

ELECTROCHEMICAL STUDY OF EUROPIUM TRICHLORIDE IN MOLTEN EUTECTIC LiCl-KCl

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Abstract

The present work is part of a research project that study the feasibility of the actinide separation from the rest of fission product contained in the nuclear spent fuel by pyrochemical processes with the aim of their transmutation. In order to design these processes it is necessary to determine basic thermodynamic data of the elements, especially actinides, in the molten salt, such as standard redox potential, standard free Gibbs energy of chloride formation, and activity coefficients of solvation. The electrochemical study of europium trichloride in molten eutectic LiCl-KCl has been performed at solid cathodes, vitreous carbon and tungsten, in a temperature range of 698-773K in order to obtain these basic properties. Here are presented some preliminary results obtained in this study, which indicate that Eu(III) is reduced to Eu(II) by a single step through a quasi-reversible reaction. The average diffusion coefficient of Eu(III) ions is $D \sim 1.3 \cdot 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ at 723 K.

Introduction

Partitioning and transmutation (P&T) concepts are being studied worldwide as they intend to reduce the inventories of actinides and long-lived fission products in nuclear waste with the aim of reducing its long-term radiotoxicity. At present, there is an increasing interest in the application of pyrochemical separation techniques in which the minor actinides are recycled and burned in dedicated reactors. The fact that the fuels proposed for such reactors will contain significant amounts of actinides, and will reach high burn-ups, makes the pyrochemical separation techniques quite attractive due to the high radiation stability of the salt solvent (chlorides or fluorides) and the resulting shorter cooling times [1,2].

Pyrochemical methods in molten chlorides have been tested in laboratory and hot pilot scale in order to separate uranium, plutonium and minor actinides from fission products. Among all the pyrochemical processes proposed, to achieve the separation of actinides, the electrorefining of U into a solid cathode and Pu and minor actinides into a liquid Cd cathode in a molten salt electrolyte, applied to metal fuels from the EBR-II reactor (IFR process), is one of the most developed [3,4].

Later on other processes such as reductive extraction using a metallic phase such as Cd or Bi and a salt phase, or the electrodeposition of TRU into molten cathodes (Cd or Bi) [5, 6, 7], and more recently the codeposition of actinides on solid cathodes (Al) [8] have been envisaged. The aim of this research is to increase the actinide separation efficiency and to minimise the lanthanide content in the product. Therefore, it is important to have an accurate thermodynamic and electrochemical data base for all the actinides and lanthanides [9, 10, 11].

In this work several electrochemical techniques have been used in order to calculate some thermodynamic properties, the mechanism of reduction, and the diffusion coefficient of Eu in the molten eutectic LiCl-KCl.

Experimental

The electrochemical experiments were carried out under argon atmosphere of high quality (<0.5 ppm water and < 0.1 ppm oxygen). The electrolyte was constituted by the eutectic LiCl-KCl (59-41% mol). Before each experiment the melt was purified by bubbling HCl(g) for at least 1 hour, then Ar (g) was bubbled (45-60 min) in order to remove the HCl dissolved into the molten bath. The mixture was placed in a vitreous carbon crucible that is introduced in a quartz cell which in turn is placed in a well type oven. Temperature control was carried out by a K type thermocouple shielded in an Al₂O₃ tube.

The electrolytic bath consisting of Eu³⁺ dissolved in LiCl-KCl eutectic was prepared by dissolving anhydrous EuCl₃ (Aldrich 99.9%) in the melt with HCl(g) or Cl₂(g)+C (s). The use of Cl₂+C was observed to be necessary in order to reach the complete dissolution of the EuCl₃; according to the literature reviewed this is due to the formation of the Eu oxychloride, EuOCl [12].

Working electrodes used in the electrochemical study were a tungsten wire (1mm) and a vitreous carbon rod (3mm). The surface area of the electrodes was determined after each experiment by measuring the immersion depth of the electrode. As counter electrode a graphite rod (3mm) was used. The reference electrode was an Ag/LiCl-KCl-AgCl (0.75 mol kg⁻¹) prepared in a PYREX glass tube.

