

Solvent Effects on the Dissociation of Benzoic Acid in Aqueous Mixtures of 2-Methoxyethanol and 1,2-Dimethoxyethane at 25 °C

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The thermodynamic dissociation constants (pK_T) of benzoic acid (HBz) have been determined at 25 °C in aqueous binary mixtures of 2-methoxyethanol (ME) and 1,2-dimethoxyethane (DME) at 10 wt% interval of organic co-solvent by solubility and spectrophotometric measurements. The pK_T values have been found to increase with an increase in the proportion of organic component in the solvent mixture, the effect being more pronounced in DME-H₂O mixtures. The results have been discussed in terms of the standard Gibbs energies of transfer of H⁺ from water to the mixed solvent [$\Delta G_T^\circ(H^+)$] and the relative values of the standard Gibbs energies of transfer of Bz⁻ [$\Delta G_T^\circ(Bz^-)$] and of HBz [$\Delta G_T^\circ(HBz)$] in all the solvent systems. The overall dissociation of benzoic acid is found to be governed by the specific ion-solvent interactions in the solvent media besides the relative solvent basicities.

Accurate solubility data have diverse applications in different branches of science and technology.^{1,2} This prompted us to determine accurately the solubility of benzoic acid, an antifungal preservative widely used in lotions and ointments, in pure and mixed solvents. In this paper an attempt has been made to determine the solubilities and thermodynamic dissociation constants of benzoic acid in ME-water and DME-water mixed solvents over the entire range of solvent compositions by means of pH and spectrophotometric measurements. The study is likely to enable us to determine the effect of solvents on the dissociation constants of benzoic acid and the free energies of transfer of benzoic acid and benzoate ion in these solvent mixtures.³

Experimental

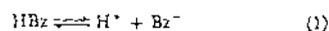
Benzoic acid (G.R.E. Merck) was recrystallised from alcohol and dried. 2-Methoxyethanol (Merck) was distilled twice and the middle fraction was used. 1,2-Dimethoxyethane (Fluka) was shaken well with FeSO₄ (A.R. BDH) for 1-2 h, decanted, and distilled. The distillate was refluxed for 12 h and then distilled over metallic sodium. Other chemicals were of analytical grade. For the determination of the solubility of benzoic acid at 25 °C in mixed solvents, saturated solutions of benzoic acid were prepared in the appropriate solvents at about 30 °C and filtered. The solution was transferred to a Campbell solubility apparatus* fitted with a sintered disc and a fine tube. The solutions were then allowed to equilibrate in a thermostatic bath maintained at 25 °C (± 0.01) for 24 h. After equilibrium was established, the solutions were filtered by inverting the apparatus (while keeping it in the thermostat). The benzoic acid content of the filtered solution was determined by titration against standard NaOH solution. The process was repeated several times for each set of measurements. The errors involved in the solubility measurements are in the range 0.1-0.3%. The solubility was also determined spectrophotometrically by measuring the OD values at 272 nm, the wavelength for the absorption maximum of benzoic acid. The band at 272 nm was assumed to be the B-band⁴ of PhCO₂H. The solubility values determined by the above two methods are within the limit of $\pm 0.2\%$. The average values are presented in column 3 of Tables 1 and 2.

* Formerly called dielectric constant.

For the determination of the dissociation constant of benzoic acid, the hydrogen ion concentration of the saturated solutions of benzoic acid in mixed solvents was measured pH-metrically using combined glass and calomel electrodes. The glass electrode has been found to function satisfactorily in aqueous binary mixtures of ME and DME. The calibration of the glass electrode and 'correction factors' in different percentages of the mixed solvents have been determined in the way suggested by Van Ultert and Haas,⁵ Irving and Manhot,⁷ and have also been described by us previously.⁸ The correction factor has been found to be slightly dependent on the nature of the solvent and the aging and asymmetry potential of the glass electrode. However, consistent and reproducible results are obtained if the 'correct factors' are determined before each set of measurements. The error range for pH measurements is usually ± 0.02 at low percentages of ME-water or DME-water mixtures and ± 0.03 at higher percentages of the mixed solvents. The relative permittivity⁹ of the solvent mixtures were taken from the literature.^{9,10}

Results and Discussion

The thermodynamic dissociation constant for the reaction



can be written as

$$K_T = \frac{C_{H^+} C_{Bz^-}}{C_{HBz}} \times \frac{\gamma_{H^+}}{\gamma_{HBz}} = \frac{C}{[C]_T - C_{H^+}} \times \frac{\gamma_{H^+}}{\gamma_{HBz}} \quad (2)$$

where $[C]_T$ = total benzoic acid concentration and C_{H^+} = concentration of H⁺ in the saturated experimental solutions determined pH-metrically. The activity coefficients of the ions at different concentrations were determined using the Davies equation,¹¹

$$-\log \gamma_{\pm} = Az_{\pm} z_{\pm} \mu^2 / (1 + \mu) - 0.2\mu \quad (3)$$

with appropriate A -values in each solvent to take into account the changed relative permittivity of the mixed solvents. The

Table 1. Solubility and pK_T^* values of benzoic acid in ME-water mixtures at 25 °C.

