

Thermodynamics of Ionization of Benzoic Acid and Some Substituted Benzoic Acids in 1,4-Dioxane–Water Mixtures

Dattatraya Vyankatesh Jahagirdar^a and Harri Lönnberg^{*,b}

^aDepartment of Chemistry, Marathwada University, Aurangabad 431004, India and ^bDepartment of Chemistry, University of Turku, SF-20500 Turku, Finland

Jahagirdar, D. V. and Lönnberg, H., 1992. Thermodynamics of Ionization of Benzoic Acid and Some Substituted Benzoic Acids in 1,4-Dioxane–Water Mixtures. – Acta Chem. Scand. 46: 399–402.

Thermodynamic parameters, ΔG^\ominus , ΔH^\ominus and ΔS^\ominus , for the dissociation of aromatic carboxylic acids and phenols have frequently been used to explain the effect of substituents on the ionization of functional groups.^{1,2} The fundamental measurements of this type were mainly carried out in aqueous solutions. More recently the effect of solvent on proto-

lytic equilibria has become a subject of considerable interest, and thermodynamic data in mixtures of water and organic solvents have been determined.^{3,4} These data have also been used to obtain values for the thermodynamic functions of transfer from the aqueous to an aqueous-organic solvent.³⁻⁵

Table 1. Standard Gibbs energy, enthalpy and entropy of ionization of benzoic acids in dioxane–water mixtures at 298.2 K.

Comp.	ϵ_r	x_D^a	$\Delta G^{\ominus b}$	ΔH^\ominus	$T\Delta S^\ominus$	ΔS^\ominus
			kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
Benzoic acid	78.2	0	24.20	0.65 ^c	–23.6	–79
	60.2	0.050	27.83	0.67	–27.2	–91
	41.5	0.112	32.73	0.88	–31.9	–107
	25.9	0.234	41.07	1.00	–40.1	–134
	10.7	0.455	53.17	1.42	–51.8	–174
	8.2	0.551	42.68	1.13	–41.6	–140
	5.6	0.648	32.90	0.75	–32.2	–108
4-Chlorobenzoic acid		0	23.07	0.92 ^d	–22.2	–74
		0.050	25.87	2.96	–22.9	–77
		0.112	29.88	5.43	–24.5	–82
		0.234	38.41	8.78	–29.6	–99
		0.455	51.24	7.85	–43.4	–146
		0.551	41.84	5.85	–36.0	–121
3-Nitrobenzoic acid		0	19.89	0.29	–19.6	–66
		0.050	23.74	0.42	–23.3	–78
		0.112	26.75	1.71	–25.0	–84
		0.234	34.69	3.26	–31.4	–105
		0.455	46.82	2.72	–44.1	–148
		0.551	43.28	2.48	–40.8	–137
4-Nitrobenzoic acid		0	18.47	0.21 ^e	–18.3	–61
		0.050	23.28	0.42	–22.9	–77
		0.112	26.88	1.37	–25.5	–86
		0.234	34.56	2.42	–32.1	–108
		0.455	46.82	1.50	–45.3	–152
		0.551	43.92	0.72	–43.2	–145
	0.648	40.96	0.04	–40.9	–137	

^aMole fraction of dioxane. ^bCalculated from $\text{p}K_a$ values reported in Ref. 6. ^cLit. 0.62 kJ mol^{-1} . ^dLit. 0.96 kJ mol^{-1} . ^eLit. 0.13 kJ mol^{-1} .

Jahagirdar *et al.*⁶ have previously described the dependence of pK_a values of substituted benzoic acids on the composition of dioxane–water mixtures. According to these workers the solvent effects on the dissociation of this class of compound are similar in the sense that the pK_a values pass through a maximum when the mole fraction of dioxane (x_D) is 0.44. This was attributed to dioxane molecules entering into the primary hydration sphere of the ionic species. To understand more about the role of solute–solvent interactions, the ΔH^\ominus values for the dissociation of benzoic acid and its 4-chloro, 3-nitro and 4-nitro derivatives have now been determined in 0, 20, 40, 60, 80 and 90% (v/v) dioxane–water mixtures at 298.2 K. These values, along with the previous data⁶ on the Gibbs energies of ionization, were used to calculate the ΔS^\ominus values.

