GLOBAL JOURNAL OF ENGINEERING SCIENCE AND RESEARCHES

THERMAL EFFECT OF CONDUCTOMETRIC STUDY OF 2:2 ELECTROLYTES IN BINARY MIXTURE OF WATER WITH N-N DIMETHYLEFORMAMIDE AT 298.15, 303.15, 308.15 K

Ritu Kumrawat*[1], Dr.Kumud Modi[2] & Dr. A.A Ansari[3]
[*1]P.M.B.Gujrati Science College, Indore
[2]P.M.B.Gujrati Science College, Indore, M.P. (INDIA)
[3]I.K. College, Indore, M.P

ABSTRACT

Molar conductivities of dilute solutions of 2:2 electrolytes i.e. $MnSO_4$, $CuSO_4$ and $ZnSO_4$ in binary mixtures of DMF and water were measured in the temperature range from 298.15, 303.15, 308.15 K . The limiting molar conductivity (Λo) were determined by the Lee-Wheaton conductivity equation. For a given dielectric the Λ_0 values for all the salts increases with increasing size of the cation and follow the order $Mn^{++} < Cu^{++} < Zn^{++}$ in DMF + H_2O mixtures

Keywords: *limiting molar conductivity, DMF, Dielectric constant,* $MnSO_4$, $CuSO_4$ *and* $ZnSO_4$*9.*

I. INTRODUCTION

In the investigation of the transport behaviour of the dilute electrolytic solutions many workers [1-8] have explained the concentration dependence of conductance data in terms of continuum theories. According to these theories, the decrease in conductance with increasing solute concentration arises from the electrostriction, relaxation and ionic association. However, these theories have been developed by many [5-8] who interpreted the magnitude of conductance behaviour in terms of ion-ion and ion- solvent interactions ,the vital roles played by the dielectric constant and the viscosity of the medium and the nature of the solute, comprehensive attentions [1-5] has been drawn to the salts of large size, particularly alkali halides and alkali earth sulphates, owing to their excellent solubility characteristics in a wide variety of solvents and their ability to form a homologous series that makes a comparative study feasible.

A thorough review on the sequence of developments of conductance equations revealed that the original Fuoss – Onsager conductance equations have been revised many times by workers like Fuoss and Krauss [9] ,Fuoss- Hasia [10] , Fuoss and Justice [11], Pitts [12] and Fernandez – Prini [13] But the problem of selecting the appropriate conductance equation suggests to review thoroughly the sequence of developments of conductance equation.

According to the Debye –Huckel- Onsager equation [14-16] the equivalent conductance, Λ is given as

$$\Lambda = \Lambda_0 - (\alpha \Lambda_0 + \beta) C^{1/2} \qquad (1)$$

Therefore, it would be of great interest to undertake an analysis of 2:2 electrolytes in terms of Fuoss -1978 and LW equations in order to examine its applicability.

For this purpose, measurements of electrical conductances of 2:2 electrolytes ($MnSO_4$, $CuSO_4$ and $ZnSO_4$) in N-N – Dimethylformamide - water(DMF-H_2O) mixtures of varying dielectric constants ($48.96 \leq D \leq 76.78$) respectively have been made as a function of concentration at 298.15, 303.15 and 308.15^{0}K.

II. EXPERIMENTAL

(1) Chemicals:

Manganese Sulphate, Copper Sulphate, and Zinc Sulphate (BDH, AG) were used as solutes while pure and distilled Dimethylformamide (E. Merck) were used to prepare the solvent mixtures.

(2) Preparation of electrolytic solutions:

All the electrolytic solutions 2: 2 salts were prepared on the basis of weight. Dimethylformamide (DMF) + water ($48.96 \leq D \leq 76.78$) mixtures of varying dielectric constants under study were also prepared. Triply distilled water (specific conductance, $3.6 \times 10^{-6} ohm^{-1}\ cm^{-1}$) was used for preparing different solvent mixtures. Then a weighed amount of solute was dissolved in 25 ml of mixed solvent in a dry vessel. Initially a concentrated electrolytic solution was prepared and solutions of different concentrations were prepared by the method of dilution.

(3) Temperature control:

All the measurements were made at different temperature (298.15^0, 303.15^0 and 308.15^0K) in a double walled thermo-stated water bath with a thermo regulator in order to maintain a uniform temperature. The overall temperature stability was found to be within ± 0.05^0C.

(4) **Measurement of conductance:**

Conductance measurements of all the electrolytic solutions were carried out by Digital Conductivity Meter (611 – EI Products INDIA) at a constant frequency of 1 KH_Z with an accuracy of ± 0.05 to 0.01 %. The Pyrex conductivity cell of cell constant 0.760 cm^{-1} was used having bright platinum disc electrodes containing about 200 ml of solutions. The cell was calibrated by method of Lind and co-workers (44) using the desi-normal potassium chloride solution.

(5) Measurement of density:

A single limbed calibrated pyknometer with a glass bulb capacity of approximately 5.786 ml volume was used for determining the densities of the solvents. The pyknometer stem of 5.5 cm length and 2 mm diameter with uniform graduations of 0.01 ml divisions so that the volume could be read upto 0.005 ml. In order to avoid the effect of air tension inside the pyknometer the cork was open for a while at each reading at corresponding temperatures.

(6) **Measurement of viscosity:**

Cannon-Ubbelohde viscometer was used for the viscosity measurement. It has been calibrated prior to use by the standard method.. The accuracy of calibrated viscometer was checked by measuring the viscosity of triply distilled water at test temperature and compared with those of the reported values . The reproducibility was found to be within ± 0.05 %.

(7) Dielectric constant :

The reported dielectric constant [45, 46] values of the solvent mixtures were used .

III. RESULTS AND DISCUSSION

1. Density and Viscosity of Solvent Mixtures –

The densities, ρ and viscosities, η of DMF + H_20 Solvent mixtures of varying dielectric constants have been measured as a function of weight percent (wt%) of DMF at 298.15, 303.15 and 308.15^0K . The densities of solvent mixtures are found to decrease with increase in wt% of DMF at different temperature. Also the viscosities of the solvent mixtures are found to increase with increase in wt% of DMF due to hydration effect of DMF resulting in an increased solvent structure.

2. Concentration Dependence of Equivalent Conductance -

The electrical conductance of dilute solutions of $MnSO_4$, $CuSO_4$ and $ZnSO_4$ in DMF + H_2O mixtures of various dielectric constant values covering the range ($48.96 \le D \le 76.78$) have been measured as a function of concentration at 298.15, 303.15 and 308.15^0K.The observed values of equivalent conductance, Λ (S cm^2 mol^{-1}) as a function of concentration, C (mol dm^{-3}) are presented in Table- II B(2) for 2:2 symmetrical electrolytes respectively.

The Λvalues have been plotted as a function of $\sqrt{C}$ in fig. – I B (2.1 to 2.15). It is evident from the Onsager plots the decrease in Λ values with increase in solute concentration of all the salts under study is supported by the Debye-Huckel theory. The decrease in ionic mobility with increasing solute concentration has been attributed to the decrease in the free ion concentration as ionic association increases by the action of long - range inter ionic forces.

For a given dielectric constant the conductance of all the salts vary consistently with increasing size of the cation and therefore follows the order $Mn^{++} < Cu^{++} < Zn^{++}$ while the conductance of a given salt decreases with decreasing dielectric constant of the medium. Higher the value of dielectric constant higher is the value of conductance observed, which attributed to the greater ionization of the solute. Lower the dielectric constant, lower is the value of conductance due to the formation of ion - dipolar pair in dipolar associated solvents as observed in present case.

3. Analysis of Conductance Data –

The concentration and temperature dependence of conductance data for $MnSO_4$, $CuSO_4$ and $ZnSO_4$ in DMF + H_2O mixtures have been first analyzed in terms of Fuoss (1978) conductance equation based on the concept of diffusion controlled steady - state approach is of the form,

$$\Lambda = [\, 1 - \alpha\,(1 - \gamma\,)]\,[\, \Lambda_0\,(\, 1 + \Delta X / X\,) + \Delta\, \Lambda_e\,] \qquad (3.1)$$

Table II B (2): -Equivalent Conductance, Λ (S cm^2 mol^{-1}) as a function of Molar concentration C (mol dm^{-3}) of $MnSO_4$, $CuSO_4$, and $ZnSO_4$ in DMF - H_2O mixtures at 298.15^{0}K , 303.15^{0}K,308.15^{0}K

$MnSO_4$				$CnSO_4$				$ZnSO_4$			
C/10^{-4}	Λ			C/10^{-4}	Λ			C/10^{-4}	Λ		
	298.15^{0}K	303.15^{0}K	308.15^{0}K		298.15^{0}K	303.15^{0}K	308.15^{0}K		298.15^{0}K	303.15^{0}K	308.15^{0}K
					10 wt% DMF + H_2O						
821.7	49.7	57.16	66.25	**821.7**	53.20	56.14	58.74	**821.7**	64.97	71.01	78.29
639.1	52.66	60.75	70.21	**547.3**	61.01	64.49	67.16	**586.9**	72.35	78.74	86.39
522.9	55.02	63.60	73.35	**410.7**	66.88	70.80	73.45	**456.4**	78.07	84.62	92.49
442.4	56.96	65.92	75.92	**328.5**	71.60	75.86	78.49	**373.4**	82.70	89.33	97.32
331.8	60.22	69.80	80.23	**271.2**	75.72	80.29	82.88	**316.0**	86.59	93.22	101.28
265.4	62.64	72.68	83.41	**232.4**	79.07	83.90	86.43	**273.8**	89.91	96.52	104.63
221.2	64.54	74.19	85.89	**203.4**	81.98	87.03	89.50	**174.2**	100.22	106.51	114.62
165.9	67.34	78.19	89.54	**180.7**	84.54	89.79	92.21	**127.8**	106.96	112.85	120.83
110.6	70.85	82.27	94.09	**112.9**	94.56	100.63	102.71	**99.36**	112.09	117.57	125.41
88.4	72.56	84.24	96.29	**82.13**	100.97	107.58	109.36	**81.3**	115.94	121.04	128.75
					20 wt% DMF + H_2O						
658.4	28.44	30.07	32.84	**658.4**	34.05	36.05	39.38	**658.4**	50.31	55.82	60.94
438.0	32.30	34.28	37.20	**438**	38.81	40.75	43.69	**470.2**	55.53	61.45	66.87
329.2	35.13	37.37	40.38	**329.2**	42.27	44.16	47.52	**365.7**	59.52	65.74	71.35
263.3	37.39	39.83	42.89	**263.3**	45.01	46.86	50.54	**299.2**	62.73	69.19	74.92
219.0	39.26	41.87	44.98	**219.0**	47.26	49.07	53.02	**253.2**	65.39	72.06	77.86
146.0	43.33	46.32	49.47	**146.0**	52.11	53.86	57.35	**207.1**	68.56	75.45	81.32
109.5	46.11	49.38	52.52	**109.5**	55.39	57.10	61.93	**175.3**	71.16	78.23	84.51
87.6	48.18	51.64	54.78	**87.6**	57.80	59.48	64.55	**125.2**	76.19	83.60	89.51
73.0	49.79	53.42	56.52	**73.0**	59.66	61.32	66.57	**79.6**	82.39	90.17	95.98
62.5	51.09	54.85	59.93	**62.5**	61.16	62.80	68.19	**68.9**	84.19	92.08	97.84
					30 wt% DMF + H_2O						
491.8	30.51	32.63	34.42	**491.8**	31.12	35.09	40.64	**491.8**	36.39	40.35	44.41
327.8	34.47	36.80	39.08	**327.8**	35.82	39.90	45.54	**351.2**	40.48	44.59	49.19
245.8	37.42	39.89	42.52	**245.8**	39.35	43.44	49.03	**273.2**	43.61	47.83	52.81
196.6	39.76	42.33	45.22	**196.6**	42.17	46.21	51.68	**223.5**	46.12	50.47	55.72
163.8	41.69	44.33	47.43	**163.8**	44.50	48.47	53.79	**189.1**	48.22	52.65	58.11
140.4	43.33	46.03	49.29	**140.4**	46.48	50.36	55.55	**163.9**	50.01	54.52	60.14
105.3	46.33	49.14	52.70	**122.8**	48.21	51.99	57.00	**117.1**	54.12	58.81	64.77
84.2	48.61	51.48	55.26	**109.2**	49.72	53.39	58.25	**91.0**	57.07	61.90	68.05
56.1	52.51	55.47	59.61	**78.2**	53.93	57.23	61.57	**63.0**	61.08	66.12	72.46
42.1	55.04	58.03	62.38	**60.1**	57.13	60.07	63.94	**48.1**	63.74	68.93	75.36

