

Full Paper

Thermodynamic and Electrical Conductivity Studies on Ion Association of zinc sulphate in N, N-Dimethylformamide –Water mixed solvents

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Article history : Received: 27/2/2017; Revised : 28/2/2017; Accepted : 3/4/2017;
Available Online ::

Abstract

The conductance of zinc sulphate in binary mixtures N, dimethylformamide –water (DMF–H₂O) using the organic solvent mass fractions of 10%, 20%, 30% and 40% at different temperatures of (298.15, 303.15, 308.15 and 313.15) K was measured experimentally. The experimental data are already analyzed through the use of Fuoss-Shedlovsky technique. Molar conductance (Λ_m), limiting molar conductance (Λ_0), the ion-pair association constant (K_A), as well as the standard thermodynamic parameters for association (ΔG_A° , ΔH_A° and ΔS_A°) were estimated and also discussed. It was observed that adding DMF to mixtures caused the molar conductance values were decreased since the relative permittivity of the solvent decreased while. Clearly strengthening the ion association at higher temperatures is basically the result of a decrease in the permittivity of the solvent. The positive values (ΔH_0) show that the association processes are endothermic naturally. Entropy change (ΔS_0) values were positive as a result of decrease in solvation of ion-pair compared to that of the free ion. This related to increase in the degree of freedom upon association.

Keywords: Molar conductance. Ion-pair association. Binary Mixed solvents. Permittivity of the solvent. Thermodynamic parameters. Fuoss-Shedlovsky.

1. Introduction

Within a wide temperature range, conductivity measurements for electrolyte solution can provide an in-depth information for analysis of the salts and explain the various ion-ion and ion-solvent interactions [1-4].

Association constant (K_A) and the thermodynamic parameters are essential where these salts work well in several applications such as pharmaceutical industries and water purification ...etc. Also, conductance studies of electrolytes over a variety of temperatures in pure

and mixed solvent media provide valuable details about their thermodynamic behavior. Studies in the association phenomena through the use of conductivity technique can result in investigate the factors affecting the thermodynamic and kinetic stability of the used salts in used solutions. Thus in this study, it was attempted to obtain good information on the association at different temperatures (298.15, 303.15, 308.15 and 313.15 K) by conductometric measurements. The limiting molar conductance and association constants of zinc sulphate in mixed solutions were driven by analyzing conductivity data relation to Fuoss- Shedlovsky equation [5-8]. The Thermodynamic functions (ΔH^0 , ΔG^0 , ΔS^0) were calculated and compared based on the interaction of solvent at a specific temperature. The comprehension of the nature of the association process is complicated by strong hydration of the free ions and Fuoss-Shedlovsky conductivity equation has been successfully employed by many researchers for the study of several electrolytes in different solutions.

2. Experimental

2.1. Chemicals

Bidistilled water was used in the preparation of mixed solvent with a specific conductivity of $0.09 \mu\text{S cm}^{-1}$ at 298.15 K. (DMF 99.9%), zinc sulphate heptahydrate (99.9%) and Potassium chloride (KCl, 99%) were supplied from Riedel-de Haën company (Germany) and also were used without further purification.

2.2. Conductivity measurements of mixed solvents

The binary mixed solvents of (DMF-H₂O) with the DMF mass fractions of 10%, 20%, 30%, and 40% were chosen to be the solvent media for this study and were prepared by mixing required volume of DMF and water (with error $\pm 0.01\%$) by applying the following equation:

