

## Thermodynamics of transfer of polar nonelectrolytes from water to aqueous salt solutions

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The Setschenow parameter and thermodynamic parameters of transfer of a number of monosubstituted benzoic acids from water to different salt solutions have been reported. The data have been rationalized by considering the structure breaking effects of the ions of the salts, the localised hydrolysis model, the internal pressure theory and Symons' theory of water structure.

Studies of the salt effect on the activity coefficient of nitrobenzoic acids<sup>1,2</sup> and acid terephthalic esters<sup>3</sup> revealed that these solutes behave differently from other acidic nonelectrolytes<sup>4-7</sup>. 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 electrolyte on the activity coefficient of the solute is determined by the extent to which the water structure is compressed 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 thus obstructed resulting in salting out. Large ions having the same charge would have the opposite effect. According to Symons<sup>9</sup> change in the availability of OH<sub>f</sub> and LP<sub>f</sub> (lone pair of electrons) in the water structure will have substantial effect on solubility. These observations led us to investigate the problem in detail by choosing a series of monosubstituted benzoic acids: methyl-, fluoro-, chloro-, bromo-, iodo-, hydroxy- and amino-benzoic acids in the presence of KF, KBr, KI, KCNS, KNO<sub>3</sub>, K<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, tetramethylammonium chloride (TMACl) and sodium formate. The Setschenow parameter and thermodynamic parameters of transfer ( $\Delta H$  and  $\Delta S$ ) of the solutes from water to aqueous salt solution were computed from the solubility measurements at 20, 25, 35 and 40°C in the absence and presence of salt in the concentration range 0.05-0.35 mol dm<sup>-3</sup>.

### Materials and Methods

All the reagents used were of AR grade. The solubility (at constant temperature maintained by a Haake bath system) was determined by the method of

Bockris<sup>10</sup> using a Hitachi 200-20 UV-visible spectrophotometer. The solute with salt solution in a boiling tube (fitted with a mercury seal apparatus to minimise the loss due to evaporation) was shaken thoroughly with an indigenously fabricated shaking machine to attain equilibrium. The solubility values were reproducible within an error of 0.5%.  $K_s$  was determined using the equation  $\lim_{[\text{salt}] \rightarrow 0} K_s / \log(S_0/S) = \log(S_0/S)/[\text{salt}]$  where S and S<sub>0</sub> are the solubility of the solute in the presence and absence of salt (Table I).

### Results and Discussion

KF and HCOONa salted in all the solutes extensively. The Setschenow equation was not obeyed with these solutes over the entire concentration range.  $\Delta H$  and  $\Delta S$  were negative. F<sup>-</sup> and HCOO<sup>-</sup> with their highly localized charge acting as a base can exhibit some sort of acid-base interaction with the proton of the carboxyl group of benzoic acids.

Excepting nitro-, bromo-, and iodobenzoic acids the Setschenow equation was obeyed for KCl, KBr, KI, KNO<sub>3</sub> and KCNS. For all nitrobenzoic acids salting-in was observed.  $K_s$  values for these salts were positive for methyl-, fluoro-, chloro-, hydroxy- and aminobenzoic acids. Positive  $\Delta H$  and  $\Delta S$  for salting-in and negative values for salting out were observed, the values being very small. In methylbenzoic acids the presence of a large apolar group can lead to intermolecular hydrophobic interaction which in turn causes increased structuredness of the surrounding water molecule. The charge:size ratio of the ions is in the order Cl<sup>-</sup> > Br<sup>-</sup> > NO<sub>3</sub><sup>-</sup> > I<sup>-</sup> > CNS<sup>-</sup>. The salting out parameter should also decrease in the same order according to the localised hydrolysis model. This

Table 1—Setschenow parameters of solutes

Solute substituted benzoic acid	KCl	KBr	KI	KCNS	KNO <sub>3</sub>	(CH <sub>3</sub> ) <sub>3</sub> -N-Cl	K <sub>2</sub> SO <sub>4</sub>	MgSO <sub>4</sub>
2-nitro-	-0.12	—	—	—	—	—	—	—
3-nitro-	-0.19	-0.26	—	—	-0.21	—	—	—
4-nitro-	-0.28	-0.36	—	—	—	—	—	—
2-methyl-	0.23	0.21	0.19	—	0.17	-0.14	0.18	0.19
3-methyl-	0.16	0.14	0.13	—	0.17	-0.13	0.25	0.25
4-methyl-	0.21	0.19	—	—	—	-0.13	0.17	0.19
2-fluoro-	0.16	0.14	0.12	0.11	0.15	-0.09	0.15	0.13
3-fluoro-	0.18	0.16	0.07	0.07	0.07	-0.12	0.18	0.17
4-fluoro-	0.28	0.23	0.19	—	0.21	-0.08	0.16	0.30
2-chloro-	0.14	0.14	—	—	—	-0.13	—	—
3-chloro-	0.13	-0.11	—	—	—	-0.20	—	—
4-chloro-	0.10	—	—	—	—	-0.32	—	—
2-hydroxy-	0.11	0.10	0.08	—	0.06	-0.20	—	—
4-hydroxy-	0.14	0.11	—	—	—	-0.22	0.11	0.26
2-amino-	0.07	-0.11	-0.07	—	—	-0.27	0.13	0.22
4-amino-	0.10	0.09	0.06	—	0.07	-0.19	0.20	0.20

