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Ionic Interactions of Fe^{2+} and Cu^{2+} in Aqueous Methanol System

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The densities and viscosities of $FeSO_4$ and $CuSO_4$ solutions in aqueous methanol (10, 30 and 50 % v/v systems) within a concentration of 1×10^{-2} to 9×10^{-2} mol/dm^3 at 30, 40 and 50 ºC have been measured. It was observed that the viscosities of solutions increase with the increase in concentration of salt and solvent composition at particular temperature. The viscosity data was used to evaluate ion-ion interactions and ion - solvent interactions in terms of A and B coefficients of Jones-Dole equation. The values of ion solvent interaction were incorporated in terms of Jones Dole coefficient 'B'. It was found that the values of B increased from $FeSO_4$ to $CuSO_4$ with the increase in temperature from 30, 40 and 50 ºC. Apparent molar volumes (ϕ_V) were derived from these data supplemented with their densities respectively. The limiting apparent molar volumes (ϕ_V^o) and experimental slopes (S_v) obtained from Masson equation have been interpreted in terms of ion-ion and ion-solvent interactions, respectively.

Key Words: Viscosities, Apparent molar volume, Excess molar volume.

INTRODUCTION

The volumetric behaviour of solutes has been proved to be very useful in elucidating the various interactions occurring in aqueous and non-aqueous solutions[1]. It has been found by a no of workers[2] that viscosity is a property of the liquid, which depends upon the intermolecular forces. The structural aspects of the liquids can also be inferred from the viscosities of solutions at different concentrations and temperatures. First frequent use of non-aqueous solvents as media for organic and inorganic reactions has led to increasing interest in the transport properties of minerals in solutions. This behaviour can be investigated by conductance and viscosity measurements, which provide in depth understanding of the nature of ion-ion and ion solvent interactions[3,4].

Even though studies on ion-solvent interactions in mixed solvents are quite extensive[5], such studies in binary solvents containing ethanol + non-aqueous ionizing cosolvent, especially where the anion of the ionizing cosolvent is the same as the anion of the salts are limited.

Studies on the apparent molar volumes of electrolytes and dependence of viscosity on concentration of solutes and temperature of solutions have been undertaken as a function of ion-ion and ion-solvent interactions[6].

As partial molar volume of a solute reflects the commulative effects[7] of ion-ion and ion-solvent interactions, it would be of interest to study partial molar volume of some strong electrolytes. Such data are expected to highlight the role of the cation and of the anion of an electrolyte in influencing its partial molar volume at infinite dilutions in water. A number of recent studies have been carried out on the behaviour of salts in various solvents.

In continuation to earlier findings[8-10], the measurement of excess molar volumes and limiting apparent molar volumes, experimental slope and viscosity B coefficient for sulfate salts at different temperatures are presented in this communication and these parameters help to obtain better insight into ion-solvent and ion-ion interactions[11].

Mandal and Sanyal[12] determined viscosities of solutions of phenol, resorcinol and *p*-cresol and benzyl alcohol at 303-313 K. They concluded that aliphatic compounds belonging to a particular homologous series exhibits an increase in B coefficient with the lengthening of hydrophobic carbon chain. Seal and Catterjee[13] worked on *o*-amino benzoic acid and found out that B coefficient of *o*-amino benzoic acid decreases with temperature.

EXPERIMENTAL

Aqueous methanol system was prepared by dissolving methanol in distilled water to obtained 10, 30 and 50 % (v/v). Solutions of $CuSO_4$ and $FeSO_4$ (0.1 mol/dm^3) were prepared using aqueous methanol medium of 10, 30 and 50 % (v/v). Different dilutions of $CuSO_4$ and $FeSO_4$ salts were made in the range of 1×10^{-2} to 9×10^{-2} mol/dm^3. The densities of these solutions ($FeSO_4$ and $CuSO_4$ of aqueous methanol solvent) were measured with the help of relative density bottle having capacity of 10 ± 0.1 mL by volume. Viscosities of different % compositions were measured within temperature range 30, 40 and 50 °C. An Ostwald viscometer (Pyrex made in England type techniconominal constant 0.05 ± 0.001 CS/CC capillary ASTMAD 445) was used for the analysis. Time of flow of solutions was measured through stopwatch having a least count of 0.5 s.