Wt% of ME	$10^2 \epsilon_1^1$	$[C_T]^*$ /mol dm ⁻³	Corrected pH of saturated solution	λ	$-2 \log \gamma_{\pm}$	pK_T^*	pK_T^*	Average pK_T^*
00	1.27	0.0285	2.90	0.509	0.03	4.23	4.21	4.22
10	1.34	0.0444	2.97	0.549	0.03	4.60	4.57	4.59
20	1.43	0.0782	2.90	0.606	0.04	4.73	4.69	4.71
30	1.56	0.1422	2.87	0.691	0.05	4.94	4.90	4.92
40	1.74	0.3973	2.84	0.813	0.06	5.34	5.31	5.33
50	1.99	0.5314	2.91	0.995	0.07	5.61	5.58	5.60
60	2.37	1.2555	2.85	1.293	0.09	5.89	5.87	5.88
70	2.92	1.4429	2.99	1.768	0.11	6.25	6.24	6.25
80	3.77	1.5965	3.30	2.593	0.11	6.91	6.88	6.90
90	5.26	2.2988	3.52	4.278	0.14	7.54	7.55	7.55
100	5.91	3.0535	—	5.087	—	—	—	—

* The uncertainty in the pK_T^* value is ± 0.02 units. * Total concentration of benzoic acid. * From solubility data. * Spectrophotometric.

Table 2. Solubility and pK_T^* values of benzoic acid in DME-water mixtures at 25 °C.

Wt% of DME	$10^2 \epsilon_1^1$	$[C_T]^*$ /mol dm ⁻³	Corrected pH of saturated solution	λ	$-2 \log \gamma_{\pm}$	pK_T^*	pK_T^*	Average pK_T^*
10	1.40	0.0486	2.93	0.587	0.04	4.57	4.54	4.56
20	1.56	0.1292	2.87	0.691	0.05	4.90	4.89	4.90
30	1.76	0.5093	2.90	0.827	0.06	5.57	5.57	5.57
40	2.01	1.2322	2.85	1.009	0.07	5.86	5.83	5.85
50	2.35	2.1032	2.82	1.277	0.10	6.06	6.03	6.05
60	2.79	2.7123	2.94	1.652	0.11	6.42	6.41	6.42
70	3.58	2.8909	3.05	2.401	0.14	6.70	6.67	6.69
80	4.79	3.5260	3.38	3.714	0.15	7.46	7.43	7.45
90	7.42	4.4288	3.90	7.160	0.16	8.61	8.62	8.62
100	14.12	3.2025	—	13.811	—	—	—	—

* The uncertainty in the pK_T^* value is ± 0.03 units. * Total benzoic acid concentration. * From solubility data. * Spectrophotometric.

activity coefficients using Debye-Huckel limiting law have also been attempted but the γ_{\pm} values by the two methods differ only in the third decimal place.

The dissociation constants of benzoic acid in the mixed solvents were also determined spectrophotometrically in the way suggested by Robinson and Biggs.¹² For this method a number of buffer solutions of known pH were employed. According to Robinson and Stokes¹³ the value of the pH of the buffer solution should be equal to the pK of the organic acid. In this investigation the range of possible pK values at 25 °C is 4.2–8.6. We have used the acetic acid-sodium acetate buffer for the pH range 4.2–4.7 and phosphate buffer solution e.g. 0.06 mol dm⁻³ potassium dihydrogen phosphate and 0.06 mol dm⁻³ disodium hydrogen phosphate for measurements outside this range. The experimental pH of the buffer solution used was close to the value of the pK of the acid in each percentage of mixed solvent. The pH values were measured with an ECIL pH meter with an accuracy of ± 0.01 pH unit. The spectrophotometric measurements were recorded with a Shimadzu UV-240 spectrophotometer maintained at 25 °C. The analytical wavelength for spectrophotometric measurement was 240 nm and the concentration of the acid was $(5-9) \times 10^{-5}$ mol dm⁻³. The thermodynamic dissociation constants (pK_T^*) of benzoic acid calculated from solubility data and determined by spectrophotometric methods in aqueous binary mixtures of ME and DME are recorded in columns 7 and 8 of Tables 1 and 2, respectively.

