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Conductometric and Thermodynamic Study of Copper and Nickel Sulfate in Aqueous Methanol Systems

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Abstract The conductivities of copper sulfate and nickel sulfate solutions in aqueous and aqueous methanol systems (0 % to 40 % v/v) were measured in concentration range ($1x10^{-3}$ to $10x10^{-3}$ $mol.dm^{-3}$) at different temperatures (298 to 323 K). Conductometric data were used for the calculation of molar conductivity at infinite dilution (Λ_m°), degree of dissociation (α) and dissociation constant (K_d). The decreased in ion–solvent interaction with the increase in temperature, for individual electrolyte attributed to the increase in limiting molar conductance. Thermodynamic parameters such as energy of activation (E_a), free energy change of activation ($\Delta G^{\#}$) and entropy change of activation ($\Delta S^{\#}$) were also calculated at various temperatures as a function of concentration of electrolytes in aqueous and aqueous methanol systems.

Keywords: *molar conductance, copper sulfate, nickel sulfate, methanol, degree of dissociation, activation parameters*

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1. Introduction

Thermodynamic and transport properties of electrolyte solutions are important for their applications in various chemical processes in industries; electrochemical processes such as electrolysis; supercritical technology, including destruction of hazardous agents and synthesis in supercritical fluids; production of energy sources, including scaling in production wells, utilization of geothermal energy or inhibition of gas hydrate formation; hydrometallurgical processes etc [1].

Transport properties as conductance can be measured at low concentrations, it helps in the study of ionic solvation and reliable values of infinite dilution are readily obtained [2]. These properties are sensitive to strong ion-solvent interactions, effective size of the ions, and also to any modification in the structure of the solvents. Conductivity is the method used in to test the quality of process water in those applications where ultrapure water is required, such as in the pharmaceutical, microelectronics, waste water treatment, sea water desalination etc [3,4].

Conductance studies of electrolytes in mixed solvents have received considerable attention in recent years. It is a simple method to study the solvents effects, nature of ion, ion-solvent interaction existing in the system, modification in the structure of a solvent due to the presence of an ion and ionic movement in a solution. The study of variation in molar conductance with temperature and solvent composition provides information about ionic mobility and solvent viscosity, hydrogen bonding capability, dielectric constant and its specific interaction with ions. The influence of various temperatures on conductivity measurement can give detailed information of ion-ion and ion-solvent interaction for different electrolytes solution [5-16].

Table 1. Relative permittivity (ε) of aqueous and aqueous methanol Systems at different temperatures

Temperature (K)	Aqueous Systems	Aqueous Methanol Systems		
		10 %	20 %	30 %
293	80.37	75.84	71.02	66.01
298	78	74.04	69.17	64.29
303	76.73	72.37	67.48	62.71
308	75.01	70.53	65.80	61.19
313	73.12	68.90	64.13	59.53

Alcohol–water systems are of great interest in physics, chemistry and biology. Alcohols are industrially and scientifically important organic compounds and their physical and chemical properties are largely determined by the hydroxyl (–OH) group. Alcohols are strongly associated in solution because of dipole–dipole interaction and hydrogen bonding. The dipole moment of alcohol molecules is due to hydroxyl (–OH) group as a result changes in relative permittivity as a function of alcohol–water composition and temperature depends on the intermolecular attraction [17]. Hydrogen bonding is

complex in liquid state and its presence brings a considerable change in the dielectric properties of liquid mixtures. Molecular mixtures (binary mixtures) bring about changes in physical properties such as density, molar volume, refractive index, dielectric permittivity, conductivity etc, and also in thermodynamic properties like entropy, free energy etc [18,19]. Akerlof [20] have reported the relative permittivity values of aqueous methanol systems at different temperatures as shown in Table 1.

Present work deals with the conductometric study of divalent salts such as copper sulfate and nickel sulfate in aqueous and aqueous methanol systems and their interaction with solvent as a function of concentration and temperature. Thermodynamic properties were also calculated through conductance data as a function of solvent compositions and temperature.