Table 1 records the standard Gibbs energies, enthalpies and entropies for the ionization of benzoic acid and some substituted benzoic acids in various dioxane–water mixtures at 298.2 K. The values of relative permittivity of the solvent mixtures are included in the same table. Evidently, the ionization enthalpies are positive and the entropies are negative over the entire range of solvent compositions studied. In other words, the dissociation process is both enthalpically and entropically unfavorable. The negative entropy change indicates an increase in order for the dissociation reaction. Apparently, ordering of solvent molecules around the H^+ and A^- ions, produced from neutral HA, is more extensive than ordering around HA, and hence the ionization generates an order in both water and dioxane–water mixtures. The data in Table 1 also show that variation of the ΔG^\ominus values, and hence the pK_a values, as a function of x_D , is mainly determined by the entropic contribution, $T\Delta S^\ominus$. The enthalpy term usually amounts to less than 10%

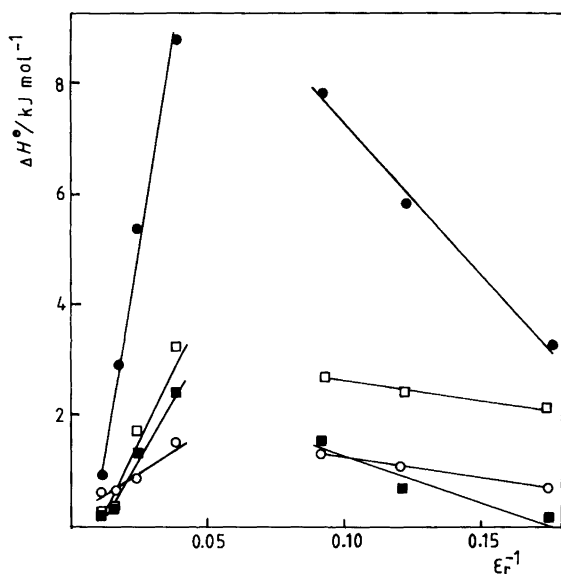


Fig. 1. Enthalpies of ionization of benzoic acids plotted against the reciprocal relative permittivity of the reaction mixture: ○, benzoic acid; ●, 4-chlorobenzoic acid; □, 3-nitrobenzoic acid; ■, 4-nitrobenzoic acid.

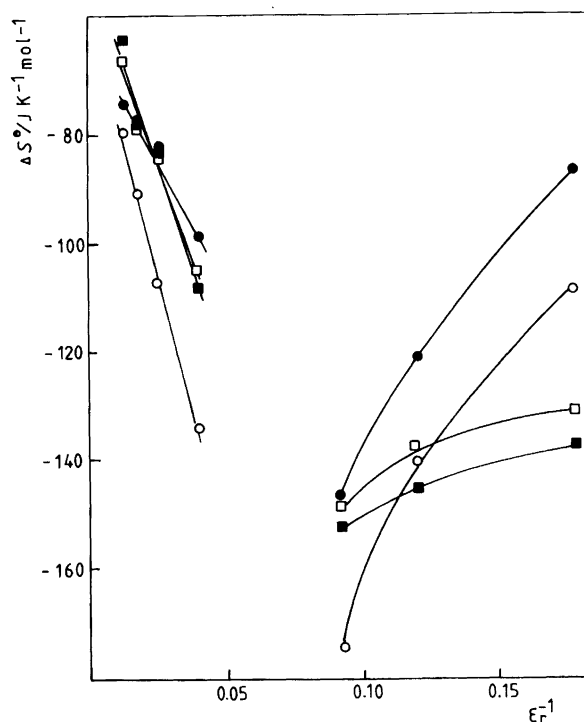


Fig. 2. Entropies of ionization of benzoic acids plotted against the reciprocal relative permittivity of the reaction mixture: ○, benzoic acid; ●, 4-chlorobenzoic acid; □, 3-nitrobenzoic acid; ■, 4-nitrobenzoic acid.

of the weakening of the acid strength that takes place when the dioxane content is increased up to $x_D = 0.44$. Only in the case of 4-chlorobenzoic acid is the enthalpy contribution as high as 25%.

