The physico-chemical properties of two types of choline-chloride (ChCl) based ionic liquids (that are actually ionic liquid analogues) were studied within 50-90°C temperature range. Density and viscosity of ChCl-CrCl₃×6H₂O mixtures with 3:1, 2:1, 1:1 and 1:2 mole ratios in composition as well as of ChCl-dihydrate oxalic acid mixtures were determined at 50-70°C. Electrochemical techniques as cyclic voltammetry and electrochemical impedance spectroscopy were applied at 60-90°C both from CrCl₃, 6H₂O binary systems (containing 2.3-2.7 M Cr³⁺ ion) and from ternary systems consisted in a ChCl-oxalic acid ionic liquid as supporting electrolyte in which 2-50 millimolar concentrations of CrCl₃, 6H₂O were dissolved. The existing ionic species of chromium and the mechanism of reduction/oxidation were discussed.

Keywords: choline chloride based ionic liquids; hexahydrate chromium trichloride; density; viscosity; chromium electrodeposition; electrode processes of chromium ions
for dissolved Cr(II) ion to be reduced to metallic state is now more narrow and therefore the Cr deposition is restricted. More recently, chromium was deposited in ionic liquids based on 1-butyl-3-methylimidazolium tetrafluoroborate and chromium (III) salts [BMim][BF4] [8-10]. However, these electrolytes with imidazolium derivatives are still a challenge for the large-scale applications, owing to the expensive costs of precursor (alkylimidazoles) and potentially toxicological and purity issues.

Ionic liquids containing mixtures with participation of choline chloride (hydroxy-ethyl-trimethyl ammonium chloride, denoted in the following as ChCl) have also received widespread attention for Cr plating due to their environmentally friendly properties and, therefore, because they may be a promising substitute of toxic Cr(VI) baths. This quaternary ammonium salt can form complexes with numerous organic compounds as hydrogen bond donors such as amides, alcohols or carboxylic acids [11,12], Abbott et al [13-15] also showed that ChCl forms eutectics with a variety of hydrated metal salts including compounds of cobalt, nickel, iron, copper, zinc, etc., and these eutectics are found to have properties similar to imidazolium-based ionic liquids. Mixtures of choline chloride with hydrated chromium chloride, nitrate, sulfate or acetate have been shown to form eutectic liquids that are air and moisture stable [14]; because these binary mixtures are not exactly ionic liquids, they are considered ionic liquid analogues [16]. The well-known advantages of ChCl – based ionic liquids and analogues, as environmentally more acceptable, have best answer the industrial requirement for large-scale application such as metal plating. Chromium can be potentially electrodeposited with high current efficiency from these ionic liquids containing chromium salts. The possible electrodeposition of thick, adherent and efficient from these ionic liquids containing chromium chloride hexahydrate (Merck, >98%) and oxalic acid (Aldrich, >98%) have been received to prepare the ionic liquids and mixtures (ionic liquid analogues). Choline chloride and hexahydrate chromium trichloride, weighed (mostly for amount of 0.4 moles mixture) and mixed in molar ratios of 3:1; 2:1; 1:1 and 1:2, were heated at approximately 90°C and maintained at this temperature for more than 30 min. With prolonged heating the liquid color at 90°C was purple due to the loss of water molecules from the coordination sphere around the chromium ion. The color turned dark green by cooling below 70°C, so that at room temperature a viscous dark green liquid is obtained; we noticed that this process of color change is reversible by heating/cooling cycling.

In order to prepare systems more diluted in chromium ion, portions of ChCl-OxA·2H2O (1:1 mole ratio) eutectic were first obtained by heating at 90°C the mixture of ChCl and dihydrate oxalic acid until a homogeneous liquid is formed. Then, the solutions containing 2-50 mM chromium chloride were prepared by dissolving the appropriate amounts of CrCl·6H2O chromium salt and stirring the mixtures at 90°C temperature. Their color is green for freshly prepared liquids, with a color intensity depending on chromium concentration; however, with prolonged time of storage in open air, the diluted solutions (2-6mM Cr ion) turn into reddish-purple colour which may be explained by conversion of CrII to superior oxidation states.