The electrochemical techniques used, i.e. cyclic voltammetry and chronopotentiometry, were carried out in an electrochemical cell having three electrode set-up and a PAR 273A potentiostat-galvanostat with a EG&E M270 electrochemical software.

Concentration of Eu was determined by ICP-MS analysis. Samples were taken from the molten salt, dissolved and diluted in nitric acid.

Results and discussion

Reversibility study

The cyclic voltammograms recorded at different scan rates (0.06-1.0 V s⁻¹) at a vitreous carbon and tungsten electrode, in a solution of EuCl₃ (6.78 10⁻² mol kg⁻¹) in LiCl-KCl are shown in Figure 1 and Figure 2 respectively. A single cathodic peak I_c is associated with an anodic peak I_a. The shape of the voltammograms is characteristic of a soluble product formation. The number of electrons exchanged in the reduction reaction was determined from the width of the peak at half height of the square wave voltammograms [1]. The number of electrons calculated that way is one, therefore, the reduction reaction produced is:

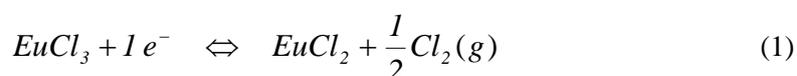
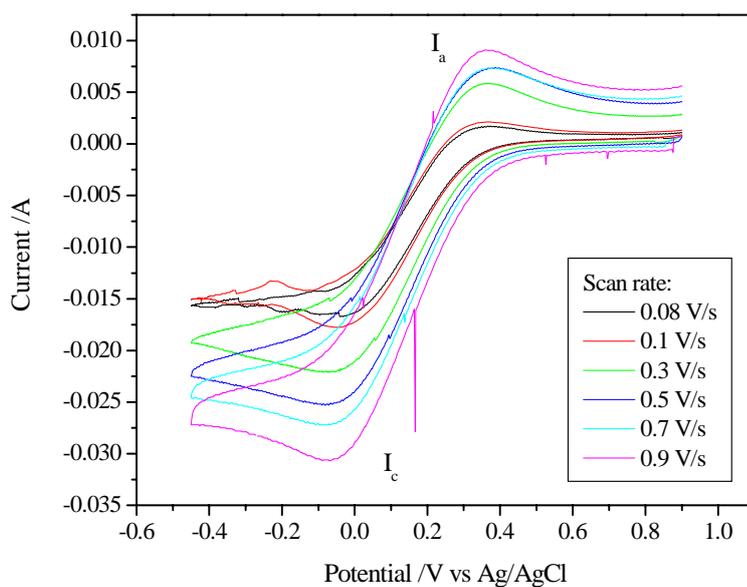
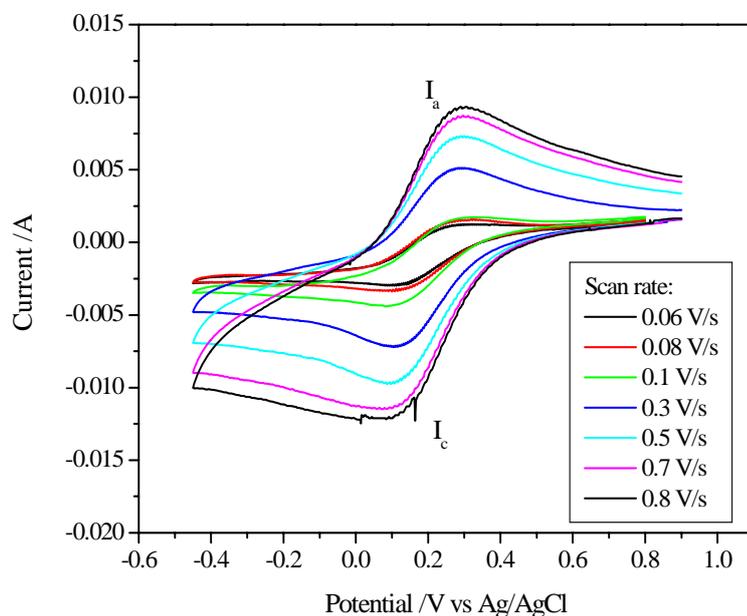


Figure 1. Cyclic voltammograms of Eu³⁺ in LiCl-KCl at 450° C



[Eu³⁺]: 6.78 10⁻² mol kg⁻¹, vitreous carbon working electrode, S= 0.7 cm².

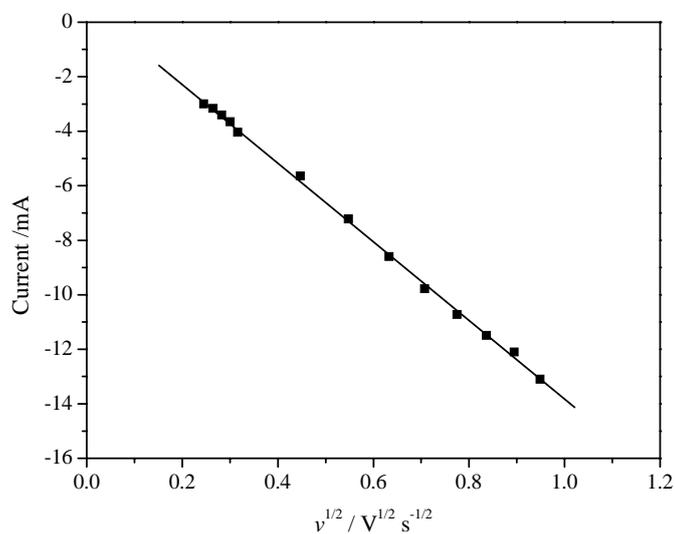
Figure 2. Cyclic voltammograms of Eu^{3+} in LiCl-KCl at 450°C



$$[\text{Eu}^{3+}] = 6.78 \cdot 10^{-2} \text{ mol kg}^{-1}, W \text{ working electrode, } S = 0.23 \text{ cm}^2$$

The analysis of these voltammograms indicates that the current of the cathodic peak (I_c) is directly proportional to the square root of the scan rate, ν [V s^{-1}], as it is shown in Figure 3, and that up to scan rates of 0.2 V s^{-1} the potential peak, E_p , is constant and independent of the scan rate. According to the theory of the linear sweep voltammetry [14], for scan rates lower than 0.2 V s^{-1} , the electrode process is reversible and controlled by the diffusion of the electroactive species. For scan rates higher than 0.2 V s^{-1} , the cathodic peak potential shifts negatively, this indicates that the system becomes quasi-reversible [13,15]. This behaviour has also been observed by S.A. Kuznetsov [16] in the equimolar NaCl-KCl melt in the temperature range 973-1123 K.

Figure 3. Variation of the current peak with the potential scan rate



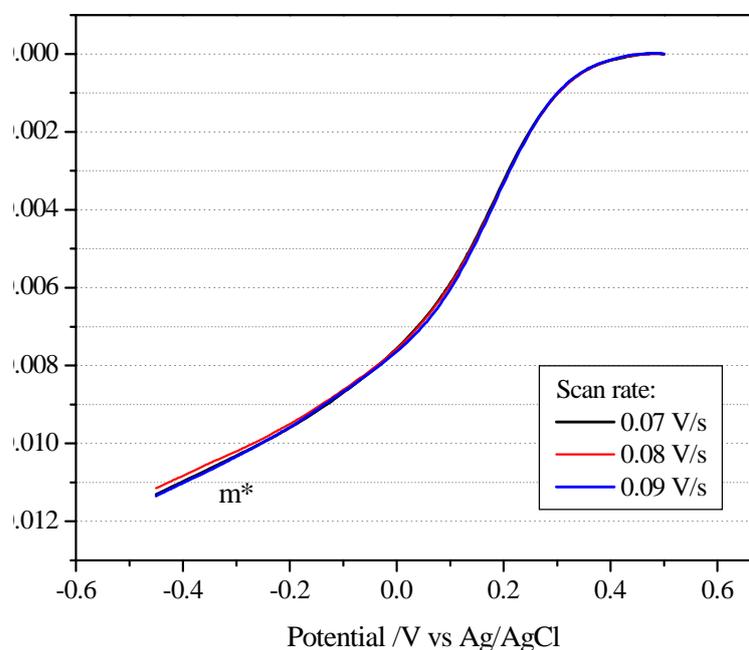
$[\text{Eu}^{3+}] = 6.78 \cdot 10^{-2} \text{ mol kg}^{-1}$, W working electrode, $S=0.23\text{cm}^2$

