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ASSOCIATION, DISSOCIATION AND HYDROGEN BONDING OF SALICYLIC ACID IN WATER-*N*,*N*-DIMETHYLFORMAMIDE MIXTURES

E.A. GOMAA, M.A. MOUSA and A.A. EL-KHOULY

Chemistry Department, Faculty of Science, Mansoura University, Mansoura (Egypt)

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ABSTRACT

The free energy of transfer (ΔG_{tr}) of salicylic acid from water to *N*,*N*-dimethylformamide (DMF) and their mixtures was calculated from the solubilities of salicylic acid in different H_2O–DMF mixtures. The maximum value of ΔG_{tr} was found to be -7.008 kcal for pure DMF. In addition to ΔG_{tr} calculations, the values of the association constant (K_{ass}) of salicylic acid were calculated from the acid concentration (solubility, S) and the pH values of the saturated solution. The highest K_{ass} value was found to be 1016.16 in pure DMF.

Moreover, the free energies of H-bonding of salicylic acid in these mixtures were calculated from the values of ΔG_{tr} and its individual terms (ΔG_{sum}).

INTRODUCTION

Many publications have reported on the behaviour of weak acids in anhydrous solvents. Interesting work has been done by Kolthoff et al. [1,2]. Aleksandrov et al. [3,4] studied the dissociation of salicylic acid in butan-2-one. Kreshkov et al. [5] studied the dissociation of amino acids (as weak acids) in mixtures of formic acid and ethyl methylketone and in mixtures of acetic acid–ethyl methylketone.

Rao et al. [6] reported some results about the dissociation constants of benzoic, salicylic, *o*- and *m*-nitrobenzoic acid in 20–50 (w/w) acetonitrile–water mixtures using the direct potentiometric method. They found that salicylic acid has an abnormal character due to the intermolecular hydrogen bonding whose values have not been reported.

EXPERIMENTAL

The aim of the present work is to study the association, dissociation and hydrogen-bonding character of salicylic acid in aqueous–aprotic solvents (i.e., H_2O–DMF mixtures). The salicylic acid and *N*,*N*-dimethylformamide

(DMF) used were supplied by Merck. The saturated solutions of salicylic acid were prepared by dissolving it in H_2O–DMF mixtures. The mixtures were then saturated with N_2 gas in closed test tubes. The tubes were placed in a shaken thermostatic water bath (Model GFL) for a period of four days, followed by another two days without shaking to reach the necessary equilibrium.

The solubility of the salicylic acid in each of these mixtures was determined gravimetrically by taking 1 ml of the saturated solution and subjecting it to complete evaporation using a small aluminium disk heated by an infrared lamp. The pH readings of these mixtures were measured using a pH-meter of the type WGP PYE (model 290).

RESULTS AND DISCUSSION

The free energies of transfer (ΔG_{tr}) of salicylic acid from water (w) to DMF and to DMF–H_2O mixtures (s) were calculated according to eqns. (1) and (2), which have been reported in the literature [7–9].

$$\Delta G_{tr} = \Delta_w^s G^0 = \left(G_s^0 - G_w^0\right) \tag{1}$$

where G_s^0 is the free energy of salicylic acid in the mixed solvent and G_w^0 is the free energy of salicylic acid in water.

$$\Delta_w^s G^0 = 2.303RT\Delta pK_{sp} \tag{2}$$

where ΔpK_{sp} is the difference between the pK_{sp} value (solubility product) of salicylic acid in pure water and those in the water–solvent mixtures. pK_{sp} was calculated by using eqn. (3).

$$pK_{sp} = \log S^2 + 2\log\gamma_{\pm} \tag{3}$$

where S and $\gamma_{\pm}$ are the molal solubility and the activity coefficient of salicylic acid, respectively.

The changes in the values of the free energy of transfer (ΔG_{tr}) can be considered as an indication of the association, particularly in cases using water–solvent mixtures [10].

