Studies in Some ' Isodielectric ' Media. Part IV.[1] Solvent Effect on the Proton Transfer Equilibria of Some Acids in Methanol–Propylene Glycol at 25 °C

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The dissociation constants ($_{s}K$) of benzoic acid, protonated (hydroxymethyl)methylamine ($TrisH^+$), and the *p*-nitroanilinium ion have been determined at 25° in the ' isodielectric ' methanol–propylene glycol solvent system by e.m.f. measurements of suitable galvanic cells in the first two cases, and by spectrophotometric measurements in the case of the latter. The solubilities of the uncharged species, benzoic acid, Tris, and *p*-nitroaniline, have also been determined at 25°. The solvent effects on the proton transfer processes of these acids have been discussed in terms of the free energies of transfer of the different species concerned from methanol to the other solvents. ' Electrostatic effect ' differences being negligibly small between these isodielectric media, specific solute–solvent interactions dictate the overall proton transfer behaviour of these acids.

SOLVENT effects on the proton transfer equilibria of different charge types of acids and bases are still an intriguing problem.[2-6] This is partly because of the difficulty in assessing the ' electrostatic effect '[5] arising from the difference in permittivity of the solvents, and partly because of our limited knowledge of the role played by the uncharged species involved in the proton transfer process. Recently it has been shown[7,8] that, for some protonated amines such as protonated Tris ($TrisH^+$) and *p*- and *m*-nitroanilinium ions (NAH^+) in aqueous mixtures of ethylene glycol (EG) and methanol, the solvent effects on the proton transfer equilibria are largely dictated by the specific solute–solvent interactions in addition to the effect of relative ' basicities '. But uncertainties in the ' electrostatic effect '[5,9] have somewhat obscured the picture, particularly for uncharged acids, where the process involves charge separation. For a better understanding of the ' chemical effects '[5] of the solvents, we have studied the proton transfer equilibria of benzoic acid, $TrisH^+$, and *p*-NAH^+ in methanol–propylene glycol, where the specific solute–solvent interactions should dictate the overall proton behaviour of these acids.

EXPERIMENTAL

Dissociation Constants of the Acids at 25°.—(i) *Benzoic acid.* The method used for determining the dissociation constant $(_{s}K)_{HA}$ of benzoic acid (HA) was exactly similar to that adopted in the case of acetic acid previously described.[10] A cell of the type A was used.

$$\text{Pt, } H_2(\text{g, 1 atm})|HA(m_1),\ NaA(m_2),\ NaCl(m_3),\ \text{solvent}|AgCl\text{–}Ag \qquad \text{A}$$

Benzoic acid (Merck, G.R.) was used without further purification. Standard solutions of benzoic acid were prepared by adding weighed amounts of solid benzoic acid to weighed amounts of the respective solvents. The strength was also checked by titrating weighed amounts of benzoic acid solution taken in water with a standard aqueous alkali solution using phenolphthalein as indicator. Other experimental details have been described.[10]

Assuming that $m_{HA} = m_1$, $m_{A^-} = m_2$, and $m_{Cl^-} = m_3$ and the ionic strength, $\mu = (m_2 + m_3)d_s$, where d_s is the density of the solvent, the $p(_{s}K)_{HA}$ values of benzoic acid in these solvents were obtained by extrapolating the plots of the function $p(_{s}K)_{HA}'$ defined by equation (1), against μ to $\mu = 0$.

$$p(_{s}K)_{HA}' = \frac{E - (_{s}E_{m}^{\circ})_{AgCl\text{-}Ag}}{2{\cdot}303RT/F} + \log m_3 + \log\frac{m_1}{m_2} = p(_{s}K)_{HA} - \log\frac{\gamma_{HA}\gamma_{Cl^-}}{\gamma_{A^-}} = p(_{s}K)_{HA} + f(\mu) \qquad (1)$$

The required values of $(_{s}E_{m}^{\circ})_{AgCl\text{-}Ag}$ and d_s have been reported earlier.[10] Table 1 shows the observed e.m.f. values (corrected for 1 atm H_2) for the corresponding buffer compositions.