2. Experimental

All glassware used were of Pyrex 'A' grade quality. Copper sulfate pentahydrate ($CuSO_4$. $5H_2O$, E. Merck, 99 % pure), Nickel sulfate heptahydrate ($NiSO_4$. $7H_2O$, E. Merck, 99 % pure) and methanol (CH_3OH) of E. Merck, A. C. S HPLC grade were used without further purification. Deionized water was used for preparation of different percentages (0 % to 40 %v/v) of aqueous methanol systems. Digital direct reading conductivity meter model HI-9813, Hanna used to measure the conductivities, having a dip type conductivity electrode with cell constant 1cm^{-1}. An Ostwald viscometer type Techniconomial constant 0.05Cs/s, capillary ASTMA D 445 USA was used to measure the viscosity. Densities were measured by relative density bottle with capacity of 10 ml by volume. Temperature was kept constant by thermostatic water bath (Circulator, model YCW- 0.1 Taiwan). A stopwatch Japan CBM Corp, QsQ having a least count of 0.01second was used for determination of time of flow of solvent.

3. Results and Discussion

Conductivities of various concentrations of electrolytes that is copper sulfate and nickel sulfate were measured, ranging from 1x10^{-3} to 10x10^{-3} mol.dm^{-3} in aqueous and aqueous methanol systems (0 %-40 %v/v) at different temperatures (298 to 323 K) with a difference of 5 K. The conductivities were used to calculate molar conductance for copper sulfate and nickel sulfate at different temperatures with different concentrations of electrolytes in aqueous methanol systems as shown in Table 2 and Table 3 respectively, by using the formula Eq. (1).

$$\Lambda_m = 1000K / C \quad (1)$$

where, Λ_m is the molar conductance, K is the specific conductance of copper sulfate and nickel sulfate, and C is the concentration of the electrolytes in mol dm^{-3}.

Molar conductance of an electrolyte solution increases with dilution and approaches a limiting value at infinite dilution [8]. This value is called molar conductance at infinite dilution (Λ_m°). Molar conductance at infinite dilution have been determined by the relation, as shown in Eq. (2).

$$\Lambda_m = \Lambda_m^\circ - [A + B\Lambda_m^\circ]C^{1/2} \quad (2)$$

where, Λ_m° is the molar conductance at infinite dilution, A and B are the constant for an electrolyte of a given valence type in each particular solution and can be calculated as in Eq. (3) and Eq. (4).

Table 2. Molar conductance of copper sulfate in aqueous and aqueous methanol Systems at different temperatures

[Salt]x10^3 (mol dm^{-3})	Molar conductance (S cm^2 mol^{-1}) at temperatures (K)					
	298	303	308	313	318	323
Aqueous System						
1.0	280	310	320	340	390	420
2.0	205	215	225	260	275	300
4.0	197	207	220	230	240	250
6.0	185	198	200	215	231	236
8.0	177	183	187	201	210	213
10	171	173	178	196	207	202
10 %(v/v) Aqueous Methanol System						
1.0	180	220	270	290	320	380
2.0	170	190	210	240	250	260
4.0	147	165	182	200	210	225
6.0	135	150	161	188	200	210
8.0	132	148	160	163	186	190
10	113	139	145	164	169	180
20 %(v/v) Aqueous Methanol System						
1.0	150	170	220	250	270	330
2.0	130	140	160	175	190	210
4.0	117	127	135	152	160	182
6.0	96.6	113	121	126	141	155
8.0	92.2	103	115	123	131	143
10	89.0	100	109	112	122	132
30 %(v/v) Aqueous Methanol System						
1.0	130	150	180	190	210	260
2.0	115	130	130	140	150	160
4.0	97.5	110	112	117	125	130
6.0	96.6	101	103	111	116	120
8.0	80.0	91.2	93.7	97.5	100	106
10	77.0	85.0	86.0	87.0	97.0	100
40 %(v/v) Aqueous Methanol System						
1.0	90.0	110	120	150	170	200
2.0	80.0	90.0	100	105	125	140
4.0	67. 5	72. 5	92. 5	97. 5	120	132
6.0	58. 3	65.0	71.6	75.0	83.3	105
8.0	56. 2	61.2	66.2	75.0	80.0	87.5
10	51.0	58.0	64.0	66.0	70.0	78.0

