

FULL PAPER

## Thermodynamic Parameters for solvation of Copper sulfate in (ethanol-water) mixed solvent at different temperatures

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**ABSTRACT:** The measurements of copper sulfate conductance have happened in binary mixed solvent with ethanol in different mass fraction 0%, 20% and 40% (W/W) (EtOH-H<sub>2</sub>O) at four different temperatures from 298.15 to 313.15°K (with a step of 5°K). The experimental data were obtained by using the Fuoss-Shedlovsky extrapolation technique. All thermodynamic parameters for association as molar conductance ( $\Lambda_m$ ), limiting molar conductance ( $\Lambda_0$ ), Walden product ( $\Lambda_0 \eta_0$ ), ion-pair association constant ( $K_A$ ), the activation energy for the transport process ( $E_a$ ) and also the standard thermodynamic parameters for an association ( $\Delta G^\circ_A$ ,  $\Delta H^\circ_A$  and  $\Delta S^\circ_A$ ) were calculated. Although we studied the effect of hydrogen bond formation in solution. The results showed that the association constant was increased with increasing temperature while the molar conductance and the limiting molar conductance values were decreased. Furthermore, the association constant values were increased, so that the association process is endothermic.

**KEYWORDS:** Limiting molar conductance, Ion-pair association Constants, Binary Mixed solvents, Walden product, Association constant.

### Introduction

Thermodynamic properties are very useful study of the intermolecular interactions and geometrical effects in the systems and thermo-physical and bulk properties of solutions. Also, they are necessary in theoretical and applied areas of research and used in many other fields of industry [1-3]. Studying the information of the transport properties (conductance, viscosity, ionic mobility) of electrolytes in aqueous and partially aqueous media tell us all about ion-ion and ion-solvent interactions in these solutions [3-9]. The Fuoss-Shedlovsky which is one of the mathematic equations of conductivity theories has been successfully used to investigate many electrolytes in solutions [9-15]. The physical properties of the binary mixed solvents like the viscosity and the relative permittivity can be varied making them more favor to solvent system for the study of ion association and ion mobility. Recently, a study of the properties

of copper sulfate has become essential in many fields such as biochemistry and other different industry. Copper sulfate used as a coloring ingredient in artworks, especially glasses and potteries and also used in firework manufacture as a blue coloring agent, but it is not safe to mix copper sulfate with chlorates when mixing firework powders [15-17].

The present article shows the effect of all parameters on the transport properties of copper sulfate in a binary mixed solvent with alcohol mass fraction 0%, 20% and 40% (W/W) (EtOH-H<sub>2</sub>O) at four different temperatures from 298.15 to 313.15°K (with a step of 5°K) by applying the Fuoss-Shedlovsky conductivity equation [18].

### Experimental

#### Chemicals

Mixed solvent was prepared using bi distilled water with a specific conductivity of 0.07  $\mu\text{S cm}^{-1}$  at 298.15°K. Ethanol (EtOH, 99.5%), Copper sulfate (CuSO<sub>4</sub>·

99.9%) and Potassium chloride (KCl,  $\geq 99\%$ ) were purchased from Sigma-Aldrich and all used without any purification.

### Solutions

Binary mixed solvent of ethanol–water with the alcohol mass fractions of 0%, 20%, and 40% were selected to be the solvent media for this study and were prepared by mixing required volume of ethanol and water (with error  $\pm 0.01\%$ ) by applying the following equation:

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

Where  $d_1$  and  $d_2$  are the density of alcohol and water respectively,  $V_1$  is the volume of alcohol which will be added to the volume  $V_2$  of water to get the mixture of the required percentage. The physical

properties, relative permittivity ( $\epsilon$ ), and viscosity ( $\eta^\circ$ ) of (ethanol–water) with the alcohol mass fractions of 0%, 20%, and 40% at temperatures from 298.15 to 313.15°K (with a step of 5°K) were discussed in Table 1 [19–21]. The unknown values of the ( $\eta^\circ$ ) and ( $\epsilon$ ) were evaluated by applying the empirical relations of these properties at the temperatures taken from the referred references. Seventeen solutions of CuSO<sub>4</sub> were prepared by mass (Mettler AE 200 balance with a sensitivity of  $\pm 0.0002$  g) with a concentration range ( $1 \times 10^{-3} - 7.1 \times 10^{-4}$  mol.dm<sup>-3</sup>) in the previously prepared mixed solvents taken a certain volume of the salt standard solution and diluted to the required volume.

