

Free Energies of Transfer of Ions from Solubility and Conductometric Measurements

A. PAL, S. K. MAITY and S. C. LAHIRI

Department of Chemistry, University of Kalyani, Kalyani-741 235

Manuscript received 10 February 1982, revised 22 October 1982, accepted 23 April 1983

Accurate values of dissociation constants of benzoic acid in methanol+water and ethanol+water mixtures were determined using Fuoss-Kraus method. Accurate values of Λ_0 of benzoic acid in different mixed solvents were determined from the relation

$$\Lambda_0(\text{benzoic acid}) = \Lambda_0(\text{HClO}_4) + \Lambda_0(\text{C}_6\text{H}_5\text{COOK}) - \Lambda_0(\text{KClO}_4)$$

utilising the Λ_0 values determined in the laboratory.

The solubilities of benzoic acid in mixed solvents were determined. The free energies of transfer of uncharged acid, $\Delta G_f^\circ(\text{HA})$, have been coupled with the free energies of transfer (ΔG_f°) for the reaction $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$ and $\Delta G_f^\circ(\text{H}^+)$ values previously determined in the laboratory, to get ΔG_f° of benzoate ion.

THE importance and limitations of the determination of free energies of transfer or medium effects of single ions are well known. The free energies of transfer of single ions can be determined using the relation

$$\Delta G_f^\circ(\text{ion}) = \Delta G_f^\circ(\text{neut}) + \Delta G_f^\circ(\text{el}) \quad \dots (1)$$

where $\Delta G_f^\circ(\text{neut})$ has been assumed to be equal to its uncharged analogue¹.

The above relation has been utilised by us to determine the free energies of transfer of benzoate ion from water to different methanol+water and ethanol+water mixtures using the solubilities of benzoic acid and the accurate values of the dissociation constants of benzoic acid determined conductometrically in different mixed solvents²⁻⁵. The results are described here.

Experimental

Potassium benzoate was prepared by mixing stoichiometric amounts of benzoic acid (G. R., E. Merck) and KOH (G. R., E. Merck) solutions. The mixture was concentrated on a water bath and cooled when crystals of potassium benzoate separated out. The salt was filtered out, recrystallized twice from alcohol+water mixture and dried. The salt was kept over H_2SO_4 in a desiccator. For the determination of Λ_0 values of potassium benzoate, the equivalent conductances of potassium benzoate in mixed solvents were determined at 298 K at different dilutions ($5 \times 10^{-2} M$ to $5 \times 10^{-4} M$). The cell constants were determined using standard procedure. Λ values were plotted against \sqrt{C} , which gave straight lines and the extrapolated values at zero concentrations gave the Λ_0 values. The conductivity measurements were done with Leeds-Northrup conductivity bridge (model 4959) with an accuracy of $\pm 0.1\%$. A 1000 cycle signal was employed.

To determine the solubility of benzoic acid at 298 K in mixed solvents, saturated solutions of benzoic acid were prepared in the appropriate solvents at 303 K and filtered. These solutions were taken in Campbell apparatus⁶ fitted with sintered disc and fine tube and allowed to equilibrate in a thermostat maintained at 298 K (± 0.01) for 24 hr. The solutions contained enough solid benzoic acid. After equilibration, the solutions were filtered by inverting the apparatus in the thermostat. The solutions were taken out and the acid content of a definite amount of the solution was determined by titration with standard caustic soda solution. The process was repeated several times for each set of experiment. The determinations were made in mixed solvents and water as well. The results are recorded in Tables 3 and 4. The error involved in the solubility measurements would be about 0.2-0.5%.

Results and Discussion

The dissociation constants of benzoic acid in different percentages of alcohol in methanol+water and ethanol+water mixtures were reported by us earlier^{2,5}. The values were determined conductometrically using Gelb's method⁴ and Fuoss-Kraus method⁵, using the equation

$$F(z) = \frac{1}{K\Lambda_0^2} \cdot \frac{C\Lambda f_{\pm}^2}{F(z)} + \frac{1}{\Lambda_0}$$

However, the Λ_0 values determined from the intercepts of the plot of $\frac{F(z)}{\Lambda}$ against $\frac{C\Lambda f_{\pm}^2}{F(z)}$ have been generally found to differ from the true Λ_0 values, leading to considerable error in K values. To overcome this, we determined the accurate values of Λ_0 of benzoic acid in different mixed solvents from the relation

$$\Lambda_0(\text{C}_6\text{H}_5\text{COOH}) = \Lambda_0(\text{HClO}_4) + \Lambda_0(\text{C}_6\text{H}_5\text{COOK}) - \Lambda_0(\text{KClO}_4) \dots (2)$$

The Λ_0 values of HClO_4 and KClO_4 have been reported^{7,8}. Λ_0 values are given in Tables 1 and 2. The Λ_0 values of benzoic acid were utilised to recalculate K values of benzoic acid in mixed solvents from the known values of slopes determined in our laboratory using Fuoss-Kraus method. The dissociation constants of benzoic acid (in methanol + water and ethanol + water mixtures) originally reported and determined using recalculated Λ_0 values of benzoic acid are recorded in Table 2.

