European Journal of Chemistry

Journal webpage: www.eurjchem.com

Conductometric, spectrophotometric and thermodynamic studies of nickel sulfate in aqueous polyvinyl alcohol + methanol systems at different temperatures

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ARTICLE INFORMATION

DOI: 10.5155/eurjchem.6.1.37-43.1146

Received: 09 September 2014
Received in revised form: 25 October 2014
Accepted: 25 October 2014
Published online: 31 March 2015
Printed: 31 March 2015

KEYWORDS
Nickel sulfate
Ionic interaction
Polyvinyl alcohol
Molar conductivity
Spectrophotometric
Thermodynamic parameters

ABSTRACT

The electrical conductance of nickel sulfate ($NiSO_4.6H_2O$) solutions in aqueous, aqueous polyvinyl alcohol (PVOH; 0.1, 0.5 and 0.9 g/dL), aqueous methanol (CH_3OH) system (30%, *v*:*v*) and aqueous PVOH+CH_3OH systems were measured in the concentration ranges 0.4×10^{-2} to 10×10^{-2} mol/L, at different temperatures (298, 303, 308, 313 and 318 K). Ionic interactions of nickel sulfate in aqueous and mixed solvent systems were measured by conductometric analysis. Different relations were used to evaluate conductometric data, for the calculation of molar conductance, molar conductance at infinite dilution ($\Lambda°_m$), degree of dissociation (α), dissociation constant (K_d) and Walden product. The increased in $\Lambda°_m$ values with the increase in percent composition of aqueous PVOH, show that PVOH interaction with solvents (water and methanol) was higher as compare to PVOH interaction with $NiSO_4$. Solvent effect was also studied by spectrophotometric analysis of $NiSO_4$ in aqueous, aqueous PVOH and aqueous PVOH + CH_3OH system. Thermodynamic parameters for dissociation process such as energy of activation ($E_a{}^{\#}$), free energy change of activation ($\Delta G_d{}^{\#}$), enthalpy change of activation ($\Delta H_d{}^{\#}$), and entropy change of activation ($\Delta S_d{}^{\#}$) were also calculated as a function of temperature and solvent composition.

Cite this: *Eur. J. Chem.* **2015**, *6(1)*, 37-43

1. Introduction

Methods of physicochemical analysis have been found to be useful tools in getting sound information about the structure of various liquids and in studying ion-solvent interactions in binary and ternary systems [1]. The physical properties of the mixed solvents are very much different from that of water. Methanol is a protic solvent, which is known to be extensively self-associated through hydrogen bonding in the pure state. The presence of a small amount of alcohol in water alters the solvent structure, by changing the hydrogen bond configurations. The addition of organic solvent to an aqueous solution of electrolyte brings about a change in ion solvation that often results in a large change in the reactivity of dissolved electrolyte [2-7].

Solute-solvent interaction has great importance in biological chemistry, physical chemistry, surface chemistry, environmental chemistry and geochemistry. According to Eigen and Tamm [8,9], the association of strongly solvated ions in aqueous solution take place by a three-step process in which the free hydrated ions initially combine with their (inner) hydration sheaths basically intact to form a double-solvent-separated ion pair (2SIP). This is followed by successive losses of water molecules to form a solvent-shared ion pair (SIP) and then a contact ion pair (CIP) as shown in Figure 1 [10,11].

Polyvinyl alcohol is a water-soluble polyhydroxy polymer, employed in practical applications because of its excellent chemical resistance and physical properties and is completely degradable. Polyvinyl alcohol serves as a thickening agent for various emulsions and suspensions and used as wet-strength adhesive. An important use of polyvinyl alcohol is as the plastic inter layer for automotive and aircraft also for coating electrical wire [12]. Divalent transition metal sulfates play a vital role in life systems as vitamins, enzymes and proteins [13]. They are widely used in agriculture as antifungal and antibacterial agents. Such solutions also find application as a mordant for dyeing as an activator for the forth flotation of various ores, as a molluscicide and for algae control.

Thermodynamic and transport properties of electrolyte solutions are important for a variety of applications in the chemical processing industries [14]. Transport properties are very useful for the study of ionic solvation. These properties can give information on the effective size of moving particles in solution and are sensitive to strong ion-solvent interactions, which not only affected by the size of the ions, and also to any

ISSN 2153-2249 (Print) / ISSN 2153-2257 (Online)
http://dx.doi.org/10.5155/eurjchem.6.1.37-43.1146

