assumption of sphericity of this charge is not true, allowing close access of solvent molecules to the charge, and Coetzee and Sharpe [34] and Farmer et al. [35] have found NMR effects suggesting specific interactions of the opposite charges with solvent molecules. Moreover, as Table 5 shows for a representative selection of large ions ($\mathrm{K^+}$ and $\mathrm{Cl^-}$ are included for comparison), significant differences in $\Delta G_t^\ominus(i)$ calculated using assumption (34) occur between ions with single charges of opposite sign and between those with double charges of opposite sign for the transfer water → water + an alcohol, or water → water + acetone: even so, because of assumption (34), the differences in Table 5 are compressed [36] compared with those found

TABLE 4

Comparison of $\Delta G_t^\ominus(\mathrm{Ph_4As \cdot BPh_4})$ with $2\Delta G_t^\ominus(\mathrm{Ph_4C})$ at 25 °C for the transfer methanol → solvent

Solvent	$\Delta G_t^\ominus(\mathrm{Ph_4As \cdot BPh_4})$ (kJ mol^{-1})	$2\Delta G_t^\ominus(\mathrm{Ph_4C})$ (kJ mol^{-1})
N,*N*-Dimethylformamide	−27.4	−18.3
N,*N*-Dimethylacetamide	−29.1	−16.0
Acetonitrile	−18.8	−5.7

TABLE 5

Comparison of $\Delta G_t^\ominus(i)$ (kJ mol^{-1}) at 25 °C for oppositely charged ions on the molar scale using the TATB method for water → water + wt.% co-solvent

i	Methanol		Ethanol[a]		Propan-2-ol[a]		Acetone[a]
	40%	60%	40%	60%	40%	60%	35%
Pr_4N^+	−4[b]	−6[b]	−5.6	−9	–	–	−10
Bu_4N^+	−6.6[b]	−11[b]	−9	−20	–	–	–
K^+	5[b]	7[b]	3.5	4.8	1.2	1.2	−3.6
Cl^-	2.6[b]	5[b]	4.8	9.3	2.8	9.4	10.6
ClO_4^-	−0.2[b]	0.6[b]	1.5	3.2	4	6	
IO_3^-	6.2[a]	–	–	–	–	–	–
BrO_3^-	4[a]	–	–	–	–	–	–
$Sb(OH)_6^-$	–	–	–	–	–	–	11
$AgCl_2^-$	–	–	1.8	4	–	–	–
$Fe(bipy)_3^{2+}$	−10[a]	−13.6[a]	−11	−15	−17	−18	–
$Fe(phen)_3^{2+}$	−13[b]	−16.3[b]	−17.6	−19.4	−22.7	−24.4	−32
$AgCl_3^{2-}$	–	–	10	19	–	–	–
$IrCl_6^{2-}$	8.4[b]	–	–	–	–	–	16.6
$ReCl_6^{2-}$	5[b]	–	7	11	–	–	–
$PtCl_6^{2-}$	–	–	13.3	–	–	–	–
$PtCl_6^{2-}$	–	–	–	–	–	–	10.7
$ReBr_6^{2-}$	4.6[b]	–	–	–	–	–	–
CrO_4^{2-}	7[a]	–	7	10	–	–	–
$Cr_2O_7^{2-}$	0.6[a]	1.8[a]	–	–	12.5	–	–
$Fe(CN)_5NO^{2-}$	6.2[a]	10.1[a]	–	–	–	–	–

[a] Ref. 11.
[b] Ref. 30.

for the same ions using the solvent-sorting procedure [1–3,13]. For the separate ions i^{z+} and i^{z-}

$$\Delta G_t^\ominus(i^{z+}) = \Delta G_t^\ominus(i^{z+})_n + \Delta G_t^\ominus(i^{z+})_e \tag{36}$$

and

$$\Delta G_t^\ominus(i^{z-}) = \Delta G_t^\ominus(i^{z-})_n + \Delta G_t^\ominus(i^{z-})_e \tag{37}$$

where subscripts n and e indicate components arising from the neutral bulk of i and from the charge on i respectively. Adding eqns. (36) and (37) gives, for the salt $i^{z+} \cdot i^{z-}$

$$\Delta G_t^\ominus(i^{z+} \cdot i^{z-}) = \Delta G_t^\ominus(i^{z+} \cdot i^{z-})_n + \Delta G_t^\ominus(i^{z+} \cdot i^{z-})_e$$

where

$$\Delta G_t^\ominus(i^{z+} \cdot i^{z-})_n = \Delta G_t^\ominus(i^{z+})_n + \Delta G_t^\ominus(i^{z-})_n$$

and

$$\Delta G_t^\ominus(i^{z+} \cdot i^{z-})_e = \Delta G_t^\ominus(i^{z+})_e + \Delta G_t^\ominus(i^{z-})_e$$

However, if, as suggested by Tables 3–5 and the results of the solvent-sorting procedure [1–3,13,37], $\Delta G_t^{\ominus}(i^{z+})_e$ is frequently negative and $\Delta G_t^{\ominus}(i^{z-})_e$ positive for the same z, a small $\Delta G_t^{\ominus}(i^{z+} \cdot i^{z-})_e$ may result even when $|\Delta G_t^{\ominus}(i^{z+})|$ and $|\Delta G_t^{\ominus}(i^{z-})|$ are numerically large with $\Delta G_t^{\ominus}(i^{z})_e$ constituting a large proportion of $\Delta G_t^{\ominus}(i^{z})$ for both i^{z+} and i^{z-}, as found for even simple inorganic ions [36]. However, Tables 3–5 indicate that $\Delta G_t^{\ominus}(i^{z+} \cdot i^{z-})_e$ will vary considerably and it would seem highly unlikely, therefore, that even an approximate agreement between $\Delta G_t^{\ominus}(\mathrm{Ph_4As^+})$ (or $\Delta G_t^{\ominus}(\mathrm{Ph_4P^+})$) and $\Delta G_t^{\ominus}(\mathrm{BPh_4^-})$ will occur universally, covering all cosolvents mixed in all proportions, as has been suggested [8–10,38].

The prospect opened by the initial good agreement for eqn. (35) in 50 wt.% dioxane by Grunwald et al. [27] does not seem to have been sustained by the examination of similar data for pure solvents and other aqueous mixtures. Tables 3–5 suggest that the caution urged at various times against the universal use of the TATB assumption by Coetzee and Sharpe [34], Strehlow et al. [33] and Farmer et al. [35] can no longer be ignored. It is also interesting to note that the strong support proposed [8,38] for the TATB method on the basis of the apparent agreement obtained between $\Delta G_t^{\ominus}(\mathrm{Ph_4As^+})$ and $\Delta G_t^{\ominus}(\mathrm{Ph_4P^+})$ using this method is not justified, as the solvent-sorting method used in this paper produces the same result [1,3,37].

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