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Thermodynamic Studies of Some Symmetrical Electrolyte's Solution in Aqueous-Organic Solvent Mixtures

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Abstract

Thermodynamic properties of the solutions of manganese sulphate ($MnSO_4$), nickel sulphate ($NiSO_4$), and zinc sulphate ($ZnSO_4$) in aqueous-organic mixtures containing 5%, 10%, 15% and 20% (*w*/w) of ethanol have been measured at 25^0C in the concentration range of $2.0x10^{-4}$ to $12.0x10^{-4}$ mol dm^{-3}. The standard Gibbs free energy, entropy and enthalpy changes were calculated from the conductance data using the values of ion-association constant by thermodynamic equations. The Gibbs free energy, entropy and enthalpy changes were investigated depending on the amount of ethanol percentage. Gibbs energy of transfer (G^0_t) from aqueous media to aqueous-organic mixtures of individual ions was also calculated in different solvent mixtures. The contributions of electrostatic and non-electrostatic part to the transfer free energy were also calculated from free energy of transfer. The values of Gibbs free energies were found negative for each electrolyte which is the sign of spontaneous association process. The values of entropies and enthalpies were found positive for each electrolyte over the entire range of solvent compositions.

Keywords: Electrolytes, ion association constant, Gibbs free energy, entropy, enthalpy, Gibbs energy of transfer.

Introduction

Thermodynamic properties for the solutions of 2:2 electrolytes in aqueous and aqueous-organic solvent mixtures are of great interest from both theoretical and practical point of view. Researches on the association/solvation of electrolytes in mixed solvent with different compositions are of great importance for obtaining information about solute-solute and solute-solvent interactions in solutions. Knowledge of the state of association of the electrolytes and their interactions with the solvent molecules is essential for making an optimal choice of solvent and electrolyte in such systems. Manganese, iron, cobalt and copper are essential in biological systems for various enzymes[1]. Cadmium and zinc

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are of interest in environmental and soil science research and have been reported as major contaminants in the subsurface environments of a number of Department of Energy sites [2]. Metal salt solutions are key components in many natural and industrial procedures [3,4]. The knowledge of their properties is very crucial for a variety of chemical processes and industrial problems. The study of electrolytes solution is basically important to understand the properties and behavior of aqueous-organic mixed solvent systems. Due to the importance in biological and industrial system it is significant to measure the thermodynamic properties for these electrolytes solutions [5]. The understanding of Gibbs energy of transfer of metal ions from water to aqueous-organic solvent mixture is necessary to know the structural features of ion-ion and ion-solvent interactions.

Solvent properties such as the viscosity and the dielectric is very important to take into consideration in order to determine the extent of solute-solvent interactions and the ionic association that allowed to understand the unique structure of the solvent. Ethanol is a polar solvent having lower dielectric constant than that of water. It associates in the liquid by hydrogen bonding. In this alcohol, ionic association is interpreted in terms of a multiple-step association process involving hydrogen-bonded solvation of anions [6]. In our previous paper, we have reported the equivalent conductance, limiting equivalent conductance and association constant data of manganese sulphate, nickel sulphate and zinc sulphate in ethanol-water mixtures with various solvent compositions at different temperatures [7]. Our present investigation is to estimate the thermodynamic properties based on association constant data of these electrolytes at a particular temperature with various solvent composition.

In this present paper, we report the thermodynamic properties of manganese sulphate, nickel sulphate and zinc sulphate solutions in ethanol-water mixtures at 30^0C. The change of standard values of Gibbs energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) are measured for various solvent compositions on the basis of ion-association constant data. The transfer of Gibbs energy (ΔG_t^0) from water to ethanol-water mixtures is also calculated to understand nature of ion-pair formation in the mixed solvent systems.

