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Molecular Interactions Of Aqueous Formic Acid

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ABSTRACT

Measurements of density, viscosity and molecular conductance were performed on aqueous formic acid solutions of different concentration at 293 K. The apparent molar volume and coefficient of Jone-Dole equation have been calculated from density and viscosity data. The behaviour of these parameters suggests the ion-solvent interaction in the system and formic acid acts as "structure maker". The presence of ion-ion pair in the system has been concluded from the conductance data. The results were also discussed in the light of Jone-Dole equation with modification and Grunberg-Nissan equation.

KEYWORDS

Formic acid;
Apparent molar volume;
Modified
Jone-Dole equation;
Gruneberg-Nissan equation;
Ion-ion pair.

INTRODUCTION

The apparent molar volume and viscosity are used as guide to the study the structural properties and interactions present in solutions. A survey of literature showed that there is lack of interaction studies of carboxylic acids in aqueous solution. Moreover, carboxylic acids-water solvent system[1] and in water systems with other co-solute[3-11] have been extensively used in the volumetric, viscometric or conductometric studies of salts of carboxylic acids. Chowdoji Rao and coworker[2] reported the apparent molar volume for formic acid. They have used Masson's equation for determination of apparent molar volume Φ_v^0 and experimental slope S_v and results have been interpreted in terms of interactions in solution. Viscosity B-coefficient of formic acid has been utilized to analyze the effect of sodium formate on solute-solvent interactions. They have concluded that the solute-solvent interactions are greater in water and decreases with increase of salts concentration, which also was evident from the volumetric results reported by the above workers. Formic acid has also been used as co-solute with other salts in viscometric, volumetric and conductometric studies[3,6,7] to investigate the nature of interaction present in solutions.

Another study[8] on carboxylic acid, the apparent molar volume of propionic acid has reported aqueous solution in presence of sodium propionate. In aqueous solution apparent molar volume of carboxylic acid was a linear function of concentration. The apparent molar volume at infinite dilution of acid was larger in presence of salts than in pure water. It was concluded that the dissociation of liquid propionic acid increased in its salt solutions. In the above study the viscosity B-coefficient has been determined and was found positive with large value, which indicates the greater solute-solvent interactions in water.

In the viscometric studies[9] it was observed that the viscosity B-coefficient of benzoate and ortho-amino benzoate ions was much larger than that of benzoic acid and ortho- amino benzoic acid, respectively. Similar difference in B- coefficient was reported for acetate ion and acetic acid[10, 11].

We have chosen formic acid as solute for viscometric and volumetric studies along with conductometric study in order to gain more information on interactions of formic acid in dilute aqueous solution. The validity of the modification in Jone-Dole equation, used with viscometric data of methanol and acetone, have also undertake with formic acid.

EXPERIMENTAL

Deionized water was distilled twice with small quantity of alkaline potassium permanganate. Finally water was distilled in corning glass apparatus with formic acid. The specific conductance of prepared distilled water for the study was in the order 2 x10^{-6} Ω cm^{-1}. The formic acid of AnalaR grade BDH was used as such and solutions were prepared by dissolving the calculated volume of acid for desire strength in distilled water. The strength of solutions was checked by titrating with standard alkali. Density measurements of solution were made using Pyknometer having capacity 15 cm^3. Pyknometer was calibrated with distilled water having density 0.9972 gm cm^{-3} and 0.9942 gm cm^{-3} at 298 K and 308 K respectively. A thermostatically controlled water bath capable of maintaining the temperature constant ± 0.01 ^{0}C was used during the studies. All weighing were made on single pan digital balance (Citizen make) with the accuracy of 0.0001g. The density values were reproducible ± 0.00002 g cm^{-3}. Viscosities were measured using an Ubbelohde type capillary viscometer (Agrwal Scientific Agra) which was calibrated with doubly distilled water by measuring reflux time using and a stop watch with a resolution of 0.1 second. The average of at least four reading reproducible within accuracy of 0.1 second was taken as the final efflux time. The conductometric measurements of formic acid solutions at different concentrations were made with a digital conductivity meter (Systronic 306). The conductivity meter was calibrated with standard KCl solution. The accuracy of meter was 0.01 m S cm^{-1} during the study. The results were checked for constant reading.