Table II (B) 2 :- Continued

MnSO$_4$				CnSO$_4$				ZnSO$_4$			
C/10^{-4}	Λ			C/10^{-4}	Λ			C/10^{-4}	Λ		
	298.15^{0}K	303.15^{0}K	308.15^{0}K		298.15^{0}K	303.15^{0}K	308.15^{0}K		298.15^{0}K	303.15^{0}K	308.15^{0}K
50 wt% DMF + H$_2$O											
382.2	13.24	11.92	11.76	**382.2**	12.96	15.32	18.66	**382.0**	17.53	24.52	25.51
286.5	14.61	13.26	13.21	**254.6**	15.16	17.48	20.48	**272.8**	19.17	26.08	27.93
229.2	15.70	14.48	14.43	**190.9**	16.86	19.13	21.79	**212.2**	20.38	27.28	29.75
191.0	16.62	15.48	15.49	**152.7**	18.26	20.48	22.79	**141.4**	22.29	29.22	32.66
127.3	18.72	17.87	18.04	**127.3**	19.44	21.59	23.59	**106.1**	23.59	30.54	34.64
95.4	20.22	19.66	19.99	**84.8**	22.21	24.15	25.31	**70.7**	25.26	32.27	37.23
76.3	21.36	21.11	21.57	**63.6**	24.23	25.96	26.43	**47.2**	26.73	33.81	39.53
63.6	22.27	22.30	22.89	**50.9**	25.81	27.34	27.23	**40.3**	27.24	34.34	40.34
47.7	23.67	24.19	25.03	**42.4**	27.11	28.44	27.85	**35.2**	27.65	34.78	40.99
33.1	25.30	26.57	27.75	**36.3**	28.20	29.36	28.34	**31.3**	28.00	35.13	41.53
60 wt% DMF + H$_2$O											
303.8	14.80	16.64	18.26	**303.8**	19.27	21.75	25.02	**303.8**	14.50	16.59	19.63
227.0	16.55	18.58	20.31	**202.5**	22.18	24.61	28.07	**182.2**	17.97	20.50	23.78
182.0	17.97	20.15	21.96	**151.9**	24.37	26.76	30.28	**130.2**	20.60	23.45	26.79
151.9	19.19	21.49	23.36	**130.2**	25.58	27.94	31.46	**86.8**	24.15	27.41	30.68
101.0	22.12	24.69	26.67	**97.0**	27.94	30.24	33.69	**65.1**	26.92	30.47	33.55
75.0	24.37	27.15	29.16	**78.1**	29.69	31.94	35.29	**52.0**	29.20	32.98	35.84
60.0	26.11	29.02	31.04	**55.0**	32.51	34.64	37.74	**43.4**	31.11	35.07	37.68
50.0	27.55	30.56	32.57	**43.4**	34.37	36.41	39.28	**37.2**	32.80	36.90	39.24
33.0	30.82	34.03	35.98	**39.0**	35.19	37.17	39.94	**32.5**	34.30	38.52	40.61
28.0	32.10	35.38	37.27	**32.0**	36.66	38.55	41.10	**28.8**	35.67	40.00	41.81

