Electrochemistry of Curium in Molten Chlorides

Alexander Osipenko\(^1\), Alexander Mayershin\(^1\), Valeri Smolenski\(^2,\star\), Alena Novoselova\(^2\) and Michael Kormilitsyn\(^1\)

\(^1\)Radiochemical Division, Research Institute of Atomic Reactors, 
\(^2\)Institute of High-Temperature Electrochemistry, Ural Division, Russian Academy of Science, Russia

1. Introduction

Molten salts and especially fused chlorides are the convenient medium for selective dissolution and deposition of metals. The existence of a wide spectrum of individual salt melts and their mixtures with different cation and anion composition gives the real possibility of use the solvents with the optimum electrochemical and physical-chemical properties, which are necessary for solving specific radiochemistry objects. Also molten alkali metal chlorides have a high radiation resistance and are not the moderator of neutrons as aqua and organic mediums [Uozumi, 2004; Willit, 2005].

Nowadays electrochemical reprocessing in molten salts is applied to the oxide and metal fuel. Partitioning and Transmutation (P&T) concept is one of the strategies for reducing the long-term radiotoxicity of the nuclear waste. For this case pyrochemical reprocessing methods including the recycling and transmutation can be successfully used for conversion more hazardous radionuclides into short-lived or even stable elements. For that first of all it is necessary to separate minor actinides (Np, Am, Cm) from other fission products (FP).

Pyrochemical reprocessing methods are based on a good knowledge of the basic chemical and electrochemical properties of actinides and fission products. This information is necessary for creation the effective technological process [Bermejo et al., 2007, 2008; Castrillejo et al., 2005a, 2005b, 2009; De Cordoba et al., 2004, 2008; Fusselman et al., 1999; Kuznetsov et al., 2006; Morss, 2008; Novoselova & Smolenski, 2010, 2011; Osipenko et al., 2010, 2011; Roy et al., 1996; Sakamura et al., 1998; Serp et al., 2004, 2005a, 2005b, 2006; Serrano & Taxil, 1999; Shirai et al., 2000; Smolenski et al., 2008, 2009].

Curium isotopes in nuclear spent fuel have a large specific thermal flux and a long half-life. So, they must be effectively separated from highly active waste and then undergo transmutation.

The goal of this work is the investigation of electrochemical and thermodynamic properties of oxide and oxygen free curium compounds in fused chlorides.
2. Experimental

2.1 Preparation of starting materials

The solvents LiCl (Roth, 99.9%), NaCl (Reachim, 99.9%), KCl (Reachim, 99.9%), and CsCl (REP, 99.9%) were purified under vacuum in the temperatures range 293-773 K. Then the reagents were fused under dry argon atmosphere. Afterwards these reagents were purified by the operation of the direct crystallization [Shishkin & Mityaev, 1982]. The calculated amounts of prepared solvents were melted in the cell before any experiment [Korshunov et al., 1979].

Curium trichloride was prepared by using the operation of carbochlorination of curium oxide in fused solvents in vitreous carbon crucibles. Cm$^{3+}$ ions, in the concentration range $10^{-2}$-$10^{-3}$ mol kg$^{-1}$ were introduced into the bath in the form of CmCl$_3$ solvent mixture.

The obtained electrolytes were kept into glass ampoules under atmosphere of dry argon in inert glove box.

2.2 Potentiometric method

The investigations were carried out in the cell, containing platinum-oxygen electrode with solid electrolyte membrane which was made from ZrO$_2$ stabilized by Y$_2$O$_3$ supplied by Interbil Spain (inner diameter 4 mm, outer diameter 6 mm). This electrode was used as indicating electrode for measuring the oxygen ions activity in the investigated melt. The measurements were carried out versus classic Cl$^-$/Cl$_2$ reference electrode [Smirnov, 1973]. The difference between indicator and reference electrodes in the following galvanic cell

$$Pt_{(s)} , O_{2(g)} | ZrO_2 \{Y_2O_3 \} \text{ Melt under test} \parallel \text{Solvent melt} | Cl_{2(g)} , C_{(s)}$$

is equal to

$$\varepsilon = \varepsilon^o - \frac{RT}{2F} \ln \frac{a_{O^{2-}} \cdot P_{Cl_2}}{a_{Cl^-} \cdot P_{O_2}}$$

(2)

where $a$ is the activity of the soluble product in the melt (in mol·kg$^{-1}$); $P$ is the gas pressure (in atm.); $\varepsilon^o$ is the difference of standard electrode potentials of the reaction 3 (in V); $T$ is the absolute temperature (in K); $R$ is the ideal gas constant (in J·mol$^{-1}$·K$^{-1}$); $n$ is the number of electrons exchanged and $F$ is the Faraday constant (96500 C·mol$^{-1}$).

$$2Cl_{(l)} + 1 / 2O_{2(g)} = O^{2-}_{(l)} + Cl_{2(g)} .$$

(3)

The value $\varepsilon^o$ of the reaction (3) is the following

$$\varepsilon^o = E^o_{Cl_2/Cl^-} - E^o_{O_2/O^{2-}} = -\frac{\Delta G^o}{2F}$$

(4)

where $\Delta G^o$ is the change of the standard Gibbs energy of the reaction 3 (in kJ·mol$^{-1}$·K$^{-1}$).
$E_{O_2/O^2^-} = E_{O_2/O^2^-}^* - \frac{RT}{2F} \ln \left[ m_{eq}(O^{2-}) \right]$ \hspace{1cm} (5)

where $E_{O_2/O^2^-}$ is the equilibrium potential of $O_2/O^2-$ system \( \text{(in V)} \); $E_{O_2/O^2^-}^*$ is an apparent standard potential of the system \( \text{(in V)} \).

The value of apparent standard potential $E^*$ in contrast to the standard potential $E^0$ describes the dilute solutions, where the activity coefficient $\gamma_{O^2^-}$ is constant at low concentrations [Smirnov, 1973] and depends from the nature of molten salts. It can be calculated experimentally with high precision according to expression (5). The introducing of oxide ions in the solution was done by dropping calculated amounts of BaO (Merck, 99.999%) which completely dissociates in the melt [Cