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Interaction Studies of Dilute Aqueous Oxalic Acid

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Abstract: Molecular conductance λ_m , relative viscosity and density of oxalic acid at different concentration in dilute aqueous solution were measured at 293 K. The conductance data were used to calculate the value association constant. Viscosity and density data were used to calculate the A and B coefficient of Jone-Dole equation and apparent molar volume respectively. The viscosity results were utilized for the applicability of Modified Jone-Dole equation and Staurdinger equations. Mono oxalate anion acts, as structure maker and the solute-solvent interaction were present in the dilute aqueous oxalic acid.

Keywords: Staurdinger equation, Modified Jone-Dole equation, Viscosity, Conductance, Oxalic acid

Introduction

Viscometric, volumetric and conductometric studies of a solute in case of aqueous solution is related to the interactions among the components of a solution¹⁻³, a knowledge of which is important in solution chemistry. In highly dilute aqueous solutions, the two properties apparent molar volume and viscosity are needed to buildup such knowledge of inter molecular interactions.

The structural and dynamic nature of water molecules in different environments is also important in such aqueous solutions. Water it self is highly associated and its tendency to associate with solute molecule is high. The organic compound, which contains carboxyl group (name derived by linking carbonyl and hydroxyl), belongs to the class of carboxylic acid. These compounds have a capacity to form hydrogen bond like water. In this study viscometric, volumetric and conductometric studies of oxalic acid were undertaken to research the intermolecular/ionic interactions/structural features focused on highly dilute aqueous media. A survey of literature showed that there is lack of interaction studies of

carboxylic acids in dilute aqueous solutions. Moreover, carboxylic acids – water solvent system⁴⁻⁶ and in water systems with other co-solute⁷⁻¹¹ have been extensively used in the volumetric, viscometric or conductometric studies of salts of carboxylic acids.

Recently, studies relating to the measurement of partial molar volume of oxalic acid in aqueous solution¹² and in aqueous solution of fructose have been reported¹¹. In both the studies the data indicates the presence of strong solute-solvent/ion-solvent interactions. Such studies are still lacking in relation to viscometric and conductometric measurements in order to ascertain the various interactions present in dilute aqueous solutions. The study has been undertaken determination of the values of the coefficients A_x and B_x for modified Jones-Dole equation as proposed in our previous study¹. The conductivity data has been measured under same experimental conditions and analyzed by the Arrhenius – Ostwald relation¹³.

Experimental

Deionised water was distilled twice with a small quantity of alkaline potassium permanganate. Finally water was distilled in corning glass apparatus with sulphuric acid. The specific conductance of prepared distilled water for the study was of the order, $2 \times 10^{-6} \Omega \text{ cm}^{-1}$ oxalic acid (GR Sarabhai M) was used as such and solutions were prepared by dissolving the calculated weight of the sample for desired strength in distilled water.

Density measurements of solutions were made using Pyknometer having capacity 15 cm^3 . Pyknometer was calibrated with distilled water having densities $0.9972 \text{ gm cm}^{-3}$ and $0.9942 \text{ gm cm}^{-3}$ at 298 K and 308 K respectively. The densities of solutions were determined from the mass of solution in the pyknometer after reaching thermal equilibrium with a thermostatically controlled water bath capable of maintaining the temperature constant $\pm 0.01^\circ\text{C}$. A Citizen make electronic balance with an accuracy of $\pm 0.0001 \text{ g}$ was used for weight determination. The density values were reproducible $\pm 0.00006 \text{ g cm}^{-3}$.

Viscosities were measured using an Ubbelohde type capillary viscometer (Agrwal Scientific Agra), which was calibrated with doubly distilled water, by measuring efflux time using a stop watch with a resolution of 0.01 second. The average of at least four reading reproducible within accuracy of 0.01 second was taken as the final efflux time.

