

Solubility and the thermodynamics of transfer of benzoic acid in mixed solvents

A Pal & S C Lahiri*

Department of Chemistry, University of Kalyani, Kalyani 741 235

Received 19 December 1986; revised 6 July 1987; rerevised 7 September 1987

The solubilities of benzoic acid in ethanol + water mixtures have been determined at three different temperatures to obtain the thermodynamic parameters (ΔG° , ΔS° , ΔH°) of transfer of benzoic acid from water to ethanol + water mixtures. The results have been interpreted in terms of the structural changes occurring in the solvent mixtures with the change in solvent composition. The activity coefficients of benzoic acid in water and mixed solvents have been found to be close to unity from theoretical calculations using the data from the literature.

The importance and varied applications of solubility measurements are well known¹. In order to understand the nature of dissolution, we have undertaken systematic studies³⁻⁵ on the solubility of benzoic acid, a compound widely used as an antifungal preservative, in different mixed solvents. The solubility values are also of relevance in understanding solute-solvent interactions.

Recently, Das *et al.*² reported the solubilities of benzoic acid in different solvents over a wide range of temperature. However, the values are limited to a few solvent concentrations and the reported accuracy (2%) of the solubility values appears to be low. This prompted us to reinvestigate the solubility values of benzoic acid in ethanol + water mixtures and the results are presented in this paper. It is known² that entropy of transfer of uncharged species may well act as a structural probe for different solvent systems. This prompted us to investigate the thermodynamics of transfer of neutral benzoic acid in ethanol + water mixtures (0-100%) and the values of thermodynamic parameters so obtained are also reported here.

Materials and Methods

Benzoic acid (GR, E Merck) was used as such. Ethanol was purified using the standard procedure. Caustic soda (GR, E Merck) solution was standardized in the usual way. The other chemicals used were also of GR quality (E Merck). The solubility values of benzoic acid were determined at 288, 293 and 298 K exactly in the same way as described in our previous communications³⁻⁵. The solubility values of benzoic acid in water and mixed solvents are recorded in Table 1.

However, small corrections arising from the dissociation of benzoic acid have been applied by measurements of H^+ ions in saturated solutions of benzoic acid pH-metrically.

The accuracy in the solubility measurements depends mainly on the accuracy in the measurement of temperature, accuracy in the transfer of solutes from the desired temperature to the temperature of actual estimation, and accuracy in the estimation.

The temperature for the solubility measurements was adjusted to $\pm 0.01^\circ C$ of the desired temperature. A 60W bulb and a toluene-mercury thermoregulator were used to maintain the temperature of the experimental thermostat which was placed in a hot-cum-cold thermostat. The temperature of the hot-cum-cold thermostat was preset at the desired temperature using a contact thermometer and relay system.

A clear solution of benzoic acid, saturated at a slightly higher temperature (about 1° higher than that of the experimental temperature), was taken in a Campbell solubility apparatus which was placed in the experimental thermostat. The solution was allowed to equilibrate for about 4 hr. It was then inverted in the thermostat for filtration. The temperature variation during filtration or centrifuging of the saturated solutions was thus avoided.

Adherence of fine particles of solute to the surface of the pipette has been observed if the saturated solutions are pipetted out at a higher temperature and drained out at a lower temperature. For this reason, experiments were carried out at room temperature or below room temperature. The errors involved in the solubility measurements are 0.2-0.5% at 298K and about 0.3-0.7% at lower temperatures. The tem-

Table 1—Solubility of benzoic acid in ethanol + water mixtures at 288, 293 and 298 K and the thermodynamic parameters of solvation of benzoic acid at 298 K

EtOH (wt%)	Solubility (mol/lit.)	ΔG° (kJ/mol)	Solubility (mol/lit.)	ΔG° (kJ/mol)	Solubility (mol/lit.)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	$T\Delta S^\circ$ (kJ/mol)
288 K			293 K		298 K			
0	0.0201	9.35	0.0240	9.09	0.0284	8.82	24.7	15.9
8.0	0.0214	9.20	0.0291	8.62	0.0389	8.05	42.2	34.2
16.4	0.0247	8.86	0.0367	8.05	0.0577	7.07	60.8	53.8
25.3	0.0531	7.03	0.0856	5.99	0.1201	5.25	68.0	62.7
34.4	0.0982	5.56	0.1920	4.02	0.3593	2.54	92.4	91.8
44.0	0.1895	3.98	0.4052	2.20	0.7785	0.62	100.8	100.2
54.1	0.8004	0.53	1.0256	-0.06	1.3061	-0.66	34.6	35.3
64.7	1.3826	-0.77	1.5467	-1.06	1.7316	-1.36	16.0	17.4
76.0	1.7990	-1.41	1.9921	-1.68	2.2034	-1.96	14.4	16.4
87.6	2.0391	-1.71	2.3403	-2.07	2.6656	-2.43	19.3	21.7
100	2.2439	-1.93	2.5042	-2.24	2.7481	-2.50	15.0	17.5

