

Ionic solvation in water + co-solvent mixtures. Part 25. Gibbs free energies of transfer of single ions from water into water + sulpholane mixtures

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Abstract

The stability of the proton in water + sulpholane mixtures relative to that in water has been investigated experimentally via equilibria established when 4-nitroaniline is introduced into water-rich acidic mixtures. Gibbs free energies of transfer from water into the mixtures $\Delta G_t^\circ(i)$ have also been calculated for Cl^- , OH^- and Rb^+ . The extra stability accorded to the proton in the mixture arises largely from the rearrangement of solvent molecules close to the proton, with the solvate species containing a sulpholane molecule having a higher stability and a lower ionic mobility than the solvate species where this is absent. The relative stabilities of the charge on organic ions is investigated and discussed in relation to the structure of the molecule bearing the charge.

INTRODUCTION

Following the application of the spectrophotometric solvent-sorting method for the determination of the Gibbs free energy of transfer of the proton from water into an aqueous mixture containing an organic co-solvent, $\Delta G_t^\circ(\text{H}^+)$, to co-solvents such as alcohols [1–3], ethers [1, 4, 5], ketones [1, 6, 7], carbonyl-ethers [8], hydroxyethers [9, 10], polyalcohols [1, 11, 12] and dimethyl sulphoxide [1], we have now extended this to the proton in mixtures of water with sulpholane. As in the earlier applications, once $\Delta G_t^\circ(\text{H}^+)$ has been determined, the Gibbs free energies of transfer of single anions can be determined using

$$\Delta G_t^\circ(\text{X}^-) = \Delta G_t^\circ(\text{HX}) - \Delta G_t^\circ(\text{H}^+) \quad (1)$$

where $\Delta G_t^\circ(\text{HX})$ can be calculated from E° data for suitable cells. The free energies of transfer of cations can then be calculated using

$$\Delta G_t^\circ(\text{M}^+) = \Delta G_t^\circ(\text{MX}) - \Delta G_t^\circ(\text{X}^-) \quad (2)$$

where $\Delta G_t^\circ(\text{MX})$ can be derived from solubility or E° measurements.

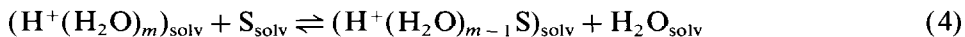
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GIBBS FREE ENERGY OF TRANSFER OF THE PROTON

This method for determining $\Delta G_{\text{t}}^{\circ}(\text{H}^+)$ was first applied to water + methanol mixtures [1, 13]. Although the hydrated proton has been assumed to be $(\text{H}_2\text{O})_4\text{H}^+$ [14], it is clear that a sphere of radius three times the radius of H_2O with its centre at the centre of H_3^+O will also contain an additional H_2O molecule, perhaps more weakly associated with H_3^+O than the other three H_2O molecules [1, 13, 15]. Hence, in considering the transfer of a spherical aqua-proton from water into a water-rich mixture also containing an organic co-solvent, the species concerned is $(\text{H}_2\text{O})_5\text{H}^+$ [15]. The Gibbs free energy of transfer of this charged sphere of radius $r = 3r_{\text{H}_2\text{O}}$ from water w into a water-rich mixture x containing a co-solvent S is given by the Born expression on the molar scale [1, 3, 11, 13, 16]

$$\begin{aligned} \Delta G(\text{Born}) &= \mu_{\text{c}}^{\circ}(\text{H}_{\text{aq}}^+)(T, P, n\text{H}_2\text{O} + n\text{S}) - \mu_{\text{c}}^{\circ}(\text{H}_{\text{aq}}^+)(T, P, \text{H}_2\text{O}) \\ &= \frac{Ne^2}{24\pi\epsilon_0 r_{\text{H}_2\text{O}}} (D_{\text{x}}^{-1} - D_{\text{w}}^{-1}) \end{aligned} \quad (3)$$

where N is Avogadro's number, ϵ_0 is the permittivity of a vacuum, e is the electronic charge and D is the dielectric constant. This transfers the proton from the (hypothetical) standard state $\gamma(\text{H}^+) = 1.00$ and $[\text{H}^+] = 1.00 \text{ mol dm}^{-3}$, with $\gamma(\text{H}^+) \rightarrow 1.0$ as $\sum [i] \rightarrow 0$ (where $i = \text{ion}$) in water, to $\gamma(\text{H}^+) = 1.00$ and $[\text{H}^+] = 1.00 \text{ mol dm}^{-3}$, with $\gamma(\text{H}^+) \rightarrow 1.0$ as $\sum [i] \rightarrow 0$ in the mixture. In such water-rich mixtures, the input of Gibbs free energy to create a hole in the mixture to receive the sphere will be balanced by the free energy decrease when the same sized hole collapses in water. However, in the mixture containing H_2O and S molecules, there will be a rearrangement of the solvent molecules surrounding and within the charged sphere from that experienced in pure water. This can be represented by the equilibrium [1, 13]



assuming now that $m \geq 5$ and that, in these water-rich mixtures, only one S molecule is involved in an exchange for an H_2O molecule in the aqua-proton. The free energy change involved for the exchange in equilibrium (4) for each mole of aqua-proton transferred is given by [1, 13]

$$\Delta G_2 = -[\text{SH}^+]RT \ln K_{\text{c}}[\text{H}_2\text{O}]_{\text{x}} F_{\text{c}} \quad (5)$$

where $\text{SH}^+ = (\text{H}^+(\text{H}_2\text{O})_{m-1}\text{S})$, $[\text{H}_2\text{O}]_{\text{x}}$ is the molar concentration of water in the mixture, and the concentration quotient K_{c} is given by

$$K_{\text{c}} = \frac{[\text{SH}^+]}{[\text{P}][\text{S}]} \quad (6)$$

where P is $\text{H}^+(\text{H}_2\text{O})_m$. The symmetrical activity coefficient term F_c is given by

$$F_c = y(\text{SH}^+)_x y(\text{H}_2\text{O})_x / y(\text{S})_x y(\text{P})_x \quad (7)$$

