Thermochimica Acta, 200 (1992) 443–459
Elsevier Science Publishers B V , Amsterdam

The stability of the proton in water + co-solvent mixtures

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(Received 30 December 1991)

Abstract

The Hammett acidity function H_0 gives an indication of the ability of a neutral molecule to be protonated and can be used to compare the relative stabilities of protons in solvents consisting of neutral molecules. The rise in H_0 when an organic, oxygen-containing base is introduced into water containing a mineral acid, accompanied by a decrease in conductivity, conforms to the existence of a solvent-sorting equilibrium around the solvated proton together with competing equilibria involving the protonation of the Hammett-indicator base by two different proton solvates. The proton solvate containing a co-solvent molecule is more stable than that without it, and the ionic mobility of the proton involved with the former is less than that in the latter. Free energies of transfer of the proton from water into the mixture $\Delta G_t^\ominus(H^+)$ calculated using this solvent-sorting method and the reference ion method ($\Delta G_t^\ominus(Ph_4As^+) = \Delta G_t^\ominus(BPh_4^-)$) are compared with the rises in H_0 in water-rich media: those using the latter method are shown to be inconsistent with the rise in H_0 for some alcohols From the extent of the conversion of the aqua-proton into the proton solvate containing the co-solvent, the factors influencing the proton–co-solvent solvate are discussed for a range of solvent compositions. The principal effect over the whole range of water-rich compositions is found to be the ability of substituent groups to supply or withdraw electron density from the basic site in the co-solvent molecule

INTRODUCTION

Because all attempts to determine free energies of transfer of ions $\Delta G_t^\ominus(i)$ from water into mixtures of water with an organic co-solvent depend on extra-thermodynamic assumptions, it is difficult to assess what the error on $\Delta G_t^\ominus(i)$ might be, even though it has been asserted that the error on $\Delta G_t^\ominus(i)$ derived from the reference ion TATB method (defined below) is less than 20% [1]. However, the measurement of the basicity of such a water + co-solvent mixture with the Hammett acidity function [2] uses no extra-thermodynamic assumptions and therefore offers a reliable assessment of the stability of the proton in the mixture relative to water. A comparison of H_0 in a range water + co-solvent mixtures with $\Delta G_t^\ominus(H^+)$

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obtained using the two main of sets of extra-thermodynamic assumptions used in water + co-solvent mixtures may, therefore, afford a method of distinguishing which set produces the more reliable values.

HAMMETT ACIDITY FUNCTION

For an indicator B, such as 4-nitroaniline, in equilibrium with its acidic form

$$BH^+ \overset{K_a}{\rightleftharpoons} B + H^+ \tag{1}$$

K_a is given by

$$K_a = \frac{a_{H^+}a_B}{a_{BH^+}} = \frac{a_{H^+}[B]\,y'(B)}{[BH^+]\,y'(BH^+)} \tag{2}$$

where a is activity and y' is the activity coefficient based on $y' \rightarrow 1$ at infinite dilution in water. For a second equilibrium such as eqn. (1) involving AH^+ and A with an equilibrium constant K_a'

$$pK_a' = pK_a - \log\frac{[BH^+]}{[B]} - \log\frac{[A]}{[AH^+]} - \log\frac{y'(BH^+)y'(A)}{y'(B)y'(AH^+)} \tag{3}$$

If the acidity function H_0 is defined by

$$H_0 = pK_a - \log\frac{[BH^+]}{[B]} \tag{4}$$

then

$$H_0 = pK_a' + \log\frac{[A]}{[AH^+]} + \log\frac{y'(BH^+)y'(A)}{y'(B)y'(AH^+)} \tag{5}$$

and pK_a' can be evaluated from the observed ratio $[A]/[AH^+]$ and H_0 determined from K_a and $[BH^+]/[B]$, provided $y'(BH^+)y'(A)/y'(B)y'(AH^+) = 1.0$, as has been found to hold for a series of related indicators B and A covering differing acidity ranges. It is generally accepted [3,4] that the Hammett acidity function gives a good indication of the ability of a neutral molecule to accept a proton and it therefore affords a method of comparing the stability of the proton in a range of solvents consisting only of neutral molecules.

THE TATB/TPTB METHOD FOR DETERMINING $\Delta G_t^{\ominus}(H^+)$

In the TATB method for determining free energies of transfer of individual ions, the free energy of transfer of the salt $Ph_4As^+BPh_4^-$

determined from solubilities is divided equally between the two ions [5].

$$\Delta G_t^\ominus(\mathrm{Ph_4As^+}) = \Delta G_t^\ominus(\mathrm{BPh_4^-}) = \tfrac{1}{2}\Delta G_t^\ominus(\mathrm{Ph_4As^+BPh_4^-}) \qquad (6)$$

Equation (6) assumes that the contribution to $\Delta G_t^\ominus(\mathrm{Ph_4As^+})$ or $\Delta G_t^\ominus(\mathrm{BPh_4^-})$ arising from the transfer of the charge on the large ion is, in either case, negligible compared with that arising from the transfer of the neutral bulk of the ion, as in eqns. (7) and (8)

$$\Delta G_t^\ominus(\mathrm{Ph_4As^+})_e \ll \Delta G_t^\ominus(\mathrm{Ph_4As^+})_n \qquad (7)$$

$$\Delta G_t^\ominus(\mathrm{BPh_4^-})_e \ll \Delta G_t^\ominus(\mathrm{BPh_4^-})_n \qquad (8)$$

where subscripts e and n indicate contributions from the charge and the neutral bulk, respectively. It is assumed that, owing to the size of the ion, the surface charge will be low enough to avoid any influence on the orientation of the solvent molecules, even with highly dipolar solvent molecules such as water, alcohols, ethers and ketones. In the TPTB method, analogous assumptions to those in eqns. (6)–(8) are applied to the ions $\mathrm{Ph_4P^+}$ and $\mathrm{BPh_4^-}$.

