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ULTRASONIC STUDIES ON MOLECULAR INTERACTION AND PHYSICO-CHEMICAL BEHAVIOUR OF SOME DIVALENT TRANSITION METAL SULPHATES IN AQUEOUS PROPYLENE GLYCOL AT 303.15K

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ABSTRACT

Density (ρ), viscosity (η) and Ultrasonic velocity (U) measurement have been measured for some divalent transition metal sulphates namely nickel sulphate ($NiSO_4$), manganese sulphate ($MnSO_4$) and cobalt sulphate ($CoSO_4$) in aqueous propylene glycol mixture (3:1 ratio) at 303.15K. Using the experimental values, the adiabatic compressibility (β), 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 constants (S_K, S_V), transfer volume ($\Delta\varphi_V^0$), B-coefficient of Jones-Dole equation were calculated and these results have been discussed in terms of ion-solvent and ion-ion interactions.

Keywords: ultrasonic velocity, apparent molar volume, transfer volume, hydration number.

INTRODUCTION

Ultrasonic velocity measurements are helpful to study the ion-solvent interactions in aqueous and non-aqueous solutions. Ultrasound has been extensively used to determine the ion solvent interactions in aqueous solution containing electrolytes[1]. In solution of ionic solute the attraction between the solute and solvent is essentially of ion-dipole interaction depends mainly on ion size and polarity of the solvent. The strength of ion-dipole attraction in directly proportional to the size of the ion, charge and the magnitude of the dipole, but inversely proportional to the distance between the ion and the dipolar molecule. The distance between the ion and the dipolar molecule. The dissolution of electrolyte in a 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 interaction in solutions. The accurate measurement of density, viscosity, ultrasonic velocity and hence the derived parameters such as adiabatic compressibility, apparent molal compressibility and apparent molal volume will give significant information regarding the state of affairs in a solution. Such studies on binary electrolytes have been made 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 physico-chemical studies of binary electrolytes cannot be so useful to get a definite conclusion regarding the structural properties and the type of interaction involved, the study of ternary electrolytes in 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 of these, ion-ion, ion-solvent interactions are of current interest. The interaction help in better understanding of the types of solute and solvent, i.e. whether the added solute modifies or distorts the structure of the solvent. Partial molar volumes of electrolytes provide valuable information about the ion-ion and ion-solvent interactions in ionic solutions[7-11]. The addition of organic solvent to an aqueous solution of electrolyte brings about the change in ion solvation that often results in a large change in the reactivity of dissolved electrolyte[12,13]. Now-a-days, propylene glycol is being used for the synthesis of nano-particles. The use of propylene glycol + water mixtures has attracted much attention in recent years as solvent in the study of physico-chemical properties of electrolytic solutions. Propylene glycol acts as reducing agent as well as stabilizing medium. Third-transition metal plays a vital role in life systems because of natural presence in vitamins, enzymes and proteins (Mn, Co, Ni, etc.). Manganese sulphate is the inorganic compound. Manganese sulphate is a by-product of various industrially significant oxidations that use manganese dioxide, including the manufacture of hydroquinone and anisaldehyde. It is evident from the prevailing literature that interaction among the metal sulphates in aqueous an attempt has been made to elucidate the ion-ion and ion-solvent interactions of $NiSO_4$, $MnSO_4$, and $CoSO_4$ in aqueous propylene glycol mixtures at 303.15K through ultrasonic velocity measurement.

The ultrasonic velocity data as such do not provide significant information about the native and relative strength of various types of intermolecular or inter ionic interactions between the components. Hence their desired parameters such as adiabatic compressibility (β), 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 constants (S_K, S_V), transfer volume ($\Delta\varphi_V^0$), B-coefficient of Jones-Dole equation have been obtained to shed more light on such interactions.

EXPERIMENTAL

All the chemicals used in this present research work are spectroscopic reagent (SR) and analytical reagent (AR) grades of minimum assay of 99.9% obtained from E-Merck, Germany and Sd Fine Chemicals, India, which are used as such without further purification. Water used in these experiments was deionized, distilled and degassed prior to making solutions. Required amount of water and propylene glycol were taken to prepare the composition of binary mixtures (Volume ratio 3:1) in a clean dry conical flask with a ground stopper. The required quantity of metal sulphates for given molarity was dissolved in binary mixture of aqueous propylene glycol and similar procedure has been adopted for different molarities of metal sulphates. For each concentration, the mass of metal sulphate can be measured using electronic digital balance having an accuracy ± 0.1 mg (Model: SHIMADZU AX200). The density was determined using a specific gravity bottle by relative measurement method with an accuracy of ±0.01 $kg\cdot m^{-3}$. An Ostwald's Viscometer (10ml capacity) was used for the viscosity measurement and efflux time was determined using a digital Chronometer to within ± 0.01s. An ultrasonic interferometer having the frequency 3MHz (MITTAL ENTERPRISES, NEW DELHI, MODEL F-81) with an overall accuracy of ± 0.1% has been used for velocity measurement. An electronically digital operated constant temperature bath (RAAGA Industries) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature. The accuracy in the temperature measurement is ± 0.1 K.

