Solvent Effect on the Dissociation of Protonated Tris(hydroxymethyl)-methylamine and *p*-Nitroanilinium Ion in Water–Ethylene Glycol Media at 25 °C

By **K. K. Kundu,*** **A. L. De,** and **M. N. Das,*** Department of Chemistry, Jadavpur University, Calcutta-32, India

The dissociation constants $({}_{s}K)_{BH^+}$ of two BH^+-type acids, protonated tris(hydroxymethyl)methylamine (tis,H$^+$) and *p*-nitroanilinium ion, have been determined at 25 °C in a series of aqueous mixtures of ethylene glycol from electrometric and spectrophotometric measurements respectively. The solvent effects on the dissociation behaviour of these acids, $\Delta G_t^{\circ}[BH^+{-}B]_{sys} = 2{\cdot}303RT[p({}_{s}K)^{N}{}_{BH^+} - p({}_{w}K)^{N}{}_{BH^+}]$, in these media result in the characteristic minima with the solvent composition. The solvent effects have been discussed in terms of the free energies of transfer (ΔG_t°) from water to the aqueous glycol solvents, of the uncharged bases (B) evaluated from the measured solubilities, of the hydrochlorides of the bases (B,HCl) computed from the corresponding values for HCl, and also of the individual ions assessed from the previous knowledge of $\Delta G_t^{\circ}(Cl^-)$. The corresponding data for tris,H$^+$ and and *m*-nitroanilinium ion in methanol–water solvents, obtained from the literature and from the present work, are also compared. The individual contributions of the different species concerned are discussed in terms of the interaction energies of the species with positive or negative charge centres of the isolated solvent dipoles. The overall behaviour of these protonated amines with different chemical nature and also with different solvophilism is found to be largely dictated by the specific solute–solvent interactions besides the effect of the relative solvent ' basicities '.

DESPITE extensive studies,[1-4] the solvent effect on the dissociation of weak acids and bases of different charge types in pure or mixed amphiprotic solvents is not yet well understood. This is particularly evident from the dissociation behaviour of many cationic acids of the type (BH^+) in some aqueous organic solvents [1-4] where the pK_{BH^+} values are found to pass through minima as the proportion of the organic component increases. This peculiar behaviour of the BH^+ type of acids is almost a common feature in aqueous mixtures of some common solvents such as methanol,[5-7] ethanol,[8-10] dioxan,[11] and acetic acid.[11]

In this paper we report our studies on the dissociation constants of two BH^+ type acids, protonated tris(hydroxymethyl)methylamine (tris,H$^+$) and *p*-nitroanilinium ion in a series of aqueous mixtures of ethylene glycol. As the ' electrostatic ' effect on the dissociation of these cationic acids should be small, it is expected [12] that the relative influence of specific solute–solvent interactions will be distinctly reflected in the dissociation constants. For ascertaining the probable contributions of the uncharged species (B) taking part in the corresponding acid–base reactions,[12] solubilities of the corresponding amines (B) in those solvents were also measured.

EXPERIMENTAL

Dissociation Constants of Tris(hydroxymethyl)methylamine.—Principle of the method. The dissociation constants $({}_{s}K)_{BH^+}$ of this acid were determined from e.m.f. measurements of the cell A, as in the case of pure water [13] or 50% methanol–water,[14] where m_1 and m_2 are the molalities of tris hydrochloride and tris respectively.

$$\text{Pt},H_2(\text{g, 1 atm})|\text{tris},H^+Cl^-(m_1),\ \text{tris}(m_2),\ \text{solvent}|\text{AgCl–Ag} \quad (A)$$

Procedure.—Methods of purification of ethylene glycol (Pure, Merck) and water, and the preparation of the solvents as well as the solutions of HCl required for the preparation of hydrochlorides of tris have been described.[15,16] Tris, commercially known as Tham (Fischer Scientific Co.), was kindly furnished by the U.S. National Bureau of Standards, and was used after being dried at 105 °C. The concentrations of the base solutions were determined by titrating weighed quantities of the solutions with a standard aqueous HCl solution with Methyl Red as indicator. Buffer solutions were prepared by mixing weighed quantities of the standard solutions of the base and HCl in the respective solvents. Buffer solutions of lower ionic strengths (μ) in each case were prepared by diluting weighed quantities of the buffer solutions with weighed quantities of the solvents. Measurements were made at 25 ± 0·1 °C. The e.m.f. values were recorded with a Rubicon potentiometer and a moving coil galvanometer (L and N). Readings were taken at intervals of 15 min until 2 or 3 successive readings were constant within ±0·1 mV. About 3—4 h were required for the attainment of equilibrium. The final readings were occasionally checked by inserting a second hydrogen electrode.

---

[1] R. P. Bell, ' The Proton in Chemistry,' Cornell University Press, Ithaca, New York, 1959.

[2] R. G. Bates, ' Determination of pH, Theory and Practice,' Wiley, New York, 1964.

[3] E. J. King, ' Acid–Base Equilibria,' Pergamon, London, 1965.

[4] R. G. Bates, ' Hydrogen-bonded Solvent System,' eds. A. K. Covington and P. Jones, Taylor and Francis, London, 1968, pp. 49—86.

[5] C. L. de Ligny, *Rec. Trav. chim.*, 1960, **79**, 731.

[6] E. E. Sager, R. A. Robinson, and R. G. Bates, *J. Res. Nat. Bur. Stand.*, 1964, **68**, *A*, 305.

[7] M. Paabo, R. G. Bates, and R. A. Robinson, *J. Phys. Chem.*, 1966, **70**, 247.

[8] B. Gutbezahl and E. Grunwald, *J. Amer. Chem. Soc.*, 1953, **75**, 559, 565.

[9] R. G. Bates and G. Schwarzenbach, *Helv. Chim. Acta*, 1955, **38**, 699.

[10] M. Merle, G. Douheret, and M. L. Dondon, *Bull. Soc. chim. France*, 1966, 159.

