



RESEARCH ARTICLE

**Apparent molar volume and viscometric study of carboxylic acid
in aqueous solution**Sunil kumar Sikarwar¹, V. R. Chourey² and A. A. Ansari³

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coefficient.***Corresponding Author****Sunil kumar Sikarwar****Abstract**

Densities and viscosities of Carboxylic acids at different temperature (298.15, 303.15, 308.15, 313.15) have been measured from experimental data. The apparent molar volume, limiting apparent molar volume, Jones-Doles A and B coefficients were calculated. The results show strong solute-solvent interaction that indicates all selecting carboxylic acids are structure makers in aqueous solution.

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Introduction

Partial molar volume provided useful information about various types of interactions occurring in solution. Ion – salvation is the back bone of solution chemistry¹⁻², these studies help us to characterize the structure and properties of the solutions. Viscometric, volumetric and conductometric studies of a solute in case of aqueous solution is related to the interaction among the components of a solution, a knowledge of which is important in solution chemistry. In highly dilute solutions, the two properties apparent molar volume and viscosity are needed to buildup such knowledge of inter molecular interactions. The structure of solution is important to understand the nature of action many carboxylic acids are produced industrially on a large scale. Carboxylic acids are used in the production of polymers, pharmaceuticals, solvents, and food additives and industrially important. It is a natural preservative/conservative and is also used to add an acidic or sour taste to foods and drinks. The study of such interactions of electrolytic behaviour in solution is very significant and useful for investigate their physicochemical behavior³⁻⁵.

MATERIALS AND METHODS

All the chemical citric acid, oxalic acid and tartaric acid were used in the present study of analytical grade. Freshly distilled water with specific conductance of $\sim 10^{-6} \Omega \text{cm}^{-1}$ was used to preparing solution throughout the experiment. The aqueous solution of carboxylic acids was made by weight and molalities were converted in to molarities using the standard expression⁶. The densities of solutions were measured at different temperature (298.15, 303.15, 308.15, 313.15) K using a viscometer made by Borosil glass. The mass measurements were done on digital electronic balance (SartoriusGC103). Viscosity determines with calibrated U shaped Ostwald viscometer with sufficiently long reflux time more than 100 sec. to avoid kinetic energy correction. The viscometer was averaged from three readings for each solution. The calibration of density bottle and viscometer⁶⁻⁷ was done by using doubly distilled water. An average of triplet measurement was taken in to account. Temperature was controlled by thermostatic water –bath.

Theory

The apparent molar volume can be calculated from density data using the following equation ⁷.

$$\phi_v = M/d_0 - 1000(d-d_0)/d_0c$$

Where d_0 and d are the densities of solvent and solution respectively; c is the molar concentration in gm./lit. and M is molecular weight of solute. The apparent molar volume can be considered to be the sum of the geometric volume of the solute molecules and changes that occur in to the solution due to its interaction with solvent. The data are filled to Masson ⁸ equation and calculate limiting partial molar volume and experimental slope by least square method.

$$\phi_v = \phi_v^0 + S_v \sqrt{C}$$

Time of flow were determined for carboxylic acids under study at chosen concentration and temperature from 20-40⁰ C. The viscosity were determined from the formula $\eta/\eta_0 = td/t_0d_0$ were η , t , d are the absolute viscosity, time of flow and density of solution, while η_0 , t_0 , d_0 are same quantities for the solvent water. The viscosity data was analyzed according to Jones- dole ⁹ equation.

$$\eta/\eta_0 = \eta_r = 1 + Ac^{1/2} + Bc$$

Where η_r is relative viscosity, c is molar concentration the constant A is the Falkenhagen coefficient and B is the Jones- dole coefficient related to the solute- solvent and solute – solute interaction respectively. Viscosity data has been analyzed with the help of Jones- dole equation from the linear plots of $[(\eta/\eta_0)-1]^{1/2}$ versus $c^{1/2}$ by computerized least square method.

RESULTS AND DISCUSSION

The value of apparent molar volume of carboxylic acid at different temperature (298.15, 303.15, 308.15, 313.15)K given in Table1. It shows ϕ_v is linear function of concentration and obeys Masson's equation.