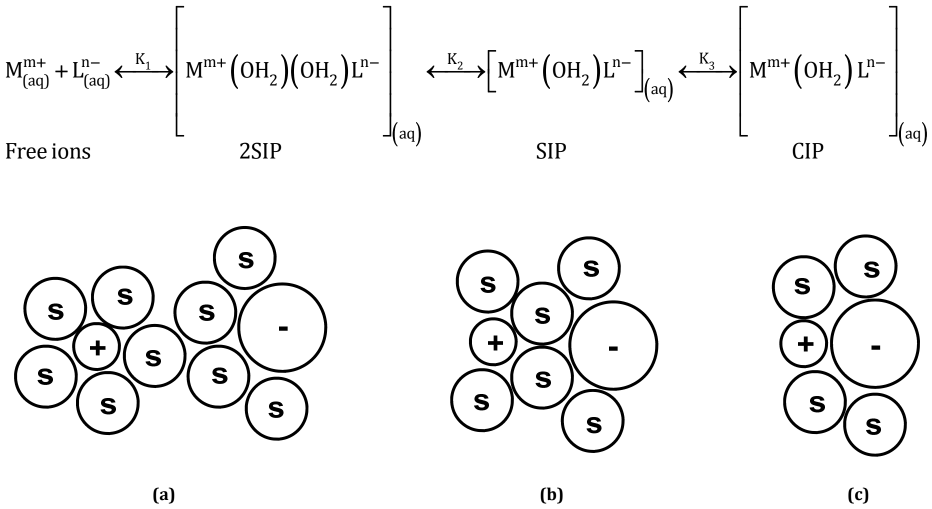

Figure 1. Schematic representation of ion pair types: (a) solvent separated (2SIP), (b) solvent shared (SIP), and (c) contact (CIP) ion pair.

modification in the structure of the solvents. The conductometric method can best be used to study the ion-solvent interactions [15-17]. Conductometric analysis of electrolytes in mixed solvents has received considerable attention in recent years. It is a simple, accurate and reliable method to study the solvents effects, nature of ion, ion-solvent interaction existing in the system, and 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 ability, dielectric constant and specific interactions of ions with the solvent. The influence of various temperatures on conductivity measurement can give detailed information of ion-ion and ion-solvent interaction for different electrolytes solution [18-30]. Molecular associations in liquid system and their variations with composition and temperature were studied by thermodynamic data [31-38].

Transition metals occupy the space between group II and group III of the periodic table and due to their unique physical and chemical properties are of great interest. They form colored compounds which are often paramagnetic and show variable oxidation states but among them nickel is stable with maximum energy and 2+ oxidation state. The dissolution of nickel sulfate in water gives solution containing the ion $[Ni(H_2O)_6]^{2+}$ ion. The interaction of nickel sulfate in mixed solvent systems is the main interest for this research. The present work deals with the study of the nature of nickel sulfate in aqueous, aqueous PVOH, aqueous methanol and aqueous PVOH + methanol systems. Ionic interactions were studied as a function of composition of solvent, concentration and temperature by conductometric method. Effect of solvent was also studied by spectrophotometric analysis of $NiSO_4$ in aqueous, aqueous PVOH and aqueous PVOH + CH_3OH system. Thermodynamic parameters also confirmed the mode of interaction in the presence of particular mixed solvent systems.

2. Experimental

All glassware used was of Pyrex A grade quality. Polyvinyl alcohol (PVOH; 98% hydrolyzed) and methanol (CH_3OH) of Merck 99.9% pure were used for the experimental work. Average molecular weight of polyvinyl alcohol at 298 K was calculated by Mark-Houwink relation.

$$[\eta]_{\text{int}} = kM_v^{\alpha} \qquad (1)$$

where, the values of k and α are 33.88×10^{-5} and 0.716 for polyvinyl alcohol at 298 K [12] and the average molecular weight thus found were approximately 46835 Da. The structural formula of polyvinyl alcohol is shown in Figure 2.

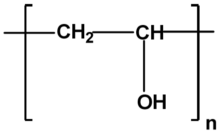

Figure 2. Structural formula of polyvinyl alcohol.

Different compositions of nickel sulfate in aqueous, aqueous PVOH (0.1, 0.5 and 0.9 g/dL) and aqueous PVOH (0.1, 0.5 and 0.9 g/dL) + CH_3OH systems (10, 20 and 30%, *v*:*v*) were prepared in doubled distilled water having a conductivity of 0.06 μS/cm. Nickel sulfate hexahydrate ($NiSO_4.6H_2O$, Mol. Wt = 262.86 g/mol) of Merck, 99% pure was used without further purification. Stock solutions of 0.01 mol/L $NiSO_4.6H_2O$ were prepared by dissolving calculated amount of nickel sulfate in aqueous, aqueous methanol and aqueous PVOH + methanol systems. Solutions in various concentration ranges from 0.4×10^{-2} to 10×10^{-2} ±0.0001 mol/L were prepared from stock solutions. Digital direct reading conductivity meter of Jenway-4510 having least count 0.01 μS/cm used to measure the conductivities. An Ostwald viscometer type Techniconomial constant 0.05 Cs/s, capillary ASTMAD 445 USA was used to measure the viscosity of solvent. The densities of solvent were measured with relative density bottle having the capacity of 10 cm^3 at different temperatures. The temperature was kept constant by keeping all solutions in thermostatic water bath (circulator, model YCW-0.1, Taiwan R. O. C.) for about 10-15 minutes and controlled within ±0.01 K. An electronic balance (Sartorius, Germany) was used for mass determination. A stopwatch Japan CBM Corp, QsQ was used for determination of time of flow of solvent. Reproducibility of the results was checked by replicate measurements. The uncertainty in the experimental data for conductivity, density and viscosity was found to be ±0.02 mS/ cm, ±0.0001 g/mL and ±0.02 mPa.s, respectively. Absorption spectra were recorded by double beam UV-Visible spectrophotometer (UV-160A, Shimadzu Co., Japan).