Experimental part

Chromium chloride, ChCl (Aldrich, 99%), chromium (III) chloride hexahydrate (Merck, >98%) and oxalic acid dihydrate (Merck) were used as received to prepare the ionic liquids and mixtures (ionic liquid analogues). Choline chloride and hexahydrate chromium trichloride, weighed (mostly for amount of 0.4 moles mixture) and mixed in molar ratios of 3:1; 2:1; 1:1 and 1:2, were heated at approximately 90°C and maintained at this temperature for more than 30 min. With prolonged heating the liquid color at 90°C was purple due to the loss of water molecules from the coordination sphere around the chromium ion. The color turned dark green by cooling below 70°C, so that at room temperature a viscous dark green liquid is obtained; we noticed that this process of color change is reversible by heating/cooling cycling.

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Densities and viscosities were determined in the temperature range of 50-70°C using an Anton Paar (model DMA 4500) vibrating-tube density meter and an Anton Paar (model AMVn) automatic microviscosimeter, respectively. The equipment for density has measured the period of vibrations of a thin metallic wire, showing the density of the electrolyte. The overall uncertainty of the density measurements was estimated to be within ±0.10 ± 0.2 g cm⁻³.
The temperature in both measuring cells was respectively controlled by integrated Peltier thermostats with ±0.05 °C accuracy.

Cyclic voltammetry measurements were carried out with scan rates in the range of 3-1000 mVs⁻¹ using a Zahner electrik IM 6 potentiostat. IR compensation was employed in all the voltammetric measurements. The electrochemical impedance spectroscopy (10 mV ac voltage, 200 kHz – 50 mHz frequency range) was also applied. In the three-electrode cell either a platinum plate (0.5-1 cm²) or a Cu disk (0.2 cm²) were working electrodes. A platinum plate and Ag wire acted as counter and quasi-reference electrodes, respectively. Prior to each measurement the working electrode was polished with 50 μm alumina paste, rinsed with HNO₃:H₂O 1:1 solution, washed with running water and distilled water, and finally dried. Electrochemical measurements were performed in the temperature range of 60-90 °C.

Results and discussions

The electrolytes used in the present work were respectively controlled by integrated Peltier thermostats with ±0.05°C accuracy.

Cyclic voltammetry measurements were carried out with scan rates in the range of 3-1000 mVs⁻¹ using a Zahner electrik IM 6 potentiostat. IR compensation was employed in all the voltammetric measurements. The electrochemical impedance spectroscopy (10 mV ac voltage, 200 kHz – 50 mHz frequency range) was also applied. In the three-electrode cell either a platinum plate (0.5-1 cm²) or a Cu disk (0.2 cm²) were working electrodes. A platinum plate and Ag wire acted as counter and quasi-reference electrodes, respectively. Prior to each measurement the working electrode was polished with 50 μm alumina paste, rinsed with HNO₃:H₂O 1:1 solution, washed with running water and distilled water, and finally dried. Electrochemical measurements were performed in the temperature range of 60-90°C.

Studies of density and viscosity for choline chloride - CrCl₃·6H₂O and choline chloride - oxalic acid binary systems

Four ChCl-CrCl₃·6H₂O binary mixtures with mole fractions of chromium trichloride increasing gradually from 0.25 (3:1 mole ratio) to 0.67 (1:2 mole ratio) were investigated. Dark green viscous liquids were obtained for these compositions at temperatures near ambient temperature. The aspect of the last compositions confirms the results of Abbott et al [16] who showed that the eutectic consisting in 1:2 mole ratio of ChCl/CrCl₃·6H₂O has freezing temperature at ca 14°C, with properties analogues with an ionic liquid. Our values of density (ρ) and dynamic viscosity (η) obtained experimentally for different choline chloride-CrCl₃·6H₂O binary systems are presented in tables 1 and 2. It can be seen that both density and viscosity vary significantly with composition and temperature. Correlation equations showing temperature dependences of density and viscosity, respectively, as well as values of the activation energy for viscosity were deduced on the basis of experimental data.

