

Salting Coefficients of 2-, 3-, and 4-Methylbenzoic Acids

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The Setschenow parameter and thermodynamic parameters of transfer of 2-, 3-, and 4-methylbenzoic acids from water to salt solutions have been reported. The data have been rationalized by considering the structure-breaking effects of the ions of the salts, the localized hydrolysis model, and the internal pressure theory.

Introduction

Studies on the salt effect on the activity coefficients of substituted benzoic acids revealed that nitrobenzoic acids (1, 2) and acid terephthalic esters (3) behave differently from others in various respects. They were salted in by many of the electrolytes. K_2SO_4 showed more salting in than other electrolytes. In none of these cases was the Setschenow equation (4) found valid over the entire concentration range. These observations led us to investigate the salt effect on the activity coefficients of 2-, 3-, and 4-methylbenzoic acids in water. The following electrolytes were employed: KCl, KBr, KI, KNO_3 , K_2SO_4 , $MgSO_4$, and tetramethylammonium chloride ((TMA)Cl). The Setschenow parameter (K_s) and the thermodynamic parameters of transfer (ΔH and ΔS) of the solute from water to aqueous salt solution have been computed from solubility measurements at various temperatures in the presence and absence of salts.

Experimental Section

All the salts employed were of AR grade. 2-Methylbenzoic acid (KL England), mp 107 °C (lit. (5) mp 105 °C), 3-methylbenzoic acid (KL England), mp 111 °C (lit. (5) mp 110 °C), and 4-methylbenzoic acid (KL England), mp 182 °C (lit. (5) mp 180 °C) were employed as such. Solutions were prepared in conductivity water. The solubility (at constant temperature (± 0.02 °C) maintained by an EK 51 Haake bath

system) was determined by the spectrophotometric method using a Hitachi 200-20 UV-visible spectrophotometer. The solute with salt solution in a boiling tube (fitted with a mercury seal apparatus to minimize the loss due to evaporation) was shaken with an indigenously fabricated shaking machine to attain equilibrium. The solubility was determined at 20, 25, 35, and 40 °C for salt concentrations from 0.05 to 0.35 mol dm^{-3} . The results were reproducible within an error of 0.5%. The probable error (6) in ΔH is 0.02 $kJ\ mol^{-1}$, while that in ΔS is 0.1 $J\ K^{-1}\ mol^{-1}$. The data are given in Table I. Since added sodium benzoate did not change the solubility of benzoic acid (7), it was concluded that the solubility is unaffected by the dissociation of the acid in solution. K_s was determined using the equation

$$\lim_{[salt] \rightarrow 0} K_s = \log(S_0/S)/[salt]$$

where S and S_0 are the solubilities of the solute in the presence and absence of salt. The values are given in Table II. The ΔH and ΔS of 1 mol of solute from water to salt solution (0.1 mol dm^{-3}) at 25 °C are also given in Table II.

Results and Discussion

All the electrolytes except (TMA)Cl salted out the solutes, and the Setschenow equation was valid from 0.05 to 0.35 mol dm^{-3} salt concentration. In methylbenzoic acids the presence of a larger apolar methyl group can lead to intermolecular

Table I. Solubility S of 2-, 3-, and 4-Methylbenzoic Acids in Salt Solutions at Different Temperatures