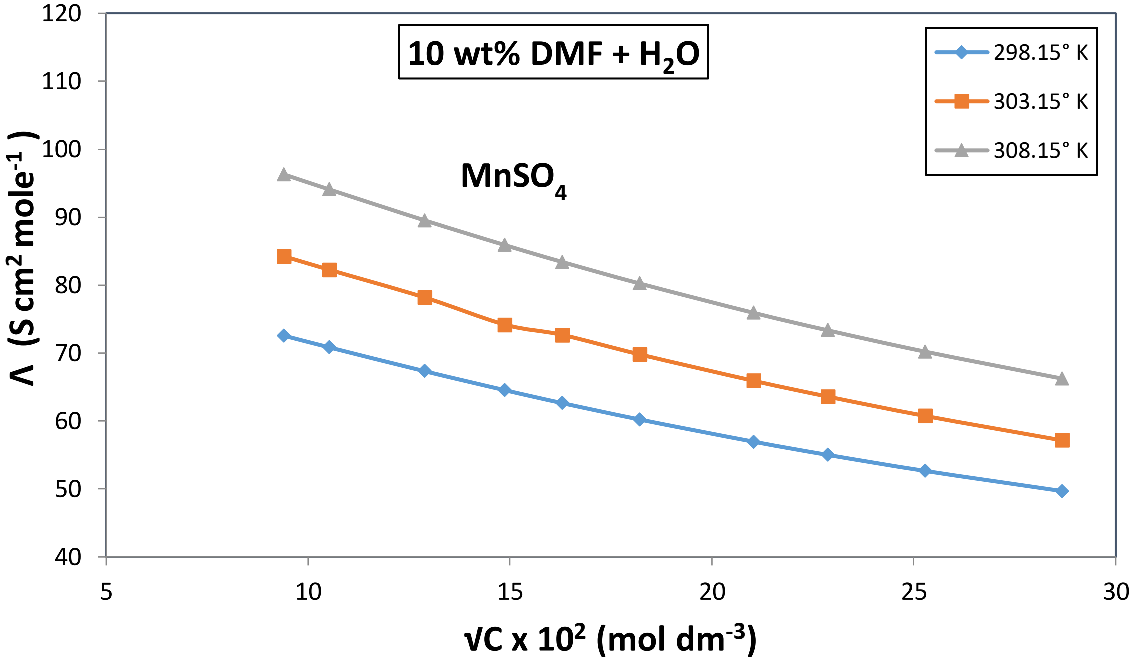

Fig. I B (2.1):-Plot of Λ vs √C for $MnSO_4$ in DMF-H_2O Mixture

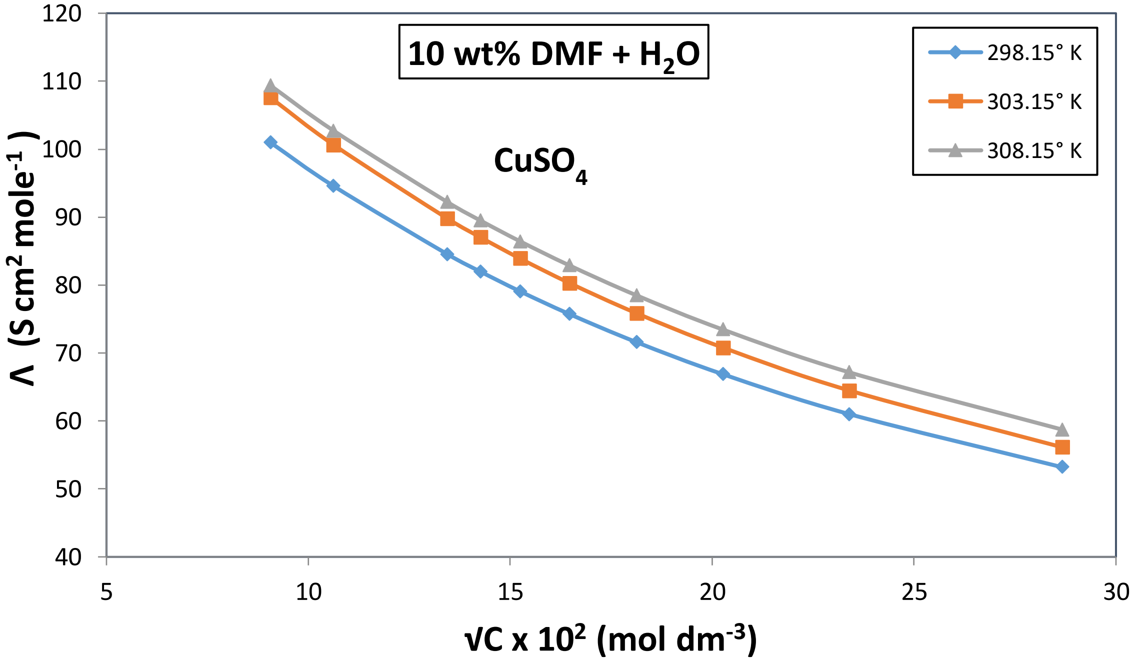

Fig. I B (2.2):-Plot of Λ vs √C for $CuSO_4$ in DMF-H_2O Mixture

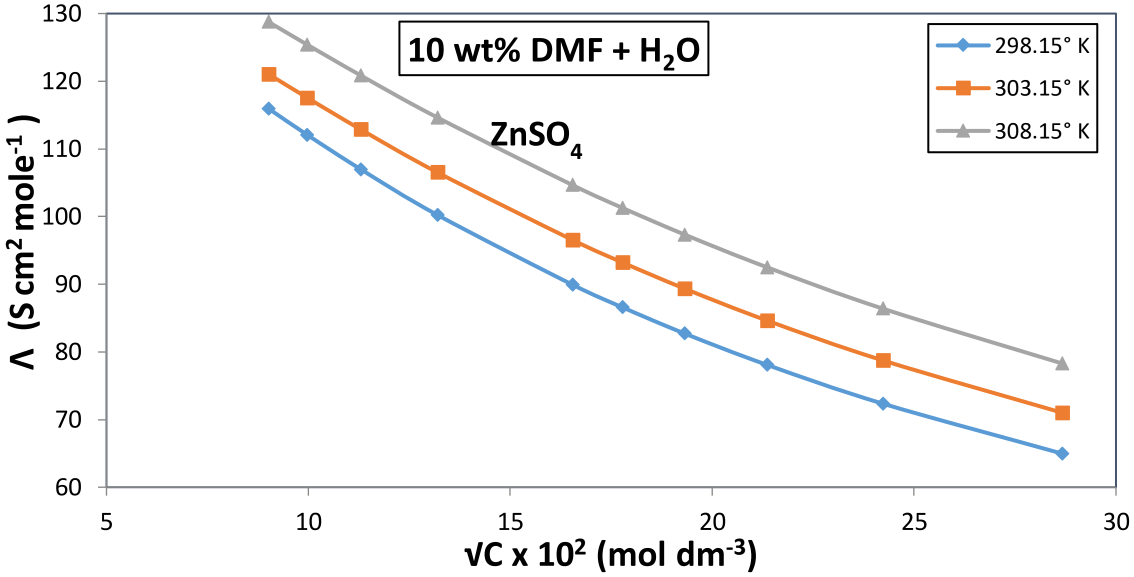

Fig. I B (2.3):-Plot of Λ vs.√C for $ZnSO_4$ in DMF-H_2O Mixture

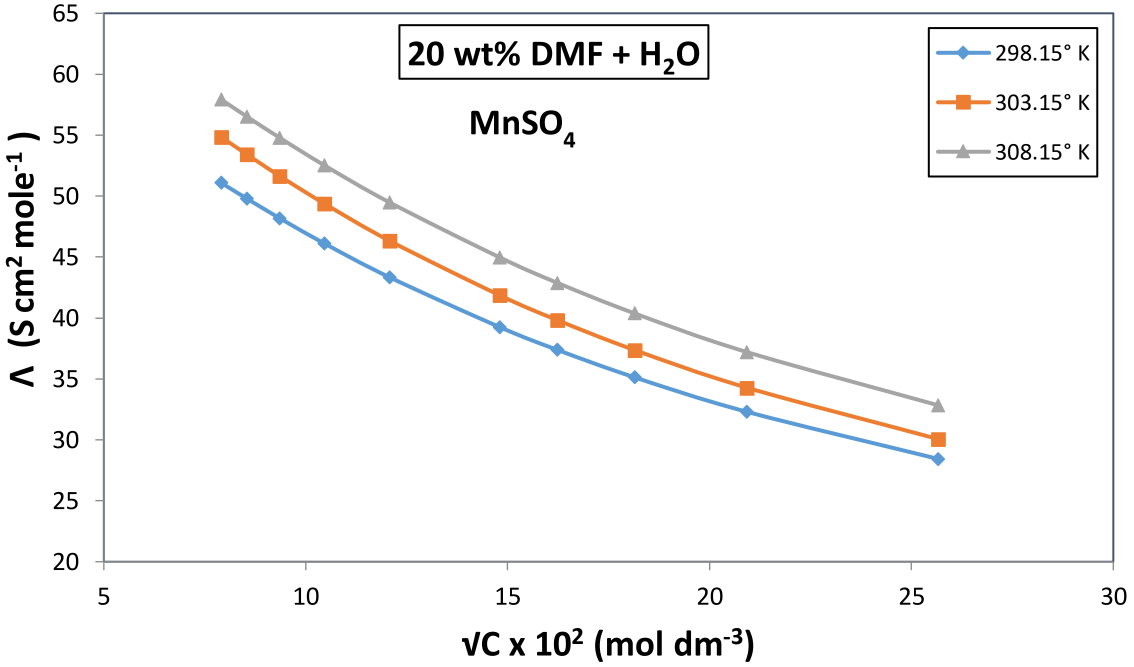

Fig. I B (2.4):-Plot of Λ vs.√C for $MnSO_4$in DMF-H_2O Mixture

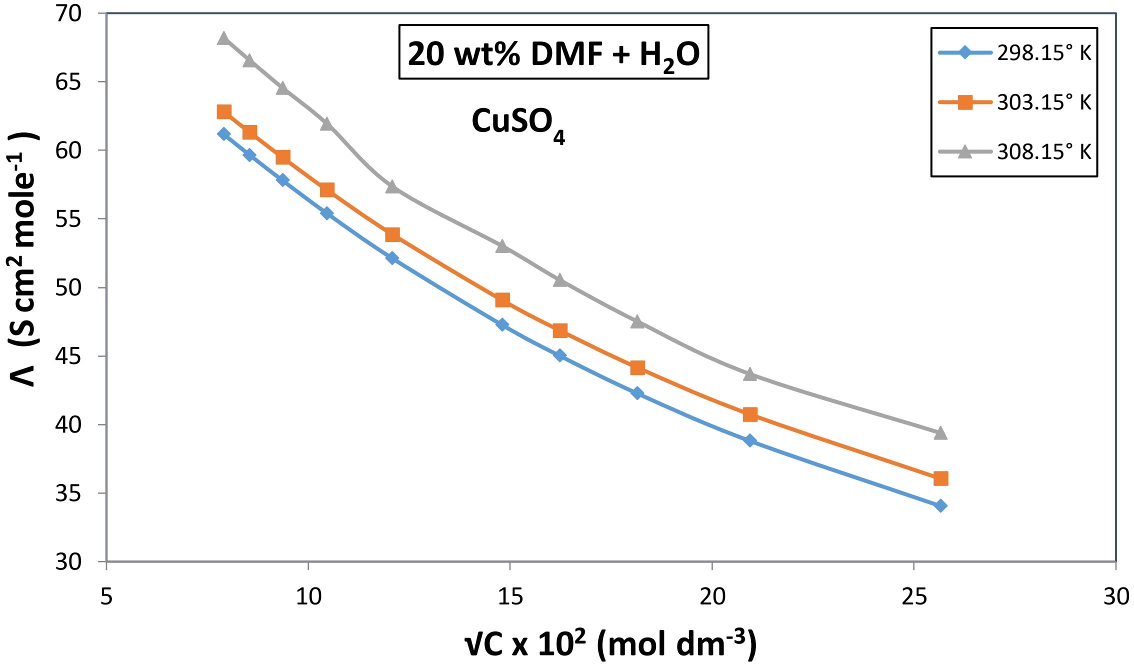

Fig. I B (2.5):-Plot of Λ vs.√C for $CuSO_4$ in DMF-H_2O Mixture

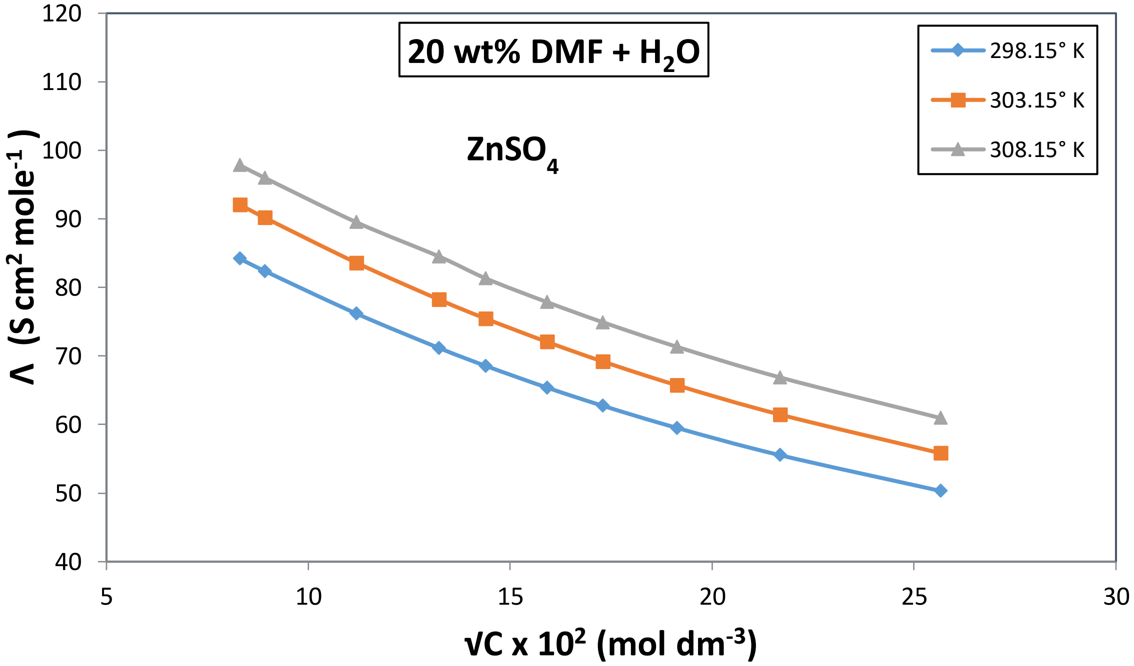

Fig. I B (2.6):-Plot of Λ vs.√C for $ZnSO_4$ in DMF-H_2O Mixture

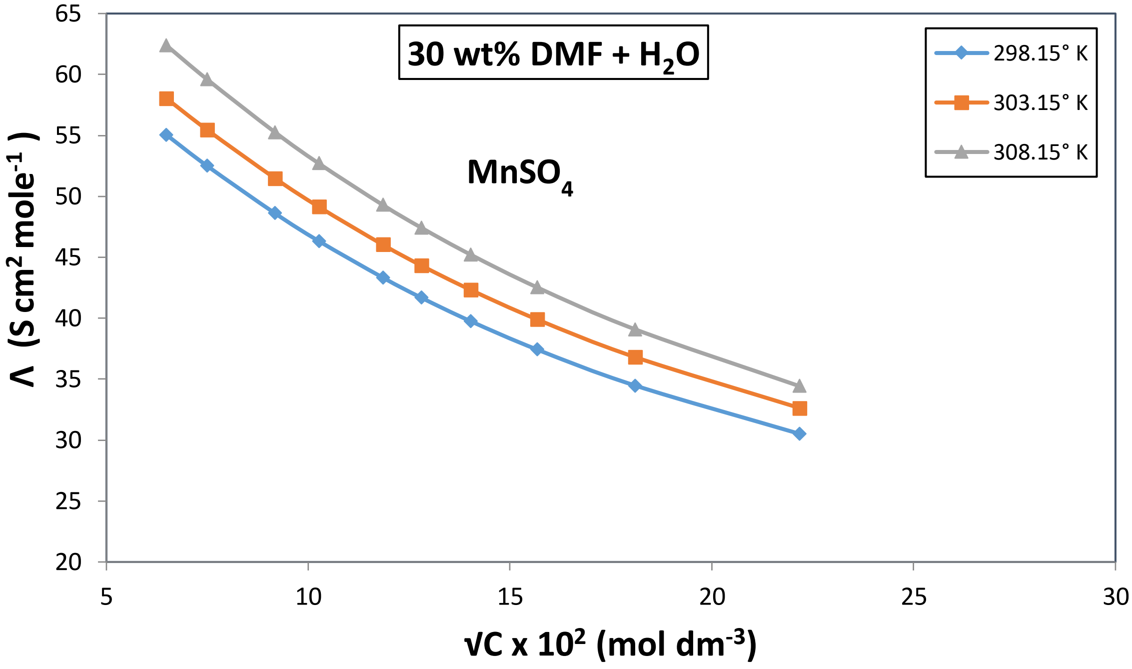

Fig. I B (2.7):-Plot of Λ vs.√Cfor $MnSO_4$in DMF-H_2O Mixture

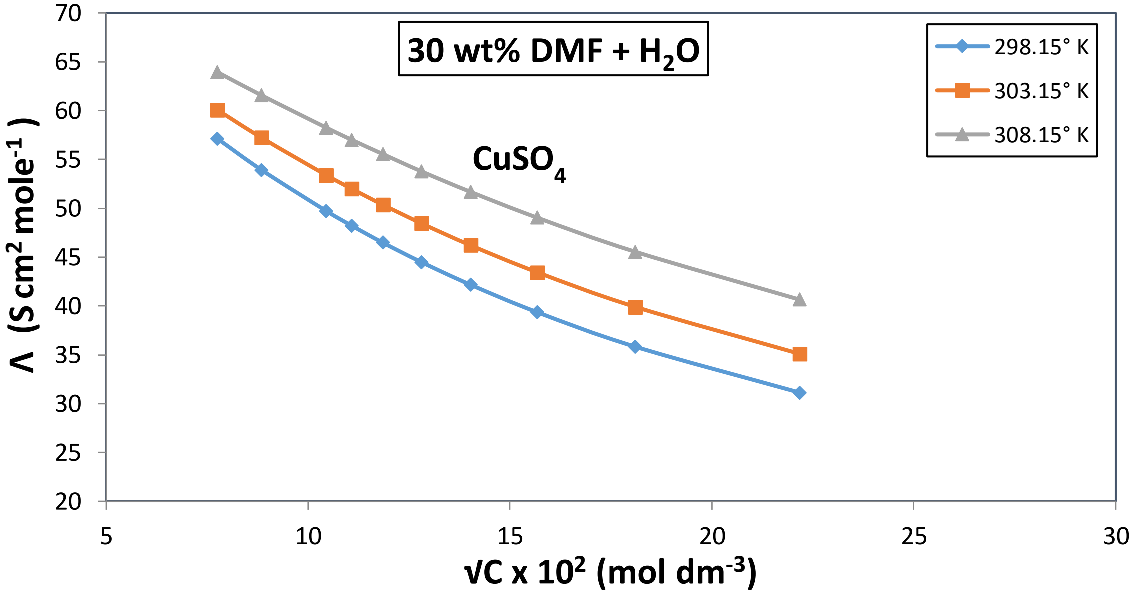

Fig. I B (2.8):-Plot of Λ vs.√C for $CuSO_4$ in DMF-H_2O Mixture

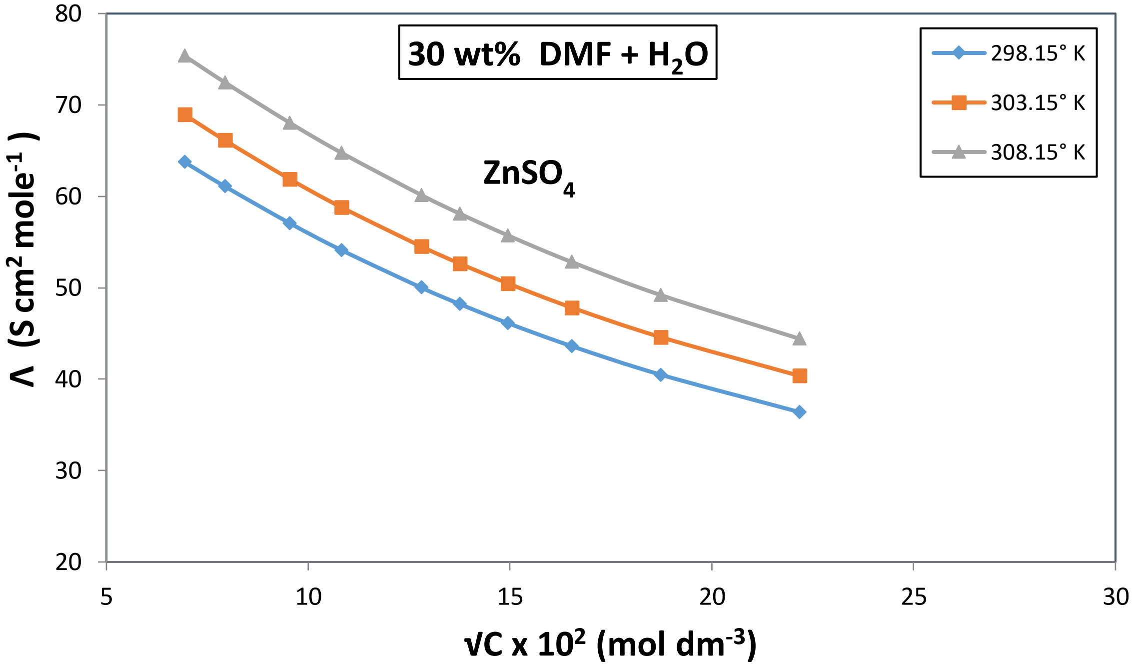