Once $\Delta G_t^\ominus(\mathrm{BPh_4^-})$ is known, $\Delta G_t^\ominus(\mathrm{K^+})$, for example, can be calculated from $\Delta G_t^\ominus(\mathrm{KBPh_4})$ and this allows the evaluation of $\Delta G_t^\ominus(\mathrm{X^-})$ from $\Delta G_t^\ominus(\mathrm{KX})$. $\Delta G_t^\ominus(\mathrm{H^+})$ can then be calculated from $\Delta G_t^\ominus(\mathrm{HX})$ determined from suitable electrolytic cells.

THE SOLVENT-SORTING METHOD FOR DETERMINING $\Delta G_t^\ominus(\mathrm{H^+})$

The transfer is considered in terms of two sequential processes. The proton in water is generally regarded as $\mathrm{H_3O^+(H_2O)_3}$ [6] which will have a pyramidal structure, as in Fig. 1(a). The overall charge will be distributed throughout the structure and, owing to the negative end of the dipole on the top water molecule being exposed, it is highly likely that an additional water molecule will be attached sufficiently strongly, as in Fig. 1(b), for the whole structure to be regarded as a sphere of radius $3r_{\mathrm{H_2O}}$, where $r_{\mathrm{H_2O}}$ is the radius of the water molecule. The transfer of this charged sphere of radius $3r_{\mathrm{H_2O}}$ between liquid water of dielectric constant D_w and the mixed

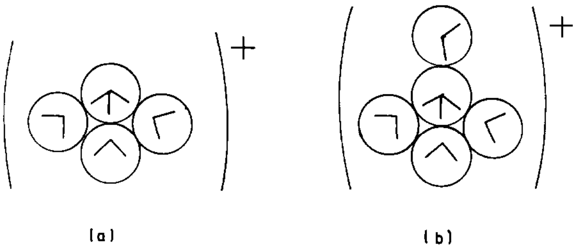

Fig 1 Representation of $\mathrm{H^+(H_2O)_4}$ (a) and $\mathrm{H^+(H_2O)_5}$ (b)

solvent of dielectric constant D_x is now considered using the Born relationship [7,8]

$$\Delta G(\text{Born}) = \frac{Ne^2}{6r_{H_2O}}\left(D_x^{-1} - D_w^{-1}\right) \tag{9}$$

In water-rich media, the free energy needed to create a hole in the mixture to receive the sphere will be exactly balanced by that gained from the collapse of the hole owing to the departure of the sphere from water.

The two components of a binary mixture consisting of water molecules and neutral molecules of a co-solvent S will now sort themselves according to

$$(H^+(H_2O)_m)_{\text{solv}} + S_{\text{solv}} \rightleftharpoons (H^+(H_2O)_{m-1}S)_{\text{solv}} + H_2O_{\text{solv}} \tag{10}$$

assuming $m \geqslant 5$ to allow for an interchange inside or outside the sphere. It is also assumed that the interchange goes no further than the replacement of one molecule of water by S. For each mole of $H^+(H_2O)_5$ transferred initially, the extent of this replacement will be indicated by the free energy change

$$\Delta G_2 = -[SH^+]RT \ln K_c[H_2O]_x F_c \tag{11}$$

where $SH^+ = (H^+(H_2O)_{m-1}S)$ and $[H_2O]_x$ is the molar concentration of water in the mixture. The concentration quotient K_c

$$K_c = \frac{[SH^+]}{[P][S]} \tag{12}$$

with $P = H^+(H_2O)_m$ and

$$F_c = y(SH^+)_x y(H_2O)_x / y(S)_x y(P)_x \tag{13}$$

It should be noted that once the aqua-proton has been transferred into the mixture, all subsequent processes, such as eqn. (10), occur in that particular mixture. Therefore, the standard states refer only to that particular mixture: for the dissolved species i, SH^+ and P, the standard state is defined by $y_x = 1.0$ and $[i] = 1.00$ with $y_x \to 1.0$ as $\Sigma[i] \to 0$; for the solvent components, H_2O and S, $y(H_2O)_x$ and $y(S)_x$ are defined by $y_x \to 1.0$ as $\Sigma[i] \to 0$ in that mixture. As each particular mixture is considered separately [8,9], the free energy of transfer of either H_2O or S into the mixture from pure water or pure S, respectively, is not involved, contrary to the suggestion by Blandamer et al. [10]. The free energy of transfer of the proton from water into the mixture on the mole fraction scale is now given by

$$\Delta G_t^{\ominus}(H^+) = \Delta G(\text{Born}) + \Delta G_2 + RT \ln(d_x M_w / d_w M_x) \tag{14}$$

where d is density, M_w is the molecular weight of water and $M_x = 100/[(\text{wt.\%}\ S/M_s) + (\text{wt.\%}\ H_2O/M_w)]$ with M_s being the molecular weight of the co-solvent. To determine $\Delta G_t^{\ominus}(H^+)$ for a range of water + co-solvent mixtures, K_c must be evaluated experimentally for each mixture. The symmetrical term F_c in eqn. (13) involving related species might be expected to approximate to unity, similar to the symmetrical terms with related species involved in the H_0 relationship [5].