The free energies of transfer for the dissociation of benzoic acid were calculated using equation (4).

$$\begin{aligned} \delta(\Delta G^{\circ}) &= \Delta G_{\text{Bz}^-}^{\circ} - \Delta G_{\text{HBz}}^{\circ} \\ &= -2.303RT(\log K_{\text{Bz}^-} - \log K_{\text{HBz}}) \end{aligned} \quad (4)$$

The free energy of transfer of neutral benzoic acid is given by

$$\Delta G_{\text{HBz}}^{\circ} = \Delta G_{\text{HBz}}^{\circ} - \Delta G_{\text{HBz}}^{\circ} = -2.303RT \log \frac{C_1}{C_w} \times \frac{f_{\text{HBz}}}{f_{\text{HBz}}} \quad (5)$$

where C_1 and C_w are the molar concentrations of undissociated benzoic acid in the solvent (s) and water (w), respectively, in a saturated solution. These are equal to the total quantity of the acid in the saturated solution less the concentration of the dissociated acid. Since the benzoic acid is present in its saturated state in respective solvents, the ratio of activity coefficient of neutral benzoic acid in the mixed solvent and in water has been assumed to be unity.¹⁴

The free-energy changes accompanying the transfer of benzoate ion from the standard state in water to that in the solvents have been calculated from the following relations:¹⁵

$$\delta(\Delta G^{\circ}) = \Delta G_{\text{H}^+}^{\circ} + \Delta G_{\text{Bz}^-}^{\circ} - \Delta G_{\text{HBz}}^{\circ} \quad (6)$$

or

$$\Delta G_{\text{Bz}^-}^{\circ} = \delta(\Delta G^{\circ}) - \Delta G_{\text{H}^+}^{\circ} + \Delta G_{\text{HBz}}^{\circ} \quad (7)$$

$\Delta G_{\text{H}^+}^{\circ}$ in equation (7) stands for the free-energy change for the transfer of 1 mol of H^+ ion from the standard state in water to the standard state in the solvent concerned and may be taken as a measure of the basicity^{16,17} of the solvent with respect to that of water. $\Delta G_{\text{H}^+}^{\circ}$ values are limited to a few (mostly low) percentages of ME-H₂O and DME-H₂O mixtures in the

Table 3. Free energies of transfer* of benzoate ion, $\Delta G_f^{\circ}(\text{Bz}^-)$, in solvent-water mixtures at 25 °C.

Wt% of solvent	$\Delta G_f^{\circ}(\text{HBz})$		$\delta(\Delta G_f^{\circ})$		$\Delta G_f^{\circ}(\text{H}^+)$		$\Delta G_f^{\circ}(\text{Bz}^-)$	
	ME	DME	ME	DME	ME	DME	ME	DME
10	-1.15	-1.38	2.11	1.94	-1.67	-1.67	2.03	2.23
20	-2.58	-3.84	2.79	3.88	-1.88	-2.57	2.09	2.61
30	-4.08	-7.16	3.99	7.70	-2.40	-3.26	2.31	3.70
40	-6.54	-9.45	6.33	9.30	-2.43	-3.99	2.12	3.84
50	-7.36	-10.77	7.87	10.44	-2.99	-4.43	3.50	4.10
60	-9.49	-11.40	9.47	12.55	-2.93	-4.57	2.91	5.72
70	-9.84	-11.56	11.58	14.09	-2.96	-4.15	4.70	6.68
80	-10.09	-12.06	15.29	18.43	-2.25	-1.42	7.45	7.79
90	-10.95	-12.62	19.00	25.11	1.75	5.46	6.26	7.03
100	-11.69	-11.52	--	--	--	--	--	--

* In kJ mol^{-1} . * Uncertainties in ΔG_f° values are of the order $\pm 0.17 \text{ kJ mol}^{-1}$.

literature. We prefer to use the $\Delta G_f^{\circ}(\text{H}^+)$ values determined by us based on the experimental measurements of transfer of BH^+ ($\text{B} = 2,2'$ -bipyridine or 1,10-phenanthroline) and related data.¹⁸ It is to be noted that $\Delta G_f^{\circ}(\text{H}^+)$ values are always determined using extra thermodynamic assumptions with their inherent limitations. But $\Delta G_f^{\circ}(\text{H}^+)$ values determined by us are consistent and in good agreement both qualitatively and almost quantitatively at low percentages of ME and DME with the available literature values^{19,20} (based on TATB assumption).

