

Ionic solvation in water + co-solvent mixtures Part 23. Free energies of transfer of single ions from water into water + diethylene glycol mixtures

Kamal H.M. Halawani and Cecil F. Wells

School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT (UK)

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Abstract

The spectrophotometric solvent sorting method for determining the free energy of transfer of the proton $\Delta G_t^\ominus(\text{H}^+)$ from water into mixtures of water with a co-solvent has been applied to mixtures of water with diethylene glycol. These values for $\Delta G_t^\ominus(\text{H}^+)$ have been used to calculate $\Delta G_t^\ominus(\text{X}^-)$ for $\text{X}^- = \text{Cl}^-$, Br^- and I^- from the data for $\Delta G_t^\ominus(\text{HX})$. The variation of these values of $\Delta G_t^\ominus(i)$ with solvent composition obtained for single ions i in these mixtures is compared and contrasted with similar variations which have been found for $\Delta G_t^\ominus(i)$ for mixtures of water with hydrophobic alcohols and for mixtures of water with other multi-hydroxy co-solvents and alkoxyethanols by correlating the different variations with the physical properties of the mixtures. To aid this, the densities of water+diethylene glycol mixtures have been measured and the relative partial molar volumes of water and glycol in the mixtures have been calculated.

Following our investigation of the effect of increasing the hydrophobicity of the co-solvent molecules on free energies of transfer of individual ionic species $\Delta G_t^\ominus(i)$ from water into water + alcohol mixtures, using the spectrophotometric solvent sorting method for determining $\Delta G_t^\ominus(\text{H}^+)$ [1,2], we have started applying this method to highly hydrophilic materials like carbohydrates and polyalcohols as co-solvents [3]. Data for $\Delta G_t^\ominus(i)$ in mixtures of water with the latter can be compared with $\Delta G_t^\ominus(i)$ in mixtures of water with ethane-1,2-diol [1,2] and with glycerol [1,2]. We now report for comparison $\Delta G_t^\ominus(i)$ determined by the solvent sorting method for mixtures of water with diethylene glycol (digol).

The solvent sorting method determines $\Delta G_t^\ominus(\text{H}^+)$ as defined in eqn. (1)

$$\Delta G_t^\ominus(\text{H}^+) = \mu_s^\ominus(\text{H}^+) - \mu_w^\ominus(\text{H}^+) \quad (1)$$

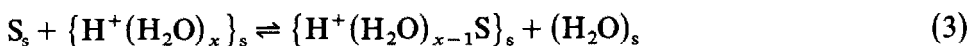
where subscripts s and w indicate the mixture and water respectively. Firstly, the standard state for the single entity of the proton solvated by water is shifted from water into the mixture by calculating the transfer free energy of

a charged sphere $P = H^+(H_2O)_5$ from water into the mixture according to the Born equation

$$\Delta G_1^\ominus (\text{Born}) = \mu_s^\ominus (P) - \mu_w^\ominus (P) = 167.6(D_s^{-1} - D_w^{-1}) \text{ kJ mol}^{-1} \quad (2)$$

where D is the dielectric constant. The standard state in either solvent is defined by $y = 1.0$ and $[P] = 1.00 \text{ mol dm}^{-3}$ with $y \rightarrow 1.0$ as $[P] \rightarrow 0$ in that solvent. It is assumed for this transfer into water-rich mixtures that the free energy of collapse of the hole vacated by P in water is equal to the free energy of formation of the hole formed in the mixture to accommodate P : this is supported by $\bar{V}_1 - V_1^\ominus$ for the water molecules remaining essentially zero for such water-rich mixtures.

The second stage of the transfer now involves the re-sorting of the solvent molecules around the proton at the new standard state in the mixture. If the co-solvent in the water-rich mixture is S , this re-sorting is envisaged as taking place in the equilibrium



where $x \geq 5$ in the mixture. Equilibrium (3) can be investigated experimentally by examining the competition of the two protonated species $P_s = H^+(H_2O)_x$ and $SH_s^+ = \{H^+(H_2O)_{x-1}S\}_s$ for a fixed added concentration c_0 of 4-nitroaniline (B) for a range of $[HCl]$ at a constant total added concentration of co-solvent $[S]_T$.



