Thermochimica Acta, 208 (1992) 323–339
Elsevier Science Publishers B.V., Amsterdam

Ionic solvation in water + co-solvent mixtures.
Part 24. Free energies of transfer of single ions from water into water + 1,2-dimethoxyethane mixtures

Cecil F. Wells

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

(Received 16 January 1992)

Abstract

The spectrophotometric solvent-sorting method for determining the free energy of transfer of the proton from water into water + co-solvent mixtures $\Delta G_t^\ominus(H^+)$ has been shown to apply to water-rich mixtures containing, 1,2-dimethoxyethane. Using $\Delta G_t^\ominus(H^+)$, values for $\Delta G_t^\ominus$(anion) and $\Delta G_t^\ominus$(cation) can be derived from the free energies of transfer of acids and salts. The free energy of transfer of the charge alone on large organic ions, $\Delta G_t^\ominus(i)_e$, has been calculated using pK_a values for organic acids in water and in the mixture in conjunction with $\Delta G_t^\ominus(H^+)$ values. These values for $\Delta G_t^\ominus(i)$ and $\Delta G_t^\ominus(i)_e$ in water + 1,2-dimethoxyethane mixtures are compared with similar free energies of transfer for ions from water into mixtures of similar co-solvents with water. To aid this comparison, values for the relative partial molar volumes of water and 2-methoxyethanol have been calculated for their mixtures.

INTRODUCTION

The observation [1–4] of a maximum in the Hammett Acidity Function H_0 in mixtures of water with an organic co-solvent suggested that the complete range of mixtures should be considered as two separate solvents, one water-rich and the other co-solvent-rich, each having its own structure, with an overlapping area around 50% composition. In our work investigating the proton in such mixtures [5–17], we have concentrated on the water-rich mixtures ($\leqslant$50 wt.% of co-solvent) where the effect of solutes on the solvent structure has been examined [18–22]. For such water-rich conditions, we found for a small fixed added concentration c_0 of a Hammett indicator B, with $[B] = c_s$ with an added co-solvent concentration $[S]_{Total}$ and an acid concentration, and $[B] = c$ at the same acid concentration but without any added co-solvent, linear plots of $cc_s/(c_s - c)$ against $c_s/(c_0 - c_s)$ are obtained (subscript s and w indicate the

---

Correspondence to: C.F. Wells, School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK.

mixture and pure water respectively). This linearity fits the equation [5–16]

$$\frac{cc_s}{(c_s-c)}=\frac{K_2F_2}{K_1F_1}\frac{c_0c_s}{(c_0-c_s)}\frac{[H_2O]_s}{[S]_{Total}}+\frac{[H_2O]c_0}{K_1F_1[S]_{Total}} \tag{1}$$

derived from the equilibria

$$\{H^+(H_2O)_x\}_{solv}+S_{solv}\overset{K}{\rightleftharpoons}\{H^+(H_2O)_{x-1}S\}_{solv}+H_2O_{solv} \tag{2}$$

$$\{H^+(H_2O)_x\}_{solv}+B_{solv}\overset{K_1}{\rightleftharpoons}BH^+_{solv}+H_2O_{solv} \tag{3}$$

$$\{H^+(H_2O)_{x-1}S\}_{solv}+B_{solv}\overset{K_2}{\rightleftharpoons}BH^+_{solv}+S_{solv} \tag{4}$$

K, K_1 and K_2 are thermodynamic equilibrium constants and the activity coefficient terms $F_1=y(B)y(P)/y(BH^+)y''(H_2O)$, where $P=H^+(H_2O)_x$, and $F_2=y(B)y(SH^+)/y(BH^+)y''(S)$, where $SH^+=\{H^+(H_2O)_{x-1}S\}$; the standard states in any water + co-solvent mixture for the dissolved species i = B, BH$^+$, P and SH$^+$ are $y=1.0$ and $[i]=1.00$ mol l^{-1} with $y\rightarrow1.0$ as $[i]\rightarrow0$ and, for H_2O and the co-solvent S, $y''\rightarrow1.0$ as Σ [dissolved species] $\rightarrow0$, all on the molar scale in the particular mixture, $[S]_{Total}$. In deriving eqn. (1) from equilibria (2)–(4), only one assumption is made [5–17], namely that

$$\frac{K_{1w}F_{1w}}{[H_2O]_w}=\frac{K_{1s}F_{1s}}{[H_2O]_s} \tag{5}$$

which is supported experimentally by the invariance of $K_{1w}F_{1w}/[H_2O]_w$ with added glycerol [5], and by the coincidence of the intercepts of the linear plots with those calculated using $K_{1w}F_{1w}/[H_2O]_w$ [5–16]. It should be noted that eqn. (5) is equivalent to

$$\frac{[BH^+]_w}{[B]_w[P]_w}=\frac{[BH^+]_s}{[B]_s[P]_s} \tag{6}$$

independent of $[H_2O]$ [17], so that the assumption suggested by Marcus [23], that $[H_2O]_w=[H_2O]_s$, is not made. Thus, Marcus' suggestion [23] of a limitation of the above treatment to very dilute solutions of S, approximating to $[H_2O]_w=[H_2O]_s$, is not valid.

Experimentally, the linear plots of $cc_s/(c_s-c)$ versus $c_s/(c_0-c_s)$ have an intercept corresponding to $[H_2O]_wc_0/K_{1w}F_{1w}[S]_{Total}$, as suggested by eqn. (5), and the ratio of slope : intercept is K_2F_2. The slope of the linear plots is given by $F_cc_0/K_c[S]_{Total}$, where the symmetrical factor $F_c=y(SH^+)y''(H_2O)/y(P)y''(S)$ and $K_c=[SH^+]/[S][P]$ [5–17].

The order of the rise in H_0 with composition in water-rich conditions with differing co-solvents [1–4] suggests that equilibrium (2) lies farther to the right, in the order MeOH < EtOH < acetone < dioxane; for a mole fraction of co-solvent $x_2 = 0.25$, H_0 rises from 1.0 in water to 1.5 for MeOH, 1.8 for EtOH, 2.1 for acetone and 2.2 for dioxane for 0.1 mol l^{-1} HCl. This correlates well with values for the concentration quotient K_c derived from the above treatment, indicating that K for equilibrium (2) becomes larger for a co-solvent ROH as the electron-releasing ability of R increases, and that the K for ROR is greater than the K for ROH [6, 7].