[11] A. K. Boni and H. A. Strobel, *J. Phys. Chem.*, 1966, **70**, 3771.

[12] P. Schindler, R. A. Robinson, and R. G. Bates, *J. Res. Nat. Bur. Stand.*, 1968, **72**, *A*, 141.

[13] R. G. Bates and H. B. Hatzer, *J. Phys. Chem.*, 1961, **65**, 667.

[14] M. Woodhead, M. Paabo, R. A. Robinson, and R. G. Bates, *J. Res. Nat. Bur. Stand.*, 1965, **69**, *A*, 263.

[15] K. K. Kundu and M. N. Das, *J. Chem. Eng. Data*, 1964, **9**, 87.

[16] S. K. Banerjee, K. K. Kundu, and M. N. Das, *J. Chem. Soc.* (*A*), 1967, 166.

Results. The e.m.f. values (E) of the cell A (corrected for 1 atm H_2 gas) in a series of aqueous glycol solvents comprising 10, 30, 50, 70, and 90% (w/w) ethylene glycol are in Table 1. The vapour pressures (p), densities (d_s), and dielectric constants (D_s) of the mixed solvents were taken from an earlier paper.[16]

The $p({}_sK)_{BH^+}$ value in each of the solvents at 25 °C was obtained from the extrapolation of the observed linear plot of the auxiliary function $p({}_sK)'_{BH^+}$, defined by equation (1), against μ to $\mu = 0$, where $({}_sE_m°)_{AgCl-Ag}$ is the standard

$$p({}_sK)'_{BH^+} = \frac{E - ({}_sE_m°)_{AgCl-Ag}}{2{\cdot}303RT/F} + \log m_{Cl^-} + \log \frac{m_{BH^+}}{m_B} - 2S_f\mu^{\frac{1}{2}} = p({}_sK)_{BH^+} - \beta\mu \qquad (1)$$

potential of the AgCl–Ag electrode on the molal scale in the solvent, m_{BH^+}, m_B, and m_{Cl^-} the molalities of tris,H$^+$, the base tris, and Cl$^-$ respectively, S_f the Debye–Hückel constant for the particular solvent and temperature, and β a constant. The $({}_sE_m°)_{AgCl-Ag}$ values in the different solvents at 25 °C were taken from a previous communication.[17] As in the case of water [13] as well as 50% water–methanol,[14] corrections due to the solubility of AgCl in tris solutions in those solvents were considered to be small. A simple calculation according to the usual relation [18] showed that the corrections for m_{S^-} due to the solvolytic reaction of the type $B + SH \rightleftharpoons BH^+ + S^-$ are negligible and so m_{BH^+} and m_B were taken to be equal to m_1 and m_2 respectively and $\mu = m_1d_s$, where d_s is the density of the solvent.[16,19] The average standard deviation of the $p({}_sK)_{BH^+}$ values, as computed from the deviations of the actual values of $p({}_sK)'_{BH^+}$ from the corresponding values on the linear plot of $p({}_sK)'_{BH^+}$ against μ for each of the solvents, amounts to about ±0·01 unit. The observed e.m.f. values against the corresponding buffer compositions in each solvent are presented in Table 1 and the $p({}_sK_{BH^+})$ values at the bottom of the respective columns containing the e.m.f. values.

Dissociation Constants of p-*Nitroanilinium Ion.—Principle of the method.* The dissociation constants $({}_sK)_{BH^+}$ of this indicator acid (BH$^+$) were determined by spectrophotometric measurements by use of a method similar to that of Bates and his co-workers.[7] The $p({}_sK)_{BH^+}$ value of this acid (BH$^+$) in any solvent can be represented by equation (2), where γ_i represents the

$$p({}_sK)'_{BH^+} = -\log m_{SH_2^+} - \log \frac{\alpha}{1 - \alpha} = p({}_sK)_{BH^+} + \log \frac{\gamma_{SH_2^+}\gamma_B}{\gamma_{BH^+}} = p({}_sK)_{BH^+} + f(\mu) \qquad (2)$$

molal activity coefficient of the respective species referred to the standard state in the respective solvent, and α and $(1 - \alpha)$ are the fractions of the indicator species present in the neutral (B) and ionized (BH$^+$) forms respectively. The ratio $\alpha/1 - \alpha$ is determinable from the measurements of spectral absorbances of the solution having the effective molal concentration of H$^+$ equal to $m_{SH_2^+}$ and of the solutions containing the completely acid and basic forms of the indicator. Since the activity coefficient factor $\log(\gamma_{SH_2^+}\gamma_B/\gamma_{BH^+})$ tends to zero at infinite dilution, the extrapolation of the plot of the auxiliary function $p({}_sK)'_{BH^+}$ of equation (2) against μ to $\mu = 0$ furnishes the $p({}_sK)_{BH^+}$ value in the particular solvent.

TABLE 1

Data for the determination of $p({}_sK)_{BH^+}$ for protonated tris in ethylene glycol–water solvent system at 25 °C. Percentages refer to the % (w/w) of ethylene glycol

$m_{Tris.HCl}$	m_{tris}	E/V
	10%	
0·1335	0·0730	0·7479
0·1070	0·0595	0·7532
0·0758	0·0415	0·7599
0·0631	0·0345	0·7639
0·0487	0·0266	0·7693
0·0378	0·0207	0·7746
0·0263	0·0144	0·7832
0·01015	0·00561	0·8038
	$p({}_sK)_{BH^+} = 8{\cdot}13$	
	30%	
0·1325	0·0828	0·7449
0·1113	0·0694	0·7484
0·1011	0·0633	0·7502
0·0855	0·0535	0·7539
0·0686	0·0429	0·7579
0·0529	0·0331	0·7638
0·0381	0·0238	0·7701
0·0190	0·0119	0·7848
	$p({}_sK)_{BH^+} = 8{\cdot}17$	
	50%	
0·1191	0·1105	0·7495
0·0983	0·0912	0·7533
0·0778	0·0723	0·7580
0·0621	0·0576	0·7626
0·0487	0·0452	0·7671
0·0351	0·0326	0·7743
0·0237	0·0220	0·7826
0·0118	0·0109	0·7975
	$p({}_sK)_{BH^+} = 8{\cdot}24$	
	70%	
0·1180	0·0831	0·7358
0·0989	0·0696	0·7401
0·0770	0·0542	0·7444
0·0563	0·0397	0·7504
0·0388	0·0273	0·7571
0·0333	0·0268	0·7592
0·0212	0·0150	0·7692
0·0106	0·00744	0·7836
	$p({}_sK)_{BH^+} = 8{\cdot}405$	
	90%	
0·1366	0·0858	0·7243
0·1145	0·0720	0·7283
0·0906	0·0570	0·7322
0·0709	0·0445	0·7358
0·0543	0·0342	0·7410
0·0380	0·0239	0·7469
0·0251	0·0158	0·7544
0·0105	0·00660	0·7709
	$p({}_sK)_{BH^+} = 9{\cdot}02$	

