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Electrochemical and thermodynamic properties of europium(III), samarium(III) and cerium(III) in 1-butyl-3-methylimidazolium chloride ionic liquid

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ABSTRACT

Electrochemical behavior of trivalent lanthanides such as europium(III), samarium(III) and cerium(III) in 1-butyl-3-methylimidazolium chloride (bmimCl) was investigated by cyclic voltammetry and chronopotentiometry at platinum working electrode in the temperature range of 343–373 K. The cyclic voltammograms of these metal ions in bmimCl at Pt electrode consisted of quasi-reversible waves occurring at a cathodic peak potential of −0.769 V, −0.547 V and −0.558 V (vs. Pd, 373 K) were attributed to the reduction of Eu(III), Sm(III) and Ce(III) to their respective divalent states. A prewave observed in the cyclic voltammogram of Eu(III) represents the reduction of Eu(III) to Eu(II) adsorbed on Pt electrode. The diffusion coefficients of these trivalents in bmimCl were determined to be of the order of $\sim 10^{-8}$ cm^2 s^{-1} by cyclic voltammetry and chronopotentiometry and the charge transfer rate constants (k_s) were determined to be of the order of $\sim 10^{-5}$ cm s^{-1} by Nicholson method. The apparent standard potentials, E^{0^*} (vs. Cl_2/Cl^-), and some thermodynamic properties of reaction of $LnCl_3$ from $LnCl_2$ were determined and the results are reported in this paper.

1. Introduction

Room temperature ionic liquids (RTILs) are finding several applications in various stages of nuclear fuel cycle. RTILs are the compounds comprising completely of ions existing in liquid state at or below the boiling point of water i.e., 373 K [1,2]. They have several attractive properties suitable for aqueous and non-aqueous reprocessing applications. RTILs are being evaluated as an alternative to the conventional diluent, n-dodecane, in aqueous reprocessing and as a substitute to the traditional high-temperature molten salts in non-aqueous reprocessing of spent nuclear fuels [3–9].

RTILs offer wide electrochemical window. From non-aqueous reprocessing point of view, Bhatt et al. [10–12] studied the electrochemical behavior of some lanthanides, La(III), Sm(III) and Eu(III) in tetra alkyl ammonium bis(trifluoromethylsulfonyl)imide ($[R_4X][NTf_2]$) ionic liquids, where X = N,P and As. The ionic liquid, tetra alkyl ammonium bis(trifluoromethylsulfonyl)imide ($[Me_4X][NTf_2]$), exhibits large electrochemical window (>5 V) and based on the observation that Eu(III) present in this ionic liquid was reduced to Eu(0), it was proposed as a substitute for high-temperature molten salts in non-aqueous reprocessing. Bhatt et al. [12] also studied the reduction of La(III), Sm(III) and Eu(III) to metallic state in the RTIL, tri methyl butyl ammonium bis(trifluoromethylsulfonyl)imide$[Me_3NBu][NTf_2]$, and reported similar results as in the previous case. Legeai et al. [13] reported the electrodeposition of lanthanum in 1-octyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ionic liquid. Nagaishi et al. [14] studied the physicochemical behavior, spectroscopic and electrochemical properties of Eu(III) as a function of water in N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)imide ($demmaNTf_2$) and $bmimNTf_2$ ionic liquids. Yamagata et al. [15] studied the electrochemical behavior of samarium, europium and ytterbium in N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ($BMPyNTf_2$), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($emimNTf_2$). We also investigated [16] the suitability of $BMPyNTf_2$ ionic liquid for the electrodeposition of lanthanides and studied the electrochemical behavior of europium(III) in the $BMPyNTf_2$ at various temperatures. It was found that Eu(III) underwent a single step quasi-reversible one-electron transfer to Eu(II) followed by a two-electron irreversible reduction to metallic europium at glassy carbon and stainless steel electrodes.

Lin and Hussey [17] studied the electrochemical and spectroscopic properties of cerium(III) in the basic $AlCl_3$-1-methyl-3-ethylimidazolium chloride and reported a quasi-reversible reduction of Ce(IV) to Ce(III) at glassy carbon, Pt and W electrodes. Schoebrechts et al. [18,19] studied the electrochemical behavior of some trivalent lanthanides ions such as Sm(III), Eu(III), Tm(III) and Yb(III) dissolved in acidic $AlCl_3$-butylpyridinium chloride and reported that they were reduced to the corresponding divalent ions at the working electrode. However, the electrochemical behavior of Eu(III), Sm(III) and Ce(III) in 1-butyl-3-methylimidazolium chloride ionic liquid have not been reported so far. The formal potential of

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$E^{0^*}_{\mathrm{Ln(III)/Ln(II)}}$ (Ln = Eu, Sm and Ce) and thermodynamic properties such as Gibbs energy and enthalpy change accompanied by reduction are not available in literature. Moreover, these lanthanides are produced in significant quantities by fission of U-235 and Pu-239. It is indeed desirable to determine the thermodynamic properties of these fission products in ionic liquid media, which are proposed as substitutes to high-temperature molten salts in non-aqueous reprocessing. Thus the objective of the present paper is to determine the formal potentials of lanthanide redox couples $\mathrm{Ln(III)} \Longleftrightarrow \mathrm{Ln(II)}$, where Ln is Eu, Sm and Ce, by transient electrochemical techniques and determine the thermodynamic values accompanying the reduction in bmimCl ionic liquid. The diffusion coefficients of trivalent lanthanides and kinetics of charge transfer at electrode–electrolyte interphase were determined and are reported in this paper.

