Dissociation of 2,4-Dinitrobenzoic Acid and D-10-Camphosulfonic Acid in Water-Methanol Mixtures at 25 °C

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The dissociation constants and the equivalent conductances of 2,4-dinitrobenzoic acid and D-10-camphosulfonic acid have been determined in water-methanol mixtures at 25 °C. The experimental data have been analyzed with the "Fuoss 78" conductance equation. The Bjerrum critical distance was accepted instead of Gurney's cosphere diameter. Values of K_A and Λ_0 are reported.

Introduction

The conductimetric determination of the thermodynamic dissociation constant of an acid HX requires the knowledge of its equivalent conductance at infinite dilution. This value can be obtained either from conductance measurements on the salts MX,MY and the strong acid HY or from measurements on the acid alone [1–3].

The simultaneous determination of K_A and Λ_0 from measurements on the acid has several advantages: The extra labor of taking measurements on the potassium and sodium salts is avoided. Besides certain salts are subject to solvolytic decomposition with the result that precise measurements of their conductance is not possible.

In order to determine the dissociation constant of an acid the equivalent conductance of the acid at several concentrations must be measured:

Then $\alpha = \Lambda/\Lambda_i$, where Λ is the equivalent conductance of the acid at a concentration c, Λ_i the equivalent conductance of the acid if it was completely ionised at a concentration αc and the α the degree of dissociation.

The value of Λ_i depends on the equation chosen for the description of the conductance curve.

According to our opinion conductance data on acids should be analysed by means of the "Fuoss 78" equation. The model upon which the equation is based takes into account the dissociation process and short range interaction which were not taken under consideration in previous equations.

The purpose of this paper is to report the conductance behaviour of 2,4-Dinitrobenzoic and D-10-Camphosulfonic acid in water-methanol mixtures at 25 °C.

Experimental

2,4-Dinitrobenzoic acid (Fluka puriss) was recrystallized twice from methanol and dried. The melting point was found to be 182 °C. D-10-Camphosulfonic acid was received from Carlo Erba R.P. it was dried under vacuum at room temperature over P_2O_5. After several pH-metric titrations by weight by a standard NaOH solution it was found to be > 99.7%.

Methanol (Merk p.a.) was passed through molecular sieves Linde 3A, distilled over sulfanilic acid and the middle fraction collected. Conductivity water was obtained from a Millipore apparatus yielding pure water of specific conductivity $5 \cdot 10^{-8}$ mho $\cdot$ cm^{-1}. The presence of dissolved atmospheric CO_2 increases the conductivity to 4.10^{-7} mho $\cdot$ cm^{-1}.

All solutions were maintained at 25° ± 0.002 °C in a Leeds and Northrup oil bath thermostat. Resistance measurements were carried out on a Jones and Joseph type alternate current bridge and the balancing point determined by a digital voltmeter. The Erlenmeyer type cells used were similar to those proposed by Dagged Bair and Kraus [4], the electrodes covered with platinum black. No extrapolation or resistance to infinite frequency was needed.

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Procedure: The water-methanol mixtures were prepared directly in the conductivity cells and maintained at 25 °C in the thermostat. The specific conductivities of the above mixtures were in the range $4 \cdot 10^{-7}$ mho · cm^{-1} (pure water) $- 5 \cdot 10^{-8}$ mho · cm^{-1} (pure methanol). During the calculations no solvent correction was made since it was due to atmospheric's CO_2 contamination. When this correction was applied it was impossible to fit the data to the equation. Weight-burette technique was employed in the incremental additions of a dilute stock solution to the conductivity cell. The cell constant was determined by the Lind, Fuoss, Zwolenik method [5].

Results

Equivalent conductances at infinite dilution Λ_0, standard deviations $\sigma_\Lambda = 100\, \sigma_\Lambda/\Lambda_0$ and association (K_A) and dissociation (K_d) constants calculated according to the "Fuoss 78" [6, 7] equation based on the "Fuoss 75" [8] model are listed in Tables 1 and 2.

Table 1. Conductance parameters for 2,4-Dinitrobenzoic acid in water-methanol mixtures at 25 °C.