As table 1 shows, the density of binary systems increased with chromium salt content and decreased with temperature. Compared to literature reports, our measured densities for 1:1 and 1:2 mixtures are very close to data obtained previously for the same systems. As an example is the value of 1.5541 gcm⁻³ for 0.667 mole fraction of chromium chloride at 60°C (table 1) compared with 1.54 gcm⁻³ reported by Abbott et al [16] for the same system. We noticed that the density lowered for mixtures richer in choline chloride (3:1 and 2:1 systems) approaching to the values of other ChCl based ionic liquids [23,24], including values of ChCl-oxalic acid system which will be discussed below (table 3). As a general observation, the obtained density values are greater than for other alkyl-imidazolium based ionic liquids [26-32] and confirm suggestion of a smaller void volume in the liquids containing choline chloride [16]. Using the density values, chromium ion molarities in ChCl-hydrated CrCl₃ mixtures have resulted in

<table>
<thead>
<tr>
<th>Mole fraction of CrCl₃·6H₂O (mole ratio of components)</th>
<th>Temperature dependence of density (values in g.cm⁻³)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.250 (3:1)</td>
<td>1.3116 1.3055 1.2999</td>
<td>0.9983</td>
</tr>
<tr>
<td>0.333 (2:1)</td>
<td>1.3603 1.3546 1.3499</td>
<td>0.9984</td>
</tr>
<tr>
<td>0.500 (1:1)</td>
<td>1.4642 1.4584 1.4525</td>
<td>0.9999</td>
</tr>
<tr>
<td>0.667 (1:2)</td>
<td>1.5600 1.5541 1.5480</td>
<td>0.9999</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mole fraction of CrCl₃·6H₂O (mole ratio of components)</th>
<th>Viscosity, mPa.s</th>
<th>Temperature dependence of density (values in g.cm⁻³)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.250 (3:1)</td>
<td>4467 1864 868</td>
<td>ln ρ = ln ρ₀ + Eₚ / R T</td>
<td>0.9184</td>
</tr>
<tr>
<td>0.333 (2:1)</td>
<td>1502 879 442</td>
<td>ln ρ = -13.607 + 6770.6 (1/T) Eₚ = 56.3 kJmol⁻¹</td>
<td>0.9921</td>
</tr>
<tr>
<td>0.500 (1:1)</td>
<td>1303 724 383</td>
<td>ln ρ = -13.811 + 6785.3 (1/T) Eₚ = 56.4 kJmol⁻¹</td>
<td>0.9984</td>
</tr>
<tr>
<td>0.667 (1:2)</td>
<td>730 359 197</td>
<td>ln ρ = -15.908 + 7267.7 (1/T) Eₚ = 60.4 kJmol⁻¹</td>
<td>0.9990</td>
</tr>
</tbody>
</table>
the range of 1.9-4.6 M, the highest value being for 1:2 mole ratio mixture at 50°C.

In all cases the density ($\rho$) is accurately correlated to the temperature ($T$) by a first-order equation:

$$\rho = a + bT$$  \hspace{1cm} (1)

This behaviour is expected because the density of an ionic liquid generally decreases with temperature due to thermal expansion which varies linearly. The obtained correlation coefficients (presented as $R^2$) are very close to unity. Similar linear dependence with temperature was also reported for the mostly of singular or binary ionic liquids [26-29]. Moreover, according to table 1 the $\rho = f(T)$ straight lines have the approximately same slope for all compositions, therefore are almost parallel. The small slope value indicates that the density of ChCl-hydrated CrCl$_3$ mixtures is quite less sensitive to temperature variation and therefore the liquid volume does not expand appreciably in the studied temperature range.

In order to study the electrochemical behaviour of chromium ionic species in more diluted ionic liquids based on choline chloride we have chosen as a solvent the eutectic mixture (1:1 mole ratio) formed by choline chloride with oxalic acid. The properties of pure ChCl-dihydrate OxA ionic liquid have been not extensively studied, and to our knowledge its density and viscosity were not reported yet in the literature. Table 3 shows the measured values of density and viscosity for ChCl-oxalic acid (1:1 mole ratio) as function on temperature. The obtained density data are situated in between the values of other ChCl-based ionic liquids recently reported [23-25], such as ChCl-urea, ChCl-ethylene glycol, ChCl-malic acid, ChCl-glycerol and also in between density values of alkyl-imidazolium based ionic liquids which are extensively studied [26-32]. The results for ChCl-OxA (1:1 mole ratio) show that the densities decrease as the temperature is raised.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$, g.cm$^{-3}$</td>
<td>25 1.24124</td>
</tr>
<tr>
<td></td>
<td>30 1.23754</td>
</tr>
<tr>
<td></td>
<td>40 1.23036</td>
</tr>
<tr>
<td></td>
<td>50 1.22337</td>
</tr>
<tr>
<td></td>
<td>60 1.21639</td>
</tr>
<tr>
<td></td>
<td>70 1.20948</td>
</tr>
<tr>
<td></td>
<td>80 1.20265</td>
</tr>
</tbody>
</table>