2. Experimental

2.1. Chemicals

All the chemicals used in this study were of analytical grade. 1-Methyl imidazole and 1-chlorobutane were procured from Fluka and Lancaster. Europium(III) Chloride, Samarium(III) Chloride and Cerium(III) Chloride were purchased from M/s. Alfa Aesar. The ionic liquid 1-butyl-3-methylimidazolium chloride (bmimCl) was synthesized as described elsewhere [3].

2.2. Voltammetric studies

Voltammetric studies were carried out in the temperature range 343–373 K. A Platinum rod (cylindrical SA = 0.082 cm^2) was used as the working electrode. A glassy carbon rod and Pd wire acted as the counter and quasi-reference electrodes, respectively. The electrochemical cell had a single leak-tight compartment and all the electrodes were placed in the same compartment. The cell was kept under argon atmosphere during entire study. IR compensation was employed in all the voltammetric measurements. Cyclic voltammograms of the solutions were recorded using Autolab (PGSTAT-030) equipped with an IF 030 interface.

3. Results and discussion

3.1. Cyclic voltammetry

The cyclic voltammograms of a solution of 50 mM Ln(III) (Ln = Eu, Sm, Ce) in bmimCl recorded at platinum working electrode at various temperatures are shown in Fig. 1. It consists (Fig. 1A) of a cathodic wave occurring at a peak potential of −0.769 V, −0.547 V and −0.558 V (vs. Pd) at 373 K are due to the reductions of Ln(III) to Ln(II) (Ln = Eu, Sm and Ce respectively). A prewave is observed in the cathodic scan of Eu(III) in bmimCl. This could be due to the reduction of Eu(III) to Eu(II)$_{\mathrm{ads}}$, which is adsorbed on platinum electrode. A postwave is also seen at higher anodic potentials upon scan reversal. Fig. 2 shows the cyclic

