ELECTRODE PROCESSES IN IONIC LIQUID SOLVENTS AS MIXTURES OF CHOLINE CHLORIDE WITH UREA, ETHYLENE GLYCOL OR MALONIC ACID

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The paper reports studies about electrochemical reduction and oxidation processes in three types of ionic liquids consisted in binary mixtures of choline chloride (ChCl) with urea, ethylene glycol (EG) and malonic acid (MA) at various molar ratios from 2:1 to 1:4. The potential windows on Pt and glassy carbon were determined at 70^{0}C by cyclic voltammetry. By comparing to those of eutectic systems, namely ChCl-urea (1:2), ChCl-EG (1:2) and ChCl-MA (1:1), voltammograms from ionic liquids with more or less ChCl content provide information about reduction of choline ion and oxidation of complexed Cl$^-$ anion.

Keywords: ionic liquids, choline chloride, urea, ethylene glycol, malonic acid, cyclic voltammetry

1. Introduction

Ionic liquids are a kind of electrolytes constituted solely from organic cations and inorganic/organic anions and have received interest over the past years due to their physicochemical properties useful for a wide range of industrial purposes. In various electrochemical applications [1] ionic liquids are promising solvents (background electrolytes) because of their non-volatility, adjustable hydrophobicity and polarity, and dissolution ability for inorganic or organic compounds. Especially in electroplating industry [2-4] where the cathodic process without hydrogen evolution interference may lead to a higher current efficiency, ionic liquids can be considered as replacement technologies for existing aqueous processes that currently utilize strong inorganic acids and highly toxic reagents. Ionic liquids containing mixtures with participation of choline chloride (*hydroxy-ethyl-trimethyl ammonium chloride*, denoted in the following as ChCl) have received widespread attention in recent years for electrodeposition or electropolishing because are easy to be prepared, have environmentally friendly

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properties, are readily biodegradable and are cheap electrolytes [5-9]. Compounds with greater ability to form hydrogen bonds (hydrogen bonds donors, HBDs) display an enhanced freezing point depression when choline chloride and a hydrogen bond donor are mixed. Thus, ChCl, as a quaternary ammonium salt, can form deep eutectics (deep eutectic solvent, DES) by mixing with numerous organic compounds such as amides, alcohols or carboxilic acids [10-12]. DES have good electrical conductivity (*ca.* 1 $mScm^{-1}$ at 30^0C [10]), confirming that the ionic species in the liquid can move independently. The viscosity and conductivity are strongly influenced by the composition and the nature of second component, and hence the fluid properties could be tailored for specific applications. The main advantage is that these eutectic ionic liquids are air and moisture stable.

Binary mixtures with other molar ratios than eutectic composition are not exactly ionic liquids in their integrality; these systems are considered ionic liquid analogues, as Abbott *et al.* [13] suggested. They may contain an excess of either ChCl, or non-dissociated second component. Moreover, it is possible to have a water content, due to the not very well dried ChCl used, or hydrated metal salts introduced in the baths for electroplating. As environmentally more acceptable electrolytes, ChCl based ionic liquids and analogues have best answer to the industrial requirement for large-scale applications such as metal plating. One of the principles of the green chemistry applied in electroplating industry is to avoid hazardous solvents and generation of waste. In this respect, ionic liquids based on ChCl have good stability and high solubility for inorganic or organic compounds. The use of ionic liquids as background electrolytes in baths may offer a convenient solution to both the vapor emission and recycling problems. Supplementary, ionic liquids can be easily recycled and reused after electrolysis. Common characteristics of ionic liquids for solvent application include a wide electrochemical window, meaning high electrochemical stability, which allows investigation of electrochemical processes that take place beyond the solvent limits.

In contrast to well explored processes during metal electrodeposition, the electrode processes of solvent in these media have not been studied extensively; there is still a vast lack of information regarding the electrochemical reduction and oxidation of ChCl based ionic liquids with no other additions, and this is related to knowledge of potential windows. In usual electrochemical surface treatments, by excessive polarizing an electrode at either cathodic or anodic potentials, the solvent is involved and its electrode processes are “side-processes”.

In this work, a study about the domain of potentials where electrochemical reduction and oxidation processes occur on Pt electrode in three types of choline chloride based ionic liquids, ChCl-urea, ChCl-ethylene glycol (EG) and ChCl-malonic acid (MA) is reported. The components were mixed in various molar ratios from 2:1 to 1:4 and the working temperature was kept constant at 70^0C. Cyclic voltammetry (CV) was the investigation technique. Comparative cyclic voltammograms were also recorded using glassy carbon electrode.