Fig. I B (2.9):-Plot of Λ vs.√Cfor $ZnSO_4$ in DMF-H_2O Mixture

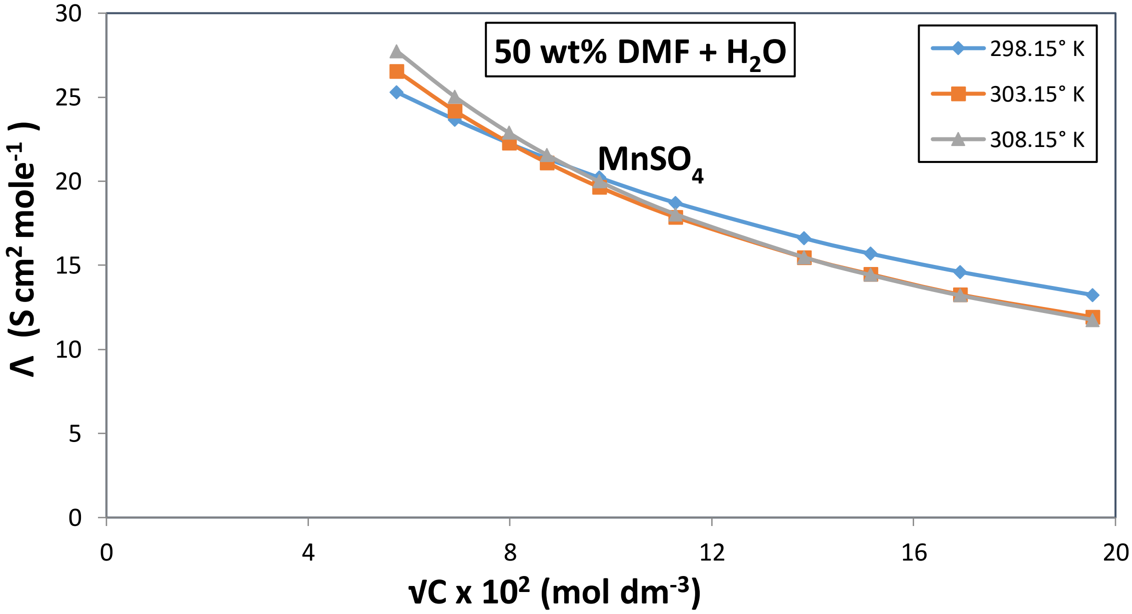

Fig. I B (2.10):-Plot of Λ vs.√Cfor $MnSO_4$in DMF-H_2O Mixture

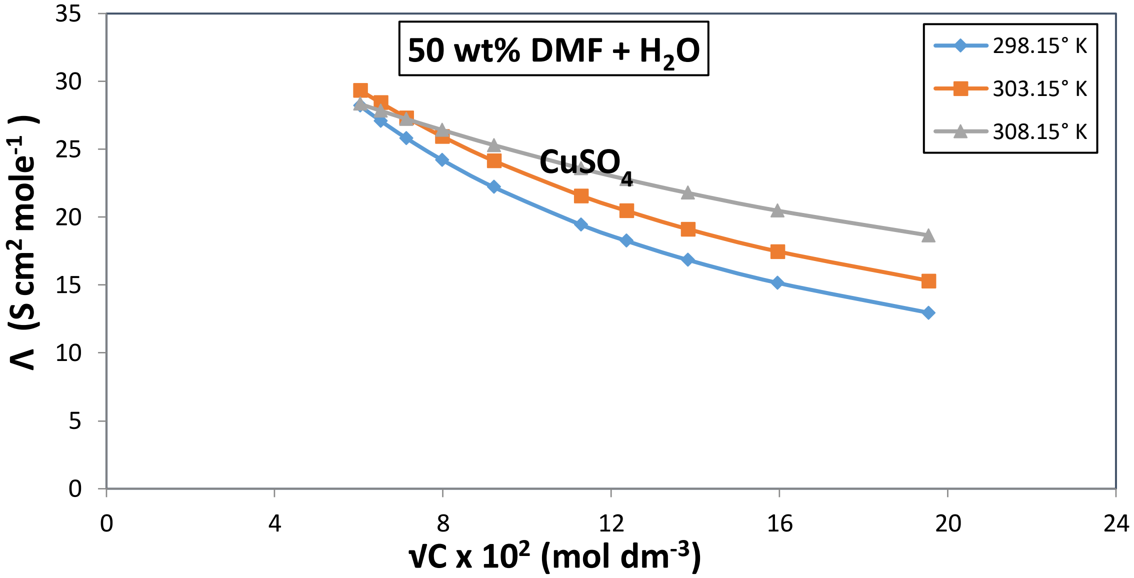

Fig. I B (2.11):-Plot of Λ vs.√Cfor $CuSO_4$ in DMF-H_2O Mixture

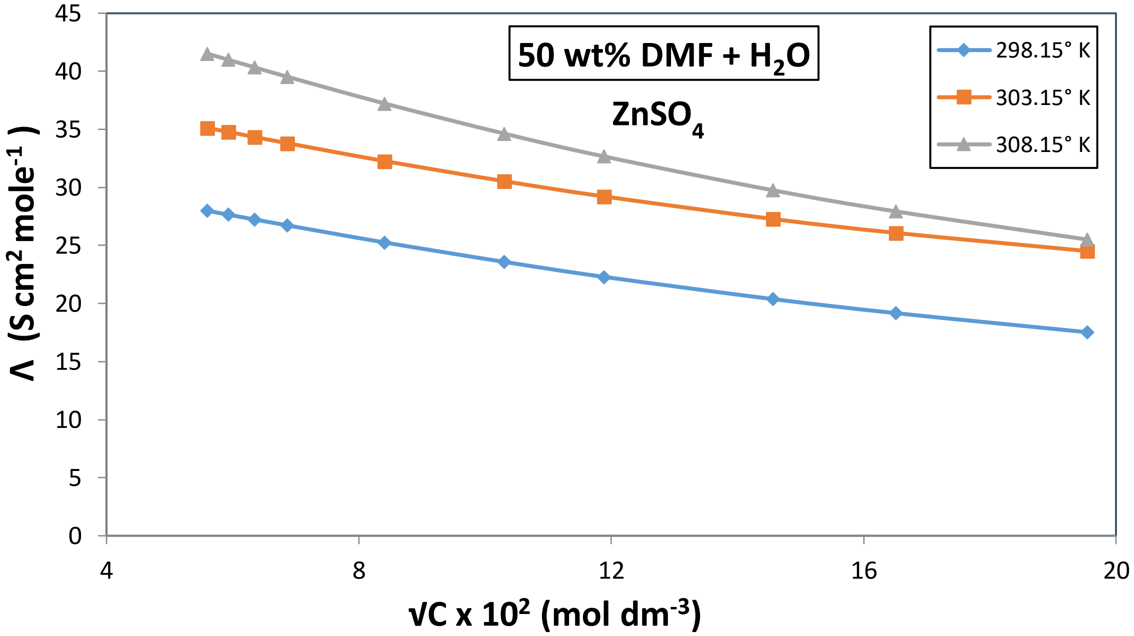

Fig. I B (2.12):-Plot of Λ vs.√Cfor $ZnSO_4$ in DMF-H_2O Mixture

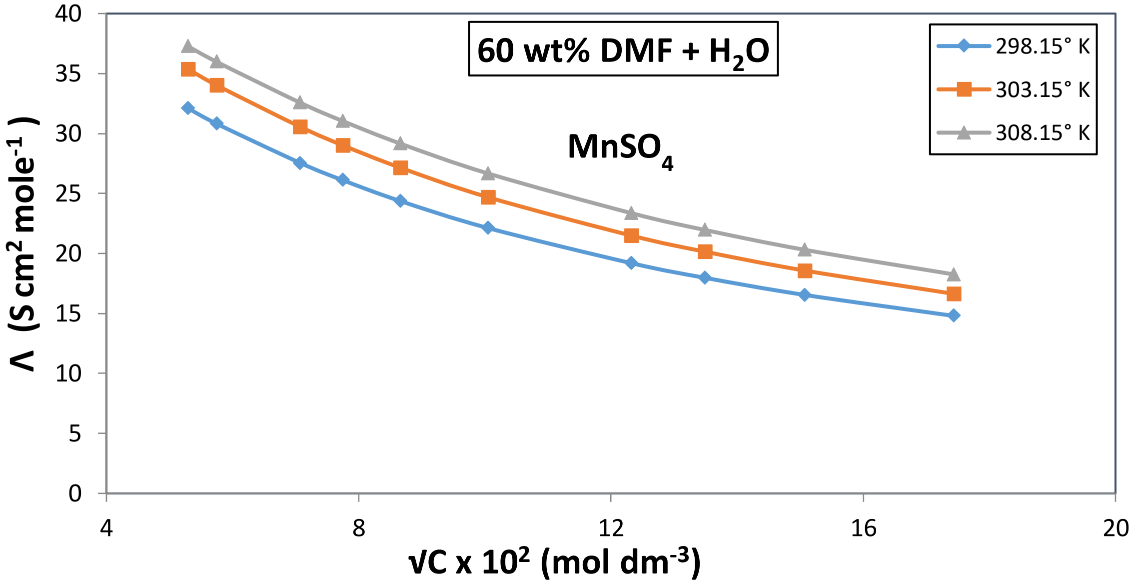

Fig. I B (2.13):-Plot of Λ vs.√Cfor $MnSO_4$in DMF-H_2O Mixture

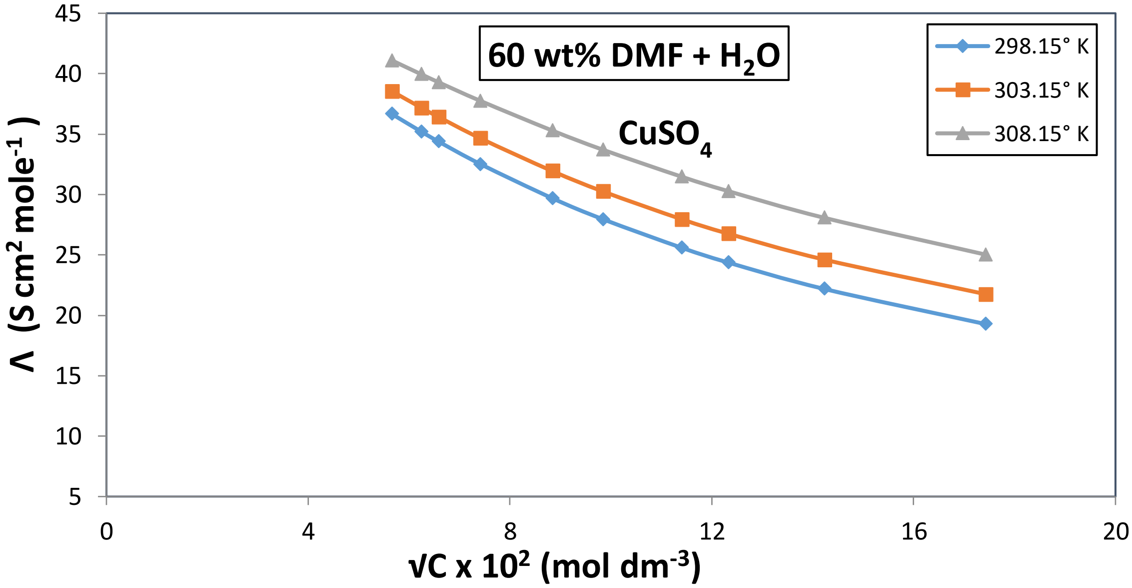

Fig. I B (2.14):-Plot of Λ vs.√Cfor $CuSO_4$ in DMF-H_2O Mixture

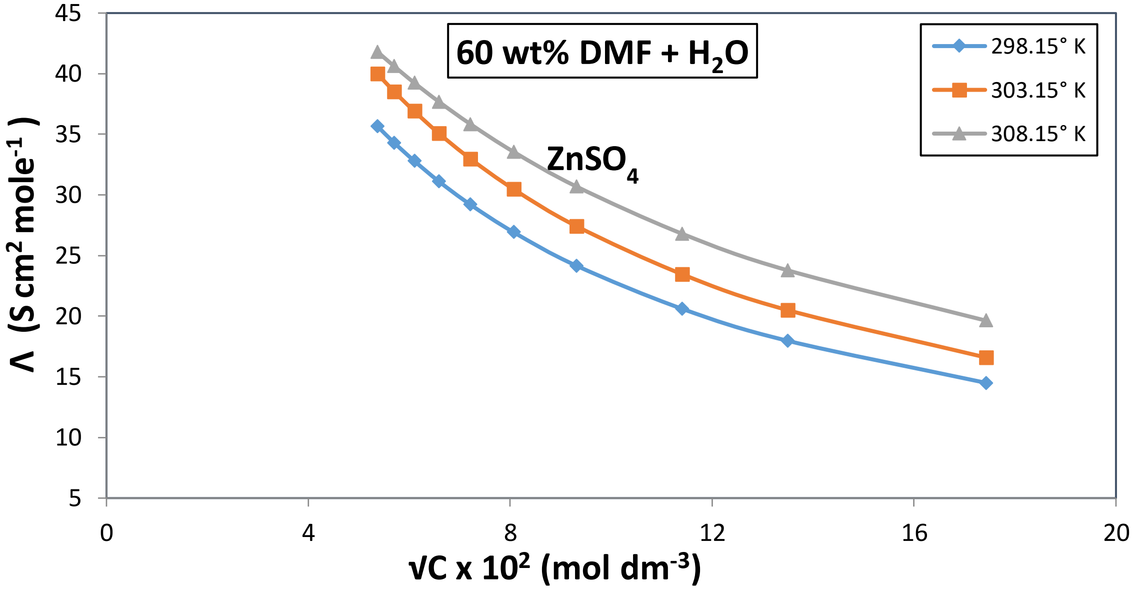

Fig. I B (2.15):-Plot of Λ vs.√C for $ZnSO_4$ in $DMF-H_2O$ Mixture

where Λ_0 stands for the limiting equivalent conductance and the term $\Delta X/X$ represents the relaxation effect, $\Delta \Lambda_e$ the electrophoretic effect, while γ denotes the fraction of solute present as free ions and α is the contact pair parameter. Both ΔX and $\Delta \Lambda_e$ depends on the values of the diameter of Gurney co-sphere (R), dielectric constant D, temperature and viscosity η, of the solvent mixtures. The parameters and auxiliary variables are related by a set of following equations,

$$K_R = (1-\alpha)\,(1-\gamma)/\,c\gamma^2\, f^{\,2}$$

$K_R = (1-\alpha)\,(1-\gamma)\,/c\gamma^2 f^2$

$= (4\pi N R^3 / 3000)\exp(\beta/R)$ (3.2)

$K_s = \alpha/(1-\alpha)$ (3.3)

Where K_R, describes the formation and separation constant of solvent separated ion - pairs by diffusion in and out of spheres of diameter (R) around the cations and K_s is the contact ion - pair formation constant describing the short - range process in which dipolar pairs form and dissociate, while γ denotes the fraction of solute present as free ion, α is the contact pair parameter, f is the activity coefficient and C is the molar concentration.