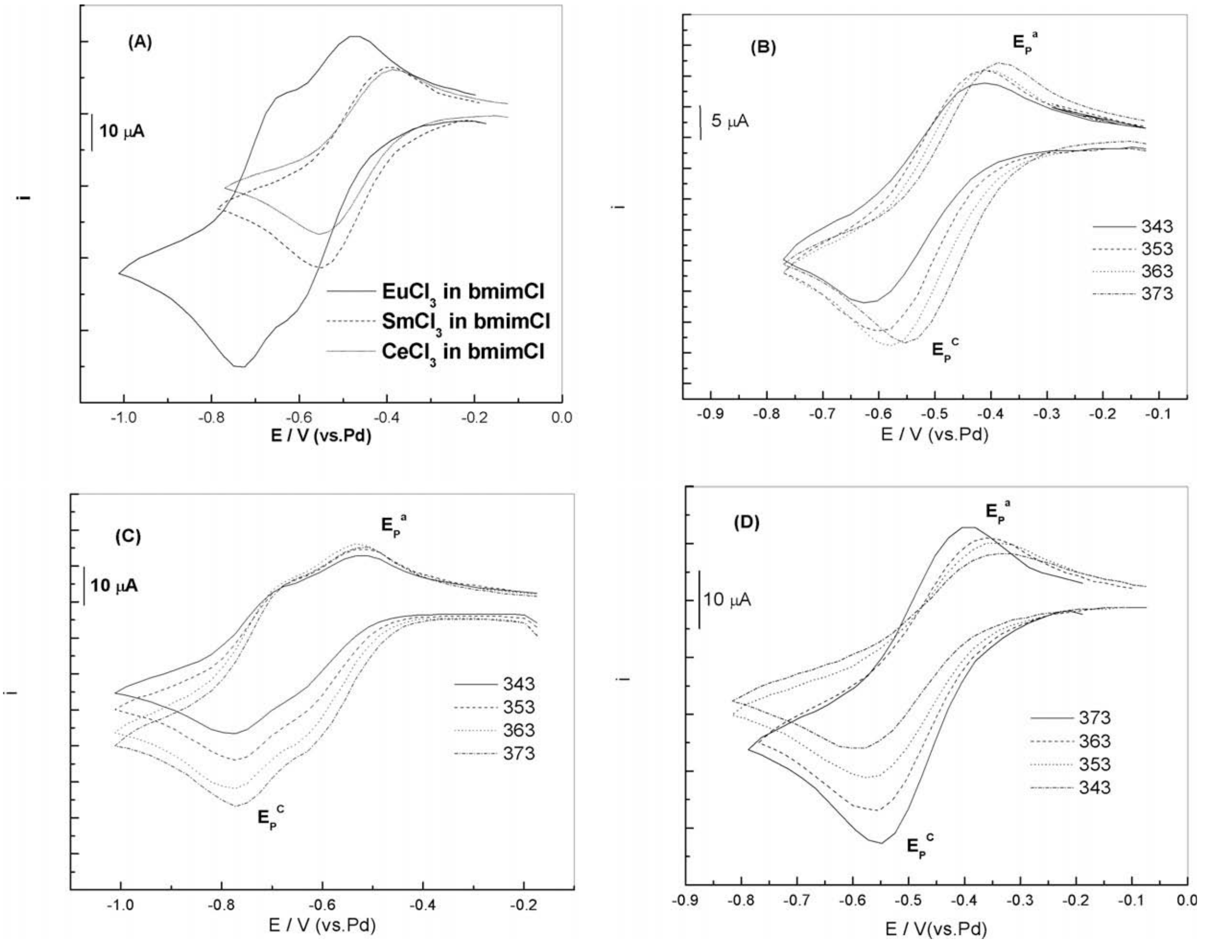

Fig. 1. Cyclic voltammograms of Ln(III) in bmimCl recorded at Pt electrode at various temperatures. (A) Cyclic voltammogram of Eu(III), Ce(III) and Sm(III) in bmimCl at 373 K, (B) cyclic voltammogram of Ce(III) in bmimCl at various temperatures, (C) cyclic voltammogram of Eu(III) in bmimCl at various temperatures, (D) cyclic voltammogram of Sm(III) in bmimCl at various temperatures.

voltammogram of Eu(III) in bmimCl as a function of bulk europium concentration. As expected a prewave and a postwave are seen at all the concentrations. The peak currents arising from the prewave and postwave are represented as $(i_p^c)_{\text{ads}}$ and $(i_p^a)_{\text{ads}}$ respectively. It is observed that the diffusion peak current, $(i_p^c)_{\text{diff}}$, increases with increase in the concentration of europium, while the adsorption peak current, $(i_p^c)_{\text{ads}}$, remains almost constant. Therefore the quotient, $(i_p^c)_{\text{diff}}/(i_p^c)_{\text{ads}}$ (ρ) when plotted against $\sqrt{v}/C_o^*$, where v and C_o^* are the scan rate and bulk concentration respectively, shown in Fig. 3, results in a straight line as expected by theory of strong adsorption of product onto the electrode by stationary electrode voltammetry [20]. The results thus indicate that Eu(III) undergoes a one-step single electron transfer reduction to $\text{Eu(II)}_{\text{ads}}$ adsorbed on platinum electrode at −0.61 V (vs. Pd).

3.2. Diffusion coefficients of Eu(III), Sm(III) and Ce(III) in bmimCl

The cathodic (E_p^c) and anodic peak (E_p^a) potentials of Eu(III), Sm(III) and Ce(III) in bmimCl obtained from Fig. 1 and the average of cathodic and anodic peak potential, $(E_p^c + E_p^a)/2$, are shown in Table 1. It is observed that the cathodic and anodic peak potentials are shifted and the average increases with increase of temperature. In all cases the magnitude $|E_p^c - E_{p/2}^c|$ is marginally larger than the value required for a reversible process (70 mV at 373 K) indicating that the reduction of these trivalents in bmimCl at platinum electrode are not reversible [21,22]. Moreover, the cathodic and anodic peak potentials are shifted marginally with increase of scan rate. A similar behavior is also observed at all the temperature ranges investigated in the present study. All these observations indicate that reduction of Eu(III), Sm(III), Ce(III) in bmimCl at platinum electrode are quasi-reversible and the reduction is not only controlled by diffusion but also by charge transfer kinetics. A relation between the cathodic diffusion peak current, $(i_p^c)_{\text{diff}}$, as a function of scan rate for a soluble–soluble irreversible systems (also applicable for quasi-reversible cases [21]) is given by Eq. (1):

$$(i_p^c)_{\text{diff}} = 0.496\, nFAC_o^* \sqrt{D_o} \sqrt{\left(\frac{\alpha n_\alpha F v}{RT}\right)}, \tag{1}$$