3. Results and discussion

Specific Conductance(L) of nickel sulfate were measured, ranging from concentrations of 0.4×10^{-2} to 10×10^{-2} mol/L in aqueous, aqueous methanol (10, 20 and 30%, *v*:*v*), aqueous PVOH (0.1, 0.5 and 0.9 g/dL) and aqueous PVOH + CH_3OH systems at different temperatures (298 to 318 K) with a difference of 5 K. The molar conductance of $NiSO_4$ were calculated from specific conductance data at different temperatures in aqueous, aqueous CH_3OH, aqueous PVOH and aqueous PVOH + CH_3OH systems as shown in Table 1 to 3, respectively, by applying relation (2):

$$\Lambda_m = \frac{1000.L}{C} \tag{2}$$

where, L is the conductivities of electrolytes, C is the concentration of electrolytes and Λ_m is the molar conductance.

Table 1. Molar conductance (Λ_m) for $NiSO_4$ in aqueous and aqueous methanol systems at different temperatures.

[Salt].10² (mol/L)	**Molar conductance (S.cm²/mol) at temperatures (K)**				
	298	**303**	**308**	**313**	**318**
Aqueous system					
0.40	152.5	152.5	155.0	157.5	160.0
0.60	131.6	133.3	134.6	138.3	140.0
0.80	122.5	123.7	125.0	126.2	128.7
1.00	114.0	117.0	118.0	119.0	121.0
2.00	94.00	94.50	95.00	95.50	96.50
4.00	76.25	74.25	73.75	73.50	69.25
6.00	67.33	66.33	66.00	65.00	64.50
8.00	60.00	58.50	56.25	56.87	55.12
10.0	53.80	53.40	51.90	50.00	49.60
Aqueous methanol system, 30% (v:v)					
0.40	82.50	85.00	87.50	90.00	92.50
0.60	75.00	76.66	78.33	80.00	81.66
0.80	71.25	72.50	75.00	76.25	77.50
1.00	65.00	66.00	68.00	69.00	70.00
2.00	53.50	54.00	55.00	56.50	57.50
4.00	45.00	45.75	46.50	47.00	47.50
6.00	39.66	41.16	41.50	42.33	43.33
8.00	37.00	37.87	38.50	38.87	39.50
10.0	34.70	35.00	35.20	35.70	35.80

Table 2. Molar conductance (Λ_m) for $NiSO_4$ in aqueous PVOH systems at different temperatures.

[Salt].10² (mol/dm³)	**Molar conductance (S.cm²/mol) at temperatures (K)**				
	298	**303**	**308**	**313**	**318**
Aqueous PVOH system, 0.1 g/dL					
0.40	155.0	155.0	157.5	160.0	162.5
0.60	138.3	140.0	143.3	146.6	148.3
0.80	123.7	125.0	126.2	127.5	130.0
1.00	118.0	119.0	120.0	122.0	124.0
2.00	95.00	95.50	96.50	97.50	98.00
4.00	76.25	75.75	75.50	75.25	75.00
6.00	67.33	66.33	66.00	65.00	64.50
8.00	60.00	58.50	56.37	56.87	55.12
10.0	53.80	53.40	51.90	50.00	49.60
Aqueous PVOH system, 0.5 g/dL					
0.40	175.0	180.0	185.0	190.0	197.5
0.60	160.0	161.6	166.6	175.0	180.0
0.80	155.0	157.5	160.0	162.5	168.7
1.00	146.0	147.0	152.0	156.0	160.0
2.00	120.0	126.5	130.0	131.5	134.0
4.00	105.0	107.5	108.0	108.5	108.7
6.00	93.66	93.33	92.66	91.50	88.83
8.00	82.75	82.25	80.37	78.50	78.00
10.0	71.90	71.80	71.50	71.20	70.50
Aqueous PVOH system, 0.9 g/dL					
0.40	200.0	200.0	207.5	210.0	217.5
0.60	175.0	180.0	185.0	191.6	193.3
0.80	162.5	168.7	170.0	172.5	176.2
1.00	157.0	159.0	160.0	162.0	165.0
2.00	128.5	133.0	133.5	134.0	135.0
4.00	109.2	109.2	109.2	109.0	109.0
6.00	96.33	95.00	94.00	93.33	92.50
8.00	85.00	84.25	83.00	81.75	80.62
10.0	72.60	72.30	71.80	71.50	71.00

Table 3. Molar conductance (Λ_m) for $NiSO_4$ in aqueous PVOH+30 % (*v*/*v*) methanol systems at different temperatures.

