A comparative study of the cathodic behaviour of EuCl$_3$ in two imidazolium chloride ionic liquids, the 1-butyl-3-methylimidazolium (C$_4$mimCl) and the 1-ethyl-3-methylimidazolium (C$_2$mimCl), on a glassy carbon electrode

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ARTICLE INFO

ABSTRACT

This work presents a comparative study of the electrochemical behaviour, on a glassy carbon electrode, of dissolved EuCl$_3$ in two chlorobasic ionic liquids, the 1-ethyl-3-methylimidazolium chloride, C$_2$mimCl, and the 1-buthyl-3-methylimidazolium chloride, C$_4$mimCl, over the temperature ranges 363–398 K and 343–363 K respectively. In both media, the electro-reduction of EuCl$_6^{3-}$ takes place via only one electrochemical step EuCl$_6^{3-}$/EuCl$_6^{4-}$. The electrochemical system EuCl$_6^{4-}$/Eu(0) has not been observed within the electrochemical window of both ILs, due to the prior reduction of the respective imidazolium cation from the solvents, which inhibits the electro-extraction of Eu(0) from the media on the GC electrode.

The paper describes how several electrochemical techniques (e.g. cyclic voltammetry (CV), convolutive potential sweep voltammetry (CPSV), steady state voltammetry (SSV), chronopotentiometry (CP) and chronoamperometry (CA)) have been used experimentally: i) verifying assumptions used in their theoretical analysis, and ii) ensuring reproducible conditions at the electrode/electrolyte interface, with the aim to obtain high-precision measurements of the diffusion coefficient of EuCl$_6^{3-}$. In order to know if there are discrepancies between the obtained data, a two-way analysis of variance, ANOVA, has been carried out. The analysis has shown that with a 95% confidence level there are no significant differences between the diffusion coefficients obtained by the different techniques. On the other hand, the diffusion coefficient of EuCl$_6^{3-}$ increases with the temperature following the Arrhenius law, being the activation energy for diffusion 40.4 ± 2.6 and 60.2 ± 1.8 kJ mol^{-1} in C$_2$mimCl and C$_4$mimCl respectively. The dimensionless Schmidt numbers, defined as the ratio between solvent viscosity and solute diffusivity ($Sc = \nu/D$), have also been calculated to characterise the solute global mass transport through its environment.

On the GC electrode, the electro-reduction of EuCl$_6^{3-}$ to EuCl$_6^{4-}$ is a quasi-reversible process. Accurate values of the kinetic parameters (i.e. the intrinsic rate constant of charge transfer, k^0, and the charge transfer coefficient, α), as well as the reversible half wave potential, E$_{1/2}^r$, have been obtained for the first time in the mentioned ionic liquids, by simulation of the cyclic voltammograms and logarithmic analysis of the voltammograms and convoluted curves.

1. Introduction

Room Temperature Ionic liquids (RTILs) commonly defined, as compounds constituted of cations and anions that melt at temperatures below 100 °C, have garnered in the last three decades much interest for use as water-free electrolytes. In comparison with conventional organic solvents, ILs exhibit particular advantages, along with minimal vapor pressure, which prevents odour problems and atmospheric pollution, nonflamability, significant chemical and thermal stability, and due to the fact that their physical and chemical properties are heavily

dependent on the specific cations and anions from which they are prepared, adjustability for tailored applications [1–3].

Resulting from their electrochemical stabilities and high ionic conductivities, ILs have also been proposed as electrolytes in electrochemical processing, being able to solve some problems of traditional liquid electrolytes [4,5]. Applications include electrodeposition of metals and alloys, electrodeposition on the nanoscale, electropolishing, electroplating, electrosynthesis of conducting polymers, membrane additives for fuel cells, dye-sensitized solar cells, electrochemical capacitors, and battery systems [3–5].

On the other hand, in the last decades there is a developing interest in using ILs in various stages of the nuclear fuel reprocessing and waste management, covering the following issues:

i) as substitutes for the inflammable volatile organic solvents (e.g. *n*-dodecane), currently employed for the liquid-liquid extraction of actinides and lanthanides in aqueous reprocessing [6–9], with the aim to reduce the chemical and radiolytic degradation of the solvent, as well as the volume of generated secondary wastes.

ii) as a possible alternative to high temperature molten salts (e.g. LiCl-KCl) in nonaqueous-based pyrochemical reprocessing [9–19]. In this way, the substitution of unsymmetrical organic cation in place of alkali metal cation of the inorganic salts, drastically reduces the melting point of the resulting organic chloride to near ambient temperature.

From these backgrounds, various ILs having a wide electrochemical window, adequate thermal and radiation stability, and ability to dissolve organic and inorganic compounds has been proposed, being between them the 1-butyl-3-methyl imidazolium chloride (C$_4$mimCl) [11,13–17,20] and the 1-ethyl-3-methyl imidazolium chloride (C$_2$mimCl) [19]. In order to evaluate the applicability of ILs, as alternative media to the conventional molten salts in the pyroreprocessing process, the knowledge of the electrochemical behaviour of actinides (Ans) and fission products (FPs), mainly lanthanides (Lns), is a major concern. Nevertheless, the reported information in C$_4$mimCl and C$_2$mimCl is scarce, ambiguous and conflicting [13–17,19].

The electroreduction of samarium (III), cerium (III) and europium (III) has been studied in C$_4$mimCl [17]. The Authors pointed out that the electroreduction of Sm(III) and Ce(III) at a Pt working electrode takes place at the same potential region in a single one-electron step, being their cathodic peak potentials (− 0,547 and − 0,558 V vs Pd at 373 K respectively). The electroreduction of Eu(III) to Eu(II) takes place at more cathodic potential values (E$_{pc}$ = − 0.769 V at 373 K) and is complicated with the adsorption of Eu(II)$_{adss}$ on the Pt electrode, giving place to a prewave and postwave in the voltammograms in the same potential region that the electrochemical waves attributed by the Authors to Sm(III)/Sm(II) and Ce(III)/Ce(II), but nothing is said about the electrochemical behaviour of the electrolyte on a Pt electrode in this potential region.

By contrast, the electrochemistry of Cerium (III) has been studied in the basic AlCl$_3$-1-methyl-3-ethylimidazolium chloride [21] and in 1-butyl-3-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide containing chloride ions [2], in both cases, it is reported that Ce(III) (i.e. CeCl$_6$$^{3−}$) is oxidized to Ce(IV) (i.e. CeCl$_6$$^{2−}$).

The electroreduction of Eu(III) and Sm(III) has also been studied in molten chloroaluminates [22–24], molten chlorides (e.g. LiCl-KCl and CaCl$_2$-NaCl) [25–26] and bis(trifluoromethylsulfonyl)imide (NTf$_2$) based ionic liquids [27] in all cases, the electroreduction of the respective Ln(III) to Ln(II) takes place following the sequence of the cathodic potential: Sm(III) > Eu(III). More recently the electroreduction of Eu(III) has been studied by Rama et al. [28] in the 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (C$_6$mim)NTf$_2$ containing tri-nbutyl phosphate and *N,N*-dihexyloctanamide ligands, the electrochemical system Eu(III)/Eu(II), free of any adsorption process, has been found quasi-reversible being the activation energy for Eu (III) diffusion 88 kJ mol$^{−1}$.

