Indian Journal of Chemistry
Vol. 34A, February 1995, pp. 134-136

Salting coefficient of hydroxybenzoic acids

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Received 6 June 1994; revised 17 August 1994; accepted 15 September 1994

The Setschenow parameter and thermodynamic parameters of transfer of 2- and 4- hydroxybenzoic acids from water to salt solutions have been reported. The data have been rationalised by considering the structure breaking effects of the ions of the salts, the localized hydrolysis model, the internal pressure theory and the theory of water structure due to Symons.

Studies of the salt effect on the activity coefficient of nitrobenzoic acids[1,2] and acid terephthalic esters[3] revealed that these solutes behave differently from other acidic nonelectrolytes[4-7]. They were salted in by many of the electrolytes. In none of these cases the Setschenow equation was found valid over the entire concentration range. These observations led us to investigate the salting coefficient of 2- and 4- hydroxybenzoic acids in water. The following electrolytes were employed: KCl, KBr, KI, KNO_3, K_2SO_4, $MgSO_4$ and tetramethylammonium chloride (TMACl). The Setschenow parameter (*K*s) and the thermodynamic parameters of transfer (ΔH_{tran} and ΔS_{tran}) of the solute from water to salt solution have been computed from solubility measurement at various temperatures in the presence and absence of salts.

Experimental

All the salts employed were of AR grade, 2-Hydroxybenzoic acid (KL, England) m.p. 159 (lit. m.p.[8] 158.3) and 4- hydroxybenzoic acid (KL, England) m.p. 214 (lit. m.p.[8] 215.5) were employed as such. Solutions were prepared in conductivity water.

Determination of solubilities

Solubility at a constant temperature (± 0.02°C) maintained by Haake EK 51 bath system was determined by spectrophotometric method using a Hitachi 200-20 UV visible spectrophotometer. The solute with salt solution in boiling tube (fitted with a mercury seal apparatus to minimise the loss due to evaporation) was shaken with an ingenously fabricated shaking machine to attain equilibrium. Solubility was determined at 20, 25, 35 and 40°C for [salt] from 0.05-0.35 mol dm^{-3}. The results were reproducible within an error of 0.5%. The probable error[9] in ΔH_{tran} was 0.02 kJ mol^{-1} while that in ΔS_{tran} was 0.1 JK^{-1}. The data are given in Table 1. *K*s was determined using the equation

Table 1—Solubility of 2- and 4- hydroxybenzoic acids in salt solutions at different temperatures (10^{-2} mol dm^{-3})

[Salt]	20°	25°	35°							40°C
	0.10	0.10								0.10
			0.05	0.10	0.15	0.20	0.25	0.30	0.35	
2-Hydroxybenzoic acid [S_o = 1.531 (20°), 1.861 (25°), 2.805 (35°) and 3.211 (40°)]										
KCl	1.531	1.861	2.822	2.798	2.800	2.739	2.698	2.664	2.624	3.197
KBr	1.573	1.909	2.886	2.860	2.827	2.787	2.762	2.728	2.704	3.260
KI	1.590	1.924	2.917	2.879	2.844	2.768	2.737	2.737	2.708	3.287
KNO_3	1.666	2.008	2.976	2.956	2.940	2.923	2.906	2.881	2.861	3.358
TMACl	1.548	1.900	2.850	2.913	2.999	3.102	3.158	3.217	3.265	3.391
K_2SO_4	1.899	2.326	3.489	3.561	3.593	3.663	3.728	3.781	3.851	4.107
$MgSO_4$	1.548	1.900	3.254	3.367	3.402	3.473	3.658	3.632	3.627	3.391
4-Hydroxybenzoic acid [S_o = 2.771 (20°), 3.688 (25°), 7.181 (35°) and 8.814 (40°)]										
KCl	2.752	3.649	7.142	7.066	6.930	6.841	6.707	6.597	6.496	8.607
KBr	2.765	3.671	7.151	7.115	6.985	6.834	6.756	6.714	6.673	8.713
TMACl	2.816	3.731	7.188	7.214	7.432	7.720	7.906	8.086	8.244	8.814
K_2SO_4	2.810	3.709	7.202	7.081	6.991	6.921	6.831	6.756	6.639	8.606
$MgSO_4$	2.739	3.621	7.089	6.939	6.714	6.482	6.289	6.097	5.922	8.489

$$\frac{\text{Lim}}{[\text{salt}] \to 0} \quad Ks = \frac{\log (S_0/S)}{[\text{salt}]}$$

where S and S_0 are the solubility of the solute in the presence and absence of salt. The equation is not obeyed at high [salt]. The values are given in Table 2. Vant Hoff reaction isochore was applied to Ks at different temperatures and ΔH_{tran} was calculated by the method of least squares. ΔG_{tran} is related to Ks by the relation

$$\Delta G_{\text{tran}} = \text{RT} \ln Ks$$

$$\Delta S_{\text{tran}} = \frac{\Delta H_{\text{tran}} - \Delta G_{\text{tran}}}{\text{T}}$$

The ΔH_{tran} and ΔS_{tran} of one mole of solute from water to salt solution (0.1 mol dm.$^{-3}$) at 25°C are also given in Table 2.

