Molecular Interionic Interaction Studies of Some Divalent Transition Metal Sulphates in Aqueous Ethylene Glycol at Different Temperatures

Thirumaran S.[1] and Sathish K.[2]
[1]Department of Physics (DDE), Annamalai University, Annamalainagar-608 002, INDIA
[2]Department of Physics, Annai College of Arts and Science, Kumbakonam-612 503, INDIA

Abstract

The present study aims for the structure-making and structure –breaking behavior of some divalent metal Sulphates in aqueous ethylene glycol at 308.15, 313.15 and 318.15K. The present investigation exploring the possible molecular interactions between the metal sulphate and ethylene glycol which is known to have much dissociation of metal sulphates in the solvent mixture. Experimental values of density, viscosity and ultrasonic velocities were carried out on the liquid ternary mixtures of water +ethylene glycol + metal sulphates namely manganese sulphate, nickel sulphate and cobalt sulphate at 308.15,313.15 and 318.15K. The binary solvent mixture of water + ethylene glycol was prepared in the constant ratio of 4:1. Metal sulphates solution was added under molality basis with these binary solvent mixtures. The related and relevant parameters correlated to our present study such as adiabatic compressibility (β), molal hydration number (n_H), apparent molal compressibility (φ_K), apparent molal volume (φ_V), limiting apparent molal compressibility (φ_K^0), limiting apparent molal volume (φ_V^0) and their associated constants (S_K, S_V), transfer volume ($\Delta_{\varphi_V^0}$) from water to aqueous solution and the viscosity B-Coefficient of Jones-Dole equations were meticulously evaluated. The molecular associations such as ion-ion, ion-solvent, solute-solvent, solute-solute etc are identified and critically discussed in terms of the structure-making and structure-breaking behaviour of metal sulphates in the solvent mixture.

Key Words: molal hydration number, adiabatic compressibility, structure-maker, viscosity B-coefficient, transfer volume, limiting apparent molal volume.

Introduction

Ultrasonic velocity measurements are extremely helpful in understanding the ion-solvent interactions in aqueous and non-aqueous solvents. This technique has been explored to determine the ion-solvent interactions in aqueous solution containing electrolyte [1]. In solvent, the attraction between the solute and solvent is essentially been of ion-dipole interaction which depends mainly on ion size and polarity of the solvent. The strength of such interactions which are proportional to the size of the ion, charge and the magnitude of distance between the ion and dipolar molecule. The electrolyte added to the solvent causes a volume contraction due to interaction between ions and solvent molecules and this may influence other acoustical properties of solution. In recent years, the studies of acoustical properties of aqueous mixed electrolytic solutions have been found to be useful in understanding the specific ion-ion and ion-solvent interactions in solutions. The experimental measurement of density, viscosity and ultrasonic velocity and the derived parameters such as apparent molal compressibility, apparent molal volume and transfer volume on these mixed solvents will provide some significant information regarding the state of affairs in a solution. Such studies on binary electrolytes have been carried out by many researchers[2-4]. However, ultrasonic velocity studies on ternary electrolytes have not received as much attention as that of binary electrolytes[5-6].

Since, molecular interaction studies of binary electrolytes cannot be so useful to obtain a definite conclusion regarding the structural properties and then types of interactions involved. The study of ternary electrolytes is gaining much importance now-a-days. Ionic association and electrostatic interactions are the prime factors that must be considered in these electrolytes. Various types of interactions exist between the ions in the solutions and these, ion-ion, ion-solvent interactions are of common interest. These interactions are helpful in better understanding the types of solute and solvent, i.e. whether the added solute modifies or distorts the structure of the solvent. Further, the addition of organic solvent to an aqueous solution of electrolyte brings about the change in ion salvation that often results in a large change in the reactivity of dissolved electrolytes[7-8]. Ethylene glycol (EG) is the simplest with dielectric constant (ϵ=38.66 (at T=293.15K) and dipole moment μ = 2020 D)[9]. It is self-associated in the pure state creating a net of hydrogen bonds which are dependent on the temperature and the presence of

electrolytes[10]. In aqueous solution, EG gives rise to two or three dimensional networks through hydrogen bonds with the consequence that the mixtures display negative deviations from ideality[11]. Now-a-days ethylene glycol(EG) is being used for the synthesis of nano particles. EG acts as dispersing, reducing as well as stabilizing medium. The nano particles are highly stable in EG and do not coagulate on long standing. Also, the divalent metal sulphates play a vital role in life systems because of their natural presence in vitamins, enzymes and proteins.(viz., Cu, Mn, Co etc.,) Manganese sulphate is an inorganic compound. It is a by-product of various industrially significant oxidations that use manganese dioxide, including the manufacture of hydroquinone and anisaldehyde. It is used in dry-cell batteries[12]. Nickel sulphate is also an inorganic compound, and is a common source of the Ni^{2+} ion for electroplating. It is decomposes at still higher temperatures to nickel oxide. These salts differ, sometimes subtly, in terms of their hydration or structural details. It is used in the laboratory. Columns used in polyhistidine-tagging, biochemistry and molecular biology. Cobalt sulphate is another inorganic compound. It is soluble in water, slightly soluble in ethanol, and especially soluble in methanol. It is used in the electroplating and electrochemical industries; as a drier for lithographic inks, varnishes, paints and linoleum; in storage batteries; and as a colouring agent in ceramics, enamels, glazes, and porcelain. In addition, cobalt sulphate has been used in animal feeds as mineral supplement[13-14].

