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Density, viscosity and electrical conductivity of three choline chloride based ionic liquids

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Three ionic liquids which are binary mixtures of 2-hydroxy-N,N,N-trimethyl-ethyl-ammonium chloride (named also choline chloride, ChCl) with oxalic acid, ethylene glycol and triethanolamine were prepared. Using a composition with 1:1 molar ratio between the components, clear and colorless liquids at room temperature were obtained. The density, viscosity and electrical conductivity were measured over the 30 to 90ºC temperature range. The temperature dependences of the measured properties were established and discussed.

Keywords: Ionic liquids; deep eutectic solvents; density; viscosity; electrical conductivity; quaternary ammonium salt; choline chloride; oxalic acid; ethylene glycol; triethanolamine

INTRODUCTION

Ionic liquids (ILs) are defined as liquids which consist solely of cations and anions and which by definition must have a melting point of 100ºC or below. Ionic liquids have properties that make them ideal for metal electrowinning: wide potential windows, high dissolving capacity for metal salts, avoidance of water and metal/water chemistry and high conductivity compared to non-aqueous solvents. The synthesis of ionic liquids based upon quaternary ammonium salts is already demonstrated [1]. In recent years, ambient temperature ionic liquids have been studied extensively for catalytic and electrochemical purposes [2-4].

It is well known that eutectic mixtures of salts have been utilized to decrease the temperature for molten salts applications. At ambient temperature, melts consisting of organic compounds named *deep eutectic solvents* (DES) can be formed between varieties of quaternary ammonium salts with a hydrogen bond donor as amide, amine, carboxylic acid or alcohol moiety [4, 5].

These DES are low melting, conductive mixtures, in their properties similar to room temperature ionic liquids. Unlike traditional ionic liquids, these eutectic mixtures are easy to prepare in a pure state. Deep eutectic solvents are cheaper to make, much less toxic and sometimes biodegradable. It was proved that both DES and usual ionic liquids are capable of dissolving many metals and metal salts. For this reason they are used for metal electrodeposition.

The principle of obtaining these mixtures can also be applied to other hydrogen donors such as amines and alcohols, in this way some deep eutectic based ionic liquids being formed.

In the present work, we focus only on 1:1 molar ratio mixtures of choline chloride with oxalic acid, ethylene glycol and triethanolamine, respectively, in an attempt to characterize their density, viscosity and conductivity as functions of temperature.

It is already known that viscosity is of key importance to the design of molten salts and ionic liquids, which tend to be more viscous than molecular liquids. The fact that ionic liquids are fundamentally different from molecular liquids means that their physical properties are also qualitatively and quantitatively different from those of molecular liquids. Therefore, the necessity of measuring their densities and transport properties is obvious. We have chosen this composition (1:1) of ionic liquids in order to establish which of them has better physico-chemical properties for being used as electrolyte in metal electrodeposition from ionic liquids. It is worth mentioning that eutectic-based ionic liquids (DES) are actually mixtures of choline chloride with oxalic acid or triethanolamine only; the studied choline chloride-ethylene glycol (1:1) ionic liquid is not a deep eutectic solvent because the corresponding eutectic composition has a molar ratio of 1:2 [4].

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EXPERIMENTAL PART

Choline chloride (ChCl) or 2-hydroxy-N,N,N-trimethylethylammonium chloride is a quaternary ammonium salt (see scheme in Fig. 1) and has a melting point (mp) of 302ºC. Choline chloride is also a complex vitamin that is added as an important nutrient in poultry, pig and other animal foods. Being a hygroscopic compound, ChCl (produced by chemical companies with 99% purity, for instance) is recrystallized from absolute ethanol, filtered and dried under vacuum prior to be used.

Oxalic acid is a relatively strong organic acid and has the appearance of white crystals with a mp of 101.5ºC.

Ethylene glycol (monoethylene glycol, MEG or 1,2-ethanediol) has a mp of -12.9ºC, thus being an alcohol widely used as an automotive engine antifreeze. In its pure form, it is an odorless, colorless, syrupy, sweet tasting and toxic liquid.