If, into one of these water + co-solvent mixtures containing a mineral acid, with equilibrium (10) in place, a small concentration of a Hammett indicator B is introduced, two additional equilibria (15) and (16) will be established

$$B_{solv} + P_{solv} \overset{K_{1x}}{\rightleftharpoons} BH^+_{solv} + H_2O_{solv} \tag{15}$$

$$B_{solv} + SH^+_{solv} \overset{K_{2x}}{\rightleftharpoons} BH^+_{solv} + S_{solv} \tag{16}$$

where K_{1x} and K_{2x} are the thermodynamic equilibrium constants in that particular mixture. Assuming the existence of equilibria (10), (15) and (16), eqn. (17) has been deduced [11]

$$\frac{c_w c_x}{c_x - c_w} = \left[\frac{K_{2x}F_{2x}}{K_{1x}F_{1x}}\right]\left[\frac{[H_2O]_x c_0}{[S]_{total}}\right]\left[\frac{c_x}{c_0 - c_x}\right] + \frac{c_0[H_2O]_x}{K_{1x}F_{1x}[S]_{total}} \tag{17}$$

relating concentrations of the unprotonated Hammett indicator B obtained with added acid in water alone, c_w, and with the same added acid concentration in the mixture containing $[S]_{total}$ of co-solvent, c_x: a fixed concentration c_0 of 4-nitroaniline is added initially to the water and to the mixture. $F_{1x} = y(B)_x y(P)_x / y(BH^+)_x y(H_2O)_x$ and $F_{2x} = y(B)_x y(SH^+)_x / y(BH^+)_x y(S)_x$, with y defined as above in the mixture. The only assumption made in the deduction of eqn. (17) is [7–9,11]

$$\frac{K_{1x}F_{1x}}{[H_2O]_x} = \frac{K_{1w}F_{1w}}{[H_2O]_w} \tag{18}$$

where subscript w indicates a value in water. The validity of this assumption is justified by the linearity obtained [11–26] in mixtures of water with a wide range of co-solvents for the plots of $c_w c_x/(c_x - c_w)$ against $c_x/(c_0 - c_x)$ with intercepts corresponding to the second term on the right-hand side of eqn. (17) using $K_{1w}F_{1w}/[H_2O]_w$ obtained in water. The slopes of these plots are equal to $c_0/K_c[S]_{total}$, which has enabled K_c to be determined directly [9,11–15]. Because eqn. (18) can be re-arranged to

$$\frac{[BH^+]_w}{[B]_w[P]_w} = \frac{[BH^+]_x}{[B]_x[P]_x} \tag{19}$$

and does not require the assumption $[H_2O]_w/[H_2O]_x = 1.0$, this method is not limited to very dilute solutions of S, as suggested by Marcus [27].

However

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

$$= \frac{y(\mathrm{B})_x y(\mathrm{BH}^+)_w}{y(\mathrm{BH}^+)_x y(\mathrm{B})_w} \frac{y(\mathrm{P})_x y(\mathrm{H_2O})_w}{y(\mathrm{H_2O})_x y(\mathrm{P})_w} \qquad (20)$$

Because $y(\mathrm{B})_x y(\mathrm{BH}^+)_w / y(\mathrm{B})_w y(\mathrm{BH}^+)_x = 1.0$ [2–4,28–31], and the symmetrical term $y(\mathrm{P})_x y(\mathrm{H_2O})_w / y(\mathrm{H_2O})_x y(\mathrm{P})_w = 1.0$ might also, therefore, be reasonably expected, then $F_{1x}/F_{1w} = 1.0$ [9]. From eqns. (18) and (19), therefore, $K_{1w}/K_{1x} = K'_{1w}/K'_{1x}$ or $K_{1w}/K'_{1w} = K_{1x}/K'_{1x}$, where $K'_1 = [\mathrm{BH}^+] \cdot [\mathrm{H_2O}]/[\mathrm{B}][\mathrm{P}]$ with $y(\mathrm{BH}^+)_w y(\mathrm{H_2O})_w / y(\mathrm{B})_w y(\mathrm{P})_w = y(\mathrm{BH}^+)_x y(\mathrm{H_2O})_x / y(\mathrm{B})_x y(\mathrm{P})_x$. By analogy, then, one might expect [9]

$$y(\mathrm{BH}^+)_x y(\mathrm{H_2O})_x / y(\mathrm{B})_x y(\mathrm{P})_x = y(\mathrm{BH}^+) y(\mathrm{S})_x / y(\mathrm{B})_x y(\mathrm{SH}^+)_x$$

with $K_{1x}/K'_{1x} = K_{2x}/K'_{2x}$ or $K_{1x}/K_{2x} = K'_{1x}/K'_{2x}$ in eqn. (17) [9], where $K'_{2x} = [\mathrm{BH}^+]_x[\mathrm{S}]_x/[\mathrm{B}]_x[\mathrm{SH}^+]_x$. Now, the slope $= F_c c_0 / K_c [\mathrm{S}]_{\mathrm{total}}$ for the linear plots of eqn. (17) and the values for $K_c F_c^{-1}$ calculated in this way agree well with $K_c = [\mathrm{SH}^+]/([\mathrm{H}^+]_{\mathrm{total}} - [\mathrm{SH}^+])([\mathrm{S}]_{\mathrm{total}} - [\mathrm{SH}^+])$ obtained with varying $[\mathrm{H}^+]_{\mathrm{total}}$ for each mixture $[\mathrm{S}]_{\mathrm{total}}$ [7–9,11–26]. This confirms, therefore, that the symmetrical $F_c = 1.0$ in eqns. (11) and (13) for all the co-solvents examined [7–9,11–26], supported by $y(\mathrm{BH}^+)_x y(\mathrm{S})_x / y(\mathrm{B})_x y(\mathrm{SH}^+)_x = 1.0$ found [31] for S being an ether with $y(\mathrm{BH}^+)_x y(\mathrm{B})_w / y(\mathrm{BH}^+)_w y(\mathrm{B})_x = 1.0$ in eqn. (20) and by other observations [7–9].

COMPARISON OF H_0 WITH $\Delta G_t^{\ominus}(\mathrm{H}^+)$ WATER + CO-SOLVENT MIXTURES

As co-solvent is added to water, H_0 increases rapidly for methanol, [32–34] ethanol, [32,35], propan-1-ol [32], propan-2-ol [32], acetone [35], dioxane [35], ethanonitrile [36], dimethyl sulphoxide [36], 2-methoxyethanol [36], *N*-methylformamide [36], ethylene carbonate [36] and ethane-1,2-diol [32]. As the co-solvent concentration rises further, H_0 reaches a maximum in the region of mole fraction of co-solvent $x_2 = 0.3$–0.5 for all except DMSO and *N*-methylformamide. Conductivity measurements with HCl in water + methanol show a decrease in conductivity over the same range of composition [34,37] but, at high concentrations of methanol, evidence for ion association between the solvated proton and Cl^- ions has been obtained [37]. Similar evidence exists for such ion association at high concentrations of ethanol [38] and of 2-methoxy-ethanol in water.

