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Electrochemistry of oxygen-free curium compounds in fused NaCl–2CsCl eutectic

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This work presents the electrochemical study of Cm(III) in fused NaCl–2CsCl eutectic in the temperature range 823–1023 K. Transient electrochemical techniques such as cyclic, differential pulse and square wave voltammetry, and chronopotentiometry have been used in order to investigate the reduction mechanism of curium ions up to the metal. The results obtained show that the reduction reaction takes place in a single step $\mathrm{Cm(III)} + 3\bar{e} \Rightarrow \mathrm{Cm(0)}$. The diffusion coefficient of $[\mathrm{CmCl_6}]^{3-}$ complex ions was determined by cyclic voltammetry at different temperatures by applying the Berzins–Delahay equation. The validity of the Arrhenius law was also verified and the activation energy for diffusion was found to be 44.46 kJ/mol. The apparent standard electrode potential of the redox couple Cm(III)/Cm(0) was found by chronopotentiometry at several temperatures. The thermodynamic properties of curium trichloride have also been calculated.

1. Introduction

Nowadays Partitioning and Transmutation (P&T) is one of the strategies for reducing the long-term radiotoxicity of nuclear waste. P&T can be successfully used for conversion of hazardous long-lived radionuclides into short-lived or even stable elements [1,2]. For that case it is necessary to separate minor actinides (Np, Am, Cm) from other fission products (FP). This process can be carried out in molten alkali metal chlorides that have a high radiation resistance and are not the moderator of neutrons such as aqueous or organic solutions. That is the reason why it is possible to reprocess nuclear waste with high actinide content and shorter cooling times in molten salt media.

Pyrochemical reprocessing methods are based on a good knowledge of the basic chemical and electrochemical properties of actinides [3–11] and fission products [12–26]. This information is necessary for the design of an effective technological process.

Curium isotopes in nuclear spent fuel have a long half-life and produce significant quantities of heat. Therefore they must be effectively separated from highly active waste and then undergo transmutation. There is only limited information about the behaviour of curium in molten salts: data about the apparent standard electrode potentials of curium–zinc alloys [27] and about the distribution number between molten salt and liquid metals [28].

The objective of the proposed investigation is to obtain data on electrochemical and thermodynamic properties of curium compounds in molten chlorides. These fundamental data can be subsequently used for feasibility assessment of the curium recovery processes in molten chlorides.

2. Experimental

The experiments were carried out under inert argon atmosphere using an electrochemical sealed quartz cell equipped with a three electrodes setup. Different transient electrochemical techniques were used such as cyclic, differential pulse and square wave voltammetry, as well as chronopotentiometry. The electrolytic bath was a mixture NaCl–2CsCl (NaCl (>99.9%), manufactured by "Reachim" plant, Mikchaylovsk, Russia and CsCl (>99.9%), manufactured by "Rare Metal Plant", Novosibirsk, Russia) with the eutectic composition (36.0:64.0 mol%). It was purified under vacuum in the temperatures range 293–673 K. Then the reagents were fused in an atmosphere of dry argon. Afterwards the solvents were purified by direct crystallization [29]. $\mathrm{Cm^{3+}}$ ions were prepared by direct addition of anhydrous $\mathrm{CmCl_3}$ to the solvent NaCl–2CsCl. The latter was prepared by direct chlorination of $\mathrm{Cm_2O_3}$ in NaCl–2CsCl eutectic in vitreous carbon crucibles. The finished product had a deep-blue colour. The content of curium in the experiments was 0.005–0.05 mol/kg. The curium concentration was determined by taking samples from the melt and analysing by radiometric method.

The electrochemical measurements were carried out using an Autolab PGSTAT302 potentiostat (Eco-Chimie) with specific GPES electrochemical software (version 4.9).

The inert working electrode was prepared using a 1.8 mm metallic W wire. It was immersed into the molten bath between

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3 and 10 mm. The active surface area was determined after each experiment by measuring the immersion depth of the electrode. The counter electrode consisted of a carbon crucible. The $2Cl^-/Cl_2$ and Ag/Ag^+ (0.75 mol/kg AgCl) electrodes were used as standard reference electrodes. The experiments were carried out in vitreous carbon crucibles; the amount of salt was 40–60 g.