As earlier discussed since so far only a few attempts have been made on ternary electrolytes system, the authors have carried out an exhaustive attempt in divalent transition metal sulphates such as manganese sulphate, nickel sulphate and cobalt sulphate in aqueous ethylene glycol at 308.15, 313.15 and 318.15K in order to elucidate the possible interionic interactions such as ion-ion, ion-solvent, solute-solvent, solute-cosolute etc., in the solvent mixture. For this, they have meticulously evaluated some of the related parameters such as adiabatic compressibility (β), molal hydration number (n_H), apparent molal compressibility (φ_K), apparent molal volume (φ_V), limiting apparent molal compressibility (φ_K^0), limiting apparent molal volume (φ_V^0) and their associated constants (S_K, S_V), transfer volume ($\Delta\varphi_V^0$) from water to aqueous solution and the viscosity B-Coefficient of Jones-Dole equations to substantiate their findings.

Material and Methods

The present study was carried out using AR/SR grade chemicals having a minimum assay of 99.9% were obtained from sigma aldrich, Gmerck and sd fine. Fresh conductivity water was used for preparing binary solvent mixture (water + ethylene glycol) at constant volume ratio of 4:1. Water used in the present investigation was deionised, distilled and was degassed prior to making solutions. Required amount of

water and ethylene glycol was taken and prepared under constant ratio of 4:1 as binary solvent mixtures in a dry conical flask with a ground stopper. Aqueous solutions which were prepared thus and immediately used on the day they were prepared. The required quantity of metal sulphates such as manganese sulphate, nickel sulphate and cobalt sulphate for a given molality (m) were dissolved in the binary solvent mixture at different temperatures.

The chemicals were weighed in an electronic digital balance (SHIMADZU AX-100, Japan Make) with a precision of 0.0001g. The density was determined using a specific gravity bottle by relative measurement method with an accuracy of $\pm0.01 kgm^{-3}$. An Ostwald's viscometer of 10ml capacity was used for the viscosity measurement. Efflux time was determined using a digital chronometer within ±0.01s. An Ultrasonic Interferometer having the fixed frequency of 2 MHz (Mittal Enterprises, New Delhi-Model: F-81) with an overall accuracy of $2ms^{-1}$ has been used for velocity measurement. An electronically digital operated constant temperature bath (RAAGA Industries, Chennai) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at desired temperature, whose accuracy is maintained at ± 0.1K.

Theory of evaluated parameters: Adiabatic compressibility (β) is given by:

$$\beta = \frac{1}{U^2\rho} \tag{1}$$

Molal hydration number (n_H) is given by:

$$n_H = \frac{n_1}{n_2}\left(1 - \frac{\beta}{\beta_0}\right) \tag{2}$$

Where β and β_0 are adiabatic compressibilities of solution and solvent respectively, n_1 and n_2 are number of moles of solvent and solute respectively.

Apparent molal compressibility (φ_K) is given by:

$$\varphi_K = \frac{1000}{m\rho_0}(\rho_0\beta - \rho\beta_0) + \left(\frac{\beta_0 M}{\rho_0}\right) \tag{3}$$

where β, ρ and β_0, ρ_0 are the adiabatic compressibility and density of solution and solvent respectively, *m* is the molal concentration of the solute and *M* the molecular mass of the solute. φ_K is the function of *m* as obtained by Gucker, 1933[15], from Debye and Huckel, 1923)[16]

Apparent molal volume (φ_V) is obtained by:

$$\varphi_V = \frac{1000}{m\rho_0}(\rho_0 - \rho) + \left(\frac{M}{\rho_0}\right) \tag{4}$$

Transfer volume ($\Delta \varphi_V^0$), of each metal sulphate from water to aqueous ethylene glycol solution were calculated using the equation

$$\Delta \varphi_V^0 = \varphi_V^0 \text{ (in aqueous ethylene glycol)} - \varphi_V^0 \text{ (in water)} \quad (5)$$

The entire viscosity data have been analysed in the light of Jones-Dole semi empirical equation (Jones and Dole, 1929)[17].

$$\frac{\eta}{\eta_0} = 1 + A m^{½} + B m \quad (6)$$

where η and η_0 are the viscosities of the solution and solvent respectively and 'm' is the molal concentration of the solute-solvent system. A is known as Falkenhagen coefficient which characterizes the ionic interaction and B is the Jones-Dole or viscosity B-coefficient which depends on the size of the solute and nature of solute-solvent interactions.