Results and Discussion

The standard Gibbs energy, enthalpy and entropy of the ion-association process were calculated from the temperature dependence of the ion-association constants (K_A). The standard enthalpy changes (ΔH^0) for each electrolyte were estimated from the slope of $\log K_A$ vs. 1/T plots (Fig.1) with the help of the following equation

$$\ln K_A = \frac{-\Delta H^0}{RT} + C$$

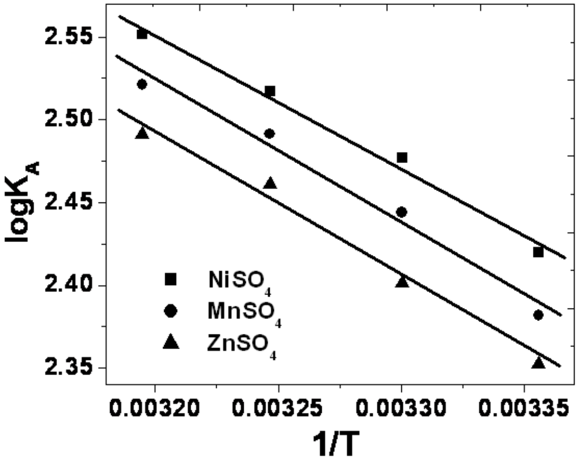

Figure 1: Plots of $\log K_A$ vs. 1/T for $NiSO_4$, $MnSO_4$ and $ZnSO_4$ in 5 wt.% of ethanol-water mixture.

The measured values of standard enthalpy changes of $NiSO_4$, $MnSO_4$ and $ZnSO_4$ solution are recorded in Table 1. It shows that all the values of ΔH^0 of each electrolyte are positive. This result indicates that the ion-association process is thermodynamically endothermic. The negative ΔH^0 is not expected from the ion-association theories [8,9]. The solvent composition dependence of ΔH^0 values for $NiSO_4$, $MnSO_4$ and $ZnSO_4$ is shown in Fig. 2. It was shown that ΔH^0 values of all the electrolytes were decreased with increase of ethanol content in the solvent mixtures. Ion-ion interaction in solution might be responsible for these positive values of ΔH^0. The calculated ΔH^0 values are found to follow the order: $ZnSO_4 > MnSO_4 > NiSO_4$.

The standard Gibbs energy changes (ΔG^0) for the ion association process were calculated from the values of association constants using the following equation:

$$\Delta G^0 = -RT \ln K_A$$

It is well known that the values of association constant of pure electrolyte are mainly influenced by the radius of the electrolyte and the dielectric constant of the solvent medium. On the other hand, there is significant evidence that some ions are solvated in the solvent medium [10], *i.e.*, each cation/anion is surrounded by a number of solvent molecules that escort the ions in solution. As a result, the values of the association constant also depend on the non-electrostatic interaction between the electrolyte and the solvent medium.

The measured values of ΔG^0 for all the electrolytes were found negative at various solvent compositions and are recorded in Table 1. It is shown that the negative ΔG^0 values increase with increase of organic portion in the solvent mixtures for each electrolyte. These findings indicate that the released solvent molecules transfer into the bulk solvent and leads to smaller ΔG^0 values. Fig. 3 represents the corresponding ΔG^0 as a function of solvent composition of ethanol in the solvent mixtures at 25^{0}C. It demonstrates that the ΔG^0 values of each electrolyte also decrease with decrease of dielectric constant of the solvent compositions. The figure shows almost linear plots except for the values in the 20 wt.% of ethanol. The negative ΔG^0 values illustrate that the ion-association process is spontaneous and the magnitude of ΔG^0 is a measure of the steady ion-pair formation. The calculated ΔG^0 values are found to follow the order: $NiSO_4$ >$MnSO_4$ >$ZnSO_4$.

Table-1. The changes of standard Gibbs energy (ΔG^0) enthalpy (ΔH^0) and entropy (ΔS^0_{298}) values of $NiSO_4$, $MnSO_4$ and $ZnSO_4$ in ethanol-water mixtures