3. Results and discussion

3.1. Study by voltammetric techniques

The reaction mechanism of the soluble–insoluble Cm(III)/Cm(0) redox system was investigated by analyzing the cyclic voltammetric curves obtained at several scan rates, Fig. 1. They show that the cathodic peak potential (E_p) is constant from 0.04 V/s up to 0.1 V/s and independent of the logarithm of potential sweep rate, Fig. 2. It means that at small scan rates the reaction Cm(III)/Cm(0) is reversible. In the range from 0.1 V/s up to 1.0 V/s the dependence is linear and shifts to the negative values with the increasing of the logarithm of the sweep rate. So in this scan range (>0.1 V/s) the reaction Cm(III)/Cm(0) is irreversible and controlled by the rate of the charge transfer. On the other hand the cathodic peak current (I_p) is directly proportional to the square root of the polarization rate (υ), Fig. 3. According to the theory of the linear sweep voltammetry technique [30] the redox system Cm(III)/Cm(0) is reversible and controlled by the rate of the mass transfer at small scan rates and is irreversible and controlled by the rate of the charge transfer at high scan rates.

The number of electrons of the reduction of Cm(III) ions for the reversible system was calculated according to [31] at scan rates from 0.04 up to 0.1 V/s:

$$E_P - E_{P/2} = -0.77\frac{RT}{nF} \tag{1}$$

where E_P is a peak potential (V), $E_{P/2}$ is a half-peak potential (V), F is the Faraday constant (96,500 C/mol), R is the ideal gas constant (J/K mol) and T is the absolute temperature (K), n is the number of exchanged electrons. The result is $n = 3.01 \pm 0.04$.

The square wave voltammetry technique was used also to determine the number of electrons exchanged in the reduction of Cm(III) ions in the molten eutectic NaCl–2CsCl. Fig. 4 shows the cathodic wave obtained at 823 K. The number of electrons exchanged is determined by measuring the width at half height of the reduction peak, $W_{1/2}$ (V), registered at different frequencies (6–80 Hz), using the following equation [32]:

$$W_{1/2} = 3.52\frac{RT}{nF} \tag{2}$$

where T is the temperature (K), R is the ideal gas constant (J/K mol), n is the number of electrons exchanged and F is the Faraday constant (C/mol).

At middle frequencies (12–30 Hz), a linear relationship between the cathodic peak current and the square root of the frequency was found. The number of electrons exchanged determined this way was close to three ($n = 2.99 \pm 0.15$).

Potentiostatic electrolysis at potentials of the cathodic peaks shows the formation of the solid phase on tungsten surface after polarization. One plateau on the dependence potential–time was obtained.

On the differential pulse voltammogram only one peak was fixed at potential range −1.5 to −2.2 V version Ag/Ag^+ reference electrode, Fig. 5. It means that the curium ion reduction at the electrode is a single step process. Thus the mechanism of the cathodic reduction of curium ions is the following:

$$\text{Cm(III)} + 3\bar{e} \Rightarrow \text{Cm(0)} \tag{3}$$

3.2. Diffusion coefficient of Cm(III) ions

The diffusion coefficient of the $[CmCl]_6^{3-}$ ion in molten NaCl–2CsCl eutectic was determined using the cyclic voltammetry technique and applying the Berzins–Delahay equation, valid for reversible soluble–insoluble system [33] at the scan rates 0.04–0.1 V/s

$$I_p = 0.61(nF)^{3/2}C_0S\left(\frac{D\upsilon}{RT}\right)^{1/2} \tag{4}$$

where S is the electrode surface area (cm^2), C_0 is the solute concentration (mol/cm^3), D is the diffusion coefficient (cm^2/s), F is the Faraday constant (96,500 C/mol), R is the ideal gas constant (J/K mol), n is the number of exchanged electrons, υ is the potential sweep rate (V/s) and T is the absolute temperature (K).

