Physical and Electrochemical Properties of 2-hydroxy-ethyl-trimethyl Ammonium Chloride **Based Ionic Liquids as Potential Electrolytes** for Metals Electrodeposition

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The present paper is a preliminary study on preparation and properties of some choline chloride based ionic liquids. Three mixtures (1:2 molar ratio) of choline chloride (2-hydroxy-ethyl-trimethyl-amonium chloride) with urea, malonic acid and citric acid were prepared and characterized. The obtained ionic liquids were clear and colorless at room temperature. Some physical properties, namely, density, electrical conductivity and viscosity of these mixtures were investigated as a function of temperature within a of 25-80°C. The Arrhenius theory and the Frenkel equation were used for understanding the transport phenomena in these ionic liquids.

Keywords: ionic liquids, choline chloride, malonic acid, urea, citric acid, density, electrical conductivity, viscosity

Ionic liquids (ILs) have received great interest recently due to their unique properties: wide liquid range, good conductivity, wide electrochemical window, non-volatility, and non-flammability [1, 11].

As a consequence, they have been studied by many researchers as a promising alternative to the conventional organic solvents [1, 4] or organic electrolytes [7-10].

Room temperature ionic liquids (RTILs) consist solely of ions and in the last few years they have also been named "low temperature molten salts". However, unlike conventional molten salts these materials often melt below 100°C. Ionic liquids (ILs) seem to be a revolution in green chemistry for less pollution and keeping a cleaner environment. There also are called "deep eutectic solvent" (DES), and are cheaper to make, much less toxic and sometimes biodegradable. It is already known that mixture of choline chloride with urea or carboxylic acids produces eutectics (namely DES) that are liquid at ambient temperature and have unusual solvent properties [12].

As ionic liquids are low or room temperature molten salts (LMS or RTMS) one can say that similarly to molten salts, eutectic mixtures of ILs are very interesting for being electrolytes in electrodeposition applications. From this point of view the physical properties (density, viscosity and electrical conductivity) are of great importance.

This paper deals with the physico-chemical properties (density, electrical conductivity and viscosity) and electrochemical behaviour of three choline chloride based ionic liquids. The three chosen mixtures prepared in the 1:2 mole ratio composition consisted in choline chloride with urea, malonic acid and citric acid, respectively. The main goal of this study is to determine which of those ionic liquids are the most suitable for being employed as electrolytes for electrochemical uses and especially for metals electrodeposition.

Experimental part Chemicals

Choline chloride (ChCl), which is 2-hydroxy-ethyltrimethyl-amonium chloride, is a quaternary ammonium salt with the molecular formula C_5H_{14} ONCl and appearance of white and deliquescent crystals. Choline chloride is a complex vitamin (B4) that is added as an important nutrient in animal feeds.

In order to obtain data to be used directly in a technological process, choline chloride (ChCl) (Sigma Aldrich 99%), malonic acid (Fluka purum >98%), citric acid (Sigma Aldrich, >98%) and urea (Sigma Aldrich, 99%) were used as purchased.

Preparation of ionic liquids

Theoretically a ionic liquid is simply obtained at 80 -110°C temperature by putting together the two components. The studied ionic liquid mixtures were formed by stirring the two components [ChCl-A (A = urea/ or malonic acid/or citric acid) and heating at ~80° C until homogenous liquids were formed [13]. Then the obtained liquids were cooled slowly. Working with (1:2 molar) compositions of ChCl-urea and ChCl-malonic acid we obtained clearly colorless ionic liquids, while for ChCl-citric acid mixture a vellow viscous liquid was obtained. The mixture of ChCl-citric acid needs heating at a temperature more than $80^{\circ}\,C$ for becoming liquid. This mixture is a very viscous yellow liquid even at 100°C and become a dense gel at 30°C. The presence of water in these ionic liquids (mainly introduced from ChCl) was appreciated (in our preliminary determinations) as maximum 5 % (in weight). This may lead to a relatively small influence to all measured properties.

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Apparatus and Procedures

The density, viscosity and electrical conductivity were measured for investigated ionic liquids within 25-80°C temperature range.

Density determinations were performed by an Archimede's principle laboratory set up. This principle states that every solid body immersed in a fluid apparently looses weight by an amount equal to that of the fluid it displaces. The measurements were performed by means of an equipment which was calibrated and tested in molten salt measurements for many years in our laboratory. This equipment was modified for ionic liquid measurements by coupling it to a temperature controller which maintained the temperature to $\pm 0.05^{\circ}$ C.

The electrical conductivity measurements were carried out by means of a WTW-Germany 350i laboratory conductometer provided with a conductivity cell TetraCon 325 (k=0.475 cm⁻¹). The ionic liquid was placed 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 viscosities were measured by using a pre-calibrated Ubbelohde Jenaer Glaswerk Schott & Gren (Germany) viscometer fixed in a special thermostated bath. Measurements of the liquid flow times were performed for at least two replicates at each temperature and the results were averaged. The experimental reproducibility of viscosity values of all ionic liquids was within 0.5%. The kinematic viscosity was converted to dynamic viscosity.

All experiments were performed in air at ambient pressure.

The dependences of density, electrical conductivity and dynamic viscosity with temperature were established for each system using the corresponding "best" equation for the same temperature range for which the investigation was carried out. The temperature-dependent equations and the standard errors of estimation (or the standard deviations) are systematized for each property.

Results and discussion

Density

The density represents a typical property for characterization of a ionic liquid which is a very important for thermodynamic computations and for technological design.

Additionally, some properties derived from density (such as thermal expansion coefficient or compresibility coefficients may give information about liquid structure and interactions.

The densities of all three binary mixtures ChCl-A (A = urea, malonic acid and citric acid) were obtained as a



Fig.1. The variation of density with temperature for (1:2 M) of ChCl-A (A = urea, malonic acid, citric acid) ionic liquids: ■= ChCl-urea; ● = ChCl-malonic acid; ▲ = ChCl-citric acid

function of temperature in the temperature range 55 - 120° C. The increase in temperature causes the density to decrease slightly. As expected, the mixture densities are related to those of solvents. Temperature dependence for the density of the studied systems are plotted in figure 1.

One can observe from figure 1 that densities are decreasing slowly with temperature for all binary ionic liquids.

In general, the density (d) decreases with temperature $(t, \circ C)$ for almost all pure substances and mixtures. In the case of mixtures involving ionic liquids, the correlation with temperature can be expressed using a linear equation:

$$d = a + bt \tag{1}$$

where parameters "a" and "b" from equation (1) were determined from the intercept and slope, respectively, of the corresponding straightlines obtained from the evolution of density with temperature. Table 1 presents the density equations for the studied ionic liquids, together with correlation coefficients and temperature ranges.

Analyzing data from figure 1 and table 1, we obtained an order of densities depending of co-solvent in series: urea < citric acid (tri-carboxylic acid) < malonic acid (dicarboxylic acid).

The densities of most ILs are higher than those of water except for pyrrolidinium dicyanodiamide and guanidinium with density ranging from 0.9 to 0.97 g . cm³; this means that the obtained density values for all three ionic liquids are in good agreement with literature data [2, 14-16]. It is interesting to note that the density of the studied ionic liquids decreases linearly with temperature but at a lower extend than for molecular organic solvents.

Table 1				
THE DENSITY EQUATIONS TOGETHER WITH CORRELATION FACTORS AND TEMPERATURE RANGES				
FOR (1:2 M) ChCI-A (A = UREA, MALONIC ACID, CITRIC ACID) IONIC LIQUIDS				

Ionic Liquid	Density equation	Correlation	Temperature (t)	
	$d (g \times cm^{-3})$	Coefficient	range	
		(R ²)	(° C)	
ChCl-urea	$d = 1.205 - 4.019 \times 10^{-4} t$	0.999	55-100	
ChCl-malonic acid	$d = 1.523 - 2.750 \times 10^{-4} t$	0.999	60-100	
ChCl-citric acid	$d = 1.393 - 8.797 \times 10^{-4} t$	0.985	80-130	



Fig.2 Electrical conductivity vs temperature for (1:2 M) of ChCl-A (A = urea, malonic acid, citric acid) ionic liquids: * =ChCl-urea; •= ChCl-malonic acid; ▲ = ChCl-citric acid

Electrical conductivity

Electrical conductivity (k) of the electrolytes is one of the most important properties for electrodeposition application. The electrolyte with higher conductivity exhibits lower ohmic drop during electrolysis and lower cell voltage so that a higher energy efficiency is expected. Figure 2 shows the plots of electrical conductivity values for the three ionic liquids as a function of temperature over the temperature range 25-110°C.

The studied ionic liquids have electrical conductivities in the range 0.014 to 6.13 $\text{mS} \times \text{cm}^{-1}$ with values increased with temperature.

