Asian Journal of Chemistry Vol. 4, No. 1 (1992) 31–34

Determination of Equivalence Conductance and Dissociation Constant from Conductance Method

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The solubility of saturated furyl acrylic acid (FAA) in water at 31°C was determined by conductometric titration using 0.1N NaOH. The equivalence conductance of FAA at infinite dilution was determined from λ_0 values of Na–FAA, HCl and NaCl at 31°C. The degree of dissociation and dissociation constant at several dilutions were determined according to Ostwald dilution law. True dissociation constant is determined by applying Debye-Hückel limiting law. The values of λ_0 and K are 394.81 and 3.963×10^{-5}, respectively.

INTRODUCTION

When any electrolyte such as an acid or a base is dissolved in a suitable solvent an ionization equilibrium is established between the free (solvated) ions and the undissociated portion of the solute such as monobasic acid.

$$HA \rightleftharpoons H^+ + A^-$$

and the ionization equilibrium constant[1] is given by

$$K = \frac{a_{H^+} \cdot a_{A^-}}{a_{HA}} \tag{1}$$

where the 'a' terms are activities of the indicated species. The constant K is referred to as the dissociation constant of HA in the given solvent at a definite temperature. Replacing activity terms as the products of molar concentration c_i and activity coefficient γ_i.

$$K = \frac{C_{H^+} \cdot C_{A^-}}{C_{HA}} \cdot \frac{\gamma_{H^+} \cdot \gamma_{A^-}}{\gamma_{HA}}$$

$$= K' \cdot \frac{\gamma_{H^+} \cdot \gamma_{A^-}}{\gamma_{HA}} \tag{2}$$

The constant K′ is the apparent dissociation constant and is in general not constant but becomes equal to the true dissociation constant when activity coefficient factor is unity *i.e.* at infinite dilution.

From conductance data on weak acid, the true dissociation constant K can be determined by applying Debye-Hückel limiting law according to eqn. 3.

$$\log K' = \log K + 2A\sqrt{\alpha c} \tag{3}$$

In the present work the equivalence conductance at infinite dilution λ_0 and the true dissociation constant K are determined from conductance data.

EXPERIMENTAL

Furyl acrylic acid (FAA) is prepared from furfural, malonic acid and pyridine as catalyst according to literature procedure[2]. FAA is purified from hot water and benzene repeatedly till m.pt. 140°C is obtained. The solubility of FAA in water is low and its solubility was determined by its saturated solution in distilled water at 31°C by conductometric titration. The solubility of FAA in water at 31°C is 0.014M.

Sodium salt of FAA was prepared from equimolar concentrations of FAA and NaOH, the solution was filtered and evaporated to dryness. A series of FAA solutions as shown in Table 1, were prepared in distilled

TABLE 1

THE CONDUCTANCE DATA OF FURYL ACRYLIC ACID AT 31°C

Concen. c	λ_c	α	$K' \times 10^5$
0.002145	56.68	0.1436	5.16
0.00286	50.22	0.1272	5.30
0.00429	41.56	0.1053	5.32
0.00715	32.72	0.0829	5.36
0.00858	30.94	0.0784	5.72
0.01001	29.66	0.0751	6.10
0.01144	27.79	0.0704	6.10
0.01287	26.33	0.0667	6.14
0.0143 (Satd.)	25.17	0.0638	6.22

water and the specific conductance of each solution was measured. The specific conductance of distilled water was subtracted from each solution.

RESULTS AND DISCUSSION

The specific conductance after correction at each dilution is used in determining λ_c values. The equivalence conductance λ_c at each dilution is determined according to eqn. 4

$$\lambda_c = \frac{1000\ K}{c} \tag{4}$$

The equivalence conductance λ_0 for Na–FAA was determined according to Debye–Hückel-Onsagar eqn.

$$\lambda_c = \lambda_0 - (a + b\lambda_0)\sqrt{c} \tag{5}$$

where a and b are constants for a given solvent and at a specified temperature. According to eqn. 5, a plot of λ_c against $\sqrt{c}$ is shown in Fig. 1. The value of λ_0 is found to be 75.5 from the intercept.