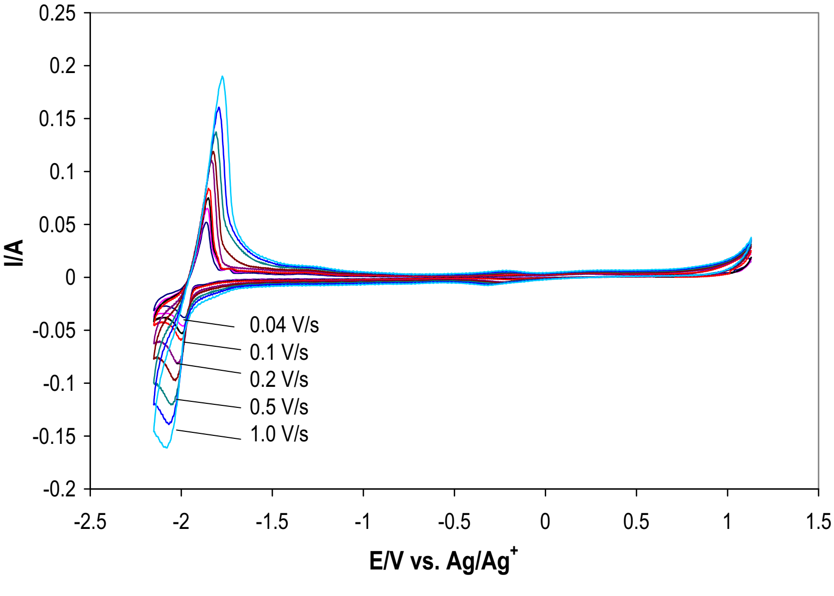

Fig. 1. Cyclic voltammograms of $NaCl–2CsCl–CmCl_3$ at different sweep potential rates at 823 K. Working electrode: W ($S = 0.31\ cm^2$). $[Cm(III)] = 4.4 \times 10^{-2}$ mol/kg.

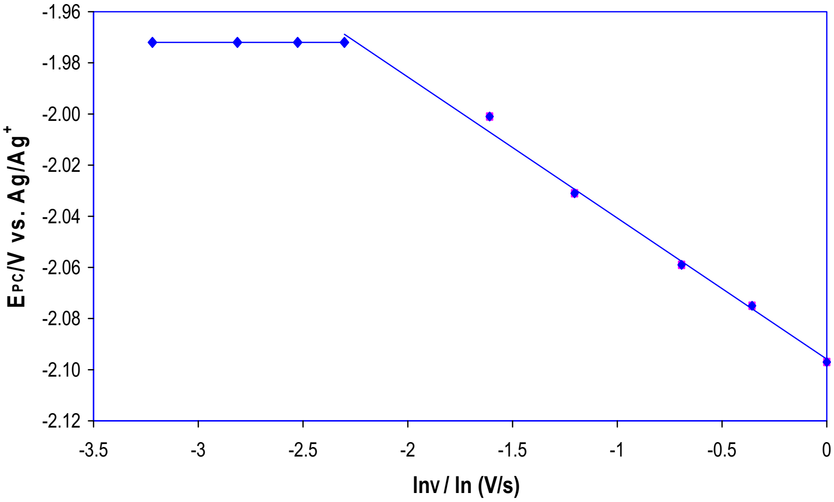

Fig. 2. Variation of the cathodic peak potential as a function neperian logarithm of the sweep rate in fused NaCl–2CsCl–CmCl$_3$ at 823 K. Working electrode: W (S = 0.59 cm^2). [Cm(III)] = 4.4 × 10^{-2} mol/kg.