For any particular $[HCl]$, if c is the concentration of B without $[S]_T$ added and c_s is the concentration of B with $[S]_T$, it has been shown that eqn. (6) is obeyed

$$\frac{cc_s}{(c_s - c)} = \frac{K_2 F_2}{K_1 F_1} \frac{c_0 c_s}{(c_0 - c_s)} \frac{[H_2O]_s}{[S]_T} + \frac{[H_2O]_s c_0}{K_1 F_1 [S]_T} \quad (6)$$

for added alcohols, ethers, ketones or others [1-4]. K_1 and K_2 are the thermodynamic equilibrium constants for equilibria (4) and (5) and $F_1 = y(B)y(P)/y(BH^+)y''(H_2O)$ and $F_2 = y(B)y(SH^+)/y(BH^+)y''(S)$, where the standard states for the dissolved species B , BH^+ , P and SH^+ are as defined above in the mixture and for H_2O and S $y'' \rightarrow 1.0$ as $\Sigma [\text{dissolved species}] \rightarrow 0$ on the molar scale in the mixture. The assumption used in deriving eqn. (6), $(K_1 F_1 / H_2O)_s = (K_1 F_1 / H_2O)_w$, is equivalent [3] to $[BH^+]_s / [B]_s [P]_s = [BH^+]_w / [B]_w [P]_w$ and does not limit the applicability of (6) to low $[S]_T$ [3].

The free energy change for the solvent sorting in the mixture is given by

$$\begin{aligned} \Delta G_2 &= [SH^+] \{ \mu_s^\ominus (H_2O) + \mu_s^\ominus (SH^+) - \mu_s^\ominus (P) - \mu_s^\ominus (S) \} \\ &= -[SH^+] RT \ln K_c [H_2O]_s F_c \end{aligned} \quad (7)$$

where $K_c = [\text{SH}^+]_s/[\text{S}]_s[\text{P}]_s$ and $F_c = \gamma(\text{SH}^+)y''(\text{H}_2\text{O})/\gamma(\text{P})y''(\text{S})$. Values for $K_c F_c^{-1}$ are derived by calculating c_0 (slope) $^{-1}$ $[\text{S}]_T^{-1}$, where the slope is that for the linear plots obtained for $cc_s/(c_s - c)$ against $c_s/(c_0 - c_s)$ used to test eqn. (6). It is confirmed that the symmetrical term $F_c = 1.0$ [1-3], as K_c calculated using eqns. (8) and (9)

$$K_c = \frac{[\text{SH}^+]}{([\text{H}^+]_T - [\text{SH}^+])([\text{S}]_T - [\text{SH}^+])} \quad (8)$$

$$[\text{SH}^+] = \frac{[\text{S}]_T}{1 + (K_2 F_2 c_0 / (c_0 - c_s))} \quad (9)$$

is equal to $K_c F_c^{-1}$ obtained using only the slopes, where $K_2 F_2$ is obtained from the slopes and intercepts of the plots of eqn. (6) and $[\text{H}^+]_T$, which equals the total added $[\text{HCl}]$.

The free energy of transfer on the mole fraction scale is now given by eqn. (10)

$$\Delta G_t^\ominus(\text{H}^+) = \Delta G(\text{Born}) - [\text{SH}^+] RT \ln K_c [\text{H}_2\text{O}]_s + RT \ln \frac{d_s M_w}{d_w M'_s} \quad (10)$$

where $[\text{SH}^+]$ is given by eqns. (11) and (12)

$$[\text{SH}^+] = 0.5 \left\{ A - (A^2 - 4[\text{S}]_T)^{1/2} \right\} \quad (11)$$

$$A = ([\text{S}]_T + 1 + K_c^{-1}) \quad (12)$$

and $[\text{H}_2\text{O}]_s$ is given by

$$[\text{H}_2\text{O}]_s = (1000d_s - [\text{S}]_T M_s) M_w^{-1} \quad (13)$$

where d is density, M_s and M_w are the molecular weights of the co-solvent and water respectively and, in eqn. (10), $M'_s = 100/((\text{wt}\% \text{S}/M_s) + (\text{wt}\% \text{H}_2\text{O}/M_w))$.