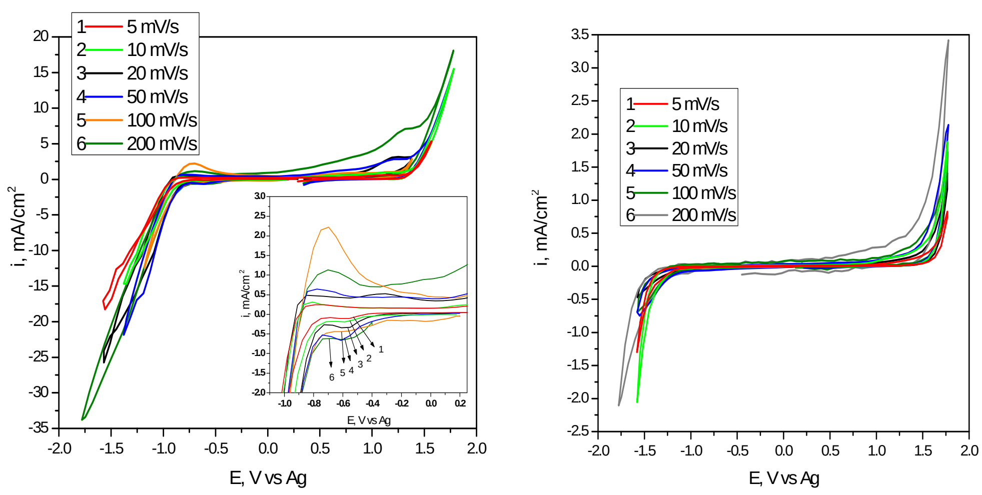
2. Experimental

Choline chloride (ChCl, 2-hydroxy-N,N,N-trimethyl-ethyl-ammonium chloride, 99%), urea, ethylene glycol (1,2 ethanediol, 99.8%), and malonic acid (MA) of analytical grade were provided by Sigma Aldrich and used as received to prepare the eutectic ionic liquids and ionic liquid analogues. Mixtures with 2:1; 1:1; 1:2; 1:3 and 1:4 molar ratios of components were prepared as three binary systems, ChCl-urea, ChCl-EG and ChCl-MA by weighing (mostly for amount of 0.4 moles) and heating at approximately 90^0C for more than 30 minutes until a homogeneous liquid is formed; by cooling at room temperature, the ionic liquid remained stable for long-term storage, reaching an equilibrium with the air moisture.

CV measurements were carried out in quiescent solutions at 70^0C constant temperature using a Zahner electrik IM 6e potentiostat. CV curves were recorded with scan rates in the range of 5-200 mVs^{-1}. In the three-electrode cell either platinum (plate of 0.5 cm^2 or disk with 3 mm diameter) or glassy carbon disk (GC, 3 mm diameter) were the working electrodes; a Pt plate with a larger surface area and an Ag wire acted as auxiliary and quasi-reference electrodes, respectively. The reference potential of silver wire in these ionic liquids is very stable and it is controlled by the activity of chloride ions. Prior to each measurement, the working electrode was polished with 50 μm alumina paste, rinsed with HNO_3:H_2O 1:1 solution, washed with running water and distilled water, and finally dried.