The results of the present work including solubility data, pH values and the values of free energy of transfer of salicylic acid in H_2O–DMF mixtures are illustrated in Table 1. It is obvious that the value of ΔG_{tr} (-7.008 kcal) corresponds to the maximum value of salicylic acid association, which refers to 100% DMF.

By calling the salicylic acid molecule HA, according to the association route reported by Aleksandrov [4], the following association can be followed

$$2HA \overset{K_{ass}}{\rightleftharpoons} H_2A_2 \overset{K'}{\rightleftharpoons} HA_2 + H^+ \tag{4}$$

TABLE 1

Solubility data, pH values and free energy of transfer values of salicylic acid in water–dimethylformamide mixtures at 25°C

Volume of DMF in mixed solvent (%)	Mole fraction of DMF (X_s)	Density of mixed solvent (ρ) [a]	Solubility (S)		pH [b]	ΔG_{tr} (kcal)
			Molar conc.	Molal conc.		
0	0	0.9971	1.498×10^{-2}	1.503×10^{-2}	2.55	0
50	0.2220	0.9949	1.4923	1.50	2.51	−5.44
60	0.3622	0.9975	2.1945	2.2	2.46	−5.895
70	0.4691	0.9890	3.3268	3.3638	2.36	−6.396
80	0.6024	0.9670	3.52012	3.640	2.26	−6.490
90	0.7730	0.9345	4.25137	4.549	2.07	−6.753
100	1.00	0.944	5.32942	5.646	1.52	−7.008

[a] From ref. 7.

[b] Measured values.

The activity coefficient ($\gamma_\pm$) can be calculated [11] if the relation log $\gamma_\pm = -0.5062\sqrt{m_0}$ is used, where m_0 is the molal concentration.

K_{ass} values were calculated from the ratios of association constant to dissociation constant (i.e., K_1/K_2) for the dimers which form a complex ion (HA_2^-) and hydrogen ion (H^+), and the values of K' (where K' is the dissociation constant of the associated acid complex, H_2A_2), are given by the following equations [3]

$$K' = a^2H^+/m_0^2 \tag{5}$$

$$paH^+ = \tfrac{1}{2}\log\frac{K_1}{K_2} - \log m_0 \tag{6}$$

$$\frac{K_1}{K_2} = K'\,K_{ass} \tag{7}$$

TABLE 2

Values of $\gamma_\pm$ (activity coefficient), aH^+ (activity of hydrogen ion obtained from pH values), k_1/k_2, K' and K_{ass} of salicylic acid in water–N,N-dimethylformamide mixtures at 25°C

Mole fraction of DMF (X_s)	$\gamma_\pm$	$-aH^+$	k_1/k_2	K' (mol l^{-1})	K_{ass} (mol l^{-1})
0	0.8669	409.259	37.837	7.4111×10^{8}	5.1055×10^{-8}
0.222	0.2399	1348.64	4.092×10^{6}	8.0837×10^{5}	5.0620
0.3622	0.1775	1625.54	1.2789×10^{7}	5.4595×10^{5}	23.425
0.4691	0.11791	1942.67	4.2707×10^{7}	3.3353×10^{5}	128.045
0.6024	0.1082	1681.89	3.7479×10^{7}	2.1349×10^{5}	175.554
0.773	0.08325	1411.23	4.1211×10^{7}	9.6243×10^{4}	428.197
1.00	0.06269	528.2	8.8936×10^{6}	8.7522×10^{3}	1016.156

where a is the activity. The values obtained for K_1/K_2, K' and K_{ass} are reported in Table 2. The maximum value of K_{ass} was found to be 1016.156 where H_2O does not exist.