[Salt].10² (mol/dm³)	**Molar conductance (S.cm²/mol) at temperatures (K)**				
	298	**303**	**308**	**313**	**318**
Aqueous PVOH+30% (v:v) methanol system, 0.1 g/dL					
0.40	90.00	92.50	95.00	97.50	100.0
0.60	83.33	85.00	86.66	88.33	90.00
0.80	75.00	76.25	77.50	78.75	81.25
1.00	70.00	71.00	72.00	73.00	75.00
2.00	56.50	57.00	58.00	59.00	60.00
4.00	45.50	46.25	47.00	47.50	48.25
6.00	41.16	41.50	41.83	42.66	43.16
8.00	38.12	38.50	38.75	38.87	39.37
10.0	35.20	35.30	35.40	35.50	35.80
Aqueous PVOH+30% (v:v) methanol system, 0.5 g/dL					
0.40	107.5	110.0	115.0	117.5	122.5
0.60	91.66	93.33	95.00	98.33	101.6
0.80	80.00	82.50	85.00	86.25	88.75
1.00	74.00	76.00	77.00	78.00	80.00
2.00	59.00	59.50	60.00	61.00	62.50
4.00	47.00	47.25	48.00	48.50	49.00
6.00	45.00	45.33	45.66	46.00	46.33
8.00	38.75	39.00	39.25	39.50	39.75
10.0	36.20	36.40	36.60	36.80	37.00
Aqueous PVOH+30% (v:v) methanol system, 0.9 g/dL					
0.40	127.5	132.5	135.0	137.5	140.0
0.60	103.3	106.6	108.3	111.6	116.6
0.80	91.25	92.50	95.00	98.75	100.0
1.00	85.00	86.00	88.00	90.00	92.00
2.00	63.00	64.00	65.00	66.50	67.00
4.00	48.50	49.75	50.25	51.00	52.00
6.00	45.66	45.83	46.00	46.16	46.33
8.00	39.25	39.50	39.75	40.00	40.50
10.0	36.80	37.00	37.10	37.20	37.30

The values of molar conductance (Λ_m) tabulated in Tables 1-3 for $NiSO_4$ in aqueous, aqueous CH_3OH, aqueous PVOH and aqueous PVOH + CH_3OH systems respectively, show that molar conductivity decreased with the increase in concentration of electrolytes in aqueous and aqueous methanol systems. This shows that with the increase in concentration there was an increased in number of ions of solute which decreased the ionic velocity due to hindrance in movement of ions or at higher concentration ion-pair formation favored thus the molar conductance decreased, while with dilution ions become free and show high values of molar conductance. Results also show that molar conductance increased with the increase in temperature due to the high mobility of the ions as a result of the increased in thermal energy, vibrational, rotational and translational energy. With the rise of temperature the viscosity of the solvent also decreased which makes the ions to move freely towards the electrodes. The decreased in values of molar conductance at higher concentration with the rise in temperature show the removal of conducting species due to favoring in ion-pair formation.

Results tabulated in Tables 1-3, show that molar conductance of nickel sulfate decreased with the increase in proportions of the aqueous methanol solvent system at the particular temperature. The trend in molar conductance is as follows: 30% < 20% < 10% < aqueous system. This behavior was due to the formation of hydrogen bond between alcohol and H_2O molecules, and thus reduced the ionic mobility results a decrease in the molar conductance values with higher percentages of the organic solvent. Further solvent viscosity 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. Increased in solvated ionic size brings about the increased in density as well as viscosity.

Table 4. Limiting molar conductance (Λ°_m) for $NiSO_4$ in aqueous, aqueous methanol and aqueous PVOH+Methanol systems at different temperatures.

Temperature (K)	**Molar conductance at infinite dilution (S.cm²/mol) in different PVOH systems**			
	0.0	**0.1**	**0.5**	**0.9**
Aqueous PVOH systems				
298	156.673(±0.07)	160.840(±0.05)	187.633(±0.07)	207.433(±0.07)
303	158.853(±0.07)	162.469(±0.01)	192.289(±0.01)	212.470(±0.05)
308	163.753(±0.07)	165.922(±0.08)	198.778(±0.02)	217.832(±0.08)
313	164.637(±0.03)	169.377(±0.03)	205.754(±0.06)	222.496(±0.04)
318	167.558(±0.02)	172.543(±0.07)	213.790(±0.05)	228.138(±0.02)
Aqueous PVOH+30% (v:v) methanol systems				
298	86.467(±0.03)	94.372(±0.08)	105.744(±0.06)	123.342(±0.08)
303	88.338(±0.02)	96.476(±0.04)	108.429(±0.01)	126.948(±0.02)
308	91.071(±0.09)	98.653(±0.07)	111.749(±0.01)	129.763(±0.07)
313	93.181(±0.09)	100.807(±0.03)	114.429(±0.01)	133.577(±0.03)
318	95.247(±0.03)	103.525(±0.05)	118.719(±0.01)	136.990(±0.05)