Perusal of Table 3. Show that the value of ϕ_v^0 for all carboxylic acids is positive in water and increase with increasing temperatures again since ϕ_v^0 is a measure of solute solvent interaction, the positive value indicate strong solute solvent interaction which suggest that the overall structural order is enhanced in aqueous solution. The presence of ion solvent interaction between the molecules promotes the structure making effect of solutes in water. ϕ_v^0 is a limiting apparent molar volume of the solute also called the apparent molar volume at infinite dilution. It is evident from table 3 that the values of S_v are positive for all carboxylic acids in aqueous solution at different temperature. Since S_v is a measure of ion-ion interaction so the results indicate the presence of weak ion-ion interaction. Since S_v is a measure of ion –ion interaction so the results indicate the presence of weak ion –ion interaction. The ϕ_v value in water in present investigation has good agreement with reported value ¹⁵⁻¹⁷. According to Gurney co-sphere overlap model the always produce overlap of the co-sphere of two ions or polar group or an ion with hydrophilic group positive volume change. On the other hand overlap of the co-sphere of an ion with that of hydrophilic groups result a negative volume change. Results indicate that ion –hydrophilic and hydrophilic interactions predominate over the ion – hydrophobic and hydrophobic- hydrophobic interactions.

$$\phi_v^0 = a_0 + a_1T + a_2T^2$$

Where T is temperature in Kelvin. The value of coefficient a_0, a_1 and a_2 are given in table , calculated by differentiating above equation with respect to temperature.

$$\phi_{E0} = (\delta\phi_{v0}/\delta T)_p = a_1 + 2a_2T$$

The Limiting apparent molar expansibilities for carboxylic acids in aqueous solution obtain at different temperature are calculated. It is found that ϕ_{E0} value increase with rise in temperature, this increase ϕ_{E0} with temperature ascribed to the presence of caging effect ¹⁰.

The structure making / breaking capacity of solute in aqueous solution may be interpreted with the help of Hepler ¹¹ equation on the basis of sign of giving expression.

$$(\delta\phi_{E0}/\delta T)_p = (\delta^2\phi_{v0}/\delta T^2)_p = -a_2$$

The sign of $(\delta^2\phi_{v0}/\delta T^2)_p$ second derivative of limiting apparent molar volume of solution with respect to temperature at constant pressure, which correspond to structure making of breaking properties of solution was determined. The determined value of $(\delta^2\phi_{v0}/\delta T^2)_p$ has been found to be positive for all three carboxylic acids structure making properties.

The value of viscosity of all studied three carboxylic acids at different temperatures (298.15, 303.15, 308.15, 313.15)K given in table 2. Viscosity of aqueous solution of carboxylic acids has been determined as a function of their concentrations. The values of coefficients A and B of the Jones – Dole equation have been determined by computerized least square method and the result has been showed in Table 3. “ B ” coefficient sare constant and characteristics’ of ion- ion and ion solvent interaction respectively. The value of A coefficients are negative and very small for all the three carboxylic acids indicating the presence of weak ion- ion interaction.

Perusal of table 3 shows that the value of B- coefficient for all carboxylic acids in aqueous solution is positive, since B is measure of solute- solvent interaction and its value depend on size and shape of solute. Positive B value indicates the existence of ion solvent interaction. A decrease in the value of B- coefficient with the rise of temperature represents structure promoting effect. This is due to ordering and a sort of enforcement of hydrogen bonded structure around the solute .At higher temperature, the surrounded sheath of solvent molecule around the water is broken and ion- solvent interaction is weakened. That further supporting earlier conclusion drawn from Δv^0 and Sv. Recently it has been emphasized by many workers ¹² that (dB/dT) is a better decisive factor for determine structure making / breaking nature of any solute rather than the B- coefficient .The value of (dB/dT) were calculated from the slope of the curve obtained by plotting B- coefficient value against temperatures and these values given in table 4. Table 3 shows at higher temperature B is less and Δv^0 is higher than at low temperature. (dB/dT) is negative underline the greater hydration at higher temperature ¹³⁻¹⁴. Higher B and negative (dB/dT) disclose the structure making capacity of carboxylic acids. These are in identical agreement with the conclusion drawn from Hepler equation as discussed earlier.

