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Molecular interionic interaction studies of Ammonium Sulphate in 15 % DMSO –water at different temperature

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Density, viscosity were measured for ammonium sulphate in 15 % DMSO-water medium at temperature 298.15 and 303.15 K. Molar volume and apparent molar volume (□°$_v$) have been calculated from density measurement and their concentration dependence are discussed. The related thermodynamic parameters such as apparent molar volume, limiting apparent molar volume, Jones dole A and B coefficient of ammonium sulphate in 15 % DMSO have been applied as a way to study different interactions. By using density and viscosity data structural interactions like solute-solute, solute-solvent have received vital importance in physical chemistry. The apparent and partial molar volume provides usefull information about various types of interactions occurring in solution. These studies are of great help in characterizing the structure and properties of solution[1,2]. Knowledge of ion-solvent interactions in aqueous and non aqueous media is considerable fundamental and technological importance. The parameters obtained by Masson equation and Jones-Dole equation are limiting apparent molar volume (□°$_v$) and their associated constant (Sv), viscosity A and B coefficient of Jones – Dole equation. The results show strong solute-solvent interactions at higher temperature 303.15 k.

Key words: Density, viscosity, limiting apparent molar volume, Jones-Dole equation, Masson equation, coefficient,

Introduction

Thermodynamics has great importance in physical chemistry as well as in solution chemistry. Accurate knowledge of the physico-chemical properties of solutions has great relevance in theoretical and applied areas of research. Such parameter is functionally dependent on temperature. Molar volume provides various types of interactions exist between solute and solution and these solute-solute and solute-solvent interactions are of current interest in all branches of chemistry. These studies help in elucidating the structure of molecule.[3,4] Thermodynamics is a fundamental subject of great importance in physical chemistry and chemical engineering. The properties of liquid mixtures basically depend on its local structure, expressed in terms of packing density and volume. It changes with composition and temperature. This change in composition changes properties like density and viscosity of mixtures. The nature and type of interactions in binary organic liquid mixtures have been studied in terms of mixing parameters such as excess molar volume.[5]

Viscosity measures the fluid quality. The important information regarding solute-solute, solute-solvent and solvent-solvent interactions in an aqueous and in nonaqueous solution study by viscometricstudy. The experimental measurement of density, viscosity and derived parameters such as apparent molar volume, this data provide some significant information regarding the state of interactions in solution.[6] Viscometric measurement of electrolyte solution have been widely used in order to obtained information regarding solute-solvent interactions.[7]

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The value of coefficient a_0, a_1 and a_2 are calculated by differentiating above equation with respect to temperature T,

□°v = 50.64 + 0.1899 T + 0.000052 T^2 4

where T is temperature.

Density data of ammonium sulphate was analyzed with the help of Masson equation. Slope Sv and intercept □°v constants are obtained by linear plots of $C^{1/2}$ Vs□v. Which is shown in fig-1 The possible explanations for positive slope that the ionic association as the concentration of the electrolyte ammonium sulphate is increased, there is weakening the ion-solvent interaction. The increase of Sv with increase of temperature suggest that more and more solute is accommodated in the void space left in associated solvent molecules and then enhance the structure of solvent molecule.

Table 1: Density ñ and viscosity s and apparent molar volume of ammonium sulphate in 15% DMSO-water at temperatures 298.15 k.

Temperature -298.15 k

Conc	ρ	□	□ᵥ
C	g cm⁻³	m Pa s	Cm³ mol⁻¹
0.008	1.02346	1.11945	-1008.5
0.01	1.02412	1.11965	-845.83
0.02	1.02885	1.12425	-590.96
0.04	1.03148	1.13225	-295.16
0.06	1.03193	1.13885	-160.74
0.08	1.03382	1.14495	-111.28
0.1	1.03672	1.15855	-91.558

Table 2: Density ñ and viscosity s and apparent molar volume of ammonium sulphate in 15 % DMSO-water at temperatures 303.15 k.

