

Thermodynamic Parameters of Transfer of 2-Nitrobenzoic Acid & 3-Nitrobenzoic Acid from Water to Aqueous Salt Solutions

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The Setschenow parameters of solubility in salt solutions and the thermodynamic parameters (25°C) of transfer from aqueous solution to aqueous salt solutions for 2-nitrobenzoic acid and 3-nitrobenzoic acid have been reported. The data have been rationalized on the basis of the localized hydrolysis model and the structure breaking action of ions of the electrolytes.

Previous work¹⁻⁴ on the effect of added salts on the activity coefficient of polar acidic nonelectrolytes has revealed that 4-nitrobenzoic acid does not obey Setschenow equation⁵ with fluorides and sulphates. With other electrolytes it is valid only for very low [electrolyte] ($\approx 0.05 \text{ mol dm}^{-3}$). Electrolytes like halides, nitrates and sulphates salt-in 4-nitrobenzoic acid¹.

In the present work corresponding studies were carried out with 2-nitrobenzoic acid and 3-

nitrobenzoic acid using the following electrolytes: KF, KCl, KBr, KI, KNO₃, K₂SO₄ and (CH₃)₄NCl. The results have been compared with those obtained with 4-nitrobenzoic acid.

2-Nitrobenzoic acid (KL England) m.p. 246° (lit.⁶ m.p. 247°) and 3-nitrobenzoic acid (KL England) m.p. 240° (lit.⁶ m.p. 240-242°) were used as such. All the salts were of AR grade. Solutions were prepared in conductivity water. The details of the experimental procedure are described elsewhere¹. The solubility measurements were carried out at 25°, 35° and 40°C. The results are reproducible within 1%. The probable error⁷ in ΔG and ΔH is ± 0.01 and 0.2 kJ mol^{-1} respectively while that in ΔS is $\pm 0.5 \text{ JK}^{-1} \text{ mol}^{-1}$.

The solubilities of 2-nitrobenzoic acid and 3-nitrobenzoic acid in the presence of electrolytes are given in Table 1. The free energies, enthalpies and entropies of transfer of one mol of the solute from aqueous solution to aqueous salt solution (0.15 mol dm^{-3}) at 25°C are given in Table 2. The Setschenow equation is obeyed even for KF and K₂SO₄. Salting-in is observed with all the electrolytes. Salting-in effect decreases in the order KF > K₂SO₄ > KI > KNO₃ > (CH₃)₄NCl > KCl = KBr. In case of 3-nitrobenzoic acid the solubility is unaffected by the addition of KCl and KBr showing that the Setschenow parameter and thermodynamic parameters of transfer have zero values. Both the acids obey the Setschenow equation

Table 1—Solubility of 2-Nitrobenzoic Acid & 3-Nitrobenzoic Acid in Salt Solutions at Different Temperatures [Solubility of 2-nitrobenzoic acid in the absence of electrolytes (10^2 mol dm^{-3}): 4.218 (25°), 5.834 (35°) and 7.096 (40°C). Solubility of 3-nitrobenzoic acid in the absence of electrolytes (10^2 mol dm^{-3}): 2.008 (25°), 2.851 (35°) and 3.401 (40°C)]

Electrolyte	Solubility (10^2 mol dm^{-3} at [salt] (mol dm^{-3}))							
	25°C		35°C				40°C	
	0.15	0.02	0.05	0.1	0.15	0.25	0.35	0.15
2-Nitrobenzoic acid								
KF	10.640	6.697	8.081	10.590	12.920	18.110	—	15.970
KCl	4.317	—	5.870	5.945	5.978	6.022	5.934	7.190
KBr	4.389	—	6.022	6.077	6.122	5.967	5.936	7.256
KI	4.561	5.989	6.089	6.221	6.299	6.421	6.480	7.550
KNO ₃	4.528	5.878	5.934	6.006	6.144	6.232	6.348	7.566
K ₂ SO ₄	5.734	6.354	6.897	7.528	7.860	8.435	8.579	9.448
(CH ₃) ₄ NCl	4.627	5.967	6.118	6.288	6.410	6.675	6.908	7.860
3-Nitrobenzoic acid								
KF	5.311	3.490	4.401	5.866	7.158	7.849	—	8.052
KI	2.131	—	2.940	2.956	3.071	3.122	—	3.660
KNO ₃	2.105	2.913	2.926	2.960	3.056	3.128	—	3.647
K ₂ SO ₄	2.139	2.976	3.058	3.139	3.149	3.164	—	3.604
(CH ₃) ₄ NCl	2.050	—	2.880	2.910	2.982	2.940	—	3.532

