

# Transference Numbers, Conductance and Viscosity Studies of Copper Sulfate in Ethylene Glycol–Water Mixtures at 20 °C

By Nikos G. Tsierkezos and Ioanna E. Molinou\*

Laboratory of Physical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, P.O. Box 64004, 157 10 Zografou, Athens, Greece

(Received May 7, 2001; accepted in revised form July 23, 2001)

## *Transference Numbers / Conductance / Viscosity / Electrolyte Solutions / Mixed Solvents*

Cell voltage (emf), conductivities and viscosities of copper(II) sulfate solutions in ethylene glycol–water mixtures have been measured at 20 °C. The transference numbers of  $\text{CuSO}_4$  have been calculated from emf measurements of concentration cells with transference. The limiting molar ( $\Lambda^\circ$ ) and ionic conductances ( $\lambda_+^\circ, \lambda_-^\circ$ ) as well as the ion association constants ( $K_A$ ) of the salt have been evaluated. The viscosity data have been analysed according to the modified Jones–Dole equation. The Stokes' radii ( $r_{Si}$ ) have been evaluated as well.

Die EMK, Leitfähigkeiten und Viskositäten von  $\text{CuSO}_4$  in Äthylenglykol Wässrige Lösungen wurden bei 20 °C gemessen. Die Überföhrungszahlen von  $\text{CuSO}_4$  wurden anhand von EMK-Messungen von Zellen ohne Überföhrung bestimmt. Die Grenzwerte der jeweiligen molaren Leitfähigkeiten ( $\Lambda^\circ$ ) sowie die Assoziationskonstanten ( $K_A$ ) des Salzes wurden in allen Lösungsmischungen berechnet. Anhand der molaren Leitfähigkeiten und der Überföhrungszahlen lässt sich die Ionenleitfähigkeiten ( $\lambda_+^\circ, \lambda_-^\circ$ ) berechnet. Die Viskositätsmessungen wurden nach der Jones–Dole Gleichung analysiert. Die Stokesschen Radii sind ebenfalls evaluiert worden.

## 1. Introduction

The study of the transport properties of electrolytes in different solvent mixtures provides information about the solvation behaviour of the ions. In a solution with mixed solvents the change of the composition makes possible the variation of the dielectric constant and the viscosity of the solvent and therefore ion-solvent interactions can be studied.

In recent years there appears a considerable interest on these studies and although conductance and viscosity measurements of 1 : 1 electrolytes in mixed

---

\* Corresponding author. E-mail: imolinou@cc.uoa.gr

solvents have been extensively investigated [1–3], the study of 2 : 2 electrolytes is limited [4, 5].

To the best of our knowledge a systematic study of the transport properties of copper(II) sulfate in mixed solvents is lacking as only few works appear in the literature [5, 6].

The aim of this work is to present measurements of conductivity, viscosity and transference numbers of copper(II) sulfate in ethylene glycol (EG)–water mixtures and thereby to obtain informations concerning the ion–solvent interactions.

Water and EG are polar solvents with similar dipole moments ( $\mu_w = 1.87$  D,  $\mu_{EG} = 2.20$  D at 20 °C) [7] but different dielectric constants ( $\epsilon_w = 80.37$ ,  $\epsilon_{EG} = 38.66$  at 20 °C) [7] owing to the different extent of the hydrogen bond net. EG is self associated in the pure state [8] ( $pK = 15.99$  at 20 °C) creating a net of hydrogen bonds which are both dependent on temperature and electrolytes [9, 10].

In previous papers [11, 12] we have reported a study of the excess thermodynamic properties of EG–water binary mixtures. The mixture was found to exhibit negative deviations, which are stronger at the water rich region, indicating interactions between water and EG molecules.

Copper sulfate shows appreciable ionic association in water and a part of this work concerns the evaluation of the association constant of the salt and its variation with the dielectric constant of the binary solvent.