The discrepancies pointed out could be due to: i) different experimental designs, ii) the purity of the ionic liquid, iii) the lack of testing conditions, iii) the interpretation of data, and iv) type of measured and controlled parameters, that give place to different relations governing the behaviour of current and/or potential. To choose the right relation and to verify its accuracy is one of the key requirements in order to obtain true electrochemical information.

The aim of this work is to carry out a comparative study of the electrochemical behaviour, of dissolved anhydrous EuCl$_3$ in two chlorobasic media (i.e. Cl$^−$ donors), C$_4$mimCl and C$_2$mimCl, on a glassy carbon electrode, in order to evaluate the applicability of imidazolium rich chloride ionic liquids, as alternative media to the conventional molten salts in the pyroreprocesing process.

2. Experimental

Two imidazolium chlorides ionic liquids were selected as electrolytic medium, C$_2$mimCl (Sigma Aldrich 98%, Mm 146.62 g/mol, CAS: 65039-09-0) and C$_4$mimCl (Sigma Aldrich 95%, Mm 174.67 g/mol, CAS: 79917-90-1). Stock solutions of europium in these ILs were prepared and stored in a homemade glove box under a N$_2$ gas atmosphere, by direct addition of anhydrous EuCl$_3$ (Sigma Aldrich 99.99% Mm 258.32 g/mol, CAS: 10025-76-0) powder, being dissolved as EuCl$_6$$^{3−}$.

A portion of the corresponding stock solution was transferred to the electrochemical conical double wall cell, Metrohm 6.1415.150, made of glass, connected to a TAMPSON TC3 thermostat to control the temperature, and dry dinitrogen (Alphagaz N$_2$ (1) purchased from Air Liquide) was bubbled through the solution continuously to ensure the absence of oxygen and water.

The working electrodes consisted of either a glassy carbon (GC) rod (d = 2 mm,) or a rotating disc electrode made of GC (d = 3 mm, 0.071 cm^2, Metrohm 61,204,310): Another GC rod (d = 3 mm,) was used as counter electrode.

For the experiments carried out in the C$_4$mimCl, a saturated AgCl│Ag electrode replaced with C$_4$mimCl was used as reference electrode, whereas in the C$_2$mimCl an Ag wire was used as a quasi-reference electrode due to the use of higher working temperatures. Although the potential adopted by this quasi-reference is undefined, it was stable on the time-scale of the experiments, not existing any chemical reaction with the media and europium species. On the other hand, because the method selected for determining the diffusion coefficient depends on the value of the current rather than the potential, the need for a reference electrode with a well-defined potential is not mandatory.

All the electrochemical experiments were carried out under a N$_2$ atmosphere, using an EG & G PAR Model 273 A potentiostat/galvanostat controlled with the PAR EG & G M270 4.6 software. The electrochemical data were analyzed with the Echem software PAR EG & G Model 271, the Cool Kinetics Analysis software 1.00, and the Condecom 2000 CV System version 1.20 EG & G Instrument.
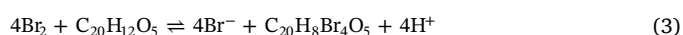
3. Results and discussion

3.1. Characterization of the electrochemical systems

The electrochemical window of C$_2$mimCl and C$_4$mimCl on a GC electrode was determined by combination of voltammetric and macro-electrolysis experiments. In both media, they are narrowed when the temperature is increased, and are limited in the anodic region by the oxidation of the chloride ions into chlorine.

$$2Cl^− − 2e^− \rightarrow Cl_2(g) \tag{1}$$

The chlorine evolution was identified in a macro-electrolysis experiment, placing in the anodic region a filter paper strip impregnated with fluorescein (C$_{20}$H$_{12}$O$_5$) and a solution of KBr. In the presence of Cl$_2$, pink eosin (C$_{20}$H$_8$Br$_4$O$_5$) is generated according to the following reactions [29]:

$$Cl_2(g) + 2Br^− \rightleftharpoons 2Cl^− + Br_2(g) \tag{2}$$

$$4Br_2 + C_{20}H_{12}O_5 \rightleftharpoons 4Br^− + C_{20}H_8Br_4O_5 + 4H^+ \tag{3}$$

In the cathodic region, the limit is due to the reduction of the respective imidazolium cation, leading in principle to the formation of their analogous radicals, which can undergo different types of reactions, as it is displayed in Fig. 1, being the most probable a radical-
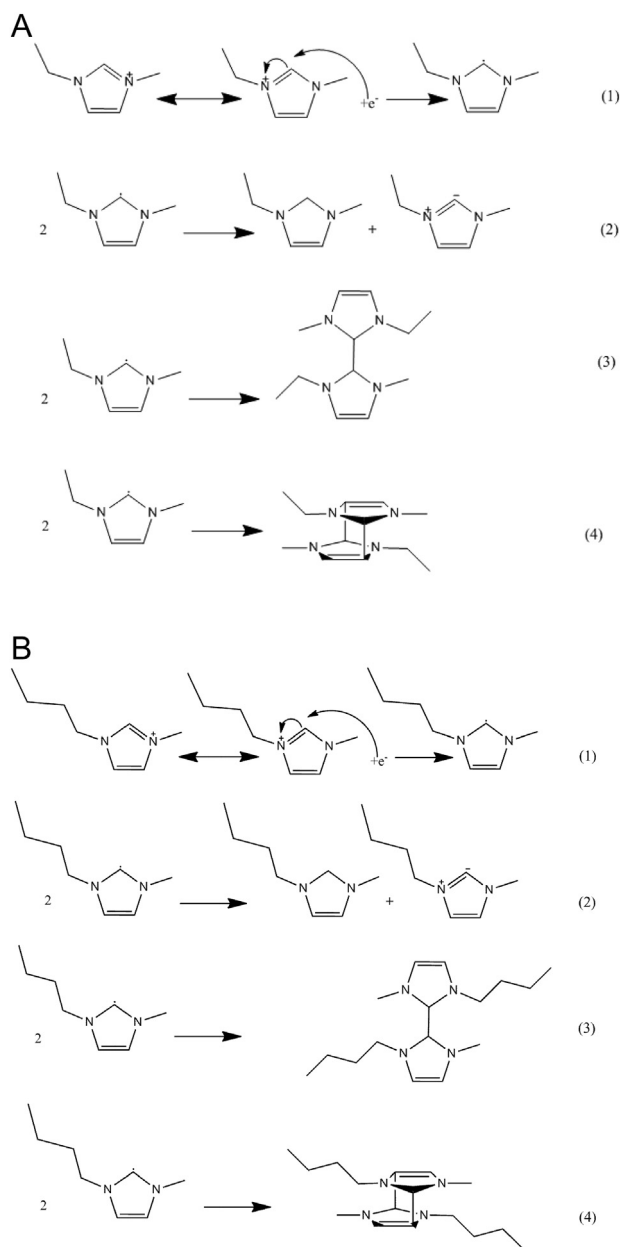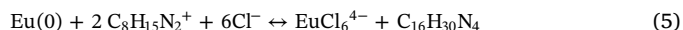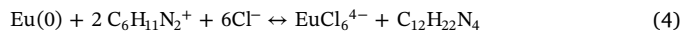
Fig. 1. Electrochemical decomposition mechanism of (a) C_2mim^+ [27], and (b) C_4mim^+ [4]. (1) formation of the imidazolium radical, (2) disproportionation reaction of two radicals, (3) coupling reaction of two radicals, (4) cage-formation reaction of two imidazolium radicals.

radical coupling reaction and a disproportionation reaction [4,30].