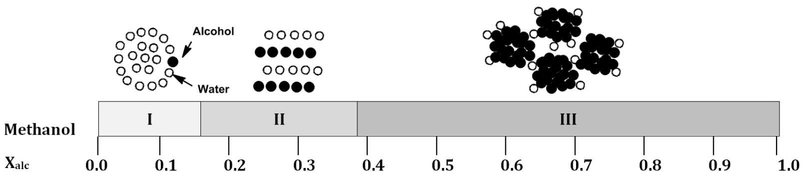

Figure 3. The CH_3OH-water mixtures are divided into three regions (I, II and III) on the basis of the clustering structures.

The increase in the viscosity made the system to have lesser conductivity. On the basis of the mass spectra for alcohol water mixtures measured at various the mole ratios, three regions I, II and III were observed [31] as shown in Figure 3. In region I, the alcohol molecules are existing as a part of inherent hydrogen bonding network of water. In the region II, the layer structure composed of the nearly equal number of alcohol and water, will be formed as stable clusters. In region III, the formation of the alcohol self-aggregating clusters becomes energetically favorable as it started from much lower concentrations. As the hydrophobicity of alcohol water mixtures increases, the region II and III shift to the lower alcoholic content.

Tsierkezos and Molinou [27] have studied the limiting molar conductance of Ni(II), Cd(II), Mn(II) and Cu(II) sulfates in methanol mixtures at 293.15 K and similar behaviour was observed. Results show that with the increase in aqueous PVOH compositions from 0.1 to 0.9 g/dL molar conductance increases. It shows that solvation of ion decreases as PVOH-water interaction increases with the increase in aqueous PVOH compositions through H-bonding. As a result of association of polymer chain with water the ions become less solvated and their mobility increased. While with the increase in aqueous methanol percent compositions 10 to 30% in composition of aqueous PVOH there is a decrease in conductance. This is also due to increase in viscosity of solvent which decreased the mobility of ions and also due to decrease in dielectric constant of medium which decreases the no of ions per cm^3 of the solution.

The conductance behaviour of many electrolytes in mixed solvent systems is reported to be influenced by a number of factors like density, viscosity, dielectric constant of the medium, ion-solvent interactions and solvent-solvent interactions. Ion-solvent interactions stabilize the ion by solvating it. The values of Λ°_m (limiting molar conductance) also depend on the composition of the binary solvent mixtures.

Resulted data was analysed to obtain molar conductance at infinite dilution (Λ°_m). Molar conductance of an electrolyte solution increased with dilution and approaches a limiting value at infinite dilution.

$$\Lambda_m = \Lambda^\circ_m - [A + B.\Lambda^\circ_m]\sqrt{C} \qquad (3)$$

where, Λ°_m is the molar conductance at infinite dilution and '*A*' and '*B*' are the constants for an electrolyte of a given valence type in each particular solution. The values of molar conductance at infinite dilution or limiting molar conductance (Λ°_m) have been determined from intercept of linear regression plots of Λ_m versus $\sqrt{C}$ and results are tabulated in Table 4. The representative plots of Λ_m versus $\sqrt{C}$ for nickel are shown in Figures 4-6. Result tabulated in Table 4 show that the molar conductance at infinite dilution decreased with the increase in solvent percent composition because of low dielectric constant of the medium which favor ion pair formation resulting a decrease in solute-solvent interactions. An ion-pair can be considered as a whole is electrically neutral and ceases to play its role in the ionic cloud. Therefore the ion-pair does not respond to an externally applied electric field and does not participate in the conduction of current. An examination of molecular models suggest that when methanol solvates the ions, perhaps a steric hindrance occurs. Because of this steric hindrance, the oxygen atoms of methanol are not in direct contact with the ions; consequently, the ions move freely and they have a tendency to associate through ion-ion interactions.

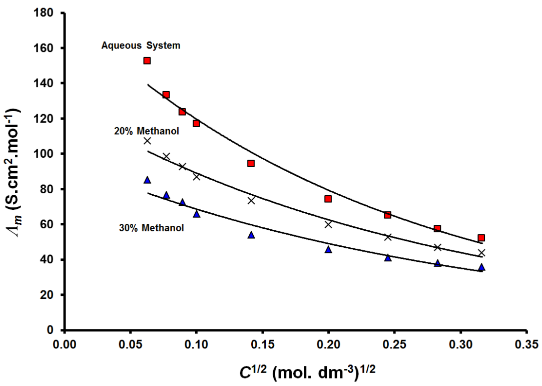

Figure 4. Plot of Λ_m versus $\sqrt{C}$ for $NiSO_4.6H_2O$in aqueous and aqueous methanol systems at 303 K.

