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Association of Salicylic Acid in Acetonitrile-Water Media

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The values of the free energy of transfer (ΔG_{tr}) of salicylic acid from water to acetonitrile in a series of acetonitrile-water mixtures have been calculated from the solubilities of salicylic acid at 25°C ± 1°C. The maximum value of the free energy of transfer is found to be $-23.729\,kJ\,mol^{-1}$ in a medium containing 80% acetonitrile. Association constant (K_{ass}) of salicylic acid has been calculated from the acid concentrations (m_0) and the *p*H-values. K_{ass} is maximum (8.58×10^3 mol/litre) in 80% acetonitrile-water medium.

A number of publications have appeared in the literature on the dissociation of weak acids in non-aqueous solvents[1-4]. Recently Rao *et al.*[5] determined the dissociation constants of benzoic, salicylic, *o*- and *m*-nitrobenzoic acids in 20-50% (v/v) acetonitrile-water mixtures using the direct potentiometric technique.

The aim of the present work is to investigate the association of salicylic acid in 60-90% (v/v) acetonitrile-water mixtures, using the solubility data.

Acetonitrile-water medium has been selected in this study since acetonitrile has several attractive physical properties like low vapour pressure and viscosity at room temperature. Further, in view of considerable differences in the dielectric constants and dipole moments of acetonitrile and water, the solubility of weak acids in these mixtures is likely to be affected.

Salicylic acid (AR, Merck) and spectroscopic grade acetonitrile (Fluka) were used. The saturated solutions of salicylic acid in 60, 70, 80 and 90% acetonitrile-water media (v/v) and in water and pure acetonitrile were prepared by dissolving the required amounts of salicylic acid under nitrogen gas. The solutions were thoroughly shaken for 4 days in a thermostat at 25°C ± 1°C and kept in the thermostat for another two days to attain equilibrium. The solubility of the acid in each of these mixtures was determined by taking 2 ml of the saturated solution, evaporating it to dryness and weighing the residue.

The free energy of transfer (ΔG_{tr}) of salicylic acid from acetonitrile (s) to water (w) was calculated[6] according to Eq. (1).

$$\Delta G_{tr} = {}^{w}_{s}\Delta G = -RT\ln a_s + RT\ln a_w \quad \ldots (1)$$

Since $pK_{sp(s)} = -\log a_s$ and $pK_{sp(w)} = -\log a_w$, Eq. 1 can be rewritten as

$$\Delta G_{tr} = 2.303\ RT\ (pK_{sp(s)} - pK_{sp(w)}) \quad \ldots (2)$$

or

$$\Delta G_{tr} = 2.303\ RT.\Delta pK_{sp} \quad \ldots (3)$$

The solubility data, *p*H values and the values of the free energy of transfer of salicylic acid in acetonitrile-water mixtures are given in Table 1. It is obvious that the maximum value of ΔG_{tr} ($-23.729\,kJ\,mol^{-1}$) is obtained in 80% acetonitrile-water mixture and this corresponds to the maximum value of the acid association according to Kim *et al.*[7,8]. Salicylic acid (HA) undergoes association according to equilibrium (4)

$$2HA \overset{K_{ass}}{\rightleftharpoons} H_2A_2 \overset{K'}{\rightleftharpoons} HA_2 + H^+ \quad \ldots (4)$$

Table 1—Solubility Data, *p*H-values and Free Energy of Transfer of Salicylic Acid in Acetonitrile-Water Mixtures at 25°C

Acetonitrile in medium (% v/v)	Mixed solvent	Solubility			*p*H	ΔG_{tr}
	mol fraction	Density	Molar conc.	Molal conc.	value	($kJ\,mol^{-1}$)
0	0	0.9971	1.7445×10^{-2}	1.7495×10^{-2}	2.55	0
60	0.341	0.8845	1.2495	1.4129	2.28	−21.744
70	0.446	0.8585	1.545	1.7996	2.18	−22.939
80	0.579	0.8307	1.7535	2.1108	1.87	−23.729
90	0.756	0.8034	1.4590	1.8169	1.10	−22.499
100	1.0	0.7769	0.5359	0.4847	0	−16.452

*ref. 6

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Table 2—Values of γ, $P_{a_{H^+}}$, K_1/K_2, K' and K_{ass} of Salicylic Acid in Acetonitrile-Water Mixtures at 25°C

Acetonitrile in medium (%, v/v)	γ	$P_{a_{H^+}}$	K_1/K_2	K' (mol/litre)	K_{ass} (mol/litre)
0	0.857	2.617	52.460	135.369×10^4	3.875×10^{-5}
60	0.250	2.902	127.139×10^4	399.680	3.181×10^3
70	0.209	2.879	185.207×10^3	233.742	7.924×10^3
80	0.184	2.636	832.067×10^3	96.966	8.580×10^3
90	0.208	1.782	121.143×10^2	18.348	6.600×10^2
100	0.244	0.353	1.193	9.574	0.1246

The association constant (K_{ass}) can be expressed by Eq. (5)

$$K_{ass} = \frac{a_{H_2A_2}}{a_{HA^2}} \quad \ldots (5)$$

The dissociation constant of the associated acid complex, H_2A_2 can be expressed by Eq (6)

$$K' = \frac{a_{H^+} \cdot a_{HA_2^-}}{a_{H_2A_2}} \quad \ldots (6)$$

Substituting for $a_{H_2A_2}$ in Eq (6) we obtain Eq. (7)

$$K' = \frac{a_{H^+} \cdot a_{HA_2}}{K_{ass} \cdot a_{HA^2}} \quad \ldots (7)$$

A comparison of the equations expressing K_1, K_2, K_3 and Eq. (7) for K' leads to the conclusion that,

$$\frac{K_1}{K_2} = K' . K_{ass} \quad \ldots (8)$$

where K_1/K_2 = association constant/dissociation constant of the dimers which form a complex ion (HA_2^-) and a hydrogen ion (H^+). Since $\gamma_{HA_2^-} = \left(\gamma_{H^+}\right.$ Eq. (6) can be written in the form:

$$K' = a_{H+}^2 / m_0^2 \quad \ldots (9)$$

Assuming that $[A^-] \ll [HA_2^-]$, then Eq. (6) can be rearranged to give Eq. (10)

$$P_{a_{H+}} = 1/2 \log \frac{K_1}{K_2} - \log m_0 \quad \ldots (10)$$

The values of K_1/K_2, K' and K_{ass} (in mol/litre) thus obtained are given in Table 2. The highest K_{ass} value is found to be 8.58×10^3 mol/litre in 80% acetonitrile-water mixture.

The values of $P_{a_{H+}}$ were calculated from the *p*H values measured for the chosen mixtures using Eq. (11)

$$P_{a_{H^+}} = pH - \log\gamma \quad \ldots (11)$$

where $\log\gamma$ is the activity coefficient of H^+, $\log\gamma = -0.5062\sqrt{m_0}$ (see ref. 9) and m_0 is the concentration of salicylic acid as mentioned before.

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