where A is the electrode area in cm^2 (0.082), C_o^* is the Ln(III) concentration in mol cm^{-3} (~50 mM), D_o is the diffusion coefficient in cm^2 s^{-1}, F is the Faraday constant, n is the number of exchanged electrons, v is the potential sweep rate in V s^{-1}, α is the charge transfer coefficient, n_α is the number of electrons transferred in the rate determining step and T is the absolute temperature in K. The value of αn_α can be determined from Eq. (2). From the slope of the straight lines, obtained from the plot of $(i_p^c)_{\text{diff}}$ against $\sqrt{v}$, the diffusion coefficients (D_o) of Eu(III), Sm(III) and Ce(III) were determined and the values are given in Table 2. It is observed that the diffusion coefficients increase with increase of temperature. Moreover, the magnitude of D_o increases in the order Ce(III) < Sm(III) < Eu(III), which is, interestingly, the order of lanthanide contraction across the series. Thus the ion with smaller radii (Eu(III)) exhibits higher diffusion coefficient as compared to Sm(III) and Ce(III). The energy of activation (E_a) determined from the slope of $\ln D_o$ against $1/T$ plot, are also tabulated in Table 2. It is observed that E_a increases in the order Ce(III) < Sm(III) < Eu(III).

$$\left|E_p^c - E_{p/2}^c\right| = \frac{1.857RT}{\alpha n_\alpha F}, \tag{2}$$

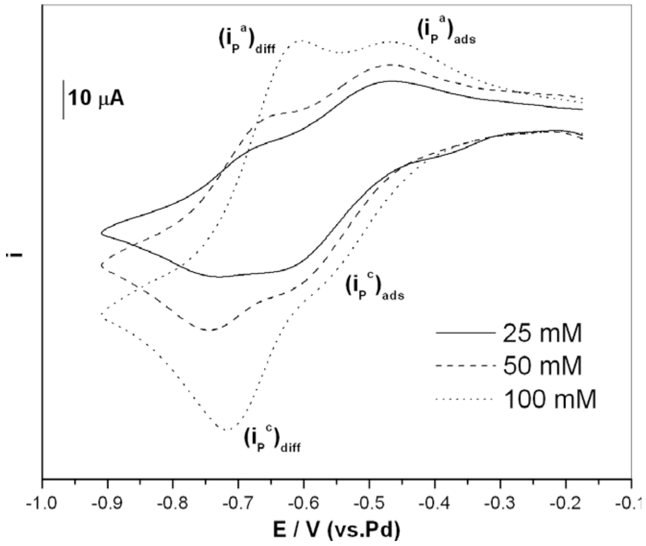

Fig. 2. Cyclic voltammograms of Eu(III) in bmimCl at 373 K at various concentrations of $EuCl_3$.

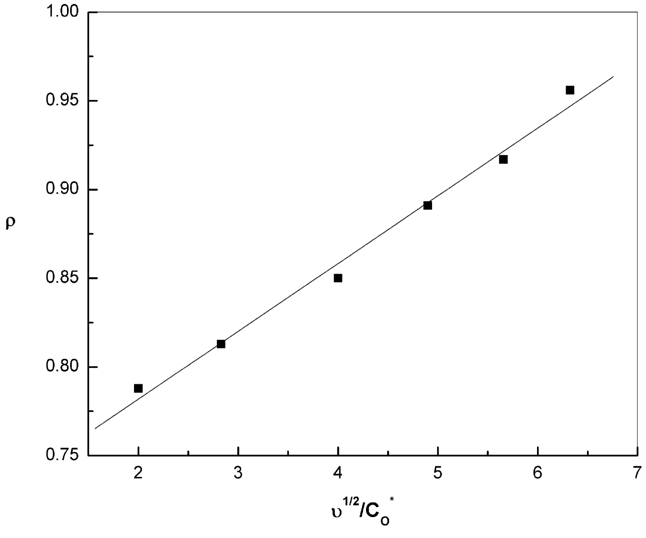

Fig. 3. Ratio of adsorption peak to diffusion peak (ρ) as a function of $v^{1/2}/C_o^*$.

3.3. Quasi-reversibility of Eu(III), Sm(III) and Ce(III) reduction

Since the reduction of trivalent lanthanides is not only controlled by diffusion but also charge transfer kinetics, as discussed above, the rate constant for the charge transfer reaction, k_s, cm s^{-1}, can be determined using Eq. (3) [22].

Table 1
The peak potentials E_p^c and E_p^a and the formal potentials for the reduction of Ce(III), Sm(III) and Eu(III) in bmimCl at Pt working electrode at various temperatures.

Metal ion	T/K	E_p^c/V	E_p^a/V	$((E_p^{c1} + E_p^{a1})/2)$/V
Ce(III)	343	−0.603	−0.435	−0.519
	353	−0.579	−0.426	−0.503
	363	−0.568	−0.421	−0.495
	373	−0.558	−0.411	−0.485
Sm(III)	343	−0.601	−0.365	−0.483
	353	−0.581	−0.376	−0.479
	363	−0.571	−0.380	−0.476
	373	−0.547	−0.401	−0.474
Eu(III)	343	−0.788	−0.520	−0.654
	353	−0.782	−0.515	−0.649
	363	−0.778	−0.509	−0.644
	373	−0.769	−0.485	−0.627

Table 2
Diffusion coefficient of Ce(III), Sm(III) and Eu(III) and charge transfer rate constant (k_s) for the reduction of trivalents in bmimCl medium at platinum electrode at various temperatures.