Free energy of transfer of the proton

With the determination of an equilibrium constant for (2), we have the possibility of relating the stability of the proton in water-rich mixtures to that in pure water. The transfer of a proton between the two liquids can be resolved into two successive processes. Firstly, a charged sphere, $H^+(H_2O)_5$ ($H^+(H_2O)_4$ with the vacant site on the pyramid occupied by a water molecule) [9, 24], is transferred from water into the mixture. This requires the creation of a cavity in the mixture to receive this sphere, followed by the collapse of the cavity vacated in water. For such water-rich mixtures of an alcoholic or ethereal co-solvent in water, the relative partial molar volume of water, $\bar{V}_1 - V_1^{\ominus}$, remains essentially zero [16, 25–30], suggesting that, although additional hydrogen bonds are formed in the water due to the presence of the co-solvent [18–22], there is little or no difference to the structural surroundings of an individual water molecule. Therefore, it is assumed that the free energy change accompanying the creation of the cavity in the water-rich mixture is exactly balanced by the free energy change accompanying the collapse of the cavity of the same size in water. The free energy of transfer of the sphere between the two liquids is then calculated using the Born equation

$$\Delta G(\text{Born}) = \mu_s^{\ominus}(\text{P}) - \mu_w^{\ominus}(\text{P}) = 167.6(D_s^{-1} - D_w^{-1})\ \text{kJ mol}^{-1} \qquad (7)$$

where D is the dielectric constant. The standard state in the mixture is as defined above for the dissolved species and that in pure water is defined by $y = 1.0$ and $[\text{P}] = 1.00$ mol l^{-1} with $y \rightarrow 1.0$ as $[\text{P}] \rightarrow 0$ in pure water.

Following this transfer, the solvent molecules in the mixture re-arrange themselves according to equilibrium (2). The free energy change for this re-arrangement is given by

$$\begin{aligned}\Delta G_2 &= [\text{SH}^+](\mu_s^{\ominus}(\text{H}_2\text{O}) + \mu_s^{\ominus}(\text{SH}^+) - \mu_s^{\ominus}(\text{P}) - \mu_s^{\ominus}(\text{S}))\\ &= -[\text{SH}^+)RT \ln K = -[\text{SH}^+]RT \ln K_c[\text{H}_2\text{O}]_s F_c \end{aligned} \qquad (8)$$

Now, K_c is given by

$$K_c = \frac{[\text{SH}^+]}{([\text{H}^+]_{\text{Total}} - [\text{SH}^+])([\text{S}]_{\text{Total}} - [\text{SH}^+])} \qquad (9)$$

and because K_2F_2 for eqn. (4) can be calculated from the ratio of slope : intercept of the linear plots of $cc_s/(c_s - c)$ against $c_s/(c_0 - c_s)$, $[SH^+]$ can be substituted into eqn. (9) from

$$[SH^+] = \frac{[S]_{Total}}{1 + K_2F_2c_s/(c_0 - c_s)} \tag{10}$$

It has been found for a wide range of co-solvents that, for water-rich mixtures, for any particular mixture $[S]_{Total}$, the K_c derived via eqns (9) and (10) for a range of [HCl] agrees well with the value for $K_cF_c^{-1}$ determined from

$$K_cF_c^{-1} = \frac{c_0}{(\text{slope})[S]_{Total}} \tag{11}$$

using the slope only from the linear plots. This supports the earlier observation [6, 7] that K_c is independent of the ionic strength with the symmetrical term $F_c = 1.0$ in water-rich mixtures [9–17]. Because K_c derived from eqn. (11) using only the slope is more accurate that K_c derived from eqns (9) and (10), $[SH^+]$ in eqn. (8) is calculated using the equations

$$[SH^+] = 0.5[A - (A^2 - 4[S]_{Total})^{1/2}] \tag{12}$$

$$A = ([S]_{Total} + 1 + K_c^{-1}) \tag{13}$$

and $[H_2O]_s$ is given by

$$[H_2O]_s = (1000d_s - [S]_{Total}M_s)M_w^{-1} \tag{14}$$

where d_s is the density of the mixture, and M_s and M_w are the molecular weights of the co-solvent and water, respectively. The free energy of transfer of the proton from water into the mixture on the mole fraction scale is given by

$$\Delta G_t^{\ominus}(H^+) = \Delta G(\text{Born}) - [SH^+]RT\ln(K_c[H_2O]_s) + RT\ln\frac{d_sM_w}{d_wM_s'} \tag{15}$$

where $M_s' = 100/\{(\text{wt.\% co-solvent}/M_s) + (\text{wt.\% } H_2O/M_w)\}$, $|\Delta G(\text{Born})| \ll |\Delta G_2|$ [9–16].

We now report the application of this technique to a double linear ether, 1,2-dimethoxyethane, using 4-nitroaniline as B with added HCl.

EXPERIMENTAL

The 1,2-dimethoxyethane used was Aldrich Gold Label 99+% spectrophotometric grade. All other materials were as described earlier for other water + co-solvent mixtures [5–16]. Concentrations of 4-nitroaniline were determined spectrophotometrically at 383 nm at 25°C [5, 6]. Mixtures of water and the ether were prepared by diluting a known volume of the ether to a fixed volume with water and the total volume added of the latter was determined experimentally to allow for the contraction.

RESULTS AND DISCUSSION

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

Following the determination of c and c_s for a range of [HCl] with the ionic strength maintained at 1.00 mol l^{-1} using the addition of NaCl for 4.34, 8.69, 17.44, 22.74, 30.68, 38.91 and 44.50 wt.% of ether, Fig. 1 shows that linear plots of $cc_s/(c_s - c)$ against $c_s/(c_0 - c_s)$ were obtained for each mixture, all having intercepts which coincided with that expected from eqn. (1) and the value of $K_{1w}F_{qw}/[H_2O]_w$ determined in water. Values for $K_cF_c^{-1}$ determined using eqn. (11) and the slopes of these plots, and values for K_2F_2 determined from the ratio of slope : intercept are collected in Table 1. K_c calculated for each [HCl] for each solvent composition using eqns (9) and (10), and the values for K_2F_2 are also given in Table 1. The mean of K_c agrees well with the $K_cF_c^{-1}$ value determined directly in the same mixture from the slope up to 30.68 wt.%. At this composition the values of K_c determined via eqns.