$$\text{DMF percentage} = (V_1 d_1) 100 / (V_1 d_1 + V_2 d_2) \quad (1)$$

Where d_1 and d_2 are the density of DMF and water respectively. V_1 is the volume of DMF which will be added to the volume V_2 of water to get the mixture of the required percentage. The physical properties, relative permittivity (ϵ), density (ρ) and viscosity (η^0) of (DMF - water) with the DMF mass fractions of 10%, 20%, 30%, and 40% at temperatures from 298.15 to 313.15 K were tabulated in Table 1 [9-12]. The unknown values of the (ρ), (η^0) and (ϵ) were evaluated by applying the empirical relations of these properties at the available temperatures taken from the referred references. The solutions of ZnSO₄ were prepared by mass (Mettler AE 200 balance with a sensitivity of ± 0.0001 g) with a concentration range ($1 \times 10^{-3} - 7.1 \times 10^{-4} \text{ mol.dm}^{-3}$) were prepared by taking certain volume of the salt standard solution and diluted to the required volume for measurements by using LF 191(Germany) conductivity meter (accuracy $\pm 0.01\%$) of a cell constant value $1 \pm 10\% \text{ cm}^{-1}$. The cell constant was determined with potassium chloride solutions. MLW 3230 ultra-thermostat was connected to the Conductivity Bridge to give constant temperature (± 0.009 °C).

Table 1: The relative permittivity (ϵ), density (ρ , g.cm⁻³) and viscosity (η , mPa s) at different temperatures of the used mixed solvents.

Solvent	T/K	E	ρ /g cm ⁻³	η /mPa s
10% (DMF-H ₂ O)	298.15	76.10	1.0129	0.7899
	303.15	74.12	1.0118	0.7451
	308.15	72.21	1.0102	0.6910
	313.15	70.31	1.0012	0.6512
20% (DMF-H ₂ O)	298.15	71.10	0.9880	0.8189
	303.15	69.12	0.9785	0.8002
	308.15	67.21	0.9719	0.7089
	313.15	66.01	0.9699	0.6812
30% (DMF-H ₂ O)	298.15	67.05	0.9668	0.8436
	303.15	65.11	0.9659	0.8036
	308.15	63.65	0.9501	0.7562
	313.15	61.13	0.9490	0.7123
40% (DMF-H ₂ O)	298.15	61.34	0.9431	0.8765
	303.15	59.76	0.9393	0.8345
	308.15	57.78	0.9342	0.8012
	313.15	55.56	0.9234	0.7988

3. Results and discussion

3.1. Estimation the limiting molar conductance

The specific conductance (K_s , $\mu\text{S cm}^{-1}$) of prepared solutions of the salt in binary mixed solvents of (DMF – water) with DMF mass fractions of 10%, 20%, 30% and 40% at different temperatures was measurement. The molar conductance (Λ_M) for ZnSO₄ solutions in binary mixed solvents at different temperatures was calculated by applying Eq. (2) and tabulated in Table 2.

$$\Lambda_m = \frac{(K_s - K_{\text{solv}}) \cdot K_{\text{cell}} \cdot 1000}{C} \quad (2)$$

Where K_s and K_{solv} are the specific conductance of the solution and the solvent, respectively; K_{cell} is the cell constant and C is the molar concentration

of the metal salt solution.

The experimental conductance data were analyzed by using Fuoss-Shedlovsky conductivity equations. The limiting molar conductance (Λ_o) were estimated for zinc sulphate solutions in (DMF-H₂O) mixed solvents at different temperatures by extrapolating the linear Onsager plot [13] between (Λ_m) and (C)^{1/2} as shown from Fig. 1 to Fig. 4.

$$\frac{1}{\Lambda_m S(Z)} = \frac{1}{\Lambda_o} + \left(\frac{K_A}{\Lambda_o^2} \right) (C \Lambda_m \gamma_{\pm}^2 S(Z)) \quad (3)$$

$$S(Z) = 1 + Z + Z^2/2 + Z^3/8 + \dots \text{ etc.} \quad (4)$$

$$Z = \frac{S(\Lambda_m C)^{1/2}}{\Lambda_o^{3/2}} \quad (5)$$

The value of (Λ_o) was used to calculate the Onsager slope (S) from the Eq. (6)

$$S = a\Lambda_o + b \quad (6)$$

$$a = 82 \times 10^4 / (\epsilon T)^{3/2} \quad (7)$$

$$b = 82.4 / \eta((\epsilon T)^{1/2}) \quad (8)$$

Where (ϵ) is the relative permittivity of the solvent, (η_0) is the viscosity of the solvent and (T) is the temperature. Using the values of (ϵ) and (η_0), the value of (S) were easily estimated. Using the data of (Λ_m), $S(z)$ and (Λ_0), the values of degree of dissociation (α) were calculated by using the following equation:

$$(\alpha) = \frac{\Lambda_m S(z)}{\Lambda_0} \quad (9)$$

Using these (α) and (ϵ) values, the mean activity coefficients (γ_{\pm}) were evaluated by means means of Eq. (10).

