

Transport properties of 2:2 symmetrical electrolytes in (water + ethylene glycol) binary mixtures at $T = 293.15$ K

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Abstract

The specific conductivities (k), the densities (ρ), and the absolute viscosities (η) of solutions of zinc(II) sulfate in (water + ethylene glycol) (EG) binary mixtures have been measured at $T = 293.15$ K. The conductivity data have been analyzed using the Lee–Wheaton conductivity equation and the limiting molar conductivities (Λ_0), the association constants (K_A), and the centre-to-centre distance of the formed ion pairs (α) have been derived. The limiting ion conductivities (λ_{\pm}°) have been evaluated and used for the calculation of the “corrected” Stoke’s radii (r_{Cor}), according to the method proposed by Robinson and Stokes. The ion mobilities have been found to be controlled completely by the bulk viscosity. The ionic association was enhanced with the increasing of the EG content in the solvent mixtures, due to the gradual decrease of the dielectric constant of the solvent medium. The formed ion pairs have been recognized to be solvent separated pairs. The viscosity data have been interpreted in terms of the Jones–Dole equation. The B_1 viscosity coefficient indicated that the Zn^{2+} ion acts as a “structure maker”.

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1. Introduction

The investigation of the transport properties of the electrolytes gives valuable information on the ion–ion and ion–solvent interactions in solution. A survey of literature shows that conductivity and viscosity studies of electrolytes in several solvent media have been performed in recent years to explore the type and the extent of the interactions in electrolyte solutions [1–17]. The limiting molar conductance, the thermodynamic association constant and the Jones–Dole viscosity coefficients are the fundamental quantities that have been extracted from these studies. Whereas the investigation of the transport properties of

symmetrical 1:1 electrolytes in binary mixtures has been the subject of numerous studies [1,3–7,9–17], 2:2 type electrolytes have not been examined so far [2,8]. Previous experience with the transport properties of electrolytes in binary mixtures of (water + methanol) [18], (water + *N,N*-dimethylformamide) [19], (water + dimethylsulfoxide) [20], and (water + ethylene glycol) [21] led us to an investigation of zinc(II) sulfate in (water + ethylene glycol) (EG) binary mixtures. The conductivity data have been analyzed using the Lee–Wheaton conductivity equation and the values of the limiting molar conductance (Λ_0), the association constant (K_A), and the centre-to-centre distance of the formed ion pairs (α) have been derived. Furthermore, the limiting ion conductivities (λ_{\pm}°) have been evaluated and used for the calculation of the Stoke’s radii ($r_{\text{St}\pm}$). The “corrected” Stoke’s radii (r_{Cor}) have been calculated according to the method proposed by Robinson and Stokes. The viscosity data have been interpreted in terms of the Jones–Dole

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equation and the corresponding B , B_i , and B_{ip} coefficients have been derived.

Glycols, the dihydroxy derivatives of the paraffins, have been the subject of considerable interest due to the versatility of these compounds as solvents in the pharmaceutical, chemical, cosmetic and food industries [22,23]. Ethylene glycol (EG) is the simplest glycol with dielectric constant $\epsilon = 38.66$ (at $T = 293.15$ K) and dipole moment $\mu = 2.20$ D [24]. The EG is self-associated in the pure state creating a net of hydrogen bonds which are dependent on the temperature and the presence of the electrolytes [25]. In aqueous solutions, EG gives rise to two or three-dimensional networks through hydrogen bonds with the consequence that the mixtures display negative deviations from ideality [26].

A literature survey revealed that conductivity studies on aqueous solutions of zinc(II) sulfate have been already reported by Acevedo *et al.* [27] and Bešter Rogač *et al.* [28]. As far as we know, viscometric and conductivity studies of zinc(II) sulfate in (water + EG) binary mixtures have not been carried out. Consequently, one of the objectives of the present paper is to provide accurate experimental conductivity and viscosity data for zinc(II) sulfate in (water + EG) binary mixtures. Furthermore, the macroscopic and the microscopic investigation of the behaviour of the solvated Zn^{2+} constitutes the main purpose of this article.

2. Experimental

2.1. Materials

Ethylene glycol (Merck, mass fraction purity 0.995) was distilled under vacuum. The purity was assessed by comparing the experimental density ($\rho = 1.11323$ g · cm⁻³), viscosity ($\eta = 20.806$ mPa · s), and refractive index ($n_D = 1.4319$) at $T = 293.15$ K with the corresponding literature values, $\rho = 1.11350$ g · cm⁻³, $\eta = 21.0$ mPa · s, and $n_D = 1.4318$ [29,24]. The agreement was satisfactory. The dried EG was stored over 0.4 nm molecular sieves. The specific conductance of the purified EG was sufficiently small 0.15 $\mu\text{S} \cdot \text{cm}^{-1}$. Water was de-ionized by an ion exchange resin and doubly distilled. The specific conductance of water was found to be 0.70 $\mu\text{S} \cdot \text{cm}^{-1}$ at $T = 293.15$ K. Zinc(II) sulfate heptahydrate $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (Riedel-de Haen, >99.8 mass%) was used without further purification.

2.2. Solutions

The (water + EG) binary mixtures were prepared by mass (± 0.0001 g). The error in the mole fraction was ± 0.0001 . A concentrated stock solution of zinc(II) sulfate was prepared by mass (± 0.0001 g) and the dilute solutions were obtained by diluting the stock solution. Under the conditions used in this work, the electrolyte was completely soluble in all the investigated mixtures. The conversion of molality to molarity was done using the density values.

The dielectric constants of the (water + EG) binary mixtures were taken from the literature [30].

2.3. Measurements

The densities of the solutions were measured with an Anton Paar (DMA 58) digital densimeter with built-in solid-state thermostat. The precision of the sample thermostat was ± 0.01 K. The densimeter was calibrated with dry air and double-distilled water at $T = 293.15$ K. The estimated uncertainty of the measured densities was ± 0.00001 g · cm⁻³.