Metal ion	T/K	$D_o \times 10^8$/cm^2 s^{-1} (CV)	E_a/kJ mol^{-1}	[a]$k_s \times 10^5$/cm s^{-1}
Ce(III)	343	1.79	18.07	1.47
	353	2.72		1.50
	363	2.84		3.23
	373	3.09		3.35
Sm(III)	343	3.17	36.43	1.71
	353	4.62		1.91
	363	7.63		2.72
	373	8.36		4.04
Eu(III)	343	4.87	54.49	5.86
	353	6.91		6.68
	363	11.0		9.83
	373	23.2		13.3

[a] k_s was determined using Eq. (3).

$$k_s = 2.18\left[D_o(\alpha n_\alpha)\frac{\nu F}{RT}\right]^{1/2} \quad \exp\left[\frac{\alpha^2 nF}{RT}\left(E_p^c - E_p^a\right)\right], \qquad (3)$$

The electrode reaction can be classified [21] as, reversible when $k_s \geqslant 0.3\ \nu^{1/2}$ cm s^{-1}, quasi-reversible when $0.3\ \nu^{1/2} \geqslant k_s \geqslant 2 \times 10^{-5}\ \nu^{1/2}$ cm s^{-1} and irreversible when $k_s \leqslant 2 \times 10^{-5}\ \nu^{1/2}$ cm s^{-1} determined using Eq. (3). The k_s values for the reduction of Eu(III), Sm(III) and Ce(III) in bmimCl at different temperatures are shown in Table 2 (scan rate 0.01 V s^{-1}). The magnitude of k_s indicate that the reduction of Ln(III) to Ln(II) (Ln = Eu, Sm and Ce) in bmimCl is quasi-reversible. It is observed that the value of k_s increases with increase of temperature. This could perhaps be due to the facilitated electron transfer at electrode–electrolyte interphase at higher temperatures.

Table 3
The rate constant k_s determined by Nicholson method for the reduction of Ce(III), Sm(III) and Eu(III) in bmimCl at Pt electrode at various temperatures. Scan rate 0.010 V s^{-1}.

Metal ion	T/K	ΔE_p^T/V	ΔE_p^{298}/V	Ψ_{298}	Ψ_T	$k_s \times 10^5$/cm s^{-1}
Ce(III)	343	0.168	0.146	0.251	0.297	3.39
	353	0.153	0.129	0.302	0.358	4.95
	363	0.147	0.121	0.350	0.426	7.79
	373	0.140	0.112	0.416	0.521	11.9
Sm(III)	343	0.236	0.205	0.114	0.131	1.82
	353	0.205	0.173	0.180	0.213	4.03
	363	0.191	0.157	0.253	0.308	6.33
	373	0.146	0.117	0.459	0.575	12.1
Eu(III)	343	0.268	0.233	–[b]	–	–
	353	0.267	0.225	–	–	–
	363	0.269	0.221	–	–	–
	373	0.284	0.227	–	–	–

[b] Could not be determined as the magnitude of ΔE_p^{298} obtained is beyond the range of Nicholson working curve.

Alternatively, the charge transfer rate constant k_s can also be determined by the method of Nicholson [23], which is widely used for quasi-reversible cases. According to Nicholson the function Ψ is