Procedure. p-Nitroaniline (AnalaR) was purified by two crystallizations from aqueous ethanol (95% v/v) and then dried *in vacuo*. A series of solutions were prepared by adding weighed amounts of standard HCl solutions and the solvent to weighed amounts of the indicator

---

[17] U. Sen, K. K. Kundu, and M. N. Das, *J. Phys. Chem.*, 1967, **71**, 3665.

[18] S. K. Banerjee, K. K. Kundu, and M. N. Das, *J. Chem. Soc.* (*A*), 1968, 139.

[19] K. K. Kundu, P. K. Chattopadhyay, Debabrata Jana, and M. N. Das, *J. Chem. Eng. Data*, 1970, **15**, 209.

(p-nitroaniline) solutions. The spectral absorbances were determined at 25 ± 0·1 °C with a Beckman model DU spectrophotometer with 1 cm cells at 380 nm where the absorbance shows a maximum for the base form.[20] The limiting absorbances of the acidic form at 380 nm, though small, were taken into account, and the absorbance readings were corrected, where necessary, for the identical total concentration of the indicator. The limiting absorbances of the acidic and basic forms of p-nitroaniline were measured in very concentrated HCl solutions (*ca.* 6M) and in very dilute sodium lyate solutions (*ca.* 0·001M) respectively. Very dilute solutions of sodium glycoxide formed by dissolving freshly cleaned pieces of sodium metal in ethylene glycol were used for obtaining the limiting absorbances of the basic form in 100% glycol.

Results. Since $\mathrm{p}({}_{\mathrm{s}}K)_{\mathrm{BH^+}}$ values for p-nitroanilinium ion ranged from 0·62 to 2·06, it was found possible to have a considerable variation in the ratios of the two forms of the indicator by simple variation of the concentration of HCl solution only. The values of the ratio $\alpha/(1-\alpha) = (D - D_1)/(D_2 - D)$ were obtained from the optical densities D_1, D_2, and D of the completely acid form (BH^+), completely base form (B), and the mixture of the two forms, measured at an identical concentration of the indicator in the same cell. The values of $-\log[\alpha/(1-\alpha)]$, molalities of HCl, the values of $-\log m_{\mathrm{SH_2^+}}$ ($m_{\mathrm{SH_2^+}}$ being the effective molality of H^+ in the solution), and $\mathrm{p}({}_{\mathrm{s}}K)'_{\mathrm{BH^+}}$ are in Table 2. The molality of the p-nitroanilinium ion at equilibrium was negligibly small with respect to the molality of HCl, so that $-\log m_{\mathrm{SH_2^+}}$ was virtually the same as that of $-\log m_{\mathrm{HCl}}$ in most cases. The values of μ were taken to be equal to $m_{\mathrm{HCl}}d_{\mathrm{s}}$. The $\mathrm{p}({}_{\mathrm{s}}K)_{\mathrm{BH^+}}$ values obtained in different solvents are recorded at the bottom of the respective columns of $\mathrm{p}_{\mathrm{s}}(K)'_{\mathrm{BH^+}}$ in Table 2. The $\mathrm{p}({}_{\mathrm{s}}K)_{\mathrm{BH^+}}$ value obtained in water at 25 °C, namely 1·00, is in fairly good agreement with the literature value.[2]

Standard Free Energy of Transfer of Uncharged Bases (Tris and p*-Nitroaniline) from Water to Glycol–Water Solvents at* 25 °C.—*Principle of the method.* The standard free-energy changes, $\Delta G_{\mathrm{t}}^{\circ}(\mathrm{B})$, accompanying the transfer of both the uncharged bases B from water to aqueous glycol solvents were obtained by the method of Bates *et al.*[12] by using the relation (3) where the subscripts s and w refer

$$\Delta G_{\mathrm{t}}^{\circ}(\mathrm{B}) = {}_{\mathrm{s}}\bar{G}^{\circ}(\mathrm{B}) - {}_{\mathrm{w}}\bar{G}^{\circ}(\mathrm{B}) = RT \ln \frac{{}_{\mathrm{w}}N_{\mathrm{B}}}{{}_{\mathrm{s}}N_{\mathrm{B}}} \qquad (3)$$

to the solvent (SH) and water respectively, $\bar{G}^{\circ}(\mathrm{B})$ the standard partial molar free energy of the base B, and N_{B} the mole fraction of the base B in the saturated solutions in the respective solvents. The validity of equation (3) depends on the ratio of the activity coefficients of the solutes being unity in the saturated solutions. Bates and his co-workers [12] point out that for tris the activity coefficient ratio in water and methanol–water is close to unity, and it may not be unreasonable to assume a similar situation in the glycol–water media. Regarding p-nitroaniline, however, no such evidence is available, and we have tacitly assumed that for this base also the activity coefficient ratio is unity.

