



Ion association and solvation behavior of copper sulfate in binary aqueous–methanol mixtures at different temperatures



Esam A. Gomaa, Mohamed A. Tahaon *

Chemistry Department, Faculty of Science, Mansoura University, 35516 Mansoura, Egypt

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ABSTRACT

The specific conductance (κ) of copper sulfate in binary mixtures (methanol–water) with the alcohol mass fractions of 0%, 20% and 40% at different temperatures of (298.15, 303.15, 308.15 and 313.15) K was measured experimentally. The conductivity data have been analyzed using the Fuoss–Shedlovsky conductivity equation. The molar conductance (Λ_M), the limiting molar conductance (Λ_0), the association constants (K_A), the Walden product ($\Lambda_0\eta_0$), and the standard thermodynamic parameters of association (ΔG°_A , ΔH°_A and ΔS°_A) were calculated and discussed. The results show that, the molar conductance and the limiting molar conductance values were decreased as the relative permittivity of the solvent decreased while, the association constant increased. Also the results show that the values of the molar conductance, the limiting molar conductance and the association constant were increased as the temperature increased indicating that the association process is an endothermic one.

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1. Introduction

Studies on electrolyte conductance of an electrolyte and the effect of ion – solvation on it in aqueous and partially aqueous media have received considerable attention in recent years as they are important both from fundamental and technological points of view [1]. The use of non-aqueous and partially aqueous solvents has been widely accepted, in place of water due to their wide applicability in various fields. It has become a practice to use solvent mixtures, water being one among the solvent mixtures [2–3]. The solvent mixtures not only give an idea about ion–solvent and solvent–solvent–interactions but also the preferential solvation of ion. The concept of ion association is widely used in solution chemistry. A literature survey shows that ion–pair or multiple-ion association phenomena and the nature of the solute–solvent interactions (in aqueous, non-aqueous and mixed solutions) have been studied conductometrically [4–10]. In the above references the electrical conductivity has been discussed largely as a function of the dielectric constant and the mathematics of conductance theories has been applied for many electrolytic systems. One of the mathematics of conductance theories is the Lee–Wheaton conductivity equation [11], which is one of the recent conductivity equations based on a more realistic picture or model in which the ions exist in one of three states: as free ions, as solvent-separated ion-pairs and/or as contact ion pairs [12]. Fuoss–Shedlovsky conductivity equation has been successfully used by many researchers for the investigation of many electrolytes in solutions in which ionic association predominates [13–19]. Alcohol–water mixtures at different temperatures exhibit a wide range of

dielectric constants, viscosity and a high degree of hydrogen bonding effect, so that the present article aims to study the effect of dielectric constants, viscosity and the hydrogen bonding on the transport properties of copper sulfate in binary mixtures methanol–water (MeOH–H₂O) with the alcohol mass fractions of 0%, 20% and 40% at different temperatures (298.15, 303.15, 308.15 and 313.15) K by applying the Fuoss–Shedlovsky conductivity equation [44].

2. Experimental

2.1. Materials and solutions

Copper sulfate pentahydrate (CuSO₄·5H₂O, 99.5%), methanol (MeOH, 99%), all were supplied from Riedel-de Haën company (Germany) and used without further purification. Bidistilled water with specific conductivity of 0.06 $\mu\text{S cm}^{-1}$ at 298.15 K was also used for the preparation of the mixed solvents. Binary mixtures of methanol–water with the alcohol mass fractions of 0%, 20% and 40% were prepared by applying the following equation:

$$\text{Alcohol percentage} = (V_1d_1)/100/(V_1d_1 + V_2d_2) \quad (1)$$

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 salts under investigation with a concentration of (8×10^{-4} , 7×10^{-4} , 6×10^{-4} , 5×10^{-4} , 4×10^{-4} , 3×10^{-4} , 2×10^{-4} , 1×10^{-4} , 1×10^{-3} , 3×10^{-3} mol·dm⁻³), were prepared by taking certain volume of the salt standard solution and diluted to the required volume for measurements by the previously prepared mixed solvents.

* Corresponding author.

E-mail address: tahaon_87@yahoo.com (M.A. Tahaon).

2.2. Conductivity measurement

The conductance measurements of the prepared salt solutions were carried out using Jenway Conductivity Bridge of a cell constant value 1 cm^{-1} and a deviation of $\pm 0.1 \mu\text{S cm}^{-1}$. The cell constant was determined with potassium chloride solutions [20]. The Conductivity Bridge was connected to MLW 3230 ultrathermostate to maintain the temperature constant at the desired temperature ($\pm 0.005 \text{ }^\circ\text{C}$).

3. Results and discussion

The physical properties, density (ρ) [20] viscosity (η) [21] and dielectric constant (ϵ) [22] of (methanol–water) with the alcohol mass fractions of 0%, 20% and 40% at temperatures of (298.15, 303.15, 308.15 and 313.15) K were tabulated in Table 1. The unavailable values of the ρ , η and ϵ were evaluated by applying the empirical relations of these properties at the available temperatures taken from the referred references. The specific conductance (κ , $\mu\text{S cm}^{-1}$) of solutions of the salt under investigation with a concentration range of ($8 \times 10^{-4} - 3 \times 10^{-3} \text{ mol L}^{-1}$) in binary mixtures of methanol–water with the alcohol mass fractions of 0%, 20% and 40% at temperatures of (298.15, 303.15, 308.15 and 313.15) K was measured experimentally. The molar conductance (Λ_m) for all studied systems was calculated by applying Eq. (2) and recorded in Tables 2, 3 and 4.