## 2. Experimental

Ethylene glycol (Merck 99.5%) was distilled under vacuum. The purity was assessed by comparing the experimental density ( $1.11323$  g cm<sup>-3</sup>), viscosity ( $20.806$  mPa s) and refractive index ( $1.4319$ ) at 20 °C, with the literature values [7]. The agreement was satisfactory. Water was deionized by an ion-exchange resin and doubly distilled. The specific conductance was found better than  $0.50$   $\mu$ S cm<sup>-1</sup> at 20 °C. Anhydrous copper(II) sulfate (Fluka 99.5%) was dried before use at 110 °C for 24 h.

All solutions were prepared by weight from a stock solution. The weighings were accurate up to  $\pm 0.0001$  g (salt) and  $\pm 0.01$  g (solvent mixtures). Molar concentrations were obtained from molality and density values with an accuracy of  $\pm 0.0001$  mol dm<sup>-3</sup>.

Densities ( $\rho$ ) were measured with an Anton Paar (DMA 58) micro-computer controlled precision densitometer, with build-in solid state thermostat. The precision of the sample thermostat was  $\pm 0.01$  °C. The DMA cell was calibrated with air and doubly distilled water at atmospheric pressure. The precision in the density was  $\pm 0.00001$  g cm<sup>-3</sup>.

Transference numbers of  $\text{SO}_4^{2-}$  ( $t_-$ ) and  $\text{Cu}^{2+}$  ( $t_+$ ) ions have been determined in the concentration range  $0.0100$  to  $0.2000$  mol dm<sup>-3</sup> in EG–water

mixtures by the emf method, in a concentration cell with transference similar to that described by Braun and Weingaertner [13]. Due to the reduced solubility of the salt in mixtures with higher than 50% w/w in EG, the evaluation of transference numbers concerning mixtures above this content, was not possible. Therefore the  $t_{\pm}^{\circ}$  values, used in the calculations of the  $\lambda_{\pm}^{\circ}$  were assumed to be equal to those obtained for the 50% w/w mixture.

The concentration of the reference solution, against which the emf of all other solutions was measured, was  $0.0020 \text{ mol dm}^{-3}$ . The copper rod electrodes were cleaned, prior to use, with dilute nitric acid, distilled water and acetone. Using a number of electrodes of the same material, the maximum bias potential observed in the cell, did not exceed 0.1 mV. The glass cell was immersed in a thermostat bath where the temperature was kept constant within  $\pm 0.01 \text{ }^{\circ}\text{C}$ . The emf of the cell was measured with a precision potentiometer (Xenon PH129). The uncertainty of the measurements was  $\pm 0.1 \text{ mV}$  and the accuracy of the transference numbers evaluated was  $\pm 0.2\%$ .

The conductance measurements were carried out with a digital bridge-type conductivity meter (Jenway PCM 3) working at a frequency of 1 kHz. The molar conductances ( $\Lambda$ ) of  $\text{CuSO}_4$  in EG–water mixtures have been measured in the concentration range  $0.0001\text{--}0.0010 \text{ mol dm}^{-3}$ . A conductance cell (dipping type) was used, with electrodes of platinum black. The cell constant ( $0.98 \pm 0.01 \text{ cm}^{-1}$ ) was determined by calibration with a  $0.01 \text{ mol dm}^{-3}$  aqueous solution of KCl at  $20 \pm 0.01 \text{ }^{\circ}\text{C}$ . The temperature of each solution became stable within 10–15 min. All measurements were corrected with the specific conductance of each solvent mixture. For the aqueous solutions hydrolysis of the salt was taken into account and the proper corrections were carried out [14]. The precision of the molar conductance was estimated as  $\pm 0.5\%$ .

The viscosities have been measured in the concentration range  $0.0010\text{--}0.1500 \text{ mol dm}^{-3}$  with a viscosity measuring unit (Schott Geräte AVS 310) equipped with an Ubbelohde capillary viscometer. The viscometer was calibrated with doubly distilled water. The time measurement tolerance was  $\pm 0.005\%$  and the display accuracy  $\pm 0.01 \text{ s}$ . The temperature was maintained constant within  $\pm 0.03 \text{ }^{\circ}\text{C}$ . The viscosities ( $\eta$ ) were averaged from four readings. The accuracy in the viscosity measurements was  $\pm 0.1\%$ .