Table 2—Calculations of the activity coefficients (γ_2) of benzoic acid in ethanol + water mixtures at 298 K

Alcohol wt%	EtOH					
	X_2	δ_m	X'_1	V_1	ϕ_1	γ_2
0	0.000	23.4	0.997	18.00	0.0179	1.009
8.0	0.033	23.06	0.995	19.32	0.0192	1.010
16.4	0.073	22.66	0.992	20.71	0.0206	1.011
25.3	0.117	22.18	0.985	22.40	0.0221	1.011
34.4	0.170	21.63	0.955	24.47	0.0234	1.011
44.0	0.235	20.96	0.905	27.05	0.0245	1.011
54.1	0.315	20.12	0.847	30.29	0.0257	1.010
64.7	0.418	19.05	0.803	34.43	0.0276	1.009
76.0	0.556	17.62	0.757	39.97	0.0302	1.007
87.6	0.740	15.70	0.712	47.46	0.0332	1.004

X_2 = Mole-fraction of the solvent, δ_m = Solubility parameter of the mixed solvents, X'_1 = Mole-fraction of the solvent in the saturated solution of benzoic acid, V_1 = Molar volume of the mixed solvents, ϕ_1 = Volume fraction of the solvent, γ_2 = Activity coefficients of benzoic acid.

perature variations were made within 10° to avoid significant error.

Results

The free energy of solvation of benzoic acid is given by Eq. 1,

$$\Delta G^\circ = -2.303 RT \log S \quad \dots (1)$$

where S is the solubility of benzoic acid expressed in molar units.

It is known that ΔC_p varies with temperature and an accurate determination of ΔH requires the measurement of solubilities over a wide range of temperatures. But the solubility values determined over a wide temperature range may be of limited accuracy leading to an error in ΔH values. The enthalpy of solvation of benzoic acid (ΔH°) has thus been determined from the slope of the plot of $-\log S$ against

$1/T$ assuming ΔH° to remain unchanged in the temperature range 288–298 K. ΔS° was obtained from the usual relationship,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \dots (2)$$

The solubility values and the thermodynamic parameters of benzoic acid in ethanol + water mixtures are recorded in Table 1.

For calculating the free energies of transfer, values of the activity coefficients of benzoic acid in different solvents are required. The activity coefficient values could not be experimentally determined but the activity coefficients (γ) of benzoic acid in these solvents have been calculated (Table 2) as described in our previous communications^{4,5} using the solubility values and the relevant data from the literature⁸. The activity coefficient values of benzoic acid in saturat-

Table 3—Thermodynamics of transfer of neutral benzoic acid from water to ethanol + water mixtures at 298 K

Ethanol (wt%)	$-\Delta G_t^\circ$ (kJ/mol)	ΔH_t° (kJ/mol)	$T\Delta S_t^\circ$ (kJ/mol)
8.0	0.8	17.5	18.3
16.4	1.8	36.2	38.0
25.3	3.6	43.3	46.9
34.4	6.1	67.7	73.8
44.0	8.2	76.1	84.3
54.1	9.5	10.0	19.5
64.7	10.2	-8.7	1.5
76.0	10.8	-10.3	0.5
87.6	11.3	-5.4	5.9
100	11.3	-9.7	1.6

ed solutions have been found to be close to unity in aqueous as well as mixed solvents.

The free energies of transfer of benzoic acid from water to mixed solvents,

$$\Delta G_t^\circ(\text{HBz}) = \Delta G_s^\circ(\text{HBz}) - \Delta G_w^\circ(\text{HBz}) \quad \dots (3)$$

have been calculated assuming the activity coefficients of benzoic acid to be unity in the saturated solutions of the respective solvents. However, corrections for the dissociation of benzoic acid have been made.

The thermodynamic parameters of transfer (ΔG_t° , ΔH_t° and ΔS_t°) of benzoic acid have been recorded in Table 3.