Temperature dependence (equation: $a + bT$) is expressed as:

$$\rho = 1.45000 - 7.010 \times 10^{-4}T \hspace{0.5cm} R^2 = 0.9999$$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$\eta$, mPa.s</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>840</td>
</tr>
<tr>
<td>30</td>
<td>416</td>
</tr>
<tr>
<td>40</td>
<td>228</td>
</tr>
<tr>
<td>50</td>
<td>138</td>
</tr>
<tr>
<td>60</td>
<td>89</td>
</tr>
</tbody>
</table>

Temperature dependence (equation: $\ln \eta = \ln \eta_0 + \frac{E_\eta}{RT}$) is expressed as:

$$\ln \eta = -13.12684 + 6201.6 \frac{E_\eta}{RT} \hspace{0.5cm} R^2 = 0.9953$$

$E_\eta = 51.56$ kJmol$^{-1}$

As figure 1a shows, viscosity decreased exponentially with temperature for all compositions of electrolytes. We tried to verify if it obeys the Arrhenius-type dependence and therefore the plotted $\ln \eta$ vs. reciprocal absolute temperature straight lines were represented in figure 1b. The activation energies for viscosity ($E_\eta$), listed also in tables 2 and 3, were calculated from the slopes of corresponding $\ln \eta - 1/T$ linear dependences. For binary systems of choline chloride with chromium salt, with an exception of 3:1 system that has the lowest content in chromium chloride, the values of $E_\eta$ are in the range of 56-60 kJmol$^{-1}$ and should be correlated to the electrostatic interactions between ionic components which are similar at these compositions. Viscosities for ChCl-OxA mixture have the lowest values in figures 1, suggesting the smallest van der Waals interactions for this ionic liquid, considered here as a supporting electrolyte for CrCl$_3$ (as chromium ion precursor).

Table 3
VALUES OF DENSITY AND VISCOSITY FOR ChCl-DIHYDRATE OxA (1:1) IONIC LIQUID AT DIFFERENT TEMPERATURES
The electrochemical behaviour of choline chloride - CrCl3·6H2O and choline chloride – dihydrate oxalic acid + CrCl3·6H2O liquid mixtures

Cyclic voltammetry was utilized to investigate electrode processes of chromium species on platinum and copper surfaces. Some electrochemical impedance (EIS) spectra were also recorded by polarizing the electrode in the potential region of interest (cathodic).

As also above discussed, we investigated four choline chloride - CrCl3·6H2O binary mixtures, prepared in molar ratios of 3:1; 2:1; 1:1 and 1:2. First, several cyclic voltammograms (CVs) obtained from the richest electrolyte in chromium species, 1:2 mixture, were presented in figure 2 by using either platinum or copper as working electrode and starting the cathodic scan from stationary electrode potential. It may be noted a very different behaviour of these two electrodes regarding the shape of cathodic branch of voltammograms. As figure 2a shows, a continuous increase of cathodic current is recorded for Pt electrode until the cathodic reverse potential (-3V) is reached. On contrary, by using copper electrode (fig. 2b) in the same 1:2 system and at the same temperature a step-wise character of Cr(III)-electro-reduction is observed. A clear cathodic peak (or a plateau) occurs in a first step; then, the cathodic current starts increasing again if the scan is extended towards more negative potentials, the second process continuing up to -2V and more negatively. We noticed that the peak current on copper increases with scan rate whereas the peak potential shifts negatively, these findings suggesting a mass transport control as well as a quasireversible behaviour for the first process.