RESULTS AND DISCUSSION

Viscometric studies

The values of η/η_0 observed at different concentration of formic acid in aqueous solution are given in TABLE 1. These values were utilized for the determination of intermolecular interactions in aqueous solution. The interaction parameters were obtained with the help of Jone-Dole equation[12] given by equation 1.

$$\frac{(\eta/\eta_O - 1)}{C^{0.5}} = A + BC^{0.5} \tag{1}$$

Where, A and B are the coefficients for the ion-ion and ion-solvent interactions respectively and c is the molar concentration of solute. The value of A and B were obtained from the intercept and slope of the linear plot of $c^{0.5}$ versus $(\eta/\eta_0 -1)/c^{0.5}$. The obtained values of constant B (0.032 $dm^{3/2}$ mol^{-1}) and A (0.0014 $dm^{3/2}$ mol^{-1}).

The obtained viscosity values have also been used to test the validity of modified Jone-Dole equation by the graph $(x_s/x_w)^{0.5}$ versus $(\eta/\eta_0 -1)/(x_s/x_w)^{0.5}$ having best correlation with coefficient value 0.9945. The value of slope B_x (1.6907) and intercept A_x

(0.0145) was obtained.

In case of formic acid the formation of dimer takes place due to the hydrogen bonding. The association of two molecules in solution is particularly important for the studies of molecular assemblies or polymers. We have applied this concept with viscometric data in Staurdinger equation for polymeric solution as test model[13] given by equation 2.

$$\eta/\eta_O = 1 + Knc \qquad (2)$$

It is evident that the applied equation is in good agreement with results. The characteristic constant for the solution of formic acid were also calculated from the slope value kn = 0.0333. According to Grunberg and Nissan[14] the value of viscosity for binary liquid mixture of component 1 and 2 is given by the equation 3.

$$\ln\eta = X_1 \ln\eta_1 + X_2 \ln\eta_2 + X_1 X_2 d_{12} \qquad (3)$$

Where, $d_{1\,2}$ is a parameter, which is regarded as a measure of the strength of interactions between dissimilar molecules. The values of $d_{1\,2}$ calculated for formic acid - water mixture with the help of equation 3 are recorded in TABLE 1, where η is the viscosity of solution, η_1 and η_2 is the pure component 1 and 2 respectively and x represents mol fractions of the components in the solutions.

Volumetric studies

The volumetric study of the solutions at same concentration in order to obtain a comparative account of experimental results was measured. The obtained values of densities are listed in TABLE 1 at different concentrations. The apparent molar volume Φ_v is given by the standard expression relation equation 4.

$$\Phi_V = \frac{M}{d_O} + \frac{1000(d_O - d)}{d_O C} \qquad (4)$$

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 Φ_v were calculated at different concentration (mol dm^3). The values obtained are given in TABLE 1 and Φ_v versus $c^{0.5}$ curve have been drawn. These plots are straight line in nature and show with correlation coefficient 0.9935 which indicates the validity of Masson's equation, equation 5, in the concentration range studied.

$$\Phi_V = \Phi_V{}^O + S_V C^{0.5} \qquad (5)$$

Where, $\Phi_v{}^0$ (intercept = 35.035 cm^{3}mol^{-1} is the apparent molar volume at infinite dilution and S_v (slope= 0.535 cm^3 l$^{1/2}$ mol$^{-3/2}$) is the slope of the plot Φ_v versus c$^{0.5}$.