**Table 1.** The relative permittivity ( $\epsilon$ ), and viscosity ( $\eta$ , mPa s) at different temperatures of the used solvents.

| Solvent                     | T/K    | $\epsilon$ | $\eta/\text{mPa s}$ |
|-----------------------------|--------|------------|---------------------|
| 0% (EtOH-H <sub>2</sub> O)  | 298.15 | 78.3       | 0.8921              |
|                             | 303.15 | 76.31      | 0.8001              |
|                             | 313.15 | 74.3       | 0.7001              |
|                             |        | 72.36      | 0.5928              |
| 20% (EtOH-H <sub>2</sub> O) | 298.15 | 77.97      | 0.9042              |
|                             | 303.15 | 76.2       | 0.8082              |
|                             | 308.15 | 74.26      | 0.7329              |
|                             | 313.15 | 70.6       | 0.6911              |
| 40% (EtOH-H <sub>2</sub> O) | 298.15 | 73.05      | 0.9209              |
|                             | 303.15 | 71.18      | 0.8193              |
|                             | 308.15 | 65.48      | 0.7478              |
|                             | 313.15 | 62.75      | 0.7092              |

### Conductivity measurement

A JENCO, Vision plus EC3175 conductance Meter of cell constant equal ( $1.05 \text{ cm}^{-1}$ ) and a deviation of ( $\pm 0.1 \mu\text{S cm}^{-1}$ ) connected to ultra-thermostat of the type Kottermann4130 (to keep the temperature constant at the desired value with a deviation  $\pm 0.005$  °C) were used for measuring the conductivity of prepared solutions. The cell was calibrated by potassium chloride solutions [22–25].

### Results and discussion

#### Calculation of limiting molar conductance

The specific conductance ( $K_s$ ,  $\mu\text{S cm}^{-1}$ ) of prepared solutions of the salt with a concentration range of ( $1 \times 10^{-3} - 7.1 \times 10^{-4}$  mol.L<sup>-1</sup>) in binary mixed solvents of (ethanol–water) with the alcohol mass fractions of 0%, 20% and 40% at different temperatures from 298.15 to 313.15°K (with a step of 5°K) was obtained. The molar conductance ( $\Lambda_m$ ) for CuSO<sub>4</sub> solutions in binary mixed solvents at different temperatures was calculated applying Eq. (2) and calculated in Table 2.

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

Where  $K_s$  and  $K_{\text{solv}}$  are the specific conductance of the solution and the solvent,

respectively;  $K_{\text{cell}}$  is the cell constant and  $C$  is the molar concentration of the metal salt solution.

The experimental conductance data were analyzed using Fuoss-Shedlovsky conductivity equations. The limiting molar conductance ( $\Lambda_o$ ) was estimated for Copper sulfate solutions in  $\text{H}_2\text{O}$  and (EtOH- $\text{H}_2\text{O}$ ) mixed solvents at different temperatures by extrapolating the linear Onsager plot [26] between ( $\Lambda_m$ ) and ( $C$ )<sup>1/2</sup> as shown in Fig. 1.

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

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

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

The value of ( $\Lambda_o$ ) was used to calculate the

Onsager slope ( $S$ ) from the Eq.(6)

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

$$a = 8.2 \times 10^5 / (\epsilon T)^{3/2} \quad (7)$$

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

Where ( $\epsilon$ ) is the relative permittivity of the solvent, ( $\eta_o$ ) is the viscosity of the solvent and ( $T$ ) is the temperature. Using the values of ( $\epsilon$ ) and ( $\eta_o$ ), the value of ( $S$ ) was easily estimated. Using the data of ( $\Lambda_m$ ),  $S(z)$  and ( $\Lambda_o$ ), the values of degree of dissociation ( $\alpha$ ) were calculated by using the following equation:

$$(\alpha) = \frac{\Lambda_m S(Z)}{\Lambda_o} \quad (9)$$

Using these ( $\alpha$ ) and ( $\epsilon$ ) values, the mean activity coefficients ( $\gamma_{\pm}$ ) were evaluated by means of Eq.(10).

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

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

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

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

**Table 2.** The molar conductance ( $\Lambda \pm 0.07$ ,  $\text{S cm}^2 \text{mol}^{-1}$ ) for copper sulfate in the used solvents at different temperatures.