In addition to the electrochemical behaviour of both ionic liquids on a GC electrode, Figs. 2–3 also depict examples of the CVs registered with a solution of $EuCl_6^{3-}$ (i.e. $EuCl_3$ dissolved in a rich chloride ionic liquid) [23,27] on a glassy carbon electrode. In both imidazolium ILs, the electro-reduction of $EuCl_6^{3-}$ takes place through only one electrochemical step giving rise to a group of signals A/A′ with the shape expected for an electrochemical system in which the oxidized and reduced species are soluble in the media, and that can be assigned to the reduction of $EuCl_6^{3-}$ and the oxidation of the electro-generated $EuCl_6^{4-}$.

As it is shown in Figs. 2–3, no other waves attributed to the reduction of the electrogenerated $EuCl_6^{4-}$ were observed within the electrochemical windows of the electrolytes. The reduction of the imidazolium cation, hinders the reduction of $EuCl_6^{4-}$ to Eu(0), therefore the reduction potential of $EuCl_6^{4-}$/Eu(0) must be more negative in

potential than those corresponding to the reduction of the respective imidazolium cation. Being not conceivable the electroextraction of metallic europium from the ILs on a GC electrode. As a result, Eu metal in contact with the IL could react with the imidazolium cation to give $EuCl_6^{4-}$ and the corresponding imidazolium radical according to the following chemical reaction, in which it has been assumed that the radicals undergo the formation of a dimer (i.e. coupling of two radicals) [4,30].

$$Eu(0) + 2\, C_6H_{11}N_2^+ + 6Cl^- \leftrightarrow EuCl_6^{4-} + C_{12}H_{22}N_4 \tag{4}$$

$$Eu(0) + 2\, C_8H_{15}N_2^+ + 6Cl^- \leftrightarrow EuCl_6^{4-} + C_{16}H_{30}N_4 \tag{5}$$

3.2. Determination of the $EuCl_6^{3-}$ diffusion coefficient, and verification of the Arrhenius law

Electrochemical techniques (e.g. cyclic voltammetry (CV), convolutive potential sweep voltammetry (CPSV), stationary voltammetry, chronopotentiometry (CP) and chronoamperometry (CA)) are suited for the determination of the diffusion coefficient of electroactive species, if and when: (i) the appropriate equations in the appropriate experimental conditions were used, and ii) the accuracy of the measurements (i.e. precision and trueness of the data) was verified. Therefore, the challenge is to identify and demonstrate which of between these techniques is the most appropriate, taken into account: the experimental verification of the assumptions used in the equations used in calculations, to ensure reproducible conditions at the electrode/electrolyte interface, simplicity of data acquisition, and accuracy of the measurements.

3.2.1. Cyclic voltammetry

Repeatability of the electrochemical response, usually reported as standard deviation, is one of the components of the precision of a measurement. It measures the closeness between consecutive measurements carried out under the same experimental conditions. In order to obtain repeatable results, the diffusion layer has to be renewed before each measurement to obtain the same electrode/electrolyte interface conditions at the beginning of each test. If the diffusion layer is not efficiently renewed the registered voltammograms become less reproducible. Repeatability of voltammetric measurements was analyzed by registering 5 consecutive cyclic voltammograms, applying the following renewal procedure of the electrode/electrolyte interface: 1) once registered the first CV of the series, the solution was stirred during 20 s without applying any voltage (i.e. open circuit potential), for the diffusion to replace the consumed electroreactants, 2) afterwards, the solution stirring was stopped and 15 s were waited before running the new measurement. After running 5 consecutive tests, all the voltammograms were compared, an example is shown in Fig. 4 in which only the first and the last CVs registered at 50 and 200 mV s^{-1} have been represented. As can be seen, at all the scan rates, the successive voltammograms and peak currents were highly repeatable.

Once verified the repeatability of the electrochemical signals, several series of voltammograms were recorded with a solution of $EuCl_6^{3-}$ at different scan rates following the renewal procedure, on a glassy carbon electrode and at the selected working temperatures (after compensation of the solution resistance which was determined by the positive feedback technique) (Figs. 5–6). It is always observed that: i) both the cathodic and anodic peak current densities increase with the rise of the scan rate, ii) $J_{pc}/v^{1/2}$ decreases as the scan rate is increased, ii) the cathodic and anodic peak potentials, E_{pc} and E_{pa}, are shifted cathodically and anodically with the increase of the scan rate, iii) the $\Delta E_p = E_{pc} - E_{pa}$ presents larger values than those expected for a reversible one-electron process, and iv) the value for $|E_p^c - E_{p/2}|$, where $E_{p/2}$ is the half-peak potential, is larger than the theoretical value expected for a one-electron Nernstian electrode process. Therefore, according to the theory of voltammetry, the reduction of $EuCl_6^{3-}$ to
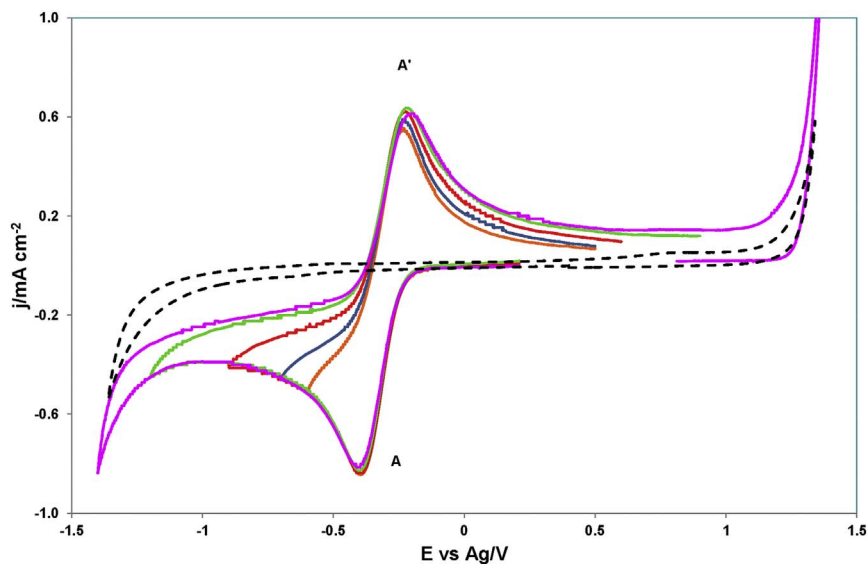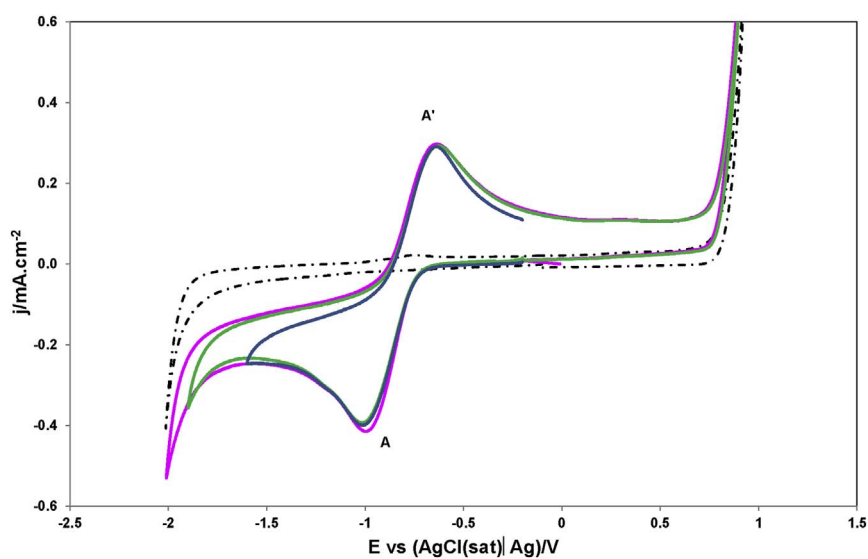
Fig. 2. Electrochemical window on a GC electrode in C_2mimCl (black dotted line) and cyclic voltammograms registered at different inversion potentials with a $EuCl_6^{3-}$ solution ($C_0 = 5,58 \times 10^{-5}$ mol cm^{-3}) in C_2mimCl at 50 mV s^{-1} and 363 K.