Wt.%	**ΔG^0_{298} in k J mol^{-1}**			**ΔH^0 in k J mol^{-1}**			**ΔS^0_{298} in J mol^{-1} K^{-1}**		
	$NiSO_4$	$MnSO_4$	$ZnSO_4$	$NiSO_4$	$MnSO_4$	$ZnSO_4$	$NiSO_4$	$MnSO_4$	$ZnSO_4$
5	-13.81	-13.59	-13.42	15.55	16.64	17.06	98.53	101.45	102.30
10	-14.58	-14.07	-13.97	11.02	11.76	12.47	85.89	86.68	88.70
15	-15.01	-14.53	-14.38	8.38	9.51	10.17	78.49	80.66	83.06
20	-15.65	-15.59	-15.48	3.93	4.40	5.48	65.70	67.08	70.32

In order to calculate the standard entropy changes (ΔS^0) of the ion-association process, we use the following equation

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T}$$

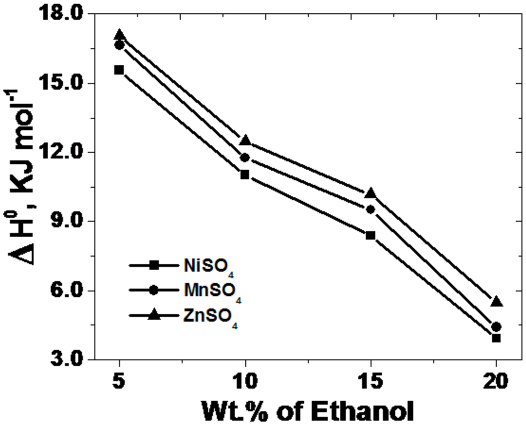

Figure 2: Plots of ΔH^0 vs. wt.% of ethanol for $NiSO_4$, $MnSO_4$ and $ZnSO_4$ at 25^{0}C.

In Table 1, the calculated ΔS^0 values of the three electrolytes are recorded. It shows that all ΔS^0 values are positive and decrease with increase of organic content in the solvent mixtures. These positive values of ΔS^0 along with ΔH^0 values indicate that the ion-association process is mainly entropy controlled. The dependence of ΔS^0 on solvent compositions are illustrate in Fig. 4. It also shows that the ΔS^0 values of all the three electrolytes decrease with decrease of dielectric constant values of the solvent mixtures which point out a deteriorating in the ion solvation. The positive ΔS^0 values of all the three electrolytes may be attributed to the increasing number of degrees of freedom upon association generally due to the release of solvent molecules. In other words, the solvation of ions is weakened as a result of the formation of ion pair. The ΔS^0 values of $NiSO_4$, $MnSO_4$ and $ZnSO_4$ in the all solvent compositions used in this study were found positive because of the decrease in solvation of the ion pairs compared to that of the free ions in the solvent mixtures [11,12]. The $\Delta S°$ values of the electrolytes are found to decrease in the following order: $ZnSO_4$ >$MnSO_4$ >$NiSO_4$, which indicates that, the degree of disordering of the ion solvation due to the formation of ion pair also decreases in the same order. There are several factors which govern the standard entropy of ion association of electrolytes like, the shape and size of the ions, charge density of ions, dispersion of the solvent molecules inside the gap of the ions and electrostriction of the solvent molecules around the ions which govern the change of standard entropy of ion-association process [13]. The entropy change may be depending on the differences of entropy between the ion-pair and the ion-solvent interactions and differences in solvent-solvent interactions.

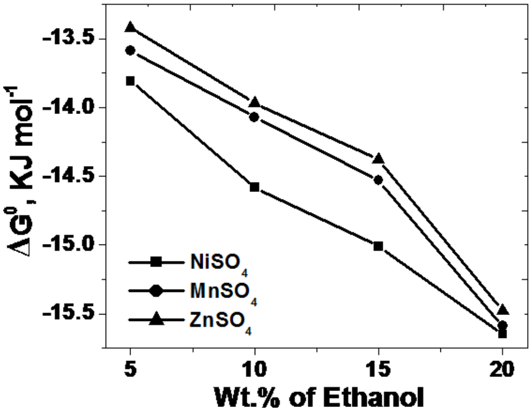

Figure 3: Plots of ΔG^0 vs. wt.% of ethanol for $NiSO_4$, $MnSO_4$ and $ZnSO_4$ at 25^0C.

