Proton-transfer Equilibria in Isodielectric Acetonitrile–Ethylene Glycol Mixtures at 298.15 K

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The dissociation constants (K_a) of tris(hydroxymethyl)methylammonium (TrisH$^+$) and *p*-nitroanilinium (pNAH$^+$) ions and *p*-nitrophenol (pNP) have been determined at 298.15 K both in ethylene glycol (EG) and its isodielectric mixtures with acetonitrile (ACN), an e.m.f. method being used for TrisH$^+$ and a spectrophotometric method for the other two acids. These K_a values have been used to derive the solvent effect on the free energies of dissociation of these acids. From independent solubility measurements on the neutral species: tris(hydroxymethyl)methylamine (Tris), *p*-nitroaniline (pNA), and pNP, the free energies of transfer of these species from EG to ACN–EG mixtures have been determined at 298.15 K. By a combination of the results of K_a and solubility measurements and with a knowledge of the free energies of transfer of the hydrogen ion evaluated earlier, the free energies of transfer of TrisH$^+$, pNAH$^+$, and pNP$^-$ (*p*-nitrophenoxide ion) in these solvents have been computed. Plots of free energies of transfer for the individual species against solvent composition reflect a wide range of solvation behaviour which has been interpreted in terms of the tendency of protic solvents like EG to solvate specifically hydrogen-bonding solutes and the tendency of dipolar aprotic solvents like ACN to solvate specifically solutes undergoing primarily dispersion interactions.

DESPITE extensive studies,[1-8] the nature of the solvent effect on the dissociation of weak acids and bases of various charge types is still incompletely understood. For example, the observed minima in the dissociation constants of BH$^+$ type acids in several mixed aqueous solvents[7a, 8-12] has often incorrectly been attributed[5,13] to the increased basicity of the mixed solvent resulting from a co-solvent-induced breakdown of water structure. It has become increasingly clear now,[7,14] however, that the apparently intriguing behaviour of dissociation constants results from the superimposition of the medium effects of the three species participating in the dissociation equilibrium and that to understand the behaviour of the composite quantity entails an understanding of the behaviour of the individual species.

The dissociation of a protogenic species HA$^{(z+1)+}$ in a protic solvent SH involves the transfer of a proton to the solvent which acts as Brönsted base [equation (1)]:

$$\mathrm{HA}^{(z+1)+} + \mathrm{SH} \rightleftharpoons \mathrm{SH}_2^{+} + A^{z+} \qquad (1)$$

where the charge z may be positive, negative, or zero. The thermodynamic dissociation constant K_a is given by equation (2) where a_i denotes the activity of the species i and for simplicity the charges have not been shown.

$$K_a = a_{\mathrm{SH}_2} \cdot a_{\mathrm{A}}/a_{\mathrm{HA}} \qquad (2)$$

The common problem encountered in the interpretation of such acid–base equilibria in mixed solvents is the uncertainty of the ' electrostatic part ' of the medium effect on the dissociation process, arising from the difference in dielectric constants of the solvents, particularly in the dissociation of uncharged acids where charge separation occurs. For this reason, studies of acid–base equilibria in isodielectric solvents should be specially informative, since here only the ' chemical ' nature of solvation of the reacting species is reflected in the observed medium effect.

In previous papers,[15] we have studied the solvent effects on the free energies of solvation of a number of electrolytes and ions in ethylene glycol (EG) and in its isodioelectric mixtures with acetonitrile (ACN), and have derived useful information regarding ion-solvation in these media. On the basis of these studies we are now able to examine the effect of this unique series of solvents on thermodynamic processes such as proton-transfer equilibria in terms of the related solute–solvent interactions. Here, we report the measurement of the dissociation constants of three weak acids, representing two charge types, in EG and its isodielectric mixtures with ACN. These, taken with associated solubility measurements on the neutral species in these solvents and the free energies of transfer of H$^+$ evaluated earlier,[15d] provided the free energies of transfer of the other species participating in the dissociation equilibria. An insight regarding the transfer behaviour of the individual species concerned in the solvents should facilitate an understanding of the overall medium effect on the proton-transfer equilibria.

Of the three acids chosen, two are of the cationic type, *viz.*, the protonated forms of tris(hydroxymethyl)-methylamine (Tris) and *p*-nitroaniline (pNA), while the third, *p*-nitrophenol (pNP), is neutral. An important distinction between pNA (or pNAH$^+$) and Tris (or TrisH$^+$) is that while the first may undergo strong dispersion interactions with the solvent, the second should be solvated primarily through hydrogen-bonding. In the present solvent system, where one solvent component (EG) is protic whereas the other (ACN) is dipolar aprotic, specific solvation of these solutes by one component or the other should give rise to some interesting trends in their respective medium effects.