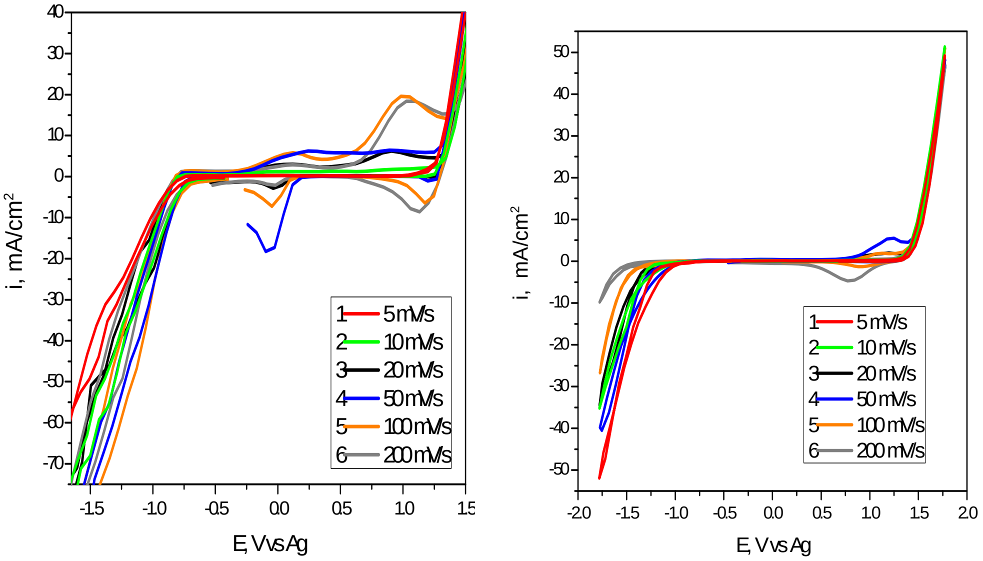
3. Results and discussion

In electrodeposition, it is important to compare the electrochemical window of the solvent and the reduction potential of the metal ion. The electrode processes at both cathodic and anodic polarization are analyzed by cyclic voltammetry technique in three kinds of ionic liquids based on choline chloride: with hydrogen bonds donors (HBD) compounds: urea, ethylene glycol and malonic acid. Voltammetric experiments were mainly carried out by scanning at first to negative potentials and only the first cycle is presented. The temperature was selected at 70^0C to favour low viscosity and good electrical conductivity of the liquid medium.



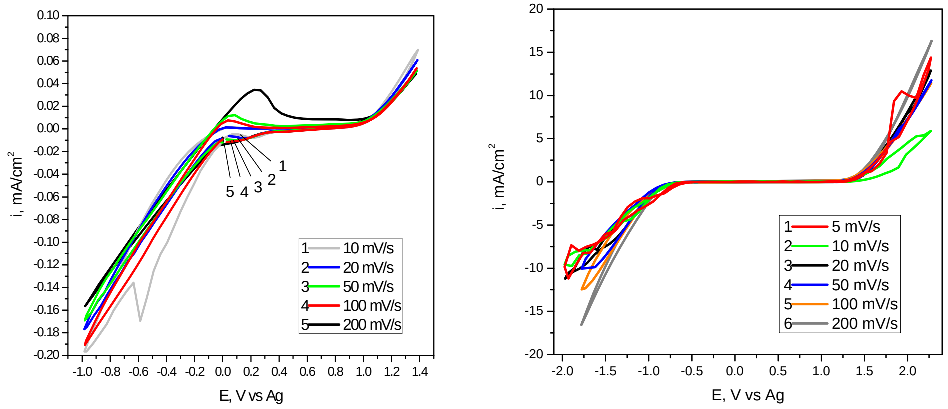
(a) (b)

Fig. 1 CVs for ChCl-urea (1:2) eutectic ionic liquid at 70^{0}C obtained with various scan rates (5-200 mVs^{-1}) using Pt electrode (a) and glassy carbon electrode (b)



(a) (b)

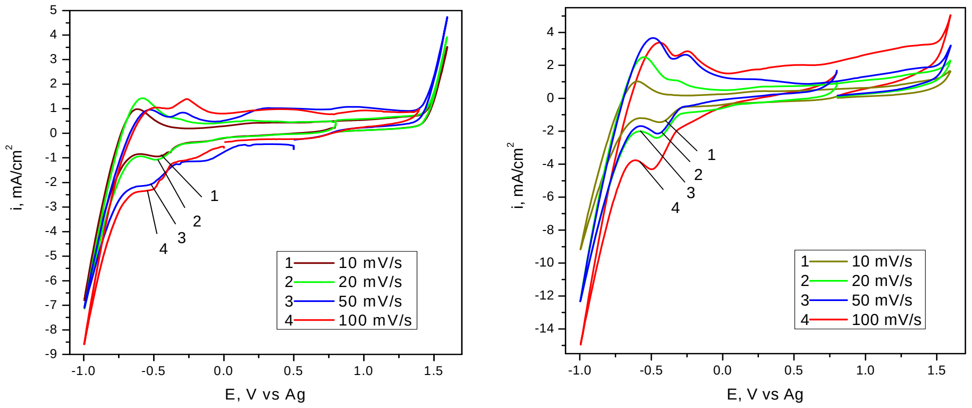
Fig. 2 CVs for ChCl-EG (1:2) eutectic ionic liquid at 70^{0}C obtained with various scan rates (5-200 mVs^{-1}) using Pt electrode (a) and glassy carbon electrode (b)