Results and Discussion

The experimental values of density (ρ), viscosity (η) and ultrasonic velocity (U) for different molalities (m) of the three divalent transition metal sulphates viz., nickel sulphate ($NiSO_4$), manganese sulphate ($MnSO_4$) and cobalt sulphate ($CoSO_4$) in aqueous ethylene glycol mixture (volume ratio 4:1) at 308.15, 313.15 and 318.15K are tabulated in table 1. The values of adiabatic compressibility (β), molal hydration number (n_H), apparent molal compressibility (φ_K), apparent molal volume (φ_V) of all the three systems are listed in table 2.similarly, the limiting molal compressibility (φ_k^0) and the limiting apparent molal volume (φ_v^0) and their associated constants S_K and S_V are listed in table 3.Similarly, the transfer volume ($\Delta\varphi_v^0$) and viscosity B coefficients of Jones-Dole equation are tabulated in table 4. and figures 1,2 and 3, show the variations of limiting apparent molal compressibility, limiting apparent molal volume and transfer volume with molal concentration of metal sulphates at different temperatures.

In all the three liquid systems (table 1), the values of density and Viscosity increases with increase in molal concentration of metal sulphates. The ultrasonic velocity (U) (From table 1) also increases with increase in the concentration of the solutes (metal sulphates) as well as rise in temperature. The increasing trend suggests a moderate strong associative nature in which the solute (metal sulphates) tends to attract the solvent (ethylene glycol) molecules [18-19]. The increase in ultrasonic velocity in these solutions may be attributed to the cohesion brought about by the ionic hydration.

When the metal sulphates are dissolved in water + ethylene glycol mixtures, the water molecules are attached to the ions strongly to the electrostatic forces, which introduce a greater cohesion in the solutions[20]. Thus, the cohesion increases, whenever an increase of solute concentration in the solution. The increased association observed in these solutions may also be due to the water structure enhancement brought about by the increase in electrostriction in the presence of ethylene glycol. The electrostriction effect which brings about the shrinkage in volume of solvent caused by the solutes such as metal sulphates is increased in mixed solvent. Similar effect was reported by earlier workers[21].

Density (ρ) is a measure of solvent-solvent and ion-solvent interactions. Increase of density with concentration indicates the increase in solvent-solvent and solute-solvent interactions, whereas the decrease in density indicates the lesser magnitude of solute-solvent and solvent-solvent interactions. Increase in density with concentration is due to the shrinkage in the volume which in turn is due to the presence of solute molecules. In other words, an increase in density may be interpreted to the structure-maker of the solvent due to the added solute. Similarly, the decrease in density with concentration indicates structure-breaker of the solvent.

Ethylene glycol is a very interesting class of solvents, due to the presence of oxy and hydroxyl groups in the same molecule which allows self-association via intra and intermolecular hydrogen bonds. The formation of intramoelcular hydrogen bonds in ethylene glycol is more favorable, when the molecules of these solvents are in the *gauche* confirmations. Probably, the addition of ethylene glycol would disrupt the self-associated structure in ethylene glycol causing the appearance in the solution of free molecules. These free molecules may interact by dipole-dipole forces and/or intermolecular hydrogen bonds forming the mixed intermolecular complexes. The same structural effects have been observed by earlier workers[22].

The perusal of table 2 illustrates the variation of adiabatic compressibility (β) with molal concentration of metal sulphates. The values of β in all the three metal sulphates systems show a decreasing trend with increasing molal concentration of solutes as well as rise in temperature. The decrease in adiabatic compressibility observed in water + ethylene glycol mixtures with metal sulphates in the present study generally confirms that conclusion drawn from the velocity data. The increase in ultrasonic velocity and decrease in β were attributed to formation of hydrogen bonds between the solute and solvent molecules. The decreasing trend of compressibility may due to the rupture of hydrogen bonds strength formed between the solute and solvent molecules.

Table-1
Values of density (ρ), viscosity (η) and ultrasonic velocity (U) at 308.15, 313.15 and 318.15 K for