$$A = \frac{82.4}{(DT)^{1/2}\eta} \quad (3)$$

$$B = \frac{8.20 \times 10^5}{(DT)^{3/2}} \quad (4)$$

where D, T and η represent the dielectric constant, absolute temperature and viscosity of the solvent respectively. The results tabulated in Table 2 and Table 3, show that molar conductance decreased with the increase in concentration of electrolytes in aqueous and aqueous methanol solvents. This shows that with the increase of concentration there is increase in number of ions of solute which decrease the ionic velocity due to hindrance in

movement of ions so molar conductance decreased while with dilution ions become free and show its high values. The behavior of electrolytes in mixed solvent system is affected by the organic solvents (methanol) which are more or less aprotic and thus the other properties like dielectric constant, attraction forces and ionic interactions can be studied by physiochemical properties of electrolytes in mixed solvent systems. Different properties such as conductivity, degree of dissociation and thermodynamic parameters can explain these forces of interactions of electrolytes with solvents.

Table 3. Molar conductance of nickel sulfate in aqueous and aqueous methanol Systems at different temperatures

[Salt]x10^3 (mol dm^{-3})	Molar conductance (S cm^2 mol^{-1}) at temperatures (K)					
	298	303	308	313	318	323
Aqueous System						
1.0	210.0	220.0	250.0	250.0	280.0	380.0
2.0	190.0	200.0	205.0	225.0	135.0	270.0
4.0	185.0	180.0	185.0	192.5	197.5	200.0
6.0	165.0	163.3	166.6	175.0	180.0	208.3
8.0	148.5	150.0	158.7	160.0	167.5	196.2
10	146.0	148.0	151.0	152.0	158.0	163.0
10 %(v/v) Aqueous Methanol System						
1.0	180.0	180.0	190.0	220.0	250.0	260.0
2.0	140.0	155.0	170.0	185.0	205.0	210.0
4.0	125.0	142.5	150.0	160.0	170.0	177.5
6.0	108.3	126.6	130.0	138.0	158.3	166.6
8.0	110.0	123.7	131.2	135.0	137.5	153.7
10	106.0	116.0	119.0	123.0	138.0	144.0
20 %(v/v) Aqueous Methanol System						
1.0	110.0	150.0	160.0	170.0	200.0	230.0
2.0	120.0	130.0	135.0	140.0	150.0	160.0
4.0	102.5	105.0	1125	117.5	137.5	147.5
6.0	83.30	98.30	105.0	115.0	118.3	123.3
8.0	81.20	87.50	95.00	98.70	113.7	120.0
10	79.00	85.0	88.00	97.00	101.0	104.0
30 %(v/v) Aqueous Methanol System						
1.0	100.0	120.0	130.0	150.0	170.0	200.0
2.0	90.00	100.0	110.0	115.0	135.0	145.0
4.0	75.00	80.00	87.50	102.5	107.5	125.0
6.0	65.00	76.60	83.30	90.00	95.00	160.0
8.0	60.00	66.20	76.20	78.70	90.00	97.50
10	59.00	64.00	700.0	73.00	81.00	88.00
40 %(v/v) Aqueous Methanol System						
1.0	80.00	100.0	110.0	120.0	140.0	170.0
2.0	75.00	85.00	90.00	95.00	100.0	115.0
4.0	60.00	65.00	72.52	75.00	82.50	92.50
6.0	55.00	58.30	61.60	66.60	70.00	78.30
8.0	47.50	53.70	57.50	62.50	72.50	76.20
10	46.00	49.00	54.00	59.00	62.00	69.00