Because the solvent-sorting equilibrium (4) occurs in the mixture, the standard state for the dissolved SH^+ and P is defined by $y_x = 1.00$ and $[\text{SH}^+]$ or $[\text{P}] = 1.00 \text{ mol dm}^{-3}$ with $y_x \rightarrow 1.0$ as $\sum [i] \rightarrow 0$, and that for the solvent components H_2O and S, $y(\text{H}_2\text{O})_x$ and $y(\text{S})_x$, is defined by $y_x \rightarrow 1.0$ as $\sum [i] \rightarrow 0$ in that particular mixture. As equilibrium (4) is considered, in turn, in each particular mixture after the transfer of the aqua-proton from the standard state in water to that in the mixture using eqn. (3), the Gibbs free energy of transfer between water and the mixture of the H_2O released on the right hand side of (4) is not invoked [1, 3, 11, 13, 16]. The Gibbs free energy of transfer of the proton from water into the particular mixture on the mole fraction scale is given by

$$\Delta G_t^\ominus(\text{H}^+) = \Delta G(\text{Born}) + \Delta G_2 + RT \ln(d_x M_w / d_w M_x) \quad (8)$$

where d is density and M is molecular weight with M_x given by

$$M_x = 100 / [(\text{wt}\% \text{S} / M_s) + (\text{wt}\% \text{H}_2\text{O} / M_w)] \quad (9)$$

To determine $\Delta G_t^\ominus(\text{H}^+)$ using eqn. (8), K_c in eqns. (5) and (6) has to be evaluated. This is achieved by using the competitive equilibria (10) and (11) of a trace concentration of a base, 4-nitroaniline, B, for SH^+ and P



B absorbs strongly at 383 nm, whilst the molar absorptivity of BH^+ is so low that it can be neglected [17]. K_{1x} and K_{2x} are thermodynamic equilibrium constants. If $F_{1x} = y(\text{B})_x y(\text{P})_x / y(\text{BH}^+)_x y(\text{H}_2\text{O})_x$ and $F_{2x} = y(\text{B})_x y(\text{SH}^+)_x / y(\text{BH}^+)_x y(\text{S})_x$, with y_x defined in each mixture as above, the relationship (12) has been found to hold [1–13, 16, 17] at each $[\text{S}]_{\text{total}}$ when a fixed total added concentration c_0 of 4-nitroaniline is used

$$\frac{c_w c_x}{c_x - c_w} = \frac{K_{2x} F_{2x} [\text{H}_2\text{O}]_x c_0}{K_{1x} F_{1x} [\text{S}]_{\text{total}}} \frac{c_x}{c_0 - c_x} + \frac{c_0 [\text{H}_2\text{O}]_x}{K_{1x} F_{1x} [\text{S}]_{\text{total}}} \quad (12)$$

where c_w is [B] determined in water alone when [HCl] is present and c_x is [B] determined in the water + co-solvent mixture containing $[\text{S}]_{\text{total}}$ for the same [HCl] used in the determination of c_w . The assumption made in deducing eqn. (12) that

$$\frac{K_{1x} F_{1x}}{[\text{H}_2\text{O}]_x} = \frac{K_{1w} F_{1w}}{[\text{H}_2\text{O}]_w} \quad (13)$$

is entirely justified by the linear plots obtained for $c_w c_x / (c_x - c_w)$ against $c_x / (c_0 - c_x)$ for a wide range of varying co-solvents S at a range of $[S]_{\text{total}}$ for each [1–13, 16, 17]. It has been shown that as eqn. (13) does not require $[\text{H}_2\text{O}]_w / [\text{H}_2\text{O}]_x = 1.00$, the use of eqn. (12) is not restricted to dilute solutions of S in water [11, 16]. It has also been shown [11, 16] that for the linear plots of $c_w c_x / (c_x - c_w)$ against $c_x / (c_0 - c_x)$, the agreement of $K_c F_c^{-1}$ calculated from the slope $= F_c c_0 / K_c [S]_{\text{total}}$ with $K_c = [\text{SH}^+] / ([\text{H}^+]_{\text{total}} - [\text{SH}^+]) ([S]_{\text{total}} - [\text{SH}^+])$ confirms the expectation that $F_c \approx 1.0$ for this symmetrical function, eqn. (7). The involvement of a species $(\text{H}^+(\text{H}_2\text{O})_{m-2}\text{S}_2)$ would not lead to the linear plots of $c_w c_x / (c_x - c_w)$ against $c_x / (c_0 - c_x)$ as found and can, therefore, be excluded.

EXPERIMENTAL

Aldrich 99% sulpholane was used without further treatment. All other materials were as described in previous publications for other water + co-solvent mixtures [1–13, 16, 17]. The concentrations of the unprotonated 4-nitroaniline (B above) in water and in the mixtures were determined spectrophotometrically with added HCl + NaCl at an ionic strength of 1.00 mol dm^{-3} at 383 nm at 25°C. Blank measurements of absorbance at 383 nm were made for identical mixtures in each case with the 4-nitroaniline omitted and applied as a correction to the measured absorbance. Mixtures were made up by volume and the contraction which occurred on mixing was determined in each case.

RESULTS AND DISCUSSION

Determination of $\Delta G_r^\circ(\text{H}^+)$

The value of c_x was determined for a range of [HCl] at an ionic strength of 1.00 mol dm^{-3} (NaCl) for 6.21, 9.86, 12.24, 18.10, 23.78, 29.33, 40.04, 45.20, 50.22, 55.12, 59.92 and 68.10 wt% sulpholane at 25°C. When combined with the values for c_w at the same [HCl] in water, linear plots of $c_x c_w / (c_x - c_w)$ against $c_x / (c_0 - c_x)$ were obtained for each $[S]_{\text{total}}$, each plot having an intercept coinciding with $c_0 [\text{H}_2\text{O}]_x / K_{1x} F_{1x} [S]_{\text{total}}$ using eqn. (13) and $K_{1w} F_{1w} / [\text{H}_2\text{O}]_w$ determined in water [13]. Examples of these plots are shown in Fig. 1. Values for $K_c F_c^{-1}$ determined from the slopes and for $K_{2x} F_{2x}$ calculated from the slope/intercept ratio are given in Table 1.

