# Solubility of 4-Nitrobenzoic Acid in Water & Salt Solutions

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Solubilities of 4-nitrobenzoic acid at 25°, 35° and 42°C have been determined in water and in the presence of several concentrations of electrolytes. The free energies, enthalpies and entropies of transfer are also reported. The data have been rationalized by considering the structure-breaking effects of the ions of the salts and the requirement of the localized hydrolysis model. The theory of Symons is not satisfactory to rationalise the experimental data.

Recently, Symons has proposed a theory of water structure and reactivity[1]. Applying this theory to predict the effect of added salts on reaction rate is beset with two difficulties. Firstly Symons has not made allowance for the added salt on the activity coefficient of the initial state of the reaction, particularly in view of Taft's work[2], although he admits the need for doing so. Secondly, the salt effect can be predicted with assurance only if full information of the mechanism of the reaction is available, which is rarely the case. A better test of the theory would be in predicting the effect of added salts on the activity coefficient of a polar non-electrolyte solute in aqueous solution.

In the present work the solubility of 4-nitrobenzoic acid in water with and without added salts has been determined. The enthalpies and entropies of transfer of the solute from aqueous solution to aqueous salt solution have also been determined by measuring the temperature coefficient of solubility.

4-Nitrobenzoic acid, m.p. 236° (lit.[3] m.p. 240°) and conductivity water were used. The salts were AnalaR equivalent. Spectral measurements were made on a Hitachi model 200-20 spectrophotometer equipped with matched cells of 1 cm path length. Temperature in the cell compartment could be controlled with an accuracy of $\pm$ 0.02°C.

Solubilities were measured essentially by the method due to Bockris *et al.*[4] and the concentrations are expressed in the molarity scale. Solubilities were measured at 25, 35 and 42°C. The results are reproducible within 1 %. The probable error[5] in $\triangle G$ and $\triangle H$ is $\pm$ 0.01 and 0.2 kJ mol$^{-1}$ and that in $\triangle S$, 0.5 JK$^{-1}$ mol$^{-1}$.

The solubilities of 4-nitrobenzoic acid in the absence of electrolytes and in the presence of electrolytes are given in Table 1. The Setschenow equation[6] is obeyed upto a concentration of 0.15 mol dm$^{-3}$ in KNO$_3$ only. With KCl, KBr, KI, NaCl and NaBr the equation is obeyed upto 0.05 mol dm$^{-3}$ because the curve connecting the points corresponding to the solubility at 0.02 and 0.05 mol dm$^{-3}$ passes through the origin on extrapolation. This was verified by the method of least squares. With the remaining salts the equation is not obeyed. Free energies, enthalpies and entropies of transfer of one mol of the solute from aqueous solution to salt solution (0.15 mol dm$^{-3}$) at 25°C are given in Table 2.

Salting-in decreases in the order KF > K$_2$SO$_4$ > MgSO$_4$ > KI > KCl > KBr = KNO$_3$ > NaBr > NaCl.

Despite the large negative value of the free energy of transfer the enthalpy term is positive (endothermic) though the entropy term is highly positive in the case of added KF. We suggest that the enhanced solubility is due to hydrogen-bonding of the proton of the carboxyl group with the F$^-$, the process requiring extra energy to desolvate the F$^-$. The endothermicity of transfer could be explained by assuming that the

Table 1—Solubility of 4-Nitrobenzoic Acid in Salt Solutions at Different Temperatures

[Solubility of 4-nitrobenzoic acid in the absence of electrolytes ($10^3$ mol dm$^{-3}$) : 1.477 (25°), 2.105 (35°) and 2.582 (42C°)]

| Electrolyte | Solubility ($10^3$ mol dm$^{-3}$) at [salt] (mol dm$^{-3}$) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 25°C | 35°C | | | | | 42°C |
| | 0.15 | 0.02 | 0.05 | 0.15 | 0.35 | 0.5 | 0.15 |
| KF | 10.175 | 4.653 | 7.851 | 14.420 | 31.398 | 40.172 | 19.942 |
| KCl | 1.586 | 2.142 | 2.195 | 2.253 | 2.232 | 2.136 | 2.516 |
| KBr | 1.565 | 2.134 | 2.165 | 2.212 | 2.200 | 2.205 | 2.398 |
| KI | 2.000 | 2.182 | 2.336 | 2.637 | 3.207 | 3.615 | 2.903 |
| KNO$_3$ | 1.731 | 2.124 | 2.131 | 2.232 | 2.326 | 2.357 | 2.724 |
| K$_2$SO$_4$ | 2.333 | 2.510 | 2.710 | 3.145 | 3.433 | 3.587 | 3.999 |
| MgSO$_4$ | 2.101 | 2.436 | 2.619 | 2.863 | 2.878 | 2.786 | 3.494 |
| NaCl | 1.609 | — | 2.177 | 2.147 | 2.079 | 1.986 | 2.628 |
| NaBr | 1.533 | — | 2.154 | 2.198 | 2.133 | 2.084 | 2.545 |