Fig. 3. Electrochemical window on a GC electrode in C_4mimCl (black dotted line) and cyclic voltammograms registered at different inversion potentials with a $EuCl_6^{3-}$ solution ($C_0 = 4,05 \times 10^{-5}$ mol cm^{-3}) in C_4mimCl at 80 mV s^{-1} and 343 K.
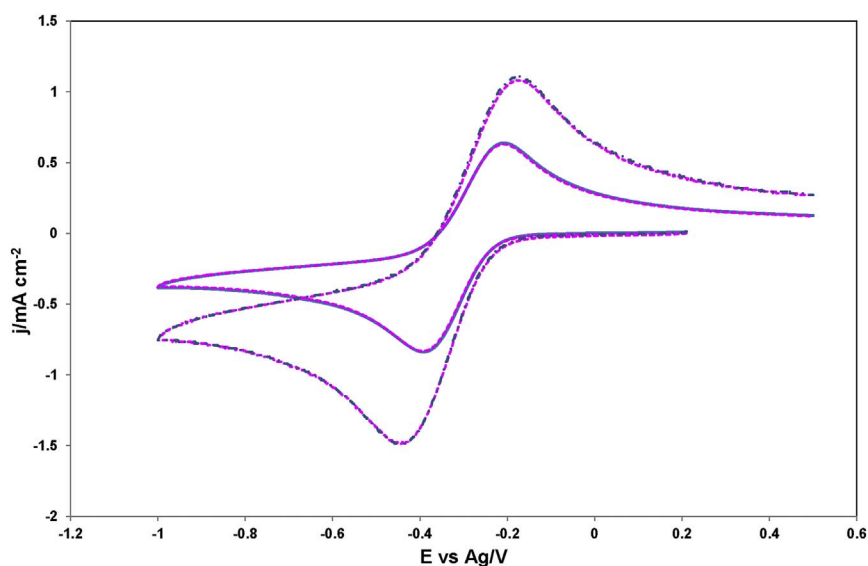

Fig. 4. Cyclic voltammograms registered with a $EuCl_6^{3-}$ solution ($C_0 = 5,58 \times 10^{-5}$ mol cm^{-3}) in C_2mimCl at 363 K and 50 mV s^{-1} and 200 mV s^{-1} and with application of the developed renewal procedure of the electrode/electrolyte interface. Pink dotted lines (---) first scan, blue dotted lines (---) fifth scan. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
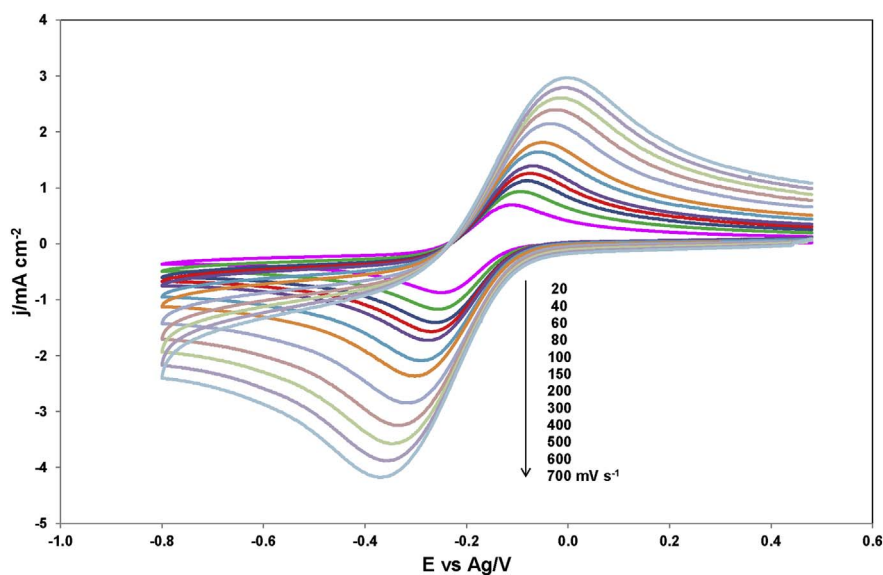
Fig. 5. Cyclic voltammograms for the reduction of $EuCl_6^{3-}$ in the C_2mimCl ($C_0 = 5.59 \times 10^{-5}$ mol cm^{-3}) at different sweep rates at 363 K using a glassy carbon electrode. Sweep rates ranging from 20 to 700 mV s^{-1}.

$EuCl_6^{4-}$ at a glassy carbon electrode is a quasi-reversible process at all the studied scan rates.

The lack of a specific equation for a quasi-reversible electrochemical exchange [31–32], avoid the calculation of the diffusion coefficient by means of this technique, being not possible to "tune" the reaction into reversible or irreversible by adjusting the useful interval of scan rates (i.e. slow and fast respectively).

3.2.2. Convolutive potential sweep voltammetry (CPSV)

Semi-integration can be a valuable adjunct to cyclic voltammetry. In this technique, all the information obtained from the wave is used, instead of the peak current and potential values as in cyclic voltammetry. The key aspect of the convolutive potential sweep voltammetry, also known as semi-integral electroanalysis, is the convoluted (semi-integrated) current m(t), where i(u) is the current from the voltammogram [33–35].

$$m(t) = \frac{1}{\pi^{1/2}} \int_0^t \frac{i(u)}{(t-u)^{1/2}} du \tag{6}$$

Fig. 7 depicts an example of the cyclic voltammograms obtained with a solution of $EuCl_6^{3-}$ in C_4mimCl and its corresponding semi-integrated curve. In the convoluted curve, the peaks has disappeared because semiintegration accurately compensates for the depletion effects that cause the current to peak. Instead, a plateau, labelled the limiting semiintegral, of height m*, is developed, irrespective of the reversibility of the electrode reaction [35], at potential values sufficiently cathodic to ensure zero surface concentration and complete concentration polarization of the reactant.