| salt | $S/(10^{-2}\ mol\ dm^{-3})$ | | | | | | | | | |
|--|-----------------------------|---------------|-------|-------|-------|-------|-------|-------|-------|-------|
| | 20 °C 0.10 | 25 °C 0.10 | 35 °C | | | | | 40 °C | | |
| | 0.05 | 0.10 | 0.15 | 0.20 | 0.25 | 0.30 | 0.35 | 0.10 | 0.10 | |
| 2-Methylbenzoic Acid [$S_0 = 0.606$ at 20 °C, 0.789 at 25 °C, 1.190 at 35 °C, and 1.383 at 40 °C] | | | | | | | | | | |
| KCl | 0.571 | 0.757 | 1.172 | 1.161 | 1.139 | 1.108 | 1.073 | 1.039 | 1.011 | 1.370 |
| KBr | 0.577 | 0.757 | 1.191 | 1.168 | 1.144 | 1.116 | 1.085 | 1.055 | 1.035 | 1.380 |
| KI | 0.584 | 0.771 | 1.226 | 1.208 | 1.202 | 1.168 | 1.145 | 1.102 | 1.072 | 1.423 |
| KNO_3 | 0.624 | 0.804 | 1.214 | 1.192 | 1.177 | 1.165 | 1.135 | 1.104 | 1.073 | 1.366 |
| (TMA)Cl | 0.609 | 0.797 | 1.198 | 1.219 | 1.250 | 1.277 | 1.292 | 1.305 | 1.319 | 1.423 |
| K_2SO_4 | 0.632 | 0.811 | 1.215 | 1.198 | 1.154 | 1.124 | 1.108 | 1.082 | 1.066 | 1.353 |
| $MgSO_4$ | 0.601 | 0.768 | 1.140 | 1.126 | 1.098 | 1.070 | 1.041 | 1.023 | 1.009 | 1.274 |
| 3-Methylbenzoic Acid [$S_0 = 0.786$ at 20 °C, 0.915 at 25 °C, 1.134 at 35 °C, and 1.263 at 40 °C] | | | | | | | | | | |
| KCl | 0.704 | 0.827 | 1.086 | 1.073 | 1.046 | 1.020 | 0.992 | 0.975 | 0.962 | 1.175 |
| KBr | 0.711 | 0.841 | 1.090 | 1.072 | 1.053 | 1.041 | 1.018 | 1.006 | 0.982 | 1.208 |
| KI | 0.761 | 0.896 | 1.184 | 1.160 | 1.151 | 1.140 | 1.122 | 1.094 | 1.070 | 1.298 |
| KNO_3 | 0.808 | 0.957 | 1.252 | 1.220 | 1.212 | 1.201 | 1.162 | 1.133 | 1.109 | 1.383 |
| (TMA)Cl | 0.758 | 0.895 | 1.144 | 1.151 | 1.175 | 1.193 | 1.211 | 1.232 | 1.251 | 1.304 |
| K_2SO_4 | 0.758 | 0.899 | 1.160 | 1.142 | 1.106 | 1.079 | 1.052 | 1.016 | 0.973 | 1.288 |
| $MgSO_4$ | 0.736 | 0.862 | 1.122 | 1.099 | 1.072 | 1.044 | 1.014 | 0.978 | 0.940 | 1.234 |
| 4-Methylbenzoic Acid [$S_0 = 0.193$ at 20 °C, 0.243 at 25 °C, 0.342 at 35 °C, and 0.392 at 40 °C] | | | | | | | | | | |
| KCl | 0.183 | 0.232 | 0.344 | 0.341 | 0.336 | 0.328 | 0.320 | 0.308 | 0.299 | 0.399 |
| KBr | 0.191 | 0.245 | 0.362 | 0.355 | 0.350 | 0.335 | 0.330 | 0.325 | 0.320 | 0.417 |
| (TMA)Cl | 0.195 | 0.246 | 0.346 | 0.349 | 0.354 | 0.359 | 0.365 | 0.371 | 0.378 | 0.401 |
| K_2SO_4 | 0.202 | 0.251 | 0.353 | 0.348 | 0.340 | 0.332 | 0.327 | 0.321 | 0.315 | 0.394 |
| $MgSO_4$ | 0.198 | 0.244 | 0.335 | 0.330 | 0.322 | 0.314 | 0.309 | 0.312 | 0.295 | 0.372 |

Table II. Setschenow Parameter (K_s) and Thermodynamic Parameters of Transfer (ΔH , ΔS) at 25 °C of 2-, 3-, and 4-Methylbenzoic Acid