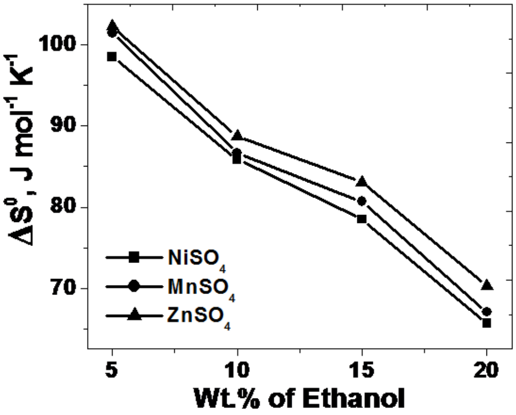

Figure 4: Plots of ΔS^0 vs. wt.% of ethanol for $NiSO_4$, $MnSO_4$ and $ZnSO_4$ at 25^0C.

In the presence of ion-ion interactions in solution the solvent molecules around the individual associating ions gain freedom due to the reduction in the electric field, which lead to increase in entropy [14]. It is evident that the enthalpic term is counterbalanced by a favorable entropy change which comes from the short- and long-range desolvation of both cation and anion ions. The attribution of $\Delta S°$ to desolvation is also supported by the positive enthalpies indicating lack of covalent bonds.

The Gibbs energy of transfer

The standard Gibbs free energy of transfer (ΔG_t^0) of each electrolyte from aqueous medium to the solvent mixtures was calculated from the following equation

$$\Delta G_t^0 = \Delta G^0_{(mixedsolvent)} - \Delta G^0_{(water)}$$

The values of ΔG^0 for water were taken from published data [15,16]. The calculated ΔG_t^0 values of the three electrolytes namely $NiSO_4$, $MnSO_4$ and $ZnSO_4$ are recorded in Table 2. It is revealed that all the values of ΔG_t^0 are found to be negative and increase with the increase of solvent composition. The dependence of the ΔG_t^0 values on the mixed solvent composition is presented in Fig. 5. As Fig. 5 shows, the ΔG_t^0 values of all the electrolytes from water to the solvent mixture are increasing negatively with the increase of the organic content in the solvent mixture. This result proposed that the electrolytes are in a lower Gibbs energy state in solvent mixtures than in aqueous medium and therefore, the transfer of ions is a spontaneous process [17,18].

Table 2: The values of changes of standard Gibbs energy of transfer (ΔG^0_t) $\Delta G^0_{t(el)}$ and $\Delta G^0_{t(ch)}$ of ion–pair formation of $NiSO_4$, $MnSO_4$ and $ZnSO_4$ in ethanol-water mixtures

Wt.%	**ΔG^0_t in J mol^{-1}**			**$\Delta G^0_{t(el)}$ in J mol^{-1}**			**$\Delta G^0_{t(ch)}$ in J mol^{-1}**		
	$NiSO_4$	$MnSO_4$	$ZnSO_4$	$NiSO_4$	$MnSO_4$	$ZnSO_4$	$NiSO_4$	$MnSO_4$	$ZnSO_4$
5	-845	-589	-769	888	793	848	-1733	-1382	-1617
10	-1610	-1065	-1311	1927	1722	1841	-3537	-2787	-3152
15	-2041	-1521	-1927	3109	2777	2969	-5149	-4298	-4896
20	-2687	-2580	-2826	4469	3992	4267	-7156	-6572	-7093

The ion-pair formation is increased with decrease of dielectric constant values of the solvent medium which is pointed out by the negative values of ΔG_t^0. Born-type electrostatic effects are responsible for the variation of ΔG_t^0 values of the electrolytes, dielectric constant of the solvent mixture, structural aspect of the solvents, favored solvation and solvent characteristics [19-23]. Gibbs free energy of transfer (ΔG_t^0) is mainly caused by electrostatic part resulting from a change in the dielectric constant of the medium which is known as electrical contribution ($\Delta G_{t(el)}^0$) and non-electrostatic part which is resulting from specific chemical interactions between the ions and the solvent molecules, which depend on the basicity of the solvent and known as chemical contribution ($\Delta G_{t(ch)}^0$) [24]. The electrostatic part of the transfer Gibbs free energy, $\Delta G_{t(el)}^0$ were measured with the help of the following equation [25]