$$\log \gamma_{\pm} = - \frac{Z_+ Z_- A \sqrt{I}}{I + Br^o \sqrt{I}} \quad (10)$$

Where Z_- , Z_+ are the charges of ions in solutions A , B are the Debye-Hückel constant.

$$A = 1.824 \times 10^6 (\epsilon T)^{-3/2} \quad (11)$$

$$B = 50.29 \times 10^8 (\epsilon T)^{-1/2} \quad (12)$$

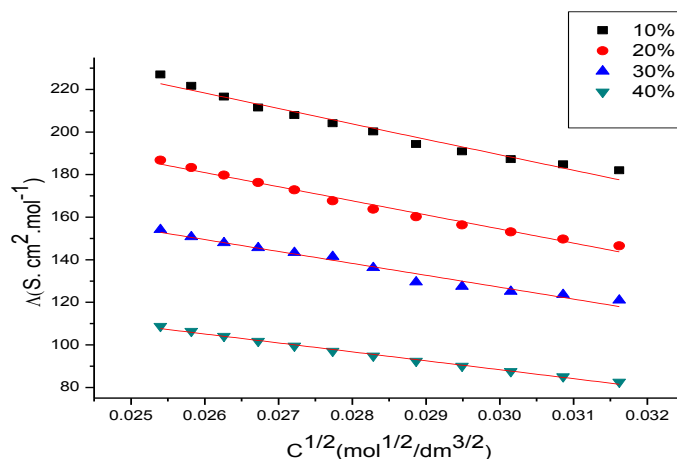


Fig. 1 The plot of (Λ) versus ($C^{1/2}$) at 298.15 K in mixed (DMF-H₂O) solvents for zinc sulphate.

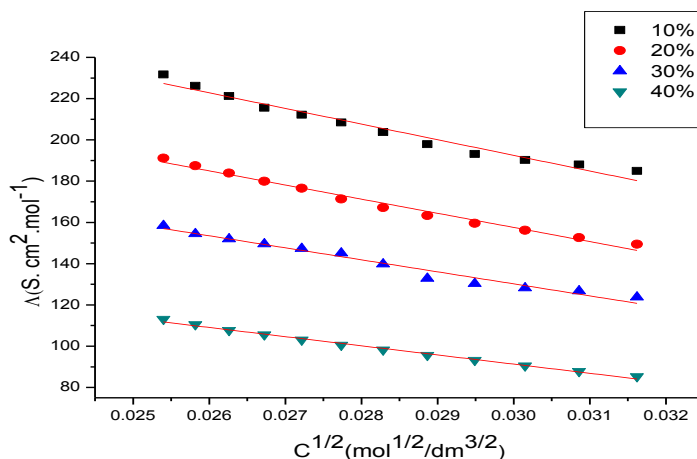


Fig. 2 The plot of (Λ) versus ($C^{1/2}$) at 303.15 K in mixed (DMF-H₂O) solvents for zinc sulphate.

