

Thermodynamics of Transfer of Aminobenzoic Acids from Water to Aqueous Salt Solutions

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The Setschenow parameter and thermodynamic parameters of transfer of 2- and 4-aminobenzoic acids from water to salt solutions have been reported. The results are discussed in terms of 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 coefficient of polar nonelectrolytes revealed that nitrobenzoic acids (1, 2) and acid terephthalic esters (3) behave differently from other acidic nonelectrolytes (4–7). 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 (8) found to be valid over the entire concentration range. These observations led us to investigate the salt effect on the activity coefficient of 2- and 4-aminobenzoic acids in water. The following electrolytes were employed: KCl, KBr, KI, KNO_3 , K_2SO_4 , $MgSO_4$, and tetramethylammonium chloride (TMACl). The Setschenow parameter (K_s) and the thermodynamic parameters of transfer ($\Delta_{tr}H$ and $\Delta_{tr}S$) of the solute from water to aqueous salt solution have been computed from solubility measurement at various temperatures.

Experimental Section

All of the salts employed were of AR grade. 2-Aminobenzoic acid (KL England) mp 145–147 °C (lit. (9) mp 147 °C) and 4-aminobenzoic acid (KL England) mp 187–189 °C (lit (9) mp 188 °C) were employed as such. Solutions were prepared in water (conductivity = $7.6 \times 10^{-4} \text{ S cm}^{-1}$). Solubility (at constant temperature (± 0.02 °C) maintained by an EK 51 Haake bath system) was determined 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 a locally fabricated shaking machine to attain equilibrium. The solubility was determined at 20, 25, 35, 40 °C for salt concentration from 0.05 to 0.35 mol dm^{-3} . The results were reproducible within an error 0.5%. The probable error (10) in $\Delta_{tr}H$ is 0.02 kJ mol^{-1} , while that in $\Delta_{tr}S$ is 0.1 J $\text{K}^{-1} \text{mol}^{-1}$. The data are given in Table 1. K_s was determined using the equation

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

where S and S_0 are the solubility of the solute in the presence and absence of salt. The values are given in Table 2. The $\Delta_{tr}H$ and $\Delta_{tr}S$ of 1 mol of solute from water to salt solution (0.1 mol dm^{-3}) at 25 °C are also given in Table 2.

Results and Discussion

Salts of KCl, KBr, and KI salted-out the solutes, obeying the Setschenow equation with initial salting-in. KNO_3 salted-out the solutes over the entire concentration range. When an electrolyte is added to an aqueous solution of the

Table 1. Solubility S of 2- and 4-Aminobenzoic Acid in Salt Solutions C at Different Temperatures ($10^2 S/\text{mol dm}^{-3}$)

salt	$C/\text{mol dm}^{-3}$									
	$t = 20$ °C		$t = 35$ °C						$t = 40$ °C	
	0.10	0.10	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.10
2-Aminobenzoic Acid [$S_0 = 2.904$ (20 °C), 3.561 (25 °C), 5.352 (35 °C), 6.550 (40 °C) mol dm^{-3}]										
KCl	2.844	3.512	5.389	5.352	5.308	5.250	5.081	4.901	4.682	6.595
KBr	2.904	3.586	5.400	5.458	5.566	5.422	5.262	5.196	5.145	6.718
KI	2.944	3.644	5.464	5.515	5.561	5.502	5.287	5.196	5.134	6.780
KNO_3	2.786	3.448	5.316	5.230	5.017	4.926	4.823	4.746	4.695	6.438
K_2SO_4	2.916	3.522	5.301	5.223	5.158	5.060	4.965	4.825	4.707	6.342
$MgSO_4$	2.839	3.449	5.312	5.184	5.071	4.926	4.785	4.600	4.501	6.254
TMACl	2.952	3.612	5.400	5.584	5.753	5.909	6.026	6.139	6.294	6.535
4-Aminobenzoic Acid [$S_0 = 3.076$ (20 °C), 3.767 (25 °C), 5.498 (35 °C), 6.631 (40 °C) mol dm^{-3}]										
KCl	2.946	3.631	5.439	5.360	5.301	5.257	5.199	5.122	5.058	6.501
KBr	2.992	3.689	5.477	5.435	5.373	5.318	5.256	5.202	5.154	6.616
KI	3.012	3.707	5.511	5.547	5.498	5.453	5.401	5.353	5.298	6.709
KNO_3	3.027	3.724	5.624	5.498	5.466	5.418	5.365	5.314	5.258	6.697
K_2SO_4	3.032	3.703	5.514	5.403	5.293	5.170	5.033	4.926	4.811	6.494
$MgSO_4$	3.056	3.738	5.531	5.427	5.440	5.195	5.071	4.945	4.822	6.525
TMACl	3.319	4.009	5.690	5.753	5.822	5.943	6.108	6.306	6.497	6.856