Table 1 also contains values for

$$K_c = [\text{SH}^+] / ([\text{H}^+]_{\text{total}} - [\text{SH}^+]) ([S]_{\text{total}} - [\text{SH}^+]) \quad (14)$$

calculated for each [HCl] at each $[S]_{\text{total}}$. To obtain these, $K_{2x} F_{2x}$ in Table 1 was used to calculate $[\text{SH}^+]$ from

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

[HCl]/ mol dm^{-3}	Wt% sulpholane (mole fraction)											
	6.21 (0.010)	9.86 (0.0161)	12.24 (0.0205)	18.10 (0.0321)	23.78 (0.0447)	29.33 (0.0586)	40.04 (0.091)	45.20 (0.110)	50.22 (0.131)	55.12 (0.156)	59.92 (0.183)	68.10 (0.242)
0.10	0.39	—	0.61	—	—	—	—	0.80	—	2.64	—	—
0.16	0.38	0.61	0.58	0.73	0.88	1.09	1.17	1.32	1.26	1.45	1.1	1.0
0.20	0.38	0.60	0.63	0.68	0.84	1.00	1.19	1.10	1.11	1.06	1.0	1.2
0.40	0.37	0.57	0.56	0.65	0.74	1.00	1.07	0.98	1.11	2.00	2.4	2.4
0.80	0.38	0.57	0.48	0.60	0.80	0.93	1.25	6.6	1.52	6.7	7.5	—
1.00	—	0.54	—	0.66	0.74	0.90	1.25	—	2.16	—	—	—
Mean K_c	0.38 ± 0.01	0.58 ± 0.03	0.57 ± 0.06	0.66 ± 0.05	0.80 ± 0.06	0.98 ± 0.07	1.19 ± 0.07	—	—	—	—	—
$K_c F_c^{-1}$	0.40 ± 0.01	0.60 ± 0.01	0.63 ± 0.01	0.69 ± 0.01	0.82 ± 0.01	1.00 ± 0.01	1.13 ± 0.01	1.22 ± 0.02	1.21 ± 0.01	1.36 ± 0.01	1.37 ± 0.02	1.38 ± 0.01
$K_2 F_2$	38.6	24.7	24.6	22.3	18.6	15.3	13.4	12.3	12.6	10.7	11.2	11.1

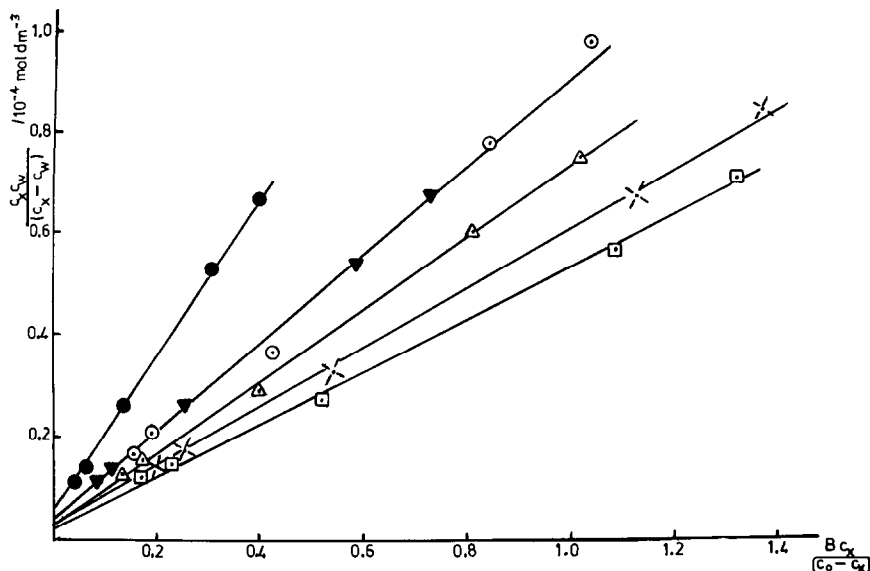


Fig. 1. Plots of $c_w c_x / (c_x - c_w)$ against $c_x / (c_0 - c_w)$ for HCl + NaCl at an ionic strength of 1.00 mol dm^{-3} and at 25°C for mixtures of water and sulpholane containing the following wt% of sulpholane: \circ , 23.78, $B = 1.00$; \times , 29.33, $B = 1.00$; \triangle , 40.04, $B = 0.50$; \square , 50.22, $B = 0.50$; \blacktriangledown , 59.92, $B = 0.20$; \bullet , 68.10, $B = 0.10$.

$$[\text{SH}^+] = \frac{[\text{S}]_{\text{total}}}{1 + \frac{K_{2x} F_{\text{ex}} c_x}{c_0 - c_x}} \quad (15)$$

Table 1 shows that, for each $[\text{S}]_{\text{total}}$, the agreement for K_c with varying $[\text{HCl}]$ is acceptable and that the mean K_c agrees with the $K_c F_c^{-1}$ obtained using only the slope for the same mixture for $[\text{S}]_{\text{total}} \leq 40 \text{ wt}\%$. For $[\text{S}]_{\text{total}} \geq 45 \text{ wt}\%$, some erratic variation of K_c with $[\text{HCl}]$ occurs at each $[\text{S}]_{\text{total}}$, as found for similar concentrations of other co-solvents. This arises from the difference ($[\text{H}^+]_{\text{total}} - [\text{SH}^+]$) in eqn. (14) becoming very small for $[\text{S}]_{\text{total}} \geq 45 \text{ wt}\%$, with attendant large errors in the calculated K_c . The agreement between the mean K_c determined via eqns. (14) and (15) with $K_c F_c^{-1}$ obtained from the slope, confirms the expected relationship $F_c \approx 1.0$ for this symmetrical term, as found with all other mixtures [1–13, 16, 17].