It is also noticeable in Fig. 7 that the backward and the forward branches of the semiintegrated cyclic voltammogram do not exactly retrace and a hysteresis behaviour occurs between them, supporting the fact that the electrochemical system $EuCl_6^{3-}/EuCl_6^{4-}$ is quasi-reversible. On the other hand, the convoluted curves of the voltammograms exhibited well defined limiting currents, whose values are independent of the scan rate. Therefore, the $EuCl_6^{3-}$ diffusion coefficient can be computed from the limiting semiintegral, of height m*, by means of Eq. (7) [31–35].

$$m^* = nFSC_0D^{1/2} \tag{7}$$

where S is the electrode area (cm^2), C_0 represents the bulk concentration (mol cm^{-3}), and D is the diffusion coefficient (cm^2 s^{-1}). The obtained results on a GC rod and a GC disc electrode, are gathered in Table 1.
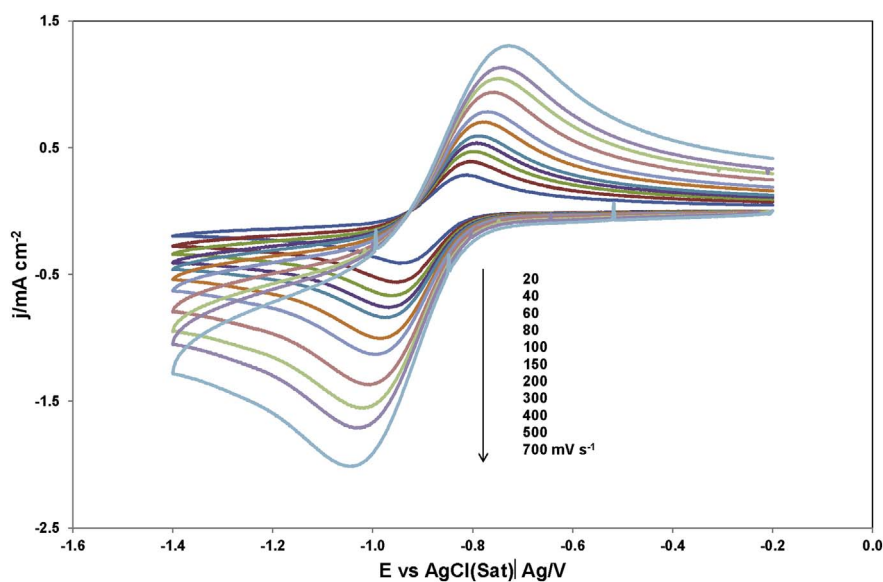

Fig. 6. Cyclic voltammograms for the reduction of $EuCl_6^{3-}$ in the C_4mimCl ($C_0 = 4.00 \times 10^{-5}$ mol cm^{-3}) at different sweep rates at 363 K using a glassy carbon electrode. Sweep rates ranging from 20 to 700 mV s^{-1}.
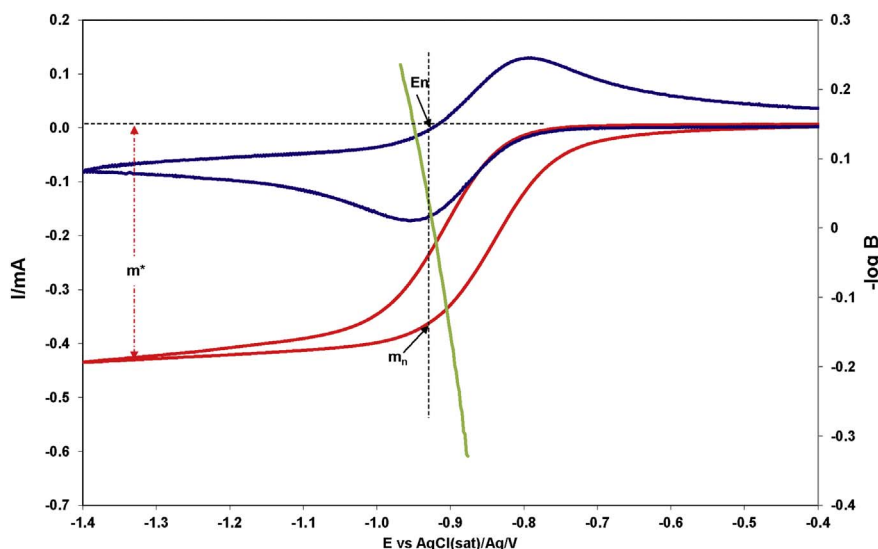
Fig. 7. Blue line cyclic voltammogram, its corresponding convoluted curve (red line) and logarithmic analysis of $EuCl_6^{3-}$ in C_4mimCl (green line). Experimental conditions: $C_0 = 4.025 \times 10^{-5}$ mol cm^{-3}; $T = 353$ K; scan rates: (pink lines) 40 and (blue lines) 150 mV s^{-1}. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.2.3. Stationary voltammetry (SV)

Stationary polarization curves on a rotating disc electrode (RDE) were also recorded with a $EuCl_6^{3-}$ solution in the C_4mimCl at various rotation speeds in the range between 500 and 3000 rpm. Examples of the linear stationary voltammograms are shown in Fig. 8. The voltammograms exhibit well defined limiting current for the reduction of $EuCl_6^{3-}$. The limiting current, I_{lim}, is proportional to the square root of the rotating disc electrode speed, according to the Levich equation [32].

$$I_{lim} = 0.62nFS\nu^{-1/6}D^{2/3}C_0\omega^{1/2} \tag{8}$$

where ν is the kinematic viscosity of the ionic liquid taken from [36], and ω is the rotating disc electrode speed (rad s^{-1}). Plots of the limiting current, I_{lim}, versus $\omega^{1/2}$ are shown in the inset of Fig. 8, the plots were linear and passed through the origin, indicating that the reduction of $EuCl_6^{3-}$ is under convective mass transport control in the potential region where the limiting current is observed. From the slopes of these plots, the diffusion coefficient of $EuCl_6^{3-}$ was determined, being the obtained values gathered on Table 1.

3.2.4. Chronoamperometry

Fig. 9 show examples of the chronoamperograms registered with a solution of $EuCl_6^{3-}$ in C_2mimCl on a GC electrode at several cathodic potentials that were chosen so that the reaction was: i) under mix control, ii) kinetically controlled, and iii) diffusion controlled. After every run the electrode was polarized for 25–30 s at a potential value sufficiently anodic to ensure zero surface concentration of the

electogenerated $EuCl_6^{4-}$, afterwards the diffusion layer was renewed following the renewal procedure indicated previously.

By plotting the current density versus $1/t^{1/2}$ at potential values in the mass-transport controlled region, where the concentration of $EuCl_6^{3-}$ is nearly zero at the electrode surface and the current is totally controlled by mass transfer (i.e. electrode kinetics no longer influence the current), it can be shown that the experimental data obey the Cottrell law [31,32].

$$j_d(t) = \frac{nFD^{1/2}C_0}{\pi^{1/2}t^{1/2}} \tag{9}$$

where $j_d(t)$ is the sampled current density at time t. The diffusion coefficient, $D_{Eu(III)}$, was calculated from the slope of the straight lines and the main results are gathered in table 1.

3.2.5. Chronopotentiometry

Despite of the uncertainty in the graphical determination of transition time, which is unavoidable when using chronopotentiometry, the diffusion coefficient of $EuCl_6^{3-}$ in C_2mimCl was also determined from the chronopotentiograms as those shown in Fig. 10, by means of Sand's equation [31,32].

$$j\tau^{1/2} = \frac{nFD^{1/2}C_0\pi^{1/2}}{2} \tag{10}$$

where J is the applied current density and τ is the transition time. The chronopotentiograms were registered at various imposed current

Table 1
Variation of the diffusion coefficient of $EuCl_6^{3-}$ with the temperature in the C_2mimCl and C_4mimCl ionic liquids calculated by different electrochemical techniques, density (ρ), dynamic viscosity (η), kinematic viscosity (ν), and Schmidt number.