Figs. 1 and 2 show the ionization enthalpies and entropies plotted against the reciprocal relative permittivity, ϵ_r^{-1} , of the solvent mixtures. The endothermic nature of the ionization reaction is initially increased with increased dioxane content, the dependence of ΔH^\ominus on ϵ_r^{-1} being approximately linear. However, in dioxane-rich solutions an inverse dependence on ϵ_r^{-1} is observed. The ΔS^\ominus values, in turn, pass through a minimum at $\epsilon_r = 0.093$. The problem of interest is why ΔS^\ominus is more negative for $x_D \approx 0.45$ than for lower and higher dioxane content. This point is discussed below in the light of the present knowledge on the structure of solvent mixtures. It should also be noted that the ionization enthalpies obtained at $x_D > 0.5$ may include a contribution of ion-pairing between sodium and benzoate ions (see the Experimental). Since the ion associations are generally endothermic processes, the real ionization enthalpies may, in dioxane rich mixtures, be smaller than the observed ones. In spite of this, the main conclusions remain valid: (i) the variation in ΔG^\ominus is mainly determined by the entropic factor, and (ii) ΔH^\ominus passes through a maximum and ΔS^\ominus through a minimum at $x_D \approx 0.5$.

Variation in the ionization enthalpies and entropies with dioxane content may be due to a change in the overall permittivity of the medium and to specific solvent–solute

interactions, among which donor-acceptor interactions play an important role. According to the classical theory of Born,⁷ a solvent is a continuous dielectric medium that only provides an electrostatic field. However, preferential solvation by one of the components of the solvent mixture may change the solvent composition in the neighbourhood of ionic solutes, and hence lead to deviation from the expected behavior. As seen from Figs. 1 and 2, the enthalpy and entropy changes for ionization of benzoic acids are approximately linearly related to reciprocal permittivity at low dioxane content, as indeed is expected on the basis of Born's theory. Accordingly, dioxane up to a mole fraction of 0.3-0.4, could be interpreted as affecting mainly the dielectric properties of the solution. However, in reality the picture of dioxane-water mixtures is more complicated. Several experimental approaches suggest that a pronounced break-down of water structure takes place upon addition of dioxane. Many physical parameters related to solvent structure pass through a maximum in the range $0.2 < x_D < 0.5$: the Kirkwood correlation parameter g reaches a maximum value at $x_D = 0.3$,⁸ the relaxation time of water in dioxane-water mixtures exhibits a maximum value at $0.3 < x_D < 0.5$,⁹ and the viscosity passes through a maximum at $0.2 < x_D < 0.3$.¹⁰ These observations have been accounted for by formation of either 1:3,¹⁰ or 1:2 and 2:2 dioxane-water adducts.¹¹ Excess thermodynamic functions of mixing water and dioxane are also consistent with the formation of a rather ordered solvent structure at $x_D \approx 0.3$.¹² The excess Gibbs energy is positive over the whole composition range, consisting of a small enthalpic contribution (negative at $x_D < 0.5$ and positive at $x_D > 0.5$) and a markedly negative entropic contribution. The latter quantity passes through a minimum at $x_D \approx 0.3$. Interestingly, the ionization of benzoic acids is both enthalpically and entropically most unfavourable at $x_D \approx 0.4$, i.e. under conditions where 1:2 and 2:2 dioxane-water adducts may be assumed to predominate. In other words, the structure-making effect of the ionization reaction is most pronounced in solvent mixtures which already have a rather ordered structure; competition of the ionic species with dioxane molecules for water molecules will still increase the order of solvent structure. At higher dioxane content, where the medium may be regarded as a mixture of dioxane molecules and 2:2 water-dioxane adducts, the enthalpy values become less positive and the entropy values less negative. Previously,⁶ it has been suggested that under such conditions dioxane molecules may enter the primary hydration sphere of the ionic species produced by dissociation of benzoic acids. If this really happens, the solvation of the ionic species may be assumed to resemble that of unionized benzoic acid, and hence the changes that dissociation of benzoic acid exerts on the solvent structure are less pronounced than at lower dioxane content. The dependence of the thermodynamics of ionization on solvent composition is rather insensitive to substituent effects.