Theory and Calculations

Using the measured data, the following volumetric, compressibility and transport parameters have been calculated using the standard relations.

Adiabatic Compressibility $$\beta = \frac{1}{U^2\rho} \quad (1)$$

Molal hydration number has been computed using the relation

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

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.

The apparent molal compressibility has been calculated from relation,

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

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[14] from Debye Huckel theory[15] and is given by

$$\varphi_K = \varphi_K{}^0 + S_K m^{1/2} \tag{4}$$

where $\varphi_K{}^0$ is the limiting apparent molal compressibility at infinite dilution and S_K is a constant. $\varphi_K{}^0$ and S_K of equation (4) have been evaluated by the least square method.

The apparent molal volume φ_V has been calculated using the relation

$$\varphi_V = \left(\frac{M}{\rho}\right) - \frac{1000\left(\rho - \rho_0\right)}{m\rho\rho_0} \tag{5}$$

The apparent molal volume φ_V has been found to differ with concentration according to Masson[16] empirical relation as

$$\varphi_V = \varphi_V^0 + S_V m^{1/2} \tag{6}$$

where φ_V^0 is the limiting apparent molal volume at infinite dilution and S_V is a constant and these values were determined by least square method.

Transfer volume of each electrolytes, $\varphi_V{}^0$ from water to aqueous solutions have been calculated by the equation $\Delta\varphi_V{}^0 = \varphi_V{}^0$ (in aqueous solution) - $\varphi_V{}^0$ (in water) (7)

The viscosity A and B coefficients for the amino acids in aqueous 1,4-dioxane solutions were calculated from the Jones-Dole equation[17].

$$\frac{\eta}{\eta_0} = 1 + Am^{1/2} + Bm \tag{8}$$

where, η and η_0 are the viscosities of the solution and solvent respectively and m is the molal concentration of the solute. A is determined by the ionic attraction theory of Falkenhagen-Vernon and therefore also called Falkenhagen coefficient[18], B or Jones-Dole coefficient is an empirical constant determined by ion-solvent interactions.

RESULTS AND DISCUSSION

The experimental values of density (ρ), for different molarity of the three metal sulphates viz., nickel sulphate ($NiSO_4$), manganese sulphate ($MnSO_4$) and cobalt sulphate ($CoSO_4$) in aqueous medium at 303.15K are shown in Table-1. Further, the values of density (ρ), viscosity (η) and ultrasonic velocity (U) of three divalent transition metal sulphates in aqueous propylene glycol mixtures (Volume ratio 3:1) are presented in Table-2. The values of adiabatic compressibility (β), 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 constants (S_K , S_V), transfer volume (ΔV_φ^0) and viscosity A and B coefficients are shown in Tables 3-4.

In all the three systems (Table-2) the values of density and ultrasonic velocity increases with increase in molal concentration of metal sulphates. The ultrasonic velocities are smaller in $NiSO_4$ than other two metal sulphates. Molecular association is thus responsible for the observed increase in ultrasonic velocity in these mixtures. The increase in ultrasonic velocity in these solutions may be attributed to the cohesion brought about by the ionic hydration.

Table-3 shows the variation of adiabatic compressibility with molar concentration of metal sulphates in aqueous propylene glycol mixtures at 303.15K. The decrease in adiabatic compressibility, observed in propylene glycol + water mixtures with metal sulphates in the present study generally confirms that conclusion drawn from the velocity data. The increase in velocity and decrease in compressibility were attributed to formation of hydrogen bonds between solute and solvent molecules. The compressibility appears to be decreasing with increase hydrogen bond strength formed by solute and solvent molecules. The adiabatic compressibility values are found greater in $NiSO_4$ which shows molecular association/interaction is strong in $NiSO_4$ than other two metal sulphates. The magnitude is in the order: $NiSO_4 > MnSO_4 > CoSO_4$.

The molecular interaction between the solute and the water molecules present in the solvent is termed as hydration. The positive values of hydration number (Table-3) indicates an appreciable solvation of solutes[19]. This is an added support for the structure intensifying property of the solutes as well as the presence of appreciable dipole-dipole interaction between solute and water molecules. From the Table-3 it is observed that the values of n_H are found to increase with increase the content of $NiSO_4$, but it found to decrease in $MnSO_4$ and $CoSO_4$. The decreasing behaviour of n_H shows the strength of interaction gets weakened in the solute-solvent molecules.