By applying Buckingham's theory [12], i.e., assuming tetrahedral solvation and cos $\theta = \pm 1$ for orientation of solvent molecules, the individual terms of the free energy of transfer can be calculated and written as reported by Kim [13]. It can be summarised as follows

$$\Delta G_{\text{charging}} = -\frac{Nq^2Z^2}{2r}\left(\frac{1}{\epsilon_s} - \frac{1}{\epsilon_w}\right) \tag{8}$$

$$\Delta G_{\text{ion-dipole}} = -4NqZ\left(\frac{\mu_s}{\sigma_s^2} - \frac{\mu_w}{\sigma_w^2}\right) \tag{9}$$

$$\Delta G_{\text{ion-induced}} = -2Nq^2Z^2\left(\frac{\alpha_s}{\sigma_s^4} - \frac{\alpha_w}{\sigma_w^4}\right) \tag{10}$$

$$\Delta G_{\text{ion-quadrupole}} = 8NqZ\left(\frac{\theta_s}{\sigma_s^3} - \frac{\theta_w}{\sigma_w^3}\right) \tag{11}$$

$$\Delta G_{\text{dipole-quadrupole}} = 3.44N\left(\frac{\mu_s\theta_s}{\sigma_s^4} - \frac{\mu_w\theta_w}{\sigma_w^4}\right) \tag{12}$$

Where ϵ is the dielectric constant, μ is the dipole moment, α is the polarizability, θ is the quadrupole moment, and σ is the value of the

TABLE 3

Physical parameters of DMF and water and X_s, X_{s1}, X_{s2}, X_{s3} and X_{s4} values in water–N,N-dimethylformamide mixtures at 25°C

TABLE 3A [13]

Physical parameter	H_2O	DMF
σ [a]	2.77	4.96
μ [b]	1.85	3.82
ϵ [c]	78.3	36.8
α [a]	1.47	7.88
θ [e]	3.84	6.08

TABLE 3B

Mole fraction of DMF (X_s)	X_{s1}	X_{s2}	X_{s3}	X_{s4}
0	0	0	0	0
0.222	0.3428	0.9754	0.2268	0.4047
0.3622	0.5581	1.5905	0.3698	0.6599
0.4691	0.7232	2.0611	0.4792	0.8552
0.6024	0.9287	2.6468	0.6154	1.0983
0.773	1.1917	3.3963	0.7897	1.4093
1.000	–	–	–	–

[a] σ = hard sphere diameter (10^{-8} cm).

[b] μ = dipole moment (10^{-18} esu).

[c] ϵ = dielectric constant.

[d] α = polarisability (10^{-24} cm^3).

[e] θ = quadrupole moment (10^{-26} esu).

TABLE 4

ΔG_t and its individual values (including $\Delta G_{\text{H-bonding}}$) (kcal mol^{-1}) of salicylic acid in H_2O–DMF mixtures at 25°C

Mole fraction of DMF	$-\Delta G$ (charging)	$-\Delta G$ (ion–dipole)	$-\Delta G$ (ion-induced)	$-\Delta G$ (ion–quadrupole)	$-\Delta G$ (dipole–quadrupole)	$-\Delta G$ (sum)	$-\Delta G_{tr}$	$-\Delta G$ (H-bonding)
0	0	0	0	0	0	0	0	0
0.222	0.00914	1.4700	0.1855	0.00044	0.00344	1.6685	5.44	3.7715
0.3622	0.01490	2.3969	0.3025	0.00071	0.00562	2.7206	5.895	3.1744
0.4691	0.01931	3.1059	0.3920	0.00094	0.00728	3.5254	6.396	2.8706
0.6024	0.02480	3.9885	0.5034	0.00118	0.00935	4.5272	6.490	1.9628
0.773	0.03182	5.1181	0.6459	0.00153	0.01199	5.8412	6.753	0.9118
1.0	0.04117	4.2947	0.1904	0.00192	0.00851	4.5365	7.008	2.4715

distance between the centre of the salicylic acid and the solvent. Subscripts w and s refer to water and solvent, respectively.

All the physical parameter data (ϵ, σ, μ, α and θ) used in this publication for the calculation of the different terms of ΔG_{tr} ($\Delta G_{\mathrm{charging}}$, $\Delta G_{\mathrm{ion-dipole}}$, $\Delta G_{\mathrm{ion\text{-}induced}}$, $\Delta G_{\mathrm{ion-quadrupole}}$ and $\Delta G_{\mathrm{dipole-quadrupole}}$) are listed in Table 3A.