A digital conductivity meter Systronic 306 with a dipping type conductivity cell having platinized electrodes was used for conductivity measurement. The temperature of solutions was kept constant with the help of a thermostat. The conductivity meter was calibrated with standard KCl solution. The accuracy of the conductivity meter was 0.01 mS cm^{-1} during the study. The results were checked for constant reading.

Results and Discussion

The apparent molar volume Φ_v of aqueous solution of oxalic acid was calculated from the observed densities of different concentrations using the following standard expression equation (1).

$$\Phi_v = \frac{M}{d_0} + \frac{1000(d_0 - d)}{d_0 c} \quad (1)$$

Where M is the molar mass of solute, d and d_0 are densities of solution and pure solvent, respectively, and c is the molarity of solute. The values of densities and calculated values are given in Table 1. The dependence of apparent molar volume on concentration of the solute is given by the equation (2), known as Masson's equation.

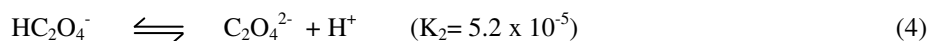
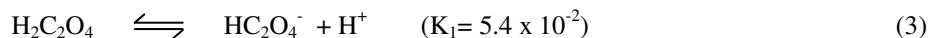
$$\Phi_v = \Phi_v^0 + S_v c^{0.5} \quad (2)$$

Table 1. Variation in density, specific conductance, and η / η_0 for different molar concentration of aqueous oxalic acid at 293 K

Conc. mol dm ⁻³	Density gcm ⁻³	Φ_v cm ³ mol ⁻¹	η / η_0	$\eta / \eta_0 - 1/c^{0.5}$	$(x_s/x_w)^{0.5}$	$\eta / \eta_0 - 1 / (x_s/x_w)^{0.5}$	Spec. Cond. mS cm ⁻¹
0.055	1.0006	46.4472	1.011	0.046904	0.031464	0.349603	13.8
0.11	1.003	46.4472	1.021	0.063317	0.044609	0.470753	21.8
0.165	1.0051	48.2686	1.031	0.076317	0.054681	0.566926	29
0.22	1.0076	47.3571	1.041	0.087412	0.063246	0.648267	35.1
0.275	1.01	47.1757	1.052	0.09916	0.070852	0.733925	41
0.33	1.0122	47.6614	1.062	0.107928	0.077717	0.797762	46.2
0.385	1.0148	46.9675	1.073	0.11765	0.084083	0.868187	51
0.44	1.017	46.3578	1.082	0.12362	0.09	0.911111	56.7
0.495	1.0192	47.6614	1.092	0.130763	0.095603	0.962309	61.8
0.55	1.0216	47.54	1.102	0.137537	0.100896	1.010942	64.7

x_s = mole fraction of solute, x_w = mole fraction of water

The values of apparent molar volume Φ_v were used for applicability of Masson's equation. The plot of $c^{0.5}$ versus Φ_v was not linear. The variation of Φ_v with $c^{0.5}$ followed a cyclic trend having maxima and minima. This type of trend resembles with the X-ray refraction data on liquids in radial distribution function which is a measure of average particle density as a function of distance from arbitrary origin. Such fluctuations of Φ_v in highly dilute aqueous media at lower concentration were also observed in case of alcohols [14] having protic nature due to the hydroxyl group. The limiting apparent molar volume (Φ_v^0) was calculated using the least square treatment to the plot of Φ_v versus $c^{0.5}$. The plot is given in Figure 1. The value obtained for Φ_v^0 and S_v for oxalic acid at 293 K are 46.618 ± 0.50 -cm³ mol⁻¹ and 1.082 ± 0.06 cm³ l^{1/2} mol^{-3/2} respectively. The positive value of Φ_v^0 indicating there by a interaction between solute and solvent molecule. The S_v indicating that the solute have good solute-solute interaction or good complex ion forming tendency. The oxalic acid ionizes in two steps; first ionization takes place one thousand times than the second.