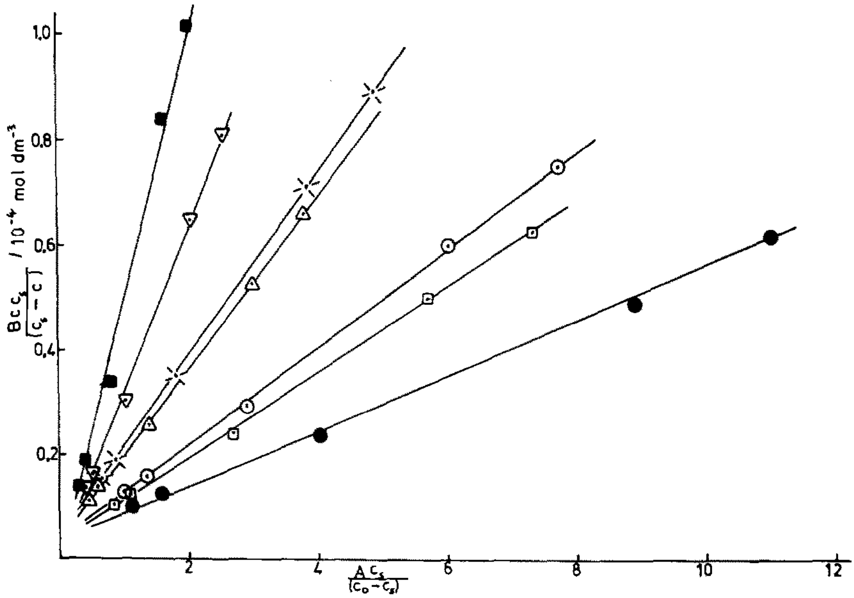

Fig. 1. Plots of $cc_s/(c_s - c)$ against $c_s/(c_0 - c_s)$ for HCl + NaCl at at ionic strength of 1.00 mol l^{-1} and at 25°C for mixtures of water with 1,2-dimethoxyethane containing the following wt.% of the di-ether: ■, 4.34, $A = 0.25$, $B = 0.34$; ∇, 8.69, $A = 0.25$, $B = 0.50$; ×, 17.44, $A = 0.25$, $B = 1.00$; ○, 22.74, $A = 0.25$, $B = 1.00$; △, 30.68, $A = B = 1.00$; □, 38.93, $A = B = 1.00$; ●, 44.50, $A = B = 1.00$.

TABLE 1

Values for K_c (l mol^{-1}), $K_cF_c^{-1}$ (l mol^{-1}) and K_2F_2 at 25°C and at an ionic strength of 1.00 mol l^{-1} for water + 1,2-dimethoxyethane mixtures at different wt.% concentrations of 1,2-dimethoxyethane (mole fraction concentrations in parentheses)

[HCl] (mol l^{-1})	Concentration of 1,2-dimethoxyethane						
	4.34 (0.0090)	8.69 (0.0185)	17.44 (0.0405)	22.74 (0.056)	30.68 (0.081)	38.91 (0.0113)	44.50 (0.138)
0.160	0.59	0.71	1.16	1.62	2.6	3.0	4.0
0.200	0.60	0.70	1.15	1.73	2.8	4.3	2.7
0.400	0.57	0.68	1.12	1.61	3.6	4.0	8.9
0.800	0.54	0.62	1.01	1.48	4.3	–	–
1.00	0.52	0.61	0.97	1.55	4.2	–	–
Mean K_c	0.56	0.66	1.08	1.60	3.5	–	–
	±0.03	±0.05	±0.08	±0.09	±0.8		
K_2F_2	26.5	22.6	13.7	9.7	5.9	3.75	2.77
$K_cF_c^{-1}$	0.58	0.68	1.12	1.58	2.59	4.08	5.5
from slope	±0.02	±0.01	±0.01	±0.01	±0.02	±0.04	±0.1

At this composition the values of K_c determined via eqns. (9) and (10) become erratic owing to the difference ($[H^+]_{Total} - [SH^+]$) in eqn. (9) becoming very small with large errors: this effect becomes accentuated for 38.91 and 44.50 wt.% mixtures, as has been found for similar compositions for mixtures of other co-solvents with water [9–16]. The good

TABLE 2

Values for the free energy of transfer (kJ mol^{-1}) of single cations from water into water + 1,2-dimethoxyethane mixtures at 25°C on the mole fraction scale

Conc. of di-ether		H^+	Li^+	Na^+	K^+	Rb^+	Cs^+	Ph_4As^+
Wt.%	Mole fraction							
4.34	0.0090	−1.58	–	–	–	–	–	–
8.69	0.0185	−3.16	–	–	–	–	–	–
10.00	0.0217	–	−2.53	−2.29	−2.30	−2.64	−2.46	−7.4
17.44	0.0405	−6.6	–	–	–	–	–	–
22.74	0.056	−8.6	–	–	–	–	–	–
30.00	0.079	–	−8.2	−7.2	−7.5	−7.8	−7.6	−17.6
30.68	0.082	−10.9	–	–	–	–	–	–
38.92	0.113	−12.2	–	–	–	–	–	–
44.50	0.128	−12.7	–	–	–	–	–	–
50.00	0.167	–	−9.6	−8.0	−8.2	−8.3	−8.5	−24.8

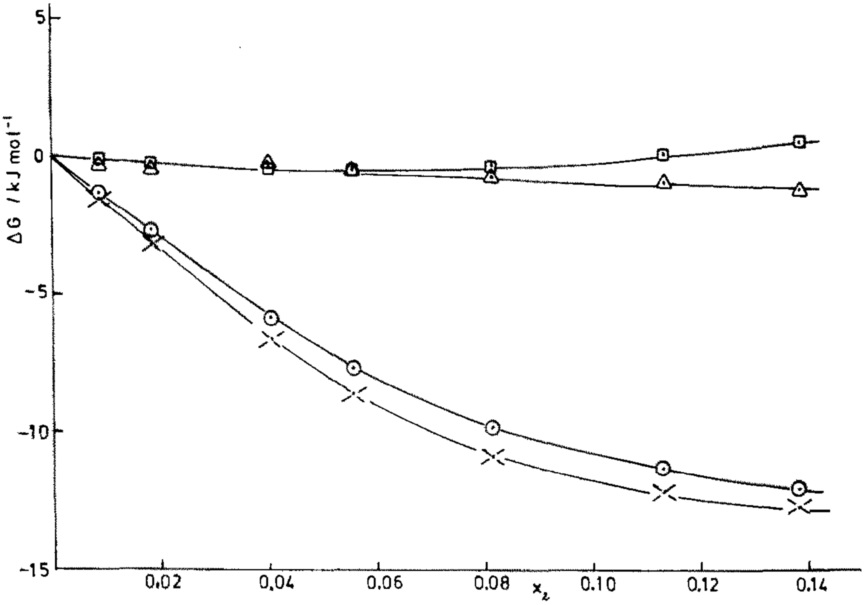

Fig. 2. Variation with mole fraction of the di-ether of $\Delta G_t^\ominus(H^+)$ (×), ΔG_2 (○), ΔG(Born) (□) and $RT \ln(d_s M_w / d_w M_s')$ (△) for mixtures of water with 1,2-dimethoxyethane at 25°C.

agreement obtained between the mean K_c and $K_c F_c^{-1}$ for 4.34, 8.69, 17.44 and 22.74 wt.% and the reasonable agreement at 30.68 wt.% supports the conclusion that the symmetrical term F_c is equal to 1.0 for water-rich mixtures of 1,2-dimethoxyethane, as found for all other co-solvents used [9–16] and expected by analogy with Hammett's symmetrical terms $y(B')y(B''H^+)/y(B'H^+)y(B'') = 1.0$ for related bases B′ and B″ [31–35].

