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GIBBS FREE ENERGIES OF SOLUTE–SOLVENT INTERACTIONS FOR SALICYLIC, SULPHOSALICYLIC AND SULPHANILIC ACIDS IN VARIOUS SOLVENTS

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ABSTRACT

Gibbs free energies of solute–solvent interactions and the Gibbs free energies of transfer for salicylic, sulphosalicylic and sulphanilic acids from water to ethanol, *N*-methypyrollidone, acetonitrile, *N,N*-dimethylformamide, dimethylsulphoxide, propylene carbonate and *N*-methylformamide were calculated from the measured solubility data at 25°C.

K (association), ΔG (electrostatic) and ΔG (neutral) were theoretically calculated for the three acids used. It is found that the ΔG of interaction and *K* values of salicylic acid are larger than those of sulphosalicylic and sulphanilic acids in the organic solvents used. This behaviour is due to both inter- and intramolecular interactions of the hydroxyl and carboxylic groups of salicylic acid with the solvent dipoles.

INTRODUCTION

A lot of publications have reported on the dissociation and association of weak acids in organic solvents. An interesting study has been made by Kolthoff et al. [1,2]. Aleksandrov et al. [3,4] studied the dissociation of salicylic acid in butan-2-one. They found that the concentration of simple ions, A^-, is very small.

Rao et al. [5] studied the dissociation of benzoic, salicylic, and *o*- and *m*-nitrobenzoic acids in 20–50% (w/w) acetonitrile–water mixtures. They found a linear relationship between p*K* values and the reciprocal of the dielectric constant ($1/\varepsilon$).

EXPERIMENTAL

Analytical grade salicylic and sulphanilic acids were provided by Merck, whereas spectroscopic grade (Uvasol) ethanol (EtOH), acetonitrile (CH_3CN),

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N-methylpyrollidone (NMepyr), *N,N*-dimethylformamide (DMF), dimethylsulphoxide (DMSO), propylene carbonate (PC) and *N*-methylformamide (NMF) were used. The sulphosalicylic acid used was from Riedel-De-Haen AG Co.

The saturated solutions of salicylic, sulphosalicylic and sulphanilic acids in water and the organic solvents provided were prepared by dissolving the required amount of solid acid in the corresponding solvent using closed test tubes saturated with an inert gas (nitrogen). The solutions were severely shaken in a thermostatted water bath for one week followed by another day without shaking to reach the necessary equilibrium. The solubility of the three acids in each of these solvents was determined either gravimetrically or volumetrically. The gravimetric measurement was carried out by taking 1 ml of the saturated solution and evaporating to dryness using small aluminium disks heated by an infrared lamp. The volumetric analysis was carried out by direct titration of 3–5 ml of the saturated acid solution with standard 0.1 N NaOH.

RESULTS AND DISCUSSION

Gibbs free energy of transfer (ΔG_{tr}) for salicylic, sulphosalicylic and sulphanilic acids from water (w) to organic solvent (s), as solvents were calculated according to eqns. (1) and (2), which have been reported in the literature [6,7]

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

since G_s^0 is the Gibbs free energy of interaction in the solvent (s) and G_w^0 is the Gibbs free energy of interaction in water (w).

$$\Delta G_{tr} = {}_{w}^{s}\Delta G^0 = 2.303RT\left(pK_{sp(s)} - pK_{sp(w)}\right) \qquad (2)$$

where $pK_{sp(s)} = -2\log m_s\gamma_{s\pm}$ and $pK_{sp(w)} = -2\log m_w\gamma_{w\pm}$; m_s and m_w are the acid concentrations (in the molal scale) in organic solvent and water, respectively; $\gamma_{s\pm}$ and $\gamma_{w\pm}$ are the activity coefficients of these acids in organic solvents and water, respectively. The activity coefficients of interaction of the acids used were calculated by using the Debye–Hückel equation [8,9]

$$\log \gamma_{\pm} = \frac{A(Z_1Z_2)I^{1/2}}{1 + BaI^{1/2}} \qquad (3)$$

Where A and B are Debye–Hückel constants, depending on the dielectric constant of the solvent and the solvated radius (a) of the acid used, and I is the ionic strength.