The free energy of transfer for the reaction



$$\Delta G_{\text{t}}^{\circ} = \Delta G_{\text{t}}^{\circ} - \Delta G_{\text{w}}^{\circ} = \Delta G_{\text{t}(\text{H}^+)}^{\circ} + \Delta G_{\text{t}(\text{A}^-)}^{\circ} - \Delta G_{\text{t}(\text{HA})}^{\circ} \quad \dots (4)$$

$$= \Delta G_{\text{t}(\text{H}^+)}^{\circ} + \Delta G_{\text{t}(\text{el})}^{\circ} \quad \dots (5)$$

[since $\Delta G_{\text{t}(\text{A}^-)}^{\circ} = \Delta G_{\text{t}(\text{HA})}^{\circ} + \Delta G_{\text{t}(\text{el})}^{\circ}$].

Thus,

$$\Delta G_{\text{t}(\text{el})}^{\circ} = \Delta G_{\text{t}}^{\circ} - \Delta G_{\text{t}(\text{H}^+)}^{\circ} \quad \dots (6)$$

$$\Delta G_{\text{t}(\text{A}^-)}^{\circ} = \Delta G_{\text{t}}^{\circ} - \Delta G_{\text{t}(\text{H}^+)}^{\circ} + \Delta G_{\text{t}(\text{HA})}^{\circ} \quad \dots (7)$$

$$\Delta G_{\text{t}(\text{HA})}^{\circ} = \Delta G_{\text{t}(\text{HA})}^{\circ} - G_{\text{w}(\text{HA})}^{\circ} \quad \dots (8)$$

$\Delta G_{\text{t}(\text{HA})}^{\circ}$ values have been determined from solubility measurements. $\Delta G_{\text{t}(\text{A}^-)}^{\circ}$ values have been calculated using $\Delta G_{\text{t}(\text{H}^+)}^{\circ}$ values determined in this laboratory.

The values are recorded in Tables 3 and 4.

The Λ_0 values of benzoic acid decrease continuously with the percentage of organic solvents though the decrease in Λ_0 values is appreciably larger in case of ethanol + water mixtures as expected. The Λ_0 values of potassium salts was found to decrease with solvent composition but began to increase at about 75 wt% methanol and continued onwards. No such trend is observed in ethanol + water mixtures.

The discrepancies in Λ_0 values determined using equation (2) and extrapolated values from Fuoss-Kraus plot and the consequent differences in pK values are presented in Tables 1 and 2.

There are wide divergence in the values of $\Delta G_{\text{t}(\text{H}^+)}^{\circ}$ in methanol + water and ethanol + water mixtures. The $G_{\text{t}(\text{H}^+)}^{\circ}$ values determined by us⁹ in ethanol + water mixtures are qualitatively and almost quantitatively in good agreement with the values reported by Popovych and Dill¹⁰ using TABBPh_4 assumption though they are at variance with the values determined by other workers^{11,12}. The $\Delta G_{\text{t}(\text{H}^+)}^{\circ}$ values determined in methanol + water mixtures are qualitatively in agreement with the values reported by Tomkins¹³, Alfenarr and Deligny¹⁴, Wells¹⁵ and Kalidas¹⁶ but considerably different from those of others¹⁷. In view of wide divergence of results in $\Delta G_{\text{t}}^{\circ}$ of ions as apparent from the literature and the recent paper of Blandamer *et al*¹⁸, our results can be said to be in very good agreement.

The $\Delta G_{\text{t}(\text{benzoate ion})}^{\circ}$ can be calculated from (1) if we can determine $\Delta G_{\text{t}(\text{el})}^{\circ}$ of the ion. The radius of benzoate ion ($r=2.75 \text{ \AA}$) has been calculated using bond-distance values. The $\Delta G_{\text{t}(\text{el})(\text{A}^-)}^{\circ}$ calculated using Born¹⁹ equation are given in Tables 3 and 4. The equation (1) leads to negative values of $\Delta G_{\text{t}(\text{benzoate})}^{\circ}$ and consequently $\Delta G_{\text{t}(\text{H}^+)}^{\circ}$ values should become positive. The results naturally contradict the values of $\Delta G_{\text{t}(\text{H}^+)}^{\circ}$, determined by a number of workers.