Determination of Solubilities.—Tris. The solubilities of tris were determined by a method similar to that of Bates

TABLE 2

Data for spectrophotometric determination of $\mathrm{p}({}_{\mathrm{s}}K)_{\mathrm{BH^+}}$ for p-nitroanilinium ion in ethylene glycol–water solvent system at 25 °C. Percentages are % (w/w) of ethylene glycol

m_{HCl} 1	$-\log m_{\mathrm{SH_2^+}}$ 2	$-\log \frac{\alpha}{1-\alpha}$ 3	$\mathrm{p}({}_{\mathrm{s}}K)'_{\mathrm{BH^+}}$ 4
0%, Indicator concn. = $1{\cdot}14 \times 10^{-4}$M			
0·1475	0·831	0·182	1·013
0·1202	0·920	0·092	1·012
0·09634	1·016	−0·006	1·010
0·07256	1·140	−0·134	1·006
0·04896	1·310	−0·305	1·005
0·02363	1·626	−0·624	1·002
			$\mathrm{p}({}_{\mathrm{w}}K_{\mathrm{BH^+}}) = 1{\cdot}00$
10%, Indicator concn. = $8{\cdot}99 \times 10^{-5}$M			
0·1413	0·850	0·137	0·987
0·1121	0·951	0·035	0·986
0·08383	1·077	−0·097	0·980
0·05709	1·243	−0·272	0·971
0·02955	1·530	−0·561	0·969
0·01402	1·853	−0·894	0·959
			$\mathrm{p}({}_{\mathrm{s}}K)_{\mathrm{BH^+}} = 0{\cdot}96$
30%, Indicator concn. = $7{\cdot}74 \times 10^{-5}$M			
0·1309	0·883	−0·002	0·881
0·1059	0·975	−0·108	0·867
0·08629	1·064	−0·194	0·870
0·06460	1·189	−0·324	0·865
0·04390	1·357	−0·506	0·851
0·02072	1·683	−0·838	0·845
0·01056	1·976	−1·136	0·840
			$\mathrm{p}({}_{\mathrm{s}}K)_{\mathrm{BH^+}} = 0{\cdot}84$
50%, Indicator concn. = $6{\cdot}77 \times 10^{-5}$M			
0·1271	0·896	−0·164	0·732
0·08536	1·069	−0·344	0·725
0·06357	1·196	−0·482	0·714
0·04221	1·374	−0·662	0·712
0·02060	1·686	−0·989	0·697
			$\mathrm{p}({}_{\mathrm{s}}K)_{\mathrm{BH^+}} = 0{\cdot}695$
70%, Indicator concn. = $4{\cdot}35 \times 10^{-5}$M			
0·1310	0·883	−0·236	0·647
0·1030	0·987	−0·347	0·640
0·08522	1·069	−0·432	0·637
0·06680	1·175	−0·540	0·635
0·04308	1·366	−0·739	0·627
0·01987	1·702	−1·078	0·624
			$\mathrm{p}({}_{\mathrm{s}}K)_{\mathrm{BH^+}} = 0{\cdot}62$
90%, Indicator concn. = $5{\cdot}23 \times 10^{-5}$M			
0·1323	0·878	0·071	0·949
0·1061	0·974	−0·043	0·931
0·08084	1·092	−0·171	0·921
0·05378	1·269	−0·345	0·924
0·04035	1·394	−0·483	0·911
0·02705	1·568	−0·665	0·903
0·01373	1·862	−0·956	0·906
			$\mathrm{p}({}_{\mathrm{s}}K)_{\mathrm{BH^+}} = 0{\cdot}90$
100%, Indicator concn. = $8{\cdot}55 \times 10^{-5}$M			
0·09118	1·040	1·164	2·204
0·07157	1·145	1·014	2·159
0·05526	1·257	0·887	2·144
0·03705	1·431	0·694	2·125
0·01860	1·730	0·361	2·091
0·00910	2·013	0·061	2·074
			$\mathrm{p}({}_{\mathrm{s}}K)_{\mathrm{BH^+}} = 2{\cdot}06$

---

[20] D. Rosenthal, H. B. Hatzer, and R. G. Bates, *J. Amer. Chem. Soc.*, 1964, **86**, 549.

et al.[12] Sufficient solid base (B) was added to 30—40 ml solvent in 100 ml well stoppered bottles, which were shaken in a mechanical shaker at a low speed for 12 h at room temperature (25—27 °C). The bottles were then thermostatted at 25 ± 0·1 °C for *ca.* 5 h. At least three weighed aliquot portions of the saturated solution from each bottle were analysed by titration with a standard aqueous HCl solution, with Methyl Orange as indicator. The operations were repeated until successive results were in agreement. Table 3 reports the solubility in each solvent in mol kg^{-1} as well as in mole fraction. The value for water is found to be 5·89 mol kg^{-1} compared with 5·78 mol kg^{-1} obtained by Bates *et al.*[12] The values of $\Delta G_t°(B)$ computed from equation (3) are also presented in Table 3.

TABLE 3

Solubilities and $\Delta G_t°(B)$ of tris and *p*-nitroaniline in ethylene glycol–water solvents at 25 °C

Wt. % ethylene glycol	tris (B)			*p*-Nitroaniline (B)		
	m_B [a]	$10^2 N_B$ [b]	$\Delta G_t°$ (B) cal mol^{-1}	$10^3 m_B$	$10^5 N_B$	$\Delta G_t°$ (B) cal mol^{-1}
0	5·892	9·594		4·267	7·686	
10	5·093	8·982	39	5·652	10·96	−211
30	3·869	8·128	98	9·709	22·21	−628
50	2·881	7·442	150	21·01	58·60	−1203
70	1·994	6·659	216	50·79	181·3	−1873
90	1·157	5·449	335	182·3	900·7	−2822
100	0·8768	5·156	368	342·9	2084	−3318

[a] m_B = Solubility in mol per kg of solvent. [b] N_B = Mole fraction of the base in the saturated solution.