For the forward scan on Pt, we can assign the continuous increase of current in the negative potentials region to a direct reduction of chromium ionic species to Cr(0), i.e. chromium metal. However, on Cu surface the first reduction step proceeds at more negative potentials than on Pt, hence the nature of support is found to have a marked influence on the reduction potentials of chromium. The cathodic detected in the potential range from -0.4V to -1V may correspond to the partial reduction of Cr(III) by the formation of relatively stable intermediates-divalent chromium insoluble species, Cr(II) ion, as literature indicated previously [1,2]. A second step on copper surface, appearing at more negative potentials than -1V, may correspond to the reduction of Cr(II) to Cr(0). According to some authors [16] it is possible that only a part of the Cr(II) solid species existing onto electrode surface to be reduced to Cr(0). In some cases using both Pt and Cu as working electrodes, the reverse scan towards positive potentials presents in the negative potential region a clear nucleation loop with crossover suggesting that a new phase, i.e. metallic chromium, is nucleated on the substrate surface.

Quite similar cyclic voltammetry results were obtained for the other studied ChCl-CrCl3·6H2O binary systems, some CV selected curves being represented in figures 3-4. All these CVs revealed the difference in cathodic behaviour of Pt and Cu electrodes, showing a continuous increase of current on Pt electrode and a peak (or a shoulder) of Cr(III)/Cr(II) reduction process on copper surface in a similar region of potentials. Regarding the anodic branches of CVs on Pt it is clearly the occurrence of one oxidation process evidenced by peaks or waves, that may be assigned to consecutive processes as following: first oxidation, located at +0,1V ÷ +0,3V, should be a dissolution of metallic chromium resulting directly Cr(III) ion. The second one may be attributed to dissolution of the amount of insoluble Cr(II) which remained onto platinum surface, resulting Cr(III) ion, too; this last oxidation process is clearly evidenced in Figure 4a and it has a quasireversible behaviour due to its shift of peak potential with scan rate (fig. 4b).
The anodic processes on copper were not evidenced due to limitation of positive scanning in order to not impurify the electrolyte by dissolution of copper support.

We present in figures 5 the Nyquist diagrams (imaginary part of impedance vs real part) and Bode diagrams (both dependences with frequency of phase angle and impedance modulus) obtained experimentally using Pt as working electrode. These EIS spectra were recorded by shifting negatively the electrode potential in the range of Cr(III) reduction. For selection of polarization potentials we used the above CVs, therefore the data presented here should be interpreted in a same manner as in cyclic voltammetry. Nyquist spectra from figure 5a show single semicircles at high frequencies, considered as capacitive loops. They are followed by linear portions attributed to formation of chromium film through which the diffusion of Cr(III) species takes place.

By polarizing the electrode more negatively, up to -1V, a sequence of decreased diameters of capacitive semicircles was recorded, meaning that the charge-transfer resistances decrease gradually. Evolution of both impedance modulus (gradual decrease, fig. 5b) and maximum of phase angle (decrease from -60° to -5°, fig. 5c) confirm the metallic behaviour of chromium deposit which is accumulated gradually onto platinum surface.

For a discussion of the electroreduction mechanism of chromium ionic species from electrolytes with different chromium salt content, we mention that the coordination of chromium in CrCl₃·6H₂O containing ionic liquids is complex and not fully understood, because a variety of complex species could be present and the proportions of H₂O and Cl⁻ in the coordination shell of chromium were not yet determined. In aqueous solutions containing chromium trichloride as solute, Elving and Zemel [33] identified for the first time in literature the aqua-complex chromium ions. They showed that the number of H₂O molecules in the Cr³⁺ chloride complexes varies from 6 to 3 and each chloride ligand which substitutes a water molecule in the first coordination sphere produces a gradual modification evidenced by UV spectroscopy. It was established that in neutral aqueous medium the predominant species in equilibrium are the two complex cations: [Cr(H₂O)₅Cl]²⁺ and [Cr(H₂O)₄Cl₂]⁺, while a single tri-chloro species (Cr(H₂O)₃Cl₃)³⁺ (trivalent cation) was only observed when the aqueous medium is very acidic, for instance the concentrated 37wt% HCl solution (12 M HCl).