(a) (b)

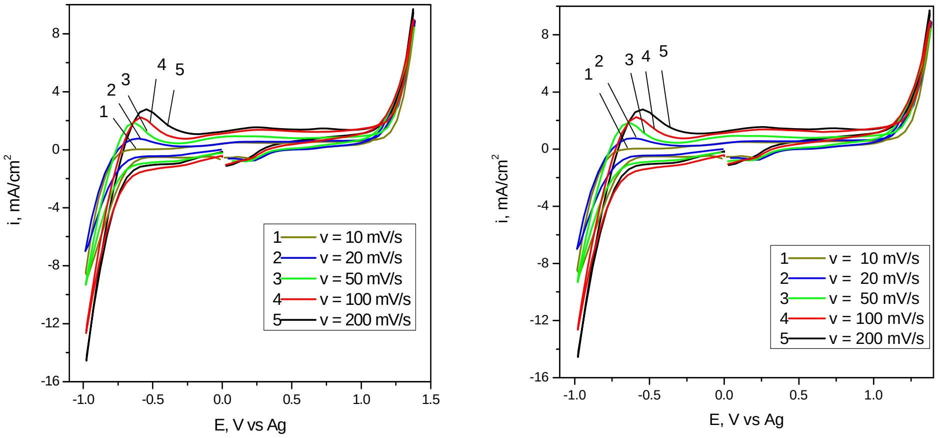
Fig. 3 CVs for ChCl-MA (1:2) eutectic ionic liquid at 70^{0}C obtained with various scan rates (5-200 mVs^{-1}) using Pt electrode (a) and glassy carbon electrode (b)

We present in Figs. 1-3 the voltammetric results for eutectic compositions which are 1:2 molar ratio (67 mol% urea or ethylene glycol) for monofunctional HBDs, and 1:1 molar ratio (50 mol% malonic acid) for difunctional HBDs. Figs. 4-6 present examples of CV curves obtained in choline chloride based solvents with other molar ratios than eutectic compositions. All figures show that the current began to continuously increase by enlarging the electrode potential range towards either negative or positive potentials. The increasing influence of the scanning rate to reduction current or oxidation current, respectively, is monotonous. In all cases, when working with glassy carbon, the current densities are lower than on Pt, leading to simpler shapes of cyclic voltammograms.



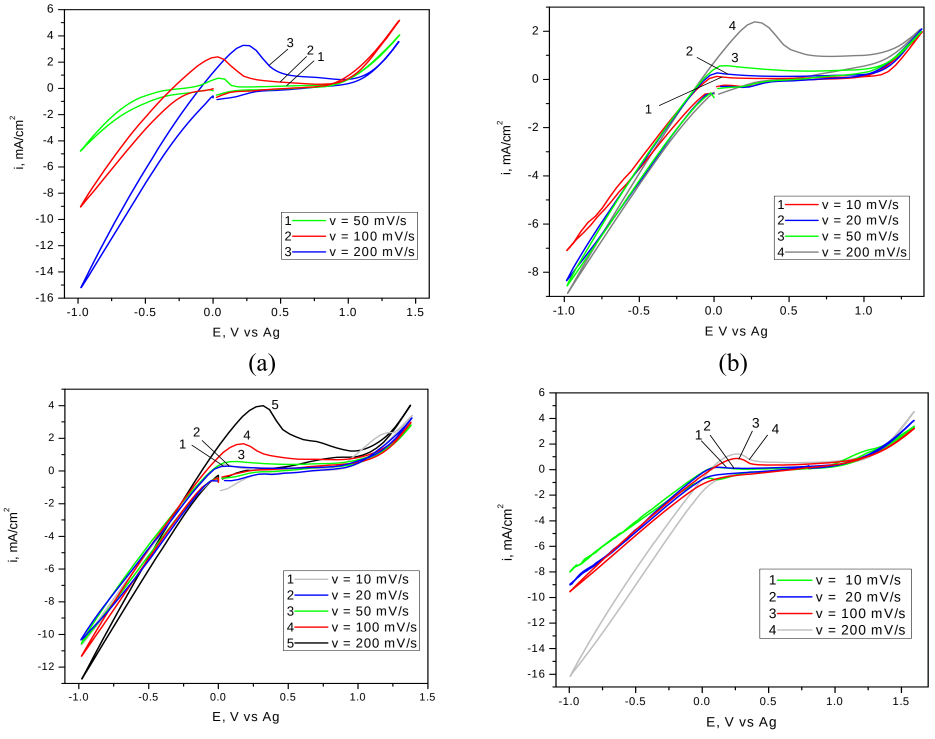
(a) (b)