Conductometric studies

The conductometric study of the aqueous formic acid at same concentration range was used for volumetric and viscometric studies. The obtained values of specific conductance at different concentration in range 0.11-mol dm^{-3} to 0.88-mol dm^{-3} at 293 K. These values were used to test the validity of Arrhenius - Ostwald relation[15] given by equation (6).

$$\frac{1}{\lambda_m} = \frac{1}{\lambda^O{}_m} \frac{C\lambda_m K_A}{\lambda^O{}_m{}^2} \qquad (6)$$

Where K_A is the association constant, $\lambda^0{}_m$ is the molecular conductance at infinite dilution, and c is the molar concentration of the electrolyte. The plot of c λ_m versus $1/\lambda_m$ is given in figure (1).

Fort and Moore[16] , Rastogi et al,[17], Ramamoorthy[18] and Subha et al,[19] reported that for any binary liquid mixtures, the positive value of Grunberg-Nissan interaction parameter $d_{1\,2}$ indicates the presence of strong interactions and the negative value of $d_{1\,2}$ indicates the presence of weak interactions between the unlike molecules. On this basis in the present study confirm the presence of strong inter-

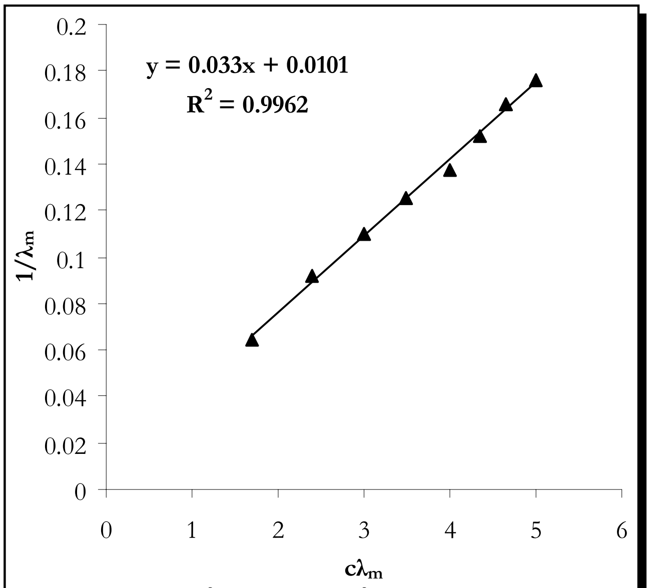

Figure 1: Plot cλ_m versus $1/\lambda_m$ for aqueous formic acid at 293 K

action between the formic acid and the water molecules. The value of interaction parameter for formic acid (d_{12}=1.28±0.10) is positive. It is evident that the interactions between formic acid and water molecule are strong. The viscosity B-coefficient for formic acid was found positive which also supports the presence of solute-solvent interactions in aqueous formic acid solution. It was observed that the value of A coefficient is positive having magnitude 0.0014 ($dm^{3/2}$ $mol^{-1/2}$) favours to the existence of very weak ion-ion interaction. The intermolecular interactions between two solute molecules or solute and solvent molecules takes place to a large extent because the acid molecule has two polar groups, carboxyl and hydroxyl. The two molecules of formic acid forms and aggregate by intermolecular hydrogen bonding or dipole-dipole interaction between water and acid molecule. The formic acid has unique characteristics among the carboxylic acid due to presence of H atom in place of alkyl group and it has structure of both carboxylic acid and aldehyde. In aqueous solutions the higher value of dielectric constant for both formic acid and water facilitate the ionization only because the further dissociation depressed by the interaction between polar groups or intermolecular hydrogen bonding. The modified Jone-Dole equation was in good agreement with the results obtained in viscometric study of formic acid. It is interesting to note the plot between $(x_s/x_w)^{0.5}$ versus $\eta/\eta_0-1/(x_s/x_w)^{0.5}$ has same nature as obtained for Jone-Dole equation. The value of B_x is 53 times of the value of B and the value of A_x is 10 time of A. These coefficients indicate the more ordered and favorable state of solution structure on adding the solute, i.e. it disrupts the original solvent structure and forms a new structure with more feasible arrangement. For pure water, majority of water molecules have four hydrogen bonds although fraction of molecule having 3 or 5 hydrogen bonds[20]. Addition of formic acid in water results the formation of H^+ and $HCOO^-$ ions, which modify the hydrogen bonded structure of water by breaking some of the hydrogen bond, which exist in pure water. The spectral studies have shown that the hydrogen bond distance in liquid water with a time scale of less than pico seconds [21]. The positive value of S_v from volumetric measurements confirms the presence of ion-ion interaction for formic acid in water and the Φ^0_v value observed by us is in the same range as reported in literature[1]. In this study the Staurdinger equation applicable for polymeric/molecular assemblies in solution have been used by us and the value of kn for formic acid was 0.0333 (dm^3 mol^{-1}).