The conductance measurements were carried out in the concentration range from (0.0001 to 0.0017) mol · dm⁻³ with a digital bridge-type conductivity meter (Jenway PCM 3) working at a frequency of 1 kHz. A conductance cell (dipping type) with electrodes of platinum black was used. The cell constant (0.98 ± 0.01) cm⁻¹ was determined by measuring aqueous solutions of potassium chloride with molarities from (0.001 to 0.100) mol · dm⁻³ at $T = 293.15$ K, according to the method of Lind and co-workers [31]. The dissolved carbon dioxide was removed by bubbling high purity nitrogen in the cell through the solution. The value of the cell constant was computed on the basis of the specific conductance of the potassium chloride solutions reported in the literature [29]. The electrode was cleaned, first with nitric acid solution (0.01 mol · dm⁻³), then with distilled water and finally was dried with acetone. The cell was thermostatted using a water bath at $T = (293.15 \pm 0.01)$ K. The temperature was controlled with a contact thermometer. All data were corrected with the specific conductance of the solvent. The correction was made by subtracting the specific conductance of the solvent medium from those of the electrolyte solutions. The molar conductivities ($\Lambda/S \cdot \text{cm}^2 \cdot \text{mol}^{-1}$) were calculated from the experimental specific conductivities ($k/S \cdot \text{cm}^{-1}$) and the concentrations ($c/\text{mol} \cdot \text{dm}^{-3}$) of the solutions using the equation, $\Lambda = 10^3 k/c$. The reproducibility of the measurements was examined by repeating each experiment two times. The uncertainty of the conductivity measurements has been estimated to be $\pm 0.2\%$.

The viscosities have been measured in a concentration range from (0.0080 to 0.2000) mol · dm⁻³ with a viscosity-measuring unit (Schott Geräte AVS 310) equipped with an Übbelohde capillary viscometer. The viscometer was calibrated with double-distilled water at $T = 293.15$ K and the constant of the viscometer has been calculated. The accuracy in the time measurement was ± 0.01 s. The viscometer was placed in a thermostat (Schott CT 050/2) electronically controlling the set temperature. The temperature was maintained constant within ± 0.03 K. The kinematic viscosities (ν) were averaged from four readings. The absolute viscosities ($\eta/\text{mPa} \cdot \text{s}$) have been calculated from the kinematic viscosities ($\nu/\text{cm}^2 \cdot \text{s}^{-1}$) and the densities ($\rho/\text{g} \cdot \text{cm}^{-3}$) using the relation: $\eta = \nu \cdot \rho$. The uncertainty in the viscosity measurements was $\pm 0.1\%$.

3. Results and discussion

3.1. Conductance measurements

The densities (ρ), the absolute viscosities (η), and the dielectric constants (ϵ) of (water + EG) binary mixtures at 293.15 K are reported in table 1. The molarities (c), the densities (ρ), the specific conductivities (k) and the molar conductivities (A) of the electrolyte in the (water + EG) binary mixtures at $T = 293.15$ K are reported in table 2. The experimental molar conductivities were analyzed by means of the Lee–Wheaton [32–34] conductivity equation in the form suggested by Pethybridge and Taba [35] (equations (1) to (5)) including the mass action law for ion association (equation (6)) and the Debye–Hückel limiting law (equation (7)):

$$A_{\text{Calc.}} = \gamma A_i, \quad (1)$$

$$A_i = A_o [1 + C_1(\beta\kappa) + C_2(\beta\kappa)^2 + C_3(\beta\kappa)^3] - \frac{\rho\kappa}{(1 + \kappa\alpha)} \left[1 + C_4(\beta\kappa) + C_5(\beta\kappa)^2 + \frac{\kappa\alpha}{12} \right], \quad (2)$$

$$\beta = \frac{|z|^2 e^2}{\epsilon_0 \epsilon k_B T}, \quad (3)$$

$$\kappa = \left(\frac{8\pi N_A e^2 |z|^2 \gamma c}{1000 \epsilon_0 \epsilon k_B T} \right)^{1/2}, \quad (4)$$

$$\rho = \frac{F \xi e |z|}{3\pi \eta_o}, \quad (5)$$

$$K_A = \frac{(1 - \gamma)}{\gamma^2 f_{\pm}^2 c}, \quad (6)$$

$$f_{\pm}^2 = \exp \left[\frac{-\beta\kappa}{(1 + \kappa\alpha)} \right], \quad (7)$$

where C_1 to C_5 are functions of the product ($\kappa \cdot \alpha$) and are given in reference [35], K_A is the thermodynamic ion-pair association constant for the equilibrium: $\text{Zn}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{ZnSO}_4$, γ the degree of dissociation, c the electrolyte concentration, f_{\pm} the mean ion activity coefficient of the dissociated species (the activity coefficient for non-conducting species is assumed to be 1), e the electronic charge, z_{\pm} the ion charge, ϵ_0 the permittivity of vacuum, ϵ the dielectric

constant of the solvent, η_o the viscosity of the solvent, F the Faraday constant, k_B the Boltzmann's constant, N_A the Avogadro's number, T the absolute temperature and the symbol ξ is equal to 1/299.79. The parameter a represents the centre-to-centre distance of the formed ion pairs. Beyond this distance, the ions are considered not to be associated.

The computations for calculating the limiting molar conductance (A_o), the association constant (K_A), and the distance parameter (a) were performed on a computer using the programme of successive approximations following the three-parameter optimization as suggested by Pethybridge and Taba [35]. The initial A_o values for the procedure were obtained from the Debye–Hückel–Onsager equation [36] followed the suggestion of Shedlovsky [37]. The formation of triple-ions was regarded as being negligible in the solvent media investigated. The calculations have been made by finding the values of A_o , K_A , and α after obtaining the minimal standard deviation (σ_A) between the calculated ($A_{\text{Calc.}}$) and the experimental ($A_{\text{Exp.}}$) conductivity values for a sequence of a values. The standard deviation σ_A is given from the following relation:

$$\sigma_A = \left[\sum_{j=1}^n (A_{j(\text{Calc.})} - A_{j(\text{Exp.})})^2 / (N_p - 1) \right]^{1/2}. \quad (8)$$

In other words, the reliable value for the distance parameter a corresponds to the minimum of the plot σ_A versus a . The value of the distance a which has been selected for the computations was ranging from 0.3 nm (the sum of the crystallographic radii of the ions) to the maximum value of 3.0 nm. Representative curves of the molar conductance (experimental and calculated values from the Lee–Wheaton equation) versus the concentration of the electrolyte in different (water + EG) binary mixtures are shown in figure 1. The hydrolysis of Zn^{2+} and SO_4^{2-} ions has been assumed to be negligible. The derived values of limiting molar conductance A_o ($\pm 0.3\%$), association constant K_A ($\pm 2\%$) and distance of closest approach of the ions (a) for zinc(II) sulfate in (water + EG) binary mixtures are reported in table 3 with their standard deviations σ_A .

The value of the limiting molar conductivity (A_o) of zinc(II) sulfate decreases as the EG content increases due to the increase of the viscosity of the solvent medium which lowers the ionic mobilities (figure 2). Consequently, the values of A_o vary almost inversely with the viscosity of the solvent medium and the Walden product ($W = \eta \cdot A_o$) has been observed to be nearly constant (table 3). An exception has been observed for the compositions 80 and 90 mass% EG. This obviously suggests that the bulk viscosity does not control the ion mobility in these binary mixtures due to an increase in the thickness of the solvate shell. A comparison of our A_o value of $(232.4 \pm 0.7) \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ in water with the A_o values of $119.29 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ and $118.64 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ (for $1/2\text{ZnSO}_4$) reported by Acevedo *et al.* [27] and Bešter Rogač *et al.* [28], respectively, reveals a satisfactory agreement.

TABLE 1

Densities (ρ), absolute viscosities (η), and dielectric constants (ϵ) of (water + ethylene glycol) (EG) binary mixtures at $T = 293.15$ K

mass% EG	$\rho/(\text{g} \cdot \text{cm}^{-3})$	$\eta/(\text{mPa} \cdot \text{s})$	ϵ^a
0	0.99820	1.008	80.37
10	1.01110	1.293	77.49
20	1.02449	1.671	74.60
30	1.01153	2.177	71.59
40	1.04989	2.837	68.40
50	1.06242	3.558	64.92
60	1.06242	4.724	61.08
70	1.08520	6.360	56.30
80	1.09534	8.003	50.64
90	1.10370	13.999	44.91

^a Literature values (reference [30]).

TABLE 2

Molarities (c), densities (ρ), specific conductivities (k), and molar conductivities (A) of zinc(II) sulfate in (water + ethylene glycol) (EG) binary mixtures at $T = 293.15$ K

$10^2 \cdot c / (\text{mol} \cdot \text{dm}^{-3})$	$\rho / (\text{g} \cdot \text{cm}^{-3})$	$10^6 \cdot k / (\text{S} \cdot \text{cm}^{-1})$	$A / (\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1})$	$10^2 \cdot c / (\text{mol} \cdot \text{dm}^{-3})$	$\rho / (\text{g} \cdot \text{cm}^{-3})$	$10^6 \cdot k / (\text{S} \cdot \text{cm}^{-1})$	$A / (\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1})$
<i>0 mass% EG</i>				<i>10 mass% EG</i>			
0.005	0.99822	11.9	221.1	0.007	1.01112	13.2	186.5
0.011	0.99823	22.9	208.5	0.013	1.01114	23.7	178.4
0.019	0.99825	39.1	211.6	0.026	1.01120	42.3	165.9
0.042	0.99829	84.0	199.1	0.056	1.01124	88.2	158.7
0.063	0.99832	121.8	192.5	0.078	1.01124	117.7	150.1
0.083	0.99836	154.0	185.8	0.102	1.01128	145.9	143.5
0.101	0.99839	183.3	180.8	0.127	1.01131	177.4	140.2
0.127	0.99841	220.1	173.6	0.158	1.01135	210.0	133.4
<i>20 mass% EG</i>				<i>30 mass% EG</i>			
0.009	1.02456	10.8	119.8	0.005	1.02378	5.2	97.2
0.013	1.02457	15.9	121.7	0.014	1.02378	13.0	92.6
0.029	1.02458	34.3	119.9	0.027	1.02379	24.3	89.6
0.055	1.02462	63.6	116.7	0.050	1.02387	41.8	83.5
0.077	1.02465	86.0	112.4	0.076	1.02390	59.8	78.8
0.104	1.02470	114.4	109.6	0.109	1.02392	81.6	75.2
0.141	1.02476	140.1	99.5	0.131	1.02397	94.3	72.2
0.162	1.02481	169.4	104.5	0.158	1.02402	111.4	70.7
<i>40 mass% EG</i>				<i>50 mass% EG</i>			
0.008	1.05180	5.4	71.6	0.011	1.06480	5.7	54.2
0.013	1.05181	9.4	70.7	0.019	1.06481	10.0	52.2
0.026	1.05184	18.0	68.2	0.028	1.06482	14.3	50.6
0.054	1.05187	34.7	63.8	0.057	1.06486	25.6	45.3
0.078	1.05197	47.9	61.1	0.084	1.06495	36.2	43.1
0.107	1.05201	63.0	59.0	0.109	1.06496	44.8	41.1
0.130	1.05207	73.1	56.2	0.138	1.06500	54.4	39.5
0.161	1.05213	87.0	54.2	0.169	1.06505	63.5	37.5
<i>60 mass% EG</i>				<i>70 mass% EG</i>			
0.010	1.07697	3.8	38.4	0.011	1.08844	2.9	27.8
0.014	1.07699	5.4	37.8	0.015	1.08845	3.9	26.6
0.027	1.07700	9.6	35.4	0.028	1.08847	6.9	24.5
0.055	1.07705	17.9	32.5	0.057	1.08851	12.4	21.9
0.081	1.07711	24.4	30.3	0.082	1.08856	16.8	20.5
0.111	1.07717	30.3	27.4	0.118	1.08860	21.8	18.5
0.134	1.07720	36.3	27.0	0.137	1.08863	24.8	18.1
0.163	1.07725	42.1	25.8	0.165	1.08869	28.6	17.3
<i>80 mass% EG</i>				<i>90 mass% EG</i>			
0.010	1.09775	1.5	15.5	0.009	1.10375	0.8	8.2
0.015	1.09776	2.2	14.7	0.014	1.10383	1.1	7.5
0.029	1.09779	3.9	13.7	0.030	1.10400	2.1	7.1
0.057	1.09783	6.9	12.0	0.065	1.10437	3.8	5.9
0.081	1.09787	9.3	11.5	0.085	1.10457	4.6	5.4
0.113	1.09791	11.3	10.0	0.113	1.10485	5.5	4.8
0.138	1.09795	13.8	10.0	0.139	1.10512	6.3	4.5
0.171	1.09800	15.9	9.3	0.167	1.10539	6.7	4.0