For two solvent mixtures, from eqns. (2) and (4)

$$\log(a_{\mathrm{H}^+})_1 - \log(a_{\mathrm{H}^+})_2 = (H_0)_2 - (H_0)_1 - \log\left(\frac{y'(\mathrm{BH}^+)}{y'(\mathrm{B})}\right)_2 \left(\frac{y'(\mathrm{B})}{y'(\mathrm{BH}^+)}\right)_1$$

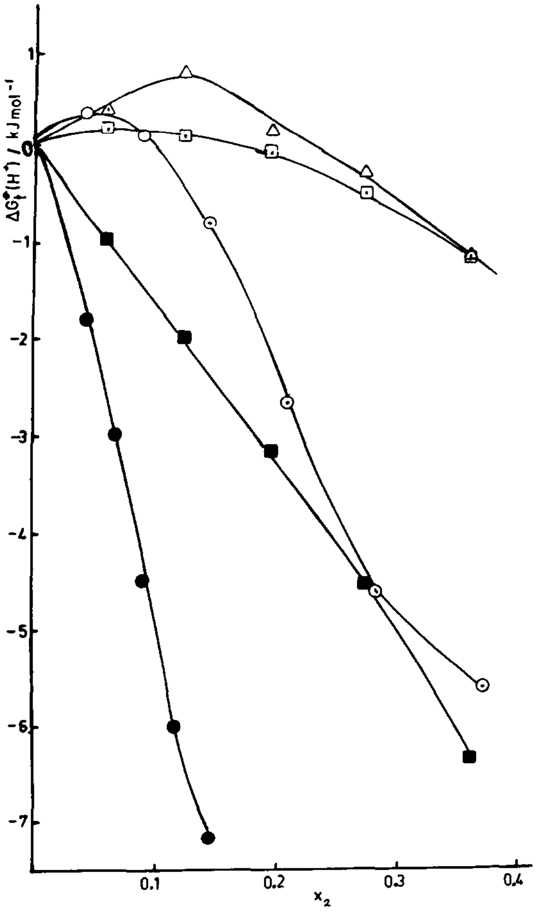

Fig. 2. A comparison of $\Delta G_t^{\ominus}(H^+)$(TATB) for water + methanol derived from the data of ref. 40 (□) and ref. 41 (△) and for water + ethanol from the data of ref 43 (○), with $\Delta G_t^{\ominus}(H^+)$(solvent-sorting) for water + methanol (■) and for water + ethanol (●)

Because the second term on the right-hand side is zero for related indicators, and, indeed, all the determinations quoted above were done with the same indicator, 4-nitroaniline, $(H_0)_2 - (H_0)_1$ will be positive, if for the same addition of protons to the solvents, $(a_{H^+})_2$ is less than $(a_{H^+})_1$. The rapid rise in H_0 at $x_2 < 0.5$ shows, therefore, that the basicity of the mixture is higher than that of pure water and, that, consequently, the proton is more stable in the mixture than in water. Using the solvent-sorting method, $\Delta G_t^{\ominus}(H^+)$ is always negative at low mole fractions of co-solvent for the co-solvents quoted above [7,13–26]: however, this is not always the case for the TATB/TPTB method.

Figure 2 shows the values for $\Delta G_t^{\ominus}(H^+)$ available for primary alcohols on the TATB scale and the solvent-sorting scale. $\Delta G_t^{\ominus}(H^+)_c$ for water + methanol on the molar scale using the TATB method is given by Abraham et al. [40] and Popovych [41]. These values are converted to the mole fraction scale using eqn. (21)

$$\Delta G_t^\ominus(H^+) = \Delta G_t^\ominus(H^+)_c + 5.71 \log \frac{M_w d_x}{M_x d_w} \tag{21}$$

with interpolated densities d_x [42]. For mole fractions $x_2 < 0.3$, $\Delta G_t^\ominus(H^+)$(TATB) values deviate little from zero, remaining ±1 kJ mol^{-1}, showing no stabilisation in the mixture: in contrast, $\Delta G_t^\ominus(H^+)$(solvent-sorting) becomes increasingly negative with considerable stabilisation at low x_2 [7,8]. $\Delta G_t^\ominus(H^+)_c$(TATB) values from Blandamer et al. [43] for water + ethanol, converted to the mole fraction scale using eqn. (21) with d_x given by Bates [44], also remains close to zero for $x_2 < 0.1$, not deviating from ±1 kJ mol^{-1} for $x_2 < 0.15$. This shows, therefore, no stabilisation in this region, where $\Delta G_t^\ominus(H^+)$(solvent-sorting) is always negative [17], showing