The decreased in limiting molar conductance as the methanol content is increased is also due to less strong hydration and presence of a short range interaction. At infinite dilution, neither the relaxation nor the electrophoretic effects are effective on the drift of ions; both these effects depend for their existence on a finite-sized ionic cloud.

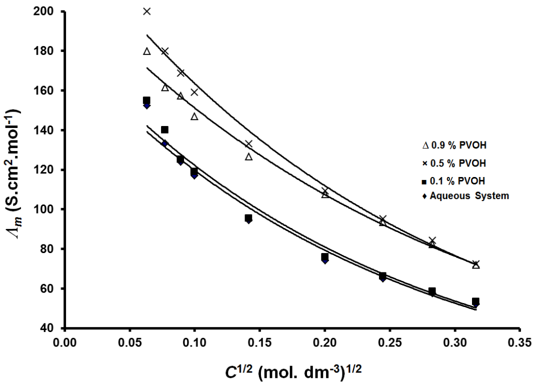

Figure 5. Plot between Molar Conductance (Λ_m) versus $C^{1/2}$ for $NiSO_4$ in aqueous and aqueous PVOH system at 303 K.

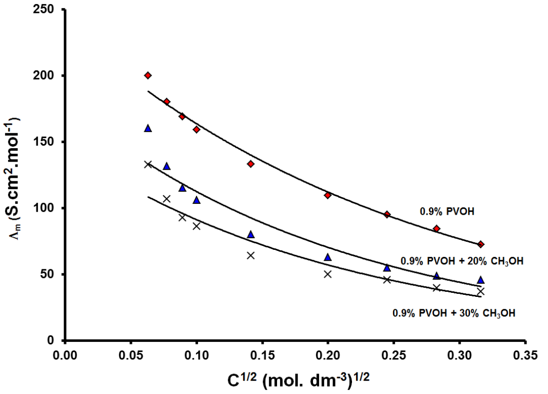

Figure 6. Plot between molar conductance (Λ_m) versus $C^{1/2}$ for $NiSO_4$ in 0.9% aqueous PVOH and 0.9% aqueous PVOH + Methanol systems at 303 K.

Walden product is helpful from the point of view of ion-solvent interaction [22]. In solutions ions are solvated, so degree of solvation as well as size of solvating molecules varies with the nature of the solvent. As regards electrolyte-solvent interactions, more information can be supplied by the dependence of Walden product changes versus composition of the mixtures. The variation of the Walden product reflects the change of total solvation. Walden product relates $\Lambda°_m$ to the viscosity of solvent by the relation.

$$\Lambda^{\circ}_{m}\eta^{\circ} = \text{Walden Product} \tag{4}$$

where, $\eta°$ is the viscosity of the solvent. The values of Walden product tabulated in Table 5 shows that its value increased with the increase in alcohol content as the higher the viscosity lesser will be the mobility of ions in the solution. Thus the decrease in conductance is more prominent when the viscosity of solvent increased. The increased in the values of Walden product indicate weak solvation while decreased in values represents strong solvation. It was also noticed that the value of Walden product decreased with increasing temperature. These negative temperature coefficients of Walden product may be related to the increase in the size of solvated ions in the mixtures as temperature increase. This is because of the variation of the proportion of the organic solvent and water molecules in the sheath of solvation with temperature.

The values of the degree of dissociation ($\alpha = \Lambda_m / \Lambda°_m$) tabulated in Table 6 show the decreased in values with the increase in percent composition of methanol. It was also observed that with the increase of alcohol content the degree of dissociation decreased because of low dielectric constant of the medium. A state of equilibrium between ionized and unionized molecule in solution is determined by the dissociation constant (K_d):

$$K_d = \left[\frac{\alpha^2}{1-\alpha}\right]C \tag{5}$$

where, K_d is the dissociation constant, (1-α) is the remaining fraction of an electrolyte un-dissociated. The values of dissociation constant for nickel sulfate ($NiSO_4.6H_2O$) are tabulated in Table 6. The variation of K_d with percent composition and temperature was observed due to the selective solvation of the ion by the solvent. The variation in values of K_d with composition is primary due to change in dielectric constant and it also indicates that the electrolyte causes reduction in the thickness of the ionic environment, surrounding ionic species. It may reduce the repulsion between different ionic species by increasing the aggregation number capacity. It may also, 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 led to decrease in values of K_d.

The effect of temperature on molar conductivity was shown by the Arrhenius relation [19,32].

$$\log \Lambda^{\circ}_{m} = \log A - \frac{E^{\#}_{a}}{2.303.R.T} \tag{6}$$

where, R is the molar gas constant, $E_a^{\#}$ is the energy of activation which determines the rate of movement of ions, A is the frequency factor and the T is the absolute temperature. The energy of activation was calculated by the plot of log $\Lambda°_m$ against $1/T$, representative plot is shown in Figure 7. The results tabulated in Table 7, show that the values of energy of activation increased from aqueous to aqueous methanol system. It shows that the rate of movement of electrolyte is slow in high percent composition of solvent (30% aqueous methanol) as compared to aqueous system. Therefore the values of limiting molar conductance for nickel in aqueous system were higher than aqueous methanol system. El-Dossoki [33] has also reported that activation energy of transport process increased as the proportion of organic solvent increased.