C_4mimCl	D $EuCl_6^{3-}$/10^{-8} cm^2 s^{-1}			C_2mimCl	D $EuCl_6^{3-}$/10^{-7} cm^2 s^{-1}		
T/K	343	353	363	363	376	387	398
CPSV[a]	4.1 ± 0.5	8.1 ± 0.8	15.1 ± 0.6	3.8 ± 0.2	6.3 ± 0.3	9.2 ± 0.6	13.2 ± 0.9
CPSV[b]	5.0 ± 0.5	11.7 ± 0.4	14.7 ± 0.2	–	–	–	–
LSV[b]	4.4 ± 0.4	7.5 ± 0.5	11.9 ± 0.9	–	–	–	–
CA[a]	3.7 ± 0.3	7.4 ± 0.8	14.0 ± 2.0	5.05 ± 1.0	6.3 ± 0.5	11.4 ± 1.3	14.0 ± 1.2
CA[b]	5.1 ± 0.3	9.5 ± 1.4	16.3 ± 1.5				
CP[a]	–	–	–	4.2 ± 0.3	6.4 ± 0.2	9.2 ± 0.3	13.1 ± 0.3
Mean value	4.5 ± 0.8	8.9 ± 1.7	14.3 ± 1.8	4.4 ± 0.8	6.3 ± 0.7	9.9 ± 1.3	13.1 ± 1.3
ρ/kg m^{-3}	1057 [35]	1051 [35]	1046 [35]	1114 [36,37]	1104 [36,37]	1096 [36,37]	1087 [36,37]
η/kg m^{-1} s^{-1}	0.27007 [35]	0.14916 [35]	0.08907 [35]	0.0429 [38]	0.0285 [38]	0.0202 [38]	0.0143 [38]
ν/cm^2 s^{-1}	2.55	1.42	0.85	0.39	0.26	0.18	0.13
SC/10^5	571.6	158.8	59.5	8.7	4.0	2.0	1.0

[a] Values obtained with a GC rod electrode.
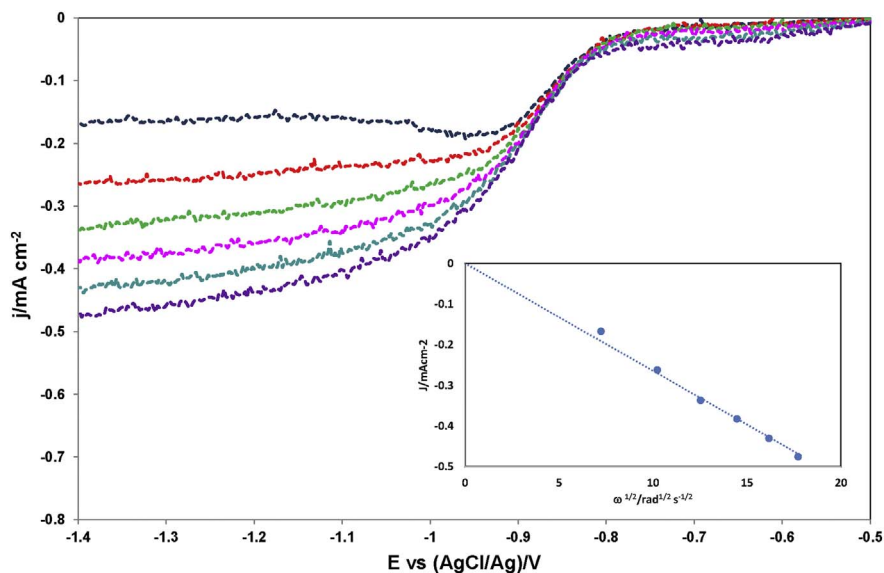[b] Values obtained with a GC disc electrode.

Fig. 8. Stationary polarization curves of $EuCl_6^{3-}$ in C_4mimCl on a rotating GC disc electrode. Experimental conditions: $C_o = 4.05 \times 10^{-5}$ mol cm^{-3}; v = 10 mV s^{-1}; T = 343 K; rotating disc electrode speeds:500, 1000, 1500, 2000, 2500 and 3000 rpm.
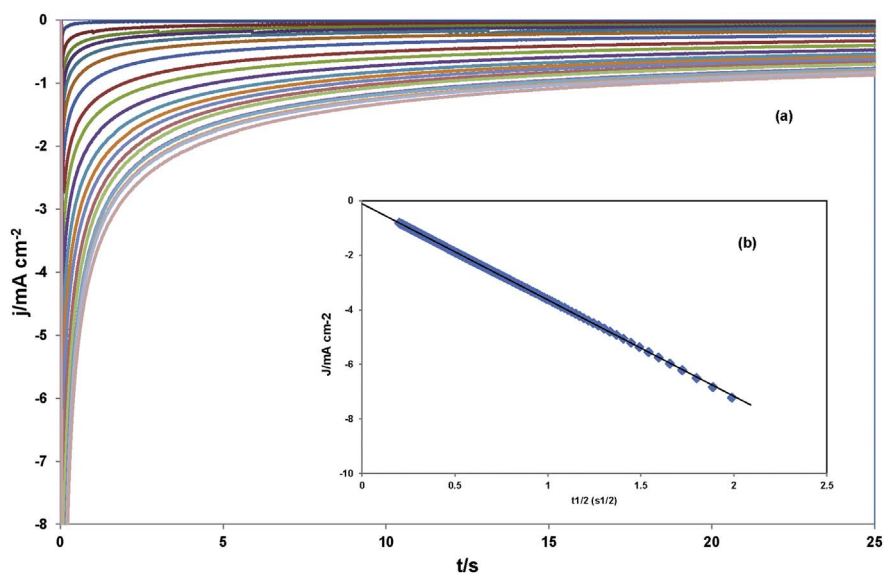

Fig. 9. Current-time transients resulted from chronoamperometric experiments for the electroreduction of $EuCl_6^{3-}$ in the C_2mimCl ($C_0 = 5.44 \times 10^{-5}$ mol cm^{-3}) at 398 K on a glassy carbon electrode at potentials ranging from -0.025 to -0.600 V vs Ag.
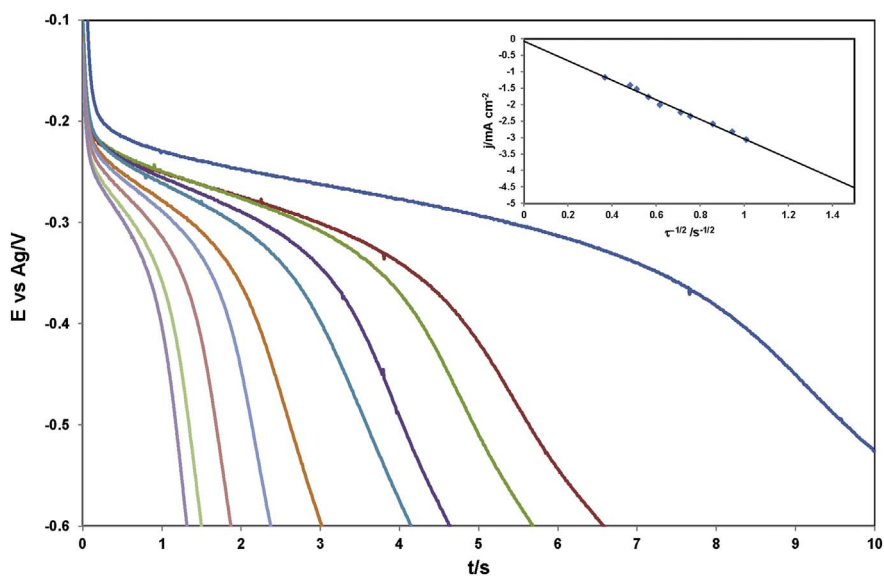