Distilled water was used in the preparation of all solutions having conductivity of 0.06 ± 0.001 mS/cm. Temperature was maintained using thermostatic bath *i.e.*, Model YCN-01, 230 volt, AC Hz 50 Amp 5 made in Taiwan.

RESULTS AND DISCUSSION

The viscosities and density data of ferrous sulfate and copper sulfate solutions having concentration range 1×10^{-2} to 9×10^{-2} mol/dm^3 in 10, 30 and 50 % aqueous methanol with in temperature of 30, 40 and 50 ºC were obtained. These results of ferrous sulfate and copper sulfate are tabulated in Tables 1 and 2. These obtained values have been calculated by using formula

$$\eta = \frac{\eta_o dt}{d_o t_o} \tag{1}$$

where η_o and η are the viscosities of solvent and solutions respectively, d_o and d are their densities, t_o and t are the corresponding flow time. The results indicate that there is a regular increment in the viscosities of ferrous and copper sulfate solutions with the increase in composition of aqueous methanol mixtures at a fixed concentration, where as the viscosities of both the two salts decreased with the rise in temperature from 30, 40 and 50 °C aqueous methanol. The density data observed for ferrous sulfate and copper sulfate solutions also show the same behaviour as decreased with the increased of temperature and with the solvent composition.

TABLE-1
VISCOSITIES OF $FeSO_4$ SOLUTIONS IN DIFFERENT % COMPOSITION OF AQUEOUS METHANOL AT DIFFERENT TEMPERATURES

Temp. (K)	Viscosities (m.p.) [Salt] × 10^2 (mol dm^{-3})]				
	1.0 ± SD	3.0 ± SD	5.0 ± SD	7.0 ± SD	9.0 ± SD
	10 % Methanol				
303	8.96 ± 0.10	9.11 ± 0.04	9.31 ± 0.05	9.52 ± 0.04	9.76 ± 0.01
313	5.91 ± 0.04	5.94 ± 0.01	6.01 ± 0.01	6.11 ± 0.05	6.29 ± 0.02
323	5.57 ± 0.01	5.64 ± 0.04	5.70 ± 0.10	5.80 ± 0.04	5.99 ± 0.03
	30 % Methanol				
303	10.60 ± 0.05	10.98 ± 0.02	11.2 ± 0.04	11.70 ± 0.10	12.03 ± 0.01
313	6.52 ± 0.02	6.70 ± 0.20	6.89 ± 0.04	7.09 ± 0.01	7.67 ± 0.01
323	6.28 ± 0.01	6.40 ± 0.02	6.52 ± 0.02	6.76 ± 0.04	6.93 ± 0.01
	50 % Methanol				
303	12.07 ± 0.04	12.58 ± 0.05	13.02 ± 0.04	13.57 ± 0.01	14.30 ± 0.01
313	7.22 ± 0.10	7.40 ± 0.03	7.69 ± 0.02	7.92 ± 0.02	8.32 ± 0.04
323	5.36 ± 0.04	5.40 ± 0.01	5.58 ± 0.02	5.78 ± 0.02	5.97 ± 0.03

The values of Jones Dole equation parameters A and B were evaluated from the slope and intercept of the linear plots of $(\eta/\eta_o - 1)/\sqrt{C}$ against square root of the salt concentrations *i.e.*