Fig. 4 CVs on Pt at 70^{0}C for ChCl-urea ionic liquid analogues with different molar ratios of components in mixture: (a) 1:3 molar ratio; (b) 1:4 molar ratio



(a) (b)

Fig. 5 CVs on Pt at 70^{0}C for ChCl-EG ionic liquid analogues with different molar ratios of components in mixture: (a) 1.5:1 molar ratio; (b) 1:1 molar ratio



(a) (b)

(c) (d)

Fig. 6 CVs on Pt at 70^{0}C for ChCl-MA ionic liquid analogues with various scan rates: (a) 2:1 molar ratio; (b) 1.5:1 molar ratio; (c) 1:2 molar ratio; (d) 1:2.5 molar ratio

Table 1

Values of voltammetric potentials on Pt at 70^{0}C showing the range of electrode processes in eutectic ionic liquids and analogues containing choline chloride

ChCl : HBD molar ratio	Scan rate, mVs^{-1}	ChCl-Urea system			ChCl-EG system		ChCl-MA system	
		Potential of cathodic shoulder or peak, V	Onset of final cathodic process, V	Onset of final anodic process, V	Onset of final cathdic process, V	Onset of final anodic process, V	Onset of final cathdic process, V	Onset of final anodic process, V
2 : 1	10	-0.56	-0.84	+1.21	-0.63	+1.12	-0.18	+1.08
	20	-0.57	-0.81	+1.28	-0.64	+1.13	-0.18	+1.00
	50	-0.59	-0.82	+1.30	-0.61	+1.15	-0.20	+1.00
	100	-0.62	-0.79	+1.30	-0.58	+1.27	-0.20	+0.98
	200	-0.70	-0.76	+1.34	-0.58	+1.13	-0.21	+0.95
1 : 1	10	-0.55	-0.83	+1.28	-0.64	+1.12	+0.10 -0.82*	+1.1 +1.46*
	20	-0.59	-0.84	+1.26	-0.64	+1.12	+0.05 -0.85*	+1.08 +1.41*
	50	-0.63	-0.80	+1.35	-0.60	+1.12	0 -0.80*	+1.05 +1.43*
	100	-0.69	-0.82	+1.35	-0.60	+1.10	-0.03 -0.83*	+1.0 +1.38*
	200	-0.73	-0.81	+1.35	-0.62	+1.15	-0.05 -0.89*	+1.0 +1.39*
1 : 2	10	-0.62	-0.84 -1.48*	+1.38 +1.65*	-0.78 -1.40*	+1.27 +1.39*	-0.02	+1.06
	20	-0.62	-0.83 -1.42*	+1.37 +1.66*	-0.77 -1.34*	1.34 +1.40*	-0.01	+1.04
	50	from -0.64 to -0.68	-0.80 -1.40*	+1.32 +1.70*	-0.75 -1.25*	+1.29 +1.40*	-0.03	+1.06
	100	from -0.64 to -0.74	-0.76 -1.35*	+1.35 +1.74*	-0.76 -1.36*	+1.34 +1.41*	-0.03	+1.06
	200	from -0.68 to -0.80	-0.78 -1.32*	+1.42 +1.76*	-0.76 -1.44*	+1.38 +1.42*	-0.02	+1.09

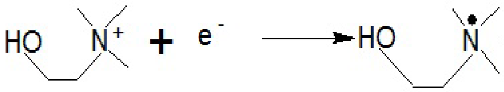
***Values on GC electrode in the same experimental conditions.**

Values of electrochemical windows were obtained by determination the cathodic and anodic limits listed in Table 1. It can be seen that using platinum electrodes, the potential window has values in the ranges of 2.1-2.2 V, 1.7-2.1 V and 1-2 V, for ChCl-urea, ChCl-EG, ChCl-MA, respectively. The corresponding values for glassy carbon electrode in such media are greater than for platinum, being in the ranges: 3.08-3.13 V, 2.65-2.86 V and 2.21-2.28 V, respectively. Such windows are not large compared to other ionic liquids, but are higher than the values in aqueous electrolytes (1.23 V).