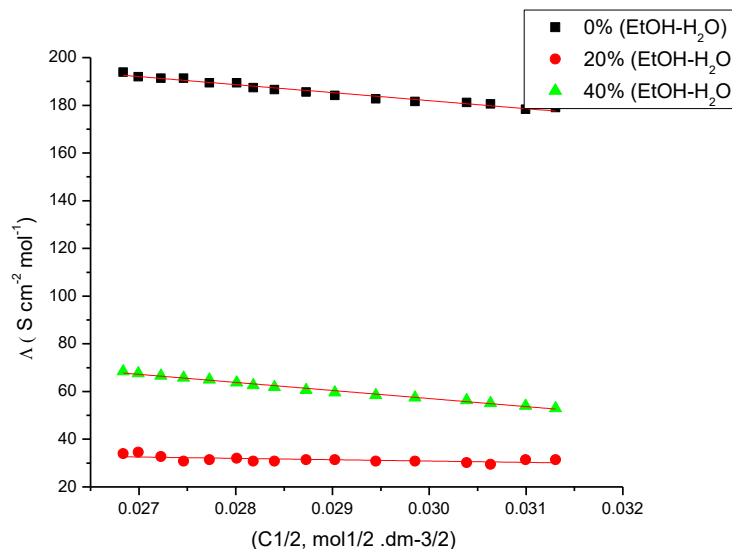
| Solvent                          | C<br>(mol. d m <sup>-3</sup> )x10 <sup>3</sup> | $\Lambda$ ( S cm <sup>2</sup> mol <sup>-1</sup> ) |        |        |        |
|----------------------------------|--|---|--------|--------|--------|
|                                  |  | 298.15  | 303.15 | 308.15 | 313.15 |
| 0% (EtOH- $\text{H}_2\text{O}$ ) | 1  | 197.70  | 201.20 | 206.00 | 210.00 |
|                                  | 0.98   | 198.54  | 202.13 | 207.05 | 211.15 |
|                                  | 0.95   | 199.08  | 202.76 | 207.80 | 212.00 |
|                                  | 0.93   | 199.63  | 203.39 | 208.55 | 212.85 |
|                                  | 0.91   | 200.86  | 204.71 | 209.99 | 214.39 |
|                                  | 0.89   | 202.05  | 205.99 | 211.39 | 215.89 |
|                                  | 0.87   | 202.75  | 206.77 | 212.29 | 216.89 |
|                                  | 0.85   | 203.16  | 207.27 | 212.91 | 217.61 |
|                                  | 0.83   | 204.12  | 208.32 | 214.08 | 218.88 |
|                                  | 0.82   | 205.43  | 209.72 | 215.60 | 220.50 |
|                                  | 0.8  | 206.00  | 210.38 | 216.38 | 221.38 |
|                                  | 0.78   | 206.93  | 211.40 | 217.52 | 222.62 |
|                                  | 0.77   | 207.61  | 212.16 | 218.40 | 223.60 |
|                                  | 0.75   | 208.03  | 212.66 | 219.02 | 224.32 |
|                                  | 0.74   | 208.85  | 213.57 | 220.05 | 225.45 |
| 0.73                             | 209.55   | 214.36  | 220.96 | 226.46 |        |
| 0.71                             | 210.00   | 214.90  | 221.62 | 227.22 |        |
| 20%(EtOH- $\text{H}_2\text{O}$ ) | 1  | 47.70   | 50.40  | 51.70  | 60.00  |
|                                  | 0.98   | 48.38   | 50.94  | 52.07  | 60.58  |
|                                  | 0.95   | 48.72   | 51.24  | 52.61  | 61.11  |
|                                  | 0.93   | 48.91   | 51.60  | 53.32  | 61.49  |
|                                  | 0.91   | 48.73   | 51.92  | 53.90  | 62.15  |