trend is observed for methyl-, hydroxy- and aminobenzoic acids. The structure breaking action of the ions of these salts increases in the order  $\text{CNS}^- > \text{I}^- > \text{Br}^- > \text{NO}_3^- > \text{Cl}^-$  and salting out pattern should be expected in the opposite direction. With halobenzoic acids the effect due to these salts was as follows: Fluorobenzoic acids were salted out and Setschenow equation was valid over the entire concentration range. The trend in the observed  $K_s$  values showed less salting out as the size of the anion increases. Bromo- and iodobenzoic acids were salted in and did not obey the Setschenow equation. The salting out phenomenon in the case of fluoro- and chlorobenzoic acids can be compared with that in hydroxybenzoic acids. The electrostriction produced by the addition of the electrolyte into the aqueous solution of the nonelectrolyte will force the latter to come out of the solution. Further  $K_s$  values must be positive for order producing ions and negative for disorder causing solutes. Since all these salts can be classified as structure breakers<sup>11</sup> salting in is effected. A regular gradation in salting action can be observed from fluoro- to iodobenzoic acids: salting out for fluoro-, initial salting in to salting out for chloro- and salting in for bromo- and iodobenzoic acids. As the size of halogen group increases the acidity of carboxyl proton increases. Data on benzaldehyde and nitrobenzene<sup>12</sup> support this argument.

All the solutes are salted in by TMACl. The Setschenow equation was valid for all solutes except nitro-, bromo- and iodobenzoic acids. Salting in by

this electrolyte is predicted by Long-McDevitt theory<sup>13</sup> and also by Bockris.  $\text{TMA}^+$  is a structure breaker<sup>11,14,15</sup> resulting in salting in.

The results with sulphates were as follows: Salting in for nitro-, chloro-, bromo-, iodo- and 2-hydroxybenzoic acids with failure of Setschenow equation; salting out for methyl-, fluoro-, amino- and 4-hydroxybenzoic acids obeying Setschenow equation.  $\text{SO}_4^{2-}$  is a powerful structure maker<sup>16</sup> reducing solubility. In nitrobenzoic acids the electron withdrawing nature of nitro group makes the carboxyl proton more acidic. Such a behaviour cannot be seen even in fluorobenzoic acids. The nitro group in nitrobenzoic acid makes the H-bond through the  $\text{OH}_f$  and the carboxyl group through the  $\text{LP}_f$  of water molecules. The inductive effect of the nitro group favours this process by making both the nitro group and the carboxyl more sensitive to H-bonding. It may be noted that the contribution to H-bonding by the two sites are not independent. The acidity of carboxyl proton plays the most important role in the salt effect of  $\text{SO}_4^{2-}$  which has been discussed in similar studies on picric acid<sup>17</sup>. The favourable effect on solubility due to the electrostatic effect will be important only when H-bonding occurs between the carboxyl group and the  $\text{LP}_f$  of water molecules. Data on phthalic acid<sup>18</sup> substantiates this argument. The intra molecular H-bonding in 2-hydroxybenzoic acid increases the acidity of carboxyl proton which increases the solubility by H-bonding through carboxyl proton which is not the case with 4-hydroxybenzoic acid. The results on the

thermodynamic parameters of transfer are in agreement with our argument.

Salting in by  $F^-$  and  $HCOO^-$  with large negative enthalpy and a quite insignificant entropy of transfer could be understood as a specific acid-base interaction involving the carboxyl proton and the anions. The breakdown of Setschenow equation with other salts can be rationalized on the basis of appreciable solubility of the solutes where this equation is not valid. The acidity of carboxyl proton decides the direction of salting process with sulphates due to its strong ability to make H-bonds with carboxyl group. The localised hydrolysis model could explain many of the observations. Symons' theory is not satisfactory to rationalize the experimental data.

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