The value of ΔG_2 can now be calculated using eqn. (5). The $K_c F_c^{-1}$ in Table 1 with $F_c \approx 1.0$ is always used, because this involves only the slope of the plots of $c_w c_x / (c_x - c_w)$ versus $c_x / (c_0 - c_x)$ rather than K_c from eqns. (14) and (15) with the more inaccurate $K_2 F_{2x}$ term obtained from the slope/intercept ratio. $[\text{SH}^+]$ in eqn. (5) is obtained from [13]

$$[\text{SH}^+] = 0.5[A - (A^2 - 4[\text{S}]_{\text{total}})^{1/2}] \quad (16)$$

with

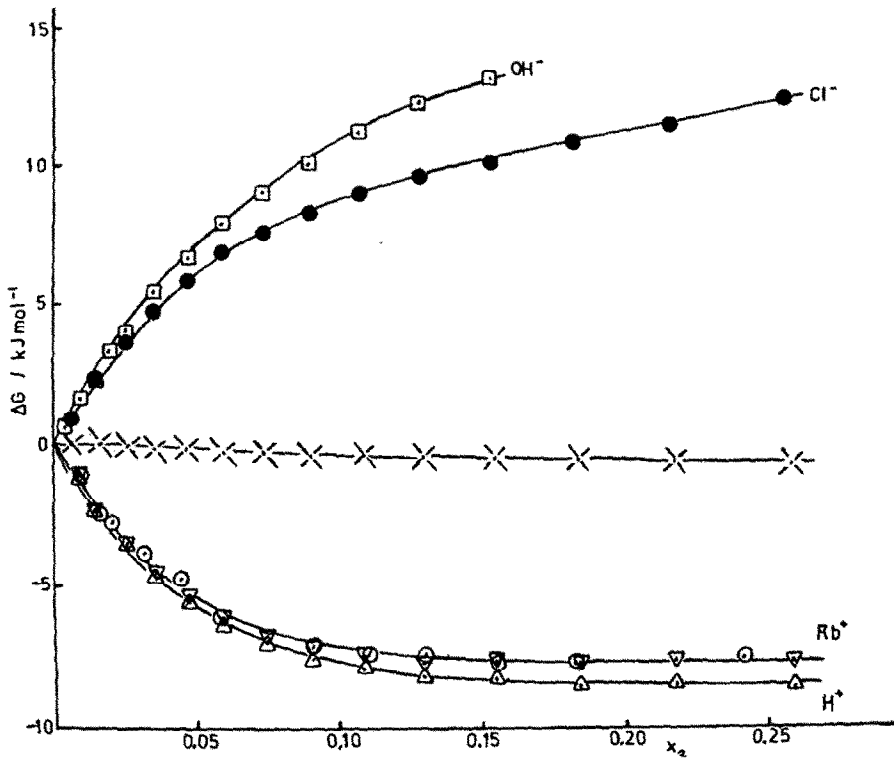


Fig. 2. The variation with mole fraction of sulpholane of: \times , $\Delta G(\text{Born})$ from eqn. (3); \circ , ΔG_2 from eqn. (5); and of the free energy of transfer at 25°C $\Delta G_i^\circ(i)$ from water into water + sulpholane mixtures for i being: Δ , H^+ ; ∇ , Rb^+ ; \square , OH^- ; and \bullet , Cl^- .

$$A = ([S]_{\text{total}} + 1 + K_c^{-1}) \quad (17)$$

and

$$[\text{H}_2\text{O}]_x = (1000d_x - [S]_{\text{total}}M_s)M_w^{-1} \quad (18)$$

The densities d_x and dielectric constants D_x of the mixtures were interpolated from the values of Tommila et al. [18]. The variations on the mole fraction scale of $\Delta G_i^\circ(\text{H}^+)$ from eqn. (8) and of ΔG_2 from eqn. (5) with the mole fraction of sulpholane are shown in Fig. 2. This shows that, as found for all other mixtures [1–13, 16, 17], $\Delta G_i^\circ(\text{H}^+) \approx \Delta G_2$ with $|\Delta G(\text{Born})| \ll |\Delta G_2|$, the difference between $\Delta G_i^\circ(\text{H}^+)$ and ΔG_2 being largely determined by the term $RT \ln(d_x M_w / d_w M_x)$ for converting from the molar scale to the mole fraction scale. The values for $\Delta G_i^\circ(\text{H}^+)$ are collected in Table 2. The error limits on ΔG_2 and, therefore, also on $\Delta G_i^\circ(\text{H}^+)$ lie well within the compass of the symbols used in Fig. 2.

TABLE 2

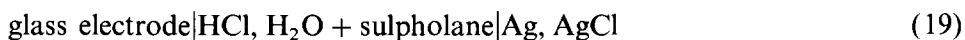
Values for the free energies of transfer $\Delta G_i^\circ(i)/\text{kJ mol}^{-1}$ of single ions from water into water + sulpholane mixtures at 25°C on the mole fraction scale

Conc. of sulpholane		H ⁺	Cl ⁻	OH ⁻	Rb ⁺
Wt%	Mole fraction				
3.00	0.0046	-0.55	-	0.66	-
5.00	0.0078	-0.97	0.97	-	-0.96
6.00	0.0095	-1.24	-	1.64	-
9.00	0.015	-2.03	-	2.26	-
10.00	0.016	-2.35	2.37	-	-2.32
12.00	0.020	-3.00	-	3.35	-
15.00	0.026	-3.57	3.64	4.04	-3.51
20.00	0.036	-4.62	4.79	5.4	-4.57
20.09	0.036	-4.63	4.77 ^a	-	-
25.00	0.048	-5.5	5.8	6.6	-5.4
30.00	0.060	-6.3	6.8	7.8	-6.2
35.00	0.075	-6.9	7.5	8.9	-6.7
40.00	0.091	-7.5	8.2	9.9	-7.1
40.00	0.091	-	8.2 ^a	-	-
45.00	0.109	-7.9	8.8	11.0	-7.4
50.00	0.130	-8.2	9.4	12.0	-7.6
55.00	0.155	-8.3	9.9	12.9	-7.6
60.00	0.184	-8.5	10.7	-	-7.8
60.00	0.184	-	10.6 ^a	-	-
65.00	0.218	-8.5	11.2	-	-7.6
70.00	0.259	-8.6	12.1	-	-7.7

^a Using E° data of ref. 20.