Molar conductance increased with the increase in temperature due to the high mobility of the ions as a result of increase in thermal energy, the vibrational, rotational and translational energy [8]. With the rise of temperature the viscosity of the solvent also decreases which makes the ions to move freely towards the electrodes. Results show that with the increase in aqueous methanol percent compositions ranging from 0 % to 40 % there is decrease in molar conductance. The solvent affects the conductance primarily through its viscosity, hydrogen bonding capability, dielectric constant and its specific interaction with ions. Viscosity of aqueous methanol system (solvent) resists the motion of ions, and dielectric properties of the solvent control the effective field strength and inter-ionic potential. They affect not only ionic viscosity but also the attraction between ions and consequently the extent of pairing specific solvation of ions can affect both mobility and association. It may also be stated that bulkier and low dielectric constant methanol entering into the solvated or hydrated ion and replaces certain water molecule from either primary or secondary hydration sheath of the ion, leading to decrease in conductance. Increase in solvated ionic size brings about the increase in density as well as viscosity. The increase in the viscosity makes the system to have lesser conductivity.

Molar conductance at infinite dilution (Λ_m°) increased with the increase in temperature while decreased with the increase of aqueous methanol percent composition (0 % to 40 %), as a result solute-solvent interactions have been decreased. The values of molar conductivity at infinite dilution have been calculated from intercept of linear plots between Λ_m versus $\sqrt{C}$ and results are tabulated in Table 4.

The representative plots of Λ_m versus $\sqrt{C}$ for copper sulfate and nickel sulfate are shown in Figure 1 and Figure 2 respectively.

Table 4. Limiting molar conductance (Λ_m°) for copper sulfate and nickel sulfate in aqueous and aqueous methanol systems at different temperatures

Aqueous Methanol Systems (% v/v)	Limiting molar conductance (S cm^2 mol^{-1}) at temperatures (K)					
	298	303	308	313	318	323
For $CuSO_4$						
00	294.94	324.03	338.78	368.37	406.57	447.34
10	206.83	245.09	299.60	329.63	479.58	412.25
20	172.80	191.56	242.21	278.38	300.08	362.40
30	168.21	200.12	199.63	214.17	234.31	282.36
40	105.64	125.86	141.64	168.94	201.75	233.64
For $NiSO_4$						
00	226.25	250.62	277.12	290.38	319.19	418.39
10	195.37	200.67	216.98	251.97	284.99	291.56
20	136.70	173.69	183.94	191.67	223.33	255.13
30	117.62	138.35	149.65	171.83	196.17	226.34
40	96.56	118.41	128.77	137.49	226.34	189.52

The increased in Λ_m° with the rise in temperature may be due to structural changes in water methanol aggregates. Ageno [21] have reported that water molecular aggregates are temperature dependent existence in the liquid. Their life is necessarily short because in the collisions due to the thermal motions some molecules can pass from one aggregate to another, only the total number of hydrogen bridges (dotted lines) remaining constant at constant temperature. The possible types of aggregates a, b, c, d and e present in water are as follows.