ΔG_2 can now be calculated for each solvent composition using eqn. (8) with $F_c = 1.0$ and $K_c F_c^{-1}$ taken from Table 1, because this value taken from the slope alone of a plot in Fig. 1 is more accurate than the mean K_c. $[H_2O]_s$ is calculated from eqn. (14) and the densities are interpolated from the published data [36, 37]. $[SH^+]$ is calculated from eqns (12) and (13), also using $K_c F_c^{-1}$ with $F_c = 1.0$. ΔG(Born) was calculated using eqn. (7) with dielectric constants interpolated from the data of Roy et al. [37]. The values for $\Delta G_t^\ominus(H^+)$ on the mole fraction scale obtained using eqn. (15) are given in Table 2.

Figure 2 shows the variation of $\Delta G_t^\ominus(H^+)$, ΔG_2, ΔG(Born) and $RT \ln(d_s M_w / d_w M_s')$ with solvent composition. This comparison shows that the ΔG_2 obtained from the solvent sorting in eqn. (2) makes the major contribution to $\Delta G_t^\ominus(H^+)$, with only a very small contribution from ΔG(Born). Thus, $|\Delta G(\text{Born})| \ll |\Delta G_t^\ominus(H^+)|$, as found for all other co-solvents in water-rich conditions [9–16].

Determination of $\Delta G_t^{\ominus}$*(anion)*

$\Delta G_t^{\ominus}(\mathrm{HCl})$ has been determined from $E^{\ominus}$ measurements [38, 39] for

$$\mathrm{Pt, H_2(1\ atm.)\ |HX, H_2O + 1,2\text{-}dimethoxyethane|\ AgX, Ag} \qquad (16)$$

with $X^- = Cl^-$ in water and in the mixtures using $\Delta G_t^{\ominus}(\mathrm{HX}) = 96.5(E_w^{\ominus} - E_s^{\ominus})$ kJ mol^{-1}.

The data for $E^{\ominus}$ of Johnson and Sen [38] is given on the molal scale and $\Delta G_t^{\ominus}(\mathrm{HX})_m$ is converted to the mole fraction scale using

$$\Delta G_t^{\ominus}(\mathrm{HX}) = \Delta G_t^{\ominus}(\mathrm{HX})_m + 11.42 \log(M_w/M_s')$$

$\Delta G_t^{\ominus}(\mathrm{Cl^-})$ is then calculated using

$$\Delta G_t^{\ominus}(\mathrm{X^-}) = \Delta G_t^{\ominus}(\mathrm{HX}) - \Delta G_t^{\ominus}(\mathrm{H^+}) \qquad (17)$$

with $X^- = Cl^-$ and the values for $\Delta G_t^{\ominus}(\mathrm{H^+})$ in Table 2. The two sets of values in Table 3 for $\Delta G_t^{\ominus}(\mathrm{Cl^-})$ are in good agreement. A similar treatment was given to $E^{\ominus}$ data [37] obtained using cell (16) with $X^- = Br^-$; $\Delta G_t^{\ominus}(\mathrm{Br^-})$ is given in Table 3. $\Delta G_t^{\ominus}(\mathrm{HI})$ values determined from $E^{\ominus}$ measurements on the cell [40]

$$\mathrm{Pt, H_2(1\ atm.)\ |KOH, KI, water + 1,2\text{-}dimethoxyethane|\ AgI, Ag}$$

have also been converted to $\Delta G_t^{\ominus}(\mathrm{I^-})$ using eqn. (17) and these values are also contained in Table 3. Values for $\Delta G_t^{\ominus}(\mathrm{F^-})$ have been determined

TABLE 3

Values for the free energy of transfer (kJ mol^{-1}) for single anions from water into water + 1,2-dimethoxyethane mixtures at 25°C on the mole fraction scale

Conc. of di-ether		F^-	Cl^-	Br^-	I^-	Pic^-	BPh_4^-
Wt.%	Mole fraction						
8.68	0.0185	–	3.46[a]	–	–	–	–
8.68	0.0185	–	3.47[b]	–	–	–	–
10.00	0.0217	4.86	–	3.12	2.26	2.20	−4.25
17.81	0.0415	–	7.1[a]	–	–	–	–
17.81	0.0415	–	7.1[b]	–	–	–	–
30.00	0.079	14.6	–	9.8	7.5	5.2	−7.9
46.52	0.148	–	14.7[a]	–	–	–	–
46.52	0.148	–	14.7[b]	–	–	–	–
50.00	0.167	19.7	–	12.6	8.5	1.71	−19.7

[a] $E^{\ominus}$ data from ref. 37. [b] $E^{\ominus}$ data from ref. 36.

from $\Delta G_t^{\ominus}(\text{KF})$ obtained [41] from $E^{\ominus}$ measurements on the cell

$$\begin{array}{l|l|c|l|l} \text{Pb(Hg),} & \text{KF,} & & \text{KF,} & \text{PbF}_2, \\ \text{PbF}_2 & \text{H}_2\text{O} + \text{1,2-dimethoxyethane} & \text{K(Hg)} & \text{water} & \text{Pb(Hg)} \end{array}$$

in water and in the mixture by using the equation

$$\Delta G_t^{\ominus}(\text{X}^-) = \Delta G_t^{\ominus}(\text{KX}) - \Delta G_t^{\ominus}(\text{K}^+) \tag{18}$$

for $\text{X}^- = \text{F}^-$ with the values for $\Delta G_t^{\ominus}(\text{K}^+)$ in Table 2 as determined below. $\Delta G_t^{\ominus}(\text{picrate})$ and $\Delta G_t^{\ominus}(\text{BPh}_4^-)$ have also been calculated using eqn. (18) with $\Delta G_t^{\ominus}(\text{K}^+)$ from Table 2 using data derived from the solubility of the potassium salts [42]. All these values for $\Delta G_t^{\ominus}(\text{X}^-)$ are collected in Table 3.

Determination of $\Delta G_t^{\ominus}$*(cation)*

$\Delta G_t^{\ominus}(\text{MCl})$ for $\text{M}^+ = \text{Li}^+$, Na^+, K^+, Rb^+ and Cs^+ have been calculated from $E^{\ominus}$ measurements [42] for the cell

$$\begin{array}{l|l|c|l|l} & \text{MCl,} & & & \\ \text{Ag,} & \text{water} + & \text{M(Hg)} & \text{MCl,} & \text{Ag} \\ \text{AgCl} & & & \text{water} & \text{AgCl} \\ & \text{1,2-dimethoxyethane} & & & \end{array}$$

and values for $\Delta G_t^{\ominus}(\text{M}^+)$ have been calculated using

$$\Delta G_t^{\ominus}(\text{M}^+) = \Delta G_t^{\ominus}(\text{MCl}) - \Delta G_t^{\ominus}(\text{Cl}^-) \tag{19}$$

with $\Delta G_t^{\ominus}(\text{Cl}^-)$ interpolated from the data in Table 3. The values for $\Delta G_t^{\ominus}(\text{M}^+)$ obtained are collected in Table 2. The $\Delta G_t^{\ominus}(\text{Ph}_4\text{As}^+)$ values in Table 2 were calculated from $\Delta G_t^{\ominus}(\text{Ph}_4\text{As}^+ \cdot \text{Pic}^-)$ (where $\text{Pic}^- = \text{picrate}$) determined from solubility measurements in water and in the mixtures [42]; and equation analogous to eqn. (19) was used with $\Delta G_t^{\ominus}(\text{Pic}^-)$ from Table 3.