The conductometric pairing constant, K_A is given by,

$$K_A = 1-\gamma/c\gamma^2 f_{\pm}^{2} \qquad (3.4)$$

The activity coefficient is given by

$$-\ln f = \beta \mathbf{K}/2(1+\mathbf{K}R) \qquad (3.5)$$

Where $\beta = e^2/DkT$

and $\mathbf{K}^2 = 8\pi\beta\gamma\eta = \pi\beta N\gamma C/125$

[Kumrawat, 6(3): March 2019]
DOI- 10.5281/zenodo.2588727

ISSN 2348 – 8034
Impact Factor- 5.070

The equation (3.1) to (3.5) have been used to find the values of three parameters (Λ_0 , K_A,R) for symmetrical electrolytes where $\gamma < 1$ and $K_A > 0.0$ which minimize the squares of the difference between observed conductance and those calculated by an equation of this form ,

$$\sigma^2_\Lambda = \Sigma^n_1 [\ \Lambda_{(cal)} - \Lambda_{(obs)}\ ]^2 / (n\text{-}p) \qquad (3.6)$$

Where, ‘n’ is the number of data points and ‘p’ is the number of parameters. The initial values of limiting equivalent conductance, Λ_0 used in the Fuoss method of analysis were obtained employing shedlovsky’s method [17] of extrapolation of the original data . The values of Λ_0 have been computed for each of the sequence of R- values of minimizing the standard deviation, $\sigma_{\Lambda.}$

The computed values of R which depend on the dielectric constant of the medium are used to find the value of R_{min} for each salt in order to obtain the final of R. Thus, in order to treat the data for R_{min} values, R will therefore be arbitrary present at the centre-to-centre distance of solvent separated pair for the system of higher dielectric constant.

$$R = a + ds \qquad \text{If } (a + ds) > \beta/2$$

Where, ‘α’ is a sum of the crystallographic radii of the ions and ‘ds’ is an average distance corresponding to the size of a cell occupied by a solvent molecule. The distance ‘ds’ is given by

$$ds = (\overline{M}\ /N\ \rho)^{1/3} = 1.183[(\overline{M}\ /\ \rho)^{1/3} A^0\ ]$$

Where M is the mean molecular weight of the solvent mixtures and ρ is the density, for the system of lower dielectric constant,

$$R = \beta/2 \qquad \text{If } (a + ds) < \beta/2$$

The computer values of the adjustable parameters Λ_0 , K_A and R along with those of σ_Λ% thus obtained are listed in Table – III A(3.1,3.2) and Table – III B(3.1,3.2) .

Similarly, each set of conductance data has been analyzed using Lee- Wheaton (LW) conductance equation [34,35] based on the Gurney co-sphere model is of the form ,

$$\Lambda = \gamma\Lambda_0\ [1+C_1(K\,R)(\beta K) + C_2(K\,R)(\beta K)^2 + C_3(KR)\ (\beta K)^3] - \rho K/(1+KR)\ \ [1 + C_4(KR)\ (\beta K) + C_5(KR)\ (\beta K)^2 + KR/12] \quad (3.7)$$

Where $\rho = |Z|\ Fe/(299.79x3\pi\eta)$, $\beta = Z^2e^2/\ DkT$,
R is the distance parameter, K is proportionate to $(\gamma C)^{1/2}$ and all other symbols have their usual meanings. The coefficient of C_1- C_5 are complex functions of $[(K\,R = 8\pi Ne^2|Z|^2\gamma C/\ 1000\ DkT)^{1/2}]$.

$$f\pm^{\,2} = \exp\,[-\ \beta\ K\ /\ (1+K\,R)]$$

$$K_A = 1 - \gamma / C\gamma^2 f_\pm^{\,2}$$

and

$$\gamma = [(1+4\ K_A C f\pm^{\,2}\,)^{1/2} - 1]\ /\ 2K_A C f\pm^{\,2}$$

The computed values of the best-fit parameters of the limiting equivalent conductance , Λ_0 , association constant , K_A and the distance parameter R along with σ_Λ% which correspond to minimum standard deviation from F-78 and LW conductance equation for 2:2 electrolytes in DMF + H_20 mixtures are listed in Table – III A (3.1 & 3.2) and Table – III B (3.1 & 3.2) respectively.

Limiting Equivalent Conductance –

The computed values of limiting equivalent conductances Λ_0 for all the 2:2 electrolytes in various DMF+H_2O mixtures are presented in Table- III B (3.1 & 3.2) respectively. It is seen that the Λ_0 values appear to follow the order similar to those of the Λ i.e. $Mn^{++} < Cu^{++} < Zn^{++}$ for 2:2 electrolytes . Moreover , the variation of Λ_0 values for 2:2 salts in all the DMF+H_2O has been found to resemble those of their corresponding Λ values at all temperature under study . It is also appears that the Λ_0 values show a consistent variation with dielectric constant of the medium i.e. decreases with decrease in the dielectric constant of the medium.

Association Constant –

The computed values of association constant K_A for all the salts under study are given in Table- III B (3.1 & 3.2). An examination of these values reveals that the ionic association obtained through F-78 equation differs in significance than those obtained from LW equation. The increase in ionic association appears to increase with the decrease in dielectric constant of the medium. Furthermore, a perusal of Table-III B (3.1 & 3.2) reveals that the K_A values for 2:2 salts in a given dielectric medium decrease with increasing size of the cations in the dielectric range ($48.96 \leq D \leq 76.78$) and follows the order $Mn^{++}.> Cu^{++} < Zn^{++}$ respectively. This anomalous behaviour of K_A values in the DMF + H_2O mixture may be ascribed to the predominant solvation of cations due to increase in the charge density with decrease in size as observed in other aqueous and aquo-organic solutions [39].

Table III B(3.1):-Best fit parameters for $MnSO_4$, $CuSO_4$, $ZnSO_4$ in DMF - H_2O mixtures at 298.15^{0}K , 303.15^{0}K,308.15^{0}K using the F78 Equation.

SALT	TEMP (^{O}K)	Λ_0 (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	R (A^o)	σ_Λ%
		10 wt% DMF + H_2O			
$MnSO_4$	298.15	84.52 ± 0.07	41.60	3.76	0.08
	303.15	98.20 ± 0.02	31.70	3.68	0.02
	308.15	111.45 ± 0.07	26.20	3.48	0.05
$CuSO_4$	298.15	137.91 ± 0.01	38.40	3.50	0.01
	303.15	143.03 ± 0.04	24.70	3.52	0.01
	308.15	145.97 ± 0.17	18.10	3.28	0.06
$ZnSO_4$	298.15	148.21 ± 0.07	13.50	3.16	0.02
	303.15	148.45 ± 0.02	15.20	3.22	0.02
	308.15	154.57 ± 0.04	13.20	3.12	0.02
		20 wt% DMF + H_2O			
$MnSO_4$	298.15	65.36 ± 0.01	52.20	4.58	0.06
	303.15	70.68 ± 0.02	48.50	4.30	0.02
	308.15	72.91 ± 0.04	47.40	4.59	0.02
$CuSO_4$	298.15	77.023 ± 0.09	50.30	4.25	0.05
	303.15	78.38 ± 0.03	38.30	4.12	0.02
	308.15	85.11 ± 0.04	46.90	3.95	0.02
$ZnSO_4$	298.15	104.57 ± 0.01	32.99	4.12	0.05
	303.15	113.15 ± 0.06	38.80	3.96	0.03
	308.15	117.96 ± 0.04	33.00	3.54	0.02
		30 wt% DMF + H_2O			
$MnSO_4$	298.15	68.54 ± 0.17	97.90	5.72	0.08
	303.15	71.54 ± 0.19	65.80	5.26	0.09
	308.15	77.82 ± 0.02	66.40	5.34	0.01
$CuSO_4$	298.15	80.27 ± 0.08	67.40	5.47	0.03
	303.15	78.20 ± 0.02	52.80	5.20	0.01
	308.15	78.72 ± 0.04	61.10	4.96	0.02
$ZnSO_4$	298.15	79.27 ± 0.03	61.70	5.22	0.02
	303.15	85.46 ± 0.05	56.10	4.68	0.03
	308.15	91.99 ± 0.02	40.48	4.96	0.01

Table III B (3.2) :-Continued

SALT	TEMP (^{O}K)	Λ_0 (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	R (A^o)	σ_Λ%
50 wt% DMF + H_2O					
$MnSO_4$	298.15	48.76 ± 0.07	230.20	6.86	0.02
	303.15	52.26 ± 0.25	102.40	6.57	0.10
	308.15	51.03 ± 0.10	96.20	6.80	0.08
$CuSO_4$	298.15	50.70 ± 0.04	95.60	6.56	0.02
	303.15	50.32 ± 0.15	79.50	6.18	0.04
	308.15	52.63 ± 0.11	49.10	6.67	0.02
$ZnSO_4$	298.15	70.73 ± 0.01	68.40	6.25	0.01
	303.15	74.84 ± 0.148	59.80	5.98	0.16
	308.15	62.96 ± 0.04	44.90	6.17	0.04
60 wt% DMF + H_2O					
$MnSO_4$	298.15	32.72 ± 0.10	273.20	8.25	0.03
	303.15	39.50 ± 0.05	220.40	8.18	0.02
	308.15	33.65 ± 0.05	172.60	7.80	0.01
$CuSO_4$	298.15	36.41 ± 0.03	155.00	7.70	0.01
	303.15	43.36 ± 0.24	99.90	7.60	0.10
	308.15	45.66 ± 0.07	60.90	7.40	0.05
$ZnSO_4$	298.15	43.72 ± 0.16	87.60	6.86	0.02
	303.15	56.42 ± 0.09	66.90	6.78	0.01
	308.15	49.04 ± 0.05	53.50	6.98	0.02

Table III B(3.2):-Best fit parameters for $MnSO_4$,$CuSO_4$,$ZnSO_4$ in DMF-H_2O mixtures at 298.15^{0}K ,303.15^{0}K,308.15^{0}K using LW Equation.