Diffusion coefficient

The diffusion coefficient of Eu (III) species was calculated by using two techniques, convolution and chronopotentiometry.

According to the convolution principle [13,17,18] the cyclic voltammogram data were transformed into a resembling steady-state voltammogram curves. The typical semi-integral curves at low scan rates at a W electrode are indicated in Figure 4, in which it is observed that the curves at different scan rates are coincident and that the limiting value of the current, m^* , is constant for scan rates lower than 0.1 V s^{-1} .

Figure 4. Semi-integrals of cyclic voltammograms at different scan rates.



EuCl₃ concentration: 6.8 10⁻² mol kg⁻¹, W working electrode, temperature 723K.

The diffusion coefficient of Eu (III) can be determined according to the convolution theory using the following equation [17,18]:

$$m^* = -nFSCD^{1/2} \quad (2)$$

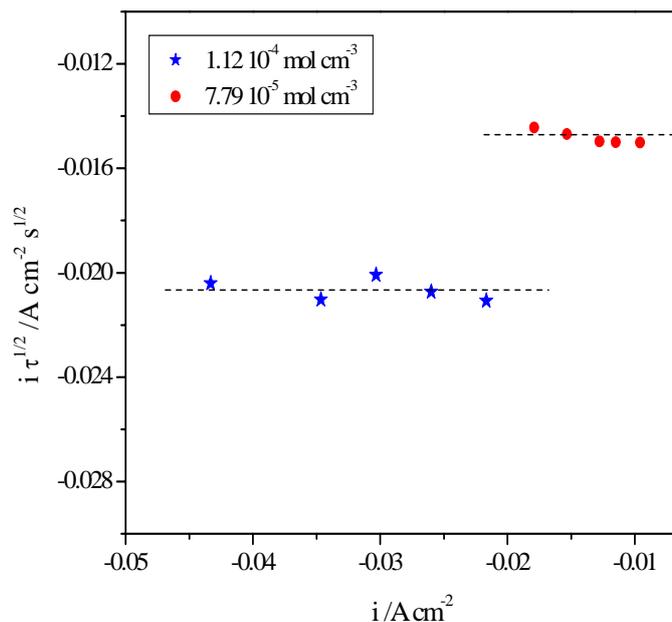
where n is the number of electrons exchanged, S the surface area of the working electrode (cm²), m* is the limiting current value of the semi-integral curve (A), F the Faraday Constant (C mol⁻¹), C the Eu(III) concentration (mol cm⁻³), and D the diffusion coefficient (cm² s⁻¹). The results obtained for both working electrodes at the temperatures tested are shown in Table 1.

Table 1. Diffusion coefficient of Eu(III) in LiCl-KCl by convolution

Temperature /K	D 10 ⁵ / cm ² s ⁻¹ (Tungsten)	D 10 ⁵ / cm ² s ⁻¹ (V. Carbon)
698	0.97	1.18
723	1.18	1.49
748	1.53	1.87
773	2.04	2.51
ΔH /kJ mol ⁻¹	-44.36	-44.55

Diffusion coefficients were also calculated by chronopotentiometry, at different imposed current densities. The product $i\tau^{1/2}$ is independent of both i , as can be observed in Figure 5 the plot of $i\tau^{1/2}$ versus i gives a straight line, for two different concentrations; based on that, the reduction of Eu(III) can be considered as a diffusion controlled process [13,19].