molality m/(×mol kg^{-1})	density ρ/(kg/m^{-3})			viscosity η/(×10^{-3} Nsm^{-2})			Ultrasonic velocity U/(m/s)		
	308.15K	313.15K	318.15K	308.15K	313.15K	318.15K	308.15K	313.15K	318.15K
System I: water (X$_1$) + ethylene glycol (X$_2$) + nickel sulphate (X$_3$) [X$_1$/X$_2$=4:1]									
0.00	1017.96	1016.04	1015.98	1.1695	1.0460	0.9562	1593.80	1596.80	1598.53
0.02	1030.74	1029.78	1029.06	1.2042	1.0994	1.0291	1600.21	1601.43	1603.00
0.04	1041.90	1040.01	1039.66	1.2674	1.1202	1.0699	1602.26	1604.91	1610.80
0.06	1052.92	1051.86	1051.46	1.3214	1.1831	1.1127	1609.86	1611.20	1617.48
0.08	1064.98	1063.98	1063.19	1.3775	1.2373	1.1355	1613.30	1615.50	1622.80
0.10	1076.05	1075.56	1074.66	1.4543	1.3021	1.1583	1619.77	1621.48	1627.20
System II: water (X$_1$) + ethylene glycol (X$_2$) + manganese sulphate (X$_3$) [X$_1$/X$_2$=4:1]									
0.00	1017.96	1016.04	1015.98	1.1695	1.0460	0.9562	1593.80	1596.80	1598.53
0.02	1029.39	1029.24	1028.25	1.2124	1.0890	1.0183	1587.21	1589.37	1604.45
0.04	1039.34	1038.93	1038.77	1.2743	1.1389	1.0791	1604.40	1605.70	1610.41
0.06	1051.98	1050.1	1049.70	1.3203	1.1816	1.1211	1609.90	1613.20	1616.91
0.08	1062.82	1061.35	1060.54	1.3954	1.2444	1.1429	1613.72	1616.23	1619.81
0.10	1073.49	1072.99	1072.35	1.4612	1.3092	1.2181	1616.11	1619.20	1621.60
System III: water (X$_1$) + ethylene glycol (X$_2$) + cobalt sulphate (X$_3$) [X$_1$/X$_2$=4:1]									
0.00	1017.96	1016.04	1015.98	1.1695	1.0460	0.9562	1593.80	1596.80	1598.53
0.02	1030.46	1029.64	1029.46	1.2137	1.0992	1.0950	1595.12	1596.94	1598.57
0.04	1042.17	1041.80	1041.40	1.1672	1.0626	1.0213	1597.30	1598.44	1600.19
0.06	1054.63	1054.15	1054.01	1.3236	1.1957	1.1154	1598.98	1600.05	1601.39
0.08	1067.26	1066.39	1065.48	1.4013	1.2503	1.1690	1599.28	1601.25	1602.42
0.10	1076.68	1076.22	1075.73	1.4448	1.2926	1.2115	1602.61	1603.27	1604.35

The molecular interaction between the solute and water molecules present in the solvent, which is termed as hydration. From table 2, it is observed that the values of hydration number (n_H) are positive in all the three liquid systems studied. The values n_H are found to be decreased with increase in molality of the metal sulphates and increase with rise in temperature. The possession of positive values of n_H indicate an appreciable salvation of solutes. This is an added support for the structure promoting nature of solutes as well as the presence of dipolar interaction between the solute and water molecules. This also suggests that compressibility of the solution will be less than that of the solvent. As a result, solutes will gain mobility and have more probability of contacting solvent molecules. This may enhance the interaction between solute and solvent molecules. The decreasing values of n_H which indicate the increase in solute-co-solute interaction. Further, the decreasing behavior of n_H suggesting that ethylene glycol has a hydration effect on the metal sulphates.

The values of apparent molal compressibility (φ_K) and apparent molal volume (φ_V) are tabulated in table 2.The following observations have been made on apparent molal

compressibility (φ_K) and apparent molal volume (φ_V) of nickel sulphate, manganese sulphate and cobalt sulphate in aqueous ethylene glycol at 308.15, 313.15 and 318.15K.

The values of the (φ_K) and (φ_v) are all negative over the entire range molality of metal sulphates. The values of φ_k are increasing with increasing molality of the solutes as well as with rise in temperature. Similarly, the values of φ_v increase with increase in content of metal sulphate and however, decrease with elevation of temperature. The maximum value of φ_v was obtained for manganese sulphate system comparing all the other metal sulphate systems, indicating that a strong molecular association is found in manganese sulphate system. Such maximum values of apparent molal volume (φ_V) are obtained for that system, which suggests ionic and hydrophobic interactions occurring in these systems, thereby indicating the presence of ion-solvent interactions. Further, the negative values of φ_v indicate electrostrictive solvation of ions[23]. From the magnitudes of (φ_v), the molecular association between the three metal sulphates systems is of the order: manganese sulphate > nickel sulphate > cobalt sulphate.

Table-2
Values of adiabatic compressibility (β), **molal hydration number** (n_H), **apparent molal compressibility** (φ_k) **and apparent molal volume** (φ_v) **at 308.15, 313.15 and 318.15 K for**