However, for ChCl-urea system Fig. 1a shows that CV curves for platinum electrode display a supplementary reduction peak (or a plateau) in the cathodic scan, located at less negative potentials (centered at *ca.* -0.6V), previous to the massive solvent reduction (which has the onset at *ca.* -0.8 V). Values of peak potentials are also listed in Table 1. Similar shapes of cathodic branches of CVs on Pt were reported by other authors [3,14], but they did not explain the nature of process. This process was not observed using glassy carbon as substrate (Fig. 1b), in concordance with other experimental works [14]. In order to elucidate the nature of this process, the CVs were recorded in mixtures of ChCl with urea having other molar ratios (ionic liquids analogues): 2:1, 1:1, 1:3 and 1:4. As it can be seen in examples shown in Figs. 4a,b, the supplementary cathodic peak was also evidenced within the same potential range. Because this reduction process was not identified in the cathodic branches of ChCl-EG and ChCl-MA, the process may be assigned to the electroreduction of neutral molecules of remained non-complexed urea existing in the ionic liquid. By comparing the CVs on Pt for systems with various molar ratios of ChCl and urea, an increasing dependence of the peak currents (or limiting currents) with the scan rate and urea concentration was noticed, suggesting a diffusion controlled process. For platinum substrate, it is possible to have an electrocatalytical activity for urea reduction in such electrolysis conditions (totally ionic medium, significant urea concentration, 70^0C).

It is worth to mention that all CVs obtained using platinum as working electrode show other supplementary waves or even peaks (more prominent for ChCl-EG system) on the entire anodic branch and on portions of the cathodic branches after reversing oxidation scan. They are certainly due to side processes of electrochemically reduced (or oxidized) products of the first sweep, and should not be taken into consideration in the evaluation of the electrochemical window. In general, the cathodic and anodic limits are attributed to the reductive reaction of the cation and oxidative conversion of the anion. Regarding different speciation in the investigated media, literature shows that during the formation of eutectics, the chloride anion is complexed by the second component of mixture (HBD); urea, ethylene glycol and malonic acid act as a hydrogen bond donors [10,12,15,16]. Abbott *et al.* [16] identified Ch^+ cations by FAB (fast atom bombardment) mass spectrometry and showed that these are only cationic species existing in ionic liquid. Of course, the choline ion moiety based on quaternary ammonium ion with functionalization on one side chain with polar group (hydroxyl group) moves independently.

For the forward voltammetric scan, the continuous increase of the current in the high negative potentials region must be ascribed by direct electroreduction of choline ion resulting a very reactive neutral radical:

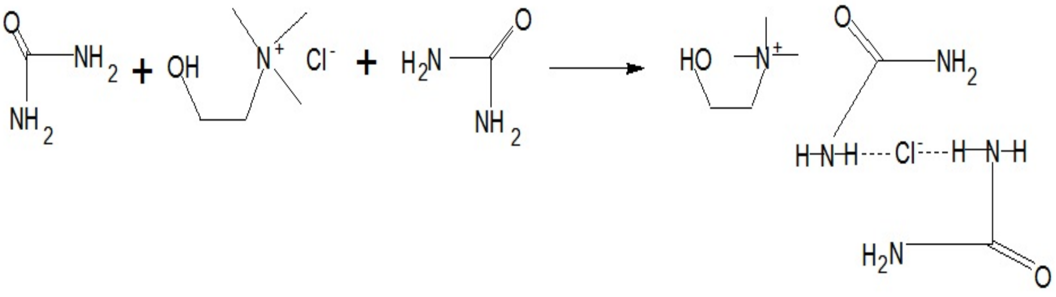


(1)

The unstable intermediate radical may convert into two parallel ways [17], producing either trimethyl amine and 3-hydroxypropyl radical or 2-dimethyl ethanolamine and methyl radical. The onset potential of cathodic reaction in both 1:2 mixtures of choline chloride with either urea, or ethylene glycol, is similar on Pt and GC electrodes (Table 1). This means that the electroreduction of glycol to its aldehyde is absent and only choline ion reduction takes place. However, the change of HBD with malonic acid has a marked effect on cathodic branch of CVs (Figs. 3 and 6) and, therefore, it narrows the potential window. Binary system of choline chloride with malonic acid contains acidic protons from dissociation of 'free' molecules of MA or of acetic acid resulted by thermal decarboxilation of MA. The smallest electrochemical window in ChCl-MA system is due to a significant increase of the cathodic current density, which has the onset at more positive potentials (see values in Table 1) than in ChCl-urea and in ChCl-EG. This proces cannot be ascribed by the choline cation reduction reaction. It is probably the electroreduction of hydrogen cations, a process in which hydrogen gas is formed; an electrocatalytic effect of platinum is expected, because the discharge of protons on Pt substrate is favored.