The dissociation constants were determined from e.m.f. measurements for TrisH$^+$, and from spectrophotometric measurements for pNAH$^+$ and pNP, while solubility measurements were carried out on the neutral compounds Tris, pNA, and pNP. The mixed solvents contained 20, 40, and 60 percent by weight of ACN, and all measurements were performed at 298.15 ± 0.05 K.

EXPERIMENTAL

The purification of the solvents EG and ACN has been described earlier.[15a] Tris (Fischer primary standard grade was used after recrystallization from 75% methanol. Tris-hydrochloride (Tris-HCl) was prepared by the slow addition of conc. HCl (AnalaR, B.D.H.) to a saturated aqueous solution of Tris; the precipitate was filtered off and recrystallized three times from water. pNA (Riedel) was twice recrystallized from 90% ethanol. pNP (Riedel) was recrystallized from benzene until perfectly white. All compounds were dried *in vacuo*. Since pNP slowly decomposes on exposure to light and air, the product used was always freshly crystallized and dried.

Dissociation Constants.—The electrometric method used for the determination of the dissociation constants of $TrisH^+$ was essentially similar to that used for the same acid in water [14c] and in 50% methanol.[8b] E.m.f. measurements were performed on the cell where m_1 and m_2 are the molalities of Tris-HCl and Tris respectively. The ratio $m_1 : m_2$ was kept constant for a given solvent, while the ionic strength was varied. E.m.f. measurements on these solutions were performed in a manner essentially similar to that earlier described.[15a] Equilibrium was reached in 7—8 h on the average. No poisoning of the hydrogen electrodes was observed.

$$\text{Pt, } H_2\text{ (g, 1 atm)/Tris-HCl } (m_1)\text{, Tris } (m_2)\text{, solvent/AgCl–Ag} \quad \text{(A)}$$

The spectrophotometric method employed for the determination of the dissociation constants of $pNAH^+$ resembled that used by Bates and his co-workers.[8a] For $pNAH^+$, a series of solutions having varying ionic strengths were prepared by mixing weighed amounts of standard solutions of pNA and HCl (G. R. Merck) with the appropriate solvent. From preliminary measurements it was found that the wavelength of maximum absorbance for pNA in these solvents is 380 nm, so all measurements were performed at this wavelength. The optical absorbances were measured in a 1.00 cm cell using a Beckmann DU (G 2400) spectrophotometer. The limiting absorbances of the undissociated forms of pNA were determined by measurement on pNA solutions containing small amounts of concentrated solutions of HCl and sodium lyate respectively. The absorbance of the undissociated form, *i.e.* $pNAH^+$, was found to be negligibly small at 380 nm and was therefore taken to be zero.

For pNP, the solutions for measurement contained pNP, Tris, and Tris-HCl dissolved in the appropriate solvent. The ionic strength was varied by varying the concentration of Tris-HCl, while the buffer ratio $m_{\text{Tris-HCl}} : m_{\text{Tris}}$ was kept at a fixed value. The spectrophotometric measurements were essentially similar to those for pNA, the wavelength chosen being 405 nm at which the dissociated form of pNP showed the maximum absorbance.

Solubilities.—For the determination of the saturated solubilities of Tris, pNA, and pNP, a small quantity of each solute was added to the appropriate solvent taken in a Jena bottle, shaken and allowed to equilibriate in a thermostat at 298.15 ± 0.05 K. Aliquots of each solution were withdrawn at 48 h intervals and estimated after appropriate dilution with a large volume of water so that the medium was essentially aqueous. For pNA and pNP, the estimation was performed spectrophotometrically at 380 and 320 nm respectively, the corresponding molar absorptivity values being 1.28×10^4 and 9.72×10^3 respectively. Tris was estimated by titration with standard aqueous HCl using Methyl Orange as indicator. The saturation equilibrium was generally reached in 7—10 days, when the solution concentrations showed no further change.