Table 2—Thermodynamic Parameters (at 25°C) of Transfer and Setschenow Parameter for the Solubility of 2-Nitrobenzoic Acid & 3-Nitrobenzoic Acid in Salt Solutions

Electrolyte	Setschenow parameter $-k$	Thermodynamic parameters		
		ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (JK ⁻¹ mol ⁻¹)
2-Nitrobenzoic Acid				
KF	2.57	-4.41	-6.52	-7.1
KCl	0.06	-0.06	-0.51	-1.5
KBr	0.06	-0.11	-0.67	-1.9
KI	0.26	-0.20	-0.73	-1.8
KNO ₃	0.21	-0.17	-0.53	-1.2
K ₂ SO ₄	1.07	-0.76	-1.02	-0.9
(CH ₃) ₄ NCl	0.18	-0.23	+0.44	+2.2
3-Nitrobenzoic Acid				
KF	3.74	-2.42	-5.47	-10.2
KI	0.16	-0.15	-0.78	-3.1
KNO ₃	0.16	-0.12	-1.25	-4.6
K ₂ SO ₄	0.59	-0.18	-0.19	-1.2
(CH ₃) ₄ NCl	0.09	-0.06	+1.04	+3.7

upto a concentration of 0.15 mol dm⁻³ with electrolytes other than KF and K₂SO₄; in the latter cases the validity is only upto a concentration of 0.05 mol dm⁻³ of the electrolyte. These were verified by the least squares method.

While solutes like benzoic acid, phthalic acid and succinic acid are salted-out the nitro acids are salted-in by the same electrolytes. The difference in behaviour can be accounted for on the basis of the difference in their hydrogen bonding abilities, as follows. In nitrobenzoic acids there are two independent sites available for hydrogen bonding with water molecules. Though phthalic acid and succinic acid also possess two sites of hydrogen-bonding the strong intramolecular hydrogen-bonding is competing with inter-molecular hydrogen bonding. The structure-breaking action⁸ of the ions of the salts would liberate water molecules which in turn would enter into hydrogen-bond interaction with the carboxyl and the nitro groups. According to the localized hydrolysis model⁹ the orientation of water molecules by the anions of the electrolytes would favour increased solubility by hydrogen-bonding with the carboxyl group. The two sites of hydrogen-bonding in nitrobenzoic acids cannot make independent contribution to the solubility because as the hydrogen-bonding occurs at one site the change in its electro-negativity will be transmitted to the other site of hydrogen-bonding. As the [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. Further, the solubilities of 2-nitrobenzoic acid and 3-nitrobenzoic acid are high enough to show considerable deviation in activity from concentration.

With KF and K₂SO₄, the increase in solubility with [salt] is due to the hydrogen-bond interaction of the proton of the carboxyl group with the anions¹. Contribution towards solubility, based on the localized hydrolysis model, due to the small sized F⁻ and highly charged SO₄²⁻ is also not ruled out since both 2-nitrobenzoic acid and 3-nitrobenzoic acid obey the Setschenow equation upto a concentration of 0.05 mol dm⁻³. With the other electrolytes the data can be rationalized on the basis of the structure-breaking effect of the ions of the salts. The structure-breaking action would decrease in the order I⁻ > Br⁻ > NO₃⁻ > Cl⁻. This would favour increased solubility in the same order. Though tetraalkylammonium ions are considered to be structure-makers¹⁰, in general, the smaller sized tetramethylammonium ion is a powerful structure-breaker¹¹. It is responsible for the higher (negative) value of the Setschenow parameter for this ion compared to that for KCl. The relative values of the salting-in parameter support the argument.

The values of the free energy of transfer are negative and follow the same order as the Setschenow parameter. The enthalpies and entropies of transfer are negative except in the case of tetramethylammonium chloride. It has already been mentioned that the enhanced solubility with KF and K₂SO₄ is due to the hydrogen-bonding of the proton of the carboxyl group with the anions. This would involve more energy to desolvate both the carboxyl group and the anions of the salts. The negative values of enthalpy and entropy of transfer indicate that this energy is insufficient to compensate for the energy gained by the hydrogen bond interaction of the proton of the carboxyl group with anions. The relative values of the thermodynamic parameters of transfer with the other electrolytes can be rationalized in terms of the structure-breaking action. This process should increase the enthalpy and entropy of transfer. The fact that the observed results are the reverse of this expectation can be accounted for by assuming that the liberated water molecules can involve themselves in hydrogen-bonding with the carboxyl and the nitro group. This process would decrease both the enthalpy and entropy of transfer. The positive values (though small) with tetramethylammonium chloride can be easily understood from the fact that tetramethylammonium ion is also a powerful structure-breaker.

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