Using the Bondi [14] model for calculating Van der Waals radii, the radius of salicylic acid was calculated and found to be 3.7 Å.

The five terms of ΔG_{tr} of salicylic acid mentioned above were calculated according to the above equations (8–12) for acid transfer from water to DMF, and their values are illustrated in Table 4.

To calculate the values of the five terms of ΔG_{tr} for the corresponding mixed solvents (i.e., H_2O–DMF mixtures) given in Table 4, the values of X_{s1}, X_{s2}, X_{s3} and X_{s4} were first calculated using eqns. (13)–(16) which have been reported by Kim et al. [7].

$$X_{\mathrm{s1}} = X_{\mathrm{s}}\left(\frac{\mu_{\mathrm{s}}}{\sigma_{\mathrm{s}}^{2}}\right)\Big/\left(\frac{\mu_{\mathrm{w}}}{\sigma_{\mathrm{w}}^{2}}\right) \tag{13}$$

where X_{s} is the mole fraction of DMF in the bulk solution.

$$X_{\mathrm{s2}} = X_{\mathrm{s}}\left(\frac{\alpha_{\mathrm{s}}}{\sigma_{\mathrm{s}}^{4}}\right)\Big/\left(\frac{\alpha_{\mathrm{w}}}{\sigma_{\mathrm{w}}^{4}}\right) \tag{14}$$

$$X_{\mathrm{s3}} = X_{\mathrm{s}}\left(\frac{\theta_{\mathrm{s}}}{\sigma_{\mathrm{s}}^{3}}\right)\Big/\left(\frac{\theta_{\mathrm{w}}}{\sigma_{\mathrm{w}}^{3}}\right) \tag{15}$$

$$X_{\mathrm{s4}} = X_{\mathrm{s}}\left(\frac{\mu_{\mathrm{s}}\theta_{\mathrm{s}}}{\sigma_{\mathrm{s}}^{4}}\right)\Big/\left(\frac{\mu_{\mathrm{w}}\theta_{\mathrm{w}}}{\sigma_{\mathrm{w}}^{4}}\right) \tag{16}$$

Then the values of X_{s}, X_{s1}, X_{s2}, X_{s3} and X_{s4} were multiplied by those of $\Delta G_{\mathrm{charging}}$, $\Delta G_{\mathrm{ion-dipole}}$, $\Delta G_{\mathrm{ion\text{-}induced}}$, $\Delta G_{\mathrm{ion-quadrupole}}$ and $\Delta G_{\mathrm{dipole-quadrupole}}$, respectively, for the transfer of salicylic acid from H_2O to DMF. The values of X_{s}, X_{s1}, X_{s2}, X_{s3} and X_{s4} are illustrated in Table 3B.

The ΔG values of hydrogen bond formation were calculated, and are tabulated in Table 4, by subtracting the value of each ΔG_{sum} from the corresponding value of ΔG_{tr} according to the following equation

$$\Delta G_{\mathrm{H\text{-}bonding}} = \Delta G_{\mathrm{tr}} - \Delta G_{\mathrm{sum}} \tag{17}$$

Generally, the results obtained from Tables 1 and 2 lead to the conclusion that salicylic acid in pure DMF has the highest association value. This association value was found to decrease as H_2O was added to DMF. Moreover, by increasing the amount of H_2O added to DMF the results of $\Delta G_{\mathrm{H\text{-}bonding}}$ (see Table 4) were found to increase. This shows that the H-bond formation is through the acid and water molecules, i.e., intermolecular H-bonding. On the other hand, the ion–dipole interaction ($\Delta G_{\mathrm{ion-dipole}}$) established between the salicylic acid molecules and the solvent molecules (i.e., DMF) was found to decrease as the amount of H_2O added to DMF was increased. At the same time, $\Delta G_{\text{H-bonding}}$ was increased. The other individual terms of ΔG_{tr} were found to be small compared to $\Delta G_{\text{ion-dipole}}$.

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