RESULTS

The e.m.f. values (E) for the cell (A) in different solvents, duly corrected to 1 atm partial pressure of hydrogen,[15a] are listed in Table 1 with the corresponding values of m_1, m_2, and μ, where μ is the ionic strength given by $\mu = m_1 . d_s$, d_s being the solvent density. An extrapolation function pK'_{BH^+} defined by the equation was constructed. Values of

TABLE 1

Necessary quantities for the evaluation of pK'_{BH^+} for Tris in ACN–EG mixtures at 298.15 K

m_1/ mol kg^{-1}	m_2/ mol kg^{-1}	μ/ mol dm^{-3}	E/V	pK'_{BH^+}
		20% ACN		
0.004 96	0.004 96	0.005 11	0.7712	10.49
0.009 64	0.009 64	0.009 93	0.7600	10.53
0.0144	0.0144	0.0148	0.7529	10.53
0.0193	0.0193	0.0199	0.7488	10.54
0.0241	0.0241	0.0248	0.7450	10.53
0.0340	0.0340	0.0350	0.7393	10.50
0.0388	0.0388	0.0400	0.7380	10.51
		40% ACN		
0.005 27	0.005 21	0.005 04	0.7550	10.62
0.0103	0.0102	0.009 85	0.7437	10.60
0.0206	0.0204	0.0197	0.7313	10.63
0.0258	0.0255	0.0247	0.7281	10.64
0.0309	0.0306	0.0295	0.7264	10.65
0.0362	0.0358	0.0346	0.7230	10.63
0.0417	0.0412	0.0399	0.7202	10.61
		60% ACN		
0.005 25	0.005 26	0.004 67	0.7369	10.85
0.0166	0.0166	0.0148	0.7150	10.83
0.0222	0.0222	0.0198	0.7142	10.89
0.0279	0.0280	0.0248	0.7101	10.88
0.0336	0.0337	0.0299	0.7090	10.90
0.0393	0.0394	0.0350	0.7058	10.88
0.0449	0.0450	0.0399	0.7007	10.82

$$pK'_{BH^+} = (E - E_m^{\circ})/k \ln 10 + \log m_1 + \log (m_1/m_2) - 2A_0B_0d_s^{-\frac{1}{2}}\mu^{\frac{1}{2}} (1 + a_0B_0d_s^{-\frac{1}{2}}\mu^{\frac{1}{2}})^{-1}/\ln 10 - 2 \ln(1 + 0.002\, M_sd_s^{-1}\mu) = pK_{BH^+} + f(\mu) \quad (3)$$

E_m° (the standard potential of the Ag–AgCl electrode), M_s (the average molecular weight of the solvent), d_s, and the characteristic solvent parameters A_0B_0 and B_0 were taken from a previous paper,[15a] and $a_0 = 0$; K_{BH^+} is the dissociation constant of $TrisH^+$.

For $pNAH^+$, a similar extrapolation function may be defined by equation (4) where $m_{SH_2^+}$ is the molality of HCl in

$$pK'_{BH^+} = -\log m_{SH_2^+} - \log [u/(u_b-u)] = pK_{BH^+} + f(\mu) \quad (4)$$

the solution and the ionic strength is given by $u = m_{SH_2^+} . d_s$; $u = D/m$ and $u_b = D_b/m_b$, where m is the total molality of pNA in any solution and m_b that in the solution containing completely dissociated pNA; D and D_b are the respective optical absorbances of these solutions. The values of $m_{SH_2^+}$, m_{ind} (*i.e.* m or m_b), μ, and D are given in Table 2. For pNP, an analogous extrapolation function pK'_{HA} may be defined

$$pK'_{HA} = pK_{B_1H^+} + \log (m_{B_1}/m_{B_1H^+}) - \log [(u - u_a)/(u_b - u)] + 2\, A_0B_0d_s^{-\frac{1}{2}}\mu^{\frac{1}{2}}(1 + a_0B_0d_s^{-\frac{1}{2}}\mu^{\frac{1}{2}})^{-1}/\ln 10 + 2k \ln (1 + 0.002\, M_sd_s^{-1}\, \mu) = pK_{HA} + f(\mu) \quad (5)$$

TABLE 2

Necessary quantities for the evaluation of pK'_{BH^+} for pNA in ACN–EG mixtures at 298.15 K