The dependence of the logarithm of the association constant of zinc(II) sulfate on the dielectric constant of the solvent medium, which is shown in figure 3, clearly demonstrates that a smaller dielectric constant of the solvent medium leads to a greater association constant of electrolyte. A continuous transition is observed from almost negligible ion association in water, $K_A = (277 \pm 6) \text{ dm}^3 \cdot \text{mol}^{-1}$, to marked association in 50 mass% EG, $K_A = (980 \pm 23) \text{ dm}^3 \cdot \text{mol}^{-1}$, and finally to strong association in 90 mass% EG, $K_A = (5155 \pm 103) \text{ dm}^3 \cdot \text{mol}^{-1}$. These results demonstrate that stronger attractive Coulom-

bic forces between the ions are developed and stable ion pairs are formed upon reducing the dielectric constant of the solvent medium [38–40]. Furthermore, it can be seen from table 3 that the distance between the ions in the ion pairs (a) is always higher than the sum of the crystallographic radii indicating that the ZnSO_4 ion pairs are solvent-separated in all the binary mixtures investigated.

To investigate the behaviour of the individual ions comprising the electrolyte, it is necessary to split the limiting molar conductances into their ionic contributions. It is well known that the cation and the anion add independently to

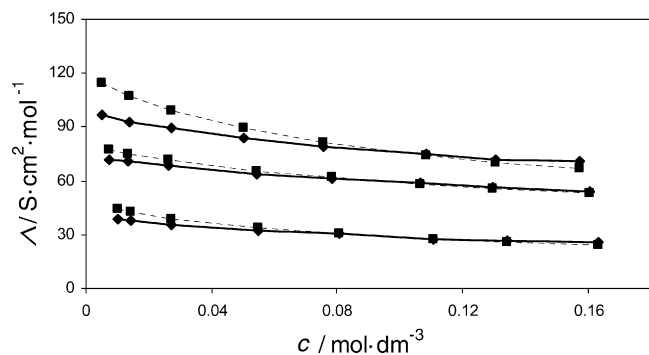


FIGURE 1. Plot of the molar conductivity (Λ) versus the concentration (c) of zinc(II) sulfate in 30, 40, and 60 mass% EG at $T = 293.15$ K. The symbols are denoted as follows: experimental Λ values (\blacklozenge), values of Λ calculated from the Lee–Wheaton equation (\blacksquare) (equations (1) to (7)).

TABLE 3

Limiting molar conductances (Λ_0), association constants (K_A), values of the Walden product ($W = \eta \cdot \Lambda_0$), centre-to-centre distances of the ion pairs (a), and standard deviations (σ_A) of zinc(II) sulfate in (water + ethylene glycol) (EG) binary mixtures at $T = 293.15$ K

mass% EG	$\Lambda_0 / (\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1})$	$K_A / (\text{dm}^3 \cdot \text{mol}^{-1})$	$W = (\eta \cdot \Lambda_0) / (\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1} \cdot \text{mPa} \cdot \text{s})$	$a / \text{\AA}$	$\sigma_A / (\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1})$
0	232.4 ± 0.7	277 ± 6	234.7	8.5	1.05
10	190.2 ± 0.6	390 ± 8	246.1	8.9	0.82
20	142.1 ± 0.4	489 ± 10	237.8	9.2	1.59
30	109.5 ± 0.3	768 ± 15	238.4	9.2	0.25
40	82.8 ± 0.2	904 ± 18	235.0	9.3	0.09
50	67.2 ± 0.2	980 ± 23	239.1	9.6	0.10
60	47.4 ± 0.2	1173 ± 23	223.8	10.3	0.06
70	37.1 ± 0.1	1369 ± 27	236.3	10.5	0.04
80	16.6 ± 0.1	2618 ± 52	148.0	10.7	0.03
90	10.3 ± 0.1	5155 ± 103	144.1	11.2	0.01

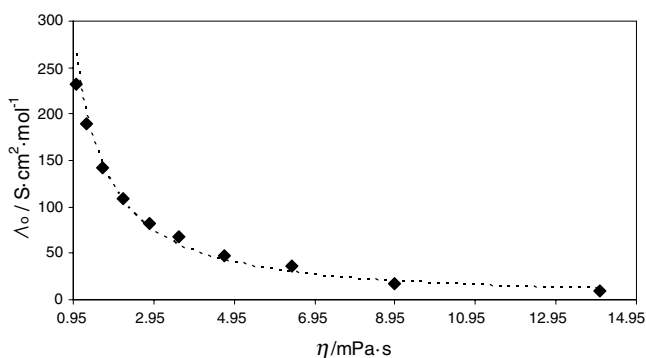


FIGURE 2. Plot of the limiting molar conductivity (Λ_0) of zinc(II) sulfate versus the viscosity (η) of the (water + ethylene glycol) (EG) binary mixtures at $T = 293.15$ K.

the molar conductivity (according to the Kohlrausch' law of the independent migration of the ions). The limiting ion conductivities of Zn^{2+} have been calculated using the limiting ion conductivities of SO_4^{2-} , which have been reported earlier [21]. The limiting ion conductivities of Zn^{2+} (λ_+°) along with those of SO_4^{2-} (λ_-°) are reported in

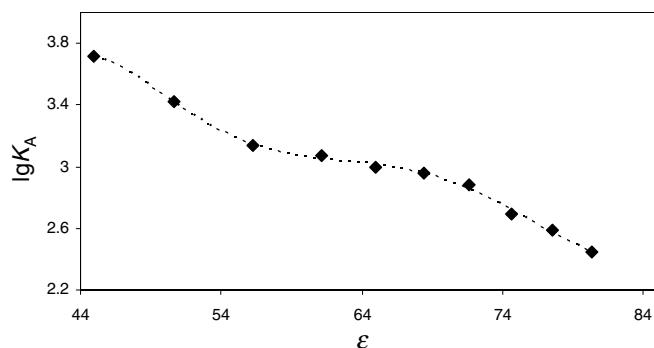


FIGURE 3. Plot of the logarithm of the association constant ($\lg K_A$) of zinc(II) sulfate versus the dielectric constant (ϵ) of the (water + ethylene glycol) (EG) binary mixtures at $T = 293.15$ K.

table 4. Taking into account that the limiting ion conductivity is a measure of the mobility of the ion, one can conclude, that the mobility of the ions decreases as the solvent medium becomes more viscous.