Determination of $\Delta G_i^\circ(i)$ for other ions i

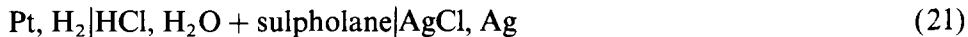
$\Delta G_i^\circ(\text{HCl})$ is obtainable for water + sulpholane mixtures from two sources. Firstly, Smits et al. [19] have calculated $\Delta G_i^\circ(\text{HCl})_c$ on the molar scale from E° values for the cell



for sulpholane concentrations in the range 0–85 wt%. After conversion of $\Delta G_i^\circ(\text{HCl})_c$ to the mole fraction scale for 5–70 wt% sulpholane using the equation

$$\Delta G_i^\circ(\text{HCl}) = \Delta G_i^\circ(\text{HCl})_c + 2RT \ln(M_w d_x / M_x d_w) \quad (20)$$

$\Delta G_i^\circ(\text{Cl}^-)$ was calculated using eqn. (1) with the $\Delta G_i^\circ(\text{H}^+)$ values in Table 2. Secondly, Tommila and Belenskij [20] have measured E_m° values for the cell



for 20–94 wt% sulpholane at 25°C. $\Delta G_t^\circ(\text{HCl})_m$ on the molality scale was calculated using

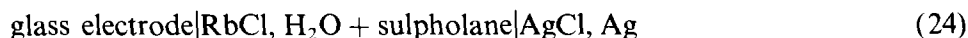
$$\Delta G_t^\circ(\text{HCl})_m = 96.5(E_w^\circ - E_x^\circ) \text{ kJ mol}^{-1} \quad (22)$$

for 20–60 wt% sulpholane with $(E_w^\circ)_m = 0.22246 \text{ V}$ [21]. These were then converted to the mole fraction scale using

$$\Delta G_t^\circ(\text{HCl}) = \Delta G_t^\circ(\text{HCl})_m + 2RT \ln(M_w/M_x) \quad (23)$$

and $\Delta G_t^\circ(\text{Cl}^-)$ calculated from eqn. (1). Both sets of values for $\Delta G_t^\circ(\text{Cl}^-)$ in Table 2 are in good agreement.

Smits et al. [22] have also determined $\Delta G_t^\circ(\text{RbCl})_c$ on the molar scale from E° measurements on the cell



over the range 0–85 wt% sulpholane. After conversion to the mole fraction scale using an equation analogous to eqn. (20), $\Delta G_t^\circ(\text{Rb}^+)$ was calculated for 5–70 wt% sulpholane using eqn. (2) with the $\Delta G_t^\circ(\text{Cl}^-)$ values given in Table 2. The resulting values are collected in Table 2.

It has also been shown [1–13] that $\Delta G_t^\circ(\text{H}^+)_m + \Delta G_t^\circ(\text{OH}^-)_m$ on the molality scale can be calculated from the ionic product on the molality scale K_{ip}^m using the equation

$$\Delta G_t^\circ(\text{H}^+)_m + \Delta G_t^\circ(\text{OH}^-)_m = RT \ln\left(\frac{K_{ip}^w}{K_{ip}^x}_m\right) + RT \ln \frac{(a_{\text{H}_2\text{O}}^x)_m^2}{m_w m_x} \quad (25)$$

where $(a_{\text{H}_2\text{O}}^x)_m$ is the activity of water in the mixture on the molality scale, and m_w and m_x are the molalities of water in pure water and in the mixture, respectively. Values for pK_{ip}^c on the molar scale [23] have been converted to the molality scale using

$$pK_{ip}^m = pK_{ip}^c + 2 \log_{10} d_x \quad (26)$$

The values for $(a_{\text{H}_2\text{O}}^x)_m$ on the mole fraction scale calculated from the activity coefficients for water in water + sulpholane mixtures [18] were converted to the molality scale using

$$(a_{\text{H}_2\text{O}}^x)_m = 55.509 a_{\text{H}_2\text{O}}^x \quad (27)$$

The values for $\Delta G_t^\circ(\text{H}^+)_m + \Delta G_t^\circ(\text{OH}^-)_m$ obtained from eqn. (25) were converted to the mole fraction scale using an equation analogous to eqn. (20), and the $\Delta G_t^\circ(\text{OH}^-)$ values calculated using eqn. (1) with the $\Delta G_t^\circ(\text{H}^+)$ values given in Table 2, are also given in Table 2.

Gibbs free energy of transfer of the charge on large ions

The Gibbs free energy of transfer of an ion can be regarded as composed of a contribution from the transfer of the electrically neutral bulk of the ion, $\Delta G_t^\circ(i)_n$, and of a contribution from the transfer of the charge on the ion, $\Delta G_t^\circ(i)_e$ [24], i.e.

$$\Delta G_t^\circ(i) = \Delta G_t^\circ(i)_n + \Delta G_t^\circ(i)_e \quad (28)$$

$\Delta G_t^\circ(i)_e$ will, of course, be influenced by the degree of localization of the charge on the ion and by its sign [25]. As it is difficult to determine directly the $\Delta G_t^\circ(i)_n$ value for a particular charged molecule [24], an indirect method has to be employed in resolving $\Delta G_t^\circ(i)$ into its components.