Temperature - 303.15 K

Conc.	ρ	□	□ᵥ
C	g cm⁻³	m Pa s	Cm³ mol⁻¹
0.008	1.02064	1.11691	-905.52
0.01	1.02096	1.11926	-729.93
0.02	1.02641	1.12524	-568.89
0.04	1.03122	1.13586	-337.97
0.06	1.02995	1.14516	-160.89
0.08	1.03064	1.15663	-96.552
0.1	1.03387	1.16562	-83.043

The negative sign of Sv suggests that the electrolytes behave as structure breakers in that particular solvent. The Sv values (ion-ion interaction) decreases as the size of the cation increases. □°v values are increased as the temperature is increases. The large □°v values of ammonium sulphate reveal the strong solute-solvent interactions and preferential solvation of ions. The apparent molar volume □v has good agreement with reported value of M. Parmar and A. khanna.[13]

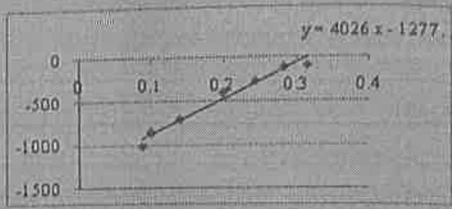

Fig-1 Plot of $C^{1/2}$ vsÕv of ammonium sulphate at 298.15 K

The results indicate as temperature is increases then □°v value increases. Solute-solvent interactions are increases. Temperature is increases then Sv value is decreases i.e ion-ion interaction decreases which are shown in table-1.

2. Viscometric Study of ammonium sulphate in solution

Time of flow of ammonium sulphate of different concentrations like 0.008 to 0.1 M was measured at temperature 303.15 and 313.15 k. The viscosity of solution were represented by equation,

$s/s_o = t\,ñ / t_o\,ñ_o$ 5

Where s, t, ñ are the absolute viscosity, time of flow and density of solution while s_o, t_o, $ñ_o$ are the same quantities for the solvent water. Viscosity of solution was calculated by using Jones- Dole equation[14]. Viscometer constant is falkenhagen coefficient and Jones-Dole coefficient. These parameters was used to interpret the solute-solute, solute-solvent interactions.

$s/s_o = sr = 1 + AC^{1/2} + BC$ 6

Where sr is relative viscosity, C is molar concentration, A is the falkenhagen coefficient which shows solute-solute interactions and B is the Jones-dole coefficient which shows solute-solvent interactions[15]. Viscosity of

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aqueous solution of ammonium sulphate in 15 % DMSO at different concentrations like 0.008 and 0.1 M were measured. The plots of $C^{1/2}$ Vs $[s/s_o -1]\ C^{1/2}$ are linear in all cases indicating Jones-Dole equation which is shown in figure2.

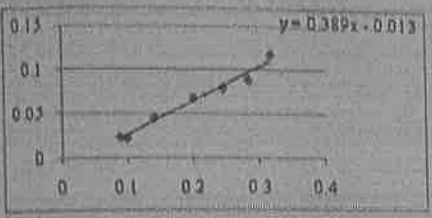

Fig-2 Plot of $C^{1/2}$ Vs $[s / s_o-1]\ C^{1/2}$ of ammonium sulphate at 298.15 K

Values of viscosity coefficient like A and B were determined by Jones-Dole equation[16,17] by using computerized least squares method which is shown in table-2

Falkenhagen and Jones-Dole coefficient are positive which indicate solute-solvent interactions. As the temperature is increases then B Coefficient is increases which show higher solute-solvent interactions. As the temperature increases the viscosity A coefficient is decreases i.e solute-solute interaction is low at high temperature.

Table.3 Limiting apparent molar volume (□°v), experimental slope (Sv) and viscosity Coefficient A and B at 303.15 and 313.15 k.