From energy of transfer of the charge alone on large organic ions

For the equilibrium

$$\text{A}^+_{\text{solv}} \overset{K_a}{\rightleftharpoons} \text{B}_{\text{solv}} + \text{H}^+_{\text{solv}}$$

for a large organic cation A^+, B resembles A^+ so closely in size and structure that the free energy of transfer of electrically neutral A $\Delta G_t^{\ominus}(\text{A}^+)_n$ is given by

$$\Delta G_t^{\ominus}(\text{A}^+)_n = \Delta G_t^{\ominus}(\text{B})$$

Consequently, the free energy of transfer of the charge alone on A

$\Delta G_t^{\ominus}(\mathrm{A}^+)_e$ is given by

$$\Delta G_t^{\ominus}(\mathrm{A}^+)_e = \Delta G_t^{\ominus}(\mathrm{A}^+) - \Delta G_t^{\ominus}(\mathrm{B}) = RT\ln(K_a^s/K_a^w) + \Delta G_t^{\ominus}(\mathrm{H}^+) \qquad (20)$$

and $\Delta G_t^{\ominus}(\mathrm{A}^+)_e$ can be calculated from measurements of K_a in water and in the mixture, and from $\Delta G_t^{\ominus}(\mathrm{H}^+)$ interpolated from the data in Table 2. Reynaud has determined K_a values in mixtures of water with 1,2-dimethoxyethane for a range of large organic cations on the molar scale [43] therefore, to produce $\Delta G_t^{\ominus}(\mathrm{A}^+)_e$, values for $-5.71\log(M_w d_s/M_s' d_w)$ must be added to the right-hand-side of eqn. (20). The resulting $\Delta G_t^{\ominus}(\mathrm{A}^+)_e$ values on the mole fraction scale are collected in Table 4.

For an equilibrium between a conjugate pair A and B^-, for a large A with $\Delta G_t^{\ominus}(\mathrm{B}^-)_n = \Delta G_t^{\ominus}(\mathrm{A})$, eqn. (21) can be applied

$$\Delta G_t^{\ominus}(\mathrm{B}^-)_e = \Delta G_t^{\ominus}(\mathrm{B}^-) - \Delta G_t^{\ominus}(\mathrm{A}) = RT\ln(K_a^w/K_a^s) - \Delta G_t^{\ominus}(\mathrm{H}^+) \qquad (21)$$

Reynaud has determined pK_a values for acetic and benzoic acids on the molar scale; to produce $\Delta G_t^{\ominus}(\mathrm{B}^-)_e$ on the mole fraction scale using eqn. (21) with $\Delta G_t^{\ominus}(\mathrm{H}^+)$ values interpolated from Table 2, $+5.71\log(M_w d_s/M_s' d_w)$ has to be added to the right-hand-side. The values of $\Delta G_t^{\ominus}(\mathrm{B}^-)_e$ obtained are included in Table 4.

TABLE 4

Values for the free energy of transfer of the charge alone $\Delta G_t^{\ominus}(\mathrm{i})_e$ (kJ mol^{-1}) for large organic ions in water + 1,2-dimethoxyethane mixtures at 25°C on the mole fraction scale at different wt.% concentrations of di-ether (mole fraction connections in parentheses)

Ion	Conc. of di-ether				
	8.76 (0.0188)	17.77 (0.0414)	27.03 (0.069)	36.56 (0.103)	46.36 (0.147)
Anilinium	−2.24	−4.67	−7.2	−7.1	−6.7
N-Methylanilinium	–	−4.33	−6.6	−6.6	−5.4
N-Ethylanilinium	–	−5.2	−7.6	−7.5	−6.3
N-2-Propylanilinium	–	−4.16	−6.3	−6.2	−4.89
N-*t*-Butylanilinium	–	−4.56	−7.0	−7.2	−6.1
N,*N*-Dimethylanilinium	−1.44	−4.16	−6.2	−5.8	−4.26
N,*N*-Diethylanilinium	−2.47	−4.84	−6.8	−5.9	−3.86
N,*N*-Di(2-propyl)anilinium	−1.84	−3.76	−5.8	−5.6	−3.97
4-Bromoanilinium	−1.67	−3.30	−5.0	−4.67	−4.03
4-Bromo-*N*,*N*-dimethylanilinium	−1.50	−3.19	−4.73	−3.70	−1.86
4-Bromo-*N*,*N*-diethylanilinium	−1.16	−2.16	−3.42	−2.27	−0.15
Pyridinium	–	−3.98	−6.3	−6.3	−5.5
Quinolinium	–	−2.96	−4.67	−4.33	−3.23
Isoquinolinium	–	−3.36	−5.1	−4.73	−3.57
Acetate	3.90	8.2	13.0	16.1	19.2
Benzoate	4.18	9.0	14.3	17.9	21.4

Comparison of values for $\Delta G_t^{\ominus}(i)$ *and* $\Delta G_t^{\ominus}(i)_e$

Figures 3 and 4 show that the variation of $\Delta G_t^{\ominus}(\mathrm{i})$ with solvent composition in water + dimethoxyethane resembles closely the variations found in mixtures of water with other co-solvents [9–16]. Thus, in Fig. 3, $\Delta G_t^{\ominus}(\mathrm{i})$ values for i = anions, are positive in the sequence $F^- > Cl^- > Br^- > I^- > Pic^-$; and $\Delta G_t^{\ominus}(\mathrm{i})$ for the hydrophobic anion BPh_4^- is negative, as shown in Fig. 4, similar to the findings with other co-solvents [9–16]. As found before [9–16], $\Delta G_t^{\ominus}(\mathrm{i})$ values for i = cations are negative with the sequence in $-\Delta G_t^{\ominus}(\mathrm{i})$ being $Ph_4As^+ > H^+ > Li^+ > Na^+$, Rb^+, Cs^+, K^+, again showing the effect of the hydrophobicity of Ph_4As^+, with $-\Delta G_t^{\ominus}(Ph_4As^+) > -\Delta G_t^{\ominus}(BPh_4^-)$, showing the effect of the positive