EXPERIMENTAL

Diethylene glycol was purified by fractional distillation under reduced pressure: the fraction used boiled at 145–146°C at a pressure of 5–6 mm of Hg. All other materials used were as described for earlier determinations of $\Delta G_t^\ominus(\text{H}^+)$ [1-3]. Concentrations of 4-nitroaniline were again determined spectrophotometrically at 383 nm at 25°C [4]. Mixtures of the water and the glycol were prepared by diluting a known volume of the glycol to a fixed volume using water; the total volume of water added was determined experimentally by examining the contraction on mixing. Densities were determined at 25°C using specific gravity bottles.

RESULTS AND DISCUSSION

Determination of $\Delta G_t^\ominus(H^+)$

Linear plots for $cc_s/(c_s - c)$ against $c_s/(c_0 - c_s)$ were obtained (Fig. 1) for measurements of c and c_s at 11.03, 21.67, 32.03, 42.13 and 61.39 wt% of diethylene glycol, and the intercepts coincided with those required by eqn. (6) using $K_1F_1/[H_2O]$ determined in pure water. Values for $K_cF_c^{-1}$ calculated from the slopes of these plots are given in Table 1. K_2F_2 calculated from the slope/intercept ratios of these plots are also given in Table 1, and these values have been used to calculate values for K_c at each $[HCl]$ for all the mixtures using eqns. (8) and (9). These values for K_c agree well amongst themselves for each mixture and the mean agrees well with $K_cF_c^{-1}$, except for some erratic behaviour among the K_c values at 61.39 wt% of glycol, where high errors in $([H^+]_T - [SH^+])$ arise due to low values for this

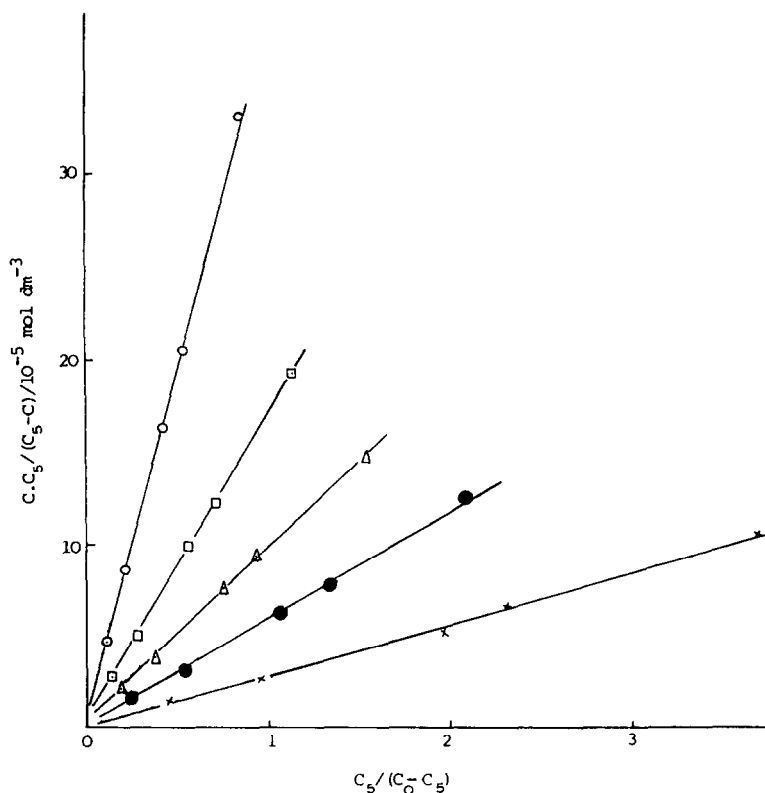


Fig. 1. Plots of $cc_s/(c_s - c)$ against $c_s/(c_0 - c_s)$ for HCl+NaCl at an ionic strength = 1.00 mol dm⁻³ and at 25°C for mixtures of water with diethylene glycol containing the following wt% of glycol: (○) 11.03; (□) 21.67; (Δ) 32.03; (●) 42.13; (×) 61.39.

