Solvational Behavior of Some Substituted Benzoic Acids in Ethanol–Water Mixtures at 298.15 K

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The effect of substitution on the solubility and dissociation constants for the reaction

$$\mathrm{HA} \rightleftharpoons \mathrm{H}^+ + \mathrm{A}^-$$
$$(\mathrm{HA} = \text{substituted benzoic acids})$$

have been studied from the measurements of pH and solubilities of substituted benzoic acids in ethanol+water mixtures (0—100 wt%). The changes in the solubility values depend on the hydrophobic character and the dielectric constant of the solvent medium. The free energies of transfer for anions have been determined from the relation

$$\Delta G^\circ_\mathrm{t}(\mathrm{dissn.}) = \Delta G^\circ_\mathrm{t}(\mathrm{H}^+) + \Delta G^\circ_\mathrm{t}(\mathrm{A}^-) - \Delta G^\circ_\mathrm{t}(\mathrm{HA})$$

using the previously determined values of $\Delta G^\circ_\mathrm{t}(\mathrm{H}^+)$. The results are discussed in the light of solute-solvent interactions.

The importance of accurate solubility data and their diverse applications in different branches of science and technology have been stressed.[1,2] However, comparatively little studies have been made to study the effects of solvents on the solubilities and dissociation constants of different substituted benzoic acids.

In course of our studies on ion–solvent interaction,[3—10] it has been observed that the determination of free energies of transfer of solute from one solvent to other and the determination of ionic free energies of transfer provide the quantitative measure of ion (or solute)–solvent interactions.

The results are reported here.

Experimental

Absolute alcohol (B.C.P.W., Calcutta) was distilled twice and the middle fraction was used. Triply distilled water was used to prepare the solution. The solvent mixtures were prepared by weight. The densities were determined using a calibrated pycnometer. The dielectric constants of the mixed solvents were taken from the literature.[11]

Substituted benzoic acids (*o*-nitro-, *m*-nitro-, *p*-nitro-, *o*-chloro-, *m*-chloro-, and *p*-chlorobenzoic acids) were of Fluka's Puriss grade and need not be purified. However, the compounds were recrystallized from ethanol–water mixtures, dried in an air oven at 390 K and kept in a vacu um desiccator. The purity of the compounds was tested from melting point determinations and volumetric titration of acids.

The solubility measurements were made in the same way as described before.[5—9] The average values of the solubility of substituted benzoic acids in water and H_2O–EtOH systems at 298.15 K are presented in Tables 1 and 2. The errors in the solubility measurements are within 0.1 to 0.3%.

The dissociation constants of the acids were determined from pH-measurements of the saturated solutions of the substituted acids using Orion Digital pH-meter (Model EA™ 940 Expandable Ion Analyser) having an accuracy of ±0.001 pH unit. The glass electrode was calibrated in H_2O–EtOH systems before use in the way suggested by Van Uitert et al.[12] and used extensively by us and others.[12—17]

The meter readings (B) of the 10^{-4} M $HClO_4$ solutions in H_2O–EtOH systems (1 M=1 mol dm^{-3}) were taken using 10^{-4} M $HClO_4$ in aqueous solutions as pH 4. The 'correction factor' ($\log U_\mathrm{H}$) is obtained using the relation

$$\begin{aligned} -\log[\mathrm{H}^+] &= B + \log U_\mathrm{H} \\ \text{or,}\quad 4 &= B + \log U_\mathrm{H} \end{aligned}$$

The H^+ concentrations in H_2O–EtOH systems were obtained by algebraic addition of $\log U_\mathrm{H}$ to the meter reading of the desired solution in the solvent mixtures. In order to obtain better accuracy, the 'correction factor' was determined before each set of measurements.