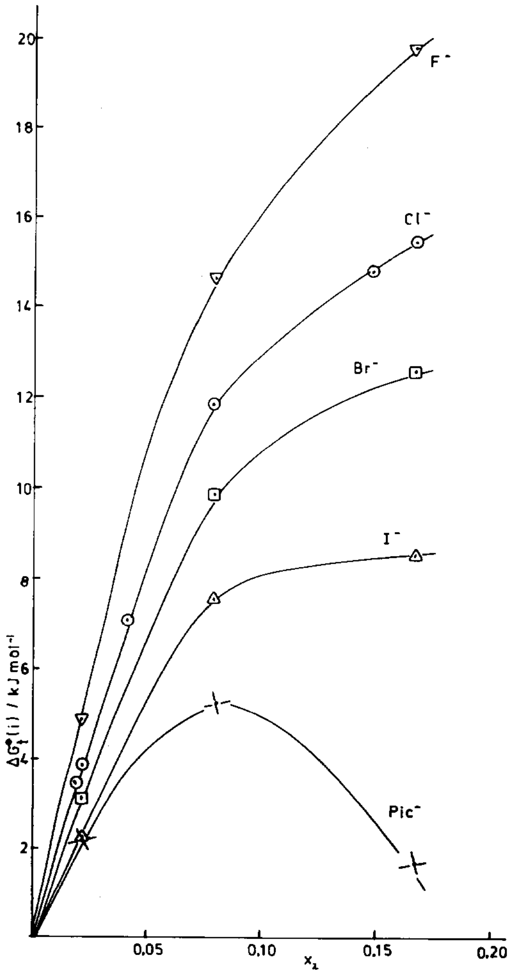

Fig. 3. Variation with mole fraction of the di-ether of $\Delta G_t^{\ominus}(\mathrm{i})$ for i = F^-, Cl^-, Br^-, I^- and picrate in mixtures of water with 1,2-dimethoxyethane at 25°C.

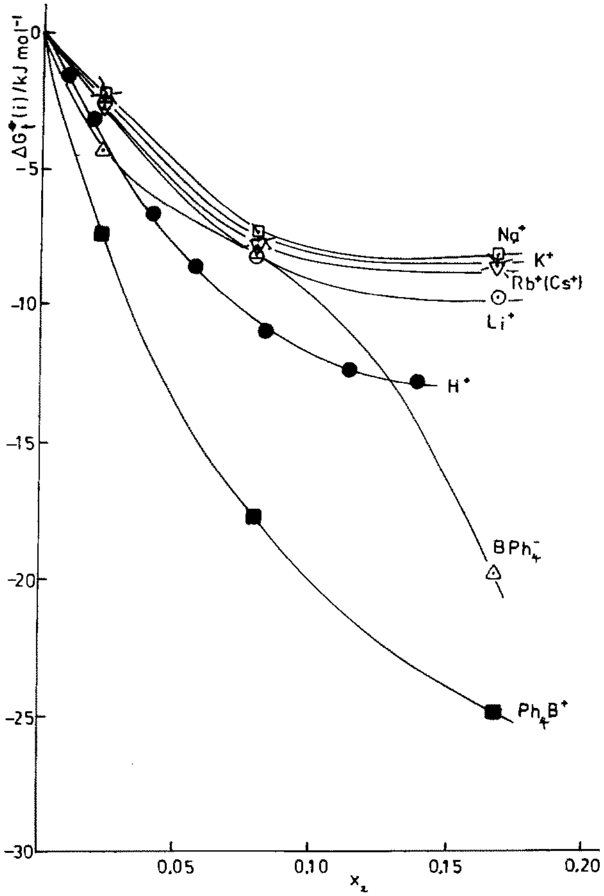

Fig. 4. Variation with mole fraction of the di-ether of $\Delta G_t^\ominus(i)$ for i = H^+, Li^+, Na^+, K^+, Cs^+, Ph_4As^+ and BPh_4^- in mixtures of water with 1,2-dimethoxyethane at 25°C.

charge over the negative charge for two ions having similar hydrophobic effects. Presumably, $\Delta G_t^\ominus(Pic^-)$ is less than $\Delta G_t^\ominus(i)$ for the halide ions owing to the effect of the hydrophobicity of the benzene ring. It should also be noted that, as in the other water-rich solvent systems [9–16], $\Delta G_t^\ominus$(anion), except for i = BPh_4^-, appears to be approaching a maximum, with an actual maximum for i = Pic^-, and $\Delta G_t^\ominus$(cation) appears to approach a minimum.

As in many other solvent systems [9–16], $\Delta G_t^\ominus(i)_e$ values in Table 4 for large organic cations are negative at low x_2 with a minimum, in this case, at $x_2 \approx 0.07$–0.09. The variation in $\Delta G_t^\ominus(i)_e$ for i = acetate or benzoate with solvent composition, resembles the variation of $\Delta G_t^\ominus(i)_e$ for anions in other water + co-solvent systems [9–16].

In comparing $\Delta G_t^\ominus(i)$ for any particular ion in water + co-solvent mixtures for a range of alcoholic co-solvents, it has been shown [6, 7] that the electron availability on the bonded oxygen atom of the co-solvent molecule is an important factor that must be considered. Another variant that must be important is the extent to which the co-solvent induces structure formation in the aqueous mixture. A range of indicators are used to assess the degree of structure formation induced by the co-solvent: the existence of and the depth of a minimum in $\bar{V}_2 - V_2^\ominus$ [25–29, 44]; a positive structural contribution to the increase in the temperature of the maximum density of water when the co-solvent is added [45]; a maximum in the ultrasonic absorption of the mixtures [46, 47]; the existence of a minimum in the excess enthalpy of mixing ΔH_M^E, and the extent to which this occurs at $x_2 < 0.5$ [25, 27, 48–51]; and the existence of a maximum in the viscosity η of the mixtures [52, 53]. For hydrophobic alcohols, all these properties indicate the enhanced formation of structure in the mixtures over that found in water, but for glycols and other polyhydroxy compounds, little if any enhanced structure is found in the mixtures. However, when one of the hydroxyl groups in ethane-1,2-diol is alkylated, $ROCH_2CH_2OH$, structure appears, as shown by the existence of a maximum in the ultrasonic absorption for R = Me or Et [46], and a sharp minimum in $\bar{V}_2 - V_2^\ominus$ for R = Et [16]: the sharp minimum in the variation of $\bar{V}_2 - V_2^\ominus$ with x_2 shown in Fig. 5 for water + 2-$MeOCH_2CH_2OH$ mixtures calculated from the density data of Shindo and Kusano [54], confirms this. As with the alcohols and glycols, $\bar{V}_1 - V_1^\ominus$ remains approx. zero during the minimum in $\bar{V}_2 - V_2^\ominus$, showing that the structural surroundings of the average individual water molecule remains little changed in water-rich mixtures from that in pure water. For 1,2-dimethoxyethane mixed with water, in addition to a sharp minimum in $\bar{V}_2 - V_2^\ominus$ at $x_2 < 0.1$ with $\bar{V}_1 - V_1^\ominus \approx$ zero [36], a maximum appears in η at $x_2 \approx 0.15$ [55], which is absent for water + glycol mixtures: similarly, dimethoxylation of diethylene glycol produces in aqueous mixtures a maximum [55] in η, a sharp mimimum in $\bar{V}_2 - V_2^\ominus$ for $x_2 < 0.1$ [55], and also a minimum in ΔH_M^E at low x_2 [56]. The variations in all these physical properties suggest that the order in which co-solvents produce an enhanced structure in water is glycol < methanol < ethanol < alkoxyalcohol < dialkoxyethane < propan-2-ol < *t*-butyl alcohol: when added to water they form stronger hydrogen bonds with water than water does with water, owing to the electron releasing effects of the alkyl groups, producing a negative excess ΔH_M^E, accompanied by a negative excess entropy of mixing. However, the alkyl groups themselves form structure by being excluded from the "flickering clusters" of structured water into the cavities between the water clusters, resulting in the decrease in $\bar{V}_2 - V_2^\ominus$, whilst the fact that $\bar{V}_1 - V_1^\ominus \approx$ zero shows that the surroundings of the average individual water molecule remain little changed from that experienced in pure water.