The radii of salicylic, sulphosalicylic and sulphanilic acids were calculated by using the Bondi [10] model for calculating the Van der Waals radii. They were found to be 3.7, 3.84 and 3.65 Å, respectively. The diameters of the solvents used were taken from the literature [11] (hard sphere diameters), calculated from the scaled particle theory. From the measured solubility data (in the molal scale), Gibbs free energies of interaction and free energies of transfer from water to organic solvent for salicylic acid were calculated and are listed in Table 1. The maximum ΔG values were found for ethanol and *N*-methylpyrollidone, and the minimum values for propylene carbonate.

The K_{ass} values were calculated theoretically after Fuoss [12] by using eqn. (4).

$$K_{\text{ass}} = 4/3\pi N_{\text{A}} a^3 \exp\left(\frac{e^2}{a\varepsilon kT}\right) \tag{4}$$

where N_{A} is Avogadro's number and a is the radius of the solvated acid. The K_{ass} values of salicylic acid are also given in Table 1.

It is thus concluded from Table 1 that increasing K_{ass} values follow increasing ΔG_{tr} values in the order

$$\text{NMepyr} > \text{DMF} > \text{DMSO} > \text{NMF} > \text{EtOH} > \text{CH}_3\text{CN} > \text{PC} > \text{H}_2\text{O}$$

On the other hand, the ΔG_{el} (electrostatic) value was calculated by eqn. (5) as explained by Abraham and Liszi [13]

$$\Delta G_{\text{el}} = Z^2/2\left(\frac{1}{\varepsilon_1} - 1\right)\left(\frac{1}{a} - \frac{1}{b}\right) + \left(\frac{1}{\varepsilon} - 1\right)\frac{1}{b} \tag{5}$$

where ε is the known bulk dielectric constant of the solvent, a is the solvated radius and $r = (b - a)$ is the thickness of the local layer. ε_1 is taken as 2 for the organic solvents [13].

The neutral free energy (ΔG_{n}) was calculated after Siekierski [14] by applying eqn. (6).

$$\Delta G_{\text{n}} = \Delta G_{\text{tr}} - \Delta G_{\text{el}} \tag{6}$$

As shown in Table 1 the ΔG_{el} values of salicylic acid are smaller than those of the neutral part.

Since the interaction between the dipoles of both salicylic acid and the solvent is an important one, $\Delta G_{\text{ion-dipole}}$ was calculated by applying [11] eqn. (7).

$$\Delta G_{\text{ion-dipole}} = -4N_{\text{A}} qZ\left(\frac{\mu_{\text{s}}}{\sigma_{\text{s}}^2} - \frac{\mu_{\text{w}}}{\sigma_{\text{w}}^2}\right) \tag{7}$$

where μ_{s} and μ_{w} are the dipole moments of the solvent and water respectively. Equation (7) is an application of Buckingham's [15] theory on assuming tetrahedral solvation and $\cos\theta = \pm 1$ for the orientation of solvent molecules. The $\Delta G_{\text{ion-dipole}}$ values are also given in Table 1 with the maximum value found on using ethanol.

In the case of sulphosalicylic and sulphanilic acids the solubility (in the

TABLE 1

Solubility data, log γ, K_{ass} and Gibbs free energies of salicylic acid in some organic solvents at 25 ± 1°C

Solvent	ε [11]	σ (Å) [11]	S [a]	log γ	ΔG [b]	ΔG_{tr} [b]	$K_{ass} \times 10^3$	ΔG_{el} [b]	ΔG_n [b]	$\Delta G_{ion\text{-}dipole}$ [b]
H_2O	78.5	2.77	0.0146	0.2229	−4.390	0	0.850	0	0	0
EtOH	24.6	4.35	2.874	0.6380	2.982	−7.372	1.170	0.067	−7.439	1.555
NMepyr	32.0	5.41	5.526	0.4584	3.266	−7.656	1.430	−0.087	−7.569	−0.404
CH_3CN	36.0	4.16	0.621	0.4410	0.637	−5.027	1.133	0.061	−5.088	−0.876
DMF	36.7	4.93	4.459	0.4120	2.886	7.276	1.310	0.077	−7.353	−0.600
DMSO	46.7	4.91	4.911	0.3240	2.761	−7.151	1.308	0.076	−7.228	−0.702
PC	64.4	5.15	0.283	0.2469	−0.818	−3.572	1.131	0.058	−3.630	−1.650
NMF	182.4	4.47	3.807	0.0854	1.811	−6.201	1.200	0.066	−6.267	−1.079

[a] Solubility in molal concentration/l.