Discussion

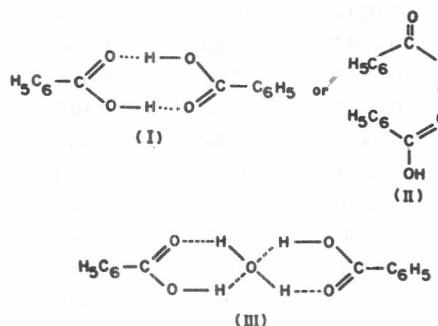
The solubility values recorded in Table 1 show that the solubility of benzoic acid increases with increase in concentration of organic solvent due to increase in hydrophobic character of the solvent mixtures. The increase in solubility of benzoic acid with increase in [organic solvent] can also be understood in terms of solubility parameter (δ)⁸. Benzoic acid ($\delta = 11.3$) with its high m.p. (394.8 K) is slightly soluble in water ($\delta = 23.4$) but highly soluble in ethanol ($\delta = 13.00$). Naturally, in mixed solvents (δ ranging between 13.0 and 23.0), solubility will be appreciable, since closer the δ -values the greater would be the solubility of benzoic acid.

The free energies of transfer of benzoic acid from aquo to aquo-organic mixtures indicate relative preference of solute for one environment over the other⁹ and give a quantitative measure of solute-solvent interactions.

The change in free energy is a measure of the tendency of two or more molecules to aggregate in aqueous solution. It is well known that organic acids like CH_3COOH , etc., form dimers in aqueous solution

due to hydrophobic interactions⁹. The dimerization of benzoic acid in nonpolar solvents is well known.

Therefore, it is responsible to assume that like CH_3COOH , $\text{C}_2\text{H}_5\text{COOH}$, etc.⁹, benzoic acid may also form cyclic dimers like (I) or (II), though no report on dimerization of benzoic acid in water is available.



It is to be noted that the replacement of H atom of formic acid, HCOOH ($pK = 3.75$) by CH_3 or C_2H_5 group changes the pK values considerably (4.76 and 4.87 for acetic acid and propionic acid respectively). The solubilities of these acids in water are high. However, the replacement of H-atom by aryl group (C_6H_5 -group) changes pK -values to a comparatively lesser extent (pK of $\text{C}_6\text{H}_5\text{COOH} = 4.20$), but the solubility is decreased enormously. This may be due to interlinking by water molecules through hydrogen bonding as shown in (III) (though the structure is not established) or it may be due to greater hydrophobic interactions. Dimerisation is expected to be less in water but may gradually increase with increase in [organic solvent]. It is not possible to say whether one H-bond or two hydrogen bonds are involved in the dimerization process, but following Schrier¹⁰, it can be said that the dimerization of benzoic acid in aqueous solution involves one hydrogen bond. The total driving force for dimerization consists of two parts—the hydrogen bond formation and the hydrophobic interaction between aryl groups⁹.

Though the dimerization process is of importance, in the absence of data on dimerization equilibria nothing specific can be said. The free energy of transfer has been found to increase with temperature up to 64 wt% of ethanol beyond which it is almost insensitive to changes in temperature.

Analysis of the thermodynamics of transfer of benzoic acid in ethanol + water mixtures is difficult. The variation of ΔG_t° , ΔH_t° and $T\Delta S_t^\circ$ with change in [ethanol] has been depicted in Fig. 1.

The results indicate that the entropy and enthalpy of solvation are maximum near about 44 wt% ($\sim X_2 = 0.2$) indicating maximum structure formation. It is also noted that both enthalpy and entropy then

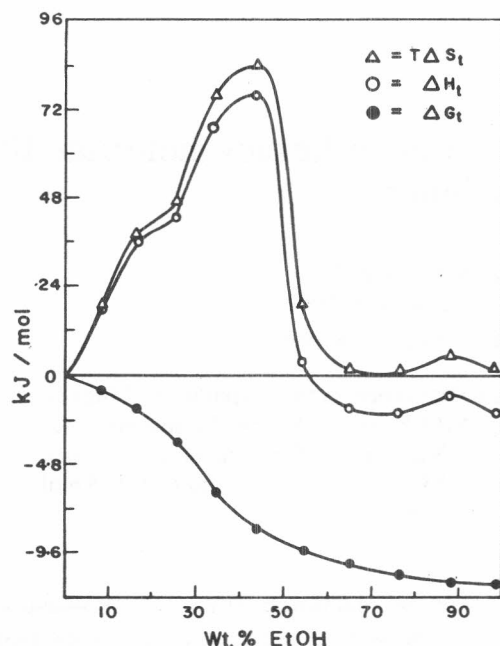


Fig.1—Plots of thermodynamic parameters against wt% of ethanol

decrease up to about 76 wt% of ethanol, but a maximum is observed at about 87 wt% ethanol, though free energy decreases continuously.