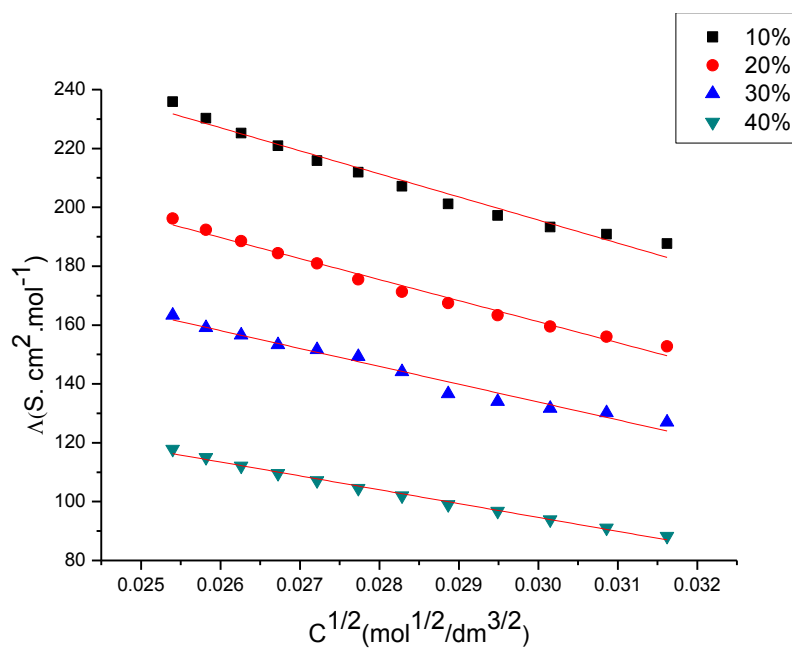


Fig. 3 The plot of (Λ) versus ($C^{1/2}$) at 308.15 K in mixed (DMF-H₂O) solvents for zinc sulphate.

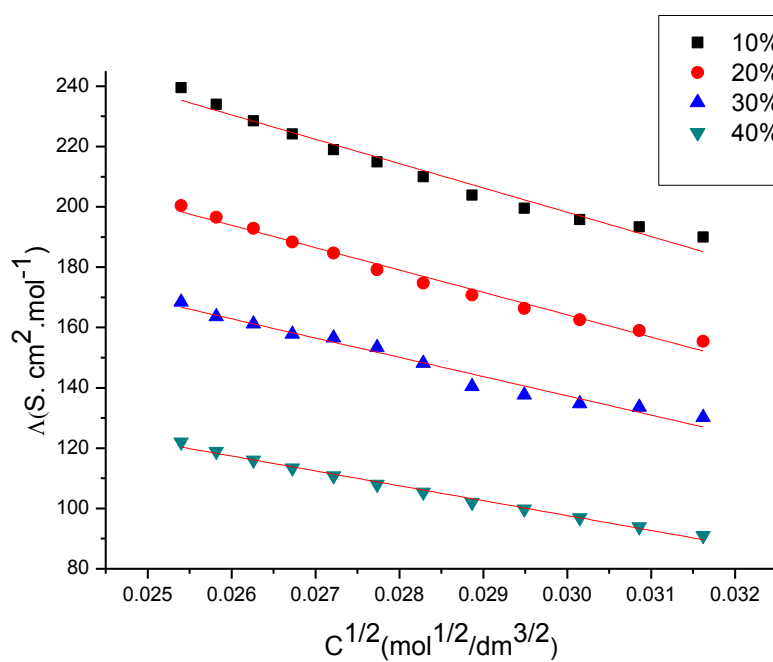


Fig. 4 The plot of (Λ) versus ($C^{1/2}$) at 313.15 K in mixed (DMF-H₂O) solvents for zinc sulphate.

Table 2 The limiting molar conductance (Λ_0 , $\pm 0.20\%$, $\text{S cm}^2 \text{mol}^{-1}$) and Fuoss–Shedlovsky parameters of zinc sulphate in the used solvents at different temperatures.

Solvent	T/K	Λ_0	S	Z	S(Z)	A	γ_{\pm}	α
10% (DMF - H ₂ O)	298.15	406.98419.80	166.90	0.0086	1.0087	0.5336	0.9008	0.4510
	303.15	430.86440.24	175.97	0.0088	1.0088	0.5415	0.9001	0.4445
	308.15		186.38	0.0090	1.0090	0.5495	0.8993	0.4395
	313.15		195.77	0.0092	1.0092	0.5583	0.8982	0.4355
20% (DMF - H ₂ O)	298.15	353.18363.33	162.94	0.0093	1.0094	0.5909	0.8945	0.4187
	303.15	375.64386.65	169.36	0.0094	1.0095	0.6013	0.8932	0.4151
	308.15		184.11	0.0098	1.0099	0.6119	0.8920	0.4105
	313.15		190.81	0.0098	1.0099	0.6137	0.8923	0.4059
30% (DMF - H ₂ O)	298.15	295.07304.93	154.68	0.0106	1.0106	0.6453	0.8860	0.4144
	303.15	315.90328.78	163.15	0.0107	1.0108	0.6577	0.8845	0.4103
	308.15		172.10	0.0109	1.0109	0.6640	0.8839	0.4064
	313.15		185.40	0.0112	1.0112	0.6886	0.8807	0.4004
40% (DMF - H ₂ O)	298.15	214.32	140.57	0.0128	1.0129	0.7374	0.8744	0.3903
	303.15	224.49	148.85	0.0129	1.0130	0.7480	0.8735	0.3849
	308.15	235.94	158.50	0.0129	1.0130	0.7677	0.8714	0.3787
	313.15	245.63	165.96	0.0130	1.01309	0.7947	0.8677	0.3753