Table 2—Thermodynamic Parameter (at 25°C) of Transfer and Setschenow Parameter for Solubility of 4-Nitrobenzoic Acid in Salt Solutions

| Electrolyte | Setschenow parameter $k$ | Thermodynamic parameters | | |
|---|---|---|---|---|
| | | $\Delta G$ kJ mol$^{-1}$ | $\Delta H$ kJ mol$^{-1}$ | $\Delta S$ JK$^{-1}$ mol$^{-1}$ |
| KF | — | —4.73 | +4.77 | +31.9 |
| KCl | 0.26 | —0.17 | —4.39 | —14.2 |
| KBr | 0.22 | —0.21 | —5.57 | —18.4 |
| KI | 0.91 | —0.80 | —8.29 | —25.5 |
| KNO$_3$ | 0.22 | —0.38 | —5.02 | —15.9 |
| K$_2$SO$_4$ | — | —1.13 | —1.17 | —0.4 |
| MgSO$_4$ | — | —0.88 | —2 34 | —5.0 |
| NaCl | 0.19 | —0.21 | —3.64 | —11.7 |
| NaBr | 0.20 | —0.13 | —3.68 | —12.1 |

energy gained by the hydrogen-bonding is insufficient to offset this requirement. The desolvation also would lead to considerable increase in entropy because of the freeing of water molecules from the hydration shell of F$^-$.

The above explanation also holds good to explain the effects of added K$_2$SO$_4$ and MgSO$_4$. Although SO$_4^{2-}$ is less electronegative than F$^-$ it has two sites available for hydrogen-bonding. The thermodynamics of transfer also support this interpretation.

The small negative value of the free energy of transfer in the case of added KI arises from mutual compensation of enthalpy and entropy terms. I$^-$ is a powerful structure-breaker[7] and this process would increase the enthalpy and entropy of transfer. The fact that the results are the reverse of this expectation can be accounted for by assuming that the liberated water molecules are involved in inter-molecular hydrogen-bonding with both the carboxyl and the nitro groups. This process would decrease both the enthalpy and entropy of transfer. The fact that the solubility increase is fairly large indicates that the second factor is more important.

The values of the Setschenow parameter and the thermodynamic parameters of transfer in the case of added KCl, KBr, KNO$_3$, NaCl and NaBr are all closely similar. The structure-breaking action will decrease in the order Br$^-$ > NO$_3^-$ > Cl$^-$ (ref. 7). According to the localized hydrolysis model, the orientation of water molecules by these ions would

increase the solubility by hydrogen-bonding with carboxyl group in the order Cl$^-$ > NO$_3^-$ > Br$^-$ and decrease the solubility by hydrogen-bonding with the nitro group in the same order[8].

One further point needs comment. Even electrolytes which behave as true salts, i.e. ions not involved in hydrogen-bonding with the substrate, fail to obey the Setschenow equation beyond 0.05 mol dm$^{-3}$. In the case of benzoic acid the Setschenow equation is valid upto a concentration of 1 mol dm$^{-3}$ (ref. 4). Such a behaviour could be ascribed to the fact that there are two independent sites available for hydrogen-bonding in p-nitrobenzoic acid. Also, when hydrogen bonding occurs at one site the change in its electronegativity will be transmitted to the group in the para-position. This means that the two sites cannot be considered to make independent contribution to the solubility. As [salt] is increased there will be change in the capacity for hydrogen-bonding of these two sites and this would result in the failure of Setschenow equation. However the applicability of Setschenow equation in the case of phthalic[9] and succinic[10] acids, which also have two sites available for hydrogen-bonding is a consequence of strong intramolecular hydrogen-bonding which is competing with intermolecular hydrogen-bonding. However, Symons' theory[1] is not satisfactory to rationalise the experimental data.

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