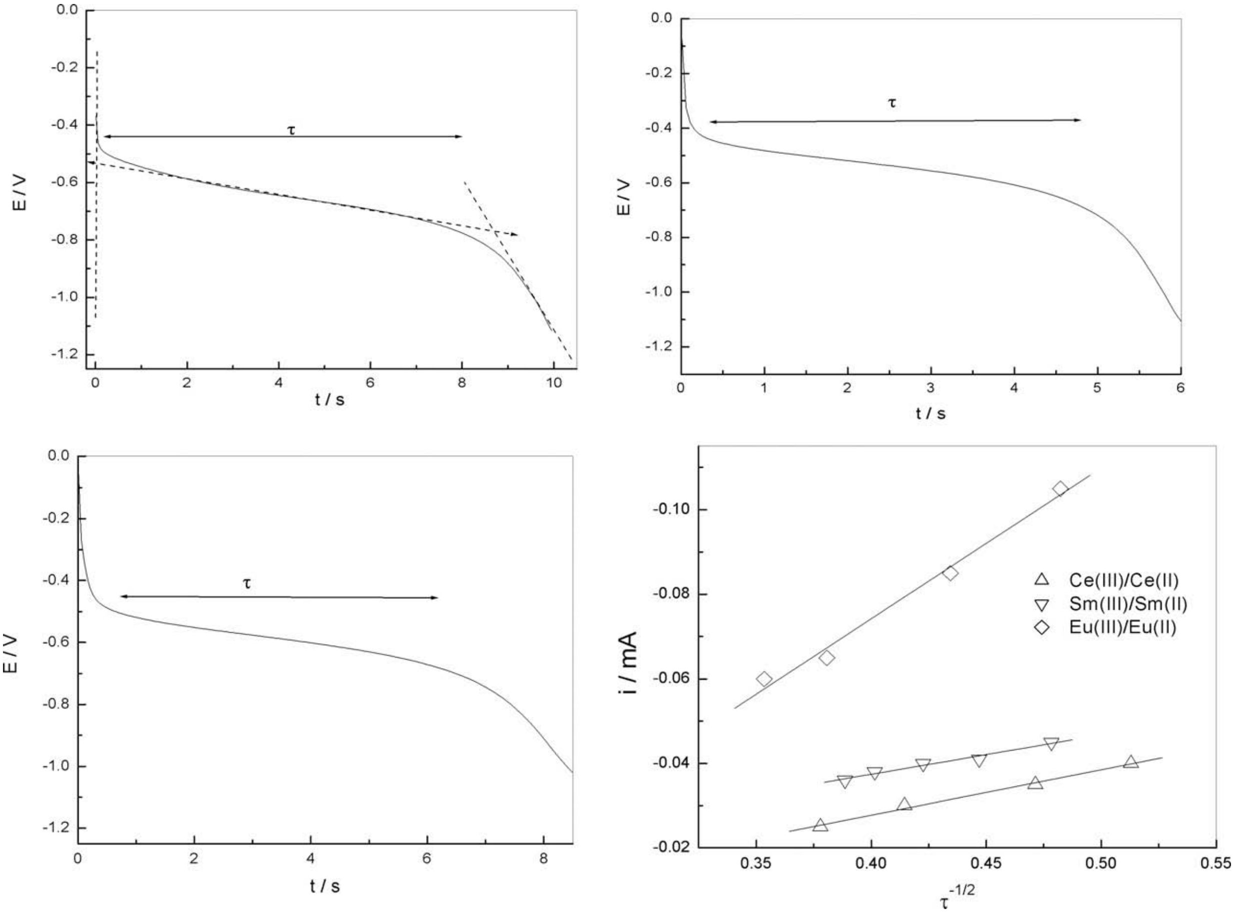

Fig. 4. Chronopotentiograms of Ln(III) in bmimCl at Pt electrode at 373 K. (A) Chronopotentiogram of Eu^{3+} in bmimCl at 373 K at Pt working electrode at applied constant current -1.0×10^{-4} A, (B) chronopotentiogram of Sm^{3+} in bmimCl at 373 K at Pt working electrode at applied constant current -7.4×10^{-5} A, (C) chronopotentiogram of Ce^{3+} in bmimCl at 373 K at Pt working electrode at applied constant current -7.0×10^{-5} A, (D) plot of i against $\tau^{-1/2}$ at 373 K.

related to the rate constant k_s by Eq. (4) and Ψ is also related to the peak potential separation $\Delta E_p^T(E_p^a - E_p^c)$.

$$\Psi = \frac{k_s\left(\frac{D_o}{D_R}\right)^{\alpha/2}}{[\pi D_o(nF/RT)v]^{1/2}}, \tag{4}$$

The values of Ψ at various magnitudes of ΔE_p are reported in a Nicholson working curve [23] at 298 K. However, the present data are generated in the temperature range of 343–373 K. Therefore, it requires the conversion of peak separation potentials ΔE_p^T to 298 K (ΔE_p^{298}) for obtaining the value of Ψ. This can be achieved by Eqs. (5) and (6), according to the procedure described elsewhere [24–26].

$$\Delta E_p^{298} = \Delta E_p^T\left(\frac{298}{T}\right), \tag{5}$$

$$\Psi_T = \Psi_{298}\left(\frac{T}{298}\right)^{1/2}, \tag{6}$$

The calculated values of ΔE_p^{298} at various temperatures are shown in Table 3. Assuming $D_o = D_R$ and from the Nicholson working curve [23] and Eqs. (4)–(6), the parameters Ψ and k_s were determined. The values of k_s, tabulated in Table 3, fall in the range $0.3\ \nu^{1/2} \geqslant k_s \geqslant 2 \times 10^{-5}\ \nu^{1/2}\ \mathrm{cm\ s^{-1}}$ confirms that reductions of Ln(III) in bmimCl are quasi-reversible. It is seen that k_s values increase with increase of temperature.