Tables 1 and 2 show that the solubility values and pK_f values of benzoic acid increase progressively with an increase in the percentage of ME or DME in the solvent. A comparison with other mixed solvents shows that the solubility values in ME-H₂O are less (but greater in DME-H₂O) than the corresponding values in alcohol-water mixtures.^{21,22} The $\Delta G_f^{\circ}(\text{H}^+)$ values becomes increasingly negative in going from water to ME-H₂O and DME-H₂O mixtures indicating that the binary mixtures are more basic than water. The basicity reaches a maximum at 80 wt% of ME (ME:H₂O ca. 1:1) and at 70 wt% DME (DME:H₂O ca. 1:2); the basicity then decreases and ultimately becomes less basic than water at about 90 wt% of organic solvents. The results also coincide with the fact that DME-H₂O is more basic than ME-H₂O mixtures.¹⁹ The changes in basicity of solvent mixtures are reflected in the pK_f values of benzoic acid. Thus the pK_f values of benzoic acid in ME-H₂O mixtures are less than those in DME-H₂O mixtures. The two solvents also differ in their relative permittivity values and solvating capabilities. The relative permittivity values of ME-water mixtures are greater than those of DME-water mixtures of similar mol% non-aqueous component; electrostatic interactions thus impart a less positive contribution to $\Delta G_f^{\circ}(\text{Bz}^-)$ in ME-H₂O than in DME-H₂O resulting in more ionization in the former than in the latter solvent system (Table 3).

The solvent effect on the dissociation equilibrium of HBz can also be seen from equation (7). The values of $\delta[\Delta G_f^{\circ}(\text{HBz} - \text{Bz}^-)]$ increase with increase in mol% of ME or DME, the rate of increase being larger at higher percentage of organic co-solvents. Since the dissociation of benzoic acid produces extra charge, it is expected that the $\delta[\Delta G_f^{\circ}(\text{HBz} - \text{Bz}^-)]$ value should necessarily increase with increase in wt% of ME or DME.

Table 3 shows that $\Delta G_f^{\circ}(\text{HBz})$ becomes increasingly negative with an increase in mol% of ME or DME, the values being less negative in ME than DME. This indicates that benzoic acid is stabilized in these mixed solvents, primarily through dispersion forces.²³ Since the number of methyl groups (relative hydrophilic -OH groups) is greater in DME, a greater

dispersion effect is expected in DME-H₂O and this may be largely responsible for the greater stability of HBz [more negative $\Delta G_f^{\circ}(\text{HBz})$] in DME-H₂O, as observed. The $\Delta G_f^{\circ}(\text{Bz}^-)$ values are predominantly positive, in agreement with the fact that ΔG_f° of anions are usually positive.^{24,25} The result indicates that the transfer of $\Delta G_f^{\circ}(\text{Bz}^-)$ is non-spontaneous from water to organic solvents.

In conclusion, the overall dissociation behaviour of benzoic acid in these two solvent systems is dictated by specific solute-solvent interactions as well as the effects of relative solvent basicity.

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Solubilities and Free Energies of Transfer for *p*-Nitro- and *p*-Chloro-benzoic Acids in Aqueous Mixtures of 2-Methoxyethanol and 1,2-Dimethoxyethane

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The solubilities of the *p*-nitro- and *p*-chloro-benzoic acids in 2-methoxyethanol (ME) + water and 1,2-dimethoxyethane (DME) + water mixtures at 25° have been measured. The thermodynamic dissociation constants of the acids have been determined from pH and solubility measurements. The free energies of transfer of *p*-nitro- and *p*-chloro-benzoate ions [$\Delta G^\circ_f(A^-)$] from water to mixed solvent systems have been evaluated from the corresponding ΔG°_f values of the acids and $\Delta G^\circ_f(H^+)$ values previously determined in all the solvent systems. The overall dissociation behaviour of these acids is found to be dictated by the specific solute-solvent interactions besides the relative solvent basicities.

SOLUBILITIES and dissociation of substituted-benzoic acids were reported earlier^{1,2} in aqueous mixtures of methanol and ethanol. In this paper we report our studies on solubilities and dissociation constants of *p*-nitro- and *p*-chloro-benzoic acids in a series of aqueous mixtures of 2-methoxyethanol (ME) and 1,2-dimethoxyethane (DME). Since the solvent effect involves $\Delta G^\circ_f(H^+)$, and $\Delta G^\circ_f(A^-)$ values have been found to be different between alcohols and studied solvent systems, it would be interesting to study the proton transfer processes in this particular class of solvent media.³ Thus a study of dissociation in these two solvent systems may be expected to reveal the specific molecular picture of solvation of the species involved in the ionisation equilibria.