MeOH wt-%	Λ_0 $\frac{\text{mho} \cdot \text{cm}^2}{\text{equiv}}$	σ_Λ %	K_A	K_D
0	377.67	0.025	23.4	4.27×10^{-2}
0	377.31	0.014	23.0	4.34×10^{-2}
20	246.23	0.023	60.21	1.66×10^{-2}
40	167.02	0.018	185.48	5.39×10^{-3}
50	139.27	0.052	327.52	3.05×10^{-3}
80	91.29	0.051	3688	2.71×10^{-4}
90	90.05	0.058	19155	5.22×10^{-5}
95	102.01	0.096	89318	1.12×10^{-5}

Table 2. Conductance parameters for D-10-Camphosulfonic acid in water-methanol mixtures at 25 °C.

MeOH wt-%	Λ_0 $\frac{\text{mho} \cdot \text{cm}^2}{\text{equiv}}$	σ_Λ	K_A	K_D
0	375.1	0.058	< 5	
20	247.76	0.023	< 5	
40	166.78	0.043	< 5	
60	119.24	0.045	< 5	
80	91.85	0.041	5.97	1.67×10^{-1}
90	88.38	0.059	12.8	8.12×10^{-2}
95	92.08	0.054	19.2	5.20×10^{-2}
98	103.48	0.054	29.0	3.44×10^{-2}
100	178.5	0.089	63.5	1.69×10^{-2}

All calculations were carried out on a Univac 1100 computer. The data set $[(c_i, \Lambda_i), d, \eta, D, T]$ (density d, viscosity η and dielectric constant D values were taken from literature [9]), was put into the program. The Λ_0 and K_A values were deduced from the equations

$$\Lambda = p(\Lambda_0(1 + \Delta X/X) + \Delta\Lambda_e)),$$
$$\gamma = 1 - K_R\, C \gamma^2 f^2/(1 - a),$$
$$K_R = (4\pi N R^3/3000) \exp(\beta/R),$$
$$-\ln f = \beta k/2(1 + k R), \quad \beta = e^2/D \varkappa T,$$
$$k^2 = 8\pi \beta \gamma n = \pi \beta N \gamma C/125,$$
$$-E_s/kT = \ln[a/(1 - a)],$$

for Λ_0 and a values which minimize

$$\sigma_\Lambda^2 = \sum_j [\Lambda j\,(\text{calcd}) - \Lambda j\,(\text{obsd})]^2/n - 2$$

for various R values (in the above equations all symbols have their usual meaning).

In case of concentrated alcoholic mixtures, 80–100 wt-% in methanol, the most convenient R value was found to be Bjerrum's critical distance $q = e^2/2 D \varkappa T$. In 0–60 wt-% methanol mixtures the most convenient R value was equal to 6 Å bearing in mind the acid's molecule size.

Discussion

2,4-Dinitrobenzoic acid behaves as a moderately strong acid in aqueous solutions and its strength diminishes as the solvent is enriched in methanol. The graph of $-\log K_d$ against $\Delta(1/D) = 1/D - 1/D_{H_2O}$ gives a straight line up to 95 wt-% (Figure 1). All of our results were obtained with acid concentrations that were below 3.5×10^{-3}, and medium effects in the calculations of Λ_0 and K_A are expected to be small [10].

The conductances of solutions of 2,4-dinitrobenzoic acid in water have been measured by Dippy et al. [11], who obtained $\Lambda_0 = 381.9$, $K_A = 38$. However they measured at much higher concentrations and this may be a reason for the discrepancy between our and their results.

The σ% $- R$ curves were horizontal lines for all solvent compositons. In this case the Bjerrum radius can be accepted. It is lower than the molecules actual size (~ 6 Å) when the solvent has a dielectric constant greater than 56.30. Thus in case of 0–50% in methanol the R value was set equal to 6 Å and in

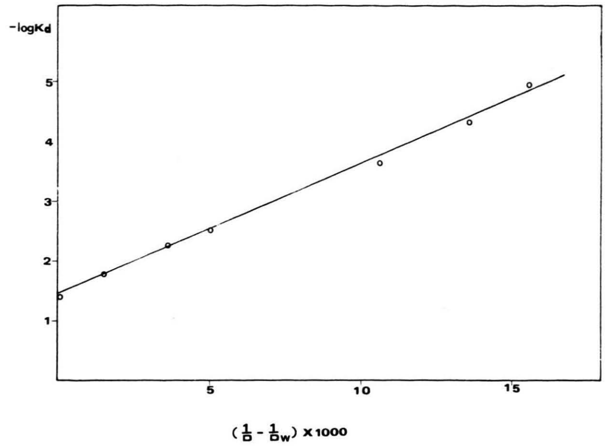

Fig. 1. Dependence of $-\log K_d$ on $1/D - 1/D_w$ for 2,4-Dinitrobenzoic acid in water-methanol mixtures.

case of more concentrated alcoholic solutions equal to the Bjerrum critical distance.