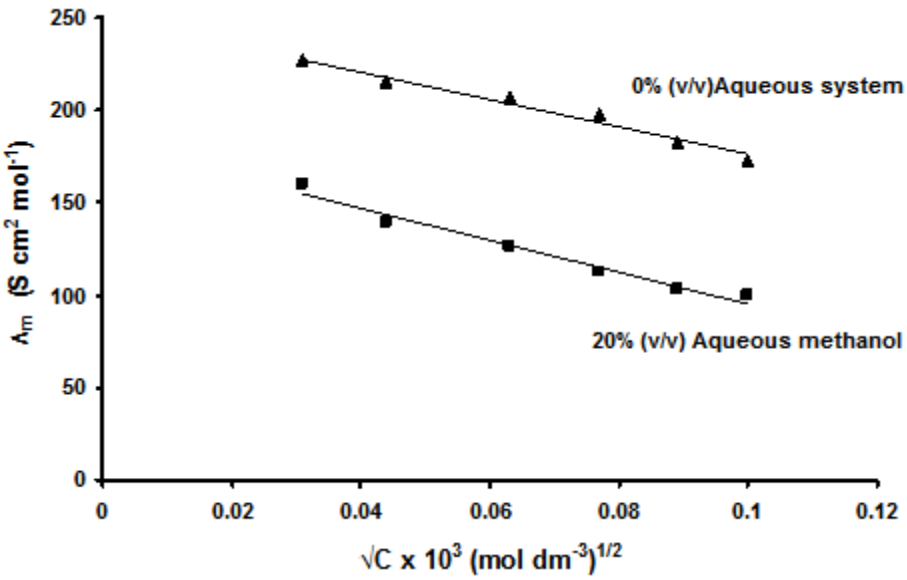


Figure 1. Plot of Λ_m versus √C for copper sulfate in aqueous and 20 %(v/v) aqueous methanol systems at 303 K

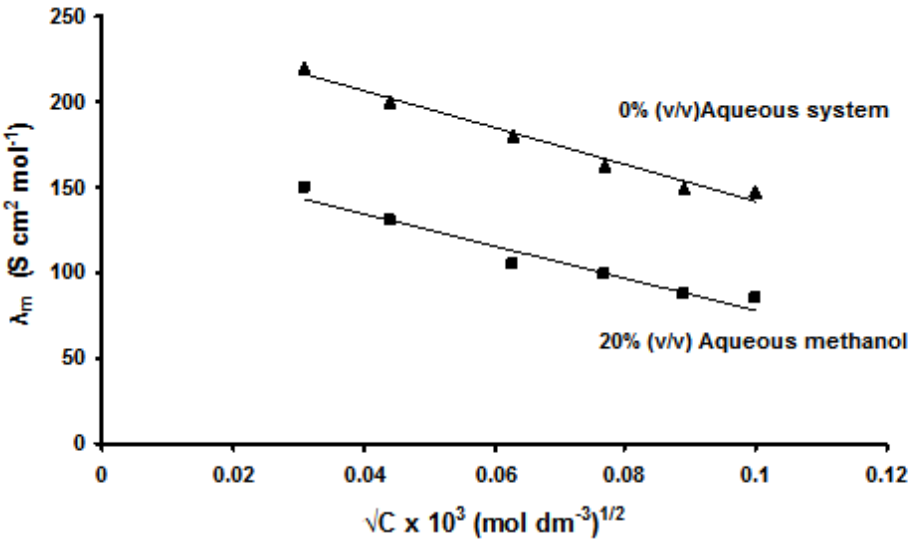
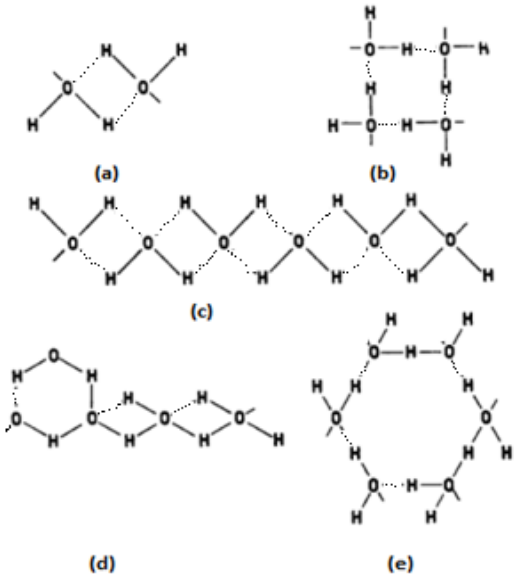
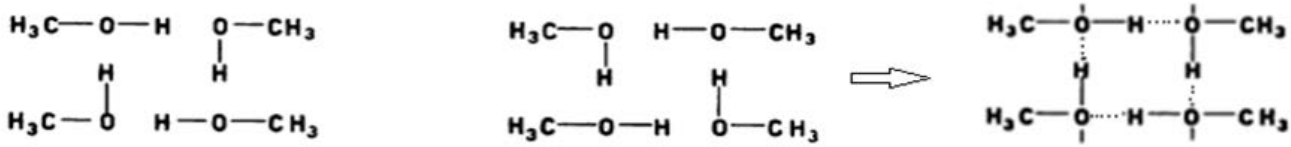