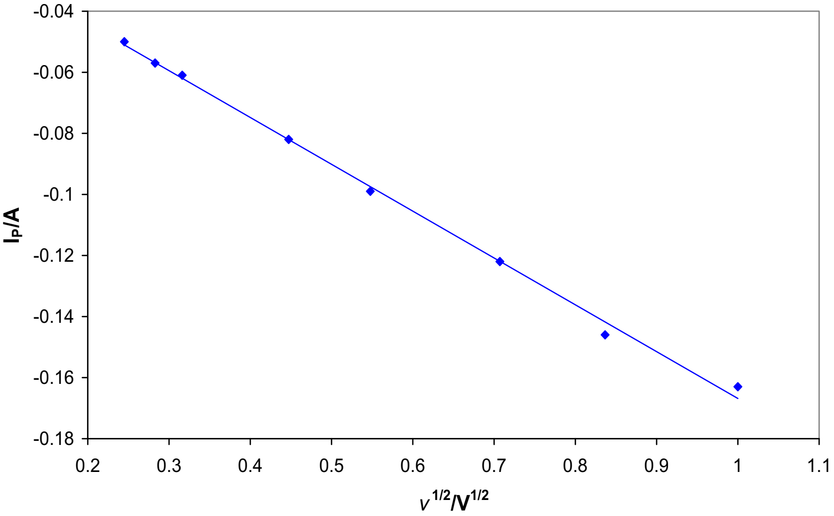

Fig. 3. Variation of the cathodic peak current as a function of the potential scan rate in fused NaCl–2CsCl–CmCl$_3$ at 823 K. Working electrode: W (S = 0.59 cm^2). [Cm(III)] = 4.4 × 10^{-2} mol/kg.

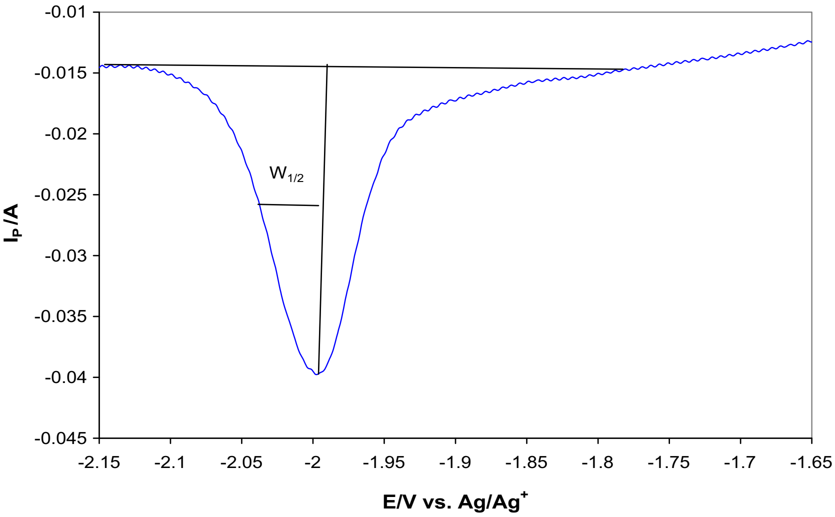

Fig. 4. Square wave voltammogram of NaCl–2CsCl–CmCl$_3$ at 25 Hz at 823 K. Working electrode: W (S = 0.29 cm^2). [Cm(III)] = 9.7 × 10^{-3} mol/kg.

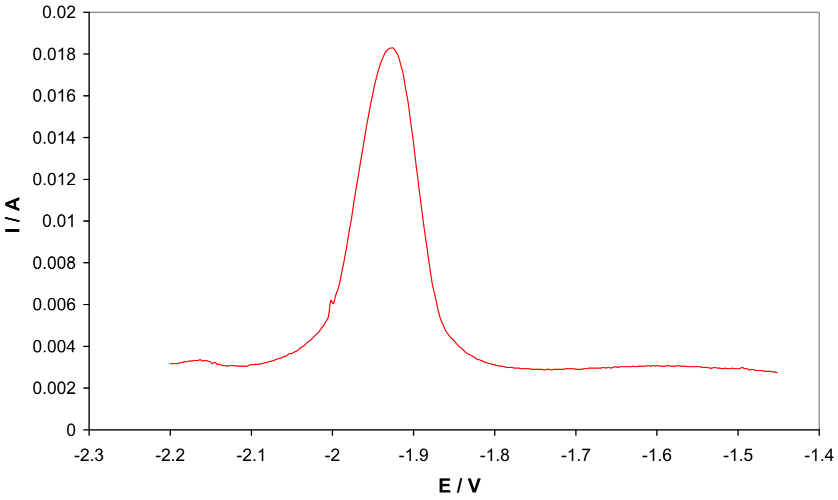

Fig. 5. Differential pulse voltammogram of NaCl–2CsCl–$CmCl_3$ melt (4.4×10^{-2} mol/kg) at 923 K.