As Λ_0 and K_A values vary relatively little, due to the variation of R, the results are not much affected by our choice.

D-10-Camphosulfonic acid behaves as a strong electrolyte in aqueous solution and in water-methanol mixtures up to 80 wt-% in methanol, where slight ion association occurs. The extent of ion association increases as the solvent mixtures are enriched in methanol.

The graph of $-\log K_d$ against $\Delta(1/D) = 1/D - 1/D_{H_2O}$ is a straight line (Figure 2). The deviation observed when the solvent is pure methanol is due to changes in ion solvation.

The dependence of Λ_0 on the methanol percentage is shown in Table 2. Λ_0 decreases as the solvent is enriched in methanol, exhibits a minimum at 90 wt-% methanol and rapidly increases in the region of pure alcohol. Conway and Bockris [12] accepted that the rate determining step for the proton transfer mechanism in alcoholic media is the rotation of hydrogen-bonded molecules round the alcoxonium ion ROH_2^+.

The normalized Walden product against the percentage of the solvent system in methanol is shown in Figure 3. The changes in the Walden product are not due to viscosity or dielectric constant variation but to the altering proton transfer mechanism (see also Shedlovsky [13, 14]).

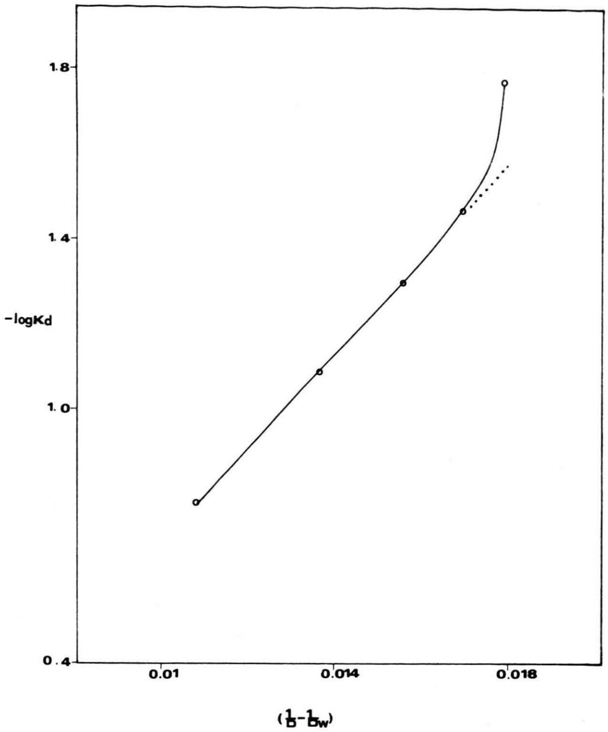

Fig. 2. Dependence of $-\log K_d$ on $1/D - 1/D_w$ for D-10-Camphosulfonic acid in water-methanol mixtures.

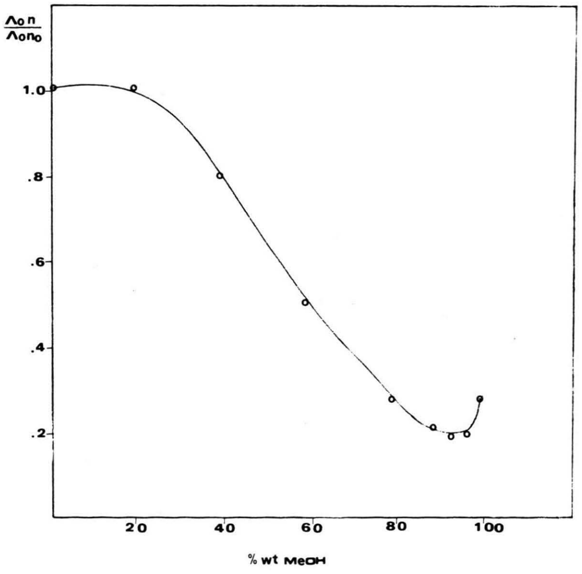

Fig. 3. Dependence of the normalized Walden product on the methanol percentage.

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