p-*Nitroaniline*. The bottles containing the solvent and the base were shaken for *ca.* 10 h in a mechanical shaker at a moderate speed, and then thermostatted at 25 ± 0·1 °C for nearly 15 days with occasional shaking. The concentrations of the solutions were determined by measuring the optical densities at 380 nm, after proper dilution with water. The whole operation was repeated until successive results were concordant. The solubilities of *p*-nitroaniline in mol kg^{-1} as well as in mole fraction and the $\Delta G_t°$ (B) values are recorded in Table 3. The solubility of *p*-nitroaniline in water is found to be 0·5888 g kg^{-1} which agrees fairly well with the literature values, 0·58 g l^{-1},[21] 0·5735 g l^{-1},[22] and 0·568 g kg^{-1}.[23]

DISCUSSION

The understanding of the solvent effect on $({}_sK_{BH^+})$ becomes relatively easier when one considers the free-energy change accompanying the transfer process (4).

$$H_3O^+(w) + SH(s) + BH^+(s) + B(w) = H_2O(w) + SH_2^+(s) + BH^+(w) + B(s) \quad (4)$$

where (s) and (w) indicate that the substances are in their standard states in the solvent SH and water respectively. The free-energy change accompanying the transfer process (4) for the acid–base system, $[BH^+–B]_{sys}$, is given by equation (5), where $\Delta G_t°(H^+)$

$$\Delta G_t°[BH^+–B]_{sys} = 2·303RT\,[p({}_sK)_{BH^+} - p({}_wK)_{BH^+}] = \Delta G_t°(H^+) + \Delta G_t°(B) - \Delta G_t°(BH^+) \quad (5)$$

stands for the free-energy change accompanying the process (6), *i.e.*, the transfer of H$^+$ from the standard state in water to that in the solvent (SH). $\Delta G_t°(H^+)$

$$H_3O^+(w) + SH(s) \longrightarrow SH_2^+(s) + H_2O(w) \quad (6)$$

May be taken to be a measure of the ' basicity ' of the solvent (SH) with respect to that of water, the basicity of the solvent and that of water being measured by the free-energy changes accompanying the processes (7) and (8) in the solvent (SH) and water respectively,

$$H^+(g) + SH(s) = SH_2^+(s) \quad (7)$$

$$H^+(g) + H_2O(w) = H_3O^+(w) \quad (8)$$

where (g) denotes that H$^+$ is in the standard state in the gaseous phase.

As the solvent effect should preferably[24] be expressed in the mole fraction scale, the values of $\Delta G_t°[BH^+–B]_{sys}$ computed by using the respective values of $p({}_sK)^N_{BH^+}$ in the mole fraction scale, obtained from the corresponding values of $p({}_sK)_{BH^+}$ in the molal scale by the usual relation[25] (Table 4). Figure 1 shows the variations of $\Delta G_t°[(BH^+–B)]_{sys}$ for both the acids with weight per cent. of ethylene glycol. For comparison, the corresponding variations for the acids tris,H$^+$ and *m*-nitroanilinium ion and in aqueous methanolic solvents[7,12] (Table 5) are also shown in Figure 1.

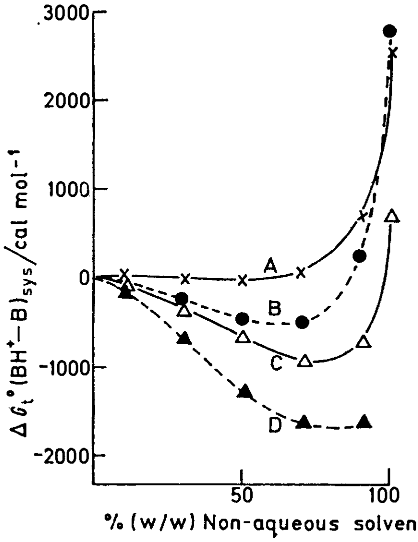

FIGURE 1 Variation of $\Delta G_t°(BH^+–B)_{sys}$ for acid–base systems as a function of concentration of non-aqueous solvent at 25 °C; A, protonated tris in aqueous glycol; B, protonated tris in aqueous methanol; C, *p*-nitroanilinium ion in aqueous glycol; D, *m*-nitroanilinium ion in aqueous methanol

Figure 1 shows that the solvent effects on the dissociation equilibria of the two BH$^+$ type acids are more or less similar in aqueous methanolic and aqueous glycolic solvents. Thus, $\Delta G_t°(BH^+–B)_{sys}$ values for

---

[21] M. A. Paul, *J. Amer. Chem. Soc.*, 1954, **76**, 3236.

[22] A. Seidell, ' Solubilities of Organic Compounds, 3rd edn., Van Nostrand, New York, 1941.

[23] A. R. Collett and J. Johnston, *J. Phys. Chem.*, 1926, **30**, 70.

[24] R. A. Robinson and R. H. Stokes, ' Electrolyte Solutions,' 2nd edn., Butterworths, London, 1965, pp. 353—354.

[25] H. S. Harned and B. B. Owen, ' The Physical Chemistry of Electrolyte Solutions,' 3rd edn., Reinhold, New York, 1958.

both the solvent systems pass through minima with the gradual addition of the non-aqueous component, the minima being more marked for *p*-nitroanilinium ion than for tris,H$^+$. The appearance of such minima for BH$^+$-type acids in aqueous organic solvents has generally been attributed to an enhanced ' basicity ' of the media resulting from a breakdown of the water structure.[4,11,17,26] The contribution of the uncharged species $\Delta G_t°(B)$ has, however, often been ignored, but the importance of this quantity for the aqueous methanolic and aqueous glycolic systems may be seen from Tables 3 and 5 and Figures 2 and 3. The $\Delta G_t°(B)$ values of tris for the aqueous methanolic system were obtained from the literature,[12] and those for *m*-nitroaniline were evaluated from solubility measurements by the same method as for *p*-nitroaniline described above.