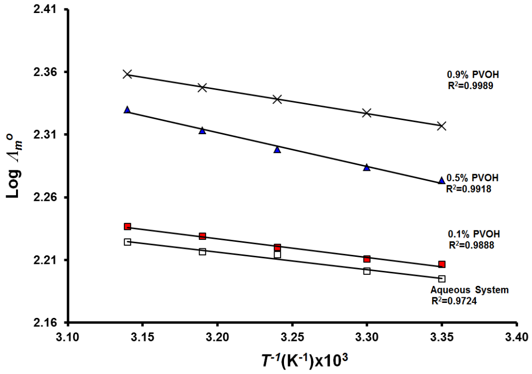

Figure 7. Plot between log limiting molar conductance versus T^{-1} for $NiSO_4$ in aqueous and aqueous PVOH systems.

Table 5. Values of Walden product ($\Lambda^\circ_m \eta^\circ$) for $NiSO_4$ in aqueous, aqueous methanol and aqueous PVOH + Methanol systems at different temperatures

Temperature (K)	**Walden product (S.cm²/mol¹.poise) for aqueous, aqueous PVOH %(*w:v*), aqueous methanol and aqueous PVOH+methanol systems**			
	0.0	**0.1**	**0.5**	**0.9**
Aqueous PVOH system				
298	1.400(±0.05)	1.474(±0.06)	2.542(±0.08)	3.173(±0.07)
303	1.272(±0.08)	1.384(±0.06)	2.055(±0.05)	2.721(±0.09)
308	1.183(±0.07)	1.272(±0.08)	1.894(±0.06)	2.343(±0.07)
313	1.080(±0.02)	1.197(±0.03)	1.771(±0.09)	2.164(±0.06)
318	1.003(±0.07)	1.119(±0.01)	1.633(±0.07)	2.007(±0.03)
Aqueous PVOH+30%(v:v) aqueous methanols				
298	2.905(±0.05)	3.510(±0.08)	5.444(±0.06)	9.769(±0.01)
303	2.823(±0.07)	3.122(±0.08)	4.230(±0.07)	7.855(±0.05)
308	2.376(±0.04)	2.840(±0.08)	3.763(±0.07)	7.129(±0.01)
313	2.251(±0.09)	2.572(±0.08)	3.511(±0.09)	6.630(±0.03)
318	2.081(±0.09)	2.404(±0.06)	3.242(±0.08)	5.908(±0.02)

Table 6. Degree of dissociation (α) and dissociation constant (K_d) for 0.01 mol/dm³ $NiSO_4$ in different solvent systems at 303 K.

Solvent system	**Degree of dissociation and dissociation constant in different solvent system**	
	$\alpha \times 10^2$	**K_d (mol/dm³) ×10²**
Aqueous	73.65	2.058
Aqueous methanol, 30% (*v:v*)	74.71	2.207
Aqueous PVOH, 0.9 g/dL	67.74	2.224
Aqueous PVOH (0.9 g/dL) + methanol (30% (*v:v*))	74.83	1.422

Table 7. Thermodynamic parameters for 0.01 (mol/dm³) $NiSO_4$ in different solvent systems at different temperatures.

Temperature (K)	**Energy of activation $E_a^\#$ (kJ/mol)**	**Enthalpy change of activation $\Delta H_d^\#$ (kJ/mol)**	**Free energy change of activation $\Delta G_d^\#$ (kJ/mol)**	**Entropy change of activation $-\Delta S_d^\#$ (kJ/mol.K)**
Aqueous				
298	2.747	0.2694	9.765	9.495
303		0.2278	9.783	9.535
308		0.1862	10.20	10.02
313		0.1447	10.33	10.19
318		0.1031	10.51	10.40
Aqueous Methanol System, 30% (v:v)				
298	3.980	1.502	9.374	7.871
303		1.460	9.608	8.147
308		1.419	9.775	8.355
313		1.377	10.04	8.662
318		1.336	10.29	8.958
Aqueous PVOH system, 0.9 g/dL				
298	3.831	1.502	9.289	7.935
303		1.460	9.588	8.276
308		1.419	9.978	8.707
313		1.377	10.24	9.019
318		1.336	10.49	9.306
Aqueous PVOH (0.9 g/dL) + Methanol system (30% (v:v))				
298	3.911	1.502	10.36	8.928
303		1.460	10.71	9.323
308		1.419	10.88	9.530
313		1.377	11.12	9.818
318		1.336	11.34	10.07

Free energy change of activation for dissociation ($\Delta G_d{}^\#$) refers to the maximum amount of energy free to do useful work:

$$\Delta G_d^\# = -2.303\, RT \log K_d \qquad (7)$$

Table 7, shows the values of free energy change of activation for dissociation of nickel sulfate. The positive values of $\Delta G_d^\#$ indicate that the dissociation process was non spontaneous and lower stability of species in solvent media. There was observed increased in values of free energy change of activation with the increase in percent composition of methanol show that ionic species are more stable in solvent mixture than in aqueous system. Thus, the resulting lower value of conductivity in solvent mixture of aqueous methanol than in aqueous system.