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

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

3.1. Limiting molar conductance

The experimental conductivities were analyzed by means of the Fuoss–Shedlovsky conductivity equations [43–44].

To start the Shedlovsky technique, the limiting molar conductance (Λ_0) at infinite dilutions were estimated for metal salt solution in H_2O , and mixed solvents at different temperatures by extrapolating the linear Onsager plot [24] between Λ_m and $C^{1/2}$ to zero concentration.

$$\frac{1}{\Lambda_m S(Z)} = \frac{1}{\Lambda_0} + \left(\frac{K_A}{\Lambda_0^2} \right) (C \Lambda_m \gamma_{\pm}^2 S(Z)) \quad (3)$$

Where

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

$$Z = \frac{S(\Lambda_m C)^{1/2}}{\Lambda_0^{3/2}} \quad (5)$$

$$S = a\Lambda_0 + b \quad (6)$$

Table 1

The relative permittivity (ϵ), density (ρ , g cm^{-3}) and viscosity (η , C.P) at different temperatures of the used solvents.

Solvent	Property	298.15 K	303.15 K	308.15 K	313.15 K
0%(MeOH–H ₂ O)	ϵ	78.3	76.51	74.76	73.05
	ρ	0.9970	0.9942	0.9912	0.988
	η	0.8904	0.7975	0.7194	0.6529
20%(MeOH–H ₂ O)	ϵ	73.74	71.84	69.94	67.54
	ρ	0.9650	0.9638	0.9620	0.960
	η	0.8566	0.7689	0.6960	0.6305
40%(MeOH–H ₂ O)	ϵ	67.88	66.09	64.33	62.63
	ρ	0.9319	0.9301	0.9287	0.9275
	η	0.8133	0.7320	0.6660	0.6016

Table 2

The limiting molar conductance's (Λ_0 , $\pm 0.25\%$, $\text{S mol}^{-1} \text{ cm}^2$) and Fuoss–Shedlovsky parameters of the studied salt in the used solvents at different temperatures.

Solvent	T/K	Λ_0	S	Z	S(z)	α	γ_{\pm}
0% (MeOH–H ₂ O)	298.15	292.74	127.86	0.0116	0.1011	0.7211	0.8811
	303.15	298.03	137.02	0.0122	0.1012	0.7148	0.8805
	308.15	308.50	147.81	0.0125	0.1013	0.6936	0.8811
	313.15	318.82	194.79	0.0087	0.1008	0.6839	0.9017
20% (MeOH–H ₂ O)	298.15	199.52	115.05	0.0145	1.0146	0.6441	0.8774
	303.15	201.14	123.93	0.0155	1.0156	0.6487	0.8753
	308.15	204.25	133.56	0.0165	1.0166	0.6487	0.8735
	313.15	207.66	148.15	0.0165	1.0167	0.6086	0.8729
40% (MeOH–H ₂ O)	298.15	112.30	103.19	0.0244	1.0247	0.7278	0.8543
	303.15	117.12	113.38	0.0254	1.0257	0.7091	0.8540
	308.15	123.41	124.12	0.0260	1.0264	0.6889	0.8538
	313.15	128.59	139.17	0.0276	1.0279	0.6159	0.8535

where

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

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

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

Using these (α) and (ϵ) values, the mean activity coefficients (γ_{\pm}) were evaluated by means of Debye–Hückel equation:

$$\log \gamma_{\pm} = - \frac{Z_+ Z_- A \sqrt{I}}{I + B r^0 \sqrt{I}} \quad (10)$$

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

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

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

K_A is the thermodynamic ion-pair association constant, α is the degree of dissociation, ϵ is the dielectric constant of the solvent. (η) is the viscosity of the solvent and (T) is the temperature [23].

The calculated and the experimental values of the limiting molar conductance as a function of the square root of the concentration were compared as noted in Fig. 1.

In comparing the obtained results for the salt under study in alcoholic–aqueous mixtures with that for the same salt in water solvent [25] at different temperatures (Table 2) we can observe that the limiting molar conductance of the studied systems in water is higher than that in alcoholic–water mixtures. This may be related to the formation of intermolecular and intramolecular hydrogen bonding with the presence of the alcohol in the solution. Also it may be related to a possibility of

Table 3

The mean ion pair association constant (K_A , $\pm 0.3\%$, $\text{dm}^3 \text{ mol}^{-1}$) used salts in the used solvents at different temperatures.

Solvent	T/K	K_A
0% (MeOH–H ₂ O)	298.15	690.569
	303.15	719.413
	308.15	819.852
	313.15	921.664
20% (MeOH–H ₂ O)	298.15	1089.35
	303.15	1093.63
	308.15	1114.63
	313.15	1383.49
40% (MeOH–H ₂ O)	298.15	1754
	303.15	1838.53
	308.15	1929.88
	313.15	1981.81

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