It has been shown [1–13] that, for an organic cation A^+ participating in a proton dissociation



provided the cation is large enough

$$\Delta G_t^\circ(A^+)_n = \Delta G_t^\circ(B) \quad (30)$$

with

$$\Delta G_t^\circ(A^+)_e = \Delta G_t^\circ(A^+) - \Delta G_t^\circ(B) = RT \ln(K_a^x/K_a^w) + \Delta G_t^\circ(H^+) \quad (31)$$

Similarly, for a large organic anion B^- formed in a proton dissociation from a neutral A [1–13]



$$\Delta G_t^\circ(B^-)_n = \Delta G_t^\circ(A) \quad (33)$$

and

$$\Delta G_t^\circ(B^-)_e = \Delta G_t^\circ(B^-) - \Delta G_t^\circ(A) = RT \ln(K_a^w/K_a^x) - \Delta G_t^\circ(H^+) \quad (34)$$

Although it is readily seen that eqn. (30) is a good approximation for cations A^+ like anilinium or quinolinium and that eqn. (33) is a good approximation for anions B^- like benzoate, it may not be so readily appreciated that eqn. (33) can also be applied when B^- is acetate. Using structural data for acetic acid [26, 27], the diameter of the sphere containing acetic acid is 0.38 nm, whereas, using structural data for the acetate ion [28] together with the radius [29] of OH^- to represent the radius of $-\text{O}^-$, the diameter of a sphere containing the acetate ion is 0.39 nm. This supports strongly the view [1–13] that eqns. (33) and (34) can be applied to the transfer of the acetate ion from water into water-rich water + co-solvent mixtures. Although the diameters of formic acid (0.18 nm) and the formate ion (0.21 nm) [26, 27] are slightly more divergent, the single point is given in Table 3.

TABLE 3
 $\Delta G_i^\circ(i)_e/\text{kJ mol}^{-1}$ values for the transfer of the charge alone at 25°C, where i is A⁺ or B⁻, from water into mixtures of water with sulpholane

A ⁺ or B ⁻	Wt% sulpholane (mole fraction)									
	12.50 (0.021)	13.55 (0.023)	25.00 (0.048)	26.25 (0.051)	37.50 (0.083)	38.26 (0.085)	49.64 (0.129)	50.00 (0.130)	60.40 (0.186)	62.50 (0.200)
Anilinium ^a	-	-2.34	-	-3.94	-	-4.60	-4.58	-	-4.09	-
<i>N</i> -Methylanilinium ^a	-	-2.28	-	-3.71	-	-4.14	-3.95	-	-3.29	-
<i>N,N</i> -Dimethylanilinium ^a	-	-2.16	-	-3.60	-	-3.97	-3.72	-	-2.94	-
3-Nitroanilinium ^b	-1.78	-	-3.07	-	-3.55	-	-	-3.37	-	-
Pyridinium ^a	-	-2.34	-	-4.05	-	-4.77	-4.75	-	-4.48	-
Quinolinium ^a	-	-1.54	-	-2.74	-	-3.23	-3.15	-	-2.83	-
Isoquinolinium ^a	-	-1.88	-	-3.14	-	-3.62	-3.55	-	-3.17	-
Acridinium ^a	-	-0.34	-	-1.31	-	-1.68	-1.67	-	-1.40	-
Formate ^c	-	-	-	-	-	-	-	-	-	15.0
Acetate ^a	-	4.22	-	7.9	-	10.8	13.3	-	15.7	16.3 ^c
Chloroacetate ^c	-	-	-	-	-	-	-	-	-	15.1
Benzoate ^a	-	4.56	-	6.7	-	11.9	14.5	-	17.0	15.1 ^c
4-Nitrobenzoate ^a	-	4.11	-	7.9	-	10.9	13.2	-	15.5	-
4-Nitrophenate ^a	-	3.65	-	7.0	-	9.5	11.7	-	13.5	13.8 ^c

Sources of pK_a data: ^a ref. 30; ^b ref. 31; ^c ref. 32.

Values of pK_a are available in water and in water + sulpholane mixtures on the molar scale [30] and on the molality scale [31, 32]. For cationic acids A^+ , those of Reynaud [30] on the molar scale are used in eqn. (31), with $-RT \ln(M_w d_x / M_x d_w)$ added to the right hand side, and those of Ang [31] on the molality scale have $-RT \ln(M_w / M_x)$ added to the right hand side. Values for $\Delta G_t^\circ(H^+)$ are interpolated from the data in Table 2 and the resulting values for $\Delta G_t^\circ(A^+)_e$ on the mole fraction scale are collected in Table 3. For electrically neutral acids, A, values for pK_a have been determined by Reynaud [30] on the molar scale and $RT \ln(M_w d_x / M_x d_w)$ is added to the right hand side of eqn. (34). The remaining pK_a for the conjugate system (32) have been determined by Bates and Pawlak [32] on the molality scale and $RT \ln(M_w / M_x)$ is added for these to the right hand side of eqn. (34). Again, the resulting $\Delta G_t^\circ(B^-)_e$ values on the mole fraction scale are collected in Table 3.