SALT	TEMP (^{O}K)	Λ_0 (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	R (A^o)	σ_Λ%
10 wt% DMF + H_2O					
$MnSO_4$	298.15	84.95 ± 0.07	40.17	3.80	0.07
	303.15	98.12 ± 0.02	30.70	3.70	0.01
	308.15	111.83 ± 0.02	25.40	3.64	0.02

$CuSO_4$	298.15	137.827 ± 0.06	36.80	3.65	0.06
	303.15	142.85 ± 0.04	24.10	3.42	0.02
	308.15	146.58 ± 0.11	18.20	3.34	0.04
$ZnSO_4$	298.15	148.005 ± 0.01	15.20	3.26	0.08
	303.15	148.28 ± 0.03	15.50	3.20	0.02
	308.15	154.32 ± 0.04	14.50	3.18	0.03
		20 wt% DMF + H_2O			
$MnSO_4$	298.15	65.417 ± 0.04	52.93	4.85	0.02
	303.15	70.61 ± 0.03	50.40	4.34	0.02
	308.15	73.01 ± 0.03	47.90	4.24	0.02
$CuSO_4$	298.15	76.941 ± 0.01	48.97	4.38	0.05
	303.15	78.50 ± 0.02	36.52	4.15	0.02
	308.15	84.99 ± 0.04	28.10	4.10	0.02
$ZnSO_4$	298.15	104.528 ± 0.07	33.24	4.15	0.03
	303.15	113.33 ± 0.05	38.80	3.85	0.03
	308.15	117.93 ± 0.04	33.20	3.58	0.02
		30 wt% DMF + H_2O			
$MnSO_4$	298.15	69.30 ± 0.02	95.30	5.72	0.01
	303.15	72.36 ± 0.05	67.60	5.40	0.03
	308.15	77.76 ± 0.02	66.10	5.34	0.01
$CuSO_4$	298.15	80.18 ± 0.08	72.50	5.47	0.03
	303.15	78.59 ± 0.04	58.20	5.16	0.02
	308.15	78.08 ± 0.02	50.60	5.10	0.01
$ZnSO_4$	298.15	79.31 ± 0.05	50.40	5.12	0.03
	303.15	85.60 ± 0.03	57.40	4.86	0.02
	308.15	91.87 ± 0.02	39.65	4.95	0.01

Table III B (3.2): - Continued

SALT	**TEMP (^{O}K)**	**Λ_0 (S cm^2 mol^{-1})**	**K_A (dm^3 mol^{-1})**	**R (A^o)**	**σ_Λ%**
		50 wt% DMF + H_2O			
$MnSO_4$	298.15	48.74 ± 0.08	169.20	6.56	0.02

	303.15	51.26 ± 0.02	119.30	6.87	0.01
	308.15	51.64 ± 0.01	110.91	6.72	0.01
$CuSO_4$	298.15	50.78 ± 0.03	99.35	6.25	0.01
	303.15	52.50 ± 0.13	72.15	6.65	0.03
	308.15	52.36 ± 0.11	62.70	6.58	0.02
$ZnSO_4$	298.15	70.31 ± 0.01	62.99	5.86	0.01
	303.15	74.61 ± 0.03	61.50	6.18	0.04
	308.15	63.57 ± 0.03	44.08	6.25	0.03
		60 wt% DMF + H_2O			
$MnSO_4$	298.15	33.67 ± 0.11	269.30	7.25	0.03
	303.15	38.69 ± 0.05	226.40	7.18	0.02
	308.15	34.15 ± 0.06	176.40	6.87	0.02
$CuSO_4$	298.15	38.96 ± 0.04	154.50	6.97	0.02
	303.15	40.75 ± 0.07	111.50	6.75	0.04
	308.15	45.69 ± 0.05	76.35	6.54	0.04
$ZnSO_4$	298.15	52.71 ± 0.14	86.60	6.56	0.01
	303.15	54.61 ± 0.08	79.65	6.36	0.01
	308.15	49.18 ± 0.04	48.63	6.26	0.01

Moreover, an increase in ionic association with increasing proportion of N,N- dimethylformamide (DMF) may be described to the predominant solvation of cations with one of the solvent molecules (DMF), which control the extent of ion-pairing. The ionic association decrease with increase in temperature for 2:2 salts in dielectric range (48.96 ≤ D ≤ 76.78).

However, the association constants obtained for all the salts (1:1 & 2:2) from F-78 and LW conductance equations are an exponential function of the dielectric constant of the medium and therefore, expressed in the following form,

$$K_A = K^0A \exp (e^2/R\,DkT) \qquad (3.7)$$

The linear plot of log$K_A$vs 1 /D [Fig.II B(3.1, 3.2,3.3)] in DMF+H_2O mixtures as reported in other solvent mixtures [45] and this linearity of the plots suggest the applicability of Bjerrum theories of ionic – association.

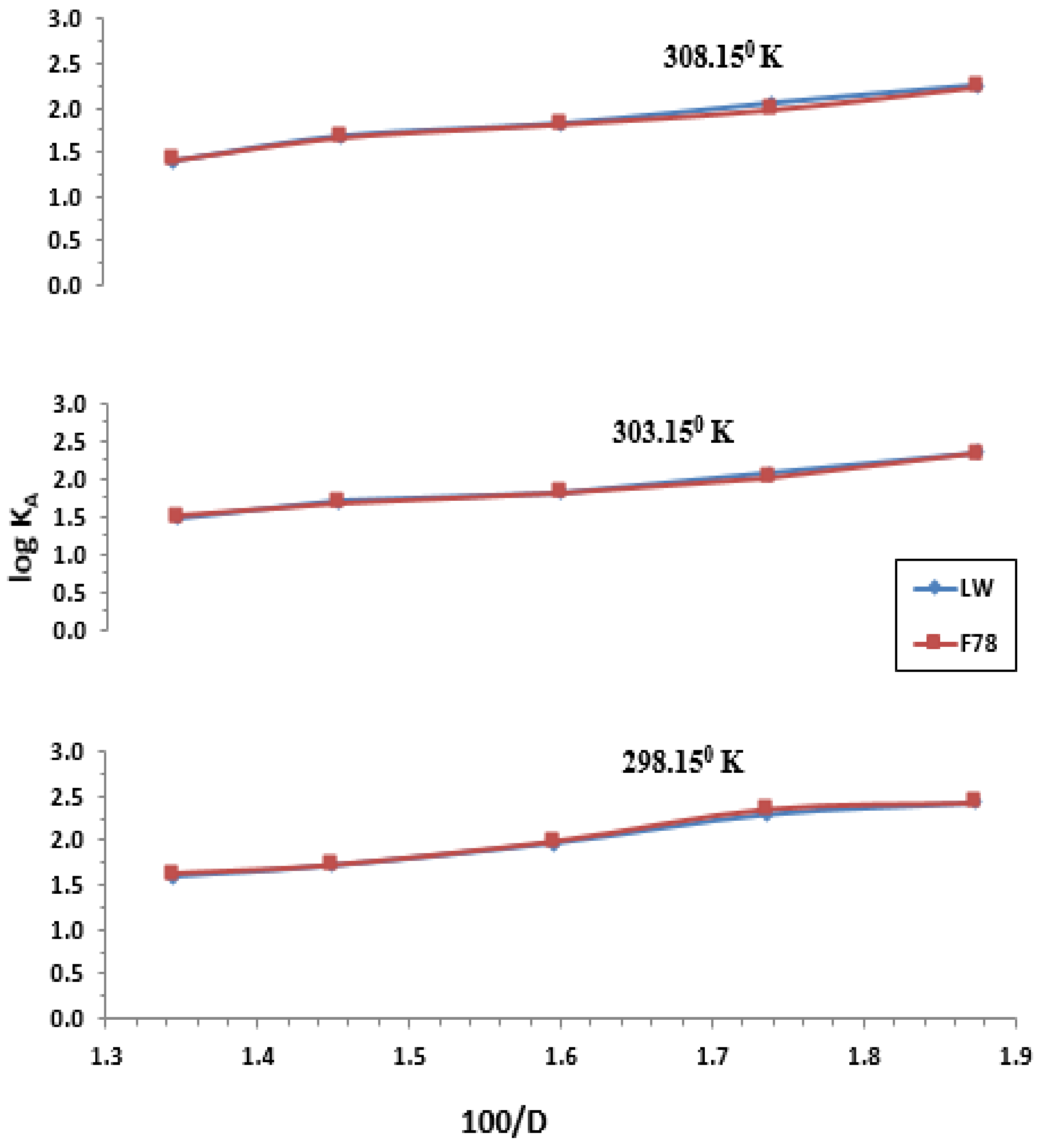

Fig. II B(3.1):-Plots of log K_A vs 1/ D for $MnSO_4$ in DMF -H_2O Mixtures at 298.15 ,303.15,308.15^{0}K

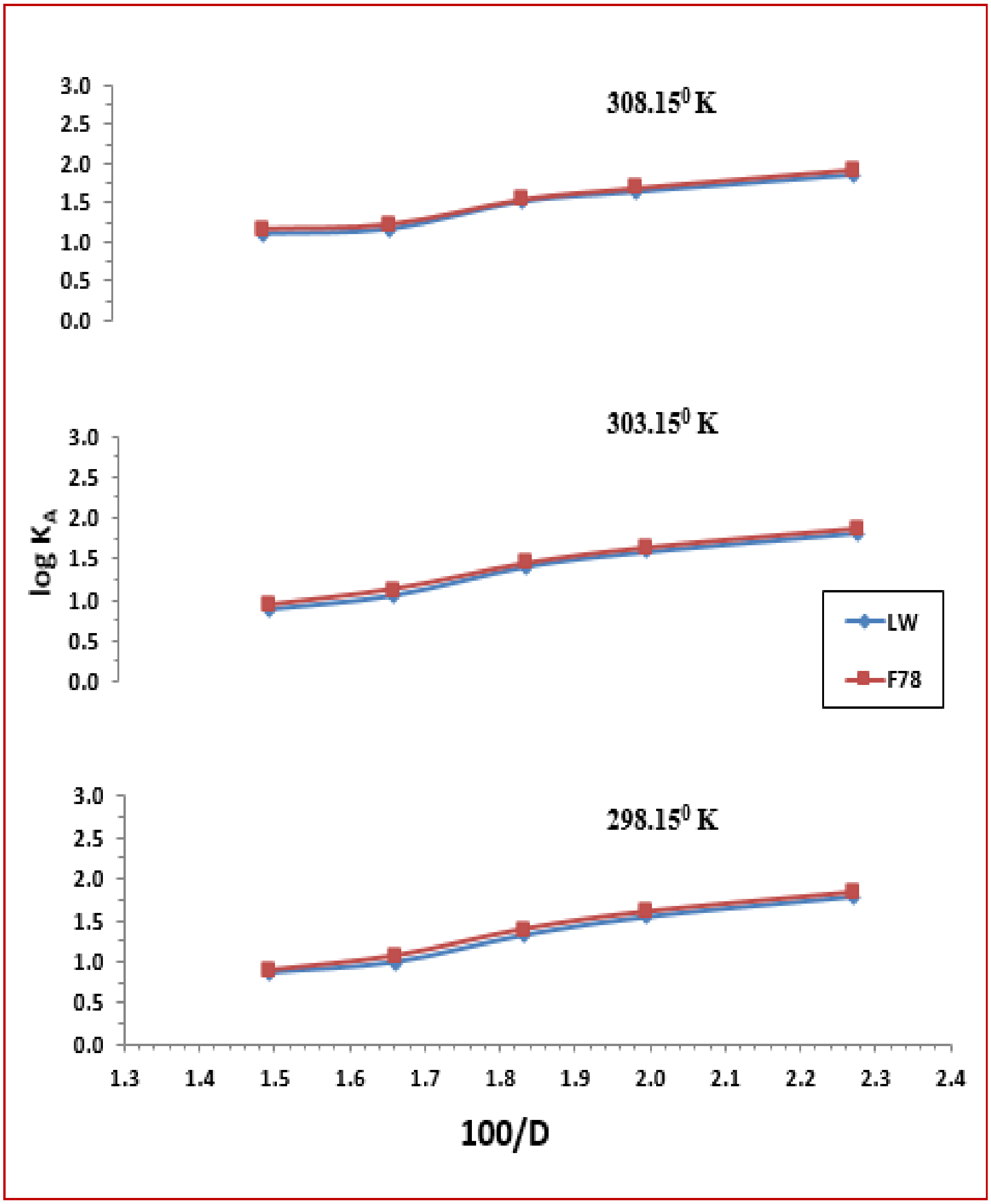

Fig. II B(3.2):-Plots of log K_A vs 1/ D for $CuSO_4$ in DMF -H_2O Mixtures at 298.15 ,303.15,308.15^{0}K