(ii) *Tris*H^+. The dissociation constants $(_{s}K)_{BH^+}$ of $TrisH^+$ in these solvents were determined at 25° by a method similar to that adopted in glycol–water solvents for this acid.[8] The e.m.f. values of the cell B, with buffer solutions

$$\text{Pt, } H_2(\text{g, 1 atm})|BH^+Cl^-(m_1),\ B(m_2),\ \text{solvent}|AgCl\text{–}Ag \qquad \text{B}$$

comprising Tris hydrochloride and Tris at different ionic strengths, were measured. The relevant experimental details have already been described.[8]

Assuming that TrisHCl is completely dissociated and that the correction due to solvolysis of Tris is negligible, the $p(_{s}K)_{BH^+}$ values were obtained by extrapolating the plot of the auxiliary function $p(_{s}K)_{BH^+}'$ defined[11] by equation (2) against μ to $\mu = 0$. Values of the Debye–Hückel

$$p(_{s}K)_{BH^+}' = \frac{E - (_{s}E_{m}^{\circ})_{AgCl\text{-}Ag}}{2{\cdot}303RT/F} + \log m_3 + \log\frac{m_1}{m_2} - 2S_{f}\mu^{\frac{1}{2}} = p(_{s}K)_{BH^+} - \beta\mu \qquad (2)$$

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[1] Part III, K. K. Kundu, A. K. Rakshit, and M. N. Das, preceding paper.

[2] R. P. Bell, ' The Proton in Chemistry,' Cornell University Press, Ithaca, New York, 1956.

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

[4] E. J. King, ' Acid-Base Equilibria,' Pergamon, London, 1965.

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

[6] H. Strehlow, ' Chemistry of Non-aqueous Solvents,' ed. J. J. Lagowski, Academic Press, New York, 1967, ch. 4.

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

[8] K. K. Kundu, A. L. De, and M. N. Das, unpublished work.

[9] J. O'M. Bockris and B. E. Conway, ' Modern Aspects of Electrochemistry,' eds. J. O'M. Bockris and B. E. Conway, Butterworths, London, 1954, vol. I, ch. 2.

[10] K. K. Kundu, A. L. De, and M. N. Das, *J.C.S. Dalton*, 1972, 373.

[11] K. K. Kundu, P. K. Chatterjee, and M. N. Das, *J. Chem. Soc.* (*A*), 1970, 2034.

constant S_f are reported in an earlier paper.[10] The observed e.m.f. values (corrected for 1 atm H_2) for the corresponding buffer compositions are presented in Table 2.

TABLE 1

Data for the determination of $p(_sK)_{HA}$ for benzoic acid (HA) in methanol–propylene glycol at 25°

m_{HA}	m_{NaA}	m_{NaCl}	E/V
	10 Wt. % PG		
0·00543	0·00710	0·00591	0·6774
0·00709	0·00927	0·00771	0·6707
0·00985	0·0128	0·0107	0·6620
0·0184	0·0240	0·0200	0·6460
0·0250	0·0327	0·0272	0·6379
0·0325	0·0424	0·0353	0·6305
			$p(_sK)_{HA} = 9·19$
	30 Wt. % PG		
0·00344	0·00548	0·00400	0·6876
0·00499	0·00794	0·00579	0·6777
0·00670	0·0107	0·00777	0·6699
0·00106	0·0168	0·0123	0·6589
0·0135	0·0216	0·0157	0·6513
0·0192	0·0305	0·0223	0·6428
0·0253	0·0402	0·0293	0·6352
			$p(_sK)_{HA} = 9·14$
	50 Wt. % PG		
0·00521	0·00539	0·00537	0·6628
0·0106	0·0109	0·0109	0·6445
0·0155	0·0160	0·0159	0·6351
0·0211	0·0219	0·0218	0·6274
0·0261	0·0270	0·0269	0·6211
0·0310	0·0321	0·0320	0·6167
0·0338	0·0349	0·0348	0·6135
			$p(_sK)_{HA} = 9·10$
	70 Wt. % PG		
0·00261	0·00304	0·00320	0·6750
0·00538	0·00627	0·00658	0·6556
0·00793	0·00924	0·00970	0·6464
0·0117	0·0137	0·0143	0·6361
0·0211	0·0246	0·0258	0·6203
0·0296	0·0345	0·0362	0·6107
			$p(_sK)_{HA} = 9·13$
	90 Wt. % PG		
0·00601	0·00332	0·00421	0·6416
0·0122	0·00675	0·00859	0·6234
0·0182	0·0101	0·0128	0·6119
0·0246	0·0136	0·0172	0·6039
0·0396	0·0219	0·0277	0·5910
0·0589	0·0326	0·0413	0·5810
			$p(_sK)_{HA} = 9·19$
	100 Wt. % PG		
0·00273	0·00367	0·00431	0·6595
0·00621	0·00791	0·00546	0·6520
0·00810	0·0103	0·00712	0·6445
0·0119	0·0151	0·0104	0·6343
0·0114	0·0154	0·0180	0·6220
0·0240	0·0305	0·0211	0·6165
0·0214	0·0287	0·0337	0·6060
			$p(_sK)_{HA} = 9·20$