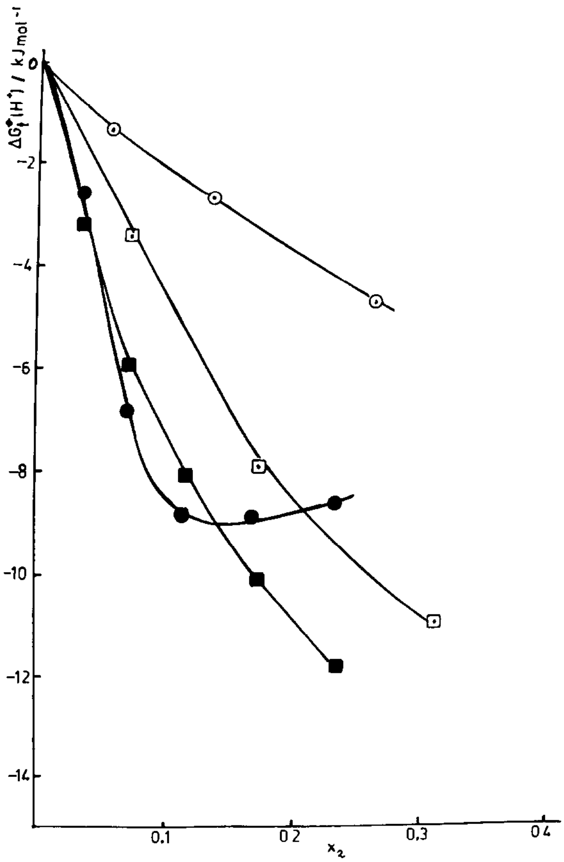

Fig 3 A comparison of $\Delta G_t^\ominus(H^+)$(TATB) for water + propan-2-ol derived from the data of ref. 43 (○) and for water + acetone from the data of ref. 45 (□), with $\Delta G_t^\ominus(H^+)$(solvent-sorting) for water + propan-2-ol (●) and for water + acetone (■).

considerable stabilisation. We must conclude, therefore, that $\Delta G_t^{\ominus}(H^+)$(TATB) values in water + methanol and in water + ethanol do not correspond with the considerable stabilisation of the proton at low x_2 shown by the rapid rise in H_0. In contrast, this rise in H_0 can be accounted for by the increasingly negative values for $\Delta G_t^{\ominus}$(H)(solvent-sorting) as H_0 rises at low x_2.

For water + propan-2-ol, $\Delta G_t^{\ominus}(H^+)_c$(TATB) of Blandamer et al. [43] corrected to the mole fraction scale is negative for $x_2 < 0.3$, as is $\Delta G_t^{\ominus}(H^+)$(solvent-sorting) (Fig. 3) [7,8]: although the latter is more negative than the former, these results do not distinguish between either method of deriving $\Delta G_t^{\ominus}(H^+)$ as an explanation for the steep rise in H_0 at low x_2. Similarly, $\Delta G_t^{\ominus}(H^+)$(TATB) for water + acetone, calculated from

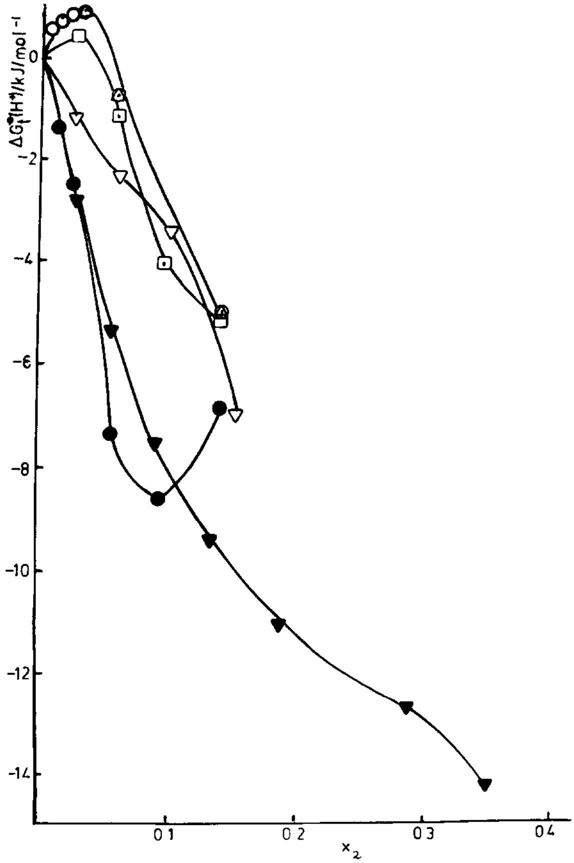

Fig 4. A comparison of $\Delta G_t^{\ominus}(H^+)$(TATB) for water + *t*-butyl alcohol derived using $\Delta G_t^{\ominus}$(HCl) of ref 51 (○), ref 52, (□) and ref 53 (△) and $\Delta G_t^{\ominus}(Cl^-)$(TATB) of ref. 43, with $\Delta G_t^{\ominus}(H^+)$(solvent-sorting) (●), and a comparison of $\Delta G_t^{\ominus}(H^+)$(TATB) (▽) derived using the $\Delta G_t^{\ominus}(OH^-)$ of ref 43 and $\Delta H_t^{\ominus}(H^+) + \Delta G_t^{\ominus}(OH^-)$ of ref 49, with $\Delta G_t^{\ominus}(H^+)$(solvent-sorting) (▼) for water + DMSO.

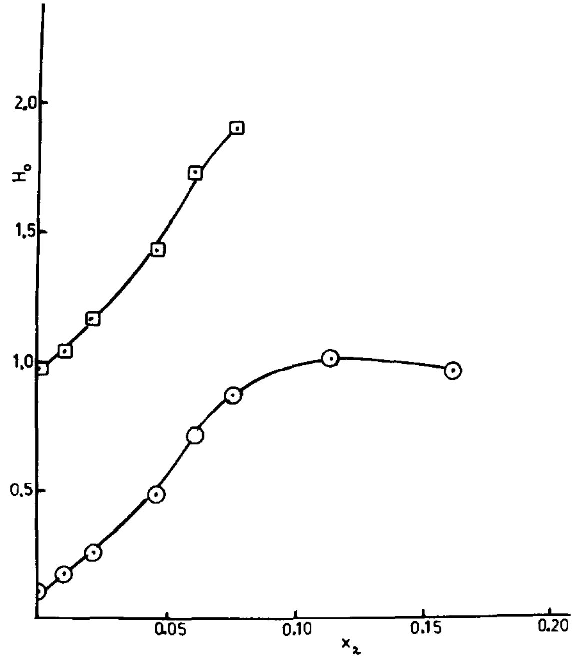

Fig. 5 Values for the Hammett acidity function H_0 in water + *t*-butyl alcohol for 0 10 mol dm^{-3} HCl (□) and 0 80 mol dm^{-}3 HCl (o) at an ionic strength of 1 00 mol dm^{-3}, determined at 25°C using 4-nitroaniline