These values are similar to those for other ILs [2, 12-13, 17]. The obtained data support the hypothesis that ionic liquids are highly conducting, confirming that the ionic species are dissociated in the liquid and can move independently.

We were able to express mathematically the temperature dependence of electrical conductivity (k, $mS \times cm^{-1}$) by polynomial equations of second degree:

$$\kappa = c + dt + et^2 \tag{2}$$

where t is the temperature (°C). Table 2 present these equations for the three studied ionic liquids, together with temperature ranges and correlation coefficients (R²).

Viscosity

Although the viscosity is an important parameter for the electrolysis process, there are very few data on the viscosity

of ionic liquids and only few papers report data for choline chloride systems [7, 8]. We succeeded to perform viscosity measurements only in the ChCl-urea and ChCl-malonic acid systems, because the mixture ChCl-citric acid was too viscous for our measurement device.

Figure 3 shows the plots of viscosity for the two ionic liquids over the temperature range 30-80°C and one can observe that the ChCl-urea mixture has lower viscosity than ChCl-malonic acid mixture.

The obtained dynamic viscosity values were found to cover the range from 50 to 740 cP, which are similar to those generally observed in ionic liquids [17, 19]. Compared with the conventional organic solutions, ILs are viscous liquids as their viscosity is of 1-4 orders of magnitude higher [19]. Unfortunately, this high viscosity will negatively affect any technological process. The viscosities of ILs are governed essentially by van der Waals interactions and H bonding and this is also valuable for our studied ionic liquids. In general, alkyl chain lengthening or fluorination of organic components makes the ionic liquid more viscous due to an increase in van der Waals interactions and hydrogen bonds [7].

For our studied ionic liquids the viscosity (η, cP) is given as a temperature (t, °C) dependence as a polynomial equation of third degree:

$$\eta = f + gt + ht^2 + it^3 \tag{3}$$

Table 3 presents these equations for dynamic viscosities of both studied ionic liquids.

Both ionic liquids have good viscosities in the temperature range 60-80° C and their dependences are similar with most of the ionic liquid viscosity evolution described in literature and also with that of molten salts [18, 20-22].

We could not find systematic data in literature about choline chloride based ionic liquids to compare our results of conductivity and viscosity; we can only compare our data with a previous work [12] refering to the ChCl-urea system. A similar evolution with temperature can be noticed for both viscosity and conductivity, with little differences in the values, which we assumed to be mainly because another kinds of devices for experimental determinations were used.

Mechanism of transport properties

One important problem for theoretical point of view is to explain the strong dependence of viscosity and electrical conductivity with temperature.

It is already known that the mechanism of the viscous flow in molten electrolytes is governed by the "hole theory".

Table 2				
POLYNOMIAL CONDUCTIVITY EQUATIONS TOGETHER WITH CORRELATION FACTORS AND				
TEMPERATURE RANGES FOR (1:2 M) ChCl-A (A=UREA, MALONIC ACID, CITRIC ACID) IONIC LIQUIDS				

Ionic liquid	Conductivity equation	Correlation	Temperature (t)	
	$\kappa (mS \times cm^{-1})$	coefficient	range	
		(R ²)	(° C)	
ChCl-urea	$\kappa = -0.598 + 0.0417t + 5.287 \times 10^{-4}t^2$	0.999	25-80	
ChCl-malonic acid	$\kappa = -0.221 + 0.0187t + 1.490 \times 10^{-4}t^2$	0.995	25-80	
ChCl-citric acid	$\kappa = 0.158 - 0.007t + 9.149 \times 10^{-5} t^2$	0.989	40-110	



Fig.3 Dynamic viscosity variation with temperature for (1:2 M) of ChCl-A (A = urea and malonic acid) ionic liquids: • = ChCl-urea; * = ChCl-malonic acid

 Table 3

 POLYNOMIAL VISCOSITY EQUATIONS TOGETHER WITH CORRELATION FACTORS AND TEMPERATURE

 RANGES FOR (1:2 M) ChCI-A (A=UREA, MALONIC ACID) IONIC LIQUIDS

Ionic liquid	Viscosity equation	Correlation	Temperature (t)
	η (cP)	coefficient	range
		(R ²)	(° C)
ChCl-urea	$\eta = 3335.8 - 135.91t + 1.894t^2 - 0.008t^3$	0.998	30-80
ChCl-malonic acid	$\eta = 1571.5 - 34.83t + 0.178t^2 + 2.925 \times 10^{-4}t^3$	0.998	40-80

By applying the Arrhenius equation to the obtained viscosities of the studied ILs, good results supporting the mechanism of viscous flow by a "hole model" were obtained.