Triethanolamine, is a tertiary amine with a mp of 0.5ºC. Like other amines, triethanolamine acts as a weak base due to the lone pair of electrons at the nitrogen atom. Triethanolamine can be abbreviated as TEOA, which can help to distinguish it from triethylamine.

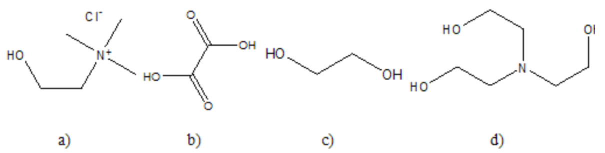

Fig. 1. Skeletal formula of DEP; a-choline chloride; b-oxalic acid; c-ethylene glycol; d-triethanolamine.

Oxalic acid anhydrous (Fluka, >97%), ethylene glycol (Fluka, >97%) and triethanolamine (Aldrich, >98%) were used as purchased. The 1:1 molar mixtures of the above substances were chosen for this study. The ionic liquids were prepared by stirring the two components at a temperature from 80 to 100ºC until a homogenous colorless liquid was formed. For all three mixtures the melting point was lower than the melting point of the components of the mixture.

The density (d), viscosity (η) and specific electrical conductivity (k), were measured by increasing and decreasing the temperature over the 30 to 80ºC temperature range in 10ºC increments for each investigated mixture and they were fitted to linear or polynomial equations.

The densities (d) were measured by the classical platinum sunker method using home-made equipment which was calibrated and tested in molten salt measurements for many years in our laboratory. The Pt sphere volume dependence on temperature was calculated according to the dependence of Pt density on temperature. Details on the employed experimental technique providing a precision of 0.2-0.3% are presented elsewhere [6-9]. This equipment was modified for ionic liquids measurements by coupling it to a temperature controller which maintained the temperature to 0.05ºC precision [10].

The viscosities (η) were measured according to [11-13] with a Cannon-Ubbelohde viscometer having a constant of 1.026. The standard deviation for ten measurements on double distilled water at 20°C, was 0.1 s. In an Ubbelohde viscometer the time that the liquid level takes to flow between two ring marks indicates the viscosity of the test fluid [11-12]. The relative standard deviation for ten measurements on double distilled water at 20°C, was <±3%. Measurements of flow times of the liquids were performed for at least two replicates at each temperature and the results were averaged.

The electrical conductivity (κ) measurements were carried out on a multichannel WTW multi 340i conductometer and pH-meter (WTW GmbH Germany) [14] provided with a WMB 340i drill and a platinized platinum electrode. The ionic liquid was put into a glass tube (introduced in a thermostated bath) with a ground joint and the measuring cell was well sealed to prevent moisture diffusion. The precision of the conductivity measurements was ±0.5%.

RESULTS AND DISCUSSION

Density

Density is an important characteristic property of any liquid. Very limited information is known about the densities of ionic liquids and DES based on choline chloride. Density values of ChCl-urea (1:2 molar ratio), ChCl-malonic acid (1:1) and ChCl-ethylene glycol (1:2) mixtures within the temperature range from 25 to 75°C were reported recently [15]. In a previous study we presented density data of ChCl-urea (1:2), ChCl-malonic acid (1:1) and ChCl- citric acid (1:1) ionic liquids [16]. We report here the density data of the binary mixtures (1:1 molar ratio) of choline chloride with oxalic acid, ethylene glycol and triethanolamine; the values obtained for these systems are presented in Fig. 2.

As can be seen from this figure, the density d (g cm^{-3}) follows a linear dependence with temperature t (ºC) according to a first-order equation:

$$d=a-bt \quad (1)$$

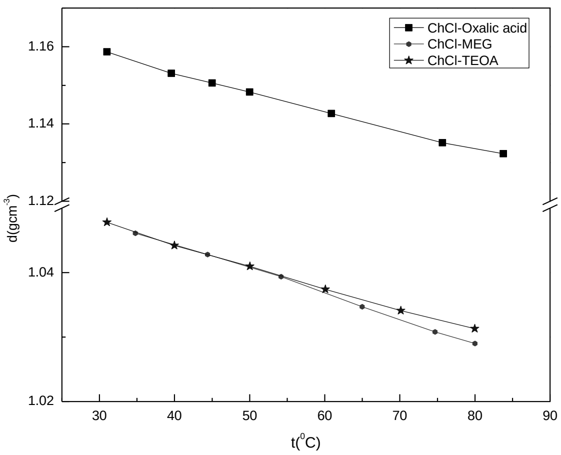

Fig. 2. Density evolution with temperature for 1:1 m ChCl-A [A=oxalic acid, etylene glycol (MEG), triethanolamine (TEOA)] ionic liquids.