$m_{SH_2^+}$/mol kg^{-1}	μ/mol dm^{-3}	$10^5 m_{ind}$/mol kg^{-1}	D	pK'_{BH^+}
		Pure EG		
0.0100	0.0111	7.27	0.591	2.032
0.0196	0.0218	7.36	0.382	2.060
0.0399	0.0443	14.57	0.397	2.113
0.0569	0.0632	15.47	0.305	2.122
0.0693	0.0769	15.90	0.257	2.133
0.0778	0.0864	15.49	0.225	2.134
Completely basic		7.06	1.190	
		20% ACN		
0.002 68	0.002 76	7.71	1.100	1.977
0.004 99	0.005 14	7.69	0.910	2.012
0.0101	0.0104	7.59	0.662	2.018
0.0201	0.0207	7.66	0.440	2.023
0.0296	0.0305	7.58	0.304	2.069
0.0498	0.0513	7.54	0.188	2.095
Completely basic		7.54	1.350	
		40% ACN		
0.005 25	0.005 02	7.68	0.748	2.080
0.009 94	0.009 50	7.66	0.529	2.117
0.0198	0.0189	7.64	0.323	2.143
0.0301	0.0288	7.78	0.244	2.130
0.0402	0.0384	7.62	0.193	2.119
0.0490	0.0469	7.54	0.144	2.174
Completely basic		7.68	1.220	
		60% ACN		
0.004 93	0.004 39	6.15	0.546	2.110
0.009 94	0.008 84	6.17	0.378	2.139
0.0198	0.0176	6.13	0.227	2.169
0.0303	0.0270	6.15	0.163	2.170
0.0403	0.0359	6.15	0.125	2.184
0.0506	0.0450	6.15	0.102	2.185
Completely basic		6.13	0.890	

as where u and u_b have similar significances as in equation (4), and $u_a = D_a/m_a$, m_a is the total molality of pNP in the solution containing the completely undissociated form, and D_a is the absorbance of this solution. K_{HA} and $K_{B_1H^+}$ are the dissociation constants of pNP and TrisH$^+$; m_{B1} and $m_{B_1H^+}$ are the molalities of Tris and TrisH$^+$ in any solution. Table 3 lists the values of μ, m_{ind}, D, and pK'_{HA} as obtained by taking $a_0 = 0$.

Dissociation constants (pK_a) of the three acids determined from the respective pK' *vs.* μ plots extrapolated to $\mu = 0$ are given in Table 4 which also shows the pK_a value for TrisH$^+$ in EG which was not determined in this study but was obtained from literature.[16a] For comparison, the pK value for pNAH$^+$ in EG obtained in an earlier study [7a] is also shown and is seen to agree with the present value within 0.02 unit. The uncertainty in these pK values is about ±0.02 unit.

The saturated solubilities (m_i) in mol kg^{-1} at 298.15 K for Tris, pNA, and pNP are presented in Table 5. These are correct to within ±2%.

The standard free energies of dissociation of each acid in a mixed solvent relative to pure EG, on the mole fraction scale, were calculated at 298.15 K by equation (6) where

$$\Delta G_t^{\circ}(A - B)_{sys} = (\ln 10)\, RT\, [\mathrm{p}({}_SK_a) - \mathrm{p}\,({}_GK_a)] - RT \ln (M_S/M_G) \quad (6)$$

${}_GK_a$ and ${}_SK_a$ are the dissociation constants in pure EG and the mixed solvent respectively, and M_G and M_S are the molecular weight of EG and the average molecular weight of the mixed solvent respectively.[15a]

The standard free energies of transfer on the mole fraction scale at 298.15 K of the neutral species Tris, pNA, and pNP were calculated by equation (7). Here the ratio of the

$$\Delta G_t^{\circ}\,(i) = RT \ln ({}_Gm_i/{}_Sm_i) - RT \ln (M_S/M_G) \quad (7)$$

activity coefficients of i in EG and in the mixed solvent has been assumed to be unity; the same assumption has been used by Bates and his co-workers [8c] and Kundu and his co-workers.[7]

TABLE 3

Necessary quantities for the evaluation of pK'_{HA} for pNP in ACN–EG mixtures at 298.15 K

μ/mol dm^{-3}	$10^5 m_{ind}$/mol kg^{-1}	D	pK'_{HA}
	Pure EG		
	$m_{Tris}/m_{TrisH^+} = 0.117$		
Completely acidic	8.54	0.930	
0.005 22	8.32	0.798	10.51
0.009 89	8.45	0.780	10.45
0.0196	8.50	0.751	10.45
0.0295	8.49	0.729	10.47
0.0393	8.59	0.722	10.50
0.0489	8.54	0.704	10.52
Completely basic	8.49	0.168	
	20% ACN		
	$m_{Tris}/m_{TrisH^+} = 0.999$		
Completely acidic	7.00	0.725	
0.004 82	6.99	0.446	10.76
0.0101	6.98	0.415	10.75
0.0196	6.97	0.387	10.77
0.0296	6.98	0.372	10.81
0.0396	7.04	0.372	10.86
0.0492	7.08	0.370	10.90
Completely acidic	6.96	0.116	
	40% ACN		
	$m_{Tris}/m_{TrisH^+} = 1.503$		
Completely acidic	7.59	0.350	
0.004 87	7.62	0.254	11.27
0.009 73	7.59	0.241	11.27
0.0195	7.64	0.234	11.31
0.0295	7.65	0.232	11.38
0.0396	7.72	0.226	11.40
0.0493	7.67	0.227	11.47
Completely basic	7.63	0.064	
	60% ACN		
	$m_{Tris}/m_{TrisH^+} = 1.497$		
Completely acidic	20.54	1.850	
0.005 03	20.49	1.475	11.75
0.009 76	20.55	1.420	11.73
0.0198	20.45	1.310	11.71
0.0297	20.61	1.275	11.74
0.0398	20.64	1.200	11.72
0.0499	20.79	1.175	11.75
Completely basic	20.35	0.256	