The relative permittivities of the solvent mixtures, used in this work were all taken from the literature [15].

### 3. Results and discussion

#### 3.1 Transference numbers measurements

The transference numbers of  $\text{SO}_4^{2-}$  ( $t_-$ ) in all solvent mixtures were calculated from emf values ( $E_c$ ) according to the equation [16, 17]

$$t_- = \frac{z_+ z_-}{(z_+ + z_-)} \frac{F}{2.303 RT} \left( \frac{dE_c}{d \log \alpha_{\pm}} \right) \quad (1)$$

**Table 1.** Limiting transference numbers of  $\text{Cu}^{2+}$  ( $t_+^\circ$ ) and  $\text{SO}_4^{2-}$  ( $t_-^\circ$ ) and the differences between Stokes' law ionic radii and crystallographic radii ( $r_{\text{St}} - r_{\text{Cr}}$ ) for  $\text{CuSO}_4$  in EG-water mixtures at 20 °C.

% w/w EG	$t_+^\circ$	$(r_{\text{St}}^+ - r_{\text{Cr}}^+)$ Å	$t_-^\circ$	$(r_{\text{St}}^- - r_{\text{Cr}}^-)$ Å
0.00	$0.373 \pm 0.004$	1.19	$0.627 \pm 0.006$	-0.35
10.00	$0.358 \pm 0.004$	1.18	$0.642 \pm 0.006$	-0.43
15.00	$0.327 \pm 0.003$	1.29	$0.673 \pm 0.007$	-0.51
20.00	$0.326 \pm 0.003$	1.29	$0.674 \pm 0.007$	-0.51
27.68	$0.324 \pm 0.003$	1.31	$0.676 \pm 0.007$	-0.52
40.00	$0.321 \pm 0.003$	1.15	$0.679 \pm 0.007$	-0.60
46.27	$0.319 \pm 0.003$	0.99	$0.681 \pm 0.007$	-0.68
50.00	$0.282 \pm 0.003$	1.31	$0.718 \pm 0.007$	-0.69
59.65		1.27		-0.70
70.00		1.24		-0.72
80.00		2.68		-0.15
90.00		3.89		0.32
100.00		7.75		1.85

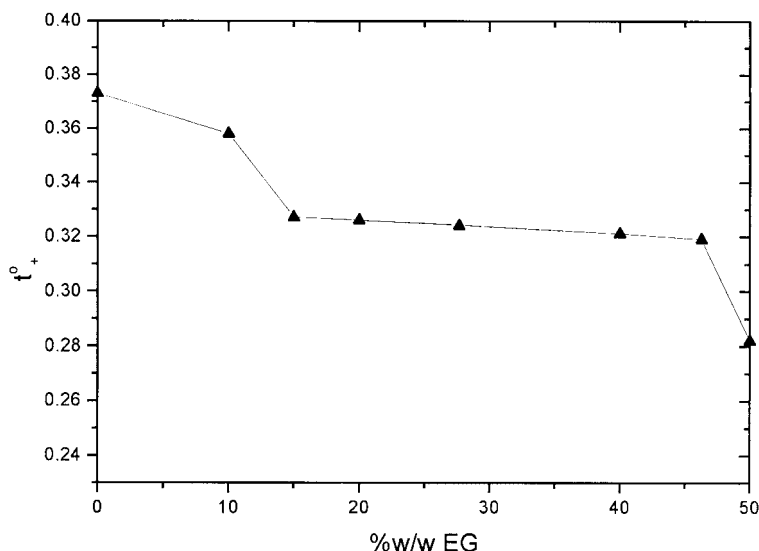
where  $\alpha_\pm$  is the activity of the  $\text{CuSO}_4$  solution. The other symbols have the usual meanings. The mean ion activity coefficients ( $\gamma_\pm$ ) and the degree of dissociation ( $\alpha_d$ ) for the calculation of the activities were determined, by using the method of successive approximations, from the equations [18]