$$\Delta G_{t(el)}^0 = 4.184x166(\frac{1}{D} - 0.0127)(\frac{1}{r_1} + \frac{1}{r_2})$$

where D is the dielectric constant of the solvent mixture and r_1 and r_2 are the ionic radii of cation and anion respectively. The measured values of $\Delta G_{t(el)}^0$ are recorded in Table 2. From this table it can be seen that the values of $\Delta G_{t(el)}^0$ are positive and increase with increase of the organic portion in the solvent medium. This results point out that the values of $\Delta G_{t(el)}^0$ are depend on the dielectric constant of the medium. It is also reported in the literature that the $\Delta G_{t(el)}^0$ values were increased with increase of organic solvent portion in the solvent mixture as the dielectric constant of the medium was decreased [26]. The calculated values of $\Delta G_{t(el)}^0$ for all the three electrolytes varied in the order of $NiSO_4$ >$ZnSO_4$ >$MnSO_4$ at all the solvent compositions studied in this work.

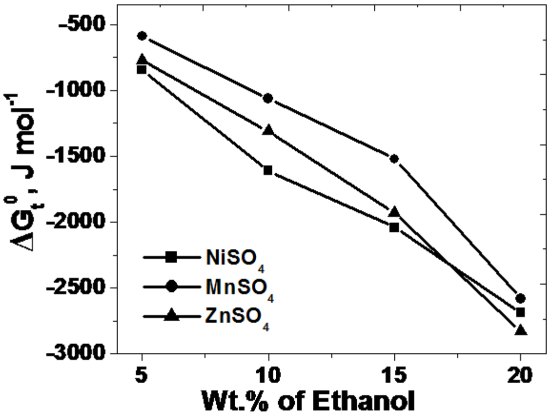

Figure 5: Plots of ΔG_t^0 vs. wt.% of ethanol for $NiSO_4$, $MnSO_4$ and $ZnSO_4$ at 25^0C.

The non-electrostatic part of the transfer Gibbs free energy, ($\Delta G_{t(ch)}^0$) were calculated by subtracting the respective $\Delta G_{t(el)}^0$ values from ΔG_t^0 values. The measured values of $\Delta G_{t(ch)}^0$ are also listed in Table 2. From this table it is seen that the values of $\Delta G_{t(ch)}^0$ are negative and it increases with the increase of organic content in the solvent mixture. The transfer Gibbs free energy is thermodynamically favorable due to the specific chemical interaction between the ions and the solvent molecules. The negative values of $\Delta G_{t(ch)}^0$ are the sign of presence of basicity in the solvent mixtures indicating that the values increase negatively with increase of solvent basicity [27]. Therefore, in view of the chemical contribution to the transfer process, the mixed solvent appears to be more basic than aqueous media. The calculated values of $\Delta G_{t(ch)}^0$ for the three electrolytes found in the order of $NiSO_4$ >$ZnSO_4$ >$MnSO_4$ in all the solvent compositions. It is demonstrated that the chemical contribution predominates over the electrostatic contribution, resulting in an overall favorable effect on transfer free energy $\Delta G_{t(ch)}^0$ from water to mixed solvent medium.

Conclusion

It may thus be concluded that the electrolytes $NiSO_4$, $MnSO_4$ and $ZnSO_4$ remain strongly associated in ethanol-water solvent mixtures to form ion pairs and the solvation of the ions is deteriorated as soon as the ion pair is formed. The values of standard Gibbs free energies, enthalpies and entropies of $NiSO_4$, $MnSO_4$ and $ZnSO_4$ in the solution process are greatly dependent on the solvent compositions. Our result revealed that the solvation of ions decreases with the increase of the organic portion in the solvent mixtures. The calculated Gibbs energy of transfer values demonstrated that the ions are in a higher Gibbs free energy state in aqueous medium than in mixed solvent medium, and the transfer of electrolytes is a spontaneous process. Further studies are necessary to reveal the exact function of solvent mixtures on the thermodynamic properties.

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