TABLE 4

pK_a Values for various acids on the molal scale in ACN–EG mixtures at 298.15 K

Wt. % ACN	TrisH+	pNAH+	pNP
0	10.475 [a]	2.04 (2.06 [b])	10.47
20	10.52	2.00	10.71
40	10.62	2.09	11.22
60	10.86	2.12	11.72

[a] Ref. 16. [b] Ref. 7*a*.

TABLE 5

Solubilities m_i/mol kg^{-1} of some neutral species in ACN–EG mixtures at 298.15 K

Wt. % ACN	Tris	pNA	pNP
0	0.665	0.343	2.87
20	0.497	0.770	4.45
40	0.281	1.36	6.01
60	0.132	1.92	6.49

Finally, using the ΔG_t^o (A–B)$_{sys}$ and ΔG_t^o (i) values just determined and the ΔG_t^o (H^+) values reported in a previous paper,[15d] the values of the standard free energy of transfer at 298.15 K on the mole fraction scale of the conjugate acids of Tris and pNP and of the conjugate base of pNP were computed using relations (8) and (9). The values of ΔG_t^o

$$\Delta G_t^o\ (BH^+\text{–}B)_{sys} = \Delta G_t^o\ (B) + \Delta G_t^o\ (H^+) - \Delta G_t^o\ (BH^+) \quad (8)$$

$$\Delta G_t^o\ (HA\text{–}A^-)_{sys} = \Delta G_t^o\ (A^-) + \Delta G_t^o\ (H^+) - \Delta G_t^o\ (HA) \quad (9)$$

(A–B)$_{sys}$, *i.e.* either ΔG_t^o (BH^+–B)$_{sys}$ (for B = pNA, Tris) or ΔG_t^o (HA–A^-)$_{sys}$ (for HA = pNP), for various ACN + EG mixtures are listed in Table 6, together with those of ΔG_t^o (B), ΔG_t^o (A^-), ΔG_t^o (BH^+), and ΔG_t^o (HA). The probable uncertainty in the values of ΔG_t^o (A–B)$_{sys}$, ΔG_t^o (B), and ΔG_t^o (HA) is ±0.16 kJ mol^{-1}.

TABLE 6

Standard free energies of transfer (kJ mol^{-1}) on the mole fraction scale in ACN–EG mixtures at 298.15 K

	B = Tris		
Wt. % ACN	ΔG_t^o (BH^+–B)$_{sys}$	ΔG_t^o(B)	ΔG_t^o (BH^+)
20	0.50	0.96	0.8
40	1.29	2.60	2.0
60	2.87	4.68	3.5

B = pNA

	B = pNA		
Wt. % ACN	ΔG_t^o (BH^+–B)$_{sys}$	ΔG_t^o (B)	ΔG_t^o (BH^+)
20	0.02	−1.76	−1.5
40	0.69	−2.95	−2.9
60	1.14	−3.60	−3.0

	HA = pNP		
Wt. % ACN	ΔG_t^o (HA–A^-)$_{sys}$	ΔG_t^o (HA)	ΔG_t^o (A^-)
20	1.61	−0.84	0.4
40	4.74	−1.37	2.7
60	7.81	−1.35	4.8

DISCUSSION

In Figure 1, ΔG_t^o (A-B)$_{sys}$ for pNA, Tris, and pNP is plotted against the mole percent of ACN in ACN–EG mixtures. The corresponding plots for pNA and Tris in the H_2O–EG system are also shown, being drawn from the results obtained earlier[7a] In the absence of ΔG_t^o (A–B)$_{sys}$ values for pNP in H_2O + EG mixtures, ΔG_t^o (A–B)$_{sys}$ values for another uncharged acid: acetic acid (HAc)[16b] have also been plotted.