The following observations have been made on φ_K and φ_V (Table-3) of metal sulphates in aqueous propylene glycol mixtures at 303.15K.

(i) the values of φ_K and φ_V are negative over the entire range of molarity.

(ii) the values of φ_K are decreases non-linearly with increasing the concentration of $NiSO_4$, but it found to be increase in $MnSO_4$ and $CoSO_4$.

(iii) the values of φ_V are decreases non-linearly with increasing the concentration of metal sulphates in all systems studied.

(iv) The magnitude of φ_K is in the order: $NiSO_4 > MnSO_4 > CoSO_4$.

All the above observations clearly suggest that the negative values of φ_K and φ_V indicates ionic and hydrophilic interactions occurring in these systems. The non-linear variations of φ_K and φ_V with respect to the solute concentration in all systems studied which indicates an existence of ion-solvent interactions. Further, the negative values of φ_V indicate electrostrictive solvation of ions[20].

The limiting apparent molar compressibility φ_K^0 provides information regarding ion-solvent interaction and S_K that of ion-ion interaction in the solutions. From the Table-4 that φ_K^0 values are negative in all the systems studied. The appreciable negative values of φ_K^0 for all studied systems reinforce our earlier view that existence of ion-solvent interaction. The magnitude of φ_K^0 is in the order: $NiSO_4 > MnSO_4 > CoSO_4$. The values of S_K exhibits negative in all systems indicate the existence of ion-ion interaction and suggest the structure making/breaking effect of the metal sulphates.

The volume behaviour of a solute at infinite dilution is satisfactorily represented by φ_V^0 which is independent of the ion-ion interactions and provides information concerning ion-solvent interactions. Table-4 reveals that the values of φ_V^0 are negative in all system studied which shows the existence of ion-solvent interaction. The S_V (Table-4) exhibits negative values in all the systems, suggesting the presence of stronger ion-ion interactions and less complex ion formation taking place in the systems.

Generally, speaking the types of interactions occurring between the divalent transition metal sulphates and aqueous propylene glycol mixture can be classified as follows:

- Ionic-Hydrophilic interactions between the ions of metal sulphates (Ni^{2+}, Mn^{2+}, Co^{2+} and SO_4^{2-}) and polar group of propylene glycol.
- Hydrophilic-hydrophobic interactions between the ions of metal sulphates and the non-polar side group of the propylene glycol.

The $\Delta\varphi_V^0$ values (Table-4) can also be explained on the basis of co-sphere overlap model[21] in terms of solute–co-solute interactions. According to this model, hydrophilic-ionic group interactions contribute positively, whereas hydrophilic-hydrophobic group interactions contribute negatively to the $\Delta\varphi_V^0$ values. In the present study, the values of $\Delta\varphi_V^0$ (Table 3.12) shows positive in $NiSO_4$, but it found to be negative in $MnSO_4$ and $CoSO_4$ mixtures. The positive contribution of $NiSO_4$ indicates the former type of interactions and negative contribution of $MnSO_4$ and $CoSO_4$ are latter type of interactions.

Viscosity is another important parameter in understanding the structure as well as molecular interactions occurring in the solutions. Viscosity variation is attributed to the structural changes. From the Table-2, it is observed that the values of viscosity increases with increasing concentration of three metal sulphates in aqueous propylene glycol solutions. 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 the Table-4, it is observed that the values of A coefficient are negative, and the values of B are positive in all systems studied. Since A is a measure of ionic interaction, it is evident that there is a weak ion-solute interaction in the mixtures studied, which is indicated by the smaller magnitude of A values. B-coefficient is also known as measure of order and disorder introduced by the solute into the solvent. It is also a measure of ion-solvent interaction and relative size of the solute and solvent molecules. The behaviour of B-coefficient in all the systems suggest the existence of strong ion-solvent interactions. The magnitude of B-values is in the order: $NiSO_4 > MnSO_4 > CoSO_4$. This conclusion is an excellent agreement with that drawn from S_K and φ_K^0 data and the larger values of B indicates structure making capacity of solute.

CONCLUSION

In summary, volume and compressibility data have been determined for divalent transition metal sulphates in aqueous propylene glycol mixtures at 303.15K and the results have been used to study the ion-solvent interaction exists in the mixture. From the magnitude of φ_K^0 and B-coefficient values it can be concluded that the existence of ion-solvent interaction is in the order: $NiSO_4 > MnSO_4 > CoSO_4$. The transfer volume $\Delta\varphi_V^0$ suggests the predominance of hydrophilic-hydrophobic interactions over ionic-hydrophilic interactions. From the co-sphere overlap model it can be concluded that ion-solvent interactions are dominating over the solute-co-solute interactions.

