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Apparent Molar Volume and Viscometric Study of Alcohols in Aqueous Solution

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Abstract

Densities and viscosities of alcohols 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 alcohols are structure makers in aqueous solution.

Key words: Limiting apparent molar volume, Hepler constant, Jones Dole coefficient.

1. Introduction

Partial molar volume provided useful information about various types of interactions occurring in solution[1-6]. Ion – salvation is the back bone of solution chemistry[7-8], 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 alcohols has gained significant popularity as a in the production of bio-diesel trans esterification & relatively safe fuel for flueless, referred as bioethanol fires. Ethanol is used in medical wipes and in most common antibacterial hand senitizer gelsare, produced industrially on a large scale. Alcohols are used in the production for manufacturing of various chemicals including butyl acrylate, butyl acetate, glycol ethers, and plasticizers it is also used as a direct solvent in paints, dyes, varnishes, coatings, and for other industrial purposes. The study of such interactions of electrolytic behaviour in solution is very significant and useful for investigate their physicochemical behavior[9-11]

2. Material and methods

All the chemical methanol, ethanol and butanol were used in the present study of analytical grade. Freshly distilled water with specific conductance of ~$10^{-6}\Omega cm^{-1}$ was used to preparing solution throughout the experiment. The aqueous solution of alcohols was made by weight and molalities were converted in to molarities using the standard expression [12]. 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 (SartoriousGC103). 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 viscometer [12-13] was done by using doubly distilled water. An average of triplet measurement was taken in to account. Temperature was controlled by thermostatic water –bath.

2.1Theory

The apparent molar volume can be calculated from density data using the following equation [13].

$$\text{Ø}v=M/d_0 -1000(d-do)/d_0c$$

Where do 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 [14] equation and calculate limiting partial molar volume and experimental slope by least square method.

$$\text{Ø}v = \text{Ø}v^0 + Sv \sqrt{C}$$

Time of flow were determined for carboxylic acids under study at chosen concentration and temperature from 20- 40^0 C. The viscosity were determined from the formula $\eta / \eta_0 = td / t_0d_0$ were n, t, d are the absolute viscosity, time of flow and density of solution, while η_0 t_0d_0 are same quantities for the solvent water. The viscosity data was analyzed according to Jones- dole [15] equation.

$$\eta / \eta_0 = \eta r = 1+ Ac^{1/2}+BC$$

Where ηr 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 $[(\eta/ \eta_{0)-1]/c}{}^{1/2}$ versus $c^{1/2}$ by computerized least square method.

3. Results And Discussion

The value of apparent molar volume of alcohols at different temperature (298.15, 303.15, 308.15, 313.15)K given in Table1. It shows Øv is linear function of concentration and obeys Masson's equation. Perusal of Table 3. Show that the value of Øv^0 for all alcohols is positive in water and increase with increasing temperatures again since Øv^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. Øv^0 is a limiting apparent molar volume of the solute also called the apparent molar volume at infinite dilution. It is evident from table that the values of Sv are positive for all alcohols in aqueous solution at different temperature. Since Sv is a measure of ion-ion interaction so the results indicate the presence of weak ion-ion interaction. Since Sv is a measure of ion –ion interaction so the results indicate the presence of weak ion –ion interaction.

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

Viscosities η (cp) of Alcohols												
Con	**298.15**			**303.15**			**308.15**			**313.15**		
	Methanol	**Ethanol**	**Butanol**	**Methanol**	**Ethanol**	**Butanol**	**Methanol**	**Ethanol**	**Butanol**	**Methanol**	**Ethanol**	**Butanol**
0.05	0.8089	1.2769	1.4362	0.8041	1.2275	1.3782	0.8006	1.1643	1.3024	0.7962	1.1375	1.2536
0.10	0.8293	1.3093	1.4806	0.8224	1.2583	1.4196	0.8160	1.2039	1.3391	0.8124	1.1624	1.2843
0.15	0.8495	1.3221	1.5370	0.8419	1.2627	1.4687	0.8354	1.2136	1.3841	0.8303	1.1782	1.3265
0.20	0.8702	1.3942	1.6097	0.8622	1.3287	1.5342	0.8582	1.2782	1.4372	0.8534	1.2254	1.3802

Table 2: Viscosities of alcohols in water at different temperature.