TABLE 1

Values for K_c , $K_c F_c^{-1}$ ($\text{dm}^3 \text{mol}^{-1}$) and $K_2 F_2$ at 25°C and at an ionic strength of 1.00 mol dm^{-3} for water + diethylene glycol mixtures

Total added acidity $[\text{H}^+]_{\text{T}}$ (mol dm^{-3})	Concentration of diethylene glycol, wt% (mole fraction)				
	11.03 (0.021)	21.67 (0.045)	32.03 (0.074)	42.13 (0.110)	61.39 (0.213)
0.100	0.383	0.445	0.51	0.65	1.45
0.160	0.377	0.435	0.54	0.59	1.36
0.200	0.380	0.441	0.53	0.59	0.82
0.400	0.370	0.421	0.487	0.53	0.82
0.800	0.349	0.407	0.467	0.57	0.91
mean K_c	0.37 ± 0.01	0.41 ± 0.01	0.51 ± 0.03	0.59 ± 0.04	1.1 ± 0.3
$K_2 F_2$	43.2	38.1	32.8	27.0	18.8
$K_c F_c^{-1}$ from slope	0.364 ± 0.003	0.41 ± 0.01	0.48 ± 0.01	0.58 ± 0.01	0.84 ± 0.02

difference under these conditions. This confirms that, as expected for such a symmetrical function [1-3], $F_c = 1.0$.

Values for ΔG_2 can now be calculated using the experimental values of $K_c F_c^{-1}$ with $F_c = 1.0$ taken directly from the slopes, together with $[\text{SH}^+]$ calculated from eqns. (11) and (12), also using these values for K_c and $[\text{H}_2\text{O}]_s$ calculated from eqn. (13) using the measured densities. ΔG_2 is plotted against mole fraction of diethylene glycol in Fig. 2.

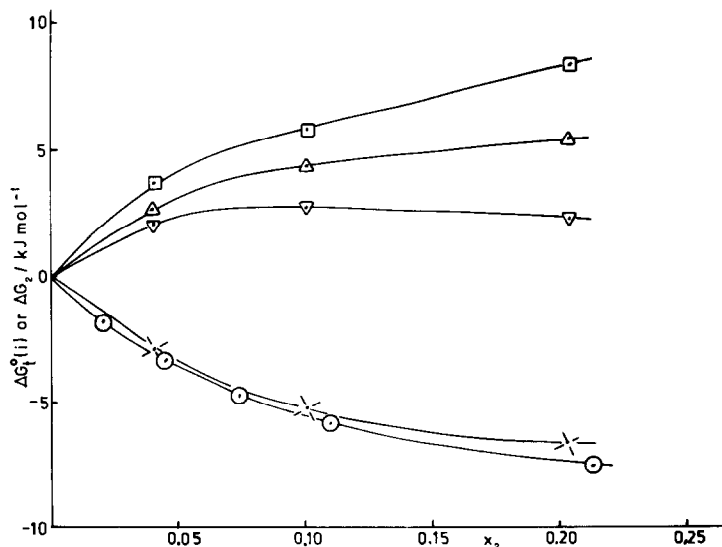


Fig. 2. The variation of ΔG_2 from eqn. (7) (\circ) and of the free energy of transfer at 25°C from water into water + diethylene glycol mixtures of H^+ (\times), Cl^- (\square), Br^- (\triangle) and I^- (∇) with the mole fraction of diethylene glycol.

