The dissociation of salicylic, 2,4-, 2,5-, and 2,6-dihydroxybenzoic acids in methanol-water mixtures at 25 °C

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The dissociation constants and the molar conductivities at the limit of zero concentration of salicylic, 2,6-, 2,5-, and 2,4-dihydroxybenzoic acids have been determined in water-methanol mixtures at 25 °C. The experimental data have been analysed with the Lee and Wheaton conductance equation.

The dissociation of acids in methanol-water mixtures varies with solvent composition in a manner which is not completely understood [1–5]. Conductimetry provides a simple and accurate method for the determination of the dissociation constant of a relatively strong acid [6–7].

In this paper we examine the behavior of salicylic, 2,4-, 2,5- and 2,6-dihydroxybenzoic acids in water-methanol mixtures at 25°.

Experimental

Salicylic acid (Fluka puriss) was recrystallised from water and dried under vacuum over P_2O_5. 2,4- and 2,5-dihydroxybenzoic acids (Fluka puriss) were recrystallised from a methanol-water mixture and dried under vacuum over P_2O_5. 2,6-dihydroxybenzoic acid (Fluka purum) was twice recrystallized from water and dried under vacuum over P_2O_5. Methanol (Merck p.a.) was dried with molecular sieves (3 Å), distilled over sulfanilic acid and the middle fraction collected. Conductivity water was obtained from a Millipore ion-exchange apparatus.

All solutions maintained at (25 ± 0.002) °C in a Leeds and Northrop oil thermostat. The resistance measurements were carried as described in Ref. [8].

Results

Values of the molar conductivities at the limit of zero concentration, Λ_0, standard deviations, σ (%), and association constants, K_A, were calculated according to the Lee and Wheaton equation [9, 10] in its series form [11]. The Λ_0 and K_A values were deduced from the equations

$$\Lambda = \gamma[\Lambda_0(1 + \Delta x/x) - \Delta\Lambda_{\mathrm{el}}]\,,$$
$$K_A = (1-\gamma)/\gamma^2 f^2 C\,,$$
$$-\ln f = b\varkappa/2(1+\varkappa R)\,, \quad b = e^2/D\,k\,T$$

for Λ_0 and K_A values which minimize

$$\sigma_\Lambda^2 = \sum_j (\Lambda_j(\mathrm{cal}) - \Lambda_j(\mathrm{obs})^2/(n-2))\,.$$

All the symbols have their usual meaning.

In the case of carboxylic acids no minimum is observed in a $R - \sigma(\%)$ plot [12, 13]. The R value was set equal to 6 Å since it is close to the mean molecular size of these acids. The conductance parameters of the acids in methanol-water mixtures are reported in Table 1.

Discussion

The strength of the acids diminishes as the solvent is enriched in methanol. We carried out measurements in solvent mixtures where the acids had a dissociation constant greater than 10^{-5} and the error of extrapolation to the Λ_0 value is small [14].

The conjugate base of salicylic acid can exist in two forms, with or without an intramolecular hydrogen bond [15]. In the case of 2,6-dihydroxybenzoic acid there always exists an intramolecular hydrogen bond providing better stability for the conjugate base. This compound has a much more acidic character than the other compounds studied, and it was possible to measure its dissociation constant over the entire range of methanol-water mixtures. 2,4-dihydroxybenzoic acid is weaker than salicylic acid because of the electron donating conjugate effect of the –OH group. In the case of 2,5-dihydroxybenzoic acid the –OH group is in the *meta* position and can influence the dissociation of the carboxylic group only indirectly through the hydrogen bond. Here the inductive and conjugate effects balance out and the dissociation constant of this acid has about the same value as salicylic acid in all the solvent mixtures studied.

The free energy of dissociation contains an electrostatic and a non-electrostatic term [5]. The

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Table 1. Conductance parameters.