[b] All ΔG values are in kcal.

TABLE 2

Solubility data, log γ, K_{ass} and Gibbs free energies of sulphosalicylic acid in some organic solvents at 25 ± 1°C

Solvent	S [a]	log γ	$K_{ass} \times 10^3$	ΔG [b]	ΔG_{tr} [b]	δG_{el} [b]	ΔG_n [b]
H_2O	0.6599	0.3039	0.359	2.7310	0	0	0
EtOH	0.2377	0.8228	0.548	4.1230	−1.3920	0.0667	−1.4580
CH_3CN	1.4440	0.5712	0.523	1.0629	1.6680	0.0608	1.6070
DMF	4.9359	0.5260	0.632	2.3790	0.3520	0.0796	0.2720
DMSO	2.2331	0.4142	0.741	2.2411	0.4899	0.0770	0.4129
PC	1.2861	0.3196	0.522	1.1665	1.5645	0.0589	1.5056
NMF	2.5689	0.1098	0.561	−1.9872	4.7182	0.0665	4.6517

[a] Solubility in molal concentration/l.

[b] All ΔG values are in kcal.

molal scale), K_{ass}, ΔG (Gibbs free energy of interaction), ΔG_{tr} (Gibbs free energy of transfer), G_{el} (electrostatic) and ΔG_n (neutral free energy) were calculated as for salicylic acid. These data are listed in Tables 2 and 3.

It was found that the solubility of sulphosalicylic acid is greater than that of salicylic and sulphanilic acids, due to the presence of an extra hydrophilic group in its structure (i.e., sulphonic group). On the other hand, K_{ass} values of sulphosalicylic acid are smaller than those of salicylic acid, due to the decrease in the electron density of both the hydroxyl and carboxylic groups in salicylic acid by the addition of an electron-withdrawing group (sulphonic group) in the *para* position in suphosalicylic acid. This decrease in the electron density favours a decrease in the intra- and inter-molecular associations of sulphosalicylic acid. The electrostatic free energy (ΔG_{el}) of sulphosalicylic acid decreases on using a solvent with a high dielectric constant, such as NMF ($\varepsilon = 182.4$), PC ($\varepsilon = 64.4$) or CH_3CN ($\varepsilon = 36$). This decrease in ΔG_{el} is followed by an increase in the intramolecular interaction, Gibbs free energy of interaction (ΔG) and Gibbs free energy of transfer (ΔG_{tr}), as shown in Table 2.

TABLE 3

Solubility data, log γ, K_{ass} and Gibbs free energies of sulphanilic acid in some organic solvents at 25 ± 1°C

Solvent	S [a]	log γ	$K_{ass} \times 10^2$	ΔG [b]	ΔG_{tr} [b]	ΔG_{el} [b]	ΔG_n [b]
H_2O	0.0812	0.3087	3.20	−3.889	0	0	0
EtOH	0.0028	0.8505	4.98	−4.610	0.721	0.066	0.65
CH_3CN	0.0015	0.5909	4.74	−6.030	2.149	0.059	2.081
DMSO	0.0065	0.4275	5.73	−4.770	0.884	0.076	0.807
PC	0.0045	0.3310	4.72	−5.472	1.583	0.284	1.299
NMF	0.1024	0.1139	5.13	−2.380	−1.509	0.065	−1.574

[a] Solubility in molal concentration/l.

[b] ΔG values in kcal.

In the case of sulphanilic acid, it was found that its solubility in the organic solvents under consideration is smaller than that of both salicylic and sulphosalicylic acids. This solubility behaviour is a result of the indirect connection of the functional group with the benzene ring in sulphanilic acid. K_{ass} values of sulphanilic acid are the lowest of the three acids used, due to the absence of hydroxyl and carboxylic groups, which increase the association ability. In view of the small solubility and K_{ass} values of sulphanilic acid, it is concluded that its Gibbs free energy of transfer and the neutral free energy are lower than those of both salicylic and sulphosalicylic acids (Table 3).

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