Fig. 10. Chronopotentiograms for the electroreduction of $EuCl_6^{3-}$ in the C_2mimCl ($C_0 = 5,58 \times 10^{-5}$ mol cm^{-3}) on a glassy carbon electrode at 363 K: applied current density ranging from -1.2 to -3.1 mA cm^{-2}.

densities when the concentration of $EuCl_6^{3-}$ in solution and the temperature of the system were kept constant. After every run the electrode and solution were summited to the same protocol described in the chronoamperometric experiments. The square root of the transition time changed linearly with the applied current density, and the diffusion coefficients was calculated by Eq. (10).

Table 1 summarizes the calculated values of the diffusion coefficient obtained by using the above electrochemical techniques. The effect of the viscosity on $EuCl_6^{3-}$ diffusion coefficients has been taken into account. As the viscosity is an intrinsic property of the solvent and the diffusion coefficient depends on the solute, the dimensionless Schmidt number that combine this two properties ($Sc = \nu/D$) was also used to characterise the solute global mass transport through its environment [36–37]. Kinematic viscosities $\nu/m^2 s^{-1}$ defined as the ratio between dynamic viscosity $\eta/kg\ m^{-1} s^{-1}$ and density $\rho/kg\ m^{-3}$ were calculated from [36,38–40] and are summarized as well in Table 1.

In order to know if there are significant differences between: i) the calculated data of the diffusion coefficients using different electrochemical techniques, and ii) the calculated data at different temperatures, a two-way (temperature - technique) analysis of variance (ANOVA) [41] was carried out. The null hypothesis was the non-existence of significant differences between the calculated units. Concerning the temperature effect, the calculated F statistics were higher than the critical F value, ($F_{cal} = 163.99 > F_{crit.} = 4.76$ in C_2mimCl and $F_{cal} = 103.41 > F_{crit.} = 4.46$ in C_4mimCl) therefore the null hypothesis must be rejected, whereas for the effect of electrochemical techniques, the calculated F statistics was lower than the critical F value ($F_{cal} = 4.72 < F_{crit.} = 5.14$ in C_2mimCl and $F_{cal} = 3.19 < F_{crit.} = 3,84$ in C_4mimCl), then the null hypothesis must be maintained, and it can be concluded that with a 95% confidence level: i) all the methods used to calculate the diffusion coefficients lead to the same values, and ii) the diffusion coefficients change with temperature, and can be related to the activation energy for diffusion, based on the Arrhenius equations:

$$C_4mimCl: logD = -0.57(\pm 0.35) - \frac{2107 \pm 135}{T} \tag{11}$$

$$C_4mimCl: logD = 1.82(\pm 0.28) - \frac{3142 \pm 99}{T} \tag{12}$$

Being the activation energy for the diffusion 40.4 ± 2.6 in C_2mimCl and $60.2 \pm 1.8\ kJ\ mol^{-1}$ in C_4mimCl.

3.3. Evaluation of the kinetic parameters relative to the reduction of Eu(III) at the glassy carbon electrode

As noted above, the electrochemical system $EuCl_6^{3-}/EuCl_6^{4-}$ is clearly quasi-reversible, being possible to obtain in practice the kinetic parameters of the one-electron transfer step (i.e. the intrinsic rate constant k^0 and the charge transfer coefficient, α,) by: i) simulation of the cyclic voltammograms and ii) from the analysis of the cyclic voltammograms and their convoluted curves.

3.3.1. Determination of the charge transfer kinetic parameters by simulation of the cyclic voltammograms

As pointed above the cyclic voltammograms were highly reproducible, therefore the information of interest (i.e. the charge-transfer rate constant, k^0, the transfer coefficient, α, as well as the reversible half-wave potential, $E_{1/2}$) can be extracted from them by comparison to simulated ones. The simulation was carried out using a simulation computer program (M271 COOL kinetic analysis software 1.10), that is based upon non-linear simplex optimization of the parameters in a normalized space derived from linear regression of the measured current on a calculated dimensionless current function [42–44]. Fig. 11 displays a representative example of these simulations, and the values of the obtained parameters are summarized in Table 2.

3.3.2. Determination of the charge transfer kinetic parameters from the analysis of the cyclic voltammograms and their convoluted curves

One application of semiintegration is the accurate determination of the Nernstian half-wave potential from a cyclic voltammogram [35]. As it is shown in Fig. 7, the cyclic voltammogram display a null potential E_n where the current trace crosses the axis. At this moment, the Nernst equation holds because there is no kinetic polarization, even though the behaviour need not be reversible elsewhere. Hence the semiintegral at this moment can provide access to $E_{1/2}$ through the equation:

$$E_{1/2}^{rev} = E_n - \frac{RT}{nF}Ln\left(\frac{m^*}{m_n} - 1\right) \tag{13}$$

where m_n is identified in Fig. 7.

By employing the semiintegral and the current in concert, it is possible to study the kinetics of the electrode reaction. In this way, Goto and Oldham [45] and Myland and Oldham [46] have derived linear plots of logarithmic functions of convoluted current as a function of E for a quasi-reversible process.
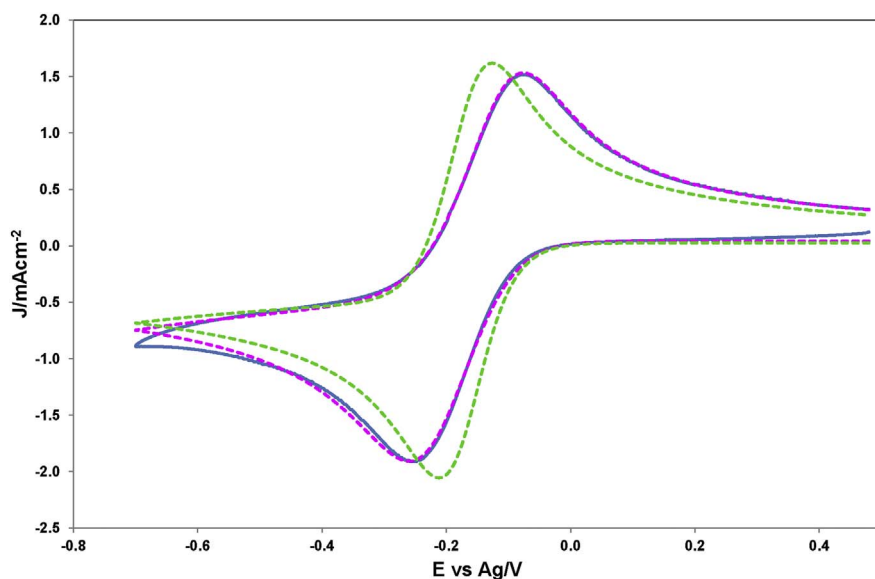

Fig. 11. Cyclic voltammograms of $EuCl_6^{3-}$ in C_2mimCl on a GC electrode. Blue line (——) experimental results obtained with compensation of the solution resistence ($C_0 = 5,58 \times 10^{-5}\ mol\ cm^{-3}$, working temperature 373 K scan rate 60 mV s^{-1}); dotted pink line (---) simulated results corresponding to a quasireversible process; dotted green line (- - -) simulated results corresponding to a reversible process. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Kinetic parameters of $EuCl_6^{3-}/EuCl_6^{2-}$ exchange in C_4mimCl and C_2mimCl.