Experimental

Materials. Benzoic acid (>99%), and 4-chloro- (>99%), 3-nitro- (>98%) and 4-nitro-benzoic acids (>99%) were commercial products of Aldrich, and were used without further purification. Dioxane was an analytical-grade product of Merck.

Calorimetric measurements. The measurements were performed on an LKB 10700-2 Batch microcalorimeter. The compartments of the reaction cell were loaded with solutions of perchloric acid and the sodium salt of benzoic acid in an appropriate dioxane-water mixture. Typically, 0.1 mol dm^{-3} and 0.08 mol dm^{-3} solutions of perchloric and the sodium salt of benzoic acid were used. The transfer of each solution, 2.00 cm^3 , was done by means of an automatic pipette. The reference cells were filled with 2 cm^3 of the same solvent mixture. The enthalpies of dilution of the sodium salt and perchloric acid were determined separately in the same solvent composition. The enthalpies of protonation were calculated by subtracting the heat evolved on dilution of the solutions of the salt and the acid from the heat evolved when the two solutions were mixed. In the concentration range employed (final concentration 0.04 mol dm^{-3}) ion association may be assumed to be almost negligible at $x_D < 0.5$. For comparison, the ion-pair formation has been estimated to be less than 15% in neat solvents of comparable permittivity (DMF, DMSO, nitrobenzene), when the concentration is 0.1 mol dm^{-3} .¹³ However, at $x_D > 0.5$ ion-pairing between sodium and benzoate ions may be extensive, and hence affect the observed values of ionization enthalpies. Since the ion association may be expected to be an endothermic process,¹³ the real ionization enthalpies may, under these conditions, be smaller than those observed.

The instrument was calibrated from measurement of ΔH^\ominus for the neutralization of a strong acid (HCl) with a strong base (NaOH).¹⁴ Each value of ΔH reported is the average of three runs, and the deviation from one experimental value to another was never more than 0.1 kJ mol^{-1} . The temperature variation of the calorimeter was $\pm 0.1 \text{ K}$.

Acknowledgements. One of the authors (D. V. J.) wishes to thank the UGC, New Delhi, India, for selecting him as a Visiting Scholar to Finland, and to the Ministry of Education, Finland, for accepting the visit.

References

1. Christensen, J. J., Izatt, R. M. and Hansen, L. D. *J. Am. Chem. Soc.* **89** (1967) 213.
2. Bell, R. P. *The Proton in Chemistry*, 2nd ed., Chapman and Hall, London 1973, Chap. 5.
3. King, E. J. *Acid-Base Equilibria*, Pergamon Press, Oxford 1965, p. 248.
4. Kundu, K. K. and Bose, K. *Can. J. Chem.* **55** (1977) 55.

SHORT COMMUNICATION

5. Jahagirdar, D. V., Arbad, B. R., Chondhekar, T. K. and Pankanti, S. U. *Indian J. Chem.* 28 A (1989) 366.
6. Jahagirdar, D. V., Shelke, D. N. and Deshpande, R. G. *J. Chem. Soc., Perkin Trans. 2* (1977) 1513.
7. Born, M. In: King, E. J., Ed., *The Encyclopaedia of Physical Chemistry and Chemical Physics*, Vol. IV, Pergamon Press, Oxford 1965, p. 146.
8. Cook, H. F. *Trans. Faraday Soc.* 47 (1951) 751.
9. Clemett, C. J., Forest, E. and Smyth, C. P. *J. Chem. Phys.* 40 (1964) 2133.
10. Mazurkiewicz, J. and Tomasik, P. *J. Phys. Org. Chem.* 3 (1990) 493.
11. Hammes, G. G. and Knoche, W. *J. Chem. Phys.* 45 (1966) 4041.
12. Franks, F. and Ives, D. J. G. *Q. Rev.* 20 (1966) 1.
13. Gordon, J. E. *The Organic Chemistry of Electrolyte Solutions*, Wiley, New York 1975, p. 389.
14. Hale, J. D., Izatt, R. M. and Christensen, J. J. *J. Phys. Chem.* 67 (1963) 2605.

Received September 10, 1991.