Figure 2. Plot of Λ_m versus √C for nickel sulfate in aqueous and 20 %(v/v) aqueous methanol systems at 303 K



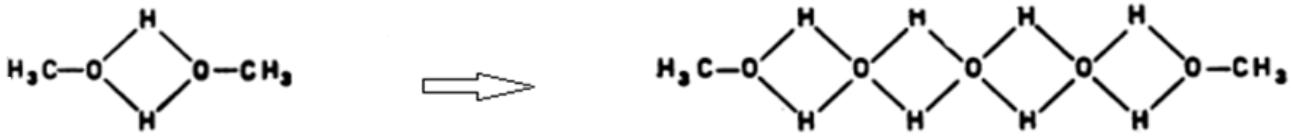
The existence of molecular aggregates in methanol were also observed by Ageno [21] whose hydrogen bridges form a tetramer ring by combining four independent molecules in two different configurations as shown below:



Four Methanol Molecules in two different configurations

Tetramer Ring

The decreased in molar conductance at infinite dilution with the increase of solvent percent composition is due to structural changes in water and methanol molecules. Ageno and Frontali [22] have also reported the dimer formation in methanol molecules but after mixing water with methanol each methanol molecule bound with water aggregates by additional H-bond as shown below:



Methanol Dimer

Water-Methanol Linear Chain

Above structures confirmed that the decreased in molar conductance at infinite dilution with methanol addition is due to prevention in resonance transfer in water molecules. It has also been observed through all structures of water and methanol that breaking of H bonds in water-water aggregates or in methanol-methanol aggregates to form water-methanol mixtures decreased the stability system.

Table 5. Values of dissociation constant (K_d) and degree of dissociation for copper sulfate in aqueous methanol systems at various temperatures

Temperature (K)	Degree of dissociation (α)	Dissociation constant K_dx10^3 (mol dm^{-3})
	Aqueous Systems	
298	0.608	7.54
303	0.566	5.93
308	0.553	5.43
313	0.546	5.25
318	0.516	4.41
323	0.477	3.05
	20 %(v/v) Aqueous Methanol Systems	
298	0.557	5.60
303	0.541	5.11
308	0.474	3.43
313	0.444	2.84
318	0.437	2.71
323	0.396	2.08

The degree of dissociation is the ratio of molar conductance at given concentration to molar conductance at infinite dilution given by the Eq. (5):

$$\alpha = \frac{\Lambda_m}{\Lambda_m^{\circ}} \tag{5}$$

where α is the degree of dissociation. The values of the degree of dissociation are tabulated in Tables 5 and 6, show the decreased in values with the increase in concentration and temperature for both electrolytes i.e. copper sulfate and nickel sulfate. As with the increase in concentration degree of dissociation decreased so the molar conductance decreased.

Table 6. Values of dissociation constant (K_d) and degree of dissociation for nickel sulfate in aqueous methanol systems at various temperatures

Temperature (K)	Degree of dissociation (α)	Dissociation constant K_dx10^3 (mol dm^{-3})
	Aqueous Systems	
298	0.657	10.01
303	0.578	6.35
308	0.572	6.13
313	0.551	5.40
318	0.524	4.63
323	0.468	3.12
	20 %(v/v) Aqueous Methanol Systems	
298	0.594	6.95
303	0.503	4.08
308	0.516	4.41
313	0.514	4.37
318	0.509	4.22
323	0.470	3.34

It was also observed that with the increase of alcohol content the degree of dissociation also decreased. Ostwald noticed a state of equilibrium between ionized and unionized molecule in solution. According to law of mass action dissociation constant is determined by the Eq. (6):

$$K_d = \left[\frac{\alpha^2}{1-\alpha}\right] C \tag{6}$$

where, K_d is the dissociation constant , (1-α) is the remaining fraction of an electrolyte un-dissociated. The values of dissociation constant for copper sulfate and nickel sulfate are tabulated in Tables 5 and 6 respectively, show an increased in the dissociation constant with the increase in concentration of electrolyte. The variation of K_d with percent composition of methanol and temperature was observed due to the selective solvation of the ion by the solvent. The variation in values of K_d with alcohol composition is primary due to change in dielectric constant and it also indicates the changes in the ionic environment, surrounding ionic species. It may reduce the