$\Delta G_t^{\ominus}(Cl^-)_c$(TATB) of Blandamer et al. [45] and $\Delta G_t^{\ominus}(HCl)_c$ of Smits et al. [46] and corrected to the mole fraction scale using the available densities [47], and $\Delta G_t^{\ominus}(H^+)$(solvent-sorting) [7,8] are both negative (Fig. 3): these, therefore, do not offer a distinction. Likewise, for water + DMSO, $\Delta G_t^{\ominus}(H^+)$(TATB), calculated from $\Delta G_t^{\ominus}(OH^-)_c$(TATB) [43] converted to the mole fraction scale using the interpolated densities [48] and $\Delta G_t^{\ominus}(H^+)$ + $\Delta G_t^{\ominus}(OH^-)$ of Woolley and Hepler [49], is negative, as is $\Delta G_t^{\ominus}(H^+)$(solvent-sorting) (Fig. 4); thus no distinction is possible. H_0 for water + *t*-butyl alcohol was calculated from the data of Wells [14] using 4-nitroaniline and HCl. Figure 5 shows that H_0 increases sharply with x_2 at low x_2, as with both propan-1-ol [32] and propan-2-ol [32] and the other alcohols [32,34,35]. For water + *t*-butyl alcohol, $\Delta G_t^{\ominus}(Cl^-)_c$(TATB) of Blandamer et al. [43] converted to the mole fraction scale using the interpolated densities [50] and combined with $\Delta G_t^{\ominus}$(HCl) derived from three different sets of data [512–53], shows that $\Delta G_t^{\ominus}(H^+)$(TATB) is positive for $x_2 \lesssim 0.05$ (Fig. 4), lying within ±1 kJ mol^{-1} for $x_2 < 0.06$. This contrasts with a negative $\Delta G_t^{\ominus}(H^+)$(solvent-sorting) for water + *t*-butyl alcohol (Fig. 4) for $x_2 < 0.12$ [8,14].

We can conclude, therefore, that, although a comparison of the two methods for acetone, propan-2-ol and DMSO as co-solvents does not distinguish between them, $\Delta G_t^{\ominus}(H^+)$ from the TATB method for methanol, ethanol and *t*-butyl alcohol as co-solvents is incapable of explaining the steep rise in H_0 at low x_2, unlike the negative values for $\Delta G_t^{\ominus}(H^+)$ from the solvent-sorting method with these three alcohols. Because of this inapplicability for these alcohols as co-solvents, the accuracy of the TATB method applied to other co-solvents must be under suspicion: certainly, a general accuracy of approx. ±20% must be a low estimate.

COMPARISON OF pK VALUES FOR THE PROTONATION OF CO-SOLVENTS

Broadly, three different sets of values for equilibrium constants exist for the protonation of organic co-solvents in mixtures with water.

Firstly, there are p*K* values derived from the observed fall in conductivity from the pure organic components towards a minimum at $x_2 > 0.9$ on the addition of water to methanol [34,54], ethanol [54,55], butan-1-ol [56], 2-methylpropan-1-ol [56], propan-2-ol [57] and pentan-1-ol [58]. The analysis of all this data depends on the original erroneous assumption of Goldschmidt [55] where the concentration of water at equilibrium was equated with that in the bulk mixture at a very low water content in the absence of the addition of the acid. Moreover, and perhaps more important, the treatment ignores the observation that H^+ and Cl^- are significantly associated in such mixtures of low dielectric constant. Also the values of $K_c' = [SH^+]/[H_2O][S] \lesssim 0.01$ are, of course, each determined in a different solvent, the pure co-solvent.

Secondly, we have the analysis of the protonation equilibria using UV, Raman, NMR and solvent extraction techniques in aqueous sulphuric acid [59]. Collections [60–62] of p*K* data show little variation with changes in the electron-releasing effects of the groups present and show the alcohols, ethers and ketones to be much less basic ($K_c' \lesssim 0.005$) than water, which is unexpected from the effect of the electron-releasing groups. This is perhaps explainable when one compares the mixtures used (30–60 wt.%, H_2SO_4) with their compositions: at this composition range (12–15 mol dm^{-3} H_2SO_4), the mixture consists [63] principally of $H_2\overset{+}{O} \cdot HSO_4^-$ and the solvation of the dissolved species will be quite different from that in water-rich media. Kolthoff and Bruckenstein's results in glacial acetic acid [64], which also show basicities of alcohols much lower than that of water (even though the order of the basicities among the alcohols is that expected from electron-releasing effects), are clearly subject to a similar criticism of a lack of comparison with water-rich media.

Thirdly, we have the determination of $K_c = [SH^+]/[P][S]$ using the solvent-sorting method with the aqua-proton P in water-rich media. From the original comparison at low concentrations of co-solvent [11,12] it was shown that both electron-releasing and stereochemical effects were impor-

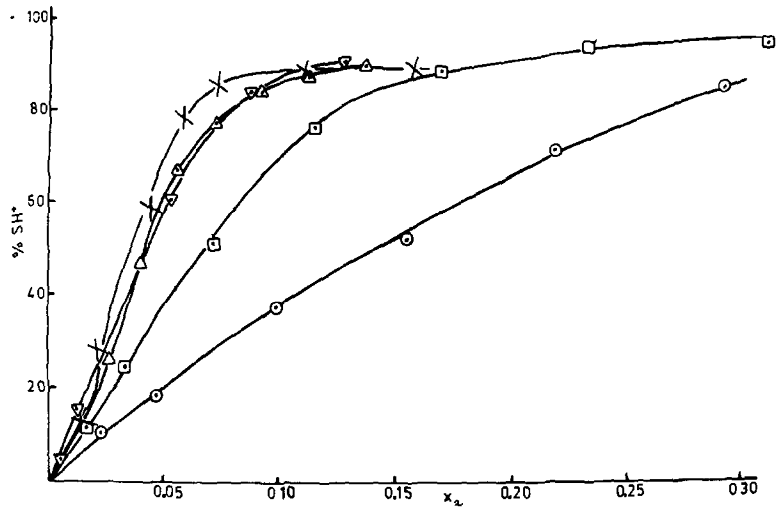

Fig 6 The variation with mole fraction of co-solvent of the percentage conversion of the solvated proton into a solvated proton containing a co-solvent molecule SH^+ for mixtures of methanol (○), ethanol (□), propan-1-ol (△), propan-2-ol (▽) and *t*-butyl alcohol (×) with water at 25°C