molality m/(×mol kg^{-1})	adiabatic compressibility β/(×10^{-10} m^2 N^{-1})			molal hydration number (n_H)			apparent molal compressibility −φ_k(×10^{-7} m^2 N^{-1})			apparent molal volume −φ_v(×m^3 mol^{-1})		
	308.15K	313.15K	318.15K	308.15K	313.15K	318.15K	308.15K	313.15K	318.15K	308.15K	313.15K	318.15K
System I: water (X_1) + ethylene glycol (X_2) + nickel sulphate (X_3) [X_1/X_2=4:1]												
0.00	3.8672	3.8600	3.8519	nil	nil	nil	nil	nil	nil	nil	nil	nil
0.02	3.7888	3.7865	3.7817	11.8239	11.0909	10.6153	-6.3465	-6.2574	-5.9985	-627.47	-675.90	-643.45
0.04	3.7386	3.7330	3.7294	9.6846	9.5820	9.4887	-5.4876	-5.4506	-5.3059	-581.68	-589.53	-582.43
0.06	3.6646	3.6622	3.6578	10.1716	9.9492	9.7835	-5.5893	-5.5637	-5.4759	-572.13	-587.32	-581.77
0.08	3.6077	3.6051	3.6006	9.7712	9.7631	9.7609	-5.4754	-5.4618	-5.3928	-571.12	-586.53	-580.58
0.10	3.5421	3.5398	3.5362	9.7931	9.7721	9.7564	-5.4568	-5.4546	-5.3808	-570.39	-585.54	-577.32
System II: water (X_1) + ethylene glycol (X_2) + manganese sulphate (X_3) [X_1/X_2=4:1]												
0.00	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil
0.02	3.7891	3.7868	3.7779	11.7631	11.3022	11.1899	-6.0755	-6.2517	-6.0253	-581.25	-649.41	-603.68
0.04	3.7341	3.7290	3.7258	10.0235	9.8838	9.7760	-5.3574	-5.4483	-5.3019	-574.90	-578.05	-560.62
0.06	3.6677	3.6635	3.6579	10.0160	9.9341	9.7786	-5.4783	-5.4569	-5.3633	-556.83	-565.26	-552.99
0.08	3.6131	3.6080	3.6013	9.5679	9.5480	9.4736	-5.3058	-5.3011	-5.2436	-550.69	-560.34	-554.67
0.10	3.5646	3.5622	3.5564	9.0551	8.9875	8.9368	-5.1349	-5.1415	-5.0922	-545.34	-557.27	-548.07
System III: water (X_1) + ethylene glycol (X_2) + cobalt sulphate (X_3) [X_1/X_2=4:1]												
0.00	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil
0.02	3.8140	3.8072	3.8002	8.0128	7.9674	7.8178	-5.0338	-5.2774	-5.1999	-613.70	-683.26	-678.87
0.04	3.7609	3.7568	3.7500	8.0052	7.7863	7.7044	-4.9983	-5.0630	-4.9558	-594.29	-633.56	-625.50
0.06	3.7086	3.7054	3.6997	7.9626	7.7762	7.6716	-4.9639	-4.9886	-4.9397	-609.11	-624.86	-623.59
0.08	3.6634	3.6573	3.6551	7.6739	7.6467	7.4398	-4.8875	-4.9237	-4.8048	-605.10	-619.16	-608.74
0.10	3.6162	3.6148	3.6115	7.5609	7.4005	7.2704	-4.7393	-4.7372	-4.6693	-576.52	-592.02	-587.83

Table-3
Values of limiting apparent molal compressibility (φ_k^0), **limiting apparent molal volume** (φ_v^0), **and their constants S_K and S_V, at 308.15, 313.15 and 318.15 K for**

system	metal sulphate	limiting apparent molal compressibility φ_k^0/(×10^{-7} m^2 N^{-1})			constant S_K/ (×10^{-7} N^{-1} m^{-1} mol^{-1})			limiting apparent molal volume φ_v^0/ (× m^3·mol^{-1})			constant S_V/ (N^{-1} m^{-1} mol^{-1})		
		308.15K	313.15K	318.15K	308.15K	313.15K	318.15K	308.15K	313.15K	318.15K	308.15K	313.15K	318.15K
I	Ni SO$_4$ +aqueous ethylene glycol	-6.7426	-6.5980	-6.1964	4.5199	4.0515	2.9012	-658.80	-716.16	-661.40	313.16	469.06	288.07
II	Mn SO$_4$ +aqueous ethylene glycol	-6.5874	-6.8941	-6.5231	4.7121	5.7970	4.7132	-615.07	-694.80	-623.70	224.70	483.99	254.35
III	CO SO$_4$ +aqueous ethylene glycol	-5.2668	-5.6515	-5.5892	1.4801	2.7884	2.8485	-663.53	-742.30	-737.86	142.53	471.32	467.48

Table-4
Values of transfer volume ($\Delta\varphi_V^0$) and A and B coefficient of Jones-Dole equation of some divalent transition metal sulphates at 308.15, 313.15 and 318.15 K for

system	metal sulphate	transfer volume $\Delta\varphi_V^0/(\times m^3\ mol^{-1})$			experimental values of $\varphi_V^0/(\times m^3\ mol^{-1})$ of metal sulphate in water			viscosity coefficient					
								A / (dm$^{3/2}$ mol$^{-\frac{1}{2}}$)			B / (dm^3 mol^{-1})		
		308.15K	313.15K	318.15K	308.15K	313.15K	318.15K	308.15K	313.15K	318.15K	308.15K	313.15K	318.15K
I	Ni SO$_4$ +aqueous ethylene glycol	-1749.64	-1833.01	-1924.67	1090.84	116.85	1263.27	-0.2314	-0.0694	0.4370	3.1332	2.5467	0.8002
II	Mn SO$_4$ +aqueous ethylene glycol	-1762.04	-1889.18	-1945.18	1146.97	1194.38	1321.48	-0.1767	-0.1356	0.1899	3.0279	2.8754	2.0354
III	CO SO$_4$ +aqueous ethylene glycol	-1617.73	-1859.86	-2135.42	954.320	1117.56	1397.56	-0.4296	-0.2444	0.0823	3.7197	2.1063	2.3469