TABLE 2

Densities (g cm^{-3}) of water + diethylene glycol mixtures at 25°C

Diethylene glycol (wt%)	Density
11.03	1.0125
21.67	1.0275
32.03	1.0435
42.13	1.0610
51.89	1.0735
61.39	1.0860
80.03	1.1060

TABLE 3

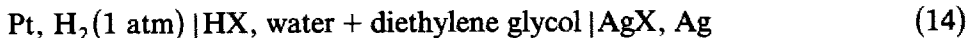
Values for the free energy of transfer of single ions from water into water + diethylene glycol mixtures at 25°C on the mole fraction scale

Concentration of glycol, wt% (mole fraction)	H^+	Cl^-	Br^-	I^-
20.00 (0.0407)	-2.93	3.68	2.71	2.02
40.00 (0.102)	-5.2	5.8	4.35	2.70
60.00 (0.203)	-6.6	8.2	5.4	2.24

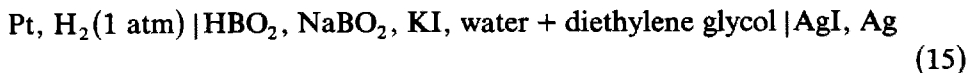
$\Delta G_t^\ominus(\text{H}^+)$ can now be calculated for any solvent composition by interpolating ΔG_2 from Fig. 2 and substituting into eqn. (10). Values for the dielectric constant needed to calculate $\Delta G(\text{Born})$ were taken from the data of Kalidas and Rao [5], and d_s to calculate the term changing $\Delta G_t^\ominus(\text{H}^+)$ from the molar scale to the mole fraction scale was interpolated from the experimental data in Table 2. The values obtained for $\Delta G_t^\ominus(\text{H}^+)$ are given in Table 3.

Determination of ΔG_t^\ominus (anion)

Values for $\Delta G_t^\ominus(\text{HX})$ are available in water + diethylene glycol mixtures for $\text{X}^- = \text{Cl}^-$, Br^- and I^- . $\Delta G_t^\ominus(\text{HCl})$ and $\Delta G_t^\ominus(\text{HBr})$ have been determined using E^\ominus values obtained for the cell (14) [5,6]



and $\Delta G_t^\ominus(\text{HI})$ from E^\ominus values for the buffered cell (15)



$\Delta G_t^\ominus(\text{X}^-)$ can then be evaluated from eqn. (16)

$$\Delta G_t^\ominus(\text{X}^-) = \Delta G_t^\ominus(\text{HX}) - \Delta G_t^\ominus(\text{H}^+) \quad (16)$$

with all free energies on the mole fraction scale and selecting $\Delta G_i^\ominus(\text{H}^+)$ from Table 3 for the correct solvent composition. The values for $\Delta G_i^\ominus(\text{X}^-)$ for $\text{X}^- = \text{Cl}^-$, Br^- and I^- are collected in Table 3.

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

The variation of $\Delta G_i^\ominus(i)$ for $i = \text{H}^+$, Cl^- , Br^- and I^- with solvent composition is illustrated in Fig. 2. Two observations can be made immediately from Fig. 2. Firstly, the major contributor to $\Delta G_i^\ominus(\text{H}^+)$ is ΔG_2 , as found for all other mixtures of water + co-solvent [1–3]. Secondly, as found for all co-solvents [1–3], $\Delta G_i^\ominus(\text{H}^+)$ is negative and $\Delta G_i^\ominus(\text{halide})$ is positive, with $\Delta G_i^\ominus(\text{I}^-)$ being negative only for mixtures of water + ethylene glycol and of water + glycerol [1].

The positive values for $\Delta G_i^\ominus(\text{X}^-)$ increase on a smooth curve with increasing mole fraction of co-solvent x_2 , and $\Delta G_i^\ominus(\text{H}^+)$ decreases on a smooth curve with increasing x_2 . For hydroxy co-solvents, this behaviour resembles more the variations of $\Delta G_i^\ominus(\text{X}^-)$ and $\Delta G_i^\ominus(\text{H}^+)$ for water + methanol [1,3], water + 2-ethoxyethanol [8] and water + 2-methoxyethanol [9]. In contrast, the variations of $\Delta G_i^\ominus(\text{X}^-)$ with x_2 in particular show a tendency to flatten off for mixtures of water with the monohydric alcohols, culminating in a maximum for the hydrophobic alcohols propan-2-ol and *t*-butyl alcohol [1,3]. The negative values for $\Delta G_i^\ominus(\text{H}^+)$ show a similar tendency towards a minimum with increasing hydrophobicity in the alcohol.