The variation of ΔG_t^o (A–B)$_{sys}$ with solvent composition for any acid–base system is observed to be sharply contrasting in the two solvent systems one of which is a non-isodielectric protic + protic combination while the other is an isodielectric protic + dipolar aprotic one. For the dissociation of HAc which involves charge separation, a large portion of the increasing ease of ionization in H_2O + EG mixtures must come from the increasing dielectric constant of the medium, whereas the isoelectric dissociations of TrisH$^+$ and pNAH$^+$, being little affected by dielectric constant changes, become readier owing to the increased solvation of the H^+ ion by increasing amounts of added water;[17] the flat portion in the curve for Tris and the upcurving portion in the curve for pNA may be attributed to the increase in ΔG_t^o (H^+) at water rich compositions.[17] On the other hand, in the isodielectric ACN–EG system, we find a decreasing ease of ionization for all three acids, pNAH$^+$, TrisH$^+$, and pNP, as the proportion of ACN in the solvent increases. Because of their closely similar structures, the dispersion interactions with the dipolar aprotic solvent ACN are likely to be similar for the two components of each of the conjugate acid–base pairs pNA–pNAH$^+$ and pNP–pNP$^-$, pNP$^-$ being the *p*-nitrophenoxide ion. Consequently, the increasing resistance to ionization must be explained by the increasing desolvation of the hydrogen ion[15d] and, for pNP, also by the increasing desolvation of the pNP$^-$ anion in ACN–EG mixtures. Similarly, the hydrogen-bonding tendencies of Tris and TrisH$^+$ are expected to be almost identical in a given solvent and here too the increasing difficulty of ionization must arise from the increasing desolvation of the hydrogen ion. To confirm these contentions, it will be necessary to examine the behaviour of the individual species concerned.

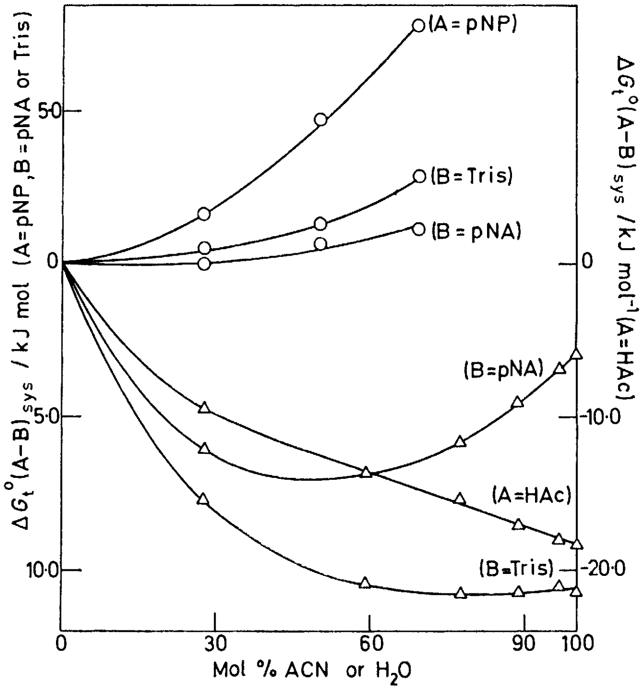

FIGURE 1 Variation of ΔG_t^o (A–B)$_{sys}$ (A = pNP, pNA, Tris, or HAc) at 298.15 K with solvent composition in ACN–EG ○ and H_2O–EG △ mixtures

In Figure 2, the free energies of transfer for the neutral species Tris, pNA, and pNP in ACN–EG mixtures are shown plotted against the mole percent of ACN. For comparison, the corresponding plots for the H_2O-EG[7a] system and the isodielectric methanol (MeOH) + propylene glycol (PG)[7b] system are also shown (excepting those for pNP for which no data are available).

In interpreting the plots shown, it must be noted that while Tris, by virtue of its three OH and one NH_2 groups, interacts with the solvent mainly through