TABLE 4

Values of $p({}_sK)^N{}_{BH^+}$ and $\Delta G_t°[BH^+–B]_{sys}$ for protonated tris and *p*-nitroanilinium ion in ethylene glycol–water solvents at 25 °C

Wt. % ethylene glycol	Protonated tris $p({}_sK)^N{}_{BH^+}$	Protonated tris $\Delta G_t°[BH^+–B]_{sys}$ cal mol^{-1}	*p*-Nitroanilinium ion $p({}_sK)^N{}_{BH^+}$	*p*-Nitroanilinium ion $\Delta G_t°[BH^+–B]_{sys}$ cal mol^{-1}
0	9·816 [a]	0	2·744	0
10	9·842	35	2·672	−98
30	9·811	−7	2·481	−359
50	9·794	−30	2·249	−675
70	9·951	48	2·066	−925
90	10·322	690	2·202	−739
100	11·682 [b]	2545	3·267	713

[a] Taken from R. G. Bates and H. B. Hetzer, *J. Phys. Chem.*, 1961, **65**, 667. [b] Taken from K. K. Kundu, P. K. Chattopadhyay, and M. N. Das, *J. Chem. Soc.* (*A*), 1970, 2034.

TABLE 5

Solubilities, $\Delta G_t°(B)$, and $\Delta G_t°$ $[BH^+–B]_{sys}$ of tris and *m*-nitroaniline in methanol–water solvents at 25 °C

Wt. % methanol	tris (B) 10^4N_B [a]	tris (B) $\Delta G_t°(B)$ cal mol^{-1}	tris (B) $\Delta G_t°[BH^+–B]_{sys}$ [b] cal mol^{-1}	*m*-Nitroaniline 10^3N_B	*m*-Nitroaniline $\Delta G_t°(B)$ cal mol^{-1}	*m*-Nitroaniline $\Delta G_t°[BH^+–B]_{sys}$ [d] cal mol^{-1}
0	94·30	0	0	1·231	0	0
10	87·56	44		1·945	−285	−149
30	73·41	148	−269	6·961	−1026	−670
50	57·02	298	−483	22·59	−1724	−1277
70	36·06	569	−513	68·10	−2377	−1622
90	15·70	1062	263	187·7	−2978	−1632
100	9·265	1334	2780 [c]	343·4	−3335	

[a] N_B = Mole fraction of the base as present in the saturated solutions; solubility data collected from P. Schindler, R. A. Robinson, and R. G. Bates, *J. Res. Nat. Bur. Stand.*, 1968, **72**, *A*, 141. [b] The required $p({}_sK)_{BH^+}$ values were obtained from the above mentioned paper. [c] The required $p(sK)_{BH^+}$ value in methanol has been taken from K. K. Kundu, A. L. De, and M. N. Das, *J.C.S. Dalton*, 1972, 386. [d] The required $p({}_sK)_{BH^+}$ values were taken from E. E. Sager, R. A. Robinson, and R. G. Bates, *J. Res. Nat. Bur. Stand.*, 1964, **68**, *A*, 303.

The relative affinities of water or the non-aqueous component towards the base (B) or its conjugate acid (BH$^+$) may be expected to arise from the relative solvating capacities of solvent dipoles exerted largely through hydrogen bond formation. The strength of hydrogen bonding should be largely guided by the relative charge densities on the oxygen and hydrogen charge centres of the isolated dipoles. Owing to the inductive effect of the methyl group in methanol, the negative charge density on the oxygen atom (${}^m\Delta_-$) is presumably somewhat greater than the corresponding quantity in water (${}^w\Delta_-$), so that the protonic character of the hydrogen atom of the hydroxy-group in methanol (${}^m\delta_+$) is weaker than that in water (${}^w\delta_+$).[27-29] Similarly, as shown earlier [27] in the case of aqueous glycolic solvent system ${}^g\Delta_- > {}^w\Delta_-$ and ${}^g\delta_+ < {}^w\delta_+$, where the superscript g refers to the glycol.

The curves for $\Delta G_t°(B)$ for the base tris in both the solvent systems (Figures 2 and 3) indicate that the base molecules are in a lower free-energy state in pure water, the effect being rather more pronounced in methanol–water than in glycol–water. This possibly arises, at least in part, from the participation of the three terminal hydroxy-groups (in the tris molecule) in the hydrogen-bonded structure of water,[12] which naturally becomes less important with the decrease in the proportion of water in the mixed medium. So far as the interaction of the NH$_2$ group in tris with the solvent molecule is concerned, the nitrogen atom with a lone pair of electrons will form a hydrogen bond with a hydrogen atom, having a stronger protonic character supplied by the solvent dipoles, and since ${}^w\delta_+ > {}^m\delta_+$ or ${}^g\delta_+$, it is expected that the transfer of tris from water to the methanolic or the glycolic solvent system will be accompanied by positive values of $\Delta G_t(B)$, as experimentally observed.

In contrast with the behaviour of tris, $\Delta G_t°(B)$ values for the nitroanilines in the respective solvent systems are found to be negative, the magnitudes increasing with increasing proportion of the non-aqueous component in the solvent mixtures. The benzene ring being hydrophobic, nitroanilines should have a greater affinity towards the organic solvents, resulting in increasingly negative contributions to $\Delta G_t°(B)$ values. The solvation will also occur through hydrogen bond formation in which the NH$_2$ as well as the NO$_2$ group

---

[26] E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1948, 1976.

[27] K. K. Kundu, A. K. Rakshit, and M. N. Das, *Electrochim. Acta*, in the press.

[28] D. Feakins and P. Watson, *J. Chem. Soc.*, 1963, 4734.

[29] D. Feakins, in ' Physico-Chemical Processes and Mixed Aqueous Solvents,' ed. F. Franks, Heinemann, London, 1967, pp. 71—91.

will be involved, and these factors should make their independent contributions to the overall values of $\Delta G_t^\circ(\mathrm{B})$. But the hydrophobism of the base is presumably the largest single factor causing an increased affinity of the base towards the organic component-rich solvent.