The temperature dependence of liquid viscosity is usually expressed by an exponential model based on the assumption that the fluid flow obeys the Arrhenius equation [21, 23].

$$\eta = A_n \times e^{\frac{z_\eta}{RT}} \tag{4}$$

where T is absolute temperature(K), A_n is a pre-exponential coefficient, E_n is activation energy for viscosity and R is the universal gas⁻¹ constant (8.314 J . K⁻¹mol⁻¹). The coefficient A_n is related to the frequency of molecular collisions in the collision theory and to entropy term in the transition state theory. The activation energy is an energy barrier, viewed as an energetic threshold.

The change in viscosity, with temperature can be also described by the logarithmic form of the Arrhenius equation:

$$\ln \eta = \ln A_{\eta} + \frac{E_{\eta}}{RT} \tag{5}$$

Therefore, according to the above equation, the log η must be also a linear function of the reciprocal of absolute temperature (1/T), [log η = log A_n + E_n / 2.303T] and from the slope and intercept of the straight line we can calculate E and A_n. Using the viscosity data we obtained the figure 4, from which the Arrhenius equations and parameters were calculated (table 4) for both ChCl-urea and ChCl-malonic acid mixtures.

As shown in table 4 the viscosity temperature dependence can be fitted by the Arrhenius equation with high precision (values around 0.99 for correlation coefficient) for studied ionic liquids.

Regarding the activation energy for viscosity, previous studies have shown that E_{η} values for ionic liquids are considerably larger than those for conventional liquids or high temperature molten salts [17, 21-23]. This is due to



Fig.4 Arrhenius plots of viscosity for (1:2 M) ChCl - A (A = urea and malonic acid) ionic liquids: • = ChCl-urea; * = ChCl-malonic acid

the large ion to hole radius ratio in ionic solvents. The difference observed between the two ionic liquids studied (with urea and malonic acid) must arise from the better ability of urea to form hydrogen bonds through its two NH₂ groups, which may explain differences in density and viscosity.

Analogous to viscosity data, the electrical conductivity of ionic liquids have been also fitted using Arrhenius [13, 24].

$$\ln \kappa = \ln A_{\kappa} - \frac{E_{\kappa}}{RT} \tag{6}$$

where A_k is a constant and $E \kappa$ is the activation energy for electrical conduction. Figure 5 shows the obtained data for all three studied ionic liquids. The values for A_k and E_k are summarized in table 5.

The obtained parameters of Arrhenius equation for conductivity data are in good agreement with data obtained

Ionic Liquid	Viscosity Arrhenius	Correlation	$A_{\eta} \times 10^7$	Eη	Temperature
	Equation	coefficient	(cP)	(KJ×mol ⁻¹)	range
	(η in cP)	(R ²)			(° C)
ChCl-urea	$\log \eta = -6.358 + 2.784 \frac{1}{T} 10^3$	0.998	4.385	53.3	25-85
ChCl-malonic acid	$\log \eta = -5.231 + 2.490 \frac{1}{T} 10^3$	0.994	58.75	47.7	40-80





Fig.5 Plots of log conductivity vs. reciprocal of absolute temperature: • = ChCl-urea; * = ChCl-malonic acid; • = ChCl-citric acid

 Table 5

 ARRHENIUS EQUATIONS FOR ELECTRICAL CONDUCTIVITY OF (1:2 M) ChCI-A (A=UREA, MALONIC ACID, CITRIC ACID) IONIC LIQUIDS

Ionic liquid	Conductivity	A _k ×10 ⁻⁵	Eκ	Correlation	Temperature
	Arrhenius equation	(mS×cm ⁻¹)	(KJ×mol ⁻¹)	coefficient (R ²)	(t) range
ChCl-urea	$\log \kappa = 5.672 - 1.701 \frac{1}{T} \times 10^3$	4.70	32.5	0.962	25-80
ChCl-malonic acid	$\log \kappa = 4.628 - 1.494 \frac{1}{T} \times 10^3$	0.42	28.5	0.985	25-80
ChCl-citric acid	$\log \kappa = 6.451 - 2.569 \frac{1}{T} \times 10^3$	28.25	49.1	0.989	40-110

in [12, 17] showing that choline chloride based ionic liquids are highly conductive media.

