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–H_2O 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 anti-fungal 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 $FeSO_4$ (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[4] fitted with a sintered disc and a fine tube. The solutions were then allowed to equilibriate 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-band[5] of $PhCO_2H$. The solubility values determined by the above two methods are within the limit of ±0.2%. The average values are presented in column 3 of Tables 1 and 2.

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 Uitert and Haas,[6] 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 permittivity† of the solvent mixtures were taken from the literature.[9,10]

Results and Discussion

The thermodynamic dissociation constant for the reaction

$$HBz \rightleftharpoons H^+ + Bz^- \qquad (1)$$

can be written as

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

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]

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

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

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† Formerly called dielectric constant.

Table 1. Solubility and $pK_T{}^a$ values of benzoic acid in ME–water mixtures at 25 °C.

Wt% of ME	$10^2\ \varepsilon_r^{-1}$	$[C_T]^b$/mol dm^{-3}	Corrected pH of saturated solution	A	$-2 \log \gamma_\pm$	$pK_T{}^c$	$pK_T{}^d$	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	—	—	—	—

[a] The uncertainty in the pK_T value is ±0.02 units. [b] Total concentration of benzoic acid. [c] From solubility data. [d] Spectrophotometric.

Table 2. Solubility and $pK_T{}^a$ values of benzoic acid in DME–water mixtures at 25 °C.

Wt% of DME	$10^2\ \varepsilon_r^{-1}$	$[C_T]^b$/mol dm^{-3}	Corrected pH of saturated solution	A	$-2 \log \gamma_\pm$	$pK_T{}^c$	$pK_T{}^d$	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	—	18.811	—	—	—	—

[a] The uncertainty in the pK_T value is ±0.03 units. [b] Total benzoic acid concentration. [c] From solubility data. [d] Spectrophotometric.

activity coefficients using Debye–Hückel limiting law have also been attempted but the $\gamma_\pm$ 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 Stokes[13] 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) × 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).

$$\begin{aligned}\delta(\Delta G^\circ) &= \Delta G_s^\circ - \Delta G_w^\circ \\ &= -2.303RT[\log K_{T(s)} - \log K_{T(w)}] \qquad (4)\end{aligned}$$

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

$$\begin{aligned}\Delta G_t^\circ(\mathrm{HBz}) &= \Delta G_s^\circ(\mathrm{HBz}) - \Delta G_w^\circ(\mathrm{HBz}) \\ &= -2.303RT \log \frac{C_s}{C_w} \times \frac{f_s(\mathrm{HBz})}{f_w(\mathrm{HBz})} \qquad (5)\end{aligned}$$

where C_s 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]

$$\delta(\Delta G^\circ) = \Delta G_t^\circ(\mathrm{H}^+) + \Delta G_t^\circ(\mathrm{Bz}^-) - \Delta G_t^\circ(\mathrm{HBz}) \qquad (6)$$

or

$$\Delta G_t^\circ(\mathrm{Bz}^-) = \delta(\Delta G^\circ) - \Delta G_t^\circ(\mathrm{H}^+) + \Delta G_t^\circ(\mathrm{HBz}) \qquad (7)$$

$\Delta G_t^\circ(\mathrm{H}^+)$ 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. $\Delta G_t^\circ(\mathrm{H}^+)$ values are limited to a few (mostly low) percentages of ME–H_2O and DME–H_2O mixtures in the

Table 3. Free energies of transfer[a] of benzoate ion, $\Delta G_t^\circ(\mathrm{Bz}^-)$,[b] in solvent–water mixtures at 25 °C.

Wt% of solvent	ΔG_t°(HBz)		$\delta(\Delta G_t^\circ)$		$\Delta G_t^\circ(\mathrm{H}^+)$		$\Delta G_t^\circ(\mathrm{Bz}^-)$	
	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	−7.26	3.99	7.70	−2.40	−3.26	2.31	3.70
40	−6.64	−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	−10.99	−12.62	19.00	25.11	1.75	5.46	6.26	7.03
100	−11.69	−11.82	—	—	—	—	—	—

[a] In kJ mol^{-1}. [b] Uncertainties in ΔG_t° values are of the order ±0.17 kJ mol^{-1}.

literature. We prefer to use the $\Delta G_t^\circ(\mathrm{H}^+)$ values determined by us based on the experimental measurements of transfer of BH^+ (B = 2,2′-bipyridine or 1,10-phenanthroline) and related data.[18] It is to be noted that $\Delta G_t^\circ(\mathrm{H}^+)$ values are always determined using extra thermodynamic assumptions with their inherent limitations. But $\Delta G_t^\circ(\mathrm{H}^+)$ 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 $\mathrm{p}K_\mathrm{T}$ 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–H_2O are less (but greater in DME–H_2O) than the corresponding values in alcohol–water mixtures.[21,22] The $\Delta G_t^\circ(\mathrm{H}^+)$ values becomes increasingly negative in going from water to ME–H_2O and DME–H_2O mixtures indicating that the binary mixtures are more basic than water. The basicity reaches a maximum at 80 wt% of ME (ME:H_2O *ca.* 1:1) and at 70 wt% DME (DME:H_2O *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–H_2O is more basic than ME–H_2O mixtures.[19] The changes in basicity of solvent mixtures are reflected in the $\mathrm{p}K_\mathrm{T}$ values of benzoic acid. Thus the $\mathrm{p}K_\mathrm{T}$ values of benzoic acid in ME–H_2O mixtures are less than those in DME–H_2O 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 $\Delta G_t^\circ(\mathrm{Bz}^-)$ in ME–H_2O than in DME–H_2O 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 $\delta[\Delta G^\circ(\mathrm{HBz} - \mathrm{Bz}^-)]$ 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 $\delta[\Delta G^\circ(\mathrm{HBz} - \mathrm{Bz}^-)]$ value should necessarily increase with increase in wt% of ME or DME.

Table 3 shows that ΔG_t°(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 is greater in DME compared with ME, a greater dispersion effect is expected in DME–H_2O and this may be largely responsible for the greater stability of HBz [more negative ΔG_t°(HBz)] in DME–H_2O, as observed. The $\Delta G_t^\circ(\mathrm{Bz}^-)$ values are predominantly positive, in agreement with the fact that ΔG_t° of anions are usually positive.[24,25] The result indicates that the transfer of $\Delta G_t^\circ(\mathrm{Bz}^-)$ 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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