The results indicate the compensation of enthalpy and entropy terms to give a simple linear free energy change.

Though it is hardly possible to correlate our data with hydrophobic interactions (HI), it is to be noted that addition of small quantities of ethanol causes a weakening of the HI. This effect is restricted to the region $0 \leq X_{\text{EtOH}} \leq 0.03$; at higher concentrations of ethanol there is a pronounced increase in the strength of the HI which persists up to $X_{\text{EtOH}} \approx 0.2$, beyond which HI becomes weak⁹.

The thermodynamics of dissolution of HBz in the solvents involves (i) rupture of bonds between solute molecules to bring the solute into the vapour phase ($\Delta H = +ve$, $\Delta S = +ve$), (ii) creation of cavity in the solvent which means rupture of H-bonds ($\Delta H = +ve$, $\Delta S = +ve$), and (iii) placement of the solute into the cavity. This step involves formation of bond between solute and solvent ($\Delta H = -ve$, $\Delta S = -ve$).

The second and third steps involve the rearrangement of the solvent molecules and are accompanied by changes in Van der Waal's forces like dipole-dipole, dispersion forces and hydrophobic bond formation.

Addition of ethanol enhances the structure formation water. This becomes maximum at about

$X_2 = 0.1$ (as shown by Arnett *et al.*¹¹) beyond which structural collapse begins. Excess enthalpy of mixing arises from H-bond formation between water molecules at the beginning. Subsequently the breaking of H-bonds of water and ethanol molecules and formation of water-ethanol hydrogen bonds occur. Finally $\text{H}_2\text{O}-\text{ROH}$ bonds are replaced by $\text{ROH}-\text{ROH}$ bonds.

Addition of benzoic acid leads to the disruption of H bonds of solvent molecules and solute molecules and the formation of new bonds between the solute and solvent. This results in an increase in enthalpy and entropy. The solubility of benzoic acid increases with the increase in ethanol content with (i) the formation of increasing number of cavities and (ii) the formation of new solute-solvent bonds.

Initially, process (i) predominates over (ii) leading to a gradual increase in enthalpy and entropy up to about 44 wt% ($X_2 = 0.2-0.3$) beyond which second term predominates leading to a decrease in enthalpy. In this region, depolymerization of the solvent molecules should lead to an entropy increase but overall decrease in the entropy values is expected due to the decrease in the total number of solvent molecules as well as increased solute-solvent bond formation.

However, it is necessary to obtain more data on the thermodynamics of transfer before useful conclusions can be drawn from such studies.

Acknowledgement

One of the authors (A.P.) wishes to thank the UGC, New Delhi for a research fellowship.

References

- 1 Kertes A S in *Solubility data series* (Pergamon Press, Oxford, New York) (vii), 1979.
- 2 Das K, Das A K, Bose K & Kundu K K, *J phys Chem*, 82 (1978) 1242.
- 3 Pal A, Maity S K & Lahiri S C, *J Indian chem Soc*, 60 (1983) 475.
- 4 Pal A & Lahiri S C, *Indian J Chem*, 25A (1986) 26.
- 5 Bhattacharyya A K, Pal A & Lahiri S C, *J Indian chem Soc*, 62 (1985) 953.
- 6 Hildebrand J H & Scott R L, *The solubility of nonelectrolytes* (Reinhold, New York) 1950, Chapters 1,2,23.
- 7 Moelwyn-Hughes E A, *Physical chemistry*, 2nd Edn (Pergamon Press, London) 1965, Chapter 17.
- 8 Martin A N, Swarbrick J & Cammarata A, *Physical pharmacy* (Lea & Febiger Philadelphia) 1969, Chapter 12.
- 9 Ben Naim A, *Hydrophobic interactions* (Plenum Press, New York and London) 1980, Chapters 1,2,3.
- 10 Schrier E E, Pottle M & Scheraga H A, *J Am chem Soc*, 86 (1964) 3444.
- 11 Arnett E M, Bentrude W G, Burke J J & Duggleby P M, *J Am chem Soc*, 87 (1965) 1541.