Table 3: The mean ion pair association constant (K_A , $\pm 0.2\%$, mol. dm^{-3}) of zinc sulphate in the used solvents at different temperatures.

Solvent	T/K	K_A
10% (DMF -H ₂ O)	298.15	3323.93
	303.15	3467.90
	308.15	3585.73
	313.15	3686.89
20% (DMF -H ₂ O)	298.15	4142.71
	303.15	4253.90
	308.15	4394.72
	313.15	4528.07
30% (DMF -H ₂ O)	298.15	4342.33
	303.15	4474.61
	308.15	4597.93
	313.15	4818.37
40% DMF -H ₂ O)	298.15	5231.18
	303.15	5440.15
	308.15	5704.29
	313.15	5888.69

It is evident from Tables 2 that the values of Λ_0 increase regularly with increase in temperature for zinc sulphate, indicating higher mobility of the ions in all solvent systems studied. This is due to the fact

that the increased thermal energy results in greater bond breaking and also variation in vibrational, rotational and translational energy of molecules lead to higher frequency and higher mobility of ions. With the rise of temperature the viscosity of the solvent also decreases which makes the ions to move freely towards the electrode.

3.2. Ion-pair association constant

The values of the ion-pair association constant (K_A) were represented in Table 3. It is clear that the association constant (K_A) values increase with increase in temperature which indicates an endothermic association process. Also this temperature dependence of the association process of ions can be explained on the basis of the interplay between dehydration and association of ions whereas the temperature increases, the dehydration and/or desolvation process of ions take place, then the ions

will have short distance of contact, therefore the association of ions increases [14-15].

It was found through conductometric data analysis zinc sulfate show more association or ion pair formation increase as the proportions of organic solvent increase in the mixtures, the mobilities of ions are decreased, giving a chance for ions to associate. This increasing in association constant values may interpreted on the basis of the interplay between association constant and strength of the ion solvation in different solvents, whereas the stronger ion is solvated, the association between cations and anions are weaker.

3.3. Thermodynamics of association

The standard Gibbs free energy of association (ΔG_A°) was calculated by using Eq. (14) for all salts under study in all solvent mixtures at all temperatures and its values were tabulated in Table 4.

$$\Delta G_A^\circ = -RT \ln K_A \quad (14)$$

Where R is the gas constant and equal (8.314 J.mol⁻¹. K⁻¹). The values of the standard enthalpy (ΔH_A°) and the standard entropy (ΔS_A°) of association process were obtained from van't Hoff equation $\left(\frac{d \ln K}{dT}\right) = \left(\frac{\Delta H_A^\circ}{RT^2}\right)$ by plotting (log K_A) versus (1/T), where the slope is equal the value of ($-\Delta H_A^\circ/2.303R$) while the entropies of association (ΔS_A°) were calculated by the use of Gibbs–Helmholtz equation Eq. (15).