Results

The thermodynamic dissociation constant for the reaction

$$\mathrm{HA} \rightleftharpoons \mathrm{H}^+ + \mathrm{A}^- \tag{1}$$
$$(\mathrm{A}^- = \text{substituted benzoate ion})$$

can be written as

$$\begin{aligned} K_\mathrm{T} &= \frac{C_{\mathrm{H}^+} \times C_{\mathrm{A}^-}}{C_\mathrm{HA}} \times \frac{f_+ \cdot f_-}{f_\mathrm{HA}} \\ &= \frac{C^2_{\mathrm{H}^+}}{(C_\mathrm{T} - C_{\mathrm{H}^+})} \times \frac{f^2_\pm}{f_\mathrm{HA}} \\ &\quad (\text{since } C_{\mathrm{H}^+} = C_{\mathrm{A}^-}) \end{aligned} \tag{2}$$

where C_T=total concentration of the acid determined from solubility measurements. C_{H^+}=concentration of

Table 1. Solubility and pK-Values of Nitrobenzoic Acids in EtOH+H_2O Mixtures at 298.15 K

wt% of EtOH	$1/\epsilon\times10^2$	A	o-$NO_2C_6H_4COOH$				m-$NO_2C_6H_4COOH$				p-$NO_2C_6H_4COOH$			
			Solubility mol dm^{-3}	Corrected pH	pK	pK_T	Solubility mol dm^{-3}	Corrected pH	pK	pK_T	Solubility mol dm^{-3}	Corrected pH	pK	pK_T
0.0	1.27	0.509	0.0334 (0.033395)	1.93	2.12	2.17 *2.17 (2.17)	0.0153 (0.015235)	2.69	3.47	3.49 *3.49 (3.49)	0.002525 (0.002516)	3.11	3.43	3.45 *3.45 (3.43)
8.0	1.35	0.5552	0.0421	1.98	2.46	2.55 (2.51)	0.0225	2.68	3.67	3.72 (3.70)	0.00305	3.09	3.51	3.54 (3.52)
16.4	1.42	0.6130	0.0482	2.03	2.65	2.73 (2.72)	0.0410	2.61	3.81	3.87 (3.86)	0.004975	3.03	3.67	3.71 (3.73)
25.3	1.53	0.6939	0.0581	2.17	3.05	3.17 (3.09)	0.0492	2.70	4.07	4.13 (4.10)	0.007425	2.98	3.76	3.81 (3.84)
34.4	1.71	0.7912	0.0627	2.30	3.36	3.46 (3.41)	0.0534	2.72	4.15	4.22 (4.28)	0.00845	3.03	3.93	3.98
44.0	1.90	0.9270	0.1942	2.22	3.71	3.84 (3.80)	0.1787	2.65	4.55	4.63 (4.61)	0.009075	3.13	4.18	4.23 (4.29)
54.1	2.14	1.133	0.5485	2.10	3.93	4.11 (4.11)	0.4365	2.55	4.74	4.87 (4.85)	0.009975	3.16	4.29	4.35 (4.41)
64.7	2.44	0.348	0.8432	2.25	4.42	4.61 (4.49)	0.8141	2.53	4.97	5.11 (5.12)	0.011025	3.21	4.39	4.46 (4.52)
76.0	2.87	1.707	1.1082	2.30	4.64	4.85 (4.72)	1.0892	2.75	5.54	5.68 (5.67)	0.022575	3.18	4.70	4.79 (4.88)
87.6	3.37	2.179	1.4821	2.35	4.87	5.14 (5.01)	1.4635	2.98	6.13	6.27 (6.26)	0.034475	3.11	4.75	4.86 (5.24)
100.0	3.95	2.792	1.6261 (1.6251)	—	—	—	1.6157 (1.6251)	—	—	—	0.05445 (0.05444)	—	—	—

*pK_T value-from Ref. 22. ( ) pK_T value-from conductance measurements. K=dissociation constant of the acid without activity correction. K_T=thermodynamic dissociation constant using activity corrections.

Table 2. Solubility and pK-Values of Chlorobenzoic Acids in EtOH+H_2O Mixtures at 298.15 K