(iii) p-*Nitroanilinium ion.* The dissociation constants $(_sK)_{BH^+}$ of *p*-$NAH^+(BH^+)$ in these solvents were determined spectrophotometrically using unbuffered solutions of HCl at different concentrations in a manner essentially similar to that in glycol–water solvents.[8] The $p(_sK)_{BH^+}$ values were obtained by extrapolation of plots of μ against $p(_sK)_{BH^+}'$ [defined by equation (3)] to $\mu = 0$.

$$p(_sK)_{BH^+}' = -\log m_{SH_2^+} - \log\frac{\alpha}{1-\alpha} = p(_sK)_{BH^+} + \log\frac{\gamma_{SH_2^+}\gamma_B}{\gamma_{BH^+}} = p(_sK)_{BH^+} + f(\mu) \quad (3)$$

The values of $-\log m_{SH_2^+}$ and $-\log[\alpha/(1-\alpha)]$ at different molalities of $HCl(m_{HCl})$ for all the solvents are given in Table 3.

TABLE 2

Data for the determination of $p(_sK)_{BH^+}$ for protonated Tris (BH^+) in methanol–propylene glycol at 25°

$m_{TrisHCl}$	m_{Tris}	E/V	$m_{TrisHCl}$	m_{Tris}	E/V
	Methanol			70 Wt. % PG	
0·00690	0·00970	0·7545	0·00683	0·00628	0·7392
0·0207	0·0291	0·7360	0·0136	0·0125	0·7279
0·0228	0·0320	0·7330	0·0220	0·0202	0·7202
0·0346	0·0486	0·7279	0·0303	0·0279	0·7152
0·0513	0·0721	0·7219	0·0375	0·0345	0·7126
0·0873	0·1226	0·7142	0·0412	0·0379	0·7116
			0·0610	0·0561	0·7072
			0·1004	0·0923	0·7008
	$p(_mK)_{BH^+} = 10·34$			$p_s(K)_{BH^+} = 10·36$	
	10 Wt. % PG			90 Wt. % PG	
0·00925	0·00879	0·7391	0·00714	0·00838	0·7509
0·0165	0·0157	0·7300	0·0124	0·0146	0·7339
0·0292	0·0277	0·7211	0·0182	0·0214	0·7276
0·0298	0·0283	0·7217	0·0255	0·0300	0·7230
0·0440	0·0418	0·7146	0·0347	0·0408	0·7197
0·0548	0·0521	0·7126	0·0348	0·0409	0·7194
0·0605	0·0574	0·7110	0·0570	0·0671	0·7133
0·1233	0·1172	0·7012	0·0992	0·1167	0·7066
	$p(_sK)_{BH^+} = 10·27$			$p(_sK)_{BH^+} = 10·47$	
	30 Wt. % PG			100 Wt % PG	
0·00795	0·00913	0·7462	0·00712	0·0114	0·7466
0·0124	0·0143	0·7385	0·0865	0·0138	0·7440
0·0263	0·0302	0·7265	0·0122	0·0194	0·7385
0·0316	0·0363	0·7244	0·0205	0·0327	0·7320
0·0459	0·0527	0·7189	0·0232	0·0369	0·7290
0·0588	0·0676	0·1753	0·0322	0·0513	0·7265
0·1045	0·1200	0·7088	0·0442	0·0705	0·7223
			0·0858	0·1368	0·7153
	$p(_sK)_{BH^+} = 10·29$			$p(_sK)_{BH^+} = 10·50$	
	50 Wt. % PG				
0·00944	0·00730	0·7311			
0·0147	0·0113	0·7238			
0·0263	0·0204	0·7147			
0·0348	0·0269	0·7104			
0·0431	0·0333	0·7082			
0·0502	0·0388	0·7064			
0·0690	0·0534	0·7022			
0·1093	0·0845	0·6950			
	$p(_sK)_{BH^+} = 10·30$				