$$-\log \gamma_\pm = \frac{2z_+z_-A_y\sqrt{\alpha_d c}}{1 + 2B_y q\sqrt{\alpha_d c}} \quad (2)$$

$$K_A = \frac{(1 - \alpha_d)}{\alpha_d^2 c \gamma_\pm^2} \quad (3)$$

where  $A_y$ ,  $B_y$  are the Debye-Hückel coefficients. The ion-size parameter ( $q$ ) was set equal to the Bjerrums critical distance, according to the suggestion of Justice [19], followed by many workers for solutions in mixed solvents [20–22]. The limiting transference numbers ( $t_-^\circ$ ) in all solvent mixtures were obtained from extrapolation, with an accuracy of  $\pm 1\%$  and are reported in Table 1. The variation of the arithmetic values with the mass fraction of EG is presented in Fig. 1.

The values seem to decrease, with the increase of the EG content. This decrease can be attributed to the gradual replacement of the water molecules of the  $\text{Cu}^{2+}$  solvation sheath by the EG molecules in the organic solvent rich region, as well as to the increased viscosity of the binary solvent mixture. The structure of EG is a spatial hydrogen-bond net [9]. In the water rich region small proportions of EG tend to increase the hydrogen bonding of water [23] leading thus to reduced mobility of the  $\text{Cu}^{2+}$  ions and consequently to decrease of the transference numbers. This conclusion can be related to the rapid in-



**Fig. 1.** Limiting transference numbers of  $\text{Cu}^{2+}$  ( $t_{+}^{\circ}$ ) for  $\text{CuSO}_4$  as a function of EG content in EG–water mixtures at 20 °C.

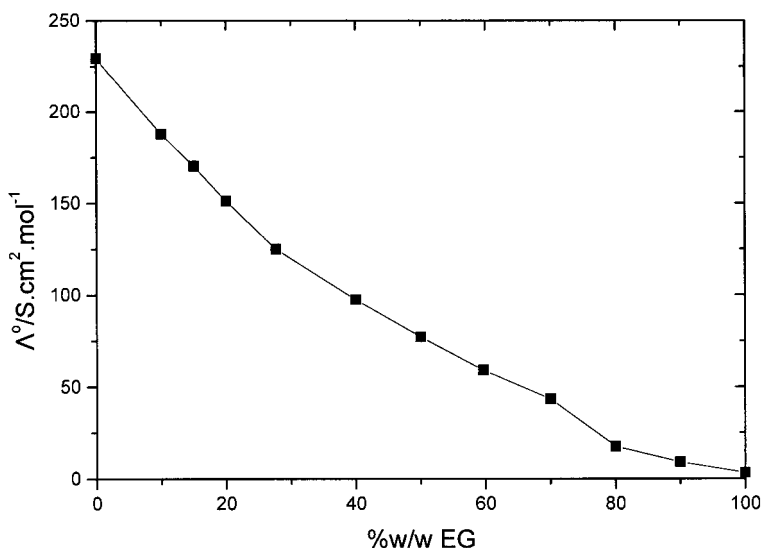
crease of the  $B_i$  coefficient, which appears within the same range of solvent composition, as is showed in Fig. 3, and is also an indication that the viscous motion dominates in the solution.

### 3.2 Conductance measurements

The experimental data were analysed, with the mass action law (Eq. (3)), the Debye–Hückel law (Eq. (2)) and the Lee-Wheaton [24, 25] conductivity equation in the form suggested by Pethybridge and Taba [26], which can be expressed as

$$\Lambda = a_d \left[ \Lambda_o \left( 1 + \frac{\Delta x}{x} \right) - \Delta \Lambda_e \right] \quad (4)$$