Figure 5. Plot of the function of $i\tau^{1/2}$ vs. i .



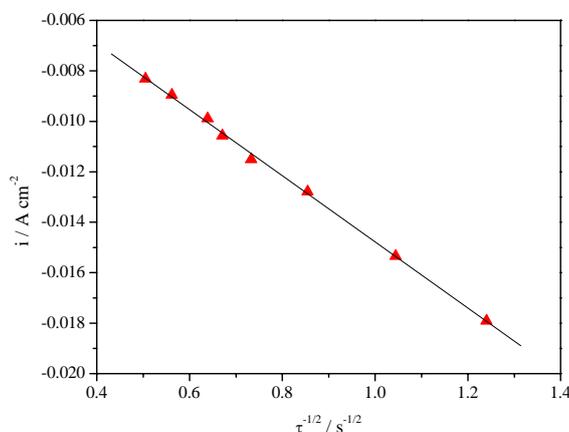
Temperature: 723K, W working electrode. Reference electrode Ag/AgCl(0.75 mol kg⁻¹).

The diffusion coefficient can be, therefore, calculated using the Sand equation [13,20]:

$$i\sqrt{\tau} = \frac{nFC\sqrt{\pi D}}{2} \quad (3)$$

i being the current density (A cm⁻²). From the slope of the plot of i versus $\tau^{-1/2}$ (Figure 6), the diffusion coefficient was calculated.

Figure 6. Dependence of current density versus $\tau^{1/2}$



EuCl₃ concentration: $4.73 \cdot 10^{-2} \text{ mol} \cdot \text{kg}^{-1}$. Temperature: 723K, W working electrode ($S = 0.78 \text{ cm}^2$)

In Table 2 are indicated the average values obtained for different temperatures and EuCl₃ concentrations

Table 2. Diffusion coefficient of Eu(III) in LiCl-KCl by chronopotentiometry

Temperature /K	$D \cdot 10^6 / \text{cm}^2 \text{ s}^{-1}$ Tungsten	$D \cdot 10^6 / \text{cm}^2 \text{ s}^{-1}$ Vitreous Carbon
698	2.04	4.10
723	2.94	6.49
748	4.92	7.42
773	5.88	11.3
$\Delta H / \text{kJ mol}^{-1}$	-66.32	-56.93

The comparison of results obtained from both techniques, Table 1 and 2, indicates that there is a great difference between them, being quite higher those obtained by convolution. The extrapolation of the results obtained by chronopotentiometry at 673K would be close to the value obtained by G.J. Janz [21] at this temperature ($1.1 \cdot 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$).

Diffusion coefficients variation with temperature follows the Arrhenius law. From the slope of the plot of $\log D$ versus $1/T$ the activation energy for diffusion has been determined according the equation [13]:

$$\log D = cte - \frac{\Delta H}{2.3 RT} \quad (4)$$

The values obtained for the activation energy using both techniques (Table 1 and Table 2) indicate that values obtained by convolution are close to those obtained by S.A. Kuznetsov [16] in NaCl-KCl in the temperature range 973-1000 K by different electrochemical techniques.