Standard Free-energies of Transfer of the Uncharged Species (Tris, p-*Nitroaniline, and Benzoic Acid) from Methanol to Methanol–Propylene Glycol at* 25°.—The free-energy change $\Delta G_t°(i)$ accompanying the transfer of the uncharged species (i) from the standard state in methanol (m) to the standard state in any of the solvents (s), *i.e.* for the process $i(m) \longrightarrow i(s)$, has been computed from the solubilities $(_sN_i)$ (in mole fraction) of these species in the solvents with respect to that in methanol $(_mN_i)$, using equation (4).[7]

$$\Delta G_t°(i) \simeq 2·303RT \log(_mN_i/_sN_i) \quad (4)$$

Solubilities of Tris and *p*-NA were determined at 25° by the respective methods adopted for glycol–water described earlier.[8] Unlike in glycol–water *p*-NA was found to dissolve readily in these completely non-aqueous solvents and much less time was necessary to attain saturation. Solubilities of benzoic acid in these solvents were determined by a similar procedure as that for Tris in glycol–water, but titration was with standard aqueous alkali. The saturation of both benzoic acid and Tris in these solvents could be effected by mild shaking for *ca.* 12 h. Since the ionization of benzoic acid is negligibly small in these solvents [$\text{p}(_{\text{s}}K)_{\text{HA}} \simeq 9$], no correction was necessary for the effective concentration of the uncharged form. The solubility of Tris in methanol obtained in this study compares fairly well with that found earlier by Bates *et al.*,[7] the values being 0·2952 and 0·2918 mol (kg-methanol)$^{-1}$ respectively. The solubilities of the substances expressed on molal and mole fraction scales are recorded in Table 4 and the values of $\Delta G_{\text{t}}°(\text{B})$ for the two bases and $\Delta G_{\text{t}}°(\text{HA})$ for benzoic acid in Table 5.

TABLE 3

Data for spectrophotometric determination of $\text{p}(_{\text{s}}K)_{\text{BH}^+}$ for p-NAH$^+$ in methanol–propylene glycol at 25°

m_{HCl}	$-\log m_{\text{SH}_2^+}$	$-\log \frac{\alpha}{1-\alpha}$	$\text{p}(_{\text{s}}K)_{\text{BH}^+}$
Methanol; [Indicator] = 4·66 × 10^{-5}M			
0·00957	2·019	−0·746	1·273
0·0242	1·616	−0·330	1·286
0·0312	1·506	−0·192	1·314
0·0451	1·346	−0·023	1·323
0·0584	1·234	0·114	1·348
0·0731	1·136	0·208	1·344
			$\text{p}(_{\text{m}}K)_{\text{BH}^+} = 1{\cdot}27$
10 Wt. % PG; [Indicator] = 3·79 × 10^{-5}M			
0·0121	1·919	−0·605	1·314
0·0247	1·607	−0·297	1·310
0·0352	1·453	−0·133	1·320
0·0453	1·344	0·009	1·353
0·0571	1·243	0·097	1·340
0·0675	1·171	0·211	1·382
0·0907	1·042	0·359	1·401
			$\text{p}(_{\text{s}}K)_{\text{BH}^+} = 1{\cdot}30$
30 Wt. % PF; [Indicator] = 3·89 × 10^{-5}M			
0·0128	1·891	−0·428	1·463
0·0255	1·594	−0·130	1·464
0·0375	1·426	−0·051	1·477
0·0532	1·274	0·215	1·489
0·0784	1·106	0·428	1·534
			$\text{p}(_{\text{s}}K)_{\text{BH}^+} = 1{\cdot}44$
50 Wt. % PG; [Indicator] = 7·82 × 10^{-5}M			
0·0130	1·886	−0·313	1·573
0·0261	1·583	−0·012	1·571
0·0396	1·402	0·197	1·599
0·0519	1·285	0·309	1·594
0·0767	1·115	0·517	1·632
0·1024	0·989	0·687	1·671
0·1227	0·911	0·774	1·685
			$\text{p}(_{\text{s}}K)_{\text{BH}^+} = 1{\cdot}55$
70 Wt. % PG; [Indicator] = 5·31 × 10^{-5}M			
0·0127	1·896	−0·182	1·714
0·0248	1·605	0·114	1·719
0·0370	1·432	0·321	1·753
0·0486	1·314	0·440	1·754
0·0944	1·025	0·807	1·832
0·1200	0·921	0·916	1·837
			$\text{p}(_{\text{s}}K)_{\text{BH}^+} = 1{\cdot}70$
90 Wt. % PG; [Indicator] = 8·93 × 10^{-5}M			
0·0137	1·862	0·006	1·868
0·0170	1·768	0·122	1·890
0·0355	1·450	0·443	1·893
0·0643	1·192	0·773	1·963
0·0798	1·098	0·884	1·982
0·0992	1·003	1·011	2·014
			$\text{p}(_{\text{s}}K)_{\text{BH}^+} = 1{\cdot}86$
100 Wt. % PG; [Indicator] = 5·55 × 10^{-5}M			
0·0201	1·696	0·410	2·106
0·0348	1·459	0·688	2·147
0·0450	1·347	0·841	2·188
0·0531	1·275	0·957	2·232
0·0631	1·200	1·044	2·244
0·0761	1·113	1·167	2·286
			$\text{p}(_{\text{s}}K)_{\text{BH}^+} = 2{\cdot}04$