3.4. Chronopotentiometry

Chronopotentiometry is used to study the electrochemical behavior of Eu(III), Sm(III) and Ce(III) in bmimCl at various temperatures at Pt working electrode. The chronopotentiograms recorded at various applied constant currents of Eu(III), Sm(III) and Ce(III), are shown in Fig. 4. The transient time (τ) shown in chronopotentiogram is a measure of time elapsed between the commencement of constant potential and the time at which the concentration of electroactive species, resulting from diffusion, reaches zero at the electrode. A relation between the applied current and transition time is given by Sand's equation (Eq. (7)) [21,22].

$$i\tau^{1/2} = \frac{nFA(D_o\pi)^{1/2}C_o^*}{2}, \tag{7}$$

The product $i\tau^{1/2}$ was constant and the plot of i against $\tau^{-1/2}$ is linear (Fig. 4). This confirms the validity of Sand's equation and enables the determination of diffusion coefficient by using Eq. (7). The D_o values obtained in a temperature range of 343–373 K are tabulated in Table 4, which are in good agreement with the values of diffusion coefficients obtained by cyclic voltammetry.

Table 4
Chronopotentiometric constant ($i\tau^{1/2}$) and diffusion coefficient of Ce(III), Sm(III) and Eu(III) obtained from chronopotentiograms at different temperatures.

Metal ion	T/K	τ/s	$i\tau^{1/2} \times 10^5$	Diffusion coefficient, $D_o \times 10^8/\mathrm{cm^2\ s^{-1}}$
Ce(III)	343	4.78	−4.37	1.65
	353	4.34	−5.00	2.16
	363	4.88	−5.52	2.62
	373	5.82	−7.24	4.51
Sm(III)	343	2.45	−7.83	5.27
	353	2.64	−8.12	5.68
	363	3.10	−8.45	6.15
	373	4.37	−9.41	7.62
Eu(III)	343	4.73	−9.78	4.36
	353	4.50	−10.6	5.12
	363	3.93	−16.9	12.9
	373	3.34	−21.9	21.9

3.5. Determination of Gibbs energy change

The trivalent lanthanides in bmimCl undergo reduction according to Eq. (8):

$$2\mathrm{LnCl_3} \Longleftrightarrow 2\mathrm{LnCl_2} + \mathrm{Cl_2} \tag{8}$$

The cathodic and anodic peak potentials are related to the apparent standard potential, $E^{0^*}_{\mathrm{Ln(III)/Ln(II)}}$, by the following expressions:

$$E_p^c = E^{0^*}_{\mathrm{Ln(III)/Ln(II)}} - 1.11\frac{RT}{nF} - \frac{RT}{nF}\ln\left(\frac{\sqrt{D_{\mathrm{Ln(III)}}}}{\sqrt{D_{\mathrm{Ln(II)}}}}\right), \tag{9}$$

$$E_p^a = E^{0^*}_{\mathrm{Ln(III)/Ln(II)}} + 1.11\frac{RT}{nF} - \frac{RT}{nF}\ln\left(\frac{\sqrt{D_{\mathrm{Ln(III)}}}}{\sqrt{D_{\mathrm{Ln(II)}}}}\right), \tag{10}$$

where

$$E^{0^*}_{\mathrm{Ln(III)/Ln(II)}} = E^{0}_{\mathrm{Ln(III)/Ln(II)}} + \frac{RT}{nF}\ln\left(\frac{\gamma_{\mathrm{Ln(III)}}}{\gamma_{\mathrm{Ln(II)}}}\right), \tag{11}$$

where $E^{0}_{\mathrm{Ln(III)/Ln(II)}}$ and γ represent standard potential and activity coefficient. Since the reduction reaction involves a single electron transfer ($n = 1$), the apparent standard potential, $E^{0^*}_{\mathrm{Ln(III)/Ln(II)}}$, determined using Eq. (12) is plotted against T in Fig. 5. It is observed that $E^{0^*}_{\mathrm{Ln(III)/Ln(II)}}$ increases with increase of T.

$$E^{0^*}_{\mathrm{Ln(III)/Ln(II)}} = \left(\frac{E_p^a + E_p^c}{2}\right) + \frac{RT}{F}\ln\left(\frac{\sqrt{D_{\mathrm{Ln(III)}}}}{\sqrt{D_{\mathrm{Ln(II)}}}}\right), \tag{12}$$

From linear regression of the experimental data, the $E^{0^*}_{\mathrm{Ln(III)/Ln(II)}}$ values are related to temperature by the following expressions:

$$E^{0^*}_{\mathrm{Ce(III)/Ce(II)}}(\mathrm{V}) = -1.752 + 1.26 \times 10^{-3}\ T(\mathrm{K}) \quad \mathrm{vs.} \quad (\mathrm{Cl_2/Cl^-}), \tag{13}$$

$$E^{0^*}_{\mathrm{Sm(III)/Sm(II)}}(\mathrm{V}) = -1.410 + 3.9 \times 10^{-4}\ T(\mathrm{K}) \quad \mathrm{vs.} \quad (\mathrm{Cl_2/Cl^-}), \tag{14}$$

$$E^{0^*}_{\mathrm{Eu(III)/Eu(II)}}(\mathrm{V}) = -1.762 + 9.0 \times 10^{-4}\ T(\mathrm{K}) \quad \mathrm{vs.} \quad (\mathrm{Cl_2/Cl^-}), \tag{15}$$

