

## Salting Coefficients of Fluorobenzoic Acids

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*The Setschenow parameter and thermodynamic parameters of transfer of 2-, 3- and 4-fluorobenzoic acid from water to salt solution are 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.*

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**KEY WORDS:** Salting in, out and coefficients; Setschenow parameter; fluorobenzoic acids; structural hydration interaction; thermodynamic parameters of transfer.

### 1. Introduction

Studies of the salt effect on the activity coefficients of substituted benzoic acids revealed that nitrobenzoic acids<sup>(1,2)</sup> and acid terephthalic esters<sup>(3)</sup> behave differently from others in various respects. They were salted in by many of the electrolytes with  $K_2SO_4$  showing more salting in than other electrolytes. In none of these cases was the Setschenow equation<sup>(4)</sup> found to be valid over the entire concentration range. These observations led us to investigate the salt effect on the activity coefficient of 2-, 3- and 4-fluorobenzoic acids in water. The following electrolytes were employed: KCl, KBr, KI, KCNS,  $KNO_3$ ,  $K_2SO_4$ ,  $MgSO_4$  and tetramethylammonium chloride (TMACl). The Setschenow parameter  $K_s$  and the thermodynamic parameters of transfer  $\Delta_t H$  and  $\Delta_t S$  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.

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## 2. Materials and Methods

All the salts employed were of AR grade. 2-Fluorobenzoic acid (KL, England) m.p. 124 (lit. m.p. 122<sup>(5)</sup>), 3-fluorobenzoic acid (KL, England) m.p. 125 (lit. m.p. 124<sup>(5)</sup>) and 4-fluorobenzoic acid (KL, England) m.p. 185 (lit. m.p. 185°C<sup>(5)</sup>) were employed as such. Solutions were prepared using conductivity water. Solubility (at constant temperature  $\pm 0.02^\circ\text{C}$ , maintained by a EK 51 Haake bath system) was determined by spectrophotometric method (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 ingeniously 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<sup>-3</sup>. The results were reproducible within an error 0.5 percent. The probable error<sup>(10)</sup> in  $\Delta_t H$  is 0.02 kJ-mol<sup>-1</sup>, while that in  $\Delta_t S$  is 0.1 J-K<sup>-1</sup>-mol<sup>-1</sup>. The data are given in Table I.  $K_s$  was determined using the equation

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

where  $S$  and  $S_0$  are the solubility of the solute in the presence and absence of salt. The values are given in Table II. The  $\Delta_t H$  and  $\Delta_t S$  of one mole of solute from water to salt solution (0.1 mol-dm<sup>-3</sup>) at 25°C are also given in Table II.

## 3. Results and Discussion

All the electrolytes except TMACl salted out the solutes and Setschenow equation was valid from 0.05 to 0.35 mol-dm<sup>-3</sup> salt concentration. When an electrolyte is added to an aqueous solution of non-electrolyte the increase in internal pressure resulting from ion water interaction compresses the water molecules and squeezes the solutes out. This effect 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 will increase the cohesive energy density. The entry of solute molecule into solution is thus obstructed causing salting out. The structure breaking action<sup>(7,8)</sup> of the ions increase in the order  $\text{CNS}^- > \text{I}^- > \text{Br}^- > \text{NO}_3^- > \text{Cl}^-$  resulting in diminishing salting out of the solutes by these salts in this order. According to localized hydrolysis model the orientation of water molecules by these ions would increase the solubility by H-bonding with the carboxyl in the order  $\text{Cl}^- > \text{NO}_3^- > \text{Br}^- > \text{I}^- > \text{CNS}^-$ .<sup>(9)</sup> The observed salt effect is the result of

Table I. Solubility of 2-,3- and 4-Fluorobenzoic Acid in Salt Solutions at Various Temperatures<sup>a</sup>

Salt	0.10	0.10	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.10
2-Fluorobenzoic Acid <sup>b</sup>										
KCl	3.95	4.87	7.06	6.95	6.82	6.73	6.64	6.57	6.49	7.99
KBr	3.98	4.91	7.19	7.00	6.84	6.72	6.63	6.58	6.51	8.07
KI	4.10	5.00	7.29	7.21	7.09	7.00	6.90	6.78	6.68	8.30
KCNS	4.13	5.10	7.34	7.29	7.16	7.03	6.92	6.86	6.76	8.40
KNO <sub>3</sub>	3.92	4.87	7.17	7.06	6.89	6.78	6.66	6.57	6.49	8.19
K <sub>2</sub> SO <sub>4</sub>	4.24	5.17	7.40	7.26	7.18	7.10	6.96	6.79	6.24	8.36
MgSO <sub>4</sub>	4.05	4.97	7.02	6.90	6.79	6.70	6.58	6.51	6.43	7.82
TMACl	4.28	5.30	7.52	7.73	7.73	7.87	7.91	8.00	8.08	8.89
3-Fluorobenzoic Acid <sup>c</sup>										
KCl	1.40	1.65	2.39	2.33	2.26	2.23	2.19	2.15	2.11	2.62
KBr	1.42	1.68	2.42	2.37	2.32	2.27	2.23	2.19	2.13	2.68
KI	1.45	1.70	2.46	2.42	2.41	2.39	2.37	2.35	2.33	2.73
KCNS	1.47	1.72	2.46	2.43	2.41	2.39	2.38	2.36	2.34	2.73
KNO <sub>3</sub>	1.44	1.70	2.45	2.43	2.41	2.39	2.37	2.35	2.33	2.74
K <sub>2</sub> SO <sub>4</sub>	1.63	1.89	2.69	2.59	2.56	2.49	2.45	2.41	2.36	2.87
MgSO <sub>4</sub>	1.52	1.75	2.41	2.36	2.31	2.27	2.22	2.17	2.14	2.58
TMACl	1.48	1.76	2.45	2.51	2.54	2.56	2.58	2.61	2.70	2.84
4-Fluorobenzoic Acid <sup>d</sup>										
KCl	4.12	5.01	7.18	6.97	6.87	6.75	6.59	6.43	6.24	7.97
KBr	4.24	5.20	7.40	7.20	6.95	6.67	6.43	6.29	6.16	8.25
KI	4.31	5.28	7.40	7.37	6.96	6.68	6.56	6.30	6.17	8.46
KNO <sub>3</sub>	4.31	5.25	7.19	7.32	6.89	6.76	6.60	6.44	6.25	8.36
K <sub>2</sub> SO <sub>4</sub>	4.84	5.83	7.93	7.85	7.72	7.50	7.45	7.24	7.11	8.86
MgSO <sub>4</sub>	4.49	5.42	7.61	7.39	7.19	6.93	6.69	6.45	6.18	8.38
TMACl	4.37	5.34	7.39	7.45	7.51	7.60	7.67	7.74	7.85	8.52