where: a and b are coefficients of the straight lines presented in Table 1.The decrease of density with increasing temperature is in a good accordance with the general evolution of both molten salts (which may be considered as high temperature ionic liquids) and ionic liquids in general [9, 14-19]. As we could not find in the literature any density data reported for these ionic liquids, we could not compare our results with those of other authors.

Viscosity

The viscosity is a parameter influencing the hydrodynamic processes in all applications of ionic liquids, for instance in electrolysis cells. Some aspects of transport phenomena in pure molten salts and ionic liquids are simpler than similar phenomena in aqueous solutions [20]. Unfortunately, there are very few data on the viscosity of ionic liquids in general and of choline chloride based ionic liquids in particular [5, 14-16, 21].

Although it was already established that the presence of water reduced the viscosity of ionic liquids [22] we did not pay attention to the quantity of water in our mixtures, as we were interested in obtaining data for a direct technological process using common available substances.

It is known that viscosity at 20-30ºC ranged between 66-1110 cP for a variety of ionic liquids [23]. As shown in Fig. 3, the viscosities of the studied 1:1 ionic liquids, reported earlier [10], change significantly as a function of temperature. Thus, the viscosity values were found to cover the range 15-130 cP, which is in good agreement with those found for ionic liquids in general [23]. This evolution with temperature is similar to that for most of the ionic liquids reported in the literature and also with that of molten salts [5, 7, 14-17, 21].

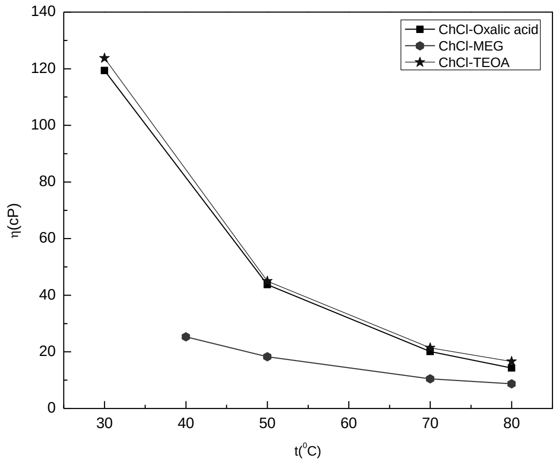

Fig. 3 Viscosity evolution with temperature for 1:1 m ChCl-A (A=oxalic acid, ethylene glycol, triethanolamine) ionic liquids.

It can be noticed that the ChCl-oxalic acid system is a low viscosity room temperature ionic liquid, whereas ChCl-ethylene glycol and ChCl-triethanolamine can be considered as high viscosity ionic liquids.

The van der Waals and hydrogen bonding interactions are believed to govern the viscosity of room-temperature ionic liquids [24]. The increase of viscosity for various ionic liquids compared to molecular solvents was attributed to enhanced van der Waals forces relative to the hydrogen bonding [25]. Regarding the influence of temperature on viscosity, the viscosity η (cP) of the studied ionic liquids is given as a polynomial temperature t (ºC) function:

$$\eta=a+bt+ct^2 \qquad (2)$$

where a, b and c are coefficients presented in Table 2.

Table 1. Constants of the equation for temperature dependence of density (g cm^{-3}) together with correlation coefficients and temperature ranges. Ionic liquids: 1:1 molar ratio choline chloride - A (oxalic acid, ethylene glycol, triethanolamine) mixtures.