TABLE 4

Solubilities of Tris, *p*-nitroaniline, and benzoic acid in methanol–propylene glycol at 25°

Wt. %	Tris		*p*-NA		Benzoic Acid	
PG	m_{B}	10^2N_{B}	m_{B}	10^2N_{B}	m_{HA}	$10N_{\text{HA}}$
0	0·2952	0·9361	0·6369	1·998	6·372	1·693
10	0·3343	1·123	0·6353	2·113	5·998	1·692
30	0·3717	1·419	0·6029	2·281	5·192	1·673
50	0·3980	1·760	0·5735	2·518	4·483	1·680
70	0·4295	2·259	0·4968	2·605	3·699	1·661
90	0·4500	2·920	0·4571	2·965	3·206	1·765
100	0·4646	3·410	0·3928	2·899	2·698	1·700

m Concentration in moles per kilogramme of solvent. *N* Denotes mole fraction of the species in the saturated solution.

TABLE 5

Standard free energies of transfer * (mole fraction scale) from methanol to methanol–propylene glycol for Tris, *p*-nitroaniline, benzoic acid, and hydrochlorides of Tris and *p*-nitroaniline at 25°

Wt. % PG	$\Delta G_{\text{t}}°(\text{B})$ Tris	$\Delta G_{\text{t}}°(\text{B})$ *p*-NA	$\Delta G_{\text{t}}°(\text{HA})$ Benzoic acid	$\Delta G_{\text{t}}°(\text{BHCl})$ TrisHCl	$\Delta G_{\text{t}}°(\text{BHCl})$ *p*-NAHCl
10	−108	−33	1	−150	−215
30	−246	−78	7	−339	−471
50	−374	−137	5	−500	−699
70	−522	−157	12	−670	−865
90	−674	−234	−24	−859	−1046
100	−766	−221	−2	−968	−1255

* $\Delta G_{\text{t}}°(\text{i})$ Values in cal mol^{-1}.

DISCUSSION

The $\text{p}(_{\text{s}}K)$ values (molal) at 25° for benzoic acid, TrisH$^+$, and *p*-NAH$^+$ in methanol, propylene glycol (PG), and various mixtures have been reported at the bottom of the respective Tables (1—3). For the sake of comparison[12] in different solvents these values have been converted to the mole fraction scale $\text{p}(_{\text{s}}K)^{\text{N}}$ by the usual relation and are recorded in Table 6. The solvent effect on the dissociation constant of the acid (A), $2{\cdot}303RT[\text{p}(_{\text{s}}K)^{N}{}_{\text{A}} - \text{p}(_{\text{m}}K)^{N}{}_{\text{A}}]$, represents the standard free-energy change for the transfer processes of the Brønsted's conjugate acid–base system $[\text{A} - \text{B}]_{\text{sys}}$, from methanol to the solvent, *i.e.* for the transfer process (5)

$$\begin{aligned}\text{MH}_2{}^+(\text{m}) + \text{SH}(\text{s}) + \text{B}(\text{m}) + \text{A}(\text{s}) \\ = \text{SH}_2{}^+(\text{m}) + \text{MH}(\text{m}) + \text{B}(\text{s}) + \text{A}(\text{m}) \quad (5)\end{aligned}$$

where (m) and (s) indicate that the substances are in the standard state in methanol and the solvent respectively.

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[12] R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' Butterworths, London, 2nd edn., 1965.

Thus (6) follows, where $\Delta G_t°(i)$ represents the free-energy

$$\Delta G_t°[A - B]_{sys} = 2{\cdot}303RT[p(_sK)^N{}_A - p(_mK)^N{}_A] \\ = \Delta G_t°(H^+) + \Delta G_t°(B) - \Delta G_t°(A) \quad (6)$$

change accompanying the transfer of any species (i) from methanol to any other solvent, SH. The values of $\Delta G_t°[A - B]_{sys}$ for the acid–base systems such as $[HA - A^-]_{sys}$ for benzoic acid and $[BH^+ - B]_{sys}$ for TrisH+ and *p*-NAH+ are given in Table 5, and their variations with wt. % PG are shown in Figure 1.