The Stokes' ionic radii ($r_{\text{St}\pm}$) of the ions have been calculated from the limiting ion conductances (λ_\pm°) using the following expression [41]:

$$r_{\text{St}\pm} = \frac{z_\pm F^2}{6\pi N_A \lambda_\pm^\circ \eta_0} \quad (9)$$

The calculated Stoke's radii ($r_{\text{St}\pm}$) of both ions are included in table 4. The Stoke's radii of SO_4^{2-} are smaller than those of Zn^{2+} leading to a greater mobility of the SO_4^{2-} ion. The

TABLE 4

Ion limiting conductances (λ_\pm°), Stoke's radii ($r_{\text{St}\pm}$) (equation (9)), corrected Stoke's radii (r_{Cor}), effective volumes (V_{Eff}) (equation (12)), and solvation numbers (S_n) (equation (11)) of Zn^{2+} and SO_4^{2-} ions in (water + ethylene glycol) (EG) binary mixtures at $T = 293.15$ K

mass% EG	$\lambda_\pm^\circ / (\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1})$	$r_{\text{St}\pm} / \text{nm}$	$r_{\text{Cor}} / \text{nm}$	$V_{\text{Eff}} / (\text{nm}^3)$	S_n
Zn^{2+}					
0	88.6 ± 0.4	0.183	0.366	0.205	8.3
10	69.6 ± 0.3	0.182	0.361	0.197	8.0
20	40.3 ± 0.2	0.243	0.436	0.347	10.2
30	24.6 ± 0.1	0.306	0.495	0.508	12.5
40	16.7 ± 0.1	0.346	0.524	0.602	13.9
50	11.8 ± 0.1	0.390	0.544	0.674	
60	7.7 ± 0.1	0.451	0.563	0.747	
70	5.9 ± 0.1	0.436	0.570	0.775	
80	3.9 ± 0.1	0.471	0.578	0.808	
90	3.7 ± 0.1	0.319	0.482	0.469	
SO_4^{2-}					
0	143.8 ± 0.6	0.113	0.249	0.065	0.6
10	120.6 ± 0.5	0.105	0.231	0.052	
20	101.8 ± 0.5	0.096	0.210	0.039	
30	84.9 ± 0.4	0.089	0.195	0.031	
40	66.1 ± 0.3	0.087	0.189	0.028	
50	55.4 ± 0.3	0.083	0.177	0.023	
60	39.7 ± 0.2	0.087	0.183	0.026	
70	31.2 ± 0.2	0.082	0.166	0.019	
80	12.7 ± 0.1	0.145	0.271	0.083	
90	6.6 ± 0.1	0.176	0.308	0.122	

crystallographic radii (r_{Cr}) of 0.075 nm for Zn^{2+} (r_{Cr}^+) and 0.230 nm for SO_4^{2-} (r_{Cr}^-) for comparison have been taken from the literature [42]. The Stoke's radii of SO_4^{2-} appear to be much smaller than its crystallographic radius, which seems rather unreasonable. This is physically unacceptable, which has also been observed by other researchers [43]. Consequently, the Stoke's radii of Zn^{2+} and SO_4^{2-} ions ($r_{St\pm}$) obtained from equation (9) need to be multiplied by the correction factor in order that this relation may provide the "correct" values of the radii of the solvated ions. This method has been described by Robinson and Stokes [44,45]. According to this method, the tetraalkylammonium ions $N(C_2H_5)_4^+$, $N(C_3H_7)_4^+$, $N(C_4H_9)_4^+$, and $N(C_5H_{11})_4^+$ are assumed not to be solvated in all solvent media due to their large size and the small surface charge. Therefore, one would expect that the Stoke's radii of these ions should be equal to their crystallographic radii. The correction factors of the Stoke's radii of Zn^{2+} and SO_4^{2-} ions have been calculated from the (r_{Cr}^+/r_{St}^+) versus r_{St}^+ linearized calibration curves of $N(C_2H_5)_4^+$, $N(C_3H_7)_4^+$, $N(C_4H_9)_4^+$, and $N(C_5H_{11})_4^+$ (figure 4). Since the limiting ion conductivities of the tetraalkylammonium ions in

(water + EG) binary mixtures are not available in the literature, these values have been calculated from the equation proposed by Gill [46,47]:

$$\lambda_+^{\circ} = \frac{z_+ F^2}{6\pi N_A \eta_0 [r_{Cr}^+ - 0.0103\epsilon - r_y]}, \quad (10)$$

where r_{Cr}^+ is the crystallographic radius of the respective ion and the value r_y is equal to 0.113 nm [46,47]. The crystallographic radii of $N(C_2H_5)_4^+$, $N(C_3H_7)_4^+$, $N(C_4H_9)_4^+$, and $N(C_5H_{11})_4^+$ (0.400, 0.452, 0.494, and 0.529) nm, respectively, have been taken from the literature [41]. The calculated values of λ_+° and r_{St}^+ of $N(C_2H_5)_4^+$, $N(C_3H_7)_4^+$, $N(C_4H_9)_4^+$, and $N(C_5H_{11})_4^+$ in the (water + EG) binary mixtures at $T = 293.15$ K are given in table 5. The "corrected" Stoke's radii (r_{Cor}) of Zn^{2+} (r_{Cor}^+) and SO_4^{2-} (r_{Cor}^-) ions are reported in table 4.

The differences between the "corrected" Stoke's radii and the crystallographic radii of Zn^{2+} and SO_4^{2-} ions are presented graphically in figure 5. The radius of the solvated Zn^{2+} is always greater than its crystallographic radius, whereas this is not true for the SO_4^{2-} . This result indicates that a solvation shell is progressively formed around

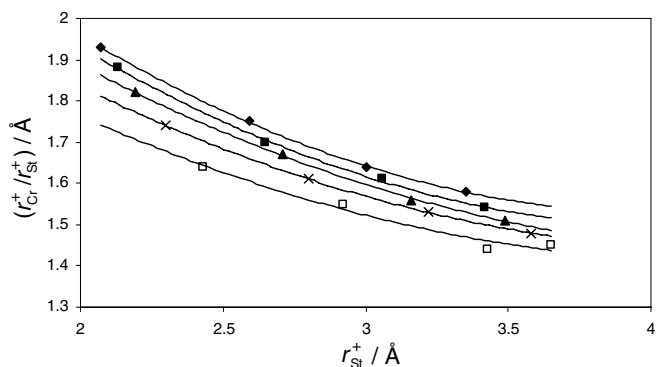


FIGURE 4. Robinson and Stokes correction factors (r_{Cr}^+/r_{St}^+) versus Stokes ionic radii (r_{St}^+) for $N(C_2H_5)_4^+$, $N(C_3H_7)_4^+$, $N(C_4H_9)_4^+$, and $N(C_5H_{11})_4^+$ in (water + ethylene glycol) (EG) binary mixtures at $T = 293.15$ K. The symbols are denoted as follows: 10 mass% EG (◆), 30 mass% EG (■), 50 mass% EG (▲), 70 mass% EG (×), and 90 mass% EG (□).