The observed increasing behavior of φ_V suggests the existence of strong ion-solvent interaction in all the three systems studied. The negative values of (φ_K) indicate ionic, dipolar and hydrophilic interactions occurring in these systems. Since more number of water molecules are available at lower concentration of ethylene glycol, the chances for the penetration of solute molecules into the solvent molecules is highly favored. The increasing values of φ_K and φ_V in the concerned systems reveal that strengthening of ion-solvent interactions existing in these mixtures. From the magnitude of φ_V, it can be concluded that a strong molecular association is found in manganese sulphate than other metal sulphate systems, suggesting that the manganese sulphate is a more effective structure-maker in the solvent mixture.
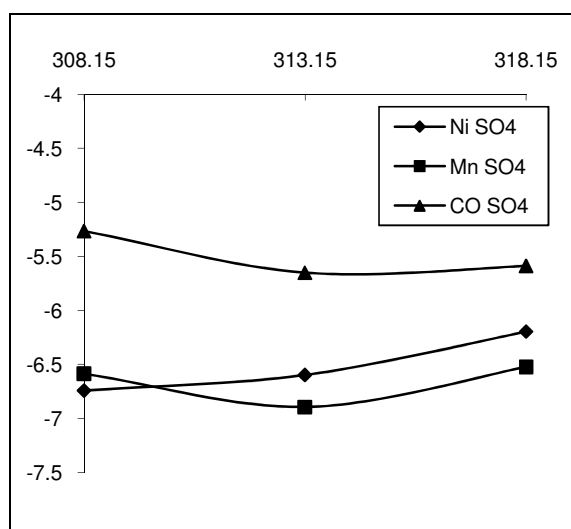

Figure-1
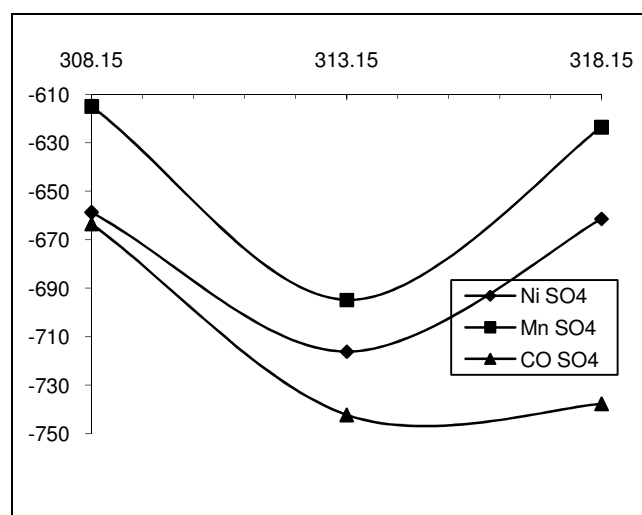**Variation of Limiting apparent molal compressibility (φ_K^0) Vs temperature in Kelvin (K)**

Figure-2
Variation of Limiting apparent molal volume (φ_V^0) Vs temperature in Kelvin (K)

The limiting apparent molal compressibility (φ_k^0) provides information regarding ion-solvent and its associated constant S_k that of ion-ion interaction in the solutions. Further, from the table 3, it is observed that φ_k^0 values are negative and from figure 1, it is seen that they behave non-linearly with rise of temperature. The appreciable negative values of φ_k^0 suggest the existence of ion-solvent interaction. Further, the values of S_k which are positive in all the three metal sulphates systems predicting the presence of weak ion-ion interaction in the mixtures.

The volume behavior of a solute at infinite dilution is satisfactorily represented by the limiting apparent molal volume (φ_v^0) values, which are independent of the ion-ion interaction and provides information concerning ion-solvent interactions. The perusal of table 3 reveals that the values of φ_v^0 are all negative in all three liquid systems studied and also it is clear from figure 2, they are behaving non-linearly with rise in temperature, which keeps the same trend as that of φ_k^0 values in all the systems studied, which further confirms the presence of strong ion-solvent interactions. Meanwhile, the value of S_v which exhibit positive values from table 3 in all the three liquid systems reflecting the existence of weak ion-ion interactions, and thus predicting the complex ion formation taking place in the systems. From the values of S_k and S_v, the magnitude of interactions between the metal suphates systems are of the order: manganese sulphate > nickel sulphate > cobalt sulphate. Hence, it is very obvious that manganese sulphate is acting as a effective structural maker in the solvent mixture (water + ethylene glycol).
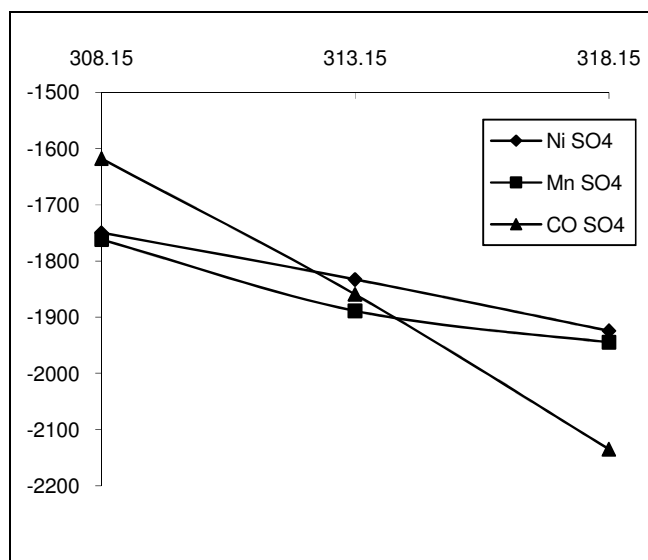