This is expected as the limitations of calculating $\Delta G_{\text{t}(\text{el})(\text{A}^-)}^{\circ}$ for an unsymmetrical ion like benzoate ion using Born equation are well known. Moreover, ion-dipole, ion-quadrupole and dispersion forces are likely to be large in case of benzoate ion. Thus, we prefer to use equation (7) to calculate

TABLE 1—EQUIVALENT CONDUCTANCES OF ELECTROLYTES AND DISSOCIATION CONSTANTS OF BENZOIC ACID AT 298K

Wt% of methanol	$\Lambda_0 \text{HClO}_4$	$\Lambda_0 \text{C}_6\text{H}_5\text{CO}_2\text{K}$	$\Lambda_0 \text{KClO}_4$	$\Lambda_0 \text{C}_6\text{H}_5\text{CO}_2\text{H}$	Λ_0 (Extrapolated)	pK (ref. 2)	pK'
8.0	381.0	120.5	121.5	380.0	360.0	4.32	4.37
16.0	331.3	109.2	98.5	342.0	308.0	4.50	4.59
25.2	280.5	95.0	87.0	288.5	263.1	4.73	4.81
34.4	228.0	83.0	80.0	231.0	218.0	4.98	5.03
44.7	195.1	77.0	75.0	197.1	182.0	5.21	5.28
54.2	171.7	77.3	71.0	178.0	157.0	5.50	5.60
64.1	151.5	73.0	68.0	156.5	136.7	5.76	5.88
75.9	131.0	81.8	75.0	137.8	118.0	6.02	6.16
87.9	117.5	99.4	92.0	124.9			

TABLE 2—EQUIVALENT CONDUCTANCES OF ELECTROLYTES AND DISSOCIATION CONSTANTS OF BENZOIC ACID AT 298K

Wt% of ethanol	$\Lambda_0 \text{HClO}_4$	$\Lambda_0 \text{C}_6\text{H}_5\text{CO}_2\text{K}$	$\Lambda_0 \text{KClO}_4$	$\Lambda_0 \text{C}_6\text{H}_5\text{CO}_2\text{H}$	Λ_0 (Extrapolated)	pK (ref. 2)	pK'
8.0	372.0	107.5	116.9	362.6	346.2	4.32	4.36
16.4	301.5	88.5	95.0	295.0	287.9	4.58	4.55
25.3	250.0	75.0	78.5	246.5	226.4	4.78	4.85
34.4	196.0	60.5	66.0	190.5	183.6	5.00	5.03
44.0	172.6	55.5	58.2	169.9	149.5	5.27	5.38
54.1	142.0	50.5	52.0	140.5	129.2	5.56	5.63
64.7	118.0	49.0	49.5	117.5	98.6	5.90	6.05
76.0	102.0	48.0	48.6	101.4			

TABLE 3—MeOH+H₂O MIXTURES AT 25° (BENZOIC ACID)

% (v/v) of alcohol	Solubility (Moles/lit)	Solubility (Molality)	ΔG° (neut.) (kJ/Mole)	ΔG°_f (neut.) (kJ/Mole)	pKa	ΔG° (acid) (kJ/Mole)	ΔG°_f (acid) (kJ/Mole)	ΔG°_f (H ⁺) (kJ/Mole)	ΔG°_f (el) (kJ/Mole) (exp.)	ΔG°_f (el) (A ⁻) using Born Eq. (kJ/Mole)	ΔG°_f (A ⁻) (kJ/Mole)
0	0.0284	0.0285	8.8246		4.20	28.96					
10	0.03560	0.03630	8.2647	-0.55	4.87	24.94	0.97	-0.58	1.50	0.18	0.94
20	0.0515	0.0584	7.3507	-1.47	4.59	26.18	2.22	-1.10	3.38	0.30	1.85
30	0.0937	0.0985	5.8667	-2.95	4.81	27.44	3.48	-1.71	5.19	0.19	2.28
40	0.1578	0.1693	4.5757	-4.24	5.03	28.69	4.73	-2.11	6.84	0.78	2.59
50	0.4329	0.4749	2.0742	-6.75	5.28	30.12	6.16	-3.01	9.17	1.03	2.42
60	0.8606	0.9662	0.3710	-8.45	5.60	31.95	7.98	-3.88	11.88	1.41	3.97
70	1.5085	1.7352	-1.0186	-9.84	5.88	33.54	9.58	-4.93	14.51	1.84	4.67
80	2.0266	2.4054	-1.7502	-10.57	6.16	35.14	11.18	-5.55	16.78	2.45	5.15
90	2.5941	3.1929	-2.3620	-11.18				-4.95		3.26	
100	3.1194	3.9658	-2.8190	-11.64							

ΔG°_f (H⁺) = Determined in our laboratory°.