Comparison of $\Delta G_t^\circ(i)$ and $\Delta G_t^\circ(i)_e$

Water-rich mixtures of water + sulpholane have a positive excess free energy of mixing ΔG_{mix}^E [18], like ΔG_{mix}^E for mixture of alcohols with water [33]. However, they differ considerably in that the excess enthalpy of mixing ΔH_{mix}^E of water + sulpholane is positive at low x_2 [18], whereas ΔH_{mix}^E for water + alcohols [33] is negative. The positive ΔG_{mix}^E value with the latter co-solvents is attained with high values for $-T\Delta S_{\text{mix}}^E$ [33], whereas $T\Delta S_{\text{mix}}^E$ values for sulpholane as co-solvent remain approximately zero [18]. Water + dimethyl sulphoxide differs again in having negative values for ΔG_{mix}^E , ΔH_{mix}^E and $T\Delta S_{\text{mix}}^E$ [34–36]. These co-solvents have rising values for the viscosity η at low x_2 [18, 35, 37] but, whereas with alcohols [35] and dimethyl sulphoxide [37] as co-solvents this leads to a maximum, with sulpholane η rises smoothly up to η for the pure co-solvent [18]. For alcohols [38] and dimethyl sulphoxide [39], the relative partial molar volume, $\bar{v}_2 - v_2^\circ$, is negative and has a minimum at low x_2 for alcohols and a kink for dimethyl sulphoxide, with the relative partial molar volume of water, $\bar{v}_1 - v_1^\circ$, remaining approximately zero; but with sulpholane [18], $\bar{v}_1 - v_1^\circ$ is positive at low x_2 with a maximum and the negative values for $\bar{v}_2 - v_2^\circ$ rise smoothly to zero. Thus, with alcohols, and possibly dimethyl sulphoxide, added to water at low x_2 , the hydrophobic part of the co-solvent molecule collects in the interstices between the Frank-type “flickering icebergs” of structured water, without disturbing the volume occupied by each water molecule, although some extra stability is introduced through $-\Delta H_{\text{mix}}^E$ in the form of more hydrogen bonding [40–44]. However, with sulpholane, the processes involved when it is added to water at low x_2 must result, on balance, in the breakage of bonds, leading to a positive ΔH_{mix} with little nett effect on $T\Delta S_{\text{mix}}^E$.

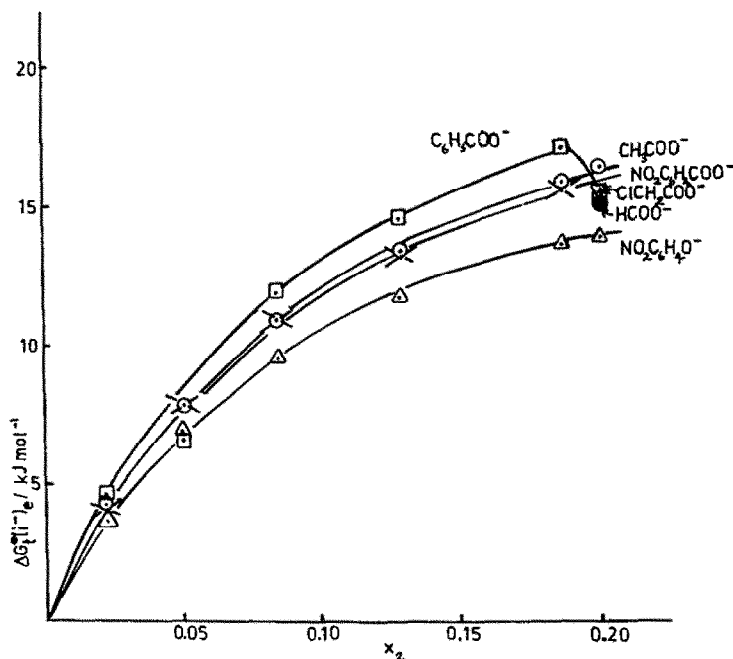
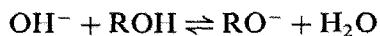


Fig. 3. The variation with mole fraction of sulpholane of the free energy of transfer of the charge alone from water into water + sulpholane mixtures for the anions: ○, acetate; □, benzoate; ×, 4-nitrobenzoate; △, 4-nitrophenate; ▽, chloroacetate; ●, formate.

Nevertheless, the behaviour of $\Delta G_i^\ominus(i)$ with varying ions i is similar in water-rich mixtures of water containing an alcohol or an ether or dimethyl sulphoxide or sulpholane. $\Delta G_i^\ominus(\text{cation})$ is usually negative, except possibly for methanol as co-solvent with some cations [1–13], and $\Delta G_i^\ominus(\text{anion})$ is usually positive, except for hydrophobic anions like BPh_4^- [1–13]. Figure 2 shows the same trend with sulpholane as co-solvent. For a protic co-solvent, $\Delta G_i^\ominus(\text{OH}^-)$ can be negative due to the extra stability in the mixture resulting from the equilibrium



but for aprotic co-solvents, as found in Fig. 2 with sulpholane, OH^- behaves like other anions and produces a positive $\Delta G_i^\ominus(\text{OH}^-)$ [1–13]. For the other co-solvents, $\Delta G_i^\ominus(\text{anion})_e$ is usually positive [1–13], as found in Fig. 3 with sulpholane as co-solvent. Figure 4 shows that $\Delta G_i^\ominus(\text{cation})_e$ is negative at low x_2 , tending to a minimum at $x_2 \approx 0.1$, similar to the behaviour of $\Delta G_i^\ominus(\text{cation})_e$ for other co-solvents mixed with water [1–13].

It is of interest to see how the free energy of transfer of the charge alone on the ion, that is the free energy of transfer of the ion minus the free energy of transfer of the electrically neutral bulk of the ion, varies with the molecular structure of the ion. Figure 3 shows that $\Delta G_i^\ominus(i)_e$ for anions is influenced little by the size of the ion and by the extent to which the charge