Models based on the theory of the Brownian motion lead to the Walden rule [2, 23] which predicts an inverse proportionality between the molar conductivity (Λ) and the viscosity (η). The validity of the Walden rule has been shown for ILs [2]. Similar to the Walden rule ($\Lambda x \eta = \text{const}$), of molecular liquids, for the ionic electrolytes was derived a new equation (called Frenkel equation):

$$k^n \times \eta = const \tag{7}$$

where: k is the electrical conductivity and η is the viscosity.

This equation assumes that the activation energies for viscous flow and ionic migration are proportional and the constant of proportionality for our studied ionic liquids, is defined as $n = E_{n}/E_{k}$. The n values can be calculated for the ChCl-urea and ChCl-malonic acid mixtures from the straight lines in figure 6, obtained from the application of equation (6) in a logarithmic form (nlogk + logn = const).

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An approximately linear correlation is observed for both ionic liquid systems, although the slopes are note worthily different. The calculated numerical values for n are 1.49 for ChCl-urea and 1.93 for ChCl-malonic acid, from straight lines in figure 6 (with R²~0.98). As n>1 this means that $E_{\eta} > E_{k}$ and the barriers for the viscous flow are larger than these involved in the ionic migration. This means that in these liquids there are not only charge carrying species simply formed by choline and chloride ions because in this case all slopes have to be similar. It seems that the chloride ion migrates in cooperation with some complexing ligands and that the protons from the carboxylic acid are not labile.

Electrochemical window

The electrochemical window of an electrolyte is the voltage range between the beginnings of its anodic oxidation and cathodic reduction. This range is important for use as a support electrolyte for many technological processes. The fundamental requirement for an ionic liquid to be useful in developing applications in electrochemistry



Fig.6. Application of Frenkel equation for the studied ionic liquids: * = ChCl-urea; • = ChCl-malonic acid



Fig.7 The electrochemical windows of ChCl-urea (a) and ChCl-malonic acid (b). Cyclic voltammograms are recorded with v = 200mV×s⁻¹, using Pt electrode (0.08 cm²), temperature 80°C

is that it should be able to offer a large electrochemical window. The electrochemical window for aqueous solutions is about 1.23V at the standard state. Electrolytes for application in electrochemical devices should be also stable during electrochemical reduction and oxidation of other contained ionic species. The electrochemical windows of the ChCl-A (A = urea, malonic acid) mixture, have been investigated using a platinum working electrode.

Figure 7 shows cyclic voltammogrames recorded in ChCl-urea (a) and ChCl-malonic acid (b) at 80°C. It may observed that 1.8 V potential window was relatively large on Pt electrode, having magnitudes of 2.2 V (+1.0 V to -1.2 V) for ChCl-urea and (+1.1V to -0.7V) for ChCl-malonic acid (electrode potentials vs. Ag quasi-reference). However, within the electrochemical windows on the cathodic branch of voltammogram obtained in ChCl-urea, a wave with small current amplitude appears that certainly increases at faster scan rates. We assumed that the existence of such wave with limiting currents less than 1mA×cm⁻² is probably due to the presence of small amount of H⁺ ions in binary ionic liquid, as a result of dissociation of water molecules that are present in liquid media. On the anodic direction, the current is almost zero within -1.0V to +1.0V potential range, with a continuous increasing at more positive values, corresponding to the possible oxidation of Cl ions. Regarding the anodic process for ChClmalonic acid system, it is clearly that at polarization more positive than +1.1V, an anodic oxidation of Cl⁻ ions appears. Also, at this moment we can say anything about the chemical nature of the reduction products of the large organic cations of ChCl-malonic acid complex that exists in the ionic medium.

Knowing that the cathodic limit is important for electrodeposition of metals, we can conclude that ChCl-A (A = urea, malonic acid) systems have relatively good electrochemical windows on Pt electrode, which renders them suitable for electrodeposition of metals such as Cu, Ni, Ag, Sn.

Conclusions

The easy synthesis, availability and biodegradability of the components of these ILs make them versatile alternatives to classical ionic liquids.

Both ionic liquids obtained from choline chloride-urea and choline chloride-malonic acid are clearly colorless and have good transport properties (density and viscosity are decreasing, while the conductivity is rising with temperature) and that make these ILs promising candidates for electro-deposition media.

The choline chloride-citric acid mixture proved not to be a good IL, because in fact it is more a gel than a liquid at room temperature and its thermophysical properties make it not suitable for electrochemical studies as it is too viscous and has a too low conductivity.