All the indicators to structure in the solvent suggest that, for hydrophobic alcohols, a maximum in structure formation occurs in the same region of composition where the tendency to an extremum in $\Delta G_i^\ominus(i)$ exists. The structural contribution to the increase in the temperature of the maximum density of water is positive [10] with a large sharp minimum in the relative partial molar volume of the alcohol, $\bar{V}_2 - V_2^\ominus$, accompanied by little variation in the relative partial molar volume of the water, $\bar{V}_1 - V_1^\ominus$ [11], and a large sharp maximum in the ultrasonic absorption [13,14]. Glycols, glycerol and methanol mixed with water show [11,15] only a small minimum in $\bar{V}_2 - V_2^\ominus$ and no maximum in the ultrasonic absorption [13]; although ethane-1,2-diol and glycerol each have a negative structural contribution to the increase in the temperature of the maximum density of water [10], other glycols have positive contributions [16] but smaller in magnitude than those found for monohydric alcohols [10]. The excess enthalpies of mixing ΔH_M^E of water with a hydroxylic co-solvent also differ for methanol and ethane-1,2-diol on the one hand and for the other monohydric alcohols on the other hand. Thus, ΔH_M^E for methanol [17] and ethane-1,2-diol [18] both have a minimum at $x_2 \approx 0.5$, but the propanols and *t*-butyl alcohol have a minimum at low x_2 and a maximum at high x_2 [12,17]. ΔH_M^E for ethanol shows an intermediate situation [17] and ΔH_M^E for polyethylene glycol [19] resembles that for ethane-1,2-diol [18]. The $\bar{V}_2 - V_2^\ominus$ [9] and ΔH_M^E [20]

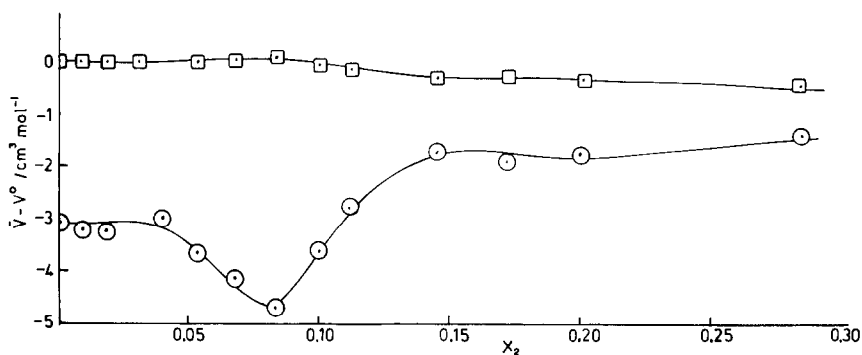


Fig. 3. The variation of relative partial molar volumes at 25°C of water (\square) and of diethylene glycol (\circ) with the mole fraction of diethylene glycol.

values for alkoxyethanols with small alkoxy groups resemble the variations found for ethane-1,2-diol.