% w/w MeOH	Salicylic acid			2–6 dihydroxybenzoic acid			2–5 dihydroxybenzoic acid			2–4 dihydroxybenzoic acid		
	Λ_0	σ(%)	K_A	Λ_0	σ(%)	K_A	Λ_0	σ(%)	K_A	Λ_0	σ(%)	K_A
0	380.2	0.02	980	385.44	0.06	196	381.36	0.03	921	374.8	0.05	2 070
20	249.1	0.05	1 800	251.50	0.06	19.4	248.02	0.01	1 700	249.51	0.07	4 150
40	170.51	0.02	4 220	170.04	0.06	30.4	166.63	0.02	4 100	167.06	0.02	10 600
60	128.95	0.07	14 000	122.67	0.03	51.6	123.73	0.02	14 500	119.92	0.02	44 500
80				97.29	0.07	254						
90				94.83	0.05	1 150						
95				104.22	0.05	5 220						
98				115.29	0.02	18 800						
100				181.67	0.02	14 800						

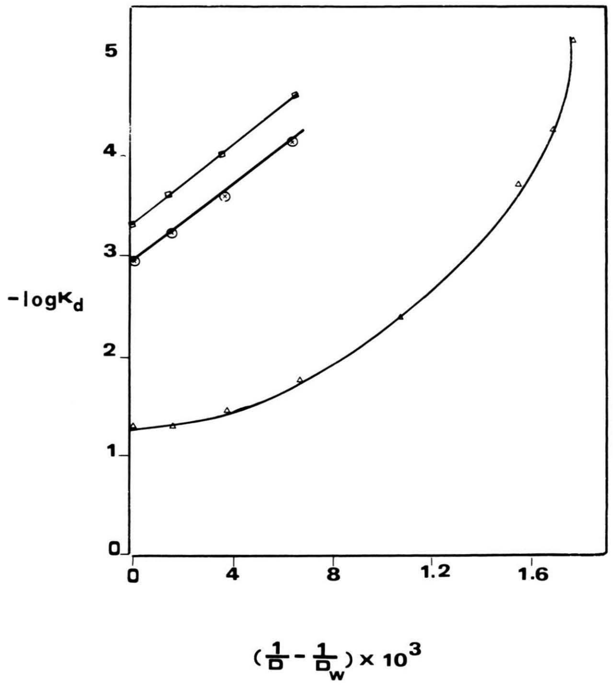

Fig. 1. Dependence of $-\log K_d$ on $I/D - I/D_w$ for salicylic (×), 2,4-dihydroxybenzoic (□), 2,5-dihydroxybenzoic (○), and 2,6-dihydroxybenzoic (△) acids in methanol-water mixtures.

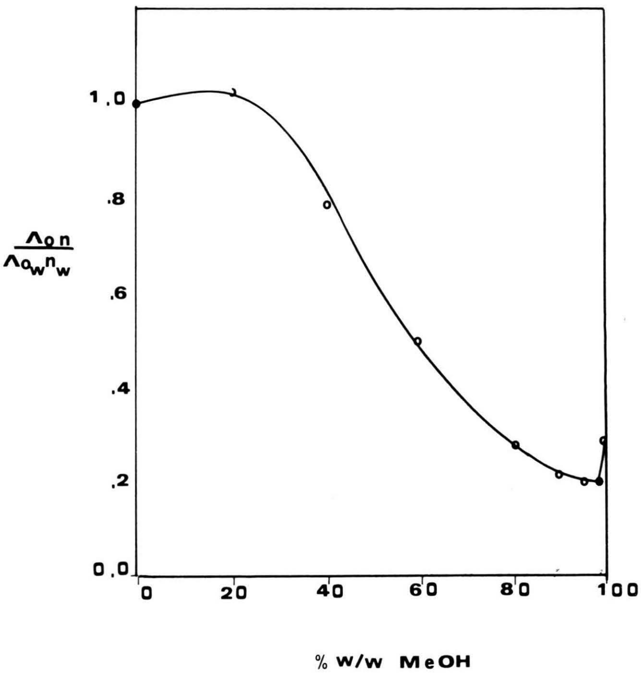

Fig. 2. Dependence of the normalized Walden product on the methanol percentage for 2,6-dihydroxybenzoic acid.

electrostatic term is given by the Born equation [16]. The non-electrostatic term includes solvation phenomena and specific solute-solvent interactions. When there is no change in solvation of an acid and its anion in a binary solvent mixture a plot of pK_A versus $(1/D - 1/D_w)$ should give a straight line. In the case of 2,6-dihydroxybenzoic acid (Fig. 1) no linear portion is found in a pK_A versus $(1/D - 1/D_w)$ plot suggesting that specific solute solvent interactions exist.

The variation of the Walden product is not due to viscosity changes, but to an altering proton transfer mechanism as the solvent is enriched in methanol [17], (Figure 2).

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