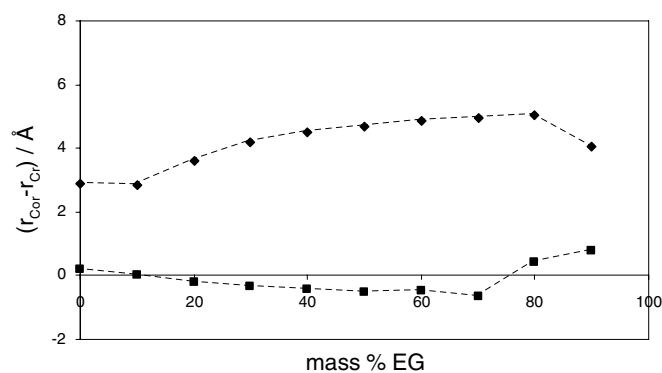


FIGURE 5. Differences between the "corrected" Stoke's radii and the crystallographic radii ($r_{Cor} - r_{Cr}$) for Zn^{2+} and SO_4^{2-} ions versus the composition of (water + ethylene glycol) (EG) binary mixtures at $T = 293.15$ K. The symbols are denoted as follows: Zn^{2+} (◆) and SO_4^{2-} (■).

TABLE 5

Calculated values of limiting ion conductances (λ_+°) (equation (10)) and Stoke's radii (r_{St}^+) (equation (9)) of $N(C_2H_5)_4^+$, $N(C_3H_7)_4^+$, $N(C_4H_9)_4^+$, and $N(C_5H_{11})_4^+$ in (water + ethylene glycol) (EG) binary mixtures at $T = 293.15$ K

mass% EG	$\lambda_+^{\circ}/(S \cdot cm^2 \cdot mol^{-1})$	r_{St}^+/nm	$\lambda_+^{\circ}/(S \cdot cm^2 \cdot mol^{-1})$	r_{St}^+/nm	$\lambda_+^{\circ}/(S \cdot cm^2 \cdot mol^{-1})$	r_{St}^+/nm	$\lambda_+^{\circ}/(S \cdot cm^2 \cdot mol^{-1})$	r_{St}^+/nm
	$N(C_2H_5)_4^+$		$N(C_3H_7)_4^+$		$N(C_4H_9)_4^+$		$N(C_5H_{11})_4^+$	
0	39.8	0.204	31.7	0.256	27.2	0.298	24.4	0.333
10	30.6	0.207	24.5	0.259	21.1	0.300	18.9	0.335
20	23.3	0.210	18.7	0.262	16.1	0.304	14.5	0.338
30	17.7	0.213	14.2	0.265	12.3	0.306	11.0	0.342
40	13.4	0.216	10.8	0.268	9.3	0.311	8.4	0.344
50	10.5	0.219	8.5	0.271	7.3	0.316	6.6	0.349
60	7.8	0.223	6.3	0.276	5.5	0.316	4.9	0.354
70	5.6	0.230	4.6	0.280	4.0	0.322	3.6	0.358
80	3.9	0.236	3.2	0.287	2.8	0.328	2.5	0.368
90	2.4	0.243	2.0	0.292	1.7	0.343	1.6	0.365

Zn²⁺ establishing, consequently, the “structure making” ability of Zn²⁺ ion. This conclusion is supported by the results of the viscosity that follow in the next pages.

The average number of the water molecules (S_n) involved in the solvation sphere of Zn²⁺ and SO₄²⁻ ions has been estimated by dividing the volume of the solvation shell (V_{Sh}) surrounding the ions by the average volume of the solvent molecule (V_S):

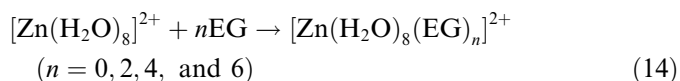
$$S_n = \frac{V_{Sh}}{V_S} = \frac{(V_{Eff} - V_i)}{V_S}, \quad (11)$$

where V_{Eff} is the effective volume of the ion and is calculated from the “corrected” Stoke’s radius (r_{Cor}) according to equation (12), and V_i is the volume of the “naked” ion and is calculated from its crystallographic radius according to equation (13):

$$V_{Eff} = \frac{4}{3}\pi r_{Cor}^3, \quad (12)$$

$$V_i = \frac{4}{3}\pi r_{Cr}^3. \quad (13)$$

The value of $S_n = 8.3$, which was found for Zn²⁺ in water, is comparable with the value of $S_n = 9.6$ reported by Marcus [42]. The calculation of S_n of the ions in (water + EG) binary mixtures have been not carried out since the solvation shells of the ions include both water and EG molecules. Anyhow, assuming that the number of the water molecules around Zn²⁺ remains the same for binary mixtures, which are rich in water (10 to 40) mass% EG, the effective volumes (V_{Eff}) of Zn²⁺ that have been found for the compositions of 10, 20, 30, and 40 mass% EG (table 4) indicate the gradual increase of the size of the solvated ion with the addition of 0, 2, 4, and 6 EG molecules, respectively:



The average volumes of the water ($V_S = 0.0245 \text{ nm}^3$) and EG ($V_S = 0.0688 \text{ nm}^3$) molecules used have been calculated using the van der Waals increments of the atoms [48]. According to the above reaction, the increase of the thickness of the solvate shell of the Zn²⁺ is a result of the complexation of water and EG through hydrogen bonding.