The oxalate mono anion formed in first step may form the neutral molecule due to internal hydrogen bond formation through hydroxyl group or it may form hydrogen bond with other mono- oxalate anion. In both the cases the hydrogen bonding justifies the solute-solute interaction as observed in the study.

If we consider that the oxalic acid molecules, mono oxalate anion/ neutral molecule and oxalate ion behave like independent molecule of solute and form molecular assemblies, we can apply the Staudinger equation (5) to the measured viscosity data of oxalic acid given in Table 1.

$$(\eta / \eta_0 - 1) = kn c \quad (5)$$

Where k is the characteristic constant, n is the monomer present in the molecular assemblies and c is mole concentration of solute. The plot (Figure 2) of concentration *versus* $(\eta / \eta_0 - 1)$ is linear with the slope value 0.183 dm³ mol⁻¹.

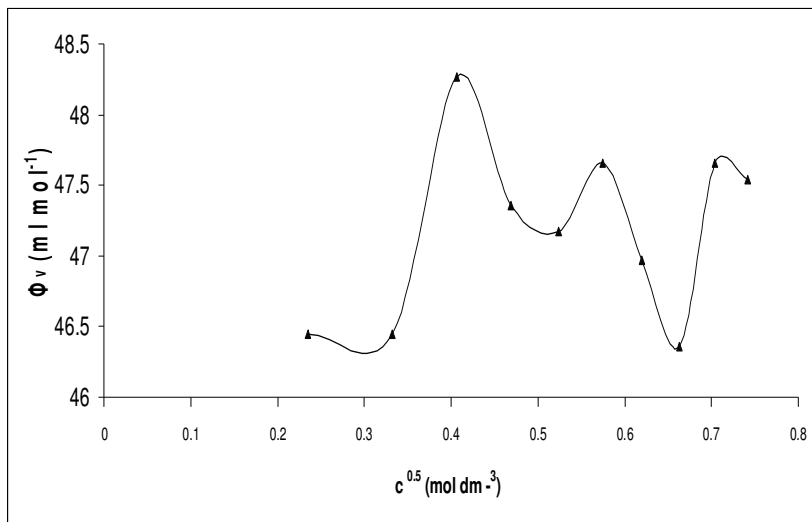


Figure 1. Plot of Φ_v versus $c^{0.5}$

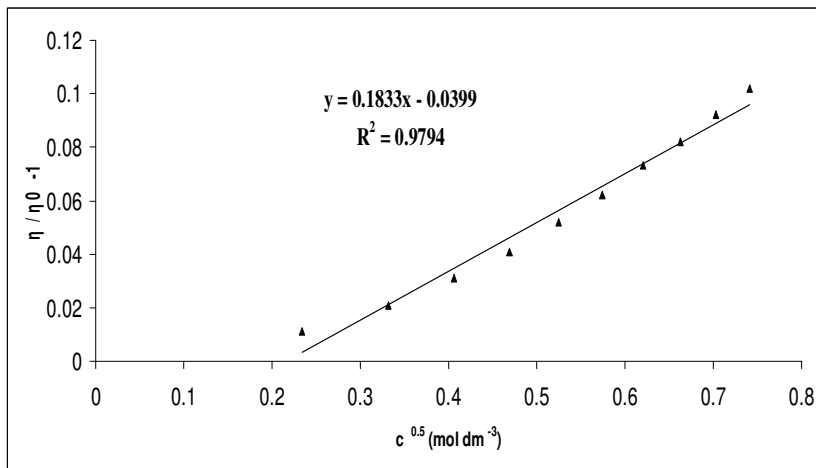


Figure 2. Plot of concentration *versus* $(\eta / \eta_0 - 1)$

The values of η/η_0 obtained at different concentration were utilized for the determination of intermolecular interactions in aqueous solution. The interaction parameters were obtained with the help of Jone-Dole equation.

$$\frac{(\eta/\eta_0 - 1)}{c^{0.5}} = A + B c^{0.5} \tag{6}$$

Where, A and B are the coefficients for the ion-ion and ion-solvent interactions respectively and c is the molar concentration. The value of A and B were obtained from the intercept and slope of the linear plots of $(\eta/\eta_0 - 1)/c^{0.5}$. The obtained values of intercept and slope are given in Figure 3.