repulsion between different ionic species by increasing the aggregation number capacity. It may also be due to bulky organic molecules, either enter the solvation shell or come out of it during the movement of the solvated ion in the bulk of the solution. In mixed solvent system decrease in hydration of ions also lead to decreased in values of K_d [6]. This decreased also indicate electrostatic ion pair formation in divalent cations [23]. Solvation of cation-solvent type is predominates over anion-solvent as sulfate anions having tetrahedral symmetry showing restriction in solvation [24].

The conductance of ions depends on the rate of movement of ions which increases with the increase in temperature as shown by the Arrhenius relation in Eq. (7) [8,9]:

$$\log \Lambda_m^\circ = \log A - \frac{E_a}{2.303RT} \quad (7)$$

where, R is the molar gas constant, E_a is the energy of activation which determines the rate of movement of ions and A is the frequency factor. The energy of activation was calculated by the plot of $\log \Lambda_m^\circ$ against 1 / T. The results tabulated in Table 7, show that the values of energy of activation increased from 0 % to 40 %, for copper sulfate and nickel sulfate. It shows that the rate of movement became slow as the composition of alcohol increased results an increased in energy of activation and decreased when rate of movement of ions is fast in low composition of alcohol system. Representative plot of energy of activation is shown in Figure 3.

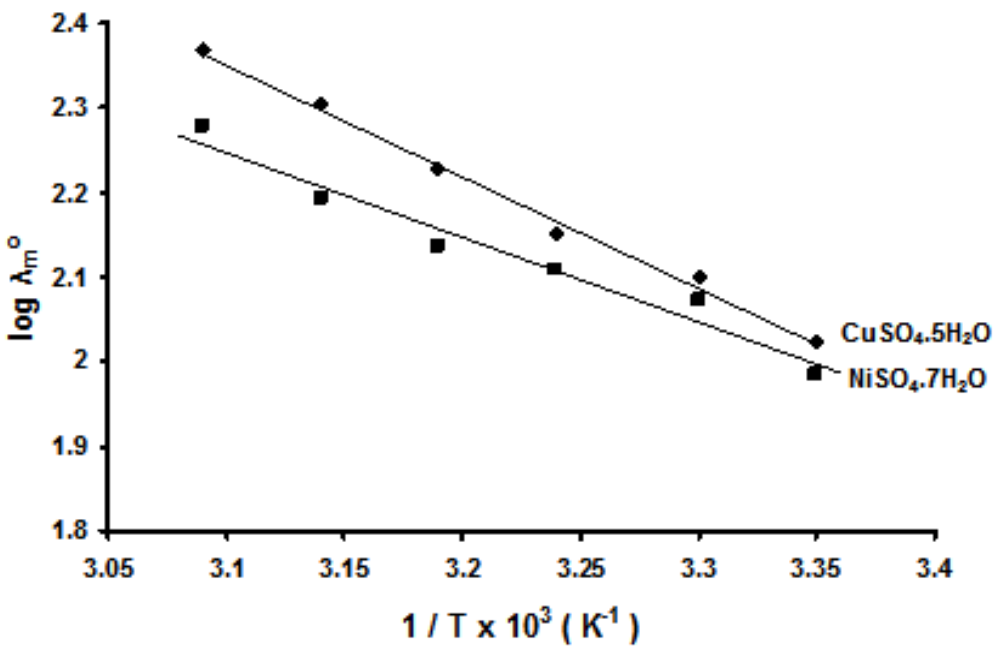


Figure 3. Plot of log Λ_m° versus 1 / T for copper sulfate and nickel sulfate in 40 %(v/v) aqueous methanol system

With the help of free energy change ($\Delta G^\#$) it is possible to predict whether the process will proceed spontaneously or not as calculated by the relation in Eq. (8) [6]:

$$DG^\# = -\ 2.303\ \mathrm{RT}\ \log K_d \quad (8)$$

Table 7. Thermodynamic parameters for copper sulfate and nickel sulfate in aqueous methanol systems at 308 K