	Technique	T/K	$E_{1/2}$ vs (AgCl(sat)│Ag)/V	α	$Logk^0/cm\,s^{-1}$
C_4mimCl	CV (kinetic analysis sofware	343	-0.859 ± 0.004	0.45 ± 0.01	-4.27 ± 0.03
		353	-0.862 ± 0.003	0.45 ± 0.01	-4.06 ± 0.02
		363	-0.860 ± 0.002	0.44 ± 0.01	-3.65 ± 0.01
	CV + CPSV	343	-0.867 ± 0.05	0.44 ± 0.02	-4.5 ± 0.04
		353	-0.867 ± 0.004	0.46 ± 0.02	-3.82 ± 0.06
		363	-0.865 ± 0.005	0.44 ± 0.04	-3.70 ± 0.13
	Technique	T/K	$E_{1/2}$ vs Ag/V	α	$Logk^0/cm\,s^{-1}$
C_2mimCl	CV (kinetic analysis sofware)	363	-0.173 ± 0.007	0.47 ± 0.01	-3.53 ± 0.01
		376	-0.161 ± 0.004	0.46 ± 0.01	-3.35 ± 0.01
		387	-0.165 ± 0.001	0.44 ± 0.01	-3.20 ± 0.01
		398	-0.160 ± 0.004	0.41 ± 0.01	-3.07 ± 0.01
	CV + CPSV	363	-0.174 ± 0.003	0.46 ± 0.05	-3.50 ± 0.16
		376	-0.160 ± 0.007	0.46 ± 0.04	-3.39 ± 0.12
		387	-0.156 ± 0.001	0.51 ± 0.03	-3.40 ± 0.23
		398	-0.157 ± 0.001	0.49 ± 0.06	-3.26 ± 0.18

The derived equation for a quasi-reversible reduction process is [45]:

$$E = E_{1/2}^r + \frac{2.3RT}{\alpha F} log \frac{k^0}{D^{1/2}} + \frac{2.3RT}{\alpha F} logB' \qquad (14)$$

where

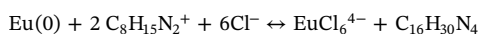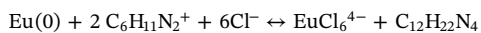$$B' = \left[\frac{m^* - m - m\ exp\left\{\frac{F}{RT}(E - E_{1/2}^r)\right\}}{I} \right] \qquad (15)$$

m is the convoluted current, m* its limiting value and I the intensity in the cyclic voltammograms. An example of the logarithmic analysis is shown in Fig. 7.

The average values of k^0 and α obtained from the plots of the potential versus the logarithmic function of convoluted current, using the diffusion coefficients values obtained before, are summarized in Table 2, being possible to see the agreement between the different calculating methods employed. According to Matsuda and Ayabe's criteria [47], the electron transfer $EuCl_6^{3-}/EuCl_6^{4-}$ can be qualified as quasi-reversible in both media on a GC electrode at the studied temperatures.

4. Conclusions

Electrochemical behaviour of Eu(III) has been studied in two alkylimidazolium chloride ionic liquids the C_2mimCl and C_4mimCl over the temperature ranges 363–398 K and 343–363 K respectively using a glassy carbon electrode. The electrochemical windows of both ionic liquids on a glassy carbon electrode are limited anodically by the oxidation of Cl^- ions into Cl_2 and cathodically by the reduction of the respective imidazolium cation.

The electroreduction of $EuCl_6^{3-}$, who is stable in both chlorobasic ionic liquids, takes place in a single electron-transfer step $EuCl_6^{3-}/EuCl_6^{4-}$. The reduction of the imidazolium cation, hinders the reduction of $EuCl_6^{4-}$ to Eu(0), therefore the $EuCl_6^{4-}/Eu(0)$ couple is more negative in potential than those corresponding to the reduction of the respective imidazolium cation. Being not conceivable the electroextraction of metallic europium from the ILs on a GC electrode. As a result, Eu metal in contact with the IL could react with the imidazolium cation to give $EuCl_6^{4-}$ and the corresponding imidazolium radical according to the following chemical reaction, in which it has been assumed that the formed radicals undergo the formation of a dimer (i.e. coupling of two radicals):

$Eu(0) + 2\ C_6H_{11}N_2^+ + 6Cl^- \leftrightarrow EuCl_6^{4-} + C_{12}H_{22}N_4$

$Eu(0) + 2\ C_8H_{15}N_2^+ + 6Cl^- \leftrightarrow EuCl_6^{4-} + C_{16}H_{30}N_4$

The applicability of several electrochemical techniques (CV, CPSV, SV, CP and CA) for accuracy measurements of the diffusion coefficient of $EuCl_6^{3-}$ in both media was investigated, and a method to improve the accuracy of the measurements has been established. The method consist of renewing the electrode/electrolyte interface, optimizing experimental parameters to ensure the validity of the assumptions used in the analysis. A two-way analysis of variance (ANOVA) showed that with a 95% confidence level: i) all the electrochemical techniques used to calculate the diffusion coefficients lead to the same values, and ii) the diffusion coefficients change with temperature. The validity of the Arrhenius law was verified, being the activation energy for diffusion of $EuCl_6^{3-}$ 40.4 ± 2.6 and $60.2 \pm 1.8\ kJ\ mol^{-1}$ in C_2mimCl and C_4mimCl respectively.

The results pointed out the effect of the solvent viscosity on the diffusion coefficient of $EuCl_6^{3-}$. A viscosity increase leads to a more difficult solute mass transport. The dimensionless Schmidt numbers, $(Sc = \nu/D)$, have also been calculated in order to characterise the solute global mass transport through its environment. The Sc variation with temperature is greater than those of the diffusion coefficient and kinematic viscosity. At a given temperature, the Sc number and the kinematic viscosity are higher in C_4mimCl than in C_2mimCl, whereas the diffusion coefficient is smaller in C_4mimCl than in C_2mimCl.

On a GC electrode, the electrochemical electron-transfer $EuCl_6^{3-}/EuCl_6^{4-}$ is a quasi-reversible process. The intrinsic rate constant of charge transfer, k^0, and the charge transfer coefficient, α, have been calculated for the first time in the mentioned ionic liquids, by simulation of the cyclic voltammograms, and from the logarithmic analysis of the cyclic voltammograms and their convoluted curves.

Taken into account that: i) the width of the electrochemical window of the C_2mimCl and C_4mimCl is relatively narrow compared to those of other ionic liquids, because oxidation of the chloride anions establishes the positive limit, and ii) coordination by the anionic hard ligand chloride, significantly stabilizes the $EuCl_6^{3-}$ (in general Ln^{3+} species, as the octahedral $[LnCl_6]^{3-}$ complexes), shifting its reduction potential to cathodic values. Neither C_2mimCl nor C_4mimCl ILs are appropriates for the electroextraction of Eu metal and in general Ln metals in pyrochemical processes.

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