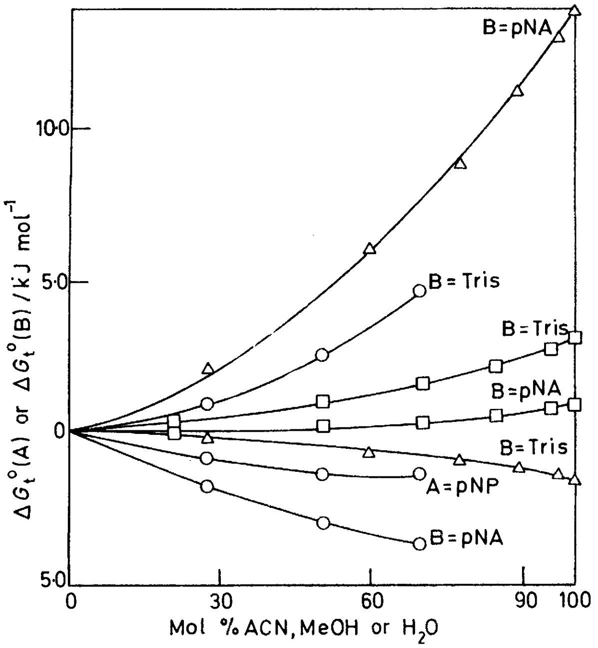

FIGURE 2 Variation of ΔG_t^o (B) (B = pNA or Tris) at 298.15 K in ACN–EG ○, H_2O–EG △, and MeOH–PG □, as well as of ΔG_t^o (pNP) at 298.15 K in ACN–EG mixtures with solvent composition

hydrogen-bonding, pNA and pNP, by virtue of their aromatic nuclei, exhibit primarily dispersion interactions with the solvent. Thus, increasing values of ΔG_t^o (Tris), *e.g.* for the ACN–EG and MeOH–PG systems, show that the hydrogen-bonding prowess of the mixed solvent in each case progressively decreases as the proportion of ACN or MeOH increases. The relative diminution of this prowess in ACN–EG mixtures far exceeds that in MeOH–PG mixtures, probably because MeOH possesses a single centre of hydrogen-bonding, EG and PG have two each, and ACN fares poorly either as a hydrogen-bond donor or acceptor.[3,18,19] On the other hand, H_2O is a better hydrogen-bonding solvent than EG, if only marginally so, as reflected in the slowly decreasing values of ΔG_t^o (Tris) with the increasing addition of H_2O to EG.

The behaviour of ΔG_t^o (pNA) in these solvent systems is seen to be strikingly different. The strength of dispersion interactions undergone with a solute increases in the sequence $H_2O < EG < ACN$ as shown by the solvation behaviour of the Ph_4As^+ or Ph_4B^- ion.[15a] This is confirmed by the sharp increase and decrease of ΔG_t^o (pNA) in the H_2O–EG and the ACN–EG systems respectively. MeOH and PG are probably equally effective (or ineffective) in undergoing dispersion interactions and virtually no change in ΔG_t^o (pNA) with solvent composition is noticed in MeOH–PG mixtures.

A further point worth noting is that although pNA and pNP have identical centres of dispersion interactions (namely, quinonoid nuclei), the relative increase of solvation of pNA exceeds that of pNP in ACN–EG mixtures, thus implying that pNA is less solvated in pure EG than pNP, even if both solutes are identically solvated through dispersion interactions in a given solvent mixture.

Figure 3 shows a comparison of ΔG_t^o (BH^+) (B = Tris, pNA) *vs.* solvent composition plots in ACN–EG and H_2O–EG mixtures. For the latter system, equation (8) was used to calculate ΔG_t^o (BH^+) values from literature values of ΔG_t^o $(BH^+–B)_{sys}$,[7a] ΔG_t^o (B),[7a] and ΔG_t^o (H^+).[17] Here, contrasting behaviour is exhibited by ΔG_t^o ($pNAH^+$) in the two systems, whereas the ΔG_t^o ($TrisH^+$) curves are very similar. What is significant is that in spite of the increasing dielectric constant, both these cationic species are desolvated on passing from EG to H_2O–EG. For $pNAH^+$, this trend may be attributed to the marked loss of dispersion interaction stability not adequately compensated for by increasing electrostatic or hydrogen-bonding effects, but for $TrisH^+$ this trend is apparently inexplicable unless we assume some sort of specific solvation with EG. In ACN–EG mixtures the decreasing ΔG_t^o ($pNAH^+$) indicates once more that dispersion interactions for this cation are overwhelmingly stronger than hydrogen-bonding so that its solvation by ACN rather than by EG is favoured. The diametrically opposite nature of the ΔG_t^o ($TrisH^+$) curve shows that the reverse is true for $TrisH^+$ and a loss of hydrogen-bonded stability in passing from EG to ACN–EG is indicated.