tant influences on K_c. All values were determined in the same highly aqueous media (< 10% by volume) and , as expected from the electron-releasing effects, alcohols, ethers and ketones were more basic than water: this corresponds to the increased stability of the protons in such media, as indicated by the increase in H_0. However, because K_c increases with increasing co-solvent content in water-rich mixtures, as required to explain the increase in H_0, a comparison of K_c values should be carried out over a range of co-solvent concentrations to investigate the influence of the molecular structure of the co-solvent.

To do this, the extents of the conversion of the aqua-proton into the proton solvate containing the co-solvent, $H^+((H_2O)_{m-1}S)$, are compared in Figs. 6–10 for a range of mixtures with water, with each co-solvent S being converted to SH^+. Figure 6 shows the influence of electron-releasing effects with alcohols as co-solvents: clearly the basicity is in the order $H_2O < MeOH \ll EtOH \ll 2\text{-}PrOH \approx 1\text{-}PrOH < t\text{-}BuOH$; the relative contraction of the differences at the end of this series may be caused by stereochemical difficulties in introducing a branched chain S into the aqua-proton $H^+(H_2O)_m$ to form $H^+(H_2O)_{m-1}S$ [12]. Figure 7 shows the influence of the presence of electron-attracting groups in reducing basicity. The second ether O makes the basicity of dioxane less than that of tetrahydrofuran and the electron-attracting effect of the $>C{=}O$ group reduces the basicity further: the lowest of these basicities results from the electron-attracting effect of the two OH groups in diethylene glycol. In Fig. 8, the basicities of urea and dimethylformamide, being greater than that of

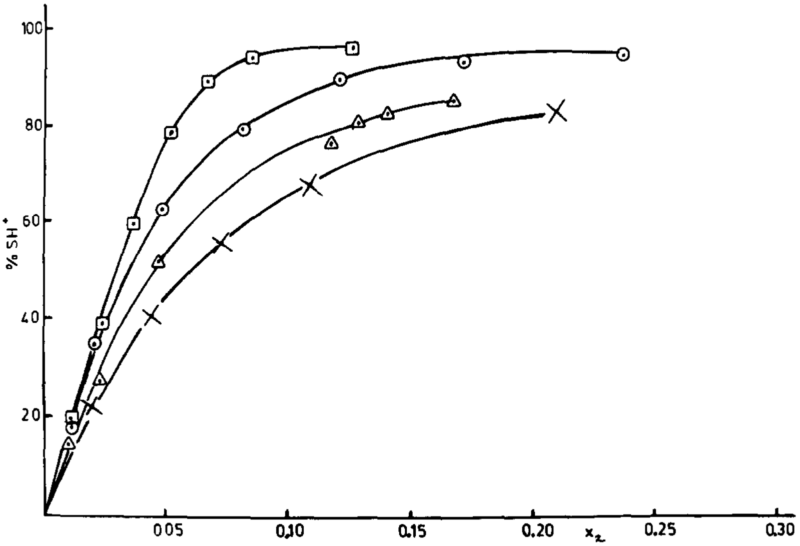

Fig. 7. The variation with mole fraction of co-solvent of the percentage conversion of the solvated proton into a solvated proton containing a co-solvent molecule SH^+ for mixtures of dioxane (o), tetrahydrofuran (□) and ethylene carbonate (△) with water at 25°C

acetone, probably reflect the greater basicity of N over O. However, the approximately equal basicities of acetone and DMSO suggest that the electron-releasing influence of the methyl groups is little changed by the

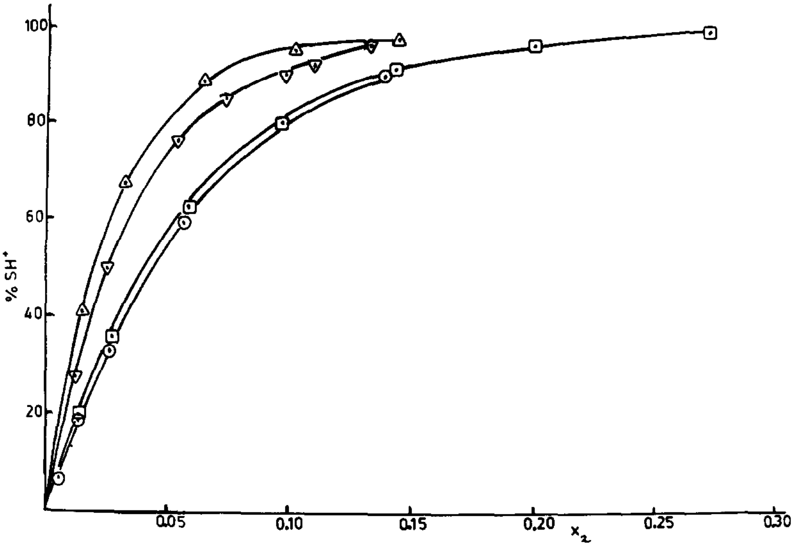

Fig. 8. The variation with mole fraction of co-solvent of the percentage conversion of the solvated proton into a solvated proton containing a co-solvent molecule SH^+ for mixtures of acetone (o), dimethyl sulphoxide (□), urea (△) and dimethylformamide (▽) with water at 25°C