wt% of EtOH	$1/\epsilon\times10^2$	A	o-ClC_6H_4COOH				m-ClC_6H_4COOH				p-ClC_6H_4COOH			
			Solubility mol dm^{-3}	Corrected pH	pK	pK_T	Solubility mol dm^{-3}	Corrected pH	pK	pK_T	Solubility mol dm^{-3}	Corrected pH	pK	pK_T
0.0	1.27	0.509	0.0210 (0.0208)	2.36	2.90	2.94 (2.94)	0.00408 (0.0041)	3.15	3.81	3.83 (3.83)	0.0008 (0.000797)	3.62	3.98	3.99 (3.98)
8.0	1.35	0.5552	0.0282	2.35	3.08	3.12	0.0048	3.17	3.96	3.98	0.0011	3.65	4.24	4.25
16.4	1.42	0.6130	0.0440	2.38	3.36	3.41	0.0073	3.18	4.18	4.20	0.0015	3.67	4.45	4.46
25.3	1.53	0.6939	0.0525	2.47	3.63	3.68	0.0152	3.12	4.40	4.43	0.0028	3.63	4.67	4.68
34.4	1.71	0.7912	0.0945	2.45	3.86	3.92	0.0628	2.96	4.71	4.75	0.0061	3.53	4.82	4.84
44.0	1.90	0.9270	0.1885	2.40	4.07	4.15	0.1350	2.90	4.91	4.96	0.0125	3.48	5.05	5.08
54.1	2.14	1.133	0.3770	2.30	4.17	4.29	0.2872	2.86	5.18	5.25	0.0190	3.50	5.27	5.30
64.7	2.44	1.348	0.4975	2.29	4.27	4.42	0.3978	2.91	5.42	5.50	0.0395	3.47	5.53	5.57
76.0	2.67	1.707	0.6385	2.30	4.40	4.60	0.4795	2.98	5.64	5.75	0.0758	3.44	5.75	5.82
87.6	3.37	2.179	0.9270	2.35	4.66	4.91	0.5195	3.02	5.75	5.87	0.1516	3.38	5.93	6.03
100.0	3.95	2.792	1.1275	—	—	—	0.6480	—	—	—	0.2895	—	—	—

H^+ ion in the saturated solution of HA.

The activity coefficients of ions $f_\pm$ in solutions of every low ionic strength (ca. 10^{-3} M) have been calculated using Davies equation[18]

$$-\log f_\pm = \frac{AZ_i^2\sqrt{\mu}}{1+\sqrt{\mu}} - 0.2\mu \tag{3}$$

with appropriate A-values in each solvent. f_{HA} has been assumed to be unity in saturated solution i.e. in the standard states of the respective solvents. Similar assumptions have been made by other workers also.[19]

The free energy of transfer for neutral substituted benzoic acids are given by

$$\begin{aligned}\Delta G_t^\circ(\mathrm{HA})_{\mathrm{neut}} &= -2.303RT\log\frac{(1-\alpha_s)\,C_s}{(1-\alpha_w)\,C_w}\times\frac{f_s(\mathrm{HA})}{f_w(\mathrm{HA})}\\ &= -2.303RT\log\frac{(1-\alpha_s)\,C_s}{(1-\alpha_w)\,C_w}\end{aligned} \tag{4}$$

where C_s and C_w are the molar solubilities of the acid in solvents and water respectively. α_s and α_w are the degrees of dissociation of acids in aqueous organic solvent and water respectively.

The free energy of transfer for the dissociation of the substituted benzoic acids have been calculated from the equation

$$\Delta G_t^\circ(1) = -2.303RT\,[\log K_\mathrm{T}(s) - \log K_\mathrm{T}(w)] \qquad (5)$$

Discussion

The solubilities and the $\mathrm{p}K_\mathrm{T}$ values of substituted benzoic acids at 298.15 K in EtOH+H_2O mixtures are presented in Tables 1 and 2. The accuracy of $\mathrm{p}K_\mathrm{T}$ values are 0.01 to 0.02. The values in aqueous solutions agree with the literature.[20—22] The sequence of the solubility of substituted benzoic acids in water is

$$o\text{-NO}_2\text{-} > o\text{-Cl-} > m\text{-NO}_2\text{-} > m\text{-Cl-} > p\text{-NO}_2\text{-} > p\text{-Cl-}$$

The sequence is usually maintained at low percentages of EtOH but the order is changed at higher percentages. Usually meta compounds are more soluble than the corresponding para compounds.

The solubilities of benzoic acids increase with the increasing hydrophobic character of the aqueous organic solvents. The variations of the solubility of the substituted benzoic acids in different substances arise from the differences in the cohesion between like solute molecules and solute-solvent interactions of various types.[23] But no quantitative correlation is possible.

The $\mathrm{p}K_\mathrm{T}$ values of substituted benzoic acids increase continuously with increase in organic co-solvent and show a linear relationship when plotted against (i) mole fraction of EtOH and (ii) $1/\epsilon$ (ϵ is the relative permittivity of the solvent) well up to ca. 40 wt% beyond which deviations from linearity occur.