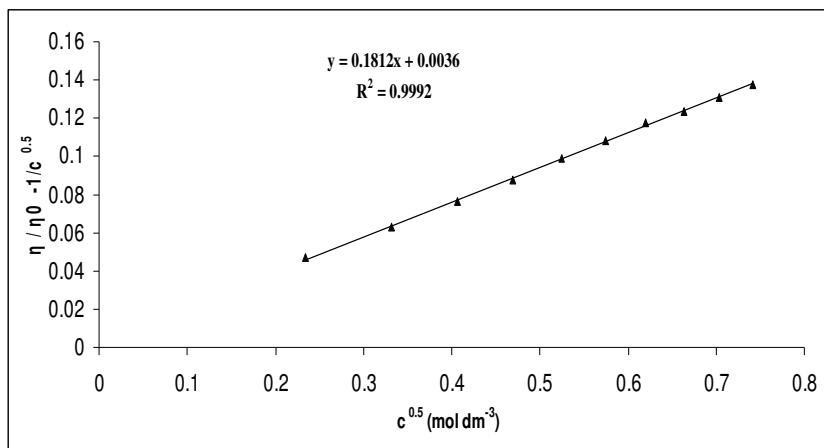


Figure 3. Linear plot of $(\eta/\eta_0 - 1)/c^{0.5}$

The values of concentration were used to calculate x_s and x_w and data obtained are recorded in Table 1. The linear plot $x_s/x_w^{0.5}$ versus $\eta/\eta_0 - 1/ x_s/x_w^{0.5}$ confirm the validity of modified Jone-Dole equation as given below.

$$\eta / \eta_0 - 1/ (x_s/x_w)^{0.5} = A_x + B_x(x_s/x_w)^{0.5} \tag{7}$$

Where A_x and B_x are the coefficient, which are the measure of the interactions present between solute-solute and solute-solvent. The plot is given in Figure 4 with slope and intercepts values.

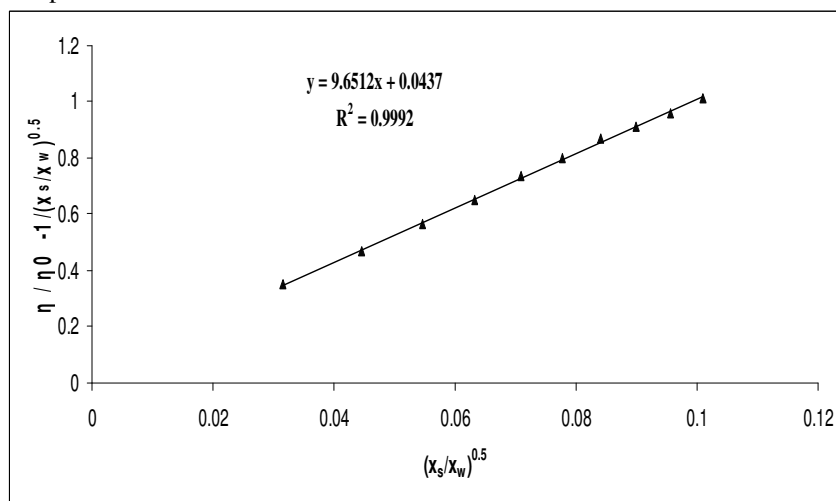


Figure 4. Plot $x_s/x_w^{0.5}$ versus $\eta/\eta_0 - 1/ x_s/x_w^{0.5}$

The values of A , A_x , B and B_x obtained in the study are positive which show the presence of ion-solvent interactions and solute-solute/ion-ion interaction. In dilute aqueous oxalic acid solution. The positive value of coefficient B also indicates that the oxalic acid behaves as structure maker in highly dilute aqueous solution. The value of A is very small which indicates the possibility of solute-solute interaction is very small in comparison to the

