

CONDUCTOMETRIC INVESTIGATIONS ON OXALIC

ACID IN 2-PROPANOL + WATER MIXTURES AT

298.15, 303.15, 308.15 AND 313.15 K

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ABSTRACT

Electrical conductivity of oxalic acid has been measured in 2-propanol + water mixtures covering the approximate range of dielectric constant $73.0 \geq \epsilon \geq 49.6$ at 298.15, 303.15, 308.15 and 313.15 K. The conductance data have been analysed by using Shedlovsky equation to obtain limiting molar conductance, association constant and Walden product. The limiting molar conductance and Walden product values were found to decrease with increase in x_{2pr} (mole fraction of 2-propanol). Oxalic acid is found to be a structure breaker in the solvent media explored. The results obtained from the study were used to elicit the nature of ion-ion and ion-solvent interactions.

Keywords: Limiting Molar Conductance, Walden Product, 2-Propanol, Oxalic Acid

I. INTRODUCTION

Investigations on transport property of an electrolyte and the effect of ion solvation on it in various aqueous and partial aqueous media have received much attention in recent years, since it gives valuable information regarding ion-ion and ion-solvent interactions [1-5]. In continuation of our works on electrolytes in 2-propanol + water mixtures, we have chosen oxalic acid as the electrolyte due to its ability to form stable complexes with various metal ions, and its substantial importance in many industrial, geological, and biological systems [6]. Moreover, it is a weak electrolyte and is expected to form hydrogen bonds with both water as well as 2-propanol. Oxalic acid on dissociation gives oxalate ion and hydrogen ion. The former is a structure breaker [7] and the latter is a kosmotrope capable of breaking hydrogen bonds. However, oxalic acid is reported to show structure breaking properties in some water + organic solvent mixtures [8]. In contrast to other dicarboxylic acids, conductance of oxalic acid in aqueous medium at 298.15 K was repeatedly measured by Ostwald [9], Collie [10], and the most extensive measurements by Darken [11]. Darken incorporated a small correction in the determined conductances considering the second dissociation of the acid. Using Quint-Viallard conductivity equation Lee and Wheaton further analysed Darken's conductance data. With an exception of Darken's work, other reports were of limited value and hence Barthel et al [6] made systematic and precise measurements of electrical conductivities of dilute aqueous oxalic acid solutions in the temperature range 298.15-308.15 K.

However, conductometric investigations on oxalic acid in 2-propanol + water mixtures are not reported in the literature. 2-Propanol + water mixtures are of special interest due to the clathrate-like structures present in them [12].

II. METHODOLOGY

Oxalic acid (Merck, AR Grade), triply distilled water (specific conductance 1×10^{-6} mho cm^{-1}) and 2-propanol purified by using standard procedure [8] were used for preparing 1M oxalic acid stock solutions in different 2-propanol + water mixtures. These solutions were further diluted to obtain solutions of desired concentrations. Conductance measurements were made using a digital microprocessor based conductivity meter (Model-308, Systronics India Limited). All the measurements were made in a thermostat maintained at the desired temperature with an accuracy of $\pm 0.1^\circ\text{C}$.

III. RESULTS AND DISCUSSION

3.1 Limiting Molar Conductance (Λ_m°)

Molar conductance of oxalic acid in 2-propanol + water mixtures were calculated using the specific conductance obtained from a direct reading digital conductivity meter at (298, 303, 308 and 313)K. The resulted molar conductance values were analysed by Shedlovsky model [13], a variant of Fuoss-Kraus model, which includes corrections for inter ionic effects on ionic mobilities and for ionic activity coefficients. Shedlovsky equation used for determining limiting molar conductance and association constant K_a is given below:

$$\frac{1}{S\Lambda_m} = \frac{1}{\Lambda_m^\circ} + \frac{C\Lambda_m S f_{\pm}^2 K_a}{\Lambda_m^{\circ 2}}$$

(1)

where

$$S = \left[\frac{\beta \sqrt{C\Lambda_m}}{2\Lambda_m^{\circ 3/2}} + \sqrt{1 + \frac{\beta^2 C\Lambda_m}{4\Lambda_m^{\circ 3}}} \right]^2 ;$$

$$\beta = \frac{8.204 \times 10^5 \Lambda_m^\circ}{(\epsilon T)^{3/2}} + \frac{82.5}{\eta(\epsilon T)^{1/2}} ;$$

$$\log f_{\pm} = \frac{-1.824 \times 10^6 (C\alpha)^{1/2} / (\epsilon T)^{3/2}}{1 + 50.24 \times 10^8 R(C\alpha)^{1/2} / (\epsilon T)^{1/2}} ;$$

$$\alpha = \frac{S\Lambda_m}{\Lambda_m^\circ} \text{ and } R = q = \frac{e^2}{2\epsilon kT}$$

where f_{\pm} is the mean activity coefficient, estimated from the extended Debye-Huckel equation; R is ion size parameter which is equal to the Bjerrum's critical distance q ; k is Boltzmann's constant and T is the temperature in Kelvin. The Shedlovsky plots are presented in Fig.1 and Λ_m° values obtained are given in TABLE 1.