TABLE 4—EtOH+ WATER MIXTURES AT 25° (BENZOIC ACID)

% (v/v) of alcohol	Solubility (Moles/lit)	Solubility (Molality)	ΔG° (neut.) (kJ/Mole)	ΔG°_f (neut.) (kJ/Mole)	pKa	ΔG° (acid) (kJ/Mole)	ΔG°_f (acid) (kJ/Mole)	ΔG°_f (H ⁺) (kJ/Mole)	ΔG°_f (exp) (kJ/Mole)	ΔG° (el) (A ⁻) using Born eq. (kJ/Mole)	ΔG°_f (A ⁻) (kJ/Mole)
0	0.0284	0.0285	8.8246		4.20	28.96					
10	0.0389	0.0397	8.0895	-0.78	4.36	24.87	0.91	-1.08	1.99	0.18	1.21
20	0.0577	0.0597	7.0669	-1.75	4.55	25.96	1.96	-1.88	3.88	0.35	2.07
30	0.1201	0.1264	5.2506	-3.57	4.85	27.67	3.70	-2.70	6.41	0.63	2.83
40	0.3593	0.3857	2.5864	-6.28	5.03	28.69	4.73	-3.38	8.12	1.09	1.83
50	0.7785	0.8556	0.6204	-8.20	5.88	30.69	6.73	-4.52	11.25	1.56	3.05
60	1.3061	1.4725	-0.6816	-9.48	5.68	32.12	8.15	-5.53	13.69	2.17	4.20
70	1.7816	2.0056	-1.3605	-10.18	6.05	34.51	10.55	-5.68	16.19	2.93	6.00
80	2.2034	2.6259	-1.9675	-10.78	6.20°	35.97	11.41	-5.53	16.94	4.01	6.16
90	2.6856	3.2769	-2.4294	-11.25	6.46°	36.88	12.92	-4.66	17.59	5.27	6.93

* = Determined from solubility and pH metrically.
 ΔG°_f (H⁺) = Determined in our laboratory°.

ΔG°_f (benzoate ion) utilizing the determined values of ΔG°_f (HA) and ΔG°_f (H⁺). The ΔG°_f (A⁻) values are predominantly positive which is in agreement with the fact that Gibbs free energies of transfer of anions are positive.

The ΔG°_f values of benzoic acid are slightly greater in ethanol + water mixtures compared to methanol + water mixtures as expected due to greater hydrophobic nature of ethanol.

Acknowledgement

The authors thank the U.G.C., New Delhi for a Research Fellowship.

References

1. S. C. LAHIRI and S. ADITYA, *J. Indian Chem. Soc.*, 1979, **56**, 1112 and references therein.
2. A. K. MANDAL and S. C. LAHIRI, *J. Prakt. Chem.*, 1977, **319**, 377.
3. A. K. MANDAL and S. C. LAHIRI, *J. Indian Chem. Soc.*, 1977, **54**, 894.

4. R. I. GELB, *Anal. Chem.*, 1971, **43**, 1110.
5. R. M. FUOSS and C. KRAUS, *J. Amer. Chem. Soc.*, 1939, **55**, 476, 2390.
6. A. N. CAMPBELL, *J. Chem. Soc.*, 1930, 179.
7. A. BHATTACHARYYA, A. K. MANDAL and S. C. LAHIRI, *Electrochim. Acta*, 1980, **25**, 1487.
8. A. BHATTACHARYYA, A. K. MANDAL and S. C. LAHIRI, *Indian J. Chem.*, 1980, **19A**, 532.
9. (a) A. K. BHATTACHARYYA, D. SENGUPTA and S. C. LAHIRI, *Z. Physik. Chem. (Leipzig)*, (in press)
 (b) D. SENGUPTA, A. PAT. and S. C. LAHIRI, *J. Chem. Soc. Dalton* (in press)
10. O. POPOVYCH and A. J. DILL, *Anal. Chem.*, 1969, **41**, 456.
11. B. GUTBEHZALL and E. GRUNWALD, *J. Amer. Chem. Soc.*, 1963, **75**, 565.
12. V. V. ALEKSANDROV and N. A. IZAMAYLOV, *Zh. Fiz. Khim.*, 1958, **32**, 404.
13. R. P. T. TOMKINS, Thesis, University of London, 1966.
14. M. ALFENAAR and C. L. DELIGNY, *Rec. Trav. Chim.*, 1967, **86**, 929.
15. C. F. WELLS, *J. C. S., Faraday I*, 1973, **69**, 934.
16. G. KALIDAS, P. SIVAPRODAS and U. V. VENKATRAM, *Z. Naturforsch.*, 1977, **32A**, 791.
17. C. M. CRISS and M. SALOMON in "Physical Chemistry of Organic Solvent Systems", (Ed.) A. K. COVINGTON and T. DICKINSON, Plenum Press, London, 1973, p. 323.
18. M. J. BLANDAMER, J. BUNGESS and A. F. DUFFIELD, *J. C. S. Dalton*, 1980, 1.
19. M. BORN, *Z. Physik.*, 1920, **1**, 45.