Table 1
Calculated values of diffusion coefficients of Cm(III) ions at different temperatures.

T/K	lg D	$D_{\mathrm{Cm(III)}}$ (cm^2/s)	E_A (kJ/mol)
1023	−4.60	2.49×10^{-5}	44.46
973	−4.88	1.33×10^{-5}	44.46
873	−5.16	6.97×10^{-6}	44.46

The estimated expression for the diffusion coefficients versus reverse temperature is the following:

$$\lg D_{[\mathrm{CmCl}_6]^{3-}} = -2.34 - \frac{2326}{T} \pm 0.02 \qquad (5)$$

The diffusion activation energy (E_A) of Cm^{3+} ions was calculated from equation:

$$-\frac{E_A}{2.303R} = \frac{\partial \log D}{\partial(1/T)} \qquad (6)$$

The activation energy of the complex curium ions depends on the value of the ionic potential of the solvent and increases in the line from LiCl to CsCl. The results of calculations of diffusion coefficients are given in Table 1.

3.3. Apparent standard potential of the redox system Cm(III)/Cm(0)

The apparent standard potential of the redox couple Cm(III)/Cm(0) was determined at several temperatures. For the measurement, the technique of open-circuit chronopotentiometry of a solution containing a $CmCl_3$ (4.4×10^{-2} mol/kg) concentration in NaCl–2CsCl was used. A short cathodic polarization was applied, 10–15 s, in order to form in situ a metallic deposit of Cm on the W electrode, and then the open-circuit potential of the electrode was measured versus time (Fig. 6). The pseudo-equilibrium potential of the redox couple Cm(III)/Cm(0) was measured and the apparent standard potential, E^*, was determined using the Nernst equation:

$$E_{\mathrm{Cm(III)/Cm(0)}} = E^*_{\mathrm{Cm(III)/Cm(0)}} + \frac{RT}{nF} \ln X_{\mathrm{CmCl}_3} \qquad (7)$$

being,

$$E^*_{\mathrm{Cm(III)/Cm(0)}} = E^\circ_{\mathrm{Cm(III)/Cm(0)}} + \frac{RT}{nF} \ln \gamma_{\mathrm{CmCl}_3} \qquad (8)$$

The apparent standard potential is obtained in the mole fraction scale versus the Ag/AgCl (0.75 mol/kg) reference electrode and then transformed into values of potential versus the $2\mathrm{Cl}^-/\mathrm{Cl}_2$