|                            |      |       |       |       |       |
|----------------------------|------|-------|-------|-------|-------|
|                            | 0.89 | 49.28 | 52.43 | 54.45 | 62.78 |
|                            | 0.87 | 49.68 | 53.02 | 54.97 | 63.37 |
|                            | 0.85 | 50.29 | 53.35 | 55.46 | 64.04 |
|                            | 0.83 | 50.76 | 53.64 | 56.04 | 64.68 |
|                            | 0.82 | 51.08 | 54.15 | 56.47 | 65.17 |
|                            | 0.8  | 51.25 | 54.50 | 57.00 | 65.63 |
|                            | 0.78 | 51.38 | 54.95 | 57.63 | 66.30 |
|                            | 0.77 | 51.74 | 55.25 | 58.50 | 66.82 |
|                            | 0.75 | 52.34 | 55.65 | 59.10 | 67.44 |
|                            | 0.74 | 52.65 | 55.89 | 59.54 | 67.91 |
|                            | 0.73 | 52.94 | 56.24 | 59.95 | 68.48 |
|                            | 0.71 | 53.06 | 56.56 | 60.48 | 68.88 |
| 40%(EtOH-H <sub>2</sub> O) | 1    | 24.70 | 25.50 | 26.90 | 27.40 |
|                            | 0.98 | 24.81 | 25.93 | 27.57 | 28.09 |
|                            | 0.95 | 25.10 | 26.57 | 27.62 | 28.56 |
|                            | 0.93 | 25.16 | 26.66 | 27.84 | 28.81 |
|                            | 0.91 | 25.41 | 26.84 | 28.27 | 29.15 |
|                            | 0.89 | 25.65 | 27.00 | 28.24 | 29.48 |
|                            | 0.87 | 25.99 | 27.49 | 28.87 | 29.56 |
|                            | 0.85 | 26.09 | 27.85 | 28.55 | 30.20 |
|                            | 0.83 | 26.16 | 28.08 | 29.16 | 30.84 |
|                            | 0.82 | 26.34 | 28.30 | 29.52 | 31.12 |
|                            | 0.8  | 26.38 | 28.50 | 30.00 | 31.13 |
|                            | 0.78 | 26.52 | 29.07 | 30.09 | 31.62 |
|                            | 0.77 | 26.65 | 29.12 | 30.55 | 32.24 |
|                            | 0.75 | 26.63 | 29.68 | 31.14 | 32.60 |
|                            | 0.74 | 26.60 | 29.43 | 31.46 | 33.21 |
|                            | 0.73 | 26.54 | 29.70 | 32.04 | 33.55 |
|                            | 0.71 | 26.60 | 29.54 | 32.20 | 33.88 |

The obtained results for Copper sulfate, Table 3, in a binary mixed solvent (EtOH-H<sub>2</sub>O) at different temperatures are different from those in case of water[27], As the limiting molar conductance of copper sulfate in (EtOH-H<sub>2</sub>O) mixtures is less than in water because conductivity values decrease when mixed solvent increases. Also conductance decrease in case of 40% than 20% in case of water and this due to formation of intermolecular and intramolecular hydrogen bonding which

make hindrance to the ions mobility. In another case of increasing content of ethanol in mixed solvent lead to reduce the solvation and dissociation of copper sulfate molecules.

Also, the limiting molar conductance for copper sulfate in all used solvents is increases with rise in temperature due to the increasing of kinetic energies of ions. The mentioned effect was supported by ionization degree ( $\alpha$ ) which is decreased by increasing the temperature.



**Fig 1.** The plot of ( $\Lambda$ ) versus ( $C^{1/2}$ ,  $\text{mol}^{1/2} \cdot \text{dm}^{-3/2}$ ) at 313.15° K in mixed (EtOH–H<sub>2</sub>O) solvents for copper sulfate.

**Table 3.** The limiting molar conductances ( $\Lambda_0$ ,  $\pm 0.25\%$ ,  $\text{S cm}^2 \text{mol}^{-1}$ ) and Fuoss–Shedlovsky parameters of copper sulfate in the used solvents at different temperature.