It can be predicted that in view of the positive A coefficient and positive S_v the formic acid forms H^+ and $HCOO^-$ ions in water, which remains in the form of ionic doublet. One ionized formic acid molecule in the form of ionic doublet interact with other ionic doublet, which attains equilibrium with hydrogen bonded water molecule or protonated water molecule in the vicinity.

In the dilute aqueous solution of formic acid the conductance increases rapidly with concentration. The conductivity data of formic acid water mixture at different concentration has been used to calculate the value of molecular conductance at infinite dilution with the help of Arrehenius - Ostwald equation (6). The value of λ^0_m is equal to 100 S cm^2. The value of λ^0_m is nearly one fourth of the molecular conductance of formic acid at infinite dilution in literature[22]. It is interpreted as an indication for the presence of association among formic acid molecules in dilute aqueous solution. An indirect conclusion can be drawn by this observation that the $HCOO^-$ ion and H^+ ion remains associated with water in the arranged form like a lattice in a crystal. The structure maker character of formic acid as reported in literature[6] was also found in agreement with our observation. This study justified the hydrogen ion-water and formate- formate ion interactions presents in dilute aqueous formic acid solution.

The existence of ion-ion pairs present in system studied also conformed by Fuoss- equilibrium[23] on the basis of slope value ($d \log \lambda_m / d \log c = -0.50$) of the plot given in figure 2 with correlation coefficient 0.9962.

In the present study, the magnitude of calculated coefficient A_x and B_x with modification in Jone-Dole equation is large in comparison to A and B values respectively, which are the measures of interactions present in solution. Thus the proposed modification leads to the more quantitative characterization of intermolecular interactions present in solution. The

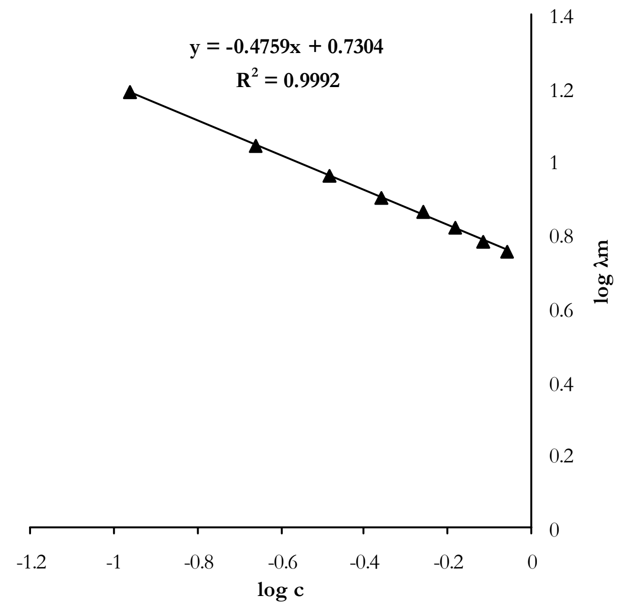

Figure 2: Plot for log λ_m versus log c for aqueous formic acid at 293 K

proposed equation can be used as a model in the studies related to interaction present in solutions.

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