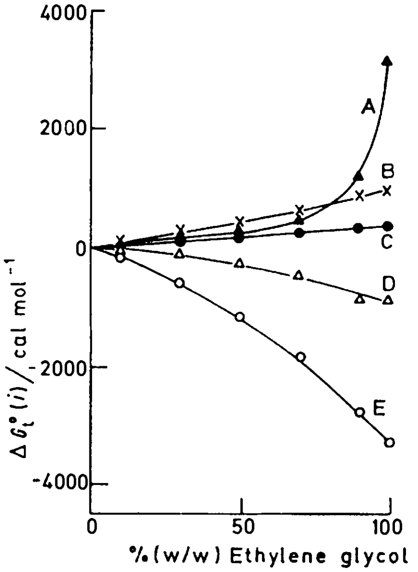

FIGURE 2 Variation of standard free energy of transfer $\Delta G_t^\circ(i)$ of some species from water to aqueous ethylene glycol at 25 °C; A, HCl; B, tris hydrochloride; C, tris; D, *p*-nitroanilinium chloride; E, *p*-nitroaniline

We now examine the values of $\Delta G_t^\circ(\mathrm{BH^+})$ of equation (5). For this purpose we have computed by equation (9) the values of $\Delta G_t^\circ(\mathrm{B,HCl})$, *i.e.*, the standard free energies of transfer of the hydrochlorides of the respective bases from water to each solvent. The

$$\Delta G_t^\circ(\mathrm{B,HCl}) = \Delta G_t^\circ(\mathrm{HCl}) + \Delta G_t^\circ(\mathrm{B}) - \Delta G_t^\circ(\mathrm{BH^+\text{-}B})_{\mathrm{sys}} \quad (9)$$

values of $\Delta G_t^\circ(\mathrm{B,HCl})$ and of $\Delta G_t^\circ(\mathrm{HCl})$ obtained from the literature [27] for both the solvent systems are presented in Table 6. The $\Delta G_t^\circ(\mathrm{HCl})$ values for the methanol–water system were obtained by interpolation. The variations in the values of $\Delta G_t^\circ(\mathrm{B,HCl})$ with the solvent composition are shown in Figures 2 and 3.

From $\Delta G_t^\circ(\mathrm{B,HCl})$, we have evaluated the values of $\Delta G_t^\circ(\mathrm{BH^+})$ for both the $\mathrm{BH^+}$ ions in the two solvent systems by utilizing the values of $\Delta G_t^\circ(\overline{\mathrm{Cl}})$, the standard free energies of transfer of the chloride ion from water to the aqueous glycolic or aqueous methanolic solvents, obtained earlier.[27] These values for the $\mathrm{BH^+}$ ions are shown in Table 7, together with the corresponding values for the $\mathrm{H^+}$ ion, $\Delta G_t^\circ(\mathrm{H^+})$.[27] Despite the uncertainties in the free-energy values for the individual ions, it is noteworthy that, like the $\Delta G_t^\circ(\mathrm{M^+})$ values for all other cations,[27] $\Delta G_t^\circ(\mathrm{BH^+})$ values are also found to be increasingly negative, the corresponding values for tris,$\mathrm{H^+}$ being more negative than for the nitroanilinium ions in both the solvent systems. The 'electrostatic' contribution to $\Delta G_t^\circ(\mathrm{BH^+})$ should obviously be positive because water has a higher dielectric than any of the mixed solvents, but the overall negative values of $\Delta G_t^\circ(\mathrm{BH^+})$ indicate that the 'primary solvation' of the $\mathrm{BH^+}$ ions arising from specific ion–dipole interactions outweigh the electrostatic or the 'secondary solvation' effect.[27-29]

Tris,$\mathrm{H^+}$ and the nitroanilinium ions are likely to be solvated in these hydroxy-solvents through the three partially protonated hydrogen atoms attached to the nitrogen atom and the negatively charged oxygen-centre of the solvent dipoles.[30] Since ${}^{m}\Delta_{-}$ or ${}^{g}\Delta_{-} > {}^{w}\Delta_{-}$, the $\Delta G_t^\circ(\mathrm{BH^+})$ values should be increasingly negative, as has been observed with both the solvent systems. In the case of nitroanilinium ions, the overall charge being positive, solvation through the interaction of the negative charge centres of the nitro-group with a positively charged hydrogen atom of the solvent dipoles should be hindered. But in the case of tris,$\mathrm{H^+}$, since the ion has three terminal hydroxy-groups and the overall species is positively charged, the solvation of this species through these terminal hydroxy-groups will also occur, imparting an increasingly negative contribution to $\Delta G_t^\circ(\mathrm{BH^+})$. Apparently, the number of solvation centres of tris,$\mathrm{H^+}$ is six and that for nitroanilinium ion is three, but even then the $\Delta G_t^\circ(\mathrm{BH^+})$ values for tris,$\mathrm{H^+}$ are found to be less negative than those for the nitroanilinium ions. This presumably suggests that the hydrophobism of the benzene ring as well as its solvophilism towards either

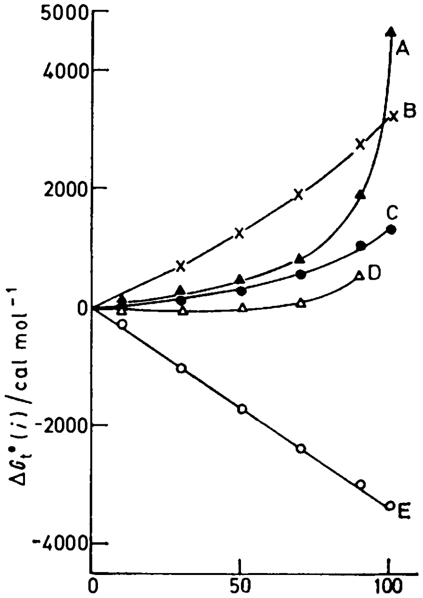

FIGURE 3 Variation of standard free energy of transfer $\Delta G_t^\circ(i)$ of some species from water to aqueous methanol; A, HCl; B, tris hydrochloride; C, tris; D, *m*-nitroanilinium chloride; E, *m*-nitroaniline

---

[30] W. Gordy, *J. Chem. Phys.*, 1939, **7**, 93.

of the organic components in the mixed media exerts a stronger influence on the $\Delta G^{\circ}_{t}(BH^+)$ values for nitroanilinium, leading to the larger negative values.