As opposite to aqueous media, for mixtures of choline chloride with hexahydrate chromium trichloride, Abbott et al. [16,17] established that the predominant chromium complex is [Cr(H₂O),Cl]⁻ anionic species cannot be excluded in the high chloride environment [16]. Regarding our studied series of ChCl-CrCl₃·6H₂O binary electrolytes this should be the case of 1:2 mole ratio where the greatest content in chloride ion exists. Thus, for this chloride rich system it is possible to formulate the formation of CrCl₄⁻ anionic species and therefore the concentration of Cr³⁺ to be decreased by the excess of chloride ion, due to an effect of changing the charge.

---

**Fig. 4.** CVs on Pt electrode (1cm²) for ChCl-CrCl₃·6H₂O (3:1) mixture, 90°C. Scan rates: (a) 3 mVs⁻¹; (b) 1- 20 mVs⁻¹; 2- 100 mVs⁻¹; 3- 200 mVs⁻¹

**Fig. 5.** EIS spectra on Pt (0.5 cm²) for ChCl-CrCl₃·6H₂O (1:2) mixture at 80°C at various polarizations: +0.1V; 0V; -0.2V; -1V. (a) Nyquist spectra; (b,c) Bode spectra
carrying species by conversion of tri-aqua into di-aqua ionic complex according to the equilibrium:

\[
\text{[Cr(H₂O)₃]Cl}_₃ \text{H₂O} + \text{Cl}^- \rightleftharpoons [\text{Cr(H₂O)₂Cl₄}]⁻ \text{H₂O} \quad (2)
\]

The data obtained at higher temperatures (85-90°C) can be related to a supplementary problem regarding the water content (introduced as hexahydrate chromium salt) of our studied liquid electrolytes; the calculated weight percentage of water is obviously increased gradually from 15.7 wt% (3:1 mole ratio) to 32.1 wt% (1:2 mole ratio) in binary ChCl-CrCl₃ systems. Abbott et al [13,16] showed that a ChCl-CrCl₃ ionic liquid cannot be formed using anhydrous chromium trichloride; therefore, ChCl-hydrated CrCl₃ mixtures may not be considered as concentrated aqueous solutions, they have properties analogous to ionic liquids. This demonstrates the role of water molecules that behave as ligands rather than solvent (free) molecules. Thus, ChCl-CrCl₃ systems are ionic liquid analogues, while the ternary mixtures ChCl-OxA-CrCl₃ which will be discussed below are nearly true ionic liquids.

By considering the ChCl-OxA supporting electrolyte with dihydrated oxalic acid used in this paper, we mention that no faradaic processes are observed on Pt electrode in this background electrolyte by polarizing in a wide range of potentials, with -0.2V and +1.3V as potential limits (fig. 6a). Only the continuous increases of currents at the cathodic and anodic limits of potential window were recorded. Obviously, the potential window of this medium should be increased in the absence of supplementary hydration water (introduced from oxalic acid) because the water molecules should favors a easier hydrogen evolution at the electrode surface. However, a narrower potential window of ChCl-OxA electrolyte was noticed by using copper electrode (fig. 6b).

The similar behaviour of ChCl-OxA ionic liquids during gradual polarization of Pt is also revealed on the electrochemical impedance (EIS) spectra that can give us information about the processes taking place in the potential range from +0.042V to -0.558V. Figures 7 and 8 show the recorded Nyquist and Bode diagrams on Pt and Cu electrodes; we have drawn in figures 7b and 8b both...
impedance modulus and phase angle vs. frequency dependences. The Nyquist spectra show only singular capacitive semicircles for all frequencies, indicating a lack of any electrode process except charging of double layer. Gradual decrease of diameters is related to an increase of the rate (exchange current) of cathodic process. The impedance modulus and phase angle maximum decrease with cathodic polarization in the same order for both electrodes. However, the nondepressed shape of semicircles in figure 7a demonstrates a good uniformity of platinum electrode surface used as cathode, whereas the depressed semicircles in figure 8b prove a degree of non-uniformity (roughness, more probably) of copper surface.

Some representative CVs obtained on Pt electrode from electrolytes containing ChCl-OxA + millimolar concentrations of CrCl₃·6H₂O salt could be seen in figures 9-11; also, figures 12 present EIS spectra for a such ionic liquid diluted in chromium species. All electrochemical tests were performed at various temperatures (60-90°C) and the scan rates in cyclic voltammetry were in the range of 3-1000 mVs⁻¹. It is expected for these ternary systems to exhibit two consecutive reduction steps, Cr(III)/Cr(II) and Cr(II)/Cr(0), and also two anodic peaks for separate dissolution of metallic chromium and of solid Cr(II) species.