Results and discussion

KCl, KBr, KI and KNO_3 salted out 2-hydroxybenzoic acid obeying Setschenow equation with initial salting in KCl and KBr salted out 4-hydroxybenzoic acid over the entire concentration range obeying Setschenow equation. Studies with KI and KNO_3 could not be carried out in the case of 4-hydroxybenzoic acid because of the strong absorption of these salts at the λ_{max} of the solute (249 nm). When an electrolyte is added to an aqueous solution of nonelectrolyte the increase in internal pressure resulting from ion water interaction compresses the water molecules and squeezes the solutes out. The effect of the salt on the activity coefficient of the solute is determined by the extent to which water structure is compacted or loosened. This in turn depends on the relative size of ion and water molecule and the charge on the ion. Small ions of high charge will make the water structure more rigid and the entry of solute molecule into solution is obstructed causing salting out. The charge: size ratio of the anion is in the order $Cl^- > Br^- > NO_3^- > I^-$. Salting out parameter should decrease in the same order which is observed. The structure breaking action of the ions increases in the order $I^- > Br^- > NO_3^- > Cl^-$. Hence the salting out pattern should be observed in the opposite direction. The observed salt effect is the resultant of the two.

TMACl salted in both the solutes. Bockris *et al*[10] attributed salting in by large TMA^+ to dispersion forces between ions and neutral solute and solvent molecules. Long- McDevitt theory[11] also predicts salting in by this ion. On the basis of localized hydrolysis model TMA^+ is a structure breaker[12-14] resulting salting in.

K_2SO_4 and $MgSO_4$ salted in 2-hydroxybenzoic acid and Setschenow equation was not valid. 4-hydroxybenzoic acid was salted out obeying Setschenow equation. SO_4^{2-} is a powerful structure maker[15]. This will reduce the solubility because the proportion of $(H_2O)_d$ molecules will be reduced. In nitrobenzoic acids the electron withdrawing nature of the nitro group makes the carboxyl proton more acidic. The nitro group makes H-bond through OH_f (Symons terminology[16]) and the carboxyl group through the LP_f of water molecules. The inductive effect of nitro group favours this process by making nitro group and carboxyl proton more sensitive to H-bonding. Contribution to solubility by the two sites are not independent. The sulphate ions increase the solubility through an electrostatic attraction between the negative end of the dipole of water molecule and H of carboxyl group. The immobilization of water molecules by SO_4^{2-} caused by H-bonding through the OH_f of water molecules will

Table 2—Setschenow parameter (Ks) and thermodynamic parameters of transfer at 25° of 2- and 4-hydroxybenzoic acids

Salt	Ks	2-Hydroxybenzoic acid		Ks	4-Hydroxybenzoic acid	
		ΔH_{tran} (kJ mol^{-1})	ΔS_{tran} (JK^{-1} mol^{-1})		ΔH_{tran} (kJ mol^{-1})	ΔS_{tran} (JK^{-1} mol^{-1})
KCl	0.11	0.17	−0.6	0.14	−0.6	−2.1
KBr	0.10	−0.46	−1.3	0.11	−0.36	−1.2
KI	0.08	−0.55	−1.6	—	—	—
KNO_3	0.06	−1.57	−4.7	—	—	—
TMACl	−0.20	−1.59	−5.5	−0.22	−0.6	−1.9
K_2SO_4	—	1.17	5.8	0.11	1.43	6.2
$MgSO_4$	—	−1.43	6.2	0.26	−1.01	−3.5

expose the LP_f site of water molecules to H-bond with carboxyl proton of the acid solute. The acidity of carboxyl proton plays the most important role in the salt effect of SO_4^{-2} which has been discussed from similar studies on picric acid[17]. The intramolecular H- bonding of 2-hydroxybenzoic acid increases the acidity of carboxyl proton ($pK_a = 2.98$). It suggests that the solubility increase is due to the increased H-bonding through this proton. The favourable effect on solubility due to electrostatic effect will be important only when H-bonding occurs between the carboxyl group and the LP_f of water molecules. Data on phthalic acid[18] substantiates this argument. The thermodynamic parameters of transfer are in agreement with the experimental data.

Acknowledgement

The authors wish to acknowledge their sincere gratitude to Dr R Anantaraman, Hon. Professor, University of Kerala, India, for his valuable suggestions.

References

1 Sugunan S, *Indian J Chem*, 22A (1983) 150.
2 Sugunan S, *Indian J Chem*, 23A (1984) 763:
3 Anantaraman R & Chandramohanakumar K (Unpublished work).
4 Sergeeva V F, *Russ Chem Revs*, 34 (1965) 309.
5 Chargkova A K & Talnikova T V, *Zh Anal Kim*, (1974) 958.
6 Ya Koreman I, *Tr Khim Teknol*, 3 (1973) 134.
7 Ya Koreman I & Makarova T V, *Zh Fiz Khim*, 48 (1974) 365.
8 *Dictionary of organic compounds*. 5th Edn (Chapman & Hall) 1982.
9 Margenau H & Murphy G M. *Mathematics for physics and chemistry* (D Van Nostrand Co), 1956, 519.
10 Bockris J O M, Bowler Reed & Kitchener J A, *Trans Faraday Soc*, 47 (1951) 184.
11 Long F A & McDevitt W, *J Am chem Soc*, 74 (1952) 1775.
12 Kay R L, *A C S Advances in Chemistry Series*, 1968, 73, 1.
13 Kay R L & Evans D F, *J phys Chem*, 70 (1966) 2325.
14 Francks F & Smith H Y, *Trans Faraday Soc*, 63 (1967) 2586.
15 Marcus Y, *Ion solvation* (Wiley Interscience, New York), 1985, 113,
16 Symons M C R, *Acc chem Res*, 14 (1983) 179.
17 Franco J, Patel N K, *Technol India*, 12 (1975) 157.
18 Ravitt R C D & Rosenblum E I, *Trans Faraday Soc*, 9 (1914) 297.