| electrolyte | K_s | $\Delta H/(\text{kJ mol}^{-1})$ | $\Delta S/(\text{J K}^{-1} \text{mol}^{-1})$ |
|--------------------------------|-------|---------------------------------|--|
| 2-Methylbenzoic Acid | | | |
| KCl | 0.23 | 1.92 | 6.0 |
| KBr | 0.21 | 1.79 | 5.7 |
| KI | 0.19 | 2.60 | 8.6 |
| KNO ₃ | 0.17 | 0.79 | 2.6 |
| (TMA)Cl | -0.14 | 0.92 | 3.2 |
| K ₂ SO ₄ | 0.18 | -2.46 | -8.1 |
| MgSO ₄ | 0.19 | -2.69 | -9.3 |
| 3-Methylbenzoic Acid | | | |
| KCl | 0.16 | 1.61 | 4.6 |
| KBr | 0.14 | 2.11 | 6.4 |
| KI | 0.13 | 2.48 | 8.2 |
| KNO ₃ | 0.17 | 2.35 | 8.3 |
| (TMA)Cl | -0.13 | 2.66 | 8.8 |
| K ₂ SO ₄ | 0.25 | -2.08 | -6.8 |
| MgSO ₄ | 0.25 | -1.71 | -5.3 |
| 4-Methylbenzoic Acid | | | |
| KCl | 0.21 | 2.89 | 9.4 |
| KBr | 0.19 | 2.62 | 8.8 |
| (TMA)Cl | -0.13 | 0.58 | 2.1 |
| K ₂ SO ₄ | 0.17 | -1.49 | -4.7 |
| MgSO ₄ | 0.19 | -3.04 | -10.2 |

hydrophobic interactions which in turn increase the "structuredness" of the surrounding water molecules. When an electrolyte is added to an aqueous solution of nonelectrolyte, the increase in internal pressure resulting from the ion-water interaction compresses the water molecules and squeezes the solutes out. This effect depends on the relative size of the ion and water molecules and the charge on the ion. Small ions of high charge will make the water structure more rigid and will increase the cohesive energy density. The entry of a solute molecule into solution is obstructed, causing salting out. The structure-breaking action (8,9) of the ions increases

in the order $\text{I}^- > \text{Br}^- > \text{NO}_3^- > \text{Cl}^-$, resulting in salting in of solutes by the ions in the same order. According to the localized hydrolysis model, the orientation of water molecules by these ions would increase the solubility by H-bonding with the carboxyl group in the reverse order. The observed salt effect is the resultant of the two. SO_4^{2-} is a structure maker (9). The immobilization of water molecules by this highly charged and compact ion increases the cohesive energy density, resulting in salting out. While KCl salted out these solutes, (TMA)Cl salted them in. The difference in behavior arises from the cationic part of the electrolyte (7). The Long-McDevitt theory (10) also predicts salting in by this electrolyte. On the basis of the localized hydrolysis model, TMA^+ is a structure breaker (8, 11, 12), resulting in salting in. The enthalpies and entropies of transfer are all positive except for sulfates. The positive values can be rationalized in terms of the structure-breaking action of the ions. The negative values for sulfates are in agreement with the structure-making action of SO_4^{2-} .

Literature Cited

- (1) Sugunan, S. *Indian J. Chem.* 1983, 22A, 150.
- (2) Sugunan, S. *Indian J. Chem.* 1984, 23A, 763.
- (3) Chandramohanakumar, K. Ph.D. Dissertation, University of Kerala, India, 1985.
- (4) Setschenow, J. Z. *Phys. Chem.* 1889, 4, 117.
- (5) *Dictionary of Organic Compounds*, 5th ed.; Chapman & Hall: London, 1982.
- (6) Margenau, H.; Murphy, G. M. *Mathematics for Physics and Chemistry*; D. Van Nostrand Co.: New York, 1956; p 619.
- (7) Bockris, J. O. M.; Bowler Reed; Kitchener, J. A. *Trans. Faraday Soc.* 1951, 47, 184.
- (8) Kay, R. L. A. *Adv. Chem. Ser.* 1968, 73, 1.
- (9) Marcus, Y. *Ion Solvation*; Wiley Interscience: New York, 1983; p 113.
- (10) Long, F. A.; McDevitt, W. F. *J. Am. Chem. Soc.* 1952, 74, 1952.
- (11) Kay, R. L.; Evans, D. F. *J. Phys. Chem.* 1966, 70, 2325.
- (12) Francks, F.; Smith, H. Y. *Trans. Faraday Soc.* 1967, 63, 2586.

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