The continuous increase of cathodic current at very negative potentials is obvious due to electrodeposition of chromium onto platinum surface by direct reduction of Cr³⁺ species. As a general rule, the cathodic current in this potential region increases with increase of temperature indicating an enhancement of diffusion of chromium ionic species in ChCl-OxA ionic liquid at higher temperatures and a facilitated electron transfer at electrode-electrolyte interphase. Another favourable influence can be attributed to the decrease of the viscosity, a fact which enhances the mass transport of the ionic species in liquid medium and, hence, the current density. This effect was frequently observed in ionic liquid-based electrolytes [8-10].

A plateau, a shoulder or even a cathodic peak, which occurred in the potential region +0.1V ÷ -0.2V on the reduction branch of voltammograms, may be assigned to the first reduction couple, Cr(III)/Cr(II). This couple is more evident at relatively higher chromium ion concentrations (50 mM or 20 mM chromium salt), at higher potential scan rates, but at lower temperatures (60-70°C), as figures 9b and 10 show. The potential of Cr(III)/Cr(II) process shifts negatively with scan rate and positively with increasing chromium salt concentration (obeying the Nernst’s law in the range of 2-50 mM chromium salt concentration), as expected. Obviously, the rate of this step, and also of the overall cathodic process is controlled by the mass transport of the trivalent-Cr complex ions to the cathode surface.

However, we noticed that along the anodic branches of voltammograms the first process of dissolution (dissolution of metallic chromium into chromium ions) is much less evidenced, with an exception of figure 9a where even two superposed waves correspond to this couple. The second anodic process, attributed to Cr(II)/Cr(III) oxidation step, appears more clearly on voltammograms. As figure 11b shows (and also fig. 9a in the reverse scan) a sharp peak, which corresponds to the oxidation of the Cr(II) formed in the forward scan that was not reduced to Cr(0), occurred at around +1V potential. With increasing scan rate its peak potential shifts gradually in the positive direction (fig. 10a, for instance) and its peak current increases proving a mass transport control. For an extensive anodic excursion of potential, such as a polarization at +2V (fig. 11a) or more positively, the increase of oxidation current produces, by reversing negatively the potential scan, a new cathodic peak which is characteristic to the products formed by oxidation of supporting electrolyte (fig. 6a for instance).

The Nyquist spectra show only singular capacitive semicircles for all frequencies, indicating a lack of any electrode process except charging of double layer. Gradual decrease of diameters is related to an increase of the rate (exchange current) of cathodic process. The impedance modulus and phase angle maximum decrease with cathodic polarization in the same order for both electrodes. However, the nondepressed shape of semicircles in figure 7a demonstrates a good uniformity of platinum electrode surface used as cathode, whereas the depressed semicircles in figure 8b prove a degree of non-uniformity (roughness, more probably) of copper surface.

Some representative CVs obtained on Pt electrode from electrolytes containing ChCl-OxA + millimolar concentrations of CrCl₃·6H₂O salt could be seen in figures 9-11; also, figures 12 present EIS spectra for a such ionic liquid diluted in chromium species. All electrochemical tests were performed at various temperatures (60-90°C) and the scan rates in cyclic voltammetry were in the range of 3-1000 mVs⁻¹. It is expected for these ternary systems to exhibit two consecutive reduction steps, Cr(III)/Cr(II) and Cr(II)/Cr(0), and also two anodic peaks for separate dissolution of metallic chromium and of solid Cr(II) species.

The continuous increase of cathodic current at very negative potentials is obvious due to electrodeposition of chromium onto platinum surface by direct reduction of Cr³⁺ species. As a general rule, the cathodic current in this potential region increases with increase of temperature indicating an enhancement of diffusion of chromium ionic species in ChCl-OxA ionic liquid at higher temperatures and a facilitated electron transfer at electrode-electrolyte interphase. Another favourable influence can be attributed to the decrease of the viscosity, a fact which enhances the mass transport of the ionic species in liquid medium and, hence, the current density. This effect was frequently observed in ionic liquid-based electrolytes [8-10].