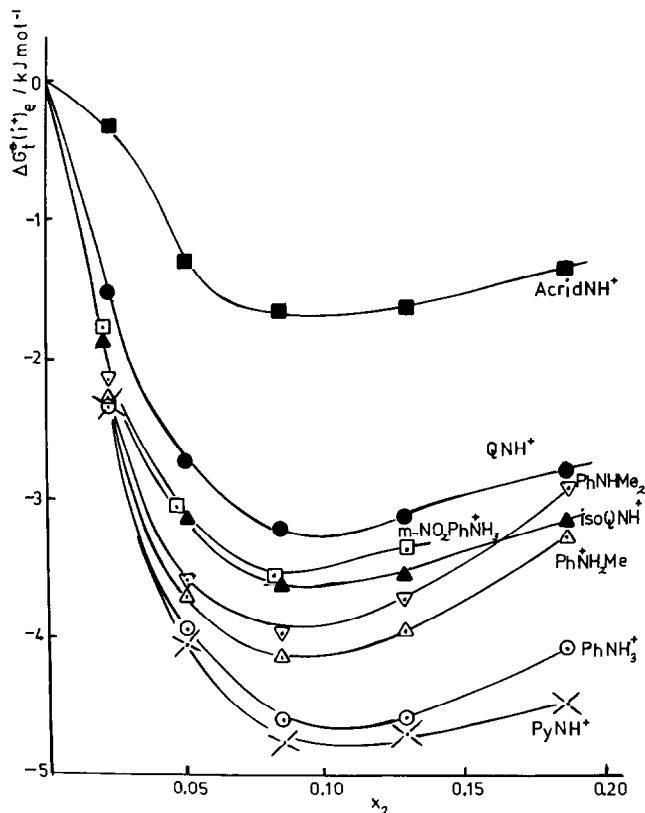


Fig. 4. The variation with mole fraction of sulpholane of the free energy of transfer of the charge alone from water into water + sulpholane mixtures for the cations: ○, anilinium; △, *N*-methylanilinium; ▽, *N,N*-dimethylanilinium; □, 3-nitroanilinium; ×, pyridinium; ●, quinolinium; ▲, isoquinolinium; ■, acridinium.

is delocalized over the whole molecule. This contrasts with the effect of similar influences on $\Delta G_{\ddagger}^{\circ}(i)_{\text{e}}$ for cations as illustrated in Fig. 4. Firstly, $-\Delta G_{\ddagger}^{\circ}(i)_{\text{e}}$ for cations decreases in the series $\text{PhNH}_3^+ > \text{PhNH}_2\text{Me}^+ > \text{PhNHMe}_2^+$. This could be interpreted as an effect of increasing size decreasing the stability of the cation in the mixture, through, say, the increasing hydrophobic effect. However, such an effect of increasing bulk should have been eliminated when $\Delta G_{\ddagger}^{\circ}(i)_{\text{n}}$ is subtracted from $\Delta G_{\ddagger}^{\circ}(i)_{\text{e}}$ in eqn. (31) and it has been shown that increasing hydrophobicity usually increases the stability of ions in water + co-solvent mixtures [1–13], contrary to the observation with this series. It seems more likely that the reduction in the stability of the charge on increasing methylation of the nitrogen atom results from the increasing electron-repelling effect tending to decrease the size of the charge. Again, Fig. 4 shows that $-\Delta G_{\ddagger}^{\circ}(i)_{\text{e}}$ for cations decreases along the series pyridinium > isoquinolinium > quinolinium > acridinium. Along this series, both the bulk of the molecule and the extent to which the

charge is dispersed over the molecule are increased. As explained above, the purely bulk effect should have been eliminated by the application of eqn. (31), so, again, it seems likely that the decrease in the stability of the ion in these mixtures along these series results from an increasing dispersal of the charge as the size of the conjugated system increases along the series [1–13].

CONCLUSION

As with the addition of a wide variety of co-solvents to acidified water [1–13] in water-rich conditions, the variation of the unprotonated form of 4-nitroaniline with acidity in each mixture obeys eqn. (12), which, in turn, requires the involvement of two different solvated forms of the proton in equilibria (4), (10) and (11) [16]. Moreover, the way in which equilibrium (4) shifts with increasing content of co-solvent in the mixture explains the sharp rise in the acidity function H_0 observed in such water-rich mixtures containing alcohols, an ether, a carbonyl compound, a sulphoxide or a nitrile [16], as now with additions of sulpholane. Figure 2 shows that, as found with all the other co-solvents [1–13], the principal component of the increase in stability of the proton on transfer from water into the aqueous mixture derives from the operation of the sorting of solvation around the proton, as in equilibrium (4). As in water + methanol [16], the rapid rise in H_0 at low x_2 is paralleled by a rapid decrease in the equivalent conductivity Λ_0 in water + sulpholane mixtures [45]. As this rapid decrease in Λ_0 occurs in both mixtures where ionic association has no influence on Λ_0 , it is ascribed to the proton in $(\text{H}^+(\text{H}_2\text{O})_{m-1}\text{S})$ having a lower mobility than the proton in $\text{H}^+(\text{H}_2\text{O})_m$ in the mixture [16].

Unfortunately, no data appear to be available with which to calculate $\Delta G_t^\circ(\text{H}^+)$ using the TATB method which depends on assumptions (35)–(37)

$$\Delta G_t^\circ(\text{Ph}_4\text{As}^+) = \Delta G_t^\circ(\text{BPh}_4^-) = 0.5\Delta G_t^\circ(\text{Ph}_4\text{As}^+\text{BPh}_4^-) \quad (35)$$

$$\Delta G_t^\circ(\text{Ph}_4\text{As}^+)_e \ll \Delta G_t^\circ(\text{Ph}_4\text{As}^+)_n \quad (36)$$

$$\Delta G_t^\circ(\text{BPh}_4^-)_e \ll \Delta G_t^\circ(\text{BPh}_4^-)_n \quad (37)$$

In this method, with $\Delta G_t^\circ(\text{Ph}_4\text{As}^+\text{BPh}_4^-)$, evaluated from solubility measurements in water and in the mixtures, the free energies of transfer of other ions, such as the proton, follow from the application of eqns. (1) and (2) to suitable $\Delta G_t^\circ(\text{HX})$ and $\Delta G_t^\circ(\text{MX})$, using $\Delta G_t^\circ(\text{Ph}_4\text{As}^+)$ and $\Delta G_t^\circ(\text{BPh}_4^-)$ derived from eqns. (35)–(37). Thus, no comparison can be made in water + sulpholane mixtures between $\Delta G_t^\circ(\text{H}^+)$ (TATB) and $\Delta G_t^\circ(\text{H}^+)$ evaluated from the solvent-sorting method used here, such has been made for other co-solvents [16]. As it was found that values for $\Delta G_t^\circ(\text{H}^+)$ (TATB) for mixtures of water with methanol, ethanol or *t*-butyl alcohol were quite unable to explain the steep rise in H_0 in such water-rich mixtures, some

doubt exists concerning the viability of assumptions (35)–(37) in such water-rich conditions with a co-solvent [16].

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