The effect of structure in the water-rich mixtures is shown in the magnitudes of the $\Delta G_t^\ominus(\text{i})$ values and their types of variation with x_2. In

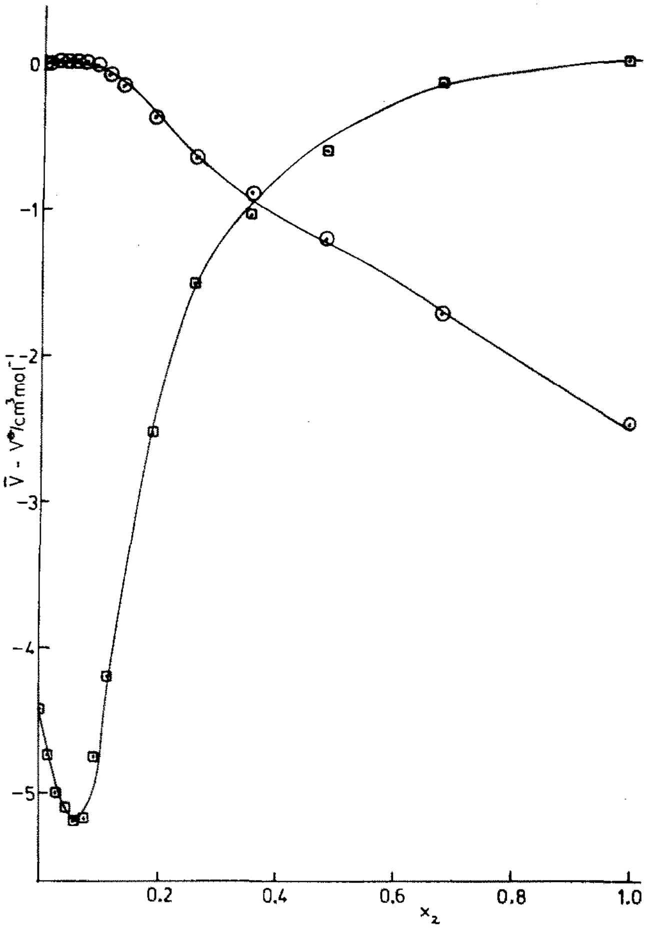

Fig. 5. Variation with mole fraction of the hydroxyether of the relative partial molar volumes of water (○) and 2-methoxyethanol (□) in their mixtures at 25°C.

general, $\Delta G_t^{\ominus}$(anion) is positive and $\Delta G_t^{\ominus}$(cation) is negative [9]. Only low values are found for glycols or glycerol as co-solvents [9]. For methanol [9], at the bottom end of the scale for structure formation with alcohols, smaller $\Delta G_t^{\ominus}$(i) values are found than with other alcohols at low x_2, but for $x_2 < 0.3$, $\Delta G_t^{\ominus}$(cation) decreases and $\Delta G_t^{\ominus}$(anion) increases continuously with increasing x_2. For the strongly structure-forming *t*-butyl alcohol and propan-2-ol as co-solvents, $\Delta G_t^{\ominus}$(cation) shows a minimum and $\Delta G_t^{\ominus}$(anion) a maximum at $x_2 \approx 0.1$–0.2 [9]; and ethanol [10] and propan-1-ol [12] show a tendency towards this. $ROCH_2CH_2OH$ with $R = Me$ [15] or Et [16] shows larger values for $\Delta G_t^{\ominus}$(i) than ethane-1,2-diol [9], with a tendency to reach limiting values for $x_2 \approx 0.15$, as does 1,2-dimethoxyethane.

Previously, the assessment of the effect of changes in the electron availability on K_c were made at very low x_2. To make an assessment at

TABLE 5

Comparison of values for K_c and $\Delta G_t^\ominus(H^+)$ for 50 wt.% mixtures of co-solvents with water at 25°C

Co-solvent	K_c (l mol^{-1})	$\Delta G_t^\ominus(H^+)$ (kJ mol^{-1})
Ethanol	1.51	−8.2
Ethane-1,2-diol	0.14	−2.2
2-Methoxyethanol	1.20	−7.7
2-Ethoxyethanol	5.2	−10.2
1,2-Dimethoxyethane	5.5	−12.7
Glycerol	<0.01	−0.5
Tetrahydrofuran	4.2 (37 wt.%)	−11.0 (37 wt.%)
Dioxane	2.17	−8.0

higher x_2, difficulties will arise due to different structural effects arising with any particular ion from the differing hydrophobicity of the co-solvent, as discussed above. However, for all co-solvents, ΔG_2 rises to a limiting value at about 50 wt.% of co-solvent, where, indeed, the maxima in the acidity function H_0 approximately occur. It would seem instructive, therefore, to compare values for K_c and $\Delta G_t^\ominus(H^+)$ in this region of composition on the limits of the water-rich region. Table 5 shows the reducing effect on the size of K_c in the presence of multiple electron-withdrawing groups with ethanol [10] > ethane-1,2-diol [9] > glycerol [5, 9], and a corresponding reduction along the series for $-\Delta G_t^\ominus(H^+)$. Converting an OH group in the diol into an ether results in an increase in both K_c and $-\Delta G_t^\ominus(H^+)$, which are further increased when the electron-releasing effect of the alkyl group is increased. Dimethoxyethane, with two linear ether groups, shows the highest value for K_c and for $-\Delta G_t^\ominus(H^+)$. A single ether oxygen atom in a ring shows high values for K_c and $-\Delta G_t^\ominus(H^+)$ [57], but both these values are reduced when a second electron-attracting oxygen atom is introduced into the ring [9].