inter molecular attraction between solute and solvent. It suggests the internal hydrogen bond formation in mono oxalate anion. The concentration range used in the study was optimum for the validity of Staurdinger, Jone-Dole equation and Modified Jone- Dole equation in which it acts as structure maker. Further addition of solute can modify the structure of water by hydration as obtained volumetrically^{10, 11} from thermal expansion. The ratio of (B_x/B) is 53.31, which is nearly equal to reported value for sugars¹.

Although the oxalic acid is a weak electrolyte, in the present study it has been concluded that the solute solvent interactions takes place with small solute-solute interactions. The carboxalate ion has resonating structure and hydrogen bond forming capability. To investigate the existence of charged assemblies specific conductance of oxalic acid was measured the data are given in Table 1. The data were analysed by the Arrhenius –Ostwald relation given by the equation. The plot $c\lambda_m$ versus $1/\lambda_m$ were linear given in Figure 5.

$$\frac{1}{\lambda_m} = \frac{1}{\lambda_m^0} + \frac{c\lambda_m K_A}{\lambda_m^0{}^2} \quad (8)$$

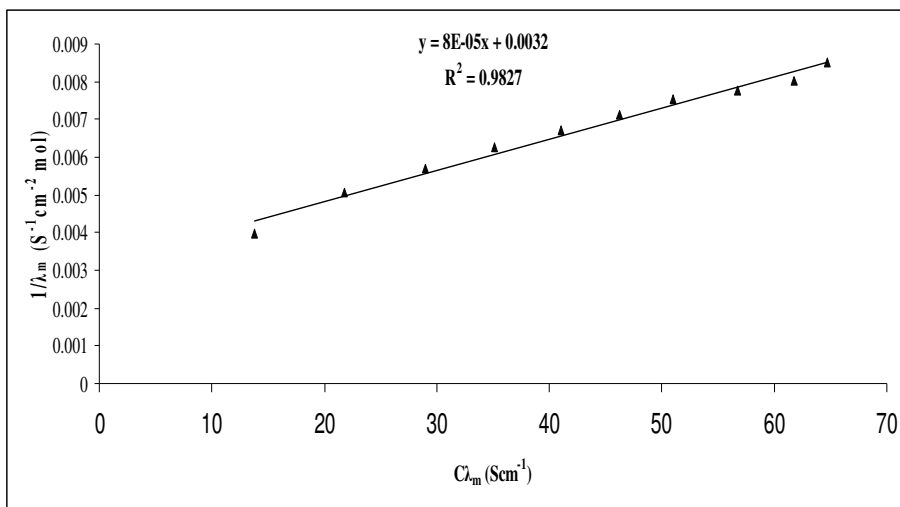


Figure 5. Plot $c\lambda_m$ versus $1/\lambda_m$

The value λ_m^0 is 312 S cm⁻¹, which is nearly double of ionic molar conductance at infinite dilution of oxalate ion. The value of K_A has significant value 7.78. The calculated value is also in agreement with the results concluded that the solute-solvent interactions exist in highly dilute aqueous solution of oxalic acid.

Conclusions

A perusal of results indicates that the B coefficient is positive and fairly large for oxalic acid in the concentration range studied, thereby showing the strong solute-solvent interaction in highly dilute aqueous solution. This is also evident from the value of Φ_v^0 . The solvent water and solute oxalic acid has protic solvent characteristics. The dissociation of acid forms mono oxalate anion, having resonating and hydrogen bond forming capacity, which can form various ionic equilibria of association or ionic doublet. The relationship between viscosity data and concentration of solute proposed by Staurdinger for poly molecular assemblies

has been also observed in the study. The experimental viscosity data is in good agreement with the Jone-Dole and Modified Jone-Dole equation.

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