3.2. Viscosity measurements

The molarities (c), the densities (ρ), the absolute viscosities (η), and the relative viscosities (η_r) of solutions of zinc(II) sulfate in (water + EG) mixtures at $T = 293.15 \text{ K}$ are reported in table 6. The viscosity data have been initially analyzed using the Jones–Dole [49] equation:

$$\eta_r = \frac{\eta}{\eta_o} = 1 + Ac^{1/2} + Bc, \quad (15)$$

where η_r is the relative viscosity of the solution, while η and η_o are the absolute viscosities of the solution and the solvent, respectively. The A coefficient represents the contribution from interionic electrostatic forces and can be calculated according to the theory of Falkenhagen using conductivity data [50]. The B coefficient represents the order or disorder of the solvent molecules in the solvation shell of the ions. In other words, the B coefficient is connected with the ion–solvent interactions. This coefficient is a specific and additive property of the ions of the electrolyte at a given temperature. The coefficients A and B have been calculated from the intercept and the slope, respectively, of the curves $[\eta_r - 1]/c^{1/2}$ versus $c^{1/2}$. The A and B values are recorded in table 7 along with their standard deviations.

The experimental values of A coefficient are positive. The B coefficient exhibits positive values and becomes more positive as the EG content increases. The positive sign indicates that the ions cause long range ordering of the solvent molecules in the secondary solvation shell acting as “structure makers”. Given that SO₄²⁻ anion is a weak “structure breaker” [51], the “structure making” behaviour can be attributed mainly to Zn²⁺. The “structure maker” behaviour of Zn²⁺ enhanced as the EG concentration increases confirming the preferential interaction of Zn²⁺ with EG molecules.

Since in the present study, the electrolyte was found to be strongly associated, the viscosity data have been further analysed using the modified Jones–Dole equation in the form of associated electrolytes:

$$\eta_r = \frac{\eta}{\eta_o} = 1 + A(\alpha_d c)^{1/2} + B_i \alpha_d c + B_{ip}(1 - \alpha_d)c, \quad (16)$$

where B_i , B_{ip} , are coefficients connected with the ion–solvent interactions and the ion–pair–solvent interactions, respectively. The A values have been calculated according to the Falkenhagen theory [50] and the degrees of dissociation (α_d) have been obtained from the association constants (see table 3). The A values calculated from the Falkenhagen equation do not agree satisfactorily with the experimental values. The plots of $[(\eta_r - 1 - A(\alpha_d c)^{1/2})/\alpha_d c]$ against $(1 - \alpha_d)/\alpha_d$ were linear and the values of B_{ip} and B_i were obtained from the slopes and the intercepts of the curves, respectively. The values of B_{ip} and B_i are reported in table 7 with their standard deviations. The coefficients B_i and B_{ip} are plotted versus the composition of the (water + EG) binary mixtures in figure 6. The B_i coefficients exhibit positive values throughout all solvent mixtures and tend to increase as the EG content increases. This result demonstrates once more that the Zn²⁺ ion acts as a “structure maker” and its ability tends to be amplified with the increase of EG content due to the preferential solvation of Zn²⁺ by EG in mixtures which are rich in EG. The B_{ip} coefficients exhibit positive values indicating the presence of solvent molecules between the formed ion pairs. The last result confirms that solvent separated pairs are formed.

TABLE 6

Molarities (c), densities (ρ), absolute viscosities (η), and relative viscosities (η_r) of zinc(II) sulfate in (water + ethylene glycol) (EG) binary mixtures at $T = 293.15$ K

$c/(\text{mol} \cdot \text{dm}^{-3})$	$\rho/(\text{g} \cdot \text{cm}^{-3})$	$\eta/(\text{mPa} \cdot \text{s})$	η_r	$c/(\text{mol} \cdot \text{dm}^{-3})$	$\rho/(\text{g} \cdot \text{cm}^{-3})$	$\eta/(\text{mPa} \cdot \text{s})$	η_r
<i>0 mass% EG</i>				<i>10 mass% EG</i>			
0.0084	0.99963	1.015	1.007	0.0085	1.01294	1.302	1.007
0.0194	1.00148	1.022	1.014	0.0196	1.01476	1.313	1.015
0.0403	1.00495	1.036	1.028	0.0388	1.01790	1.331	1.029
0.0545	1.00737	1.045	1.037	0.0545	1.02045	1.345	1.040
0.0714	1.00943	1.054	1.046	0.0667	1.02243	1.358	1.050
0.0795	1.01140	1.062	1.054	0.0787	1.02432	1.367	1.057
0.0979	1.01439	1.074	1.065	0.0974	1.02742	1.387	1.073
0.1391	1.02110	1.103	1.094	0.1350	1.03374	1.422	1.100
0.1756	1.02712	1.127	1.118	0.1770	1.03974	1.468	1.135
0.1998	1.03093	1.144	1.135	0.2025	1.04412	1.484	1.148
<i>20 mass% EG</i>				<i>30 mass% EG</i>			
0.0098	1.02614	1.684	1.008	0.0087	1.03932	2.197	1.009
0.0215	1.02803	1.700	1.018	0.0205	1.04149	2.218	1.018
0.0397	1.03098	1.724	1.032	0.0387	1.04417	2.251	1.034
0.0542	1.03314	1.748	1.046	0.0546	1.04693	2.282	1.048
0.0656	1.03517	1.757	1.052	0.0668	1.04896	2.303	1.057
0.0772	1.03704	1.772	1.061	0.0773	1.05041	2.328	1.069
0.0983	1.04038	1.800	1.077	0.0938	1.05133	2.361	1.084
0.1384	1.04670	1.855	1.110	0.1373	1.05988	2.440	1.120
0.1791	1.05249	1.907	1.141	0.1729	1.06555	2.524	1.159
				0.2071	1.07123	2.573	1.181
<i>40 mass% EG</i>				<i>50 mass% EG</i>			
0.0080	1.05308	2.865	1.010	0.0086	1.06381	3.594	1.010
0.0200	1.05510	2.896	1.020	0.0200	1.06558	3.638	1.022
0.0397	1.05802	2.947	1.038	0.0390	1.06856	3.723	1.046
0.0548	1.06046	2.989	1.053	0.0608	1.07105	3.767	1.059
0.0672	1.06247	3.024	1.066	0.0667	1.07286	3.815	1.072
0.0783	1.06416	3.055	1.076	0.0782	1.07463	3.858	1.084
0.0984	1.06731	3.118	1.099	0.0976	1.07766	3.934	1.106
0.1371	1.07332	3.239	1.141	0.1424	1.08392	4.091	1.150
0.1716	1.07937	3.337	1.176	0.1757	1.08976	4.247	1.194
0.2101	1.08468	3.438	1.211	0.2123	1.09514	4.404	1.238
<i>60 mass% EG</i>				<i>70 mass% EG</i>			
0.0086	1.07559	4.781	1.012	0.0080	1.08615	6.443	1.013
0.0197	1.07745	4.840	1.025	0.0198	1.08805	6.534	1.027
0.0402	1.08030	4.953	1.049	0.0397	1.09101	6.706	1.054
0.0550	1.08303	5.011	1.061	0.0545	1.09331	6.820	1.072
0.0614	1.08409	5.093	1.078	0.0657	1.09497	6.909	1.086
0.0777	1.09060	5.138	1.088	0.0784	1.09684	7.021	1.104
0.0981	1.09838	5.185	1.098	0.0968	1.09960	7.158	1.125
0.1407	1.09568	5.495	1.164	0.1379	1.10566	7.516	1.181
0.1729	1.10126	5.699	1.207	0.1778	1.11157	7.890	1.240
0.2144	1.10666	6.010	1.272	0.2164	1.11712	8.281	1.302
<i>80 mass% EG</i>				<i>90 mass% EG</i>			
0.0079	1.09647	8.067	1.008	0.0089	1.10717	14.237	1.017
0.0194	1.09822	8.240	1.030	0.0191	1.10868	14.447	1.032
0.0407	1.10130	8.500	1.063	0.0406	1.11171	14.923	1.066
0.0547	1.10322	8.667	1.083	0.0564	1.11394	15.270	1.091
0.0652	1.10488	8.777	1.097	0.0659	1.11523	15.487	1.106
0.0783	1.10672	8.919	1.115	0.0799	1.11724	15.817	1.130
0.0972	1.10940	9.112	1.139	0.0986	1.11985	16.265	1.162
0.1391	1.11541	9.543	1.193	0.1391	1.12534	17.252	1.232
0.1760	1.12071	9.950	1.244	0.1744	1.13041	18.211	1.301
0.2184	1.12670	10.441	1.305	0.2202	1.13679	19.077	1.363