Table 2. Setschenow Parameter (K_s) and Thermodynamic Parameters of Transfer ($\Delta_{tr}H$ and $\Delta_{tr}S$) at 25 °C of 2- and 4-Aminobenzoic Acid

salt	2-aminobenzoic acid			4-aminobenzoic acid		
	K_s	$\Delta_{tr}H/\text{kJ mol}^{-1}$	$\Delta_{tr}S/\text{J mol}^{-1}\text{K}^{-1}$	K_s	$\Delta_{tr}H/\text{kJ mol}^{-1}$	$\Delta_{tr}S/\text{J mol}^{-1}\text{K}^{-1}$
KCl	0.07	1.11	3.4	0.10	0.89	2.7
KBr	0.16	0.97	3.3	0.09	0.92	2.9
KI	0.17	0.64	2.7	0.06	1.28	4.2
KNO_3		0.88	2.7	0.07	1.01	3.3
K_2SO_4	0.13	-1.32	4.5	0.20	-0.201	-0.8
$MgSO_4$	0.22	-0.64	-2.2	0.20	-0.370	-1.3
TMACl	-0.27	-0.72	-2.3	-0.17	-1.56	-4.7

a nonelectrolyte, the increase in internal pressure resulting from ion–water interaction compresses the water molecules and squeezes the solutes out. The effect of the salt on the activity coefficient of the solute is determined by the extent to which the water structure is compacted or loosened. This in turn 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 the entry of solute molecule into solution is obstructed, causing salting-out. The charge:size ratio of the anion is in the order $Cl^- > Br^- > NO_3^- > I^-$. Salting-out parameters should decrease in this order, which is observed. The structure breaking action of the ions decreases in the order $I^- > Br^- > NO_3^- > Cl^-$. Hence the salting-out pattern should be observed in the opposite direction. The observed salt effect is the result of the two.

Tetramethylammonium chloride salted-in the solutes, obeying the Setschenow equation. Bockris *et al.* (11) attributed salting-in by the large tetramethylammonium cation to dispersion forces between ions and neutral solute and solvent molecules. Long-McDevitt theory (12) also predicts salting-in by this ion. On the basis of localized hydrolysis model TMA⁺ is a structure breaker (13-15) resulting in salting-in.

Sulfates salted-out the solutes, obeying the Setschenow equation. SO₄²⁻ is a powerful structure maker (16). This will reduce the solubility because the proportion of free water molecules will be reduced. The immobilization of water molecules by the highly charged and compact sulfate ion increases the cohesive energy density, forcing the solute to be squeezed out of the cavity in solution, resulting in salting-out. Since Mg²⁺ is a powerful structure maker and K⁺ is a structure breaker, MgSO₄ produces more salting-out than K₂SO₄. When the solutes are salted-out by the electrolyte, both enthalpy and entropy of transfer are positive except for the case of sulfates. The values are negative for salting-in. Sulfate ion is a powerful structure maker and has two sites for H-bonding. So the enthalpy of transfer should have contributions from two compensating effects, namely an endothermic component due to the desolvation of sulfate ion and an exothermic component due to the greater H-bonding with the solute molecules; the latter should be dominant, leading to a net negative

enthalpy of transfer. The liberated water molecules should be under the influence of the strong electric field of sulfate ions, causing a partial ordering and decreasing the entropy of transfer.

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