In previous investigations, values for $\Delta G_t^\ominus(i)_e$ have been examined for (a) changes occurring for an increase in size of the molecule without any change in the extent of the distribution of the charge, and (b) changes where both an increase in size and in the extent of the distribution of the charge occur [9–16, 58]. For (a), although the data in Table 4 show that there is an overall tendency for $-\Delta G_t^\ominus(i)_e$ to decrease with increasing size, this does not occur in specific series except for $BrPh\overset{+}{N}H_3$ > $BrPh\overset{+}{N}HMe_2$ > $BrPh\overset{+}{N}HEt_2$. For (b), $\Delta G_t^\ominus(\text{anion})_e$ changes little with change in the size and the extent of distribution of the charge.

REFERENCES

1 E.A. Braude and E.S. Stern, J. Chem. Soc., (1948) 1976.
2 P. Salomoa, Acta Chem. Scand., 11 (1957) 125.

3 R.G. Bates and G. Schwarzenbach, Helv. Chim. Acta, 38 (1955) 699.
4 H. Strehlow, Zeit. Phys. Chem. N.F., 24 (1960) 240.
5 C.F. Wells, Trans. Faraday Soc., 61 (1965) 2194.
6 C.F. Wells, Trans. Faraday Soc., 62 (1966) 2815.
7 C.F. Wells, Trans. Faraday Soc., 63 (1967) 147.
8 C.F. Wells, J. Phys. Chem., 77 (1973) 1994.
9 C.F. Wells, Aust. J. Chem., 36 (1983) 1739.
10 C.F. Wells, J. Chem. Soc. Faraday Trans. 1, 80 (1984) 2445.
11 G.S. Groves and C.F. Wells, J. Chem. Soc. Faraday Trans. 1, 81 (1985) 3091.
12 I.M. Sidahmed and C.F. Wells, J. Chem. Soc. Faraday Trans. 1, 82 (1986) 439.
13 G.S. Groves, K.H. Halawani and C.F. Wells, J. Chem. Soc. Faraday Trans. 1, 83 (1987) 1281.
14 I.M. Sidahmed and C.F. Wells, J. Chem. Soc. Faraday Trans. 1, 84 (1988) 1153.
15 K.H. Halawani and C.F. Wells, J. Chem. Soc. Faraday Trans. 1, 85 (1989) 2185.
16 J. Saxton and C.F. Wells, J. Chem. Soc. Faraday Trans. 1, 86 (1990) 1471.
17 K.H. Halawani and C.F. Wells, Thermochim. Acta, 155 (1989) 57.
18 H.S. Frank and M.W. Evans, J. Chem. Phys., 13 (1945) 507.
19 H.S. Frank and W.-Y. Wen, Discuss. Faraday Soc., 24 (1957) 133.
20 G. Némethy and H.A. Sheraga, J. Chem. Phys., 36 (1962) 3382, 3401.
21 G. Némethy, Angew. Chem. Int. Ed. Engl., 6 (1967) 195.
22 W. Laiden and G. Némethy, J. Phys. Chem., 74 (1970) 3501.
23 Y. Marcus, Ion Solvation, Wiley, Chichester, 1985, pp. 160–161.
24 C.F. Wells, J. Chem. Soc. Faraday Trans. 1, 69 (1973) 984.
25 A.G. Mitchell and W.F.K. Wynne-Jones, Discuss. Faraday Soc., 15 (1953) 161.
26 V.S. Griffiths, J. Chem. Soc., (1954) 860.
27 J. Kenttämaa, E. Tommila and M. Martti, Ann. Acad. Sci. Fenn., (1959) No. 93.
28 K. Nakanishi, Bull. Chem. Soc. Jpn., 33 (1960) 793.
29 A. Ray and G. Némethy, J. Chem. Eng. Data, 18 (1973) 309.
30 D.A. Bush and C.F. Wells, J. Chem. Soc. Faraday Trans. 1, 86 (1990) 941.
31 L.P. Hammett, Physical Organic Chemistry, McGraw-Hill, New York, 1940, Chapt. 9.
32 E.M. Arnett, Prog. Phys. Org. Chem., 1 (1963) 223.
33 M.A. Paul and F.A. Long, Chem. Rev., 57 (1957) 1.
34 M.J. Jorgensen and D.R. Hartter, J. Am. Chem. Soc., 85 (1963) 878.
35 E.M. Arnett and G.W. Mach, J. Am. Chem. Soc., 88 (1966) 1177.
36 W.J. Wallace and A.L. Mathews, J. Chem. Eng. Data, 8 (1963) 496.
37 R.N. Roy, E.E. Swenson, G. LaCross and C.W. Krueger, Adv. Chem. Ser., 155 (1976) 220.
38 D.A. Johnson and B. Sen, J. Chem. Eng. Data, 13 (1968) 376.
39 R.N. Roy and A.L.M. Bothwell, J. Chem. Eng. Data, 16 (1971) 347.
40 J. Datta and K.K. Kundu, Can. J. Chem., 59 (1981) 3149.
41 A. Bhattacharya, K. Das, A.K. Das and K.K. Kundu, Bull. Chem. Soc. Jpn., 54 (1981) 2194.
42 A. Bhattacharya, A.K. Das and K.K. Kundu, Indian J. Chem., 20A (1981) 353.
43 R. Reynaud, C.R. Acad. Sci. Paris C, 263 (1966) 105; Bull. Soc. Chim. Fr., (1967) 4597.
44 K. Nakanishi, N. Kato and M. Maruyama, J. Phys. Chem., 71 (1967) 814.
45 G. Wada and S. Umeda, Bull. Chem. Soc. Jpn., 35 (1962) 646.
46 J.H. Andreae, P.D. Edmonds and J.F. McKellar, Acustica, 15 (1965) 74.
47 M.J. Blandamer, Introduction to Chemical Ultrasonics, Academic Press, London, 1973, Chapt. 11.
48 R.F. Lama and B.C.-Y. Ju, J. Chem. Eng. Data, 10 (1965) 216.
49 K. Rehm and H.-J. Bittrich, Z. Phys. Chem., 251 (1972) 109.

50 H. Nakayama and K. Shinoda, J. Chem. Thermodyn., 3 (1971) 401.
51 G.N. Malcolm and J.S. Rowlinson, Trans. Faraday Soc., 53 (1957) 921.
52 A.E. Dunstan, Z. Phys. Chem., 49 (1904) 590; 51 (1905) 732.
53 F.S. Jerome, J.T. Tseng and L.T. Fan, J. Chem. Eng. Data, 13 (1968) 496.
54 Y. Shindo and K. Kusano, J. Chem. Eng. Data, 24 (1979) 106.
55 W.J. Wallace and A.L. Mathews, J. Chem. Eng. Data, 9 (1964) 267.
56 W.J. Wallace and T.J. Vellenga, J. Chem. Eng. Data, 16 (1971) 331.
57 I.M. Sidahmed and C.F. Wells, J. Chem. Soc. Faraday Trans. 1, 83 (1987) 439.
58 C.F. Wells, Thermochim. Acta, 53 (1982) 67; 130 (1988) 127.