Mixtures of water with diethylene glycol resemble those for water with ethane-1,2-diol in not having [21] the maximum in the variation of viscosity η with composition found for water + alcohol mixtures [12,22]. Moreover, ΔH_M^E for water + diethylene glycol [23] resembles that for water + ethane-1,2-diol [18], water + methanol [17] or water + alkoxyethanol [20]. Although densities are available for some mixtures of water with diethylene glycol for glycol-rich conditions [24], our measurements in Table 2 supply more data for water-rich conditions. The data of Gallant [24] at 25°C for 40, 60 and 80 wt% of diethylene glycol agree well with our values, but Gallant's value at 20 wt% [24] deviates from the plot of our densities vs. composition. Moreover, Gallant's value for pure diethylene glycol [24] deviates from the other values [25]. Using our densities in Table 2 we have calculated $\bar{V}_1 - V_1^\ominus$ and $\bar{V}_2 - V_2^\ominus$. Figure 3 shows that there is a shallow minimum in $\bar{V}_2 - V_2^\ominus$ at $x_2 \approx 0.08$, whilst $\bar{V}_1 - V_1^\ominus$ shows little change in the water-rich region, resembling the variations in mixtures of water with ethane-1,2-diol [11,15], methanol [11] and 2-ethoxyethanol [9].

It seems, therefore, that the tendency for $\Delta G_i^\ominus(i)$ to reach an extremum at low x_2 , found for the hydrophobic monohydric alcohols such as propan-2-ol and *t*-butyl alcohol, can be correlated with a sharp minimum in $\bar{V}_2 - V_2^\ominus$ at low x_2 and with a sharp maximum in the ultrasonic absorption at a slightly higher x_2 at which, approximately, a sharp minimum in ΔH_M^E occurs. This latter sharp minimum in water-rich conditions is followed by a maximum in ΔH_M^E in alcohol-rich conditions. The restriction imposed on the alcohol at low x_2 in the mixture, leading to the minimum in $\bar{V}_2 - V_2^\ominus$, probably arises mainly from the exclusion of the hydrocarbon tails from the "flickering icebergs" of structured water [26] into the intermediate cavities, with the negative ΔH_M^E arising from the stronger hydrogen bonding between the alcohol and water compared with that in the pure alcohol. One reason for

this must be the electron releasing alkyl group increasing the electron density on the hydroxyl oxygen, and thereby increasing the strengths of hydrogen bonds with the alcohol. These effects at low x_2 stabilize the proton in the mixture compared with water by pushing equilibrium (3) to the right. As the cavities between the "icebergs" of structured water fill with hydrocarbon tails, causing an expansion of the cavities by breaking up the "icebergs", $\bar{V}_2 - V_2^\ominus$ rises and $-\Delta H_M^E$ gets smaller due to the enthalpy input to the breakage of the hydrogen bonds of the water, which results, in the case of the alcohols with larger hydrocarbon tails, in a positive ΔH_M^E at higher x_2 . This change to the nature of the solvating medium from predominately aqueous to a broken down water structure with larger clusters of hydrocarbon tails causes equilibrium (3) to relax back towards the left, leading to lower values for $-\Delta G_t^\ominus(\text{H}^+)$. For anions, the effects are in the reverse directions, the changes in solvation first destabilizing the anion in the mixture relative to pure water, with this destabilization decreasing as the media changes as x_2 rises.

For methanol [11,17], ethane-1,2-diol [11,18], glycerol [11,27], alkoxyethanols [9,20] and diethylene glycol [20,23], with their lower ratio of hydrocarbon content to hydrogen bonding capacity, little restriction on the hydrocarbon tails occurs in the cavities between the "icebergs", resulting in only a low negative value for $\bar{V}_2 - V_2^\ominus$, but hydrogen bonding between the co-solvent and water continues across the whole composition range, producing a single broad minimum in ΔH_M^E . This delays the transition from one solvating medium to another until higher x_2 than those found for the more hydrophobic alcohols, and the destabilization of the proton and the stabilization of anions which occur at higher x_2 for the hydrophobic alcohols do not occur for the media with $x_2 < 0.25$ investigated here for diethylene glycol. Methanol [1,2], 2-methoxyethanol [8] and 2-ethoxyethanol [9] resemble diethylene glycol. For ethane-1,2-diol [1,2], extrema show at $x_2 \approx 0.25$ for some ions and, although smooth variations of $\Delta G_t^\ominus(i)$ with x_2 occur with glycerol, $\Delta G_t^\ominus(\text{I}^-)$ is negative [1].

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