where  $\Delta x/x$  and  $\Delta \Lambda_e$  are the relaxation and electrophoretic term, respectively. The limiting molar conductances ( $\Lambda^{\circ}$ ) and the ion-association constants ( $K_A$ ) of  $\text{CuSO}_4$  were obtained as the best fit parameters which minimize the standard deviations. The uncertainty in the  $\Lambda_o$  and  $K_A$  values was  $\pm 0.7\%$  and  $\pm 0.2\%$  respectively. The derived values, along with their standard deviations and the literature data are reported in Table 2. It can be observed that ionic association occurs in all mixtures. Due to Jahn-Teller effect, the  $\text{Cu}^{2+}$  cation adopts a distorted octahedral symmetry, resulting in an extra stabilized solvated  $d^9$  system, which in turn leads to solvent separated ion pairs [27].



**Fig. 2.** Limiting molar conductances ( $\Lambda^\circ$ ) of  $\text{CuSO}_4$  as a function of EG content in EG-water mixtures at 20 °C.

The dependence of  $\Lambda^\circ$  values against the EG content of the mixture is presented in Fig. 2.

The limiting ion conductances ( $\lambda_{\pm}^\circ$ ) have been calculated by combining the  $\Lambda^\circ$  values of the salt, with the limiting transference numbers ( $t_{\pm}^\circ$ ) and are listed in Table 2.

### 3.3 Viscosity measurements

The viscosity data were analyzed using the Jones–Dole equation [28]

$$\eta_r = 1 + Ac^{1/2} + Bc \quad (5)$$

where  $\eta_r$  is the relative viscosity of the solution, A coefficient is a measure of ion-ion interactions and B depends on the specific electrolyte and the temperature and consequently is a measure of ion-solvent interactions. The A and B values derived from (5) are given in Table 3. The A values thus obtained, agree with those calculated, only for pure water. The agreement is poor in solutions rich in organic cosolvent, an observation mentioned by other workers too [21, 29].

As ionic association occurs in all mixtures investigated, the modified Jones–Dole equation should be used

$$\eta_r = 1 + A(\alpha_d c)^{1/2} + B_i \alpha_d c + B_{ip}(1 - \alpha_d)c \quad (6)$$

**Table 2.** Limiting molar conductances ( $\Lambda^\circ$ ), association constants ( $K_A$ ) with their standard deviations ( $\sigma_A$ ) and limiting-ion conductances ( $\lambda_+^\circ, \lambda_-^\circ$ ), for  $\text{CuSO}_4$  in EG–water mixtures at 20 °C.