TABLE-2
VISCOSITIES OF $CuSO_4$ SOLUTIONS IN DIFFERENT % COMPOSITION OF AQUEOUS METHANOL AT DIFFERENT TEMPERATURES

Temp. (K)	Viscosities (m.p.) [Salt] × 10^2 (mol dm^{-3})]				
	1.0 ± SD	3.0 ± SD	5.0 ± SD	7.0 ± SD	9.0 ± SD
10 % Methanol					
303	4.79 ± 0.01	5.01 ± 0.02	5.47 ± 0.02	5.80 ± 0.01	6.30 ± 0.04
313	4.39 ± 0.03	4.45 ± 0.02	4.76 ± 0.04	4.96 ± 0.01	5.38 ± 0.04
323	4.33 ± 0.02	4.26 ± 0.04	4.46 ± 0.02	4.71 ± 0.01	5.14 ± 0.02
30 % Methanol					
303	8.49 ± 0.02	8.73 ± 0.01	9.00 ± 0.04	9.56 ± 0.04	9.94 ± 0.02
313	7.70 ± 0.04	7.72 ± 0.01	8.00 ± 0.01	8.28 ± 0.02	8.86 ± 0.01
323	6.56 ± 0.01	6.39 ± 0.02	6.66 ± 0.02	6.97 ± 0.04	7.28 ± 0.02
50 % Methanol					
303	12.47 ± 0.01	12.70 ± 0.02	13.17 ± 0.01	13.51 ± 0.04	14.27 ± 0.04
313	8.58 ± 0.02	8.68 ± 0.02	8.91 ± 0.03	9.12 ± 0.01	9.64 ± 0.05
323	7.14 ± 0.04	7.06 ± 0.10	7.14 ± 0.04	7.36 ± 0.01	7.79 ± 0.01

$$\left(\frac{\eta}{\eta_o}\right) = 1 + A\sqrt{C} + BC \qquad (2)$$

$$\left(\frac{\eta}{\eta_o} - 1\right) = A\sqrt{C} + BC \qquad (3)$$

$$(\eta_{sp}/\sqrt{C}) - A + B\sqrt{C} \qquad (4)$$

The values of A at different temperatures 30, 40 and 50 ºC for 10, 30 and 50 % aqueous methanol mixtures are tabulated in Table-3. These results show that the values of 'A' increases, increasing the composition of solvent *i.e.* the values of 'A' increased as increasing kinetic energy of the ions and high dissociation energy at particular temperature. As a result the concentration of aqueous methanol mixtures is increased as the dielectric constant of the medium decreases.

The values of 'B' in Jones Dole equation are tabulated in Table-4. The results show that the values of 'B' decreased with solvent composition of 10, 30 to 50 % and the same decrease in values is reported with temperature rise from 30, 40 and 50 °C. This indicates that electrostrictive solvation is more at higher temperatures *i.e.* the solvent molecules are strongly attached to solute, which does not expand with rise in temperature. The high charge density on the small cation gives rise to strong electrostatic interaction in solution *i.e.* the smaller the ion the stronger the ion solvent dipole interaction and larger the size of solvated ion in the solution.

TABLE-3

VALUES OF 'A' OF THE JONES DOLE EQUATION

Temperature (K)	Values of 'A' of the Jones Dole equation $(mol^{-1}\ dm^3)^{½}$	
	$FeSO_4$ ± SD	$CuSO_4$ ± SD
	10 % Methanol	
303	-0.46 ± 0.01	-1.76 ± 0.02
313	-0.21 ± 0.01	-0.85 ± 0.01
323	0.02 ± 0.01	-1.09 ± 0.01
	30 % Methanol	
303	- 0.62 ± 0.01	-1.37 ± 0.01
313	- 0.48 ± 0.02	-1.11 ± 0.02
323	- 0.34 ± 0.01	-0.85 ± 0.01
	50 % Methanol	
303	-0.05 ± 0.02	-0.91 ± 0.01
313	0.13 ± 0.01	-0.63 ± 0.02
323	0.07 ± 0.02	-0.34 ± 0.01

TABLE-4

VALUES OF 'B' OF THE JONES DOLE EQUATION

Temperature (K)	Values of 'B' of the Jones Dole equation $(mol^{-1}\ dm^3)^{½}$	
	$FeSO_4$ ± SD	$CuSO_4$ ± SD
	10 % Methanol	
303	2.54 ± 0.3	6.34 ± 0.2
313	2.37 ± 0.2	5.91 ± 0.1
323	2.19 ± 0.2	5.25 ± 0.2
	30 % Methanol	
303	2.10 ± 0.3	4.69 ± 0.1
313	2.00 ± 0.1	4.42 ± 0.1
323	1.98 ± 0.1	4.21 ± 0.2
	50 % Methanol	
303	1.41 ± 0.2	3.16 ± 0.3
313	1.36 ± 0.1	2.96 ± 0.2
323	1.30 ± 0.1	2.53 ± 0.2

The contents of Tables 3 and 4 clearly demonstrate that copper ion being smaller in size has more positive values of 'B' compared to ferrous ion, which is larger in size.