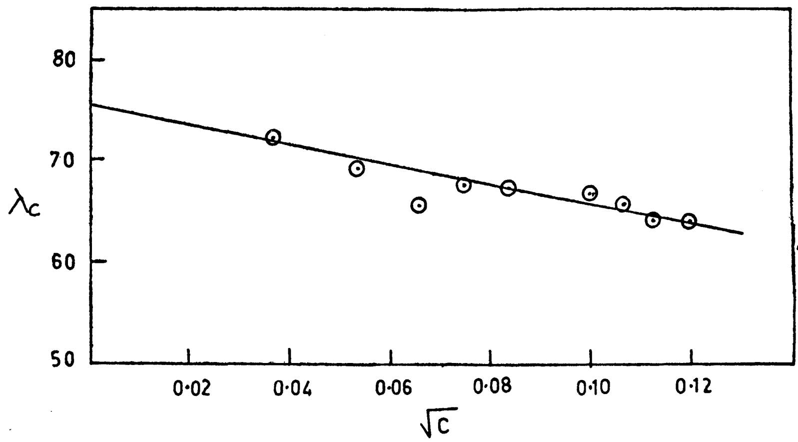

Fig. 1 A plot of λ_c against $\sqrt{c}$ for Na–FAA at 31°C.

The values of λ_0 for NaCl and HCl at 31°C are calculated from the ionic conductance and temperature coefficient α, according to eqn. 6.

$$\lambda_t = \lambda_{25}[1 + \alpha(t - 25)] \tag{6}$$

The values of λ_{25} and α were collected from the literature[2] and t is the temperature of experiment. The values of λ_0 for NaCl and HCl at 31°C are 138.86 and 458.17 respectively. The value of λ_0 for FAA is determined from the λ_0 values of Na–FAA, NaCl and HCl according to eqn. 7:

$$(\lambda_0)\ \text{FAA} = (\lambda_0)\ \text{Na–FAA} + (\lambda_0)\ \text{HCl} - (\lambda_0)\ \text{NaCl} \tag{7}$$

The λ_0 value of FAA calculated according to eqn. 7 is 394.81 at 31°C. This value is utilized in calculating the degree of dissociation α at a given dilution. The degree of dissociation α is the ratio of λ_c to λ_0.

The apparent dissociation constant K′ can be determined according to Ostwald dilution law:

$$K' = \frac{\alpha^2 C}{1 - \alpha} \tag{8}$$

The value of K′ determined according to eqn. 8 for each dilution is reported in Table 1.

The true dissociation constant K can be determined according to eqn. 3. In order to apply eqn. 3, a knowledge of K′ and α is required and these are determinable quantities from conductance data. According to eqn. 3, a plot of log K′ against $\sqrt{\alpha c}$ is shown in Fig. 2. The plot is a

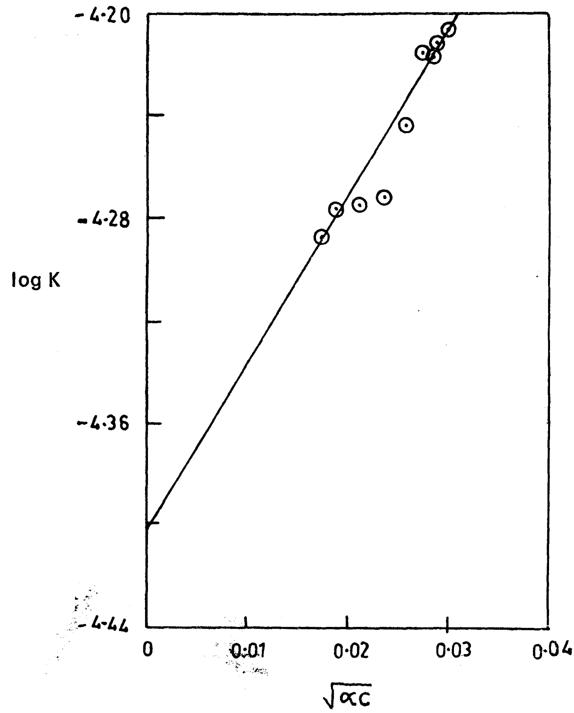

Fig. 2 A plot of log K′ against $\sqrt{\alpha c}$ for FAA at 31°C

straight line, within the range of D–H limiting law, with intercept equal to log K. The value of K is found to be 3.963×10^{-5}.

REFERENCES

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[*Received*: 14 September 1989; *Accepted*: 15 September 1990] AJC–224