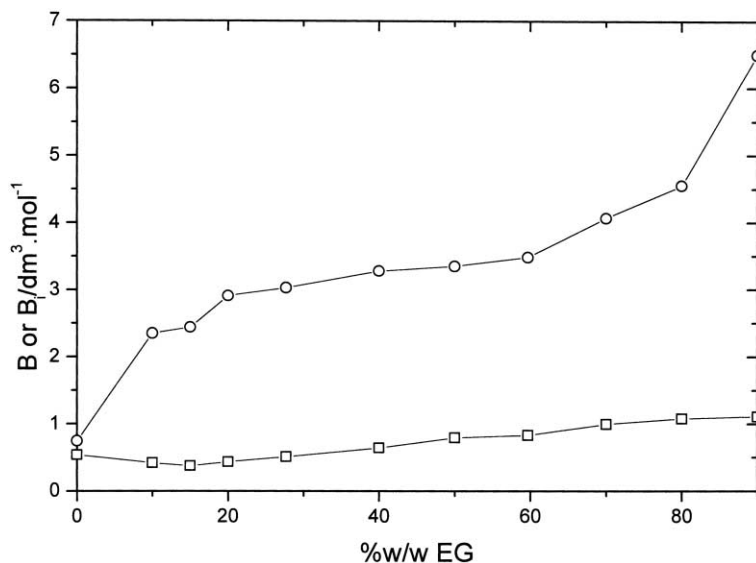
% w/w EG	$\Lambda^\circ$ $\text{S cm}^2 \text{ mol}^{-1}$	$\lambda_+^\circ$ $\text{S cm}^2 \text{ mol}^{-1}$	$\lambda_-^\circ$ $\text{S cm}^2 \text{ mol}^{-1}$	$K_A$ $\text{dm}^3 \text{ mol}^{-1}$	$\sigma_A$
0.00	$229.3 \pm 1.6$ $266.16 \pm 0.04^a$	$85.5 \pm 0.6$	$143.8 \pm 1.0$	$253 \pm 1$ $188 \pm 0.2^a$	0.3268
10.00	$187.8 \pm 1.3$	$67.2 \pm 0.5$	$120.6 \pm 0.8$	$289 \pm 1$	0.5057
15.00	$170.2 \pm 1.2$	$55.7 \pm 0.4$	$114.5 \pm 0.8$	$344 \pm 1$	0.2843
20.00	$151.1 \pm 1.1$	$49.3 \pm 0.3$	$101.8 \pm 0.7$	$368 \pm 1$	0.1994
27.68	$125.1 \pm 0.9$	$40.5 \pm 0.3$	$84.6 \pm 0.6$	$588 \pm 1$	0.1692
40.00	$97.4 \pm 0.7$	$31.3 \pm 0.2$	$66.1 \pm 0.5$	$642 \pm 1$	0.0387
50.00	$77.1 \pm 0.5$	$21.7 \pm 0.2$	$55.4 \pm 0.4$	$950 \pm 2$	0.0382
59.65	$59.1 \pm 0.4$	$16.7 \pm 0.1$	$42.4 \pm 0.3$	$1512 \pm 3$	0.0332
70.00	$43.4 \pm 0.3$	$12.2 \pm 0.1$	$31.2 \pm 0.2$	$1792 \pm 4$	0.0272
80.00	$17.7 \pm 0.1$	$4.99 \pm 0.04$	$12.7 \pm 0.1$	$1839 \pm 4$	0.0141
90.00	$9.20 \pm 0.06$	$2.59 \pm 0.02$	$6.61 \pm 0.05$	$2408 \pm 5$	0.0055
100.00	$3.29 \pm 0.02$	$0.93 \pm 0.01$	$2.36 \pm 0.02$	$5024 \pm 10$	0.0007

<sup>a</sup> at 25 °C (Ref. [5]).

**Table 3.** Viscosity coefficients A, B,  $B_i$  and  $B_{ip}$ , for  $\text{CuSO}_4$  in EG–water mixtures at 20 °C.

% w/w EG	A $(\text{dm}^3 \text{ mol}^{-1})^{1/2}$	B $\text{dm}^3 \text{ mol}^{-1}$	$B_i$ $\text{dm}^3 \text{ mol}^{-1}$	$B_{ip}$ $\text{dm}^3 \text{ mol}^{-1}$
0.00	$0.019 \pm 0.001$	$0.538 \pm 0.005$	$0.75 \pm 0.01$	$0.48 \pm 0.01$
10.00	$0.071 \pm 0.005$	$0.418 \pm 0.004$	$2.35 \pm 0.05$	$-0.35 \pm 0.01$
15.00	$0.083 \pm 0.005$	$0.374 \pm 0.004$	$2.44 \pm 0.05$	$-0.17 \pm 0.01$
20.00	$0.100 \pm 0.007$	$0.434 \pm 0.004$	$2.91 \pm 0.06$	$-0.23 \pm 0.01$
27.68	$0.125 \pm 0.008$	$0.512 \pm 0.005$	$3.03 \pm 0.06$	$0.36 \pm 0.01$
40.00	$0.076 \pm 0.005$	$0.644 \pm 0.006$	$3.28 \pm 0.07$	$0.15 \pm 0.01$
50.00	$0.075 \pm 0.005$	$0.796 \pm 0.008$	$3.35 \pm 0.07$	$0.50 \pm 0.01$
59.65	$0.047 \pm 0.003$	$0.834 \pm 0.008$	$3.49 \pm 0.07$	$0.43 \pm 0.01$
70.00	$0.073 \pm 0.005$	$0.998 \pm 0.009$	$4.07 \pm 0.08$	$0.85 \pm 0.02$
80.00	$0.087 \pm 0.006$	$1.080 \pm 0.010$	$4.55 \pm 0.09$	$0.60 \pm 0.01$
90.00	$0.110 \pm 0.007$	$1.109 \pm 0.010$	$6.49 \pm 0.13$	$0.82 \pm 0.02$