The values of densities for ferrous sulfate and copper sulfate in different % composition of methanol 10, 30 and 50 % at 30, 40 and 50 °C have been used to calculate the apparent molar volume (ϕ_V) of the salts using equation,

$$\varphi_V = \frac{M}{d_o} - \frac{1000(d - d_o)}{c\, d_o} \quad (5)$$

where M is the molecular weight of the solute, C the molar concentration of the solution and other symbols have their usual significance. The plots of against square root of molar concentration ($C^{1/2}$) were found to be linear with positive slopes for the ferrous sulfate and copper sulfate. The limiting apparent molar volume (ϕ_V^o) were calculated using least square treatment to the plots of ϕ_V *vs.* $C^{1/2}$ using Masson's equation,

$$\phi_v = \phi_v^o + S_v c^{1/2} \quad (6)$$

where S_v is a constant, dependent on charge and salt type and it can be related to ion-ion interactions, ϕ_V^o is related to ion solvent interactions. The values of ϕ_V^o and S_v are listed in Tables 5 and 6. It is evident from the data that negative values of S_v at all temperatures for ferrous sulfate and copper sulfate indicate the presence of weak ion-ion interactions in both ferrous sulfate and copper sulfate. As expected S_v values decrease with rise in temperature in different solvent compositions for both the salts, which is attributed to increase in solvation of ions and more violent thermal agitation at higher temperatures resulting in diminishing the force of ion-ion interactions (ionic dissociation).

TABLE-5
PARTIAL MOLAR VOLUMES (ϕ_V^o), EXPERIMENTAL SLOPES (S_v) FOR $FeSO_4$ SOLUTIONS IN DIFFERENT COMPOSITION OF METHANOL AT VARIOUS TEMPERATURES

Temperature (K)	ϕ_V^o (× 10^{-2}) ± SD	S_v (× 10^{-2}) ± SD
	10 % Methanol	
303	07.99 ± 2.2	-83.41 ± 3.0
313	17.02 ± 1.2	-88.93 ± 4.8
323	25.54 ± 2.4	-90.06 ± 4.5
	30 % Methanol	
303	23.44 ± 2.3	-100.84 ± 5.6
313	32.29 ± 2.5	-106.69 ± 4.4
323	41.01 ± 3.0	-107.55 ± 3.4
	50 % Methanol	
303	24.55 ± 2.5	-107.96 ± 1.2
313	35.01 ± 2.2	-123.09 ± 2.5
323	45.20 ± 1.5	-126.84 ± 2.5

TABLE-6

PARTIAL MOLAR VOLUMES (ϕ_V^o), EXPERIMENTAL SLOPES (S_v) FOR $CuSO_4$ SOLUTIONS IN DIFFERENT COMPOSITION OF METHANOL AT VARIOUS TEMPERATURES

Temperature (K)	ϕ_V^o ($\times 10^{-2}$) ± SD	S_v ($\times 10^{-2}$) ± SD
	10 % Methanol	
303	06.90 ± 1.0	-34.16 ± 2.0
313	15.85 ± 1.6	-55.13 ± 2.5
323	19.68 ± 1.2	-56.77 ± 1.5
	30 % Methanol	
303	14.99 ± 1.5	-66.19 ± 3.0
313	20.43 ± 2.5	-67.49 ± 2.5
323	26.66 ± 2.0	-68.59 ± 3.0
	50 % Methanol	
303	15.13 ± 3.0	-11.30 ± 3.5
313	27.02 ± 2.5	-113.72 ± 2.5
323	34.42 ± 1.5	-115.61 ± 2.0

To examine the ion solvent interactions the values of ϕ_V^o can be used. It is evident from Tables 5 and 6 that the values of ϕ_V^o are positive and large for both the ferrous sulfate and copper sulfate at different temperatures indicating the presence of strong ion-solvent interactions. These interactions strengthen with the rise in temperature, which is attributed to increase in solvation with increasing temperature. This also indicates that the solvent molecules are loosely attached to solute, which expands with increase of temperature, thus resulting in higher values of ϕ_V^o at higher temperature.

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