| Solvent                    | T/K    | $\Lambda_0$ | S        | Z      | S(Z)   | A      | $\gamma_{\pm}$ | A      |
|----------------------------|--------|-------------|----------|--------|--------|--------|----------------|--------|
| 0% (EtOH-H <sub>2</sub> O) | 298.15 | 257.28      | 119.5995 | 0.0112 | 1.0113 | 0.6744 | 0.9446         | 0.6744 |
|                            | 303.15 | 266         | 129.7038 | 0.0117 | 1.0118 | 0.6733 | 0.9439         | 0.6733 |
|                            | 308.15 | 271.27      | 139.612  | 0.0123 | 1.0124 | 0.6657 | 0.9433         | 0.6657 |
|                            | 313.15 | 284.37      | 156.4985 | 0.0131 | 1.0131 | 0.6559 | 0.9429         | 0.6559 |
| 20%(EtOH-H <sub>2</sub> O) | 298.15 | 82.53       | 78.8631  | 0.0218 | 1.0218 | 0.5146 | 0.9466         | 0.6152 |
|                            | 303.15 | 90.71       | 88.2674  | 0.0219 | 1.0219 | 0.5195 | 0.9469         | 0.5974 |
|                            | 308.15 | 109.22      | 100.196  | 0.0310 | 1.0310 | 0.5269 | 0.9502         | 0.5130 |
|                            | 313.15 | 118.14      | 109.65   | 0.0312 | 1.0313 | 0.5548 | 0.9483         | 0.4951 |
| 40%(EtOH-H <sub>2</sub> O) | 298.15 | 41.64       | 71.2528  | 0.0398 | 1.0401 | 0.5674 | 0.9397         | 0.6495 |
|                            | 303.15 | 54.13       | 82.4694  | 0.0339 | 1.0345 | 0.5754 | 0.9416         | 0.5913 |
|                            | 308.15 | 59.64       | 94.6348  | 0.0325 | 1.0330 | 0.6364 | 0.9407         | 0.5009 |
|                            | 313.15 | 67.71       | 103.0415 | 0.0296 | 1.0302 | 0.6621 | 0.9415         | 0.4497 |

**Table 4.** The mean ion pair association constant ( $K_A$ ,  $\pm 0.3\%$ ,  $\text{mol} \cdot \text{dm}^{-3}$ ), Walden product ( $\Lambda_0 \eta$ ,  $\text{S} \cdot \text{mol}^{-1} \cdot \text{cm}^2 \text{Pa} \cdot \text{s}$ ) and the hydrodynamic radii ( $R_H$ ) of copper sulfate in the used solvents at different temperatures.

| Solvent                    | T/K    | $K_A$    | $\Lambda_0 \eta$ | $R_H$  |
|----------------------------|--------|----------|------------------|--------|
| 0% (EtOH-H <sub>2</sub> O) | 298.15 | 922.7565 | 227.5228         | 0.0036 |
|                            | 303.15 | 930.4575 | 212.8266         | 0.0038 |
|                            | 308.15 | 975.102  | 195.9112         | 0.0042 |
|                            | 313.15 | 1034.417 | 178.6279         | 0.0046 |
| 20%(EtOH-H <sub>2</sub> O) | 298.15 | 1304.18  | 74.6236          | 0.0109 |
|                            | 303.15 | 1446.256 | 73.120           | 0.0112 |
|                            | 308.15 | 2357.14  | 70.004           | 0.0117 |
|                            | 313.15 | 2633.162 | 68.142           | 0.0120 |
| 40%(EtOH-H <sub>2</sub> O) | 298.15 | 1481.593 | 38.3463          | 0.0213 |
|                            | 303.15 | 1515.638 | 34.3483          | 0.0238 |
|                            | 308.15 | 2597.16  | 34.099           | 0.0240 |
|                            | 313.15 | 3530.324 | 31.0466          | 0.0264 |

### Ion-pair association constant

The mean values of the ion-pair association constant ( $K_A$ ) of systems under study were represented in Table 4. It was seen that the association constant for copper sulfate in the used solvents raises with raising temperature which indicates an endothermic association process. This temperature dependence of the association process of ions can be explained from the relation between desolvation and association of ions whereas the temperature increases, the desolvation process of ions takes place, the ions will be closer than before, therefore the association of ions increases.

For all the studied systems, the association constant increases as the proportions of organic solvent increase at the same temperature with an exception in the case of 20% (EtOH-H<sub>2</sub>O). This increase in association constant values may be related to decreasing in relative permittivity by increasing the proportions of organic solvent and decreasing ions mobility which give chance for ions to associate. Moreover, this can be interpreted on the basis of the interplay between association constant and strength of the ion solvation in different solvents, whereas the stronger ion is solvated, the association becomes weaker between cations and anions

The association constant values for copper sulfate in 20% (EtOH-H<sub>2</sub>O) is lower than values of association constant in water. This may be related to the interaction between ethanol and water at a low concentration from ethanol which are affected by the cage-like structures formation and are known as (icebergs) around the hydrophobic ends of the ethanol. Moreover, they can affect the mobility of ions and decrease association constant [28].