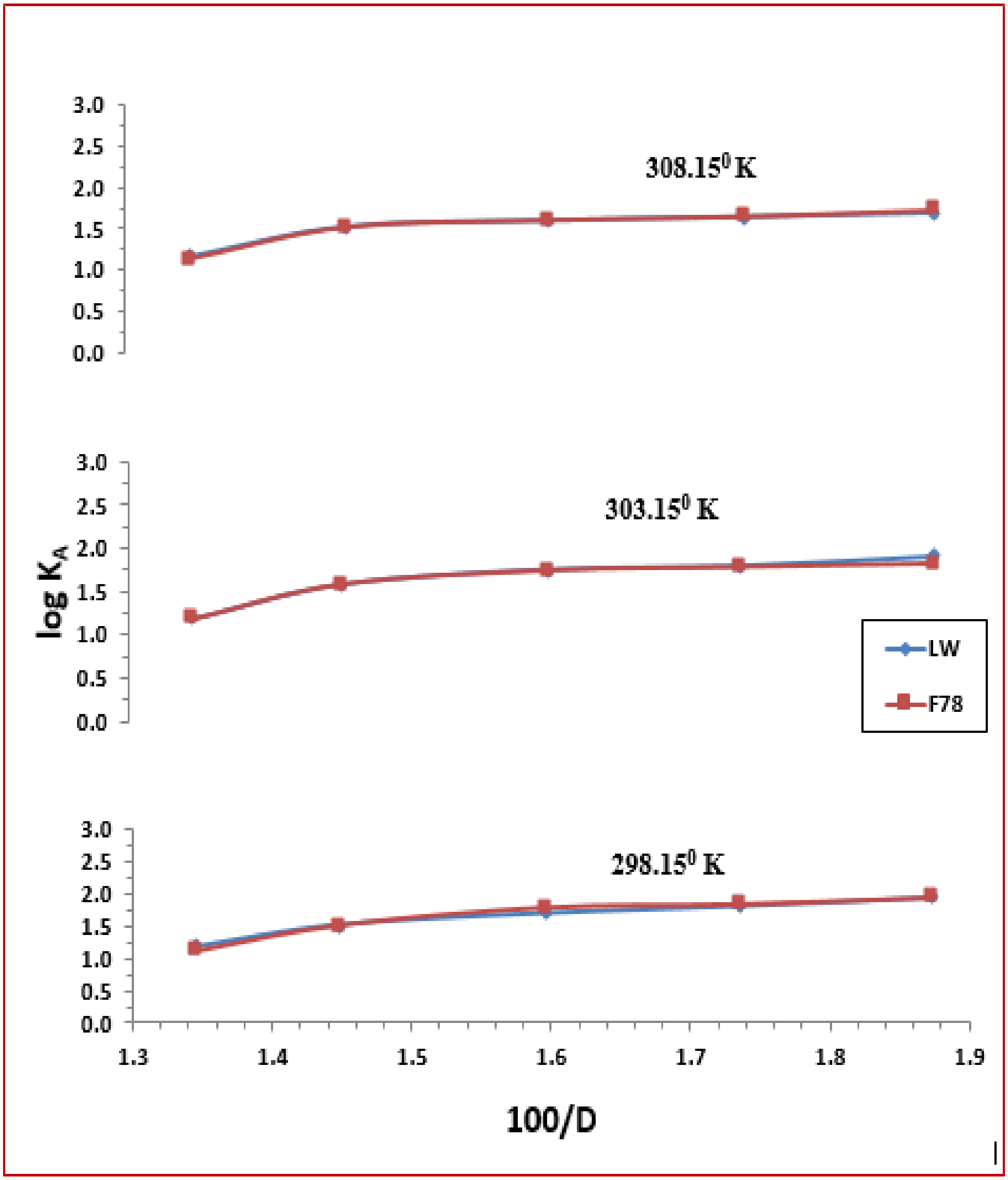

Fig. II B (3.3):-Plots of log K_A vs 1/ D for $ZnSO_4$ in DMF -H_2O Mixtures at 298.15 ,303.15,308.15^{0}K

IV. CONCLUSION

The conductance data for symmetrical 2:2 electrolytes ($MnSO_4$, $CuSO_4$ and $ZnSO_4$) in DMF + H_2O have been analyzed by minimization technique using the Fuoss – 1978 (F-78) and the Lee – Wheaton (LW) conductance equations. The values of limiting equivalent conductance, Λ_0, the thermodynamic ion – association constants , K are computed. The significance of these parameter is discussed to provide some insight on the magnitude of the ionic association and ion – solvent interactions. For a given dielectric the Λ_0 values for all the salts increases with increasing size of the cation and follow the order $Mn^{++} < Cu^{++} < Zn^{++}$ in DMF + H_2O mixtures.

The overall association behavior of these salts have been found to increase with decrease in dielectric constant of the medium. Thus, the F-78 equation appears to be better suited for understanding the behavior of conductances of such systems in all respects because it includes the solvated radii ion present in the solution in diffusion – controlled steady state and gives significantly better – fit parameters as compared to those of LW conductance equation.

REFERENCES

1. *D.F. Evans, C. Zawoyski and R. L. Kay, J. Phys. Chem., 69, 3878 (1965); ibid., 4216*
2. *R. L. Kay and D.F. Evans, J. Phys. Chem., 70, 366 (1966); ibid., 2325*
3. *D. F. Evans and P. Gardam. J. Phys. Chem, 72, 3281 (1968); ibid., 73,158 (1969)*
4. *R. L. Kay and D.F. Evans and G.P. Cunnigham, J. Phys. Chem.,73, 3322 (1969)*
5. *R. F. Serieno, P.W. Greeo, and R.C. Mamajeek, J. Phys. Chem., 75, 1722 (1971)*
6. *D. F. Evans, J.Thomos, J.A. Nadas, and M.A. Matesich , J. Phys. Chem, 75, 1714 (1971)*
7. *D. F. Evans and J. A. Nadas, J. Phys. Chem., 75, 1708 (1971)*
8. *B. K. Barkar and J.A. Carire , J. Phys. Chem., 77, 1884 (1973)*
9. *R. M. Fuoss and C.A. Kraus, J. Am.Chem. Soc., 79, 3304 (1957)*
10. *R. M. Fuoss and K. L. Hsia, Proc. Natt. Acad. Sci. USA., 57,1550 (1967)*
11. *J. C. Justice and R. M. Fuoss, J.Phys. Chem., 67, 1707 (1963)*
12. *E. Pitts, Proc. Ray. Soc. London, Ser (A), 243, 217 (1953)*
13. *R. Fernandez-Prini, Faraday Trans-I, 65, 3311 (1969)*
14. *P. Debye and E. Huckel, Z. Physik, 24,185, 305 (1923)*
15. *L. Onsager, Z. Physik, 26, 388 (1926)*
16. *L. Onsager, Trans. Faraday Soc., 23, 341 (1927)*
17. *T. Shedlovsky, J. Am. Chem. Soc., 54,1405 (1932)*
18. *L. Onsager and R. M. Fuoss, J. Phys. Chem., 36, 2689 (1932)*
19. *L. Onsager, Z. Physik, 28, 277 (1927)*
20. *R.M. Fuoss and L. Onsager, Proc. Natt. Acad. Sci, U.S., 41, 274 (1955)*
21. *R. M. Fuoss and L. Onsager, J. Phys. Chem., 61, 668 (1957)*
22. *R. M. Fuoss and F. Accascina, Electrolytic Conductance, Interscience Publishers, New York (1959)*
23. *Y. C. Chin And R. M. Fuoss, J. Phys. Chem, 72, 4123 (1968)*
24. *R. M. Fuoss, J. Am. Chem., Soc., 79, 3301 (1957)*
25. *T. L. Broadwater and R. L. Kay, J. Phys. Chem., 74, 3802 (1970)*
26. *J. E. Lind and R. M. Fuoss , J. Phys. Chem., 65, 999 (1961)*
27. *R. M. Fuoss, J. Am. Chem. Soc., 80, 3163 (1958)*
28. *R. M. Fuoss, J. Am. Chem. Soc., 81, 2659 (1959)*
29. *E. Renard and J. C. Justice, J. Soln. Chem., 3, 633 (1974)*
30. *M. C. Justice, R. Buryed and J. C. Justice, Electrochemica Acta, 16, 687 (1971)*
31. *J. C. Justice and R. M. Fuoss, J. Phys. Chem., 67, 1707 (1963)*
32. *A. D. Aprano, J. Komiyama and R. M. Fuoss, J. Soln. Chem., 4, 279 (1975)*
33. *A. D. Aprano and R. M. Fuoss, J. Soln. Chem., 3, 45 (1974)*
34. *C. J. James and R. M. Fuoss, J. Soln. Chem., 4, 91 (1975)*
35. *R. M. Fuoss, Proc. Natt. Acad., Sci, 75, 16 (1978)*
36. *Das D., J.Sol.Chem., 37(2008)947-955.*
37. *De R., Guha C. and Das B., J.Sol.Chem., 35(2006)1505-1514.*
38. *A. Bhttarai and J. Raut, J. of Alpine Chemistry, 2, 44 (2011)*
39. *J. I. Bat, M. N. Manjunatha, Indian J. Chem. Tech., 17, 462 (2010)*

40. *V. Sokol, R. Tomas, P. Boskovic, Acta. Chem. Slos., 59, 920 (2012)*
41. *A. Prkie, V. Sokol, P. Boskovic, Int. J. Electrochem Sci., 8, 4886 (2013)*
42. *B. A. Akrawi, S. M. Khalil, A. M. Dawood, Prof., J. Sci., 16, 155 (2005)*
43. *Int. J. Electrochem. Sci., 8, 10961 (2013)*
44. *M. S. Niazi, J. Chem. Soc. Pak, 15, 123 (1993)*
45. *M. R. Canon, R. E. Manning and J. D. Ball, Analyst Chem., 32, 355 (1960).*