Figure 4 presents a collection of the various free energies of transfer arrived at in this study by direct experiment or by indirect derivation. In the ultimate analysis, it now becomes clear that the features present in the ΔG_t^o $(A–B)_{sys}$ curves arise from the superimposition of the features of the individual curves for ΔG_{to} (A), ΔG_t^o (B), and ΔG_t^o (H^+). As conjectured earlier, the relative changes of solvation of the cationic acids BH^+ from EG to ACN–EG mixtures are not much

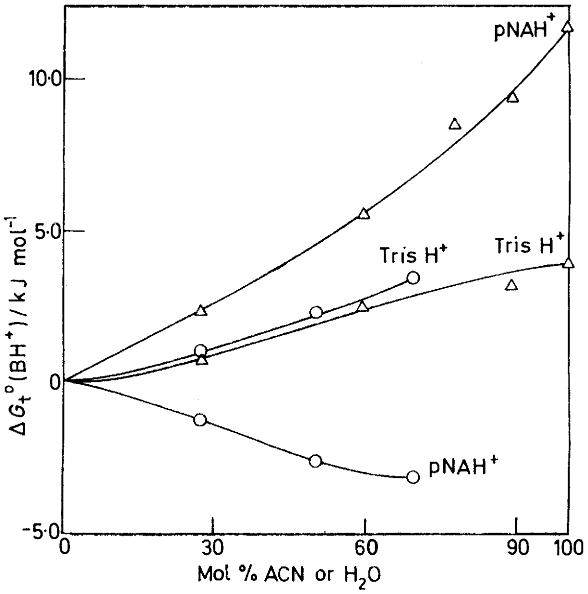

FIGURE 3 Variation of ΔG_t^o (BH^+) at 298.15 K (B = pNA or Tris) with solvent composition in ACN–EG ○, and H_2O–EG △

different from those of their conjugate bases B, so that ΔG_t^o $(BH^+-B)_{sys}$ is almost wholly dictated by ΔG_t^o (H^+). Now since the values of ΔG_t^o (H^+) were obtained [15d] using the tetraphenylarsonium tetraphenylboride assumption,[20a] such close correlation between ΔG_t^o $(BH^+-B)_{sys}$ and ΔG_t^o (H^+) is strongly indicative of the effectiveness of this assumption in estimating ionic ΔG_t^o values, as suggested by Popovych [20b] who found a similar correlation for several primary ammonium acids in aqueous mixtures of methanol and ethanol.

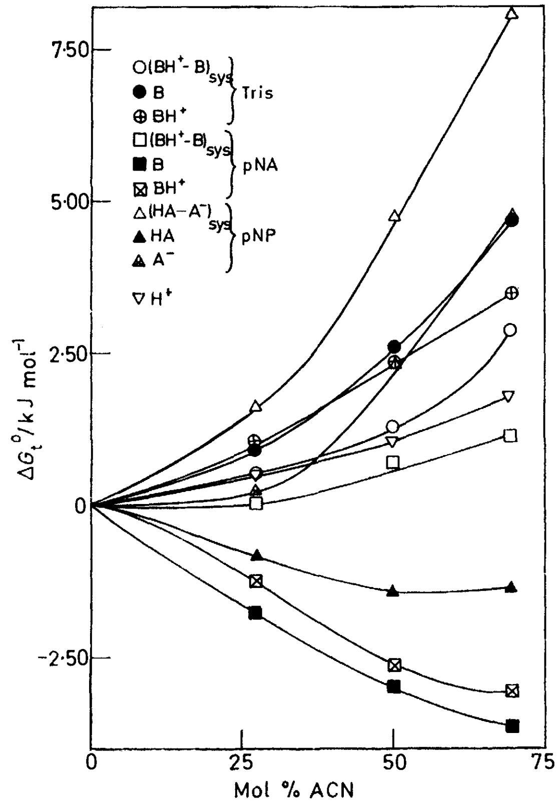

FIGURE 4 Variation of ΔG_t^o $(A-B_{sys})$, ΔG_t^o (A), ΔG_t^o (B), and $\Delta G_t^o(H^+)$ at 298.15 K with mol % ACN in ACN-EG mixtures

On the other hand, we find widely different curves for ΔG_t^o (pNP) and ΔG_t^o (pNP^-). While increasing dispersion interactions with ACN increasingly stabilize the neutral pNP molecule in ACN-EG mixtures, the pNP^- ion, in spite of its aromatic nucleus, is strongly desolvated as the ACN content of the solvent increases. This emphasizes the strong anion-desolvating characteristics of a dipolar aprotic solvent like ACN [3,18,19,21] which outweighs the effect of dispersion interactions in this case. It is pertinent to note that the picrate ion (Pi^-) was found to undergo increased solvation at intermediate compositions of the ACN-EG system before being increasingly desolvated at higher ACN proportions.[15a] This difference between these two ions of a similar nature arises most probably from the more extensive charge delocalization achieved by the Pi^- ion compared to the pNP^- ion, which enables the former to mask successfully its anionic character, at least up to moderate concentrations of ACN, in favour of its tendency to undergo increased dispersion interactions with the solvent.

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