<sup>a</sup> Units: 10<sup>-2</sup> mol·dm<sup>-3</sup>. <sup>b</sup>  $S_0 = 4.24$  (20°), 5.19 (25°), 7.37 (35°) and 8.45 (40°). <sup>c</sup>  $S_0 = 1.48$  (20°), 1.72 (25°), 2.40 (35°) and 2.68 (40°). <sup>d</sup>  $S_0 = 4.39$  (20°), 5.32 (25°), 7.29 (35°) and 8.31 (40°).

the two effects. Sulphate ion is a powerful structure maker.<sup>(8)</sup> The immobilization of water molecules by highly charged and compact SO<sub>4</sub><sup>2-</sup> increases the cohesive energy density resulting in salting out. While KCl salted out the fluorobenzoic acids TMACl salted in. The difference in behavior arises from the cationic part of the electrolyte.<sup>(9)</sup> The Long-McDevitt theory<sup>(10)</sup> also predicts salting in by this ion. On the basis of localized hydrolysis model<sup>(7,11,12)</sup> TMA<sup>+</sup> is a structure breaker resulting in salting in.

The enthalpies and entropies of transfer are all positive except for sulphates. The structure breaking action of the ions of the salts would

Table II. Setschenow and Thermodynamic Parameters of Transfer at 25°C of 2-, 3- and 4-Fluorobenzoic Acid

Salt	$K_s$	$\Delta_t H$	$\Delta_t S$	$K_s$	$\Delta_t H$	$\Delta_t S$	$K_s$	$\Delta_t H$	$\Delta_t S$
	2-Fluorobenzoic			3-Fluorobenzoic			4-Fluorobenzoic		
KCl	0.16	0.50	1.1	0.18	0.11	3.4	0.28	0.94	2.7
KBr	0.14	0.60	1.5	0.16	1.43	4.5	0.23	0.91	2.8
KI	0.12	0.56	1.6	0.07	1.45	4.8	0.19	0.87	3.2
KCNS	0.11	0.66	2.1	0.07	0.83	2.8			
KNO <sub>3</sub>	0.15	1.78	5.4	0.07	1.92	6.3	0.21	1.33	4.4
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.15	-0.92	-3.1	0.18	-1.08	-2.9	0.16	-1.34	-3.8
MgSO <sub>4</sub>	0.13	-1.27	-4.7	0.17	-2.64	-8.7	0.30	-0.60	-18.6
TMACl	-0.09	1.63	5.7	-0.12	1.93	6.6	-0.08	1.19	4.1

liberate water molecules which in turn can enter into H-bond interaction with the carboxyl and fluoro group. The endothermicity can be understood from the fact that the energy gained by H-bonding is insufficient to compensate for that required to free water molecules. The free water molecules would also increase the entropy. The negative values for sulphate ions are in agreement with its structure making action.<sup>(8)</sup>

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#### References

1. S. Sugunan, *Indian J. Chem.* **22A**, 150 (1983).
2. S. Sugunan, *Indian J. Chem.* **23A**, 763 (1984).
3. R. Anantaraman and K. Chandramohanakumar, unpublished work.
4. J. Setschenow, *Z. Phys. Chem.* **4**, 117 (1989).
5. *Dictionary of Organic Compounds*, 5<sup>th</sup> edn., (Chapman and Hall, New York, 1982).
6. H. Margenau and G. M. Murphy, *Mathematics for Physics and Chemistry* (D. Van Nostrand, 1956) p. 519.
7. R. L. Kay, *ACS Advances in Chemistry Series* **73**, 1 (1968).
8. Y. Marcus, *Ion Solvation* (Wiley, New York, 1985) p. 113.
9. J. O. M. Brockris, J. Bowler-Reed, and J. A. Kitchener, *Trans. Faraday Soc.* **47**, 184 (1951).
10. F. A. Long and W. McDevitt, *J. Am. Chem. Soc.* **74**, 1775 (1952).
11. R. L. Kay and D. F. Evans, *J. Phys. Chem.* **70**, 2325 (1966).
12. F. Franks and H. Y. Smith, *Trans. Faraday Soc.* **63**, 2586 (1967).