From these expressions, the standard Gibbs energy of the reaction $\mathrm{LnCl_2} + ½\mathrm{Cl_2} \rightarrow \mathrm{LnCl_3}$ can be determined by using Eq. (16), with the assumption that the solution is dilute and involvement of activity coefficients are negligible.

$$\Delta G^0_{\mathrm{LnCl_3}} = -nFE^{0^*}_{\mathrm{Ln(II)/Ln(III)}}, \tag{16}$$

where $E^{0^*}_{\mathrm{Ln(II)/Ln(III)}}$ apparent standard potential of oxidation of Ln(II) to Ln(III). The expressions for the standard Gibbs energy of the reaction, $\Delta G^0_{\mathrm{LnCl_3}}$, as a function of T as given below:

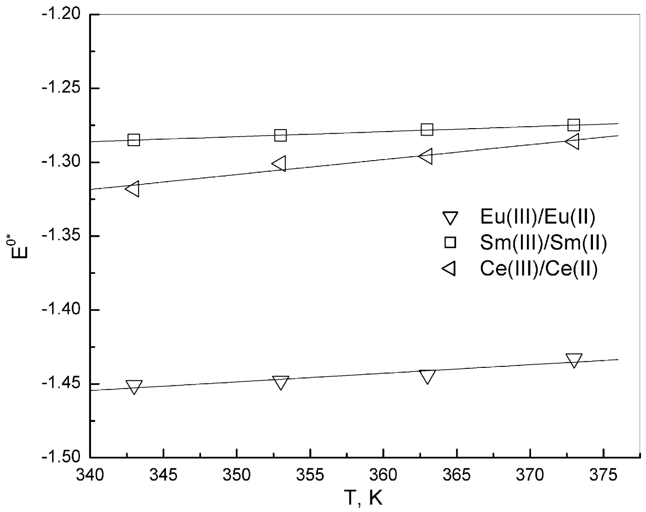

Fig. 5. Plot of E^{0^*} against T.

$$\Delta G^0_{SmCl_3}(\text{kJ mol}^{-1}) = -136.06 + 0.0376\,T(\text{K}), \tag{17}$$

$$\Delta G^0_{CeCl_3}(\text{kJ mol}^{-1}) = -169.07 + 0.1216\,T(\text{K}), \tag{18}$$

$$\Delta G^0_{EuCl_3}(\text{kJ mol}^{-1}) = -170.33 + 0.0868\,T(\text{K}), \tag{19}$$

The second terms on the right hand side of Eqs. (17)–(19) represent the standard entropy change ($\Delta S^0_{LnCl_3}$) for the reaction of $LnCl_2 + ½\,Cl_2 \rightarrow LnCl_3$. It is observed that $\Delta S^0_{LnCl_3}$ is negative indicating that the reaction involves decrease of entropy, as expected. Chlorine being a gas having higher disorder reacts with $LnCl_2$ leads to the formation of less disordered $LnCl_3$. However, it is difficult to understand the variations in entropy values (slopes) for the lanthanides investigated in the present study.

4. Conclusions

The electrochemical behavior of Eu(III), Sm(III) and Ce(III) in bmimCl at Pt working electrode at various temperatures was studied by cyclic voltammetry and chronopotentiometry. The trivalent samarium and cerium underwent a single step one-electron quasi-reversible transfer to divalent ion at platinum working electrode. However, europium(III) reduction resulted in the adsorption of the reduced product $Eu(II)_{ads}$ on platinum electrode. As a consequence, a prewave and post wave were observed in the cyclic voltammograms of Eu(III) in bmimCl. The diffusion coefficient and electron transfer rate constant for the reduction of Ln(III)–Ln(II) were determined to be of the order 10^{-8} cm^2 s^{-1} and 10^{-5} cm s^{-1} respectively at 343 K and their magnitudes increased with increase of temperature. The apparent standard potentials of $E^{0^*}_{Ln(III)/Ln(II)}$ were determined to be

$$E^{0^*}_{Ce(III)/Ce(II)}(\text{V}) = -1.752 + 1.26 \times 10^{-3}\,T(\text{K}) \quad \text{vs.} \quad (Cl_2/Cl^-),$$

$$E^{0^*}_{Sm(III)/Sm(II)}(\text{V}) = -1.410 + 3.9 \times 10^{-4}\,T(\text{K}) \quad \text{vs.} \quad (Cl_2/Cl^-),$$

$$E^{0^*}_{Eu(III)/Eu(II)}(\text{V}) = -1.762 + 9.0 \times 10^{-4}\,T(\text{K}) \quad \text{vs.} \quad (Cl_2/Cl^-),$$

and the Gibbs energy changes accompanied by the reaction were determined from apparent standard potentials.

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