Experimental

ME (G.R., E. Merck) was distilled twice and the middle fraction was utilised. DME (Fluka, Purum) was first shaken with FeSO₄ (AnalaR) for 1-2 h, decanted and then distilled; the distillate then refluxed for 12 h and distilled over metallic sodium. Other chemicals were of analytical grade. Double-distilled water from all-glass distilling sets was used for preparing the solutions.

p-Chlorobenzoic acid (Fluka, Puriss) and *p*-nitrobenzoic acid (G.R., E. Merck) were crystallised from ethanol-water mixtures. The purity of the samples was tested by melting point determination. The solubilities of *p*-nitro- and *p*-chloro-benzoic acids were determined with the help of a Campbell solubility apparatus⁴. The solutions were taken in stoppered bottles, and shaken in a mechanical shaker for 12 h at room temperature (27-35°). The bottles were then thermostated at 25±0.01° for 24 h with occasional shaking and then filtered by

inversion of the apparatus at the same temperature. The concentrations of the saturated solutions from each bottle were determined by titration with a standard (0.1-0.01 *N*) caustic soda solution using phenolphthalein as indicator. The operations were repeated until successive results were in agreement. Four sets of experiments were performed for each percentage of the solvent mixture. The solubilities of *p*-nitro- and *p*-chloro-benzoic acids in molarity are recorded in Tables 1 and 2, respectively. The solubilities in water are found to be 0.0025 and 0.0008 mol dm⁻³, respectively (Tables 1 and 3) which agree fairly well with the literature values^{5,6}.

pH of the saturated solutions of the acids for each percentage of the mixed solvents were measured using a ECIL pH-meter having an accuracy of ±0.01 pH unit. Proper calibration of the glass-calomel electrode and appropriate corrections⁷ for the change of the solvent compositions were made. The measurements were made at 25±0.01°. The dielectric constants of the solvent mixtures were taken from the literature^{6,7}.

Results and Discussion

The thermodynamic dissociation constant for the reaction,



(A⁻ = substituted benzoate ion) can be written as

$$K_T = \frac{C_{H^+} \times C_{A^-}}{C_{HA}} \times \frac{f_{\pm}^2}{f_{HA}} = \frac{C_{H^+}^2}{[C]_T - C_{H^+}} \times f_{\pm}^2 \quad (2)$$

where, $[C]_T$ is total *p*-nitro- or *p*-chloro-benzoic acid concentration, and C_{H^+} the concentration of $[H^+]$ in the saturated experimental solutions determined pH-metrically. The mean molar activity coefficients of the ions at different concentrations in aqueous

TABLE 1—SOLUBILITY AND *pK* VALUES OF *p*-NITROBENZOIC ACID IN ME+ WATER AT 25°

ME wt%	$1/\epsilon \times 10^3$	<i>A</i>	Solubility mol dm ⁻³	$-2\log f_{\pm}$	Corrected pH	<i>pK</i>	<i>pK_T</i>
00	1.27	0.509	0.002 5 (0.002 516) ^a	0.02	3.12	3.48	3.50
10	1.84	0.549	0.002 8	0.03	3.13	3.57	3.60
20	1.43	0.606	0.003 9	0.03	3.12	3.73	3.76
30	1.56	0.691	0.011 9	0.04	3.05	4.16	4.20
40	1.74	0.813	0.014 6	0.04	3.14	4.42	4.46
50	1.99	0.995	0.025 9	0.05	3.24	4.88	4.93
60	2.37	1.293	0.051 8	0.05	3.23	5.17	5.23
70	2.92	1.768	0.093 0	0.06	3.33	5.63	5.71
80	3.77	2.593	0.198 4	0.10	3.43	6.15	6.25
90	5.26	4.278	0.373 9	0.12	3.72	7.01	7.13
100	5.91	5.087	0.488 4	—	—	—	—

^aRef. 2.TABLE 2—SOLUBILITY AND *pK* VALUES OF *p*-NITROBENZOIC ACID IN DME+ WATER AT 25°

DME wt%	$1/\epsilon \times 10^3$	<i>A</i>	Solubility mol dm ⁻³	$-2\log f_{\pm}$	Corrected pH	<i>pK</i>	<i>pK_T</i>
10	1.40	0.587	0.003 1	0.03	3.15	3.68	3.71
20	1.56	0.691	0.004 2	0.04	3.15	3.84	3.88
30	1.76	0.827	0.012 3	0.05	3.12	4.30	4.36
40	2.01	1.009	0.039 4	0.05	3.07	4.59	4.64
50	2.35	1.277	0.037 9	0.06	3.19	4.95	5.01
60	2.79	1.652	0.182 1	0.09	3.09	5.44	5.53
70	3.58	2.401	0.330 0	0.12	3.15	5.82	5.94
80	4.79	3.714	0.653 4	0.15	3.37	6.56	6.71
90	7.42	7.160	0.750 9	0.19	3.75	7.38	7.57
100	14.12	18.811	0.832 4	—	—	—	—