TABLE 7

Viscosity coefficients A , B , B_i , and B_{ip} (equations (15) and (16)) of zinc(II) sulfate in (water + ethylene glycol) (EG) binary mixtures at $T = 293.15$ K

mass% EG	$10^2 \cdot A / (\text{mol}^{-1/2} \cdot \text{dm}^{3/2})$	$B / (\text{mol}^{-1} \cdot \text{dm}^3)$	$B_i / (\text{mol}^{-1} \cdot \text{dm}^3)$	$B_{ip} / (\text{mol}^{-1} \cdot \text{dm}^3)$
0	0.9 ± 0.2	0.65 ± 0.02	0.84 ± 0.04	0.60 ± 0.02
10	0.7 ± 0.2	0.72 ± 0.02	0.86 ± 0.04	0.70 ± 0.03
20	0.6 ± 0.2	0.78 ± 0.02	0.88 ± 0.04	0.77 ± 0.03
30	0.3 ± 0.1	0.88 ± 0.03	0.98 ± 0.05	0.86 ± 0.03
40	0.10 ± 0.02	1.00 ± 0.03	1.11 ± 0.06	0.98 ± 0.04
50	0.20 ± 0.05	1.08 ± 0.03	1.19 ± 0.06	1.06 ± 0.04
60	0.20 ± 0.05	1.18 ± 0.04	1.38 ± 0.07	1.14 ± 0.05
70	0.3 ± 0.1	1.33 ± 0.04	1.53 ± 0.08	1.31 ± 0.05
80	1.3 ± 0.3	1.38 ± 0.04	1.62 ± 0.08	1.40 ± 0.05
90	0.10 ± 0.02	1.66 ± 0.05	1.82 ± 0.08	1.64 ± 0.06

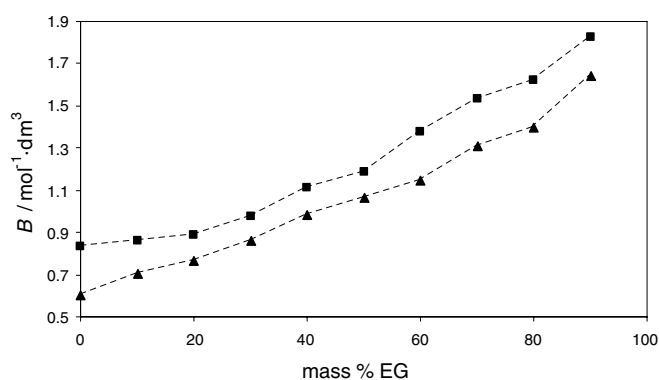


FIGURE 6. Coefficients B_i and B_{ip} of zinc(II) sulfate versus the composition of (water + ethylene glycol) (EG) binary mixtures at $T = 293.15$ K. The symbols are denoted as follows: B_i (■) and B_{ip} (▲).

4. Conclusions

In the present work, conductance, density, and viscosity measurements of solutions of zinc(II) sulfate in (water + EG) binary mixtures have been performed at $T = 293.15$ K to obtain information on the ion–ion and ion–solvent interactions. The results provide an insight on the effect of the dielectric constant and viscosity of the solvent medium on the association and the transport properties of zinc(II) sulfate. The Lee–Wheaton [32–34] conductivity equation has been used for the determination of the limiting molar conductances (A_o), the association constants (K_A), and the centre-to-centre distance of the formed ion pairs (α). The Jones–Dole [49] equation has been used for the calculation of the B , B_i , and B_{ip} viscosity coefficients. The following conclusions can be drawn on the basis of the results discussed. The zinc(II) sulfate tends to be associated with the increase of the EG content in the solvent mixtures due to the gradual decrease of the dielectric constant of the solvent medium. The ion pairs that are formed are solvent separated. The mobilities of the free ions are completely controlled by the bulk viscosity. The B_i viscosity coefficient exhibits a positive sign over the whole composition range, demonstrating the ability of the ions to orientate the solvent molecules in the secondary solvation shell. This behaviour is

mainly attributed to the Zn^{2+} ion which acts as a “structure maker”. The last conclusion is supported by the “corrected” Stoke’s radii of the Zn^{2+} ion. The “structure making” ability of the Zn^{2+} ion seems to be amplified with the increase of the EG content due to the preferential solvation of Zn^{2+} by EG molecules.

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