### Triple-ion association constant

From Fuoss equation [25], the triple ion association constant ( $K_3$ ) for copper sulfate was calculated. The triple ion formation can be neglected due to the small values of triple ion association.

### Walden Product

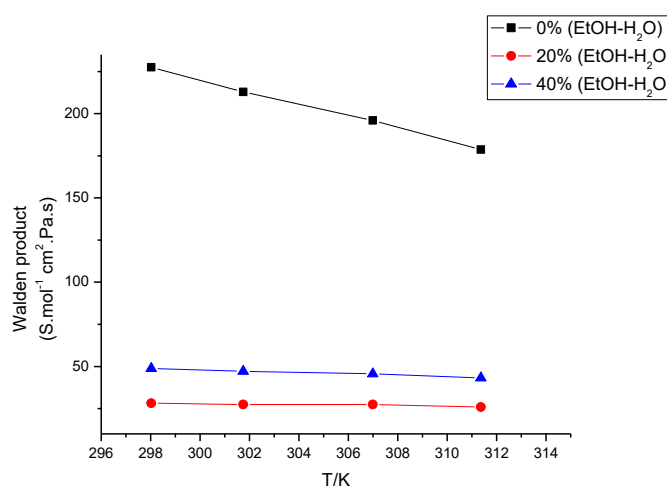
The Walden product ( $\Lambda_0 \eta_0$  or  $\lambda_0 \eta_0$ ) is very important from the point of view of ion-solvent interaction [29, 30]. The Walden product ( $\Lambda_0 \eta_0$ ) is expected to be constant for a given electrolyte in a series of solvent mixtures in which the ion-solvent interactions are uniform due to the Walden product which is the product of ion conductance due to the viscosity of the medium. Besides, it should be independent of the nature of the solvent and the molar conductance of ion at infinite dilution depending only on mobility of ions. Walden has written his rule in the form of Eq.(13).

$$\Lambda_0 \eta_0 = 0.82 \left[ \frac{1}{r_s^+} + \frac{1}{r_s^-} \right] \quad (13)$$

The factor  $\left( \frac{1}{[1/r_s^+ + 1/r_s^-]} \right)$  is a measure of the hydrodynamic radii ( $R_H$ ) of the ions,  $r$  is the radius of a hypothetical sphere that diffuses with the same speed as the particle under study. In practice, the solute molecules in solution are solvated and dynamic. So, the radius calculated from the diffusion properties of the particle is indicative of the apparent size of the dynamic hydrated/solvated particle and the hydrodynamic radius. This means that the hydrodynamic radius ( $R_H$ ) includes both solvent (hydro) and shape (dynamic) effects. The values of Walden product and hydrodynamic radii for the salts and ions under study were calculated and listed in Table 4 and represented in Figure 2. The inverse behavior of the hydrodynamic radii with Walden product was reported by many authors [31,33].

The obtained value of Walden product decreased by increasing the temperature. This may be related to the increase in the size of solvated ions in the mixtures as we raise the temperature which occurred due to the variation of the proportion of the ethanol and H<sub>2</sub>O molecules in the sheath of solvation with temperature. Walden product is affected by two factors: limiting molar conductance which is directly proportional to temperature, and viscosity which is inversely proportional to temperature. From this observation, we can conclude that the viscosity value is the most effective factor

on the inverse proportional behavior of the Walden product with the temperature. The decrease in values of Walden product with increasing proportion of methanol in the order: 0% > 20% > 40% can be explained from the fact that increasing the content of organic solvent leads to a bigger size of solvation shells around cation which reduces its mobility as well as Walden product [34]. Many authors reported the change in Walden product with temperature, solvent composition and nature of electrolyte [35,36].



**Figure 2.** The plot of Walden product ( $\Lambda_0 \eta$ ) vs. temperature (T/K) for copper sulfate in the used solvents.

### Thermodynamics of association

The standard Gibbs free energy of association ( $\Delta G_A^\circ$ ) was calculated using Eq. (13) for all salts under study in all solvent mixtures at all temperatures. The values were tabulated in Table 5.

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

Here, R is the gas constant and equal (8.314 J.mol<sup>-1</sup>.K<sup>-1</sup>). The values of the standard enthalpy ( $\Delta H_A^\circ$ ) and the standard entropy ( $\Delta S_A^\circ$ ) of association process were obtained from van't Hoff equation ( $\frac{d \ln K}{dT} = \frac{\Delta H_A^\circ}{RT^2}$ ) by plotting (log K<sub>A</sub>) versus (1/T), where the slope is equal to the value of ( $-\Delta H_A^\circ/2.303R$ ), the entropies of association

( $\Delta S_A^\circ$ ) were calculated by the use of Gibbs–Helmholtz equation Eq. (15).