TABLE 3—SOLUBILITY AND *pK* VALUES OF *p*-CHLOROBENZOIC ACID IN ME+ WATER AT 25°

Solvent wt%	$1/\epsilon \times 10^3$	<i>A</i>	Solubility mol dm ⁻³	$-2\log f_{\pm}$	Corrected pH	<i>pK</i>	<i>pK_T</i>
00	1.27	0.509	0.000 8 (0.000 797) ^a	0.01	3.62	3.99	4.00
10	1.34	0.549	0.001 3	0.01	3.78	4.61	4.63
20	1.43	0.606	0.002 6	0.02	3.70	4.78	4.80
30	1.56	0.691	0.005 6	0.02	3.67	5.07	5.09
40	1.74	0.813	0.011 2	0.03	3.62	5.28	5.31
50	1.99	0.995	0.016 2	0.03	3.75	5.71	5.74
60	2.37	1.293	0.033 4	0.03	3.85	6.22	6.25
70	2.92	1.768	0.053 5	0.04	3.87	6.47	6.51
80	3.77	2.593	0.126 8	0.06	3.92	6.94	7.00
90	5.26	4.278	0.258 9	0.07	4.13	7.67	7.74
100	5.91	5.087	0.403 1	—	—	—	—

^aRef. 4.TABLE 4—SOLUBILITY AND *pK* VALUES OF *p*-CHLOROBENZOIC ACID IN DME+ WATER AT 25°

DME wt%	$1/\epsilon \times 10^3$	<i>A</i>	Solubility mol dm ⁻³	$-2\log f_{\pm}$	Corrected pH	<i>pK</i>	<i>pK_T</i>
10	1.40	0.587	0.001 5	0.01	3.82	4.77	4.78
20	1.56	0.691	0.003 0	0.02	3.83	5.12	5.14
30	1.76	0.827	0.007 1	0.02	3.72	5.28	5.30
40	2.01	1.009	0.020 2	0.03	3.67	5.64	5.67
50	2.35	1.277	0.048 4	0.04	3.65	5.98	6.02
60	2.79	1.652	0.094 6	0.05	3.71	6.39	6.44
70	3.58	2.401	0.263 1	0.06	3.74	6.90	6.96
80	4.79	3.714	0.510 7	0.07	4.09	7.88	7.96
90	7.42	7.160	0.631 8	0.09	4.37	8.54	8.63
100	14.12	18.811	1.036 9	—	—	—	—

and mixed solvents have been determined using the Debye-Hückel limiting law,

$$-\log f_{\pm} = A \sqrt{\mu} \quad (3)$$

with appropriate A values in mixed solvents calculated from the dielectric constant values in the literature. The activity coefficients of neutral benzoic acid have been assumed to be unity in the saturated solutions of benzoic acid in the respective solvents. The ionic strengths of the solutions have been determined from C_{H^+} values based on equation (1). The dissociation constant values of both the acids determined by the solubility measurements in aqueous mixtures of ME and DME have been recorded in Tables 1-4.

The free energies of transfer for the dissociation of substituted benzoic acids have been calculated using equation (4),

$$\Delta G_t^{\circ}(1) = \Delta G_s^{\circ} - \Delta G_w^{\circ} \\ = -2.303 RT [\log K_{T(s)} - \log K_{T(w)}] \quad (4)$$

The standard free energies of transfer of p -nitro- and p -chloro-benzoic acids from water to mixed solvents were calculated using the relation,

$$\Delta G_t^{\circ}(\text{HA}) = \Delta G_s^{\circ}(\text{HA}) - \Delta G_w^{\circ}(\text{HA}) \\ = -2.303 RT \log \frac{C_s}{C_w} \times \frac{f_s(\text{HA})}{f_w(\text{HA})} \quad (5)$$

where, C_s and C_w are solubilities of the acid in water and respective solvents in molar scale. However, the validity of this relation depends on the assumption that the ratio of the activity coefficients of the neutral acid in the saturated solutions in the mixed solvent and in water is unity⁸.