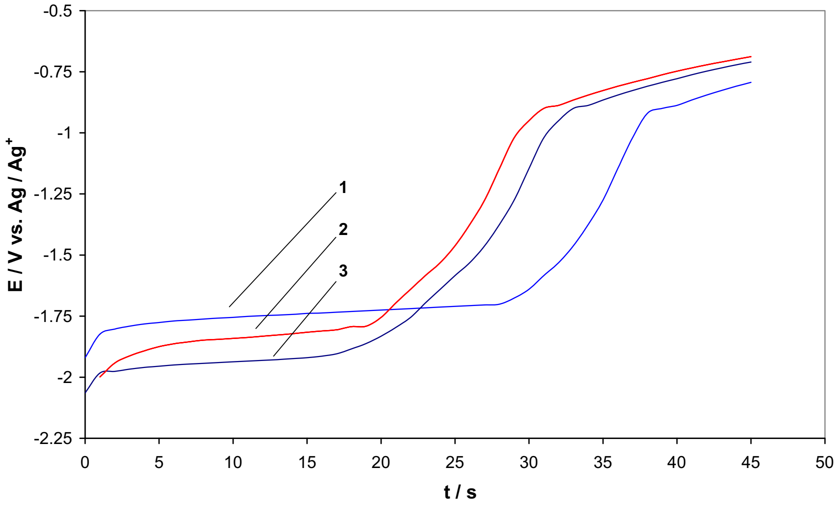

Fig. 6. The potential–time dependences after anodic polarization of W working electrode in NaCl–2CsCl–$CmCl_3$ melt at different temperatures. [Cm(III)] = 4.4×10^{-2} mol/kg. The value of polarization is equal −2.1 to −2.2 V. The time of polarization is equal 5–15 s. 1–823 K; 2–923 K; 3–1023 K.

reference electrode scale. For this purpose special measurements were carried out for building the temperature dependence between Ag/AgCl (0.75 mol/kg) and $2Cl^-/Cl_2$ reference electrodes. From the experimental data obtained in this work in the temperature range 823–1023 K the following empirical equation for the apparent standard potential of the Cm(III)/Cm(0) system versus the $2Cl^-/Cl_2$ reference electrode was obtained using [34]:

$$E^*_{\mathrm{Cm(III)/Cm(0)}} = -(3.407 \pm 0.005) + (5.42 \pm 0.14) \times 10^{-4}T \pm 0.002\ V \quad (9)$$

The comparison of our result in NaCl–2CsCl eutectic with the literature data for couples Pu^{3+}/Pu^0 [8] and U^{3+}/U^0 [25] in LiCl–KCl eutectic at 823 K gives the following values: $E^*_{\mathrm{Cm}^{3+}/\mathrm{Cm}} = -2.961\ V$; $E^*_{\mathrm{Pu}^{3+}/\mathrm{Pu}} = -2.742\ V$; $E^*_{U^{3+}/U} = -2.487\ V$.

The shift of the value of apparent standard redox potential of actinides to more negative values in line U–Pu–Am–Cm [35] also observes with the increasing the relative stability of actinides complex ions in line LiCl–NaCl–KCl–RbCl–CsCl [36]. Our results are in a good agreement with the ones reported by Smirnov [37].

3.4. Thermodynamic properties

The apparent standard Gibbs energy of formation $\Delta G^*_{\mathrm{CmCl_3}}$ is calculated according to:

$$\Delta G^*_{\mathrm{CmCl_3}} = nFE^*_{\mathrm{Cm(III)/Cm(0)}} \quad (10)$$

The least square fit of the standard Gibbs energy versus the temperature allowed us to determine the values of ΔH and ΔS more precisely by the following equation:

$$\Delta G^*_{\mathrm{CmCl_3}} = \Delta H^*_{\mathrm{CmCl_3}} - T\Delta S^*_{\mathrm{CmCl_3}} \quad (11)$$

from which the values of enthalpy and entropy of formation can be obtained:

$$\Delta G^*_{\mathrm{CmCl_3}} = -986.4 + 0.174T \pm 0.6\ \mathrm{kJ/mol} \quad (12)$$

4. Conclusions

The electrochemical behaviour of $CmCl_3$ in molten NaCl–2CsCl eutectic has been investigated using inert (W) electrode in a range of temperatures 823–1023 K. Different behaviour was found for the reduction process. At low scan rates (<0.1 V/s) Cm(III) ions are reversibly reduced to metallic curium in a single step, but at scan rates (>0.1 V/s) this reaction is irreversible.

The diffusion coefficient of Cm(III) ions was determined at different temperatures by cyclic voltammetry. The diffusion coefficient showed a temperature dependence in accordance with the Arrhenius law. The activation energy for diffusion process was found to be 44.46 kJ/mol.

Potentiostatic electrolysis showed the formation of curium deposits on inert electrodes.

The apparent standard potential and the Gibbs energy of formation of $CmCl_3$ have been measured using the chronopotentiometry at open-circuit technique.

The obtained fundamental data can be subsequently used for feasibility assessment of the curium recovery processes in molten chlorides.

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