Aqueous Methanol Systems (%v/v)	Energy of activation (E_a) (kJ mol^{-1})	Free energy change of activation ($\Delta G^\#$) (kJ mol^{-1})	Entropy change of activation ($\Delta S^\#$) (kJ mol^{-1} K^{-1})
[$CuSO_4$] = 8 x 10^{-3} (mol dm^{-3})			
00	13.24	-13.56	39.88
10	14.32	-14.14	38.70
20	23.71	-14.53	41.73
30	25.30	-14.64	42.26
40	25.42	-14.61	43.86
[$NiSO_4$] = 8 x 10^{-3} (mol dm^{-3})			
00	14.60	-13.04	37.20
10	17.49	-12.56	37.86
20	17.88	-13.89	42.31
30	19.45	-14.00	43.05
40	20.45	-14.98	46.65

Table 7 shows the values of free energy change of activation ($\Delta G^\#$) for copper sulfate and nickel sulfate. There is a decreased in values of free energy change of activation by increasing percent composition of methanol for both electrolytes was observed. Negative values of free energy change of activation show that dissociation process is spontaneous in aqueous and aqueous methanol systems. Entropy change of activation ($\Delta S^\#$) in Eq. (9) is a measure of randomness or disorderness of a system.

$$\Delta S^\# = \frac{\Delta H^\# - \Delta G^\#}{T} \quad (9)$$

Enthalpy was calculated by plotting log K_d Vs 1/ T as shown in Figure 4. Entropy change of activation increased with the increase in temperature (298 to 323 K) and percent composition 0 % to 40 % for copper sulfate and nickel sulfate are tabulated in Table 7. The increased in values of entropy change of activation with percent composition of methanol shows that randomness or disorderness of the system increased as association of the solvent increases, which causes more hindrance in the flow of the ions results in the decreased in conductivity.

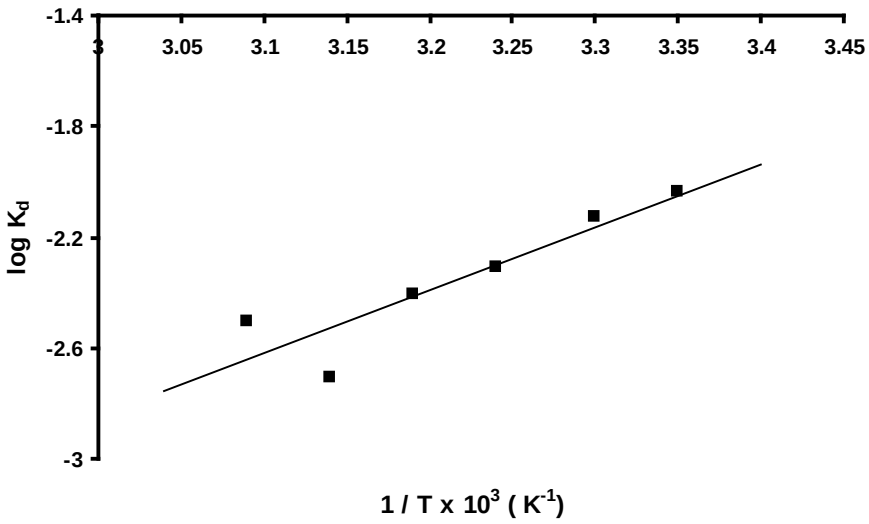


Figure 4. Plot of log K_d versus 1 / T for 8 x 10^{-3}(mol dm^{-3}) copper sulfate in 10 %(v/v) aqueous methanol system

4. Conclusion

It was found through conductometric data analysis for divalent salts that is copper sulfate and nickel sulfate show more association or ion pair formation in aqueous methanol systems as compare to aqueous system. The behavior of these salts also affected by the structural changes in water methanol aggregation by the addition of methanol in water. The increased in entropy change of activation with percent composition of methanol also confirmed the changes in solvent system.

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