TABLE 6

Values of $p(_sK)^N{}_A$ and $\Delta G_t°[A - B]_{sys}$ * for benzoic acid, TrisH+, and *p*-NAH+ in methanol–propylene glycol at 25°

Wt. % PG	Benzoic acid		TrisH+		*p*-NAH+	
	$p(_sK)^N{}_{HA}$	$\Delta G_t°[HA - A^-]_{sys}$	$p(_sK)^N{}_{BH^+}$	$\Delta G_t°[BH^+ - B]_{sys}$	$p(_sK)^N{}_{BH^+}$	$\Delta G_t°[BH^+ - B]_{sys}$
0	10·770 [a]	0	11·834	0	2·764	0
10	10·658	−153	11·738	−131	2·768	9
30	10·551	−299	11·701	−181	2·851	119
50	10·446	−442	11·646	−256	2·896	180
70	10·399	−506	11·629	−280	2·969	280
90	10·364	−554	11·644	−259	3·034	368
100	10·319	−615	11·619	−293	3·159	539

* $\Delta G_t°[A - B]_{sys}$ values are expressed in cal mol^{-1}.

[a] Taken from A. L. Bacarella, E. Grunwald, H. P. Marshall, and E. L. Purlee, *J. Org. Chem.*, 1955, **20**, 747.

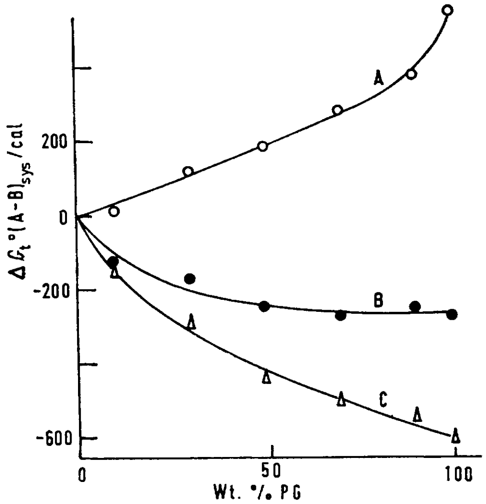

FIGURE 1 Variation of $\Delta G_t°(A - B)_{sys}$, for different acid–base systems as a function of wt. % PG at 25°: A, *p*-NAH+; B, TrisH+; C, Benzoic acid

The curves in Figure 1 and the corresponding data in Table 5 indicate that the behaviour of both types of acid in this solvent system is significantly different from that in aqueous organic solvents.[3,5,6,8] Thus, the values of $\Delta G_t°[BH^+ - B]_{sys}$, instead of passing through a minimum, as is usual in most aqueous organic solvents, with increasing proportion of the organic components, increase almost monotonically in the case of *p*-NAH+, and for TrisH+ decrease sharply at first and less so towards low concentrations of methanol. This may at first sight be taken as indirect evidence that the appearance of the minimum is in some way related to the unusual influence of water[5] on the proton transfer processes in aqueous organic mixtures. Similarly, the values of $\Delta G_t°[HA - A^-]_{sys}$ for the uncharged benzoic acid reflect more of the specificity of solute–solvent interactions than possible electrostatic effects, since the process involves the transfer of two charged species in the same direction [equation (6)].

The variations of the values of $\Delta G_t°(i)$ for the uncharged species (i) with increasing proportion of PG are illustrated in Figure 2. The corresponding values for HCl obtained from Part I[10] and those for the respective hydrochlorides of the bases (Table 6) computed by equation (7), are also illustrated in Figure 2.

$$\Delta G_t°(BHCl) = \Delta G_t°(HCl) + \Delta G_t°(B) - \\ \Delta G_t°[BH^+ - B]_{sys} \quad (7)$$

It can be seen from Figure 2 that the variation of $\Delta G_t°(HA)$ is almost unaffected by the change of solvent composition. This indicates that the relative solvation of benzoic acid either by methanol or PG does not differ