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

The thermodynamic parameters of association values showed the effect of temperature when increased in the negative values of the associating free energy ( $\Delta G_A^\circ$ ) as the temperature rise from 298.15 to 313.15 K. It was found that the association processes in all studied systems are spontaneous processes and the associating free energy becomes more negative with the increase in temperatures. This indicates that an ion-pair association is favored with lowering the dielectric constant of the medium.

The association processes are endothermic in nature due to the positive value of ( $\Delta H^{\circ}_A$ ). A positive entropy values ( $\Delta S^{\circ}_A$ ) can be explained on the assumption that iceberg structure around the cation is broken when association takes place leading to an increase in the degree of disorderliness and the positive ( $\Delta H^{\circ}_A$ ) and ( $\Delta S^{\circ}_A$ ) values are in a good agreement with several theories in many solvents. Positive

values of ( $\Delta H^{\circ}_A$ ) and ( $\Delta S^{\circ}_A$ ) for association can be attributed to counter balance of the enthalpy term by a favorable entropy change resulting from the short- and long-range desolvation of both ions. Positive ( $\Delta S^{\circ}_A$ ) values attributed to desolvation of both ions are also supported by the positive enthalpy values indicating a lack of covalent bonds.

**Table 5.** The thermodynamic parameters of association ( $\Delta G^{\circ}_A, \pm 0.33\%$ ), ( $\Delta H^{\circ}_A, \pm 0.22\%$ ) and ( $\Delta S^{\circ}_A, \pm 7.42\%$ ) for copper sulfate in used solvents at different temperatures.

| Solvent                    | T/K    | $\Delta G^{\circ}_A$    | $\Delta H^{\circ}_A$    | $\Delta S^{\circ}_A$   |
|----------------------------|--------|-------------------------|-------------------------|------------------------|
|                            |        | (KJ.mol <sup>-1</sup> ) | (KJ.mol <sup>-1</sup> ) | (J.mol <sup>-1</sup> ) |
| 0% (EtOH-H <sub>2</sub> O) | 298.15 | -16.9269                | 6.0219                  | 76.6707                |
|                            | 303.15 | -17.2317                |                         | 76.7067                |
|                            | 308.15 | -17.636                 |                         | 76.7741                |
|                            | 313.15 | -18.0759                |                         | 76.9531                |
| 20%(EtOH-H <sub>2</sub> O) | 298.15 | -17.7846                | 30.4706                 | 160.796                |
|                            | 303.15 | -18.3432                |                         | 161.014                |
|                            | 308.15 | -19.898                 |                         | 161.94                 |
|                            | 313.15 | -20.5089                |                         | 162.67                 |
| 40%(EtOH-H <sub>2</sub> O) | 298.15 | -17.8737                | 62.238                  | 265.018                |
|                            | 303.15 | -18.749                 |                         | 265.34                 |
|                            | 308.15 | -20.147                 |                         | 265.588                |
|                            | 313.15 | -21.2724                |                         | 266.661                |

## Conclusions

In this paper, conductivity measurements for copper sulfate in a binary mixed solvent with alcohol mass fraction of 0%, 20%, and 40% (EtOH-H<sub>2</sub>O) at different temperatures from 298.15 to 313.15 K (with a step of 5 K) have been reported. The conductivity data have been analyzed using Fuoss – Shedlovsky equation. The extent of ion-pairing in copper sulfate solutions under study depends on the nature of the (ion-solvent) and (solvent-solvent) interaction taking place in the solution. Furthermore, it depends on the relative permittivity and the properties of the medium. The association constant increases as the temperature increases and as the proportion of methanol increases. Also, the unusual behavior of 20% (EtOH-H<sub>2</sub>O) mixed solvent have been studied. The values of Gibbs free energy of association ( $\Delta G^{\circ}_A$ ) which become more

negative give an indication of the association process and is spontaneous in nature. The positive value of entropy change ( $\Delta S^{\circ}_A$ ) is indicating that the entropy is the driving force for the association process. The positive value of the enthalpy change ( $\Delta H^{\circ}_A$ ) indicates that the association process is endothermic.

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