System	Coefficients of Eq. (1)		Correlation Coefficient (R)	Temperature range t (ºC)
	a	$b\cdot10^4$		
ChCl-oxalic acid	1.1733	4.9573	0.9986	30-90
ChCl-ethylene glycol	1.0593	3.7831	0.9991	30-80
ChCl-triethanolamine	1.0572	3.2694	0.9994	30-80

Table 2. Constants of the equation for temperature dependence of viscosity (cP), together with the correlation coefficients and the temperature ranges. Ionic liquids: 1:1 molar ratio choline chloride - A (oxalic acid, ethylene glycol, triethanolamine) mixtures.

System	Coefficients of Eq. (2)			Correlation coefficient (R)	Temperature range t (ºC)
	a	b	c		
ChCl-oxalic acid	305.050	7.781	0.052	0.9995	30-80
ChCl-ethylene glycol	69.281	-1.449	0.009	0.9995	40-80
ChCl-triethanolamine	319.502	-8.229	0.009	0.9995	30-80

We can describe the change in viscosity with temperature by an expression derived from an Arrhenius dependence [8]:

$$\ln\eta = \ln\eta_0 + E_\eta/RT \qquad (3)$$

where η_0 is a constant and E_η is the activation energy of the viscous flow.

Fig.4 shows that all data for viscosity obey well Eq. 3 (with correlation coefficients R>0.99), which points to the validity of an Arrhenius temperature dependence for all studied ionic liquids, in accordance with other literature data on deep eutectic solvents or ionic liquids [5, 14-17]. It is clear that an increase in temperature diminishes the strength of interactions between the cation and the anion and should result in lower viscosity values [25, 26]. These results suggest that slow mass-transfer processes occurring at room temperatures, due to high viscosity of ionic liquids, will be accelerated at elevated temperatures. For choline chloride-oxalic acid (1:1) mixture, the data obtained in this study are similar to the literature data [5].

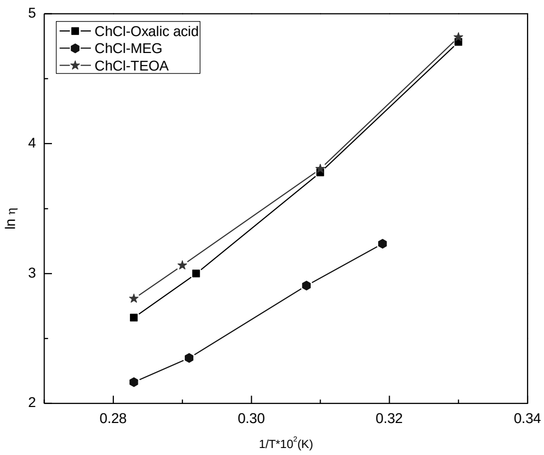

Fig. 4 Arrhenius plots of viscosity for ChCl-A (A=oxalic acid, ethylene glycol, triethanolamine) ionic liquids.

Specific electrical conductivity

The literature [3-5] indicates values of electrical conductivities for DES and common ionic liquids in the range of 0.1-14 mS cm^{-1}; of course, they should change with composition and temperature. Fig. 5 shows the plots of conductivity for the three ionic liquids studied by us in the temperature range from 30 to 80ºC. It is obvious that the choline chloride-ethylene glycol mixture has the highest electrical conductivity in the studied series, whereas the choline chloride-triethanolamine system has the lowest electrical conductivity.

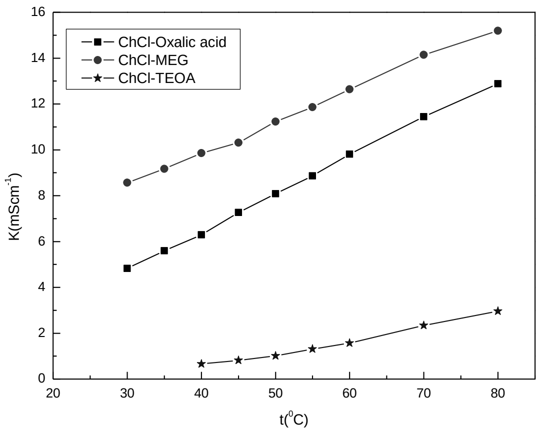

Fig. 5 Conductivity evolution with temperature for 1:1 ChCl-A (A=oxalic acid, ethylene glycol, triethanolamine) ionic liquids.