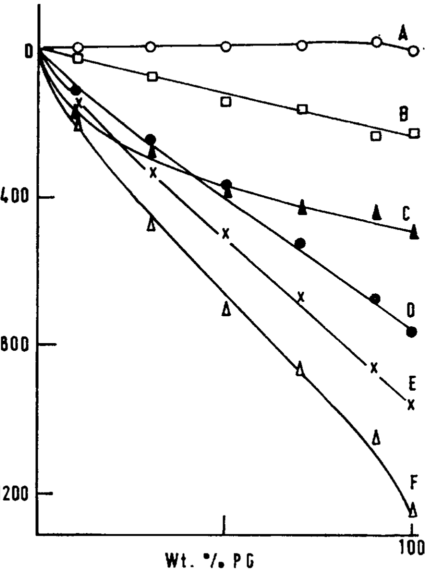

FIGURE 2 Variation of standard free energy of transfer $\Delta G_t°(i)$ of: A, Benzoic acid; B, *p*-NA; C, HCl; D, Tris; E, TrisHCl; F, *p*-NAHCl, from methanol to methanol–propylene glycol as a function of wt. % PG, at 25°

appreciably, and the relative solvophilicity of the phenyl group towards methanol or PG is balanced by the corresponding solvophilicity of $-CO_2H$ group towards PG or methanol.

The $\Delta G_t°(B)$ values for both the bases decrease almost monotonically with increasing proportion of PG, though the values for Tris are much more negative than the corresponding values for *p*-NA. This shows that the greater affinity of Tris for PG than for methanol is comparatively larger than that of *p*-NA. However, the situation is reversed for the corresponding hydrochlorides, *p*-NAHCl having larger affinity than TrisHCl for PG. Thus the values of $\Delta G_t°(BHCl)$ for TrisHCl are slightly more negative than the corresponding values for $\Delta G_t°(B)$, whereas the values for *p*-NAHCl are much more negative than for *p*-NA.

Since *p*-NA exists as a partially quinonoid form it is likely to be solvated through the positively charged amino-group preferentially by methanol, as ${}^{m}\Delta^- > {}^{g}\Delta^-$,[1] and at the same time through the negatively charged O-atoms of the $-NO_2$ group preferentially by the glycol, as ${}^{g}\delta^+ > {}^{m}\delta^+$.[1] As a result, the individual contributions to $\Delta G_t°(B)$ acting in opposition should impart a balancing effect. The observed $\Delta G_t°(B)$ values thus seem to indicate that the solvophilicity of *p*-NA towards PG probably exceeds that towards methanol.

In the case of Tris the solvation should largely involve the N-atom of the $-NH_2$ group and the bridge forming H-atom supplied by the solvent molecules. Moreover since ${}^{g}\delta^+ > {}^{m}\delta^+$,[1] the resulting magnitudes of $\Delta G_t°(B)$ should be increasingly negative, as are observed. The relative positions of the curves of $\Delta G_t°(B)$ for *p*-NA and Tris further suggest that the solvation of Tris is also likely to occur through three more centres corresponding to the three terminal $-OH$ groups in the molecule.[8]

Cl^- Being common, the relative positions of $\Delta G_t°(BHCl)$ (Figure 2) for the hydrochlorides of the bases suggest that the corresponding positions of $\Delta G_t°(BH^+)$ are the reverse of those for the pure bases. Utilizing the values of $\Delta G_t°(Cl^-)$,[1] $\Delta G_t°(BH^+)$ values for both the protonated amines have been evaluated, and are recorded in Table 7. In spite of the uncertainties in the individual ion values, it is interesting to note that $\Delta G_t°(BH^+)$ values are increasingly positive with increasing proportion of PG. This implies that like alkali-metal cations,[1] BH^+ ions are methanophilic. The values of $\Delta G_t°(TrisH^+)$ are more positive than the corresponding values for *p*-NAH$^+$. Since both the amines are primary, the protonated species will undergo solvation through the three H-atoms attached to the N-atom and the negatively charged O-atoms of solvent dipoles. For positively charged TrisH$^+$ solvation may also occur through the terminal $-OH$ groups, and the solvent dipoles with more negatively charged O-centres will have larger interaction energies. Thus, as ${}^{m}\Delta^- > {}^{g}\Delta^-$, one can visualize a similar picture for BH^+ as postulated for alkali-metal cations.[1] While the probable centres of solvation of BH^+ ions in the case of TrisH$^+$ are six those in the case of *p*-NAH$^+$ are only three. The solvophilicity of the phenyl group towards methanol and PG may or may not exert any detectable influence on $\Delta G_t°(BH^+)$ values for *p*-NAH$^+$. It would be expected that $\Delta G_t°(BH^+)$ values for TrisH$^+$ would have larger positive magnitudes compared to those for *p*-NAH$^+$.