$$\Delta G_A^\circ = \Delta H_A^\circ - T\Delta S_A^\circ \quad (15)$$

The decrease in (ΔG_0) values for zinc sulphate to more negative values with increasing temperature favors the transfer of the released solvent molecules into bulk solvent and leads to a smaller (ΔG_0) values. The positive value of (ΔH_A°), indicates the ion association processes are endothermic in nature. A positive entropy values (ΔS_A°) can be explained on the assumption that iceberg structure around the cation is broken when association takes place leading to an increase in the degree of disorderliness and the positive (ΔH_A°) and (ΔS_A°) values are in a good agreement with several theories in many solvents [16]. Positive values of (ΔH_A°) and (ΔS_A°) for association can be attributed to counterbalance of the enthalpy term by a favorable entropy change resulting from the short- and long-range desolvation of both ions. (ΔS_0) values were positive because of decrease in the solvation of ion-pair compared to that of the free ion [17-19]. This may be attributed to increase in the degree of freedom upon association, mainly due to the release of solvent molecules. The unusual behavior of 10% (DMF-H₂O) mixed solvents may be attributed to less formation of hydrogen bond in this case. Applying Fuoss-Shedlovsky theory here for symmetric electrolytes as zinc sulfate gave variation in calculated data and more easier thermodynamic individual parameters calculations than other theories like Lee, Fuoss Kraus , Fuoss Edleson [11-14] and Fuoss-Hsia-Fernández-Prini theory (FHFP) [20].

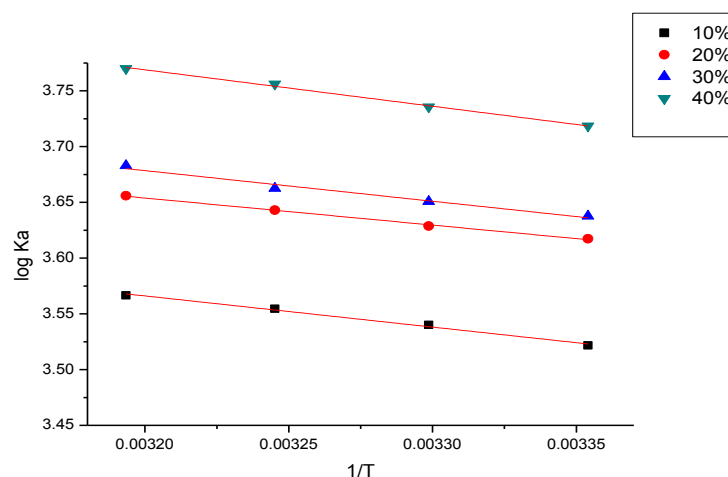


Fig. 5 Relation of ($\log k_a$) vs. ($1/T$) in mixed solvents for zinc sulphate.

Table 4 The thermodynamic parameters of association (ΔG_A° , $\pm 0.33\%$), (ΔH_A° , $\pm 0.22\%$) and (ΔS_A° , $\pm 7.42\%$) for zinc sulphate in used solvents at different temperatures.

Solvent	T/K	ΔH_A°	ΔG_A°	ΔS_A°
		(KJ.mol ⁻¹)	(KJ.mol ⁻¹)	(J.mol ⁻¹)
10% (DMF -H ₂ O)	298.15	5.3529	-20.1041	85.3835
	303.15		-20.5481	85.4399
	308.15		-20.9726	85.4313
	313.15		-21.3854	85.3853
20% (DMF -H ₂ O)	298.15	4.6464	-20.6500	84.8448
	303.15		-21.0631	84.8081
	308.15		-21.4939	84.8302
	313.15		-21.9205	84.8380
30% (DMF -H ₂ O)	298.15	5.2585	-20.7667	87.2893
	303.15		-21.190	87.2479
	308.15		-21.6098	87.1925
	313.15		-22.0824	87.3095
40% (DMF -H ₂ O)	298.15	6.2540	-21.2284	92.1766
	303.15		-21.6831	92.156
	308.15		-22.1623	92.2159
	313.15		-22.6047	92.1564

4. Conclusions

Conductivity measurements for zinc sulphate in (DMF-H₂O) mixtures of 10%, 20%, 30% and 40% at different temperatures have been reported. Thermodynamic parameters (ΔH_0 , ΔG_0 , ΔS_0) were calculated to explain the limiting equivalent conductance (Λ_0) and ion association constant (K_A) by using

Fuoss – Shedlovsky equation. The extent of ion-pairing in zinc sulphate solutions under study depends on the nature of the (ion-solvent) and (solvent-solvent) interaction taking place in the solution. Furthermore, it depends on the relative permittivity and the properties of the medium. The association constant increases as the temperature increases.

Also, the positive values of (ΔH_0) for zinc sulphate show that the association processes are endothermic in nature from the calculated entropy change (ΔS_0).

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