Figure-3

Variation of Transfer volume ($\Delta \varphi_V^0$) Vs temperature in Kelvin (K)

The following types of interactions which may be presumed occurring between the divalent transition metal sulphates and aqueous ethylene glycol mixture can be taking place as, First are is Ionic-hydrophilic interactions between the ions of metal sulphates (Ni^{2+}, Mn^{2+}, CO^{2+} and SO^{2-}) and polar group of ethylene glycol and second type is Hydrophilic-hydrophobic interactions between the ions of metal sulphates and the non-polar group of ethylene glycol.

These tendencies can also be explained using the co-sphere model[24-25]. According to this model, hydrophilic-ionic group of interactions contribute positively, whereas, ionic-hydrophobic group of interactions contribute negatively to the transfer volume studies ($\Delta\varphi_v^o$), regarding the solute-co-solute interactions. In our present investigation, one can easily notice from figure 3, these $\Delta\varphi_v^o$ values are found to be negative in all three metal sulphates systems and decrease with rise in temperature. This clearly suggests that the latter types of interaction are dominating over the former. Also the decreasing trend of $\Delta\varphi_v^o$ values over of the elevation of temperature indicating the weakening of ion-ion interactions in the mixture. This supports once again our earlier view obtained from the values of S_k and S_v.

Viscosity is an important parameter in understanding the structure as well as molecular interactions occurring in the solutions. From table 1, it is observed that the values of viscosity (η) increases with increase in solute concentration in all the systems and decreases with rise in temperature. This increasing trend indicates the existence of molecular interaction occurring in these systems. In order to shed more light on this, the role of viscosity B-coefficient has also been obtained. From table 4, it is observed that the values of A coefficient are negative and B-coefficients of Jones-Dole[17] equations are positive in all the three metal sulphates systems. Since A is a measure of ionic interaction, it is evident that there is a weak ion-ion interaction present in the liquid mixtures. The behaviour of B-coefficient in all the three liquid systems suggests the existence of strong solute-solvent interaction. Further, the decreasing values of η with rise in temperature in the present study may attributed that it may be probably due to greater thermal agitation and reduction of attractive forces between the ions.[26] From the magnitude of B values in these systems, the molecular interaction between the metal sulphates systems in the present investigation is of the order: manganese sulphate > nickel sulphate > cobalt sulphate. The above conclusion is an excellent earlier agreement with that drawn from φ_v, φ_v^o S_k, and S_v data.

Conclusion

The present investigation of molecular interactions of some divalent transition metal sulphates in aqueous ethylene glycol at varying temperatures can be summarised as following: In the present system of manganese sulphate mixture is a an

effective structure-maker in aqueous ethylene glycol mixture over the other two metal suphates systems. The transfer volume studies which predict the solute-co-solute interactions suggesting that ionic-hydrophobic interaction are existing in all the three metal sulphates systems in the present study. Strong inter-ionic interactions such as solute-solvent, ion-solvent interactions are existing, however, a weak ion-ion interaction is noticed in the present system of mixtures. The elevation of temperature leads to the weakening of molecular associations in the present system of mixtures due to thermal dispersion forces. In the present system of liquid mixtures, it is very obvious that the molecular interaction follows the order: manganese sulphate > nickel sulphate > cobalt sulphate [$MnSO_4$ > Ni SO_4 > CO SO_4].

References

1. Endo H. and Otoliko Namoto, Structural absorption of ultrasonic waves in aqueous solutions of alkali halides, *J. Chem. Soc. Faraday Trans.***2**, **77,** 217-226 **(1981)**

2. Kannappan V. and Chidambara vinayagam S., Ultrasonic study of ion-solvent interactions in aqueous and non-aqueous solutions of transition and inner transition metal ions, *Ind. J. Pure & Appl. Phys.,* **44,** 670-676 **(2006)**

3. Ravichandran S. and Ramanathan K., Ultrasonic investigations of $MnSO_4$, $NiSO_4$ and $CuSO_4$ aqueous in polyvinyl alcohol solution at 303K, *Rasayan Journal of Chemistry, 3(2),* 375-384 **(2010)**

4. Parmar M.L., Praveen Sharma and Guleria M.K., A comparative study of partial molal volumes of some hydrated and anhydrous salts of transition metal sulphates and magnesium sulphate in water at different temperatures, *Ind. J. Chem.,* **48A,** 57-62 **(2009)**