TABLE 7

Standard free energies of transfer * of some individual ions from methanol to methanol–propylene glycol at 25°

Wt. % PG	$\Delta G_t°(BH^+)$ *p*-NAH$^+$	$\Delta G_t°(BH^+)$ TrisH$^+$	$\Delta G_t°(A^-)$ Benzoate ion	$\Delta G_t°(S^-)$ [a]
30	0·26	0·39	−0·75	−0·71
50	0·60	0·80	−1·35	−1·24
70	1·09	1·29	−2·01	−1·87
90	1·42	1·61	−2·54	−2·39
100	1·67	1·96	−3·03	−2·82

* $\Delta G_t°(i)$ Values are expressed in kcal g-ion^{-1}.

[a] The required values for $\Delta G_t°[SH - SH]_{sys}$ are from ref. 13.

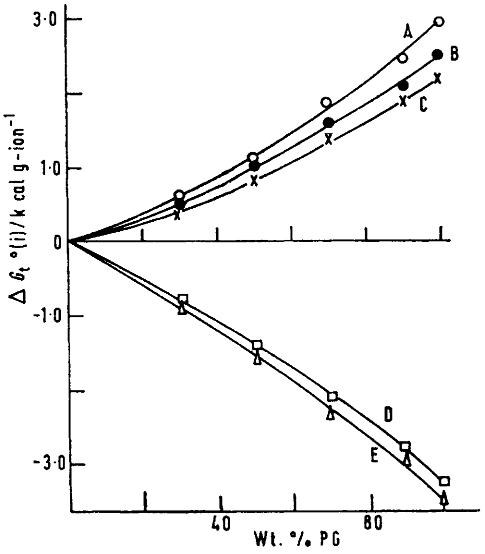

FIGURE 3 Variation of $\Delta G_t°(i)$ of some ions from methanol to methanol–propylene glycol at 25°: A, H$^+$; B, TrisH$^+$; C, *p*-NAH$^+$; D, S^- (lyate ion); E, A^- (benzoate ion)

Again utilizing the values of $\Delta G_t°(H^+)$,[1] the values of $\Delta G_t°(A^-)$ for the benzoate ion (A^-) have been evaluated and are reported in Table 7. The variation of these values with wt. % PG is also illustrated in Figure 3. It can be seen that $\Delta G_t°(A^-)$ values become increasingly negative with increasing proportion of PG. This suggests that like other anions [1] benzoate is glycophilic and is solvated through hydrogen bond formation involving positively charged H-centres of the solvent dipoles and the negative charge centre of $-CO_2^-$ group, as ${}^{g}\delta^+ > {}^{m}\delta^+$.

It appears that the resulting curves and magnitudes of $\Delta G_t°[A - B]_{sys}$ for the neutral acid HA as well as for the protonated amines (BH^+), different both in chemical nature and solvophilic character, are largely dictated by

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[13] K. K. Kundu, A. L. De, and M. N. Das, *J.C.S. Dalton*, 1972, 378.

the specific solute–solvent interaction besides the relative basicities embodied in the term $\Delta G_t°(H^+)$, especially where the ' electrostatic effect ' is relatively small.

As the values of $\Delta G_t°(H^+)$, which represent the basicity of the solvents with respect to that of methanol, become increasingly positive (Table 7, Part III), it has been inferred earlier [1] that PG is less basic than methanol and that the relative basicity of the solvent decreases with increasing proportion of PG.

Again, as indicated in Part II,[13] the values of $\Delta G_t°(S^-)$ (the acidity of the solvents relative to that of methanol), when evaluated by subtracting the values of $\Delta G_t°(H^+)$ from the corresponding values of $\Delta G_t°[SH - SH]_{sys}$,[13] are indeed found to be increasingly negative with increasing proportion of PG (Table 7). This suggests that the relative acidity of the mixed solvents increases with increasing proportion of PG. This implies that the acidity of PG is higher than that of methanol. This is also in accord with our earlier conjecture [1] namely, ${}^{g}\delta^{+} > {}^{m}\delta^{+}$, as visualized from the structural consideration of the isolated dipoles of PG and methanol. But whether the properties pertaining to isolated solvent molecules are equally meaningful for the bulk solvent is open to question.[14] The systematic trend in the observed results presented above seems to suggest that the general conclusions derived above may be considered as quite plausible.

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[0/1550 *Received, September 2nd,* 1970]

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