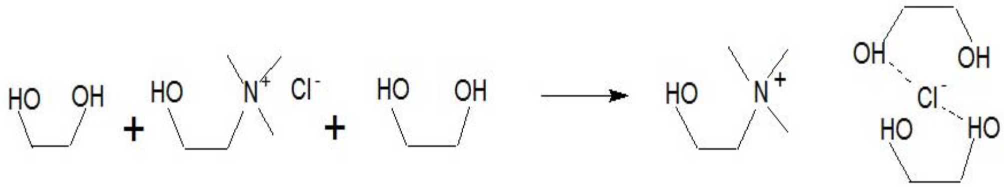
Figs. 1-6 and Table 1 show that the anodic process starts at various potentials depending on the chemical nature and concentration of donor molecules capable of forming hydrogen bonds with chloride ions. Hydrogen bonding interactions between hydrogen belonging to the complexing agent (such as urea, ethylene glycol or malonic acid) and Cl^- ions lead to a charge delocalization and an effective decrease of the interaction with the choline cation. Comparing ChCl-urea and ChCl-EG, the onset of chloride ion entity oxidation on Pt is similar, taking place at potentials in the range +1.3 ÷ +1.4 V. However, using glassy carbon electrode, the potential of the onset of oxidation process varies from +1.65 ÷ +1.76 V (ChCl-urea) to 1.34 ÷ +1.39 (ChCl-EG). This may be an evidence that urea acts as a stronger ligand for Cl^- ion than ethylene glycol. Conversely, in ChCl-MA system, the potentials of the onset of oxidation are less positive (*ca.* +1.0 V). The different potentials recorded for the onset of anodic process by diferent degrees of complexation of chloride anion that may have different structures were explained.

Unfortunately, still little is known regarding the speciation of complex anions and few studies have quantified the proportion of these complexes and non-complexated Cl⁻ ion. For ChCl-urea, Shamsuri [15] proposed the formation of complexes as products from the following reaction:



(2)

Similarly, we suggest for the other investigated systems, ChCl-EG and ChCl-MA, a coupling of choline chloride with ethylene glycol or malonic acid, according to the following schemes:



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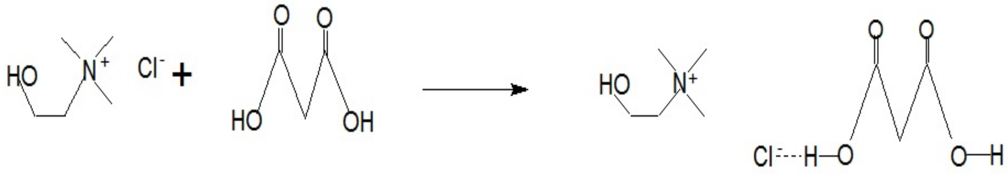

(4)

It is obviously a difference between the mixtures with 1:2 molar ratio (ChCl-urea and ChCl-EG) and ChCl-MA mixture which has 1:1 molar ratio, and this consists in H atoms non-participating in hydrogen bonding of chloride ion. This may also explain the differences in electrochemical window between ChCl-MA and the other two systems.

4. Conclusions

Cyclic voltammograms recorded in ionic liquids obtained by mixing choline chloride with urea, ethylene glycol or malonic acid in various molar ratios (from 2:1 to 1:4) evidenced cathodic and anodic limits of potential, where reduction of choline cation and chloride complexed anion take place. Scanning rate and variation of molar ratio have little influence. Values of electrochemical windows for ChCl-urea, ChCl-EG and ChCl-MA using platinum or glassy carbon electrode were determined. It was found that potential windows in ChCl-MA are clearly narrower mainly due to the change of the cathodic mechanism – reduction of protons takes place instead of reduction of choline ion. A supplementary cathodic process occuring on CVs from ChCl-urea is attributed to the reduction of 'free' molecules of urea. Increased current with scan rate and urea concentration suggest a diffusion controlled process. Schemes for complex formation during cupling choline chloride with ethylene glycol or malonic acid were proposed in a similar manner as for the complexation with urea.

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