5. Kelei Zhuo, Yujan Chen, Wenhao Wang and Jianji Wang, Volumetric and viscometric and viscosity properties of $MgSO_4$/ $CuSO_4$ in sucrose + water solutions at 298.15K, *J. Chem. Eng. Data,* **53,** 2022-2028 **(2008)**

6. Tongfan Sun and Amyn S. Teja, Density, viscosity and thermal conductivity of aqueous ethylene, diethylene and triethylene glycol mixtures between 290K and 450K, *J. Chem. Eng. Data,* **48,** 198-202 **(2003)**

7. Cox B.G. and Waghorne W.E., Thermodynamics of ion-solvent interactions, *Chem. Soc. Rev.* **9,** 381-411 **(1980)**

8. Lav Y.K., Saluja P.P.S, Kebarle P., The proton in dimethyl sulfoxide and acetone results from gas – phase ion equilibriums involving (Me_2SO) nH^+ and (Me_2CO)nH^+, *J. Am. Chem. Soc.,* **102(25),** 7429-7433 **(1980)**

9. CRC Hand Book of Chemistry and Physics, 74th ed., CRC Press, Boca Raton, FL, **(1993-1994)**

10. Alexandr V. Lebed, Oleg N. Kalugin and Ivan N. Vynnik, Properties of 1-1 electrolytes solutions in ethylene glycol at temperatures from 5ºC to 175ºC Part 1 conductance measurements and experimental data treatment, *J. Chem. Soc. Faraday trans.,* **94,** 2097-2101 **(1998)**

11. Tsierkezos N.G., Molinou I.E., Thermodynamic properties of water + ethylene glycol at 283.15, 293.15, 303.15 and 313.15K, *J. Chem. Eng. Data,* **43,** 989-993 **(1998)**

12. Arno H. Reidies., Manganese compounds Ullmann's Encyclopedia of chemical Technology, Wiley-VCH, Weinheim **(2007)**

13. Budavari S.M, O' Neal J, Smith A, Heckelman PE, eds. The Merch Index 12th ed. White House Station NJ: Merck, 414 **(1996)**

14. Richardson H.W. Cobalt compounds. In Kirk-Othmer Encyclopedia of Chemical Technology, New York: John Wiley and Sons, **7,** 229-249 **(2003)**

15. Gucker F.T, The apparent molal heat capacity, volume and compressibility of electrolytes, *J. Chem. Rev.,* **134,** 114-130 **(1933)**

16. Debye D. and Huckel C, Theory of electrolytes II. The limiting law of electrical conductivity, *Physik. Z,* **24,** 305-325 **(1923)**

17. Jones G. and Dole M., The viscosity of aqueous solutions of strong electrolytes with special reference to barium chloride, *J. Am. Chem. Soc.,* **51,** 2950-2964 **(1929)**

18. Yan Z., Wang J. and Jinsuo L., Apparent molal volumes and viscosities of some α-amino acids in aqueous sodium butrate solutions at 298.15K, **46,** 217-222 **(2001)**

19. Banipal T.S, Damanjit Kaura, Banipal P.K. and Gagandeep Singha, Thermodynamic and transport properties of l-serine and l-threonine in aqueous sodium acetate and magnesium acetate solutions at T = 298.15 K, *J.Chem. Thermodyn.,* **39,** 371-384 **(2007)**

20. Ragouramane D. and Srinivasa Rao A., Ultrasonic studies on the influence of some aminoacids on molecular interactions in aqueous solutions of ethanol, *Ind. J. Chem.,* **37A,** 659-662 **(1998)**

21. Thirumaran S. and Inbam P., Thermodynamic and transport studies on some basic amino acids in aqueous

sodium acetate solution at different temperatures, *Ind.J. Pure & Appl. Phys.*, **49,** 451-459 **(2011)**

22. Cezary M. Kinart, Magdalena Klimczak and MartaMaj, Viscosity of binary mixtures of 2-ethoxy ethanol with ethylene glycol, diethylene glycol, triethylene glycol and tetraethylene glycol at T = (293.15 K, 298.15 K, and 303.15K), *Phys. & Chem. Liq.,* **47(1),** 84-94 **(2009)**

23. Dhanalakshmi, Jasmine Vasantharani E., Analysis of apparent molal volume and apparent molal compressibility of quaternary ammonium salt in non-aqueous medium, *J. Pure & Appl. Ultrason.,* **21,** 79-82 **(1999)**

24. Hakin A.W, Michelle M. Duke, Sheri A. Klassen, Robert M. McKay and Kathryn E. Press, Apparent molar heat capacities and volumes of some aqueous solutions of aliphatic amino acids at 288.15, 298.15, 313.15, and 328.15 K, *Canadian Journal of Chemistry*, **72,** 362–368 **(1994)**

25. Gurney R.W., Ionic Processes in Solutions, Mc Graw-Hill, New York (Chapter-I), **(1953)**

26. Motin M.A., Temperature and concentration dependence of apparent molar volumes and viscosities of NaCl, NH_4Cl, $CuCl_2$, $CuSO_4$ and $MgSO_4$ in pure water and water + urea mixtures, *J. Chem. Eng. Data,* **49,** 94-98 **(2007)**