It is to be noted that $\mathrm{p}K_\mathrm{T}$ values of *p*-nitrobenzoic acid are much higher than those for *o*-nitrobenzoic acid in water rich solvents but the reverse is true beyond ca. 60 wt% of ethanol. High solubilities of *o*-nitrobenzoic acid in these solvent mixtures may be the reason for it but the correctness of the results was confirmed by conductometric determination of $\mathrm{p}K_\mathrm{T}$ values using Fuoss–Kraus method.[24]

Transfer free changes of electrolytes may give little idea regarding solvent effects on solute–solvent interactions but the transfer free energy changes of single ions have enormous potentialities in quantitative correlations between the equilibrium constants, rate constant etc.[25] However, the single ion values of organic ions are more important as most of the compounds of biological interest are organic ions.

Thus, attempts have been made to determine the single ion values of substituted benzoate ions. We have from Eq. 1

$$\Delta G_\mathrm{t}^\circ(1) = \Delta G_\mathrm{t}^\circ(\mathrm{H}^+) + \Delta G_\mathrm{t}^\circ(\mathrm{A}^-) - \Delta G_\mathrm{t}^\circ(\mathrm{HA}) \qquad (6)$$

or,

$$\Delta G_\mathrm{t}^\circ(\mathrm{A}^-) = \Delta G_\mathrm{t}^\circ(1) - \Delta G_\mathrm{t}^\circ(\mathrm{H}^+) + \Delta G_\mathrm{t}^\circ(\mathrm{HA}) \qquad (7)$$

$\Delta G_\mathrm{t}^\circ(\mathrm{H}^+)$ values have been taken from the works in our laboratory.[7] The values of $\Delta G_\mathrm{t}^\circ(\mathrm{A}^-)$ of substituted benzoate ions are given in Table 3. The uncertainties in the experimentally determined values of $\Delta G_\mathrm{t}^\circ(1)$ and $\Delta G_\mathrm{t}^\circ(\mathrm{HA})$ are small. The accuracy of $\Delta G_\mathrm{t}^\circ(\mathrm{A}^-)$ depends mainly on the accuracy of $\Delta G_\mathrm{t}^\circ(\mathrm{H}^+)$ values.

Single ion values can not be determined thermodynamically. The single ion values are always obtained using extrathermodynamic assumptions and the accuracy of the values are invariably dependent on the assumptions involved. Due to this limitation, the single ion values can not be exact. But inspite of limitations, $\Delta G_\mathrm{t}^\circ(\mathrm{A}^-)$ values calculated by us have been found to be predominantly positive i.e. the transfer process from water to mixed solvents is unfavourable, a fact generally observed in practice.[5,25—28] It is expected that the stabilization of anion due to hydrogen bonding in aqueous system decreases as we go from aqueous to aqueous organic solvents of decreased hydrogen bonding capability and increased basicity. Thus the results reported by us can be regarded fairly good. $\Delta G_\mathrm{t}^\circ(\mathrm{A}^-)$ values have been found to be maximum in the region 34—44 wt% of ethanol where the characteristic changes in the solvent properties are observed. The addition of ethanol is known to strengthen the three dimensional structure of water. The maximum structure formulation occurs in the region of 34—44 wt% of ethanol and thereafter depolymerization of water takes place. There are reflected in the ultrasonic absorption and excess properties of mixing.[27—31]

Since the electrostatic contributions are likely to be the same for benzoic acid and substituted benzoic acids, the energy changes due to structural variations of the solvent mixtures resulting from substituent effects should be totally reflected in the changes in nonelectrostatic components. The variation of the nonelectrostatic components with solvent-composition can be had from the relation

$$\begin{aligned}\delta\Delta G_\mathrm{t}^\circ(\text{non-el}) &= \Delta G_\mathrm{t}^\circ(1)(\text{subs. acid}) \\ &\quad - \Delta G_\mathrm{t}^\circ(\text{benzoic acid})\end{aligned} \qquad (8)$$

and is shown in Fig. 1. $\Delta G_\mathrm{t}^\circ$(benzoic acid) values have been taken from our earlier communication.[5]

The values of $\delta\Delta G_\mathrm{t}^\circ$(non el) represent the structural variations of the solvent-mixtures resulting from interactions of the substituent groups in the parent molecule. It is apparent that the behavior of the chloro and nitro groups is different and obviously dependent on the ortho, meta or para positions.