The enthalpy change of activation for dissociation "$\Delta H_d^\#$" was calculated by Equation (8),

$$\Delta H_d{}^\# = E_a^\# - R.T \qquad (8)$$

The values of enthalpy change of activation for dissociation of nickel sulfate were shown in Table 7. The values for$\Delta H_d^\#$ decreased with the increase in temperature indicate the endothermic nature of ionic process. The low value of enthalpy change of activation shows that ion-dissociation decreased and ion–association increased, in high percent composition of methanol. Entropy change of activation for dissociation"$\Delta S_d^\#$" is a measure of randomness or disorderness of a system significantly connected with solvent structural perturbation and calculated by the relation:

$$\Delta S_d^\# = \frac{\Delta H_d^\# - \Delta G_d^\#}{T} \qquad (9)$$

Entropy change of activation increased with the increase in percent composition (0 to 30%) for nickel sulfate is also tabulated in Table 7. The increased in percent composition of aqueous methanol results an increase in the values of entropy change of activation as solvent structure disturbed by the change in percent composition of methanol in aqueous medium, which caused more hindrance in the flow of the ions and responsible for the decreased in conductivity of electrolytes i.e. $NiSO_4$in aqueous methanol system.

Table 8. Condutometric data comparison with literature.

Solvent system	Λ_m (S.cm^2/mol) Reported	Solvent system	Λ_m (S.cm^2/mol) Observed
Aqueous	203.0 (293.15 K) 0.001 mol/dm^3	Aqueous	152.5 (298 K) 0.004 mol/dm^3
X = 0.1233 Aq. methanol	116.0 (293.15 K) 0.001 mol/dm^3 [29]	Methanol 20% (*v:v*)	115.0 (298 K) 0.008 mol/dm^3

The results of present work can be compared with earlier work in many respects. The results are compared with respect to influence of solvent and temperature on conductance as shown in Table 8. Akilan *et al.* [11] have studied that in $NiSO_4$, $CoSO_4$ and $CuSO_4$ solutions three ion pair types exist simultaneously depending on temperature and concentration range as in present work observed ion pair formation may occur with the rise of temperature, concentration and with the change in medium. Saeed *et al.* [12] observed through viscometric data that at higher concentration of PVOH, strong association of polymer with water was present as compared to solvent interaction with ions. While show small interaction with ions at lower concentration of PVOH, as observed in present work though conductometric data. Pan *et al.* [35] studied the electrical conductance of nicotinic acid in aqueous PVOH also concluded that with the addition of PVOH degree of dissociation decreases. In the present work it was also found that degree of dissociation decreased for divalent transition metal sulfates. Bešter-Rogač *et al.* [7] have also reported the negative entropy change of activation for divalent transition metal sulfates in water as obtained in the present work.

3.1. Spectral analysis of $NiSO_4$ in aqueous, aqueous PVOH and aqueous PVOH + methanol systems

For the confirmation of divalent metal sulfate-polyvinyl alcohol complexation, spectroscopic analysis was carried out. Geckeler [36] and Lin *et al.* [37] have studied the polymer-ion complexation.

Results indicate that there was no significant change in the values of λ_{max} = 393.5 nm, obtained in aqueous, aqueous PVOH and aqueous PVOH + methanol systems for $NiSO_4$ solutions which confirm that divalent transition metal salt is stable in aqueous, aqueous PVOH and aqueous PVOH + methanol system and no side reaction or any other product formation occur.

4. Conclusion

It was concluded that molar conductance of $NiSO_4$ at different temperatures decreased with the increase in percent composition of aqueous methanol and concentration of the electrolyte, the decrease in molar conductance was due to strong H-bonding between water and methanol, which is also confirmed by increased in values of Walden product with increase in percent composition of aqueous methanol. The strong interaction between water and alcohol by hydrogen bonding decreased the dielectric constant of water as a result degree of dissociation decreased. Result obtained from energy of activation $E_a^{\#}$ also show that in aqueous methanol system rate of mobility of ion decreased as increased in the energy of activation of copper sulfate and nickel sulfate in aqueous methanol solvent was observed. Other thermodynamic parameters like $\Delta G_d^{\#}$, $\Delta H_d^{\#}$ and $\Delta S_d^{\#}$ also confirmed the strong interaction between water and alcohol.

Acknowledgements

Summyia Masood would like to thank for the research grant provided by the Dean of Science (DFS), University of Karachi.

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