We can propose in this case a linear dependence of the specific conductivity (κ) on temperature (t ºC) which is given by eq. 4:

$$\kappa = a + bt \qquad (4)$$

where a and b are the coefficients presented in Table 3 together with temperature ranges and corresponding correlation factors (R).

Table 3. Constants of the equation for temperature dependence of specific conductivity, together with correlation factors and temperature ranges for 1:1 choline chloride-A (oxalic acid, ethylene glycol, triethanolamine) mixtures.

System	Coefficients of Eq.4		Correlation factor (R)	Temperature range t (ºC)
	a	b		
ChCl-Oxalic Acid	-0.0334	0.1624	0.9995	30-80
ChCl-Ethylene Glycol	4.2715	0.1390	0.9992	30-80
ChCl-Triethanolamine	-1.9698	0.0611	0.9980	40-80

We can observe that the conductivity values obtained for the studied ionic liquids (ChCl-A) are similar to those for other ionic liquids reported previously [3, 5, 15, 16, 21, 27].

Analogous to the viscosity data, the electric conductivity data of ionic liquids at various temperatures were fitted according to an Arrhenius equation [26]:

$$\ln\kappa = \ln\kappa_0 - E_K/RT \qquad (5)$$

where E_K is the activation energy for electrical conduction.

Fig. 6 shows that the graphical representations for all studied ionic liquids fit Eq.5 accurately, which is in a good agreement with other conductivity data for ionic liquids [5, 15-17, 21].

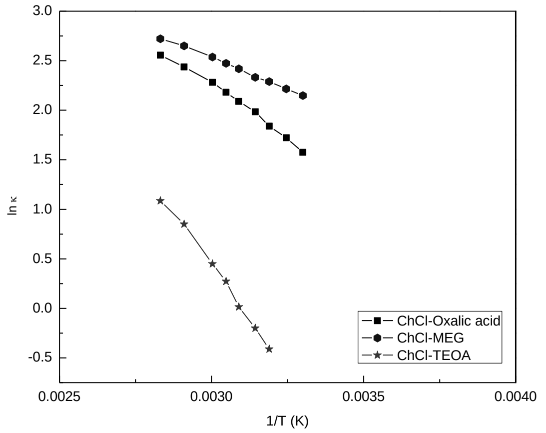

Fig. 6 Plot of log conductivity *vs.* reciprocal of absolute temperature for the DES studied.

CONCLUSIONS

The values of physical properties (density, viscosity and electrical conductivity) of three 1:1 molar mixtures of choline chloride with oxalic acid (OA), ethylene glycol (EG) and triethanolamine (TEOA), respectively, were found to be of the same order of magnitude as those of other ionic liquids and DES and are also dependent on temperature.

Both the density and viscosity of these mixtures decrease with increasing temperature, while electrical conductivity increases with temperature.

A comparison of the properties of the three studied ionic liquids leads to the following series:

$$d_{TEOA} < d_{EG} < d_{OA} \qquad (6)$$

$$\eta_{EG} < \eta_{OA} < \eta_{TA} \qquad (7)$$

$$\kappa_{TEOA} < \kappa_{OA} < \kappa_{EG} \qquad (8)$$

Obviously, the choline chloride-ethylene glycol system is the most suitable one for electrochemical purposes. It seems, however, not to be proper as an electrolyte because of its high viscosity and low electrical conductivity. The system choline chloride-oxalic acid is an intermediate electrolyte proposed for electrodeposition and may be advantageous, despite its relatively high density and viscosity.

We mention once again that some of these data are obtained for the first time experimentally as they have not yet been reported in any of the literature consulted.

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Authors contribution to the achievement of this work is equal.