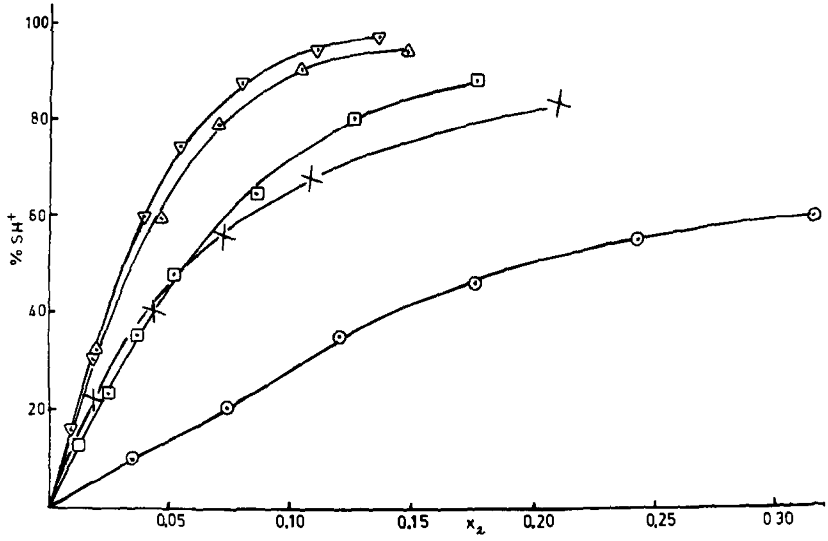

Fig 9 The variation with mole fraction of co-solvent of the percentage conversion of the solvated proton into a solvated proton containing a co-solvent molecule SH^+ for mixtures of ethane-1,2-diol (o), 2-methoxy-ethanol (□), 2-ethoxyethanol (△), 1,2-dimethoxyethane (▽) and diethylene glycol (×) with water at 25°C

change in the atom intermediate between them and the basic site. Figure 9 shows the influence of the electron-attracting OH group with ethane-1,2-diol having the lowest basicity. Alkylation of the OH groups shows the

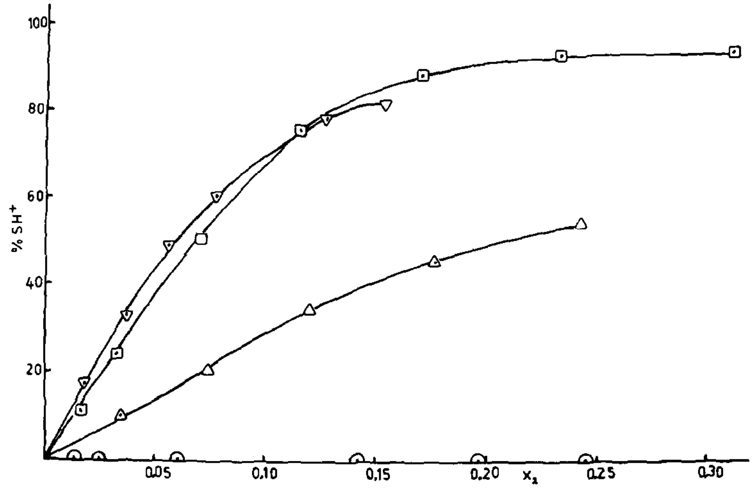

Fig 10. A comparison of the percentage conversion of the solvated proton into a solvated proton containing a co-solvent molecule SH^+ for additions of glycerol (o), ethanol (□), ethane-1,2-diol (△) and ethanonitrile (▽) to water at 25°C

increasing influence of the electron-releasing groups at the basic site in increasing the basicity OH < MeO < EtO, the methyl group on both OH groups providing the highest basicity with dimethoxyethane: an additional electron-attracting OH group in 2-ethoxyethanol reduces the basicity for diethylene glycol. Again, in Fig. 10, the increasing presence of electron-attracting OH groups reduces the basicity in the order EtOH > ethane-1,2-diol > glycerol. Similar effects to that using glycerol are found with other polyhydroxy compounds [9].

The formation of such protonated solvates containing the co-solvent explains [65] the kinetic effect of changes of acidity in several reactions and it has been shown that the determination of the protonation equilibrium constant for acetone using a variety of techniques produces good agreement with the values for K_c derived from the solvent-sorting method [66]. Moreover, as expected from the presence of the positive charge on the protonated solvate containing an alcohol molecule, the susceptibility to oxidation of the alcohol in the solvate is much reduced compared with alcohol molecules outside the protonated solvate [67–72].

CONCLUSIONS

Figures 6–10 show that, irrespective of the co-solvent concentration, the principal effect on the basicity of the co-solvent molecules in water-rich media is the presence of electron-releasing or electron-attracting groups. With the exception of glycerol and other polyhydroxy compounds with multiple electron-attracting groups, all these co-solvents have basicities greater than that of water and this is responsible for the increase in H_0 in these solutions. $\Delta G_t^{\ominus}(H^+)$ values derived using the TATB method show no stabilisation of the proton in these water-rich mixtures containing methanol, ethanol or *t*-butyl alcohol, in contrast to $\Delta G_t^{\ominus}(H^+)$ derived using the solvent-sorting technique. This raises doubts about the capability of the TATB method of representing accurately the free energies of transfer of ions from water into such aqueous mixtures containing a co-solvent.

The rapid increase in H_0 and the relative stability of the proton in the mixture with respect to that in water, is parallelled by a rapid decrease in the conductivity: Figs. 6–10 suggest that this arises from a lower mobility in the water-rich medium of the proton in $H^+(H_2O)_{m-1}S$ compared with that in $H^+(H_2O)_m$. The slight rise in conductivity and the decrease in H_0 in co-solvent-rich solutions is difficult to interpret quantitatively due to ion association occurring between the proton and its counter anion in this medium: nevertheless, it does suggest that the different solvation pertaining in this medium compared with that in a water-rich medium causes a shift in the partition of the proton between water molecules and co-solvent molecules and an increase in the mobility of the proton.

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