where  $B_i$ ,  $B_{ip}$ , are coefficients connected with the ion–solvent interactions and the ion-pair–solvent interactions, respectively. The A values were calculated from the Falkenhagen–Vernon equation [30] and the degrees of dissociation ( $\alpha_d$ ) were obtained from the association constants ( $K_A$ ). The plot of  $[\eta_r - 1 - A(\alpha_d c)^{1/2} c^{-1}]$  against  $\alpha_d$  is linear and the values  $B_{ip}$  and  $B_i$  are obtained as the intercepts at  $\alpha_d = 0$  and  $\alpha_d = 1$ , respectively. In Table 3 are given the values of  $B_i$  and  $B_{ip}$  with their standard deviations for the entire composition range



**Fig. 3.** B coefficients (□) and  $B_i$  ionic association coefficients (O) of the Jones–Dole equation for  $\text{CuSO}_4$  in EG–water mixtures at 20 °C.

investigated. The B and the  $B_i$  coefficients are plotted versus % w/w EG in Fig. 3.

The B and  $B_i$  coefficients are positive throughout all solvent mixtures indicating a structure making behaviour of the salt. As  $\text{SO}_4^{2-}$  ions are weak structure breakers [31], the structure making behaviour can be attributed mainly to  $\text{Cu}^{2+}$ , which in this case causes long range ordering of the solvent molecules. The resulting viscosity increase (Fig. 3) corresponds to a  $\text{Cu}^{2+}$  mobility reduction reflected in decreased transference numbers (Fig. 1).

Using the limiting ion conductances the Stokes' ionic radii,  $r_{\text{St}}$ , ( $r_{\text{St}} = zF^2/6\pi N\lambda^\circ\eta$ ) for  $\text{Cu}^{2+}$  and  $\text{SO}_4^{2-}$  ions, have been calculated. The differences between Stokes' law ionic radii,  $r_{\text{St}}$ , and crystallographic radii,  $r_{\text{Cr}}$ , ( $r_{\text{Cu}^{2+}} = 0.73 \text{ \AA}$ ,  $r_{\text{SO}_4^{2-}} = 1.49 \text{ \AA}$ ) [7, 32] are given in Table 1. The Stokes' radii for the  $\text{Cu}^{2+}$  ion are greater than the crystallographic, whereas this is not true for the  $\text{SO}_4^{2-}$  ion. This result confirms the solvation ability of the  $\text{Cu}^{2+}$  and indicates the structure making behaviour which can be attributed mainly to this ion.

## Conclusion

The present work has provided information on the solvation behaviour of  $\text{CuSO}_4$  in ethylene glycol–water mixtures. The  $K_A$  values indicated ion asso-



ciation of the salt throughout all solvent compositions tested. The transference numbers as well as the molecular conductivities of the salt decreased with the increase of the ethylene glycol content of the solvent mixture, indicating that the viscous motion dominates in the solution. The viscosity data have been analysed by the Jones–Dole equation, and the  $B_i$  and  $B_{ip}$  coefficients calculated, were positive throughout all solvent mixtures, indicating that  $\text{CuSO}_4$  behaves as a “structure maker”. The solvation ability and consequently the structure making behaviour seems to be attributed mainly to the  $\text{Cu}^{2+}$  ion.

### Acknowledgement

This work was financially supported by the Special Research Account of the National and Kapodistrian University of Athens.