Equation (5) indicates that in addition to $\Delta G_t^{\circ}(B)$ and $\Delta G_t^{\circ}(BH^+)$, the other quantity involved in the value of $\Delta G_t^{\circ}[BH^+-B]_{sys}$ is $\Delta G_t^{\circ}(H^+)$ which may be taken to be a measure of the ' basicity ' of the solvent relative to that of water, as suggested by equations (6)—(8). Table 7 shows that the $\Delta G_t^{\circ}(H^+)$ values for both the solvent systems become increasingly negative up to *ca.* 80% (w/w) of the respective organic solvents, beyond which the values assume less negative magnitudes resulting in distinct minima. The ' electrostatic ' contribution to $\Delta G_t^{\circ}(H^+)$ arising from the difference in the dielectric constants of water and any mixed medium should be positive, increasing in magnitude as the proportion of water in the solvent mixture decreases. The stronger protophilism of either of the organic solvents, however, outweighs the ' electrostatic ' effect, so that at any composition the overall $\Delta G_t^{\circ}(H^+)$ values remain negative. In view of our concept that ${}^{m}\Delta_{-} > {}^{w}\Delta_{-}$ or ${}^{g}\Delta_{-} > {}^{w}\Delta_{-}$, the protophilism of the mixed media should regularly increase with the increasing proportion of methanol or glycol in the solvent mixture. The situation may, however, be complicated, if any substantial change occurs in the liquid structure on the addition of the organic solvent to water or *vice versa.* In that case, the release of free solvent dipoles as a result of a partial breakdown of the liquid structure or the freezing of solvent dipoles as a consequence of the formation of a more rigid structure may affect the overall ' basicity ' of the solvent mixture.[4,31-34] This structural factor combined with the ' electrostatic ' effect may be partly responsible for the fact that a monotonic increase in the negative values of $\Delta G_t^{\circ}(H^+)$ does not occur with increasing amounts of methanol or glycol in the medium. The problem, however, is involved.[35] Nevertheless, it appears that the overall behaviour of these protonated amines with different chemical nature as well as with different solvophilism is largely dictated by solute–solvent interactions in addition to the effect of the relative solvent basicities.

TABLE 6

Standard free energy of transfer $\Delta G_t^{\circ}(i)$ (mole fraction scale) from water to aqueous organic solvents for HCl and B,HCl (tris and nitroanilines) at 25 °C

	Water to aqueous glycol			Water to aqueous methanol		
Wt. % organic	$\Delta G_t^{\circ}(HCl)$ [a] / kcal mol^{-1}	$\Delta G_t^{\circ}(B,HCl)$ / kcal mol^{-1} B = tris	$\Delta G_t^{\circ}(B,HCl)$ / kcal mol^{-1} B = *p*-nitroaniline	$\Delta G_t^{\circ}(HCl)$ [b] / kcal mol^{-1}	$\Delta G_t^{\circ}(B,HCl)$ / kcal mol^{1} B = tris	$\Delta G_t^{\circ}(B,HCl)$ / kcal mol^{-1} B = *m*-nitroaniline
10	0·08	0·08	−0·03	0·10		−0·03
30	0·17	0·27	−0·10	0·27	0·68	−0·08
50	0·25	0·43	−0·29	0·44	1·22	−0·01
70	0·42	0·59	−0·53	0·81	1·89	0·06
90	1·20	0·84	−0·88	1·92	2·75	0·57
100	3·12	0·94	−0·91	4·67 [c]	3·23	

[a] Ref. 27. [b] Taken from ref. 27 with interpolation when required. [c] Computed from the $({}_{s}E^{\circ}{}_{AgCl-Ag}$ values in water and methanol taken from R. A. Robinson and R. H. Stokes, ' Electrolyte Solutions,' Revised edn., Butterworths, London, 1965.

TABLE 7

Standard free energy of transfer $\Delta G_t^{\circ}(i)$ [a] of some individual ions from water to aqueous organic solvents at 25 °C

	Water to aqueous glycol			Water to aqueous methanol		
Wt. % organic solvents	$\Delta G_t^{\circ}(H^+)$ [b] / kcal g-ion^{-1}	$\Delta G_t^{\circ}(BH^+)$ / kcal g-ion^{-1} B = tris	$\Delta G_t^{\circ}(BH^+)$ / kcal g-ion^{-1} B = *p*-nitroaniline	$\Delta G_t^{\circ}(H^+)$ [c] / kcal g-ion^{-1}	$\Delta G_t^{\circ}(BH^+)$ / kcal g-ion^{-1} B = tris	$\Delta G_t^{\circ}(BH^+)$ / kcal g-ion^{-1} B = *m*-nitroaniline
10						
30	−1·73	−1·63	−2·00	−2·20	−1·87	−2·63
50	−2·49	−2·31	−3·03	−4·35	−3·57	−4·80
70	−4·22	−4·05	−5·17	−5·05	−4·11	−5·84
90	−5·30	−5·66	−7·38	−4·98	−4·15	−6·33
100	−4·37	−6·55	−8·40			

[a] Probable uncertainties are of the order ±0·20 kcal g-ion^{-1}. [b] Taken from ref. 27. [c] Taken from ref. 27, with interpolation where necessary.

The work was financed by the National Bureau of Standards, Washington, D.C., U.S.A.

[2/409 *Received, 22nd February,* 1972]

---

[31] O. Popovych, *Critical Rev. in Analyt. Chem.*, 1970, **1**, 73.

[32] E. M. Arnett and D. R. McKelvey, *J. Amer. Chem. Soc.*, 1965, **87**, 1393.

[33] A. Ben-Naim, *J. Phys. Chem.*, 1965, **69**, 1922.

[34] F. Franks and D. J. G. Ives, *Quart. Rev.*, 1966, **20**, 1.

[35] F. Franks, in ref. 29, pp. 50—70.