Acknowledgement: This work was supported by the Romanian Ministry of Education and Science-National Center of Programs Managing with founds provided by the PNCDI-2 Romanian Partnership Programmes - Project nr.31066/2007-2010-IONLICSURF.

References

1. WELTON, T., Chem. Rev., 99, 1999, p.2071

2. ANTHONY, J.L., BRENNECKE, J.F., HOLBREY, J.D., MAGINN, E.J., MANTZ, R., ROGERS, R.D., TRULOVE, P.C., VISSER, A.E., WELTON, T., in: Ionic Liquids in Synthesis; P. Wasserscheid, T. Welton Eds., Wiley-VCH Verlag, Weinheim, 2003, p.41

3. SONG, C.E., YOON, M.Y., CHOI, D.S., Bull. Korean Chem. Soc., 26, 2005, p.1321

4. JORAPUR, Y.R., CHI, D.Y., Bull. Korean Chem. Soc., 27, 2006, p.345. 5. WASSESCHEID, P., KEIM, W., Angew.Chem. Int. Ed., 39, 2000, p.3772.

6. DYSON, P.J., Transition Met.Chem., 27, 2002, p.353

7. BONHÔTE, P., DIAS, A.P., ARMAND, M., PAPAGEORGIOU, N., KALYANASUNDARAM, K., GRATZEL, M., Inorg. Chem., 35, 1996, p.1168 8. LEE, J.S., LEE, H.N., QUAN, D., KIM, H.S., KIM, H., J.Ind.Eng.Chem., 10, 2004, p.1086

9. BUZZEO, M.C., EVANS, R.G., COMPTON, R.G., Chem.Phys.Chem., 5, 2004, p.1106

10. BUZZEO, M.C., EVANS, R.G., Electrochemical Aspects of Ionic Liquids, Wiley- Interscience, Hoboken, 2005, p.173

11. WEBBER, A., BLOMGREN, G.E., Advance in Lithium-Ion Batteries, Eds. van Schalkwijk, W. A., Scrosati, B.,; Kluwer Academic/Plenum Publishers, New York, 2002, p.185

12. ABBOTT, A.P., CAPPER, G., DAVIES, D.L., RASHEED, R.K., TAMNYRAJAH, V., Chem.Commun., 1, 2003, p.70

13. SUOSIANG, Z., NING, S., XUESHONG, H., XINGMEI, L., XIANPING, Z., J.Phys.Chem.Ref.Data, 35, 2006, p.1475

14. POPESCU, A.M., CONSTANTIN, V., OLTEANU, M., BARAN, A., IOVESCU, A., DUTU, M., DUMITRACHE, R., Intern. Conf. Phys. Chem.-

ROMPHYSCHEM 13, Bucharest, Romania, 2008, **S5**, p101

15. MARSH, K.N., BOXALL, J.A., LICHTENTALER, R., Fluid Phase Equilibria, **219**, 2004, p.93

16. WILKES, J. Mol. Cat. A-CHEM., **214**, 2004, p.11

17. ABBOTT, A.P., BOOTHBY, D., CAPPER, G., DAVIES, D.L., RASHEED, R.K., J. Am. Chem. Soc., **126**, 2004, p.9142

18. ABBOTT, A.P., BARRON, J.C., RYDER, K.S., WILSON, D., Chem. Eur. J., **13**, 2007, p.6495

19. CIOCIRLAN, O., IULIAN, O., Rev. Chim. (Bucharest), **59**, no. 1, 2008, p.45

- 20. GENG, Y., CHEN, S., TENFANG, W., DAHONG, Y., CHANGJUN, P.,
- HONGLAI, L., YING, H., J. Molec. Liq., 143, 2008, p.100
- 21. POPESCU, A.M., Rev. Roum. Chim., 44, 1999, p.765

22. JOHNSON, K., DRIVER, G., Proceed. Intern. Symp. Ionic Liquids,

- Ed. Norvegian Univ. Sci. Tech, Trondheim, Norway, 2003, p.233
- 23. JANZ, G.J., TOMKINS, R.P.T., ALLEN, C.B., DOWNEY, J.R., GARDNER, G.L., KREBS, U., SINGER, S.K., J.Phys.Chem. Ref. Data, Molten Salts, 1975, **4**, p.881

24. BOCKRIS, J.O'M., REDDY, A.R., Modern electrochemistry, Plenum Press, NY, 1970, Vol.1, p.547

Manuscript received: 9.08.2010