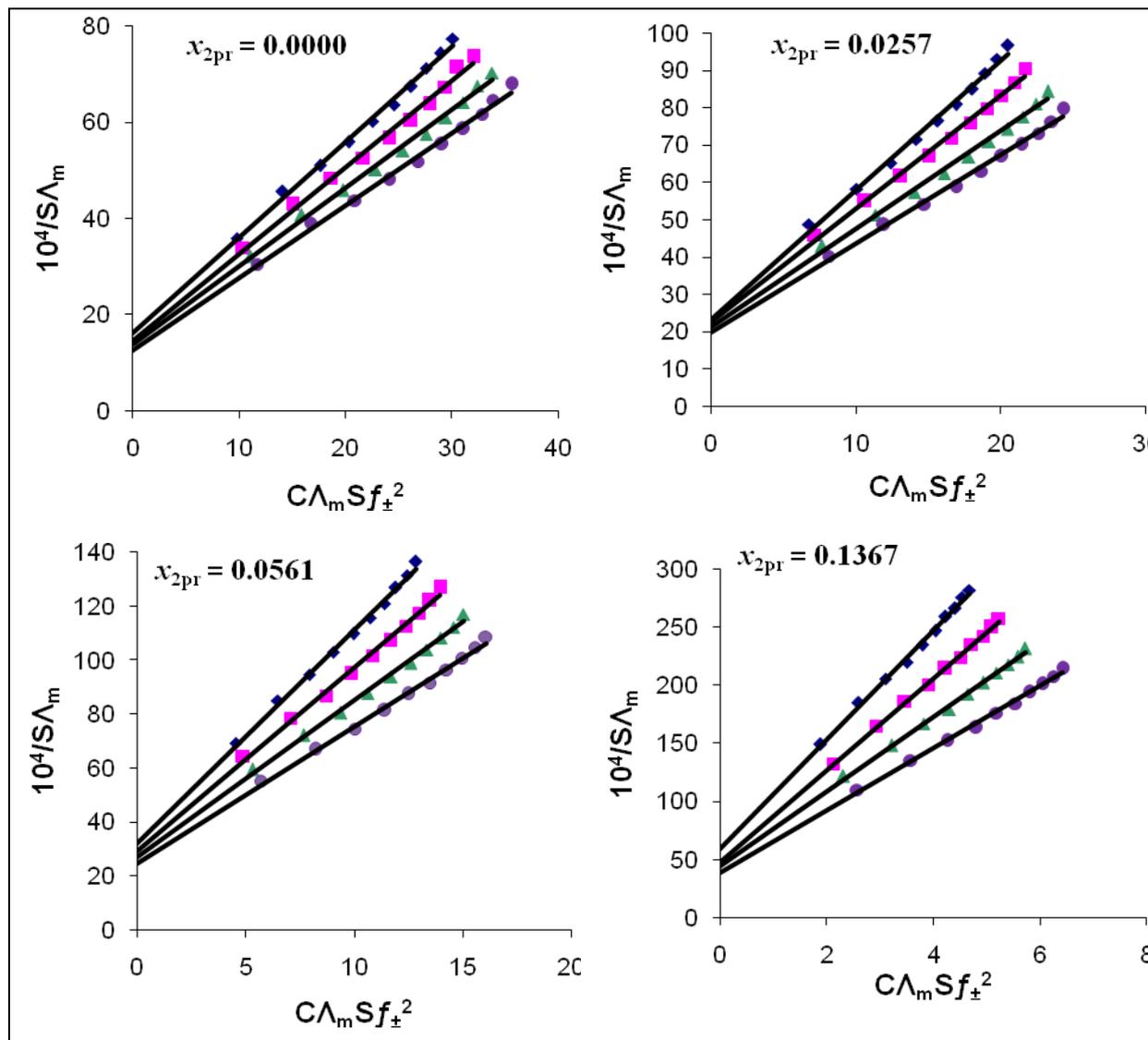


Fig. 1: Plot of $1/S\Lambda_m$ (ohm cm^{-2} mol) Vs $C\Lambda_m S f_{\pm}^2$ for oxalic acid in 2-propanol + water mixtures at Different Temperatures

As expected the limiting molar conductance values are quite large mainly due to the presence of highly conducting hydrogen ions. The anomalously large mobility of proton in aqueous medium is often explained in terms of Grotthus mechanism and quantum mechanical tunneling [14]. The increase in dissociation and ionic mobility caused the limiting molar conductance to show sharp increase with increase in temperature. A sharp decline in limiting conductance is noticed with increasing x_{2pr} . Various factors such as decrease in dielectric constant, increased viscosity of solvent mixture [1], increased basicity, destruction of tetrahedral-like structure of water and increased solvated ion size must have played a critical role in reducing the conductance. It is also known that the anomalous conductivity of proton declines with increasing alcohol content [15]. Limiting conductance is not reported beyond 0.1367 mole fraction of 2-propanol due to poor linearity of the Shedlovsky plot.