Formal standard redox potential

In the eutectic LiCl-KCl only the oxidation states of Eu(III) and Eu(II) has been observed, the potential of the Eu(II)/Eu(0) system is more negative than -2.7 V versus AgCl/Ag electrode [22]. The apparent standard potential of the redox couple Eu(III)/Eu(II) has been determined using the following equation [16]:

$$E'_{Eu(III)/Eu(II)} = (Ep^c + Ep^a) / 2 + 2.3 RT / nF \log(D_{ox} / D_{red})^{1/2} \quad (5)$$

Values of $D_{Eu(II)}$ were estimated from the current intensity peaks of the cyclic voltammograms at 0.1 Vs⁻¹ using the Randles-Sevcik equation [13,20]:

$$ip = 0.4463 (nF)^{3/2} (RT)^{-1/2} SCD^{1/2} \nu^{1/2} \quad (6)$$

Table 3 shows the results obtained at different temperatures for the two electrode tested, in molal scale, versus Cl₂/Cl⁻ reference.

Table 3. Formal standard redox potential $E'^{\circ}_{Eu(III)/Eu(II)}$ versus Cl₂/Cl⁻ electrode.

T /K	Tungsten		Vitreous carbon	
	$E'^{\circ}_{Eu(III)/Eu(II)}$	$\gamma 10^3$ (EuCl ₃)	$E'^{\circ}_{Eu(III)/Eu(II)}$	$\gamma 10^3$ (EuCl ₃)
698	-0.864	0.808	-0.884	0.579
723	-0.848	1.054	-0.858	0.879
748	-0.817	1.708	-0.843	1.140
773	-0.800	2.178	-0.817	1.687

The potential value obtained at 723K with the vitreous carbon electrode is good agreement with the one obtained by K.E. Johnson et al. [23] in this melt at the same temperature at Pt electrode.

The standard free energy of formation, $\Delta G^{\circ}_{EuCl_3}$, is calculated according to:

$$\Delta G^{\circ}_{EuCl_3} = nFE'_{Eu(III)/Eu(II)} \quad (7)$$

The plot of the $\Delta G^{\circ}_{EuCl_3}$ as a function of temperature shows a linear dependence, and can be expressed by the following expression:

$$\Delta G^{\circ}_{EuCl_3} = \Delta H^{\circ}_{EuCl_3} - T \Delta S^{\circ}_{EuCl_3} \quad (8)$$

from which the values of enthalpies ($\Delta H^{\circ}_{EuCl_3}$) and entropies ($\Delta S^{\circ}_{EuCl_3}$) of formation are obtained for both electrodes.

$$\begin{aligned} \Delta G^{\circ}_{EuCl_3} &= 137.09 - 0.075 T \quad /kJ mol^{-1} && \text{for vitreous carbon electrode.} \\ \Delta G^{\circ}_{EuCl_3} &= 130.87 - 0.069 T \quad /kJ mol^{-1} && \text{for tungsten electrode} \end{aligned}$$

Activity coefficients of EuCl_3 in the LiCl-KCl, γ_{EuCl_3} , have been calculated from the difference between the Gibbs free energy of formation obtained from the electrochemical measurements and the Gibbs free energy of formation for pure compounds at the liquid state obtained from literature [24]

$$RT \ln \gamma_{\text{EuCl}_3} = \Delta G_{\text{EuCl}_3}^{\circ} - \Delta G_{\text{EuCl}_3}^*$$
 (9)

The activity coefficient values obtained are shown in Table 3, it is observed for both electrodes an increase of the values as the temperature increases which indicate a decrease of the strength of the chloride ions complex formed by the EuCl_3 with the temperature.

Conclusion

The electrochemical behaviour of EuCl_3 has been investigated in molten LiCl-KCl in the temperature range 698-773K. It has been observed that Eu(III) is reduced to Eu(II) by a single step with exchange of one electron, presenting the reduction reaction a reversible behaviour for low sweep potential rate and a quasi-reversible behaviour for higher scan rates. The average diffusion coefficient of EuCl_3 calculated is close to $1.3 \cdot 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$. Apparent standard potential has been calculated by the cyclic voltammetry technique, the value obtained at 723K with the vitreous carbon electrode is in good agreement with the data found in the literature. Activity coefficients of EuCl_3 indicate that this ion forms complexes with the chloride ions, EuCl_6^{3-} , of the molten bath, and that the strength of these complexes decreases with the increase of the temperature.

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