The free energy change accompanying the transfer of benzoate ion from the standard state in water to that in mixed solvent has been calculated using equation (7),

$$\Delta G_t^{\circ}(1) = \Delta G_t^{\circ}(\text{H}^+) + \Delta G_t^{\circ}(\text{A}^-) - \Delta G_t^{\circ}(\text{HA}) \quad (6)$$

$$\Delta G_t^{\circ}(\text{A}^-) = \Delta G_t^{\circ}(1) - \Delta G_t^{\circ}(\text{H}^+) + \Delta G_t^{\circ}(\text{HA}) \quad (7)$$

$\Delta G_t^{\circ}(\text{H}^+)$ stands for free energy change for the transfer of H^+ from the standard state in water to that in the solvent and may be taken as a measure of the basicity of the solvents with respect to that of water. The $\Delta G_t^{\circ}(\text{H}^+)$ values have been determined in our laboratory based on the experimental measurements of transfer of BH^+ ($\text{B} = 2,2'$ -bipyridyl) from water to mixed solvents with necessary physical parameters determined as well as taken from the literature⁹. The values of $\Delta G_t^{\circ}(\text{HA})$, $\Delta G_t^{\circ}(\text{H}^+)$, $\Delta G_t^{\circ}(1)$ and $\Delta G_t^{\circ}(\text{A}^-)$ have been recorded in Tables 5-8.

The solubility values (Tables 1-4) of the acids increase with the increase in the organic solvent content of the mixed solvents and show linear relationship when plotted against (i) mole-fraction and (ii) $1/\epsilon$ well upto ~ 70 wt% beyond which deviation occurs. It is observed that the solubility increases with decreasing dielectric constant of the medium. This increase might be due to the solute-solvent interactions, and the preferential solvation

TABLE 5—FREE ENERGY OF TRANSFER OF ANION $\Delta G_t^{\circ}(\text{A}^-)$ OF p -NITROBENZOIC ACID (in kJ) IN ME+H₂O AT 25°

ME wt%	$\Delta G_t^{\circ}(\text{HA})$	$\Delta G_t^{\circ}(1)$	$\Delta G_t^{\circ}(\text{H}^+)$	$\Delta G_t^{\circ}(\text{A}^-)$
10	-0.28	0.57	-1.33	1.62
20	-1.10	1.48	-2.47	2.85
30	-3.87	3.99	-3.48	3.60
40	-4.37	5.48	-4.19	5.30
50	-5.79	8.16	-5.69	8.06
60	-7.51	9.87	-7.06	9.42
70	-8.96	12.61	-9.14	12.79
80	-10.84	16.32	-11.63	17.11
90	-12.41	20.71	-13.23	21.53
100	-13.07	—	—	—

TABLE 6—FREE ENERGY OF TRANSFER OF ANION $\Delta G_t^{\circ}(\text{A}^-)$ OF p -NITROBENZOIC ACID (in kJ) IN DME+H₂O AT 25°

DME wt%	$\Delta G_t^{\circ}(\text{HA})$	$\Delta G_t^{\circ}(1)$	$\Delta G_t^{\circ}(\text{H}^+)$	$\Delta G_t^{\circ}(\text{A}^-)$
10	-0.53	1.20	-2.15	2.82
20	-1.29	2.17	-3.55	4.53
30	-3.95	4.85	-5.09	5.99
40	-6.11	6.50	-6.78	7.17
50	-6.74	8.62	-8.48	10.36
60	-10.63	11.58	-10.27	11.22
70	-12.10	13.92	-12.82	14.64
80	-13.79	18.32	-14.63	19.16
90	-14.11	23.22	-17.62	25.70
100	-14.39	—	—	—

TABLE 7—FREE ENERGY OF TRANSFER OF ANION $\Delta G_t^{\circ}(\text{A}^-)$ OF p -CHLOROBENZOIC ACID (in kJ) IN ME+H₂O AT 25°

ME wt%	$\Delta G_t^{\circ}(\text{HA})$	$\Delta G_t^{\circ}(1)$	$\Delta G_t^{\circ}(\text{H}^+)$	$\Delta G_t^{\circ}(\text{A}^-)$
10	-1.20	3.54	-1.33	3.67
20	-2.92	4.56	-2.47	4.11
30	-4.82	6.22	-3.48	4.88
40	-6.54	7.47	-4.19	5.12
50	-7.45	9.93	-5.69	8.17
60	-9.25	12.84	-7.06	10.65
70	-10.42	14.32	-9.14	13.04
80	-12.55	17.12	-11.63	16.20
90	-14.32	21.34	-13.23	20.25
100	-15.42	—	—	—