REFERENCES

1. A. P. Abbott, G. Capper, D. L. Davies, R. Rasheed, *Inorg. Chem.*, **43**, 3447 (2004).
2. J. Dupont, R. F. de Souza, P. A. Z. Suarez, *Chem. Rev.*, **102**, 3667 (2002).
3. P. Wasserscheid and P. Welton eds., Ionic Liquids in Synthesis, Wiley-VCH Verlag, Weinheim, 2003.
4. F. Endres, A. P. Abbott, D. R Mac Farlane eds., Electrodeposition from Ionic Liquids, Wiley-VCH Verlag, Weinheim, 2008.
5. A. P. Abbott, D. Boothby, G. Capper, D. L. Davies, R. Rasheed, *J. Am. Chem. Soc.*, **126**, 9142 (2004).
6. I. Murgulescu, S. Zuca, *Rev. Roum. Chim.*, **4**, 227 (1959).
7. A. M. Popescu, BS chemistry thesis-Viscosity of molten alkaly fluoride, Bucharest, Romania, 1977.
8. S. Zuca, R. Borcan, *Rev. Roum. Chim.*, **15**, 1681 (1970).
9. A. M. Popescu, *Rev. Roum. Chim.*, **44**, 765 (1999).
10. A. M. Popescu, V. Constantin, M. Olteanu, A. Baran, A. Iovescu, M. Dutu, R. Dumitrache, in: *International Conference of Physical Chemistry-ROMPHYSCHEM 13, 3-5 Sept. 2008, Bucharest, Romania, S5, Book of abstracts, p.101.*
11. A. M. James, Practical Physical Chemistry, 2nd ed., J. & A. Churchill Ltd, London, Chap. 5.2, 1967, p. 79.
12. Determination of kinematic viscosity using the Ubbelohde viscometer, DIN 51562-1, 1999.
13. Glass Capillary Kinematic Viscometers-Specifications and Operating Instructions, ISO 3105, 1994.
14. A. M. Popescu, V. Constantin, *Chem. Res. Chinese U.*, **30**, 119 (2014).
15. O. Ciocirlan, O. Iulian, O. Croitoru, *Rev. Chim. (Bucharest)*, **61**, 721 (2010).
16. A. M. Popescu, V. Constantin, A. Florea, A. Baran, *Rev. Chim. (Bucharest)*, **62**, 531 (2011).
17. Y. Geng, S. Chen, W. Tengfang, Y. Dahong, P. Changjun, L. Honglai, H. Ying, *J. Molec. Liq.*, **143**, 100 (2008).
18. M. Olteanu, R. Borcan, M. Constantinescu, S. Zuca, *Rev. Roum. Chim.*, **39**, 673 (1994).

19. J. Jacquemin, P. Husson, A. A. H. Padua, V. Majer, *Green Chem*., **8**, 172 (2006).
20. J. O'M Bockris, A. R. Reddy, Modern Electrochemistry, 1st ed., Plenum Press, NY, 1970, 1, Chapter 6.
21. A. P. Abbott, G. Capper, D. L. Davies, R. Rasheed, V. Tambyrajah, *Chem. Commun.*, **1**, 70 (2003).
22. K. R. Seddon, S. Annegret, M. J. Tores, *Pure Appl .Chem.*, **72**, 2275 (2000).
23. W. M. Reichert, *Green Chemistry*, **3**, 156 (2001).
24. P. Bonhote, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Gratzel, *Inorg. Chem.*, **35**, 1168 (1996).
25. J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker, R. D. Rogers, *Green Chem*., **3**, 156 (2001).
26. A. G. Fadeev, M. M. Meager, *Chem. Commun.*, **3**, 295 (2001).
27. P. Wasserscheid, T. Welton, *Angew. Chem. Int. Ed.*, **39**, 3272 (2000).
28. J. O'M Bockris, E. H. Crook, H. Bloom, N. E. Richards, *Proc. R. Soc.*, A255, 558 (1960).

ПЛЪТНОСТ, ВИСКОЗИТЕТ И ЕЛЕКТРОПРОВОДНОСТ НА ТРИ ЙОННИ ТЕЧНОСТИ НА ОСНОВАТА НА ХОЛИН-ХЛОРИД

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(Резюме)

Получени са три йонни течности, представляващи бинарни смеси от 2-хидрокси-N,N,N-триметил-етил-амониев хлорид (наричан още холин-хлорид, ChCl) с оксалова киселина, етиленгликол и триетаноламин. Приготвени са смеси в моларно отношение 1:1 между компонентите, представляващи бистри и безцветни течности при стайна температура. Техните плътности, вискозитет и електропроводност са измерени при температури в интервала 30 до 90ºC. Обсъдени са температурните зависимости на измерените характеристики.