### References

1. D. S. Gill, K. S. Arora, J. Tewari and B. Singh, *J. Chem. Soc., Faraday Trans.* **84** (1988) 1729.
2. D. S. Gill, R. Singh, V. Ali, J. Singh and S. K. Rehani, *J. Chem. Soc., Faraday Trans.* **90** (1994) 583.
3. D. S. Gill and M. S. Bakshi, *J. Chem. Soc., Faraday Trans. 1* **85** (1989) 2297.
4. C. Quintana, M. L. Llorente, M. Sanchez and A. Vivo, *J. Chem. Soc., Faraday Trans. 1* **82** (1986) 3307.
5. M. S. K. Niazi and M. Hussain, *J. Chem. Eng. Data* **39** (1994) 48.
6. R. L. Blokhra, Y. P. Sehgal and V. K. Kuthiala, *Electrochim. Acta* **21** (1976) 1079.
7. *CRC Handbook of Chemistry and Physics*, CRC Press., Inc., 74<sup>th</sup> ed. (1993–94).
8. K. K. Kundu, P. K. Chattopadhyay, D. Jana and M. N. Das, *J. Phys. Chem.* **74** (1970) 2633.
9. A. V. Lebed, O. N. Kalugin and I. N. Vyunnik, *J. Chem. Soc., Faraday Trans.* **94** (1998) 2097.
10. O. N. Kalugin, A. V. Lebed and I. N. Vyunnik, *J. Chem. Soc., Faraday Trans.* **94** (1998) 2103.
11. N. G. Tsierkezos and I. E. Molinou, *J. Chem. Eng. Data* **43** (1998) 989.
12. N. G. Tsierkezos and I. E. Molinou, *J. Chem. Eng. Data* **44** (1999) 955.
13. B. M. Braun and H. Weingartner, *J. Solution Chem.* **14** (1985) 675.
14. B. B. Owen and R. W. Gurry, *J. Am. Chem. Soc.* **60** (1938) 3074.
15. G. Akerlof, *J. Am. Chem. Soc.* **54** (1932) 4125.
16. D. S. Gill and M. S. Bakshi, *J. Chem. Soc., Faraday Trans. 1* **84** (1988) 3517.
17. D. S. Gill and M. S. Bakshi, *J. Chem. Soc., Faraday Trans. 1* **85** (1989) 2285.
18. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, Butterworths Publications Ltd, 2<sup>nd</sup> ed. (1959) p. 393.
19. J. C. Justice, *Electrochim. Acta* **16** (1971) 701.
20. D. S. Gill and M. B. Sekhri, *J. Chem. Soc., Faraday Trans. 1* **78** (1982) 119.
21. D. S. Gill and A. N. Sharma, *J. Chem. Soc., Faraday Trans. 1* **78** (1982) 475.
22. J. Barczynska, A. Bald and A. Szejgis, *J. Chem. Soc., Faraday Trans.* **86** (1990) 2887.
23. J. B. Hasted, *Aqueous Dielectrics*, Chapman and Hall, 1<sup>st</sup> ed. (1973) p. 190.
24. W. H. Lee and R. J. Wheaton, *J. Chem. Soc., Faraday Trans. II* **74** (1978) 743.

25. W. H. Lee and R. J. Wheaton, *J. Chem. Soc., Faraday Trans. II* **74** (1978) 1456.
26. A. D. Pethybridge and S. S. Taba, *J. Chem. Soc., Faraday Trans. 1* **76** (1980) 368.
27. M. Magini, *J. Chem. Phys.* **74** (1981) 2523.
28. G. Jones and M. Dole, *J. Am. Chem. Soc.* **51** (1929) 2950.
29. J. Crudden, G. M. Delaney, D. Feakins, P. J. O'Reilly, W. E. Waghorne and K. G. Lawrence, *J. Chem. Soc., Faraday Trans. 1* **82** (1986) 2195.
30. H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold Publishing Corporation, USA (1943) p. 176.
31. H. S. Frank and W.-Y. Wen, *Discuss. Faraday Soc.* **24** (1957) 133.
32. A. F. Wells, *Structural Inorganic Chemistry*, Oxford University Press, Great Britain (1962) p. 57.