TABLE 8—FREE ENERGY OF TRANSFER OF ANION $\Delta G_t^{\circ}(\text{A}^-)$ OF p -CHLOROBENZOIC ACID (in kJ) IN DME+H₂O AT 25°

DME wt%	$\Delta G_t^{\circ}(\text{HA})$	$\Delta G_t^{\circ}(1)$	$\Delta G_t^{\circ}(\text{H}^+)$	$\Delta G_t^{\circ}(\text{A}^-)$
10	-1.56	4.45	-2.15	5.04
20	-3.28	6.50	-3.55	6.87
30	-5.41	7.42	-5.09	7.10
40	-8.00	9.53	-6.78	8.31
50	-10.17	11.53	-8.48	9.84
60	-11.83	13.92	-10.27	12.86
70	-14.36	16.89	-12.82	15.35
80	-16.00	22.54	-14.63	21.17
90	-16.53	26.42	-17.62	27.51
100	-17.76	—	—	—

of the solute molecules by the organic solvent at the higher percentages of the mixed solvents may cause this deviation. However, it is interesting to note that the solubility of the respective acid is greater in DME or DME+H₂O mixtures compared to that in ME or ME+H₂O mixtures, the values

being greater for *p*-nitrobenzoic acid than *p*-chlorobenzoic acid. The number of CH₂ groups relative to that of hydrophilic OH groups being greater in DME, a greater dispersion effect is expected in DME+H₂O and this may be largely responsible for the greater stability of the acids (more negative $\Delta G_f^\circ(\text{HA})$) in DME+H₂O compared to ME+H₂O as observed. Again, the difference in the behaviour of the solubilities of *p*-chloro- and *p*-nitro-benzoic acids in the solvent systems can be qualitatively explained on the basis of solute-solvent dipole interactions and the relative solvent basicities. The $\Delta G_f^\circ(\text{H}^+)$ values are found to be increasingly negative both in ME+H₂O and DME+H₂O indicating increased stabilisation of H⁺ in the mixed solvents. The $\Delta G_f^\circ(\text{H}^+)$ values indicate that the solvent mixtures become increasingly basic in character compared to water as the organic solvent component increases. The changes of the basicity of the solvent mixtures are reflected in the free energy of transfer of H⁺ ion and the solubility values of the acids. Presence of nitro group than the chloride group in the *para*-position of the benzene ring increases the polarity of that solute molecule to a large extent and the basicity is much greater in DME than in ME leading to an increase in solubility with increase in DME content of the solvent medium, the rate of increase being larger at higher percentage of the mixed solvents.

It can be seen from Tables that the pK_T values increase continuously with the increase in the percentage of organic solvent and show a linear relationship when plotted against $1/\epsilon$ at low percentages but deviations occur at higher percentages. It is also observed that the pK_T values are in the order, DME+H₂O > ME+H₂O mixtures, the values being greater for *p*-chlorobenzoic acid than *p*-nitrobenzoic acid, contrary to the solubility values of these acids in these solvent mixtures. The two solvents differ in their dielectric constant values and solvating capabilities. The dielectric constant of ME+H₂O is greater than DME+H₂O of similar mol % non-aqueous component, electrostatic interactions thus impart less positive contribution to $\Delta G_f^\circ(\text{A}^-)$ in ME+H₂O than in DME+H₂O resulting in more ionisation in the former than in the latter solvent system. However, the behaviour as reflected in the relative pK_T values of *p*-chloro-

and *p*-nitro-benzoic acids may be attributed to relative destabilisation of anions in these solvent systems and the results indicate their order to be Cl⁻ > NO₂⁻. The destabilisation of the anions are the results of decreased acidity of aquo-cosolvent mixture.

Tables 5-8 show the increasingly negative magnitudes of $\Delta G_f^\circ(\text{HA})$ with increase in mol% of ME or DME, the values being less negative in ME than DME. This indicates the stabilisation of these acids in these mixed solvents, primarily through dispersion forces¹⁰ and the basicity of the solvents are reflected on the ΔG_f° values, DME+H₂O is less acidic than ME+H₂O. The $\Delta G_f^\circ(\text{A}^-)$ values are predominantly positive and it is in agreement with the fact that ΔG_f° of anions are usually positive¹¹. The results indicate that the transfer of $\Delta G_f^\circ(\text{A}^-)$ is non-spontaneous from water to mixed solvents.

In conclusion, it may be said that the overall dissociation behaviour in these two solvent systems is dictated by specific solute-solvent interactions besides the effects of relative solvent basicities.

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