The free energy of transfer of molecules and ions usually give the quantitative measure of solute–solvent or

Table 3. Free Energy of Transfer of Anion $\Delta G^\circ_t(\mathrm{A}^-)$ of Substituted Benzoic Acid (in kJ mol^{-1}) from Water to EtOH+H_2O Mixtures at 298.15 K

wt% of EtOH	ΔG°_t (H^+)[a]	ΔG°_t (Bz^-)[b]	ΔG°_t (o-$\mathrm{NO_2Bz}^-$)	ΔG°_t (m-$\mathrm{NO_2Bz}^-$)	ΔG°_t (p-$\mathrm{NO_2Bz}^-$)	ΔG°_t (o-ClBz^-)	ΔG°_t (m-ClBz^-)	ΔG°_t (p-ClBz^-)
8.0	−1.08	1.21	2.68	1.43	1.13	1.38	1.54	1.77
16.4	−1.83	2.07	4.12	1.56	1.64	2.68	1.65	2.95
25.3	−2.70	2.83	7.04	3.46	2.09	4.65	2.39	3.44
34.4	−3.38	1.83	9.18	4.45	3.39	5.24	1.86	3.20
44.0	−4.52	3.05	9.69	4.93	5.80	5.98	2.30	3.93
54.1	−5.53	4.20	9.67	5.10	7.27	6.07	3.09	5.15
64.7	−5.63	6.00	11.55	5.02	7.75	6.23	3.81	4.98
76.0	−5.53	6.16	12.14	6.46	7.75	6.54	4.56	4.69
87.6	−4.66	6.33	12.21	9.22	6.23	6.52	4.29	3.30

a) Ref. 7. b) Ref. 5.

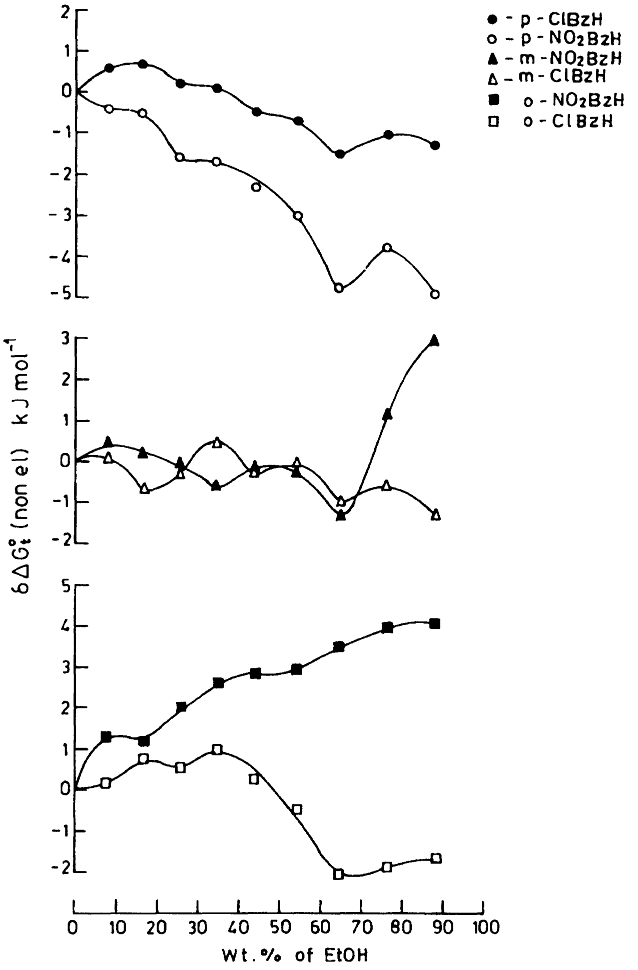

Fig. 1. Plots of non electrostatic components ($\delta\Delta G^\circ_t$) of substituted Benzoic Acids against wt% of EtOH.

ion solvent interactions which, however, include free energy change due to cavity formation in the solvent to accommodate the molecule or ion in question in addition to interaction energies. It is natural to expect better insight from the interaction energies.

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