Table 1: Experimental molar conductance at infinite dilution (Λ_m° : mho cm² mol⁻¹) for oxalic acid in 2-propanol + water mixtures at different temperatures obtained from Shedlovsky model

| T (K) | x_{2pr} | | | |
|--------|-----------|--------|--------|--------|
| | 0.0000 | 0.0257 | 0.0561 | 0.1367 |
| 298.15 | 615 | 430 | 308 | 166 |
| 303.15 | 681 | 446 | 339 | 206 |
| 308.15 | 733 | 475 | 367 | 222 |
| 313.15 | 797 | 511 | 404 | 258 |

3.2 Association Constant (K_a)

Association constants calculated from the Shedlovsky model is given in TABLE 2. Association is expected to predominate over dissociation since the electrolyte under consideration is weak. Except for $x_{2pr} = 0.0257$, association constant is found to increase with increase in temperature suggesting the endothermic nature of the system. Similar behavior is reported for tartaric acid in water + methanol/ethanol systems [16]. The trends in the variation of K_a with respect to mole fraction of 2-propanol is rather amusing. The initial addition of 2-propanol to water is found to reduce the association constant as against the usual increasing trend with declining dielectric constant. Thus the computed K_a values at $x_{2pr} = 0.0257$ and $x_{2pr} = 0.0561$ are lower than expected. The minimum K_a values noticed at $x_{2pr} = 0.0257$ can be explained on the basis of changes in water structure induced by the small quantities of 2-propanol added. Water is a highly associated solvent due to the presence of hydrogen bonds that helps in the formation of polymeric aggregates of water. Hence pure water can stabilize the ion-pairs by forming chain structure around it [17]. On adding small amounts of 2-propanol, depolymerisation of water chain occurs and hence ion-pairs are less stabilized. Larger K_a values found at $x_{2pr} = 0.1367$ is due to the predominating influence of decrease in dielectric constant favouring association.

Table 2: Experimental values of K_a for oxalic acid in 2-propanol + water mixtures at different temperatures

| T (K) | x_{2pr} | | | |
|--------|-----------|--------|--------|--------|
| | 0.0000 | 0.0257 | 0.0561 | 0.1367 |
| 298.15 | 74.99 | 64.22 | 74.93 | 129.43 |
| 303.15 | 83.35 | 60.30 | 77.92 | 168.19 |
| 308.15 | 87.61 | 59.43 | 77.97 | 157.59 |
| 313.15 | 95.59 | 62.18 | 82.65 | 177.98 |

3.3 Walden Product

Walden product was calculated for oxalic acid in different compositions of 2-propanol + water mixtures at four different temperatures using the formula:

$$\text{Walden product} = \Lambda_m^\circ \eta_o \quad (2)$$

where η_o is the viscosity coefficient of solvent mixture. The linear plot of Walden product versus temperature

provided in Fig. 2 is having negative slope indicating structure breaking behavior of oxalic acid in aqueous as well as in 2-propanol + water mixtures. The Walden product is found to decrease with increasing x_{2pr} and consequently solvation is strengthened in that direction. The momentous deviation from Walden rule with increasing mole fraction of 2-propanol may be a consequence of change of ion solvation and of the solvent structure [18].

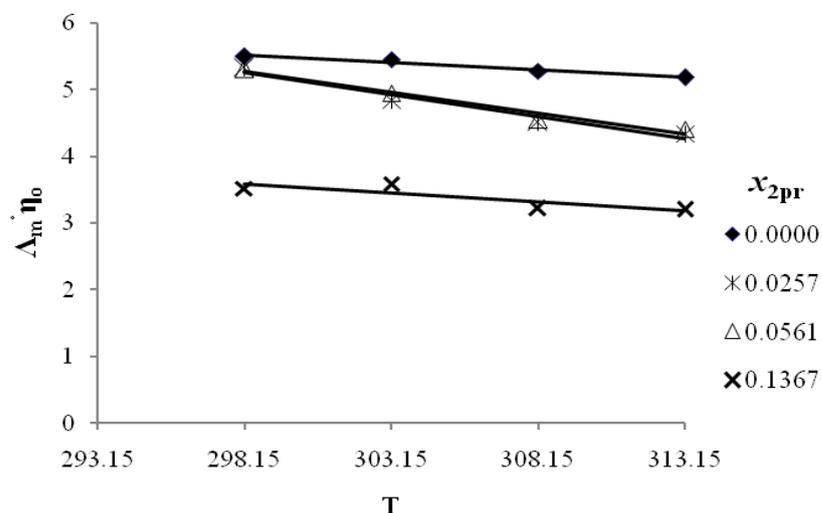


Fig. 2: Plot of walden product ($S\text{ cm}^2\text{ mol}^{-1}\text{ poise}$) vs temperature (K) for oxalic acid in 2-propanol + water mixtures

IV. CONCLUSIONS

The sharp decline in conductance with respect to increase in 2-propanol content in the solvent mixture is explained on the basis of different factors influencing ionic conductance. The endothermic nature of the system is evident from the K_a values for different systems at different temperatures. The structure breaking character is established from the variation of Walden product with temperature.

V. ACKNOWLEDGEMENTS

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