A plateau, a shoulder or even a cathodic peak, which occurred in the potential region +0.1V ÷ -0.2V on the reduction branch of voltammograms, may be assigned to the first reduction couple, Cr(III)/Cr(II). This couple is more evident at relatively higher chromium ion concentrations (50 mM or 20 mM chromium salt), at higher potential scan rates, but at lower temperatures (60-70°C), as figures 9b and 10 show. The potential of Cr(III)/Cr(II) process shifts negatively with scan rate and positively with increasing chromium salt concentration (obeying the Nernst’s law in the range of 2-50 mM chromium salt concentration), as expected. Obviously, the rate of this step, and also of the overall cathodic process is controlled by the mass transport of the trivalent-Cr complex ions to the cathode surface.

However, we noticed that along the anodic branches of voltammograms the first process of dissolution (dissolution of metallic chromium into chromium ions) is much less evidenced, with an exception of figure 9a where even two superposed waves correspond to this couple. The second anodic process, attributed to Cr(II)/Cr(III) oxidation step, appears more clearly on voltammograms. As figure 11b shows (and also fig. 9a in the reverse scan) a sharp peak, which corresponds to the oxidation of the Cr(II) formed in the forward scan that was not reduced to Cr(0), occurred at around +1V potential. With increasing scan rate its peak potential shifts gradually in the positive direction (fig. 10a, for instance) and its peak current increases proving a mass transport control. For an extensive anodic excursion of potential, such as a polarization at +2V (fig. 11a) or more positively, the increase of oxidation current produces, by reversing negatively the potential scan, a new cathodic peak which is characteristic to the products formed by oxidation of supporting electrolyte (fig. 6a for instance).
Although the ternary electrolyte ChCl-OxA.2H2O+CrCl3 contains some percentages of water concentration, in a proportion which increases with chromium salt concentration, the presence of water only decreases the electrochemical window but no peaks attributable to the reduction or oxidation of water were detected in the cyclic voltammograms.

The Nyquist and Bode spectra represented in figures 12 may be easier interpreted on the basis of the above discussion of both ChCl-CrCl3.6H2O and ChCl-OxA.2H2O binary systems. Similar to the other chromium salt containing mixtures, for the ChCl-OxA.2H2O+10 mM CrCl3.6H2O system the Nyquist spectra consist in portions of semicircles continued rapidly with straightlines; with negative polarization (from 0V to -0.8V) the semicircles become smaller and linear portions longer, showing clearly the formation of chromium film onto platinum. The curves of phase angle in Bode diagrams exhibit a decreased maxima with values started from -70° (characteristic of capacitive behaviour, absence of any film), continued to -60 and -20° (when the first nuclei of electrolycrystallized chromium are produced) and finish to -14° (characteristic of metallic film formation).

Conclusions

The densities and viscosities of four binary mixtures of choline chloride-CrCl3.6H2O (with molar ratios from 1:2 to 3:1) as well as density and viscosity of choline chloride-oxalic acid dihydrate (selected as solvent for dissolving chromium trichloride) were measured in the temperature range of 50-70°C. The densities decreased linearly with increasing temperature, whereas viscosities obey Arrhenius-type dependence. Data for density and viscosity are comparable with other ionic liquids.

Cyclic voltammograms at 80-90°C obtained from binary mixtures riched in chromium species, especially choline chloride-CrCl3.6H2O (1:2) mixture, showed very different electrodeposition behaviour by using either platinum or copper as working electrodes. The continuous increase of cathodic current on Pt is attributed to chromium electrodeposition by direct reduction of Cr3+ species. Using copper as substrate, a two-step Cr(III) electroreduction was observed, with peak (or a plateau) occurring in a first step, soluble Cr(III) → insoluble Cr(II) species, and a continuous increase of current (Cr(II) → Cr(0) step) if the scan is extended cathodically.

Ternary mixtures containing choline chloride - oxalic acid dihydrate + 2-50 mM CrCl3.6H2O salt show, in voltammograms recorded at 60-90°C on platinum, plateau or even cathodic peaks, which may be also attributed to the first reduction couple, Cr(III)/Cr(II). This couple is more evident at relatively higher chromium ion concentrations (50 mM or 20 mM chromium ion), at higher potential scan rates, but at lower temperatures (60-70°C).

References

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