T	□°v	Sv	B	A
K	$cm^3 mol^{-1}$	$cm^3 L^{1/2} mol^{-3/2}$	$dm^3 mol^{-1}$	$dm^{3/2} mol^{-1/2}$
298.15	-1277.9	4026.2	0.3894	-0.0134
303.15	-1118.0	3567.2	0.5205	-0.0161

CONCLUSION

Density, viscosity and apparent molar volume is increases as the concentration of ammonium sulphate is increases in 15 % DMSO. As temperature is increases density and viscosity of ammonium sulphate in 15 % DMSO is decreases. Falkenhagen coefficient and Jones-Dole coefficient at different temperature shows solute-solvent interactions are stronger at higher temperatures. At lower temperature ion-ion interaction arepresent.s

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The dependence of concentration of viscosity in concentrated electrolyte solution was studied by V Vand[8]. Interactions of electrolytes in binary mixtures of two liquids have been studied in terms of B coefficient of viscosity. Viscometric method used to study the behavior of certain electrolyte dissolved in binary mixtures. Density was analyzed in terms of Masson equation and viscosity was analyzed in terms of Jones-Dole equation.

Experimental

Material and Methods

Commercially available AR grade chemicals dimethylsulphoxide (DMSO) obtained from E-Merck chemical company and double distilled water were used for preparing the electrolyte solutions. DMSO is aprotic solvent and is strongly associated due to highly polar sulphoxide group. Water was distilled in quick fit apparatus over alkaline $KMnO_4$ followed by further distillation[9].

The aqueous solution of ammonium sulphate was obtained by accurately weight amount of ammonium sulphate were dissolved in particular solvent to give 1 M concentration. The ammonium sulphate is used as electrolyte was supragradequality 99.5 % pure. (E-Merck Chem.) After formation of 1M stock solution of ammonium sulphate, it is used for preparation of different concentrations 0.008M to 0.1M. The concentrations were obtained by using dilution technique. The solutions were stored in dark colour amber bottles which are kept in dry box.

Bicapillarypycnometer was used for measurement of density at temperature 298.15 and 303.15 K. The mass were measured by using Dhona electronic balance. Viscosity measurements are carried out by using Ubbelohde viscometer. The experimental measurements of flow time of the solution between two points on the viscometer were performed at three times for each solution and the average results were noted. Time was monitored by using stopwatch. Th[illegible] of glassware's like pycnometer and viscometer[10] was carried out by using double distilled water. An average of three readings was taken. The density and viscosity measurements were carried out in a glass side thermostatic water-bath.

Results and Discussion

The densities and viscosities of ammonium sulphate of different concentrations like 0.008 to 0.01M in 15 % aqueous DMSO were determined at temperature 298.15 and 303.15 K. It is observed from table- 1 that densities ñ and viscosities s increase with increase in molarities of ammonium sulphate.

1. Apparent molar volume of ammonium sulphate solution

The apparent molar volume (□v) was determined from density of solution using following equation[11]

$$\square v = M/\tilde{n}_o - 1000(\tilde{n}-\tilde{n}_o)/\tilde{n}_o C \quad ....1$$

Where $\tilde{n}_o$ and $\tilde{n}$ are the densities of solvent and solution respectively, C is the molar concentration and M is molecular weight of solute. An apparent molar volume property of solution component is quantity with the purpose of isolating the contribution of each component to the nonideality of the mixture. Apparent molar volume at different temperature is given in table 1 and table 2. Apparent molar volume of solute changes with the square root of the molar concentration and obeys Masson equation.[12]

$$\square v = \square^{o} v + S_v (C)^{1/2} \quad ....2$$

Where □°v is limiting apparent molar volume of the solute and Sv is the experimental slope. The □vvalue has been positive and increases with increasing concentration of electrolyte ammonium sulphate. Apparent molar volume of the solution of ammonium sulphate in DMSO-water mixture at 298.15 and 303.15 k are reported.

Limiting apparent molar volume (□°v) of ammonium sulphate in DMSO – water solution is depending on temperature which can be represented by following equation.

$$\square^{o} v = a_0 + a_1 T + a_2 T^2 ... \quad ....3$$