Apparent molar volume Øv(Cm^{3}mol-$^{1)}$												
Con.	**298.15**			**303.15**			**308.15**			**313.15**		
	Methanol	**Ethanol**	**Butanol**	**Methanol**	**Ethanol**	**Butanol**	**Methanol**	**Ethanol**	**Butanol**	**Methanol**	**Ethanol**	**Butanol**
0.05	44.50	57.89	93.78	45.34	57.98	93.91	45.52	58.06	94.05	45.52	58.16	94.19
0.10	45.12	58.70	95.10	45.96	58.79	95.22	46.15	58.87	95.36	46.15	58.97	95.49
0.15	45.59	59.33	96.11	46.44	59.41	96.23	46.63	59.49	96.37	46.63	59.59	96.49
0.20	46.00	59.84	96.96	46.84	59.94	97.08	47.04	60.01	97.22	47.04	60.11	97.33

The Øv value in water in present investigation has good agreement with reported value [21-23]. 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.

$$Øv^0 = a_0+a_1T+a_2T^2$$

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 temperatue.

$Ø_{E0} = (\delta Øv_0 / \delta T)p = a_1 + 2a_2T$

The Limitting apparent molar expansibilities for carboxylic acids in aqueous solution obtain at different temperature are calculated. It is found that $Ø_{E0}$ value increase with rise in temperature, this increase $Ø_{E0}$ with temperature ascribed to the presence of caging effect [16].

The structure making / breaking capacity of solute in aqueous solution may be interpreted with the help of Hepler [17] equation on the basis of sign of giving expression.

$(\delta Ø_{E0}/\delta T)\ p = (\delta 2Øv_0 / \delta T^2)p = -a_2$

The sign of $(\delta 2Øv_0 / \delta T^2)p$ 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 $(\delta 2Øv_0 / \delta T^2)p$ 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 sa re 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 $Øv^0$and Sv. Recently it has been emphasized by many workers [18] 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 ploting B- coefficient value against temperatures and these values given in table 4. Table 3 shows at higher temperature B is less and Øv is higher than at low temperature. (dB/dT) is negative underline the greater hydration at higher temperature [19-20].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 explaination had drawn from stereo chemical, kinetic and thermo dynamical studies[21-23] alcohols. Hydrophobic hydration of alcohols depends on their confirmation and configuration of hydroxy group. The hydration of alcohols has been explained with the help of concept of compatibility through specific hydration model [24-26].

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

Alcohol	$Øv_0$ (cm^3mol^{-1})				Sv (cm^3 lit $^{1}/_{2}mol^{-3/2}$)				B (m^3mol^{-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**
Methanol	43.00	43.84	43.92	44.00	6.71	6.72	6.73	6.81	0.311	0.328	0.422	0.442
Ethanol	55.94	56.03	56.11	56.22	8.72	8.73	8.75	8.76	0.332	0.393	0.396	0.472
Butanol	90.61	90.74	90.89	91.05	14.06	14.16	14.19	14.21	0.172	0.437	0.438	0.537

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

Alcohol	HEPLER CONSTANT				(dB/dT)
	298.15 K	**303.15K**	**308.15 K**	**313.15 K**	
Methanol	0.19073	0.20094556	0.201548044	0.201554048	-0.0152
Ethanol	0.15030488	0.15090932	0.15090933	0.15125648	-0.0188
Butanol	0.234172274	0.234780762	0.234984926	0.23517508	-0.0198

4. 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 Øv0.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 Jones-dole and Modified Jone- Dole equation. On according to further discussion these all carboxylic acids are structure promoter solute & their capacity lie in the order methanol < ethanol < butanol.

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