Table-1 Values of density (ρ) of some divalent transition metal sulphates in aqueous medium at 303.15 K

M/ (mol. dm^{-3})	ρ/(kg.m^{-3})		
	$NiSO_4$ + Water	$MnSO_4$ + Water	$CoSO_4$ + Water
0.00	995.7	995.7	995.7
0.02	998.7	999.4	1000.5
0.04	1000.7	1001.0	1002.3
0.06	1001.8	1003.9	1005.2
0.08	1005.5	1007.2	1008.8
0.10	1007.6	1011.7	1011.8

Table-2. Values of density (ρ) viscosity (η) and ultrasonic velocity (U) of metal sulphates in aqueous propylene glycol mixtures (3:1 ratio) at 303.15K for

M/ (mol. dm^{-3})	ρ/(kg.m^{-3})	η/(×10^{-3} Nsm^{-2})	U/(ms^{-1})
System I: $NiSO_4$ + water + propylene glycol			
0.00	1019.6	1.7678	1626.4
0.02	1020.8	1.7743	1632.2
0.04	1022.4	1.7848	1636.2

0.06	1023.2	1.8106	1639.8
0.08	1024.4	1.8378	1645.2
0.10	1030.3	1.8681	1657.0
System II : $MnSO_4$ + water + propylene glycol			
0.00	1019.6	1.7678	1626.4
0.02	1020.1	1.7710	1627.2
0.04	1021.8	1.7815	1628.8
0.06	1022.7	1.7935	1630.3
0.08	1023.9	1.8098	1632.2
0.10	1025.2	1.8220	1633.2
System III : $CoSO_4$ + water + propylene glycol			
0.00	1019.6	1.7678	1626.4
0.02	1021.2	1.7768	1637.2
0.04	1022.7	1.7910	1642.3
0.06	1025.6	1.8115	1649.4
0.08	1030.4	1.8666	1658.2
0.10	1032.8	1.8809	1668.0

Table-3. The values of adiabatic compressibility (β), hydration number (n_H), apparent molal compressibility (φ_K), and apparent molal volume (φ_V) of metal sulphates in aqueous propylene glycol mixtures at 303.15K

M/ (mol. dm^{-3})	β/(×10^{-10} m^2 N^{-1})	n_H	$-\varphi_V$ / (×10^{-3} m^3 mol^{-1})	$-\varphi_V^0$ /(×10^{-3} m^3 mol^{-1})
System I: $NiSO_4$ + water + propylene glycol				
0.00	3.7078	-	-	-
0.02	3.7023	3.35	3.6591	23.9
0.04	3.3889	5.72	6.7251	52.6
0.06	3.6789	5.82	6.6955	49.4
0.08	3.6660	6.34	7.1796	51.3
0.10	3.6569	6.15	7.1264	53.4
System II : $MnSO_4$ + water + propylene glycol				
0.00	3.7078	-	-	-
0.02	3.6772	18.45	17.4819	57.5
0.04	3.6535	16.46	16.1206	67.0
0.06	3.6346	14.79	14.3819	57.3
0.08	3.6066	15.33	14.8319	57.2
0.10	3.5350	20.91	21.1711	101.7
System III : $CoSO_4$ + water + propylene glycol				
0.00	3.7078	-	-	-
0.02	3.6533	32.89	30.1592	76.5
0.04	3.6253	24.97	23.4433	74.0
0.06	3.5840	25.02	24.2699	95.3
0.08	3.5296	27.00	27.1843	128.2
0.10	3.4801	27.58	27.5702	125.1

Table-4 Values of limiting apparent molar compressibility (φ_k^0), limiting apparent molar volume (φ_v^0), constants S_K and S_V, transfer volume ($\Delta\varphi_V^0$) and viscosity A and B coefficients of Jones-Dole equations of some divalent transition metal sulphates in aqueous propylene glycol mixtures at 303.15K

Systems	φ_k^0 /($\times10^{-8}$ m^2N^{-1})	S_k/($\times10^{-6}$ N^{-1} m^{-1}. mol^{-1})	$-\varphi_v^0$/($\times10^{-3}$ $m^3.mol^{-1}$)	$-S_v$/($m^3lt^{½}$. $mol^{-3/2}$)	$\Delta\varphi_V^0$/ ($\times10^{-3}$ m^3. mol^{-1})	A/($dm^{3/2}$. $mol^{-1/2}$)	B/(dm^3. mol^{-1})
$NiSO_4$ + aqueous propylene glycol	-1.9547	-18.2321	12.1	0.1435	152.1	-0.0582	4.9160
$MnSO_4$ + aqueous propylene glycol	-14.3396	-10.3671	35.0	0.1477	-2176.1	-0.1151	0.9008
$CoSO_4$ + aqueous propylene glycol	-24.7938	-7.3038	18.8	0.3418	-2750.8	-0.1296	0.1055

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