According to volumetric and viscometric behavior these non electrolyte solute act overall as water structure builder due to hydrophobic hydration and hydrogen bonding between solute and water molecules. Similar explanation had drawn from stereo chemical, kinetic and thermo dynamical studies ¹⁵⁻¹⁷ of carboxylic acids. Hydrophobic hydration of carboxylic acids depends on their confirmation and configuration of hydroxy group. The hydration of carboxylic acids has been explained with the help of concept of compatibility through specific hydration model ¹⁸⁻²⁰.

Table 1: Apparent molar volume of Carboxylic Acids in water at different temperature.

Conc	Apparent molar volume Δv^0 (Cm ³ mol ⁻¹)											
	298.15			303.15			308.15			313.15		
	Citric Acid	Oxalic Acid	Tartaric Acid	Citric Acid	Oxalic Acid	Tartaric Acid	Citric Acid	Oxalic Acid	Tartaric Acid	Citric Acid	Oxalic Acid	Tartaric Acid
0.05	53.13	49.97	75.23	55.38	50.05	81.22	58.88	50.39	83.01	61.11	50.40	85.37
0.10	54.01	50.69	76.46	56.21	50.77	82.42	59.68	51.10	84.17	61.87	51.11	86.52
0.15	54.68	51.24	77.39	56.85	51.32	83.33	60.29	51.67	85.06	62.45	51.65	87.40
0.20	55.25	51.71	78.19	57.39	51.78	84.10	60.81	52.11	85.82	62.94	52.12	88.14

Table 2: Viscosities of Carboxylic Acids in water at different temperature.

Con.	Viscosities η (cp) of Carboxylic Acids											
	298.15			303.15			308.15			313.15		
	Citric Acid	Oxalic Acid	Tartaric Acid	Citric Acid	Oxalic Acid	Tartaric Acid	Citric Acid	Oxalic Acid	Tartaric Acid	Citric Acid	Oxalic Acid	Tartaric Acid
0.05	1.614	1.793	1.219	1.403	1.729	1.1886	1.269	1.623	1.1522	1.162	1.4997	1.0835
0.10	1.673	1.853	1.264	1.458	1.784	1.2293	1.269	1.686	1.1939	1.2035	1.5586	1.1294
0.15	1.728	1.901	1.298	1.499	1.831	1.2580	1.311	1.729	1.2276	1.238	1.5972	1.1789
0.20	1.780	1.954	1.329	1.541	1.902	1.2837	1.340	1.806	1.2563	1.269	1.6292	1.2078

Table 3: Partial molar volumes at infinite dilution, experimental slope Sv and B coefficient of carboxylic acids in water at different temperature.

Carboxylic Acid	Φv_0 (cm ³ mol ⁻¹)				Sv (cm ³ lit ^{1/2} mol ^{-3/2})				B (m ³ mol ⁻¹)			
	298.15	303.15	308.15	313.15	298.15	303.15	308.15	313.15	298.15	303.15	308.15	313.15
Citric Acid	51.01	53.37	56.95	59.29	8.17	8.65	9.00	9.50	0.201	0.207	0.239	0.277
Oxalic Acid	48.23	48.32	48.67	48.69	7.67	7.70	7.75	7.79	0.204	0.212	0.460	0.535
Tartaric Acid	77.28	78.35	80.20	82.61	12.38	12.57	12.88	13.22	0.205	0.279	0.496	0.691

Table 4: Values of Hepler constants and (dB/dT) for studied carboxylic acids.

Carboxylic Acid	HEPLER CONSTANT				(dB/dT)
	298.15 K	303.15 K	308.15 K	313.15 K	
Citric Acid	0.009823898	0.079878222	0.071074487	0.010824702	- 0.0434
Oxalic Acid	0.00660531	0.03323472	0.013226634	0.003206578	-0.00768
Tartaric Acid	0.012814302	0.026621402	0.036837616	0.006421162	- 0.04954

CONCLUSION

A perusal of results indicates that the B coefficient is positive and fairly large for carboxylic acids in the concentration range studied, thereby showing the strong solute- solvent interaction in highly dilutes aqueous solution. This is also evident from the value of Φv^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 Staudinger for poly molecular assemblies has been also observed in the study. The experimental viscosity data is in good agreement with the Jones-dole and Modified Jones- Dole equation. On according to further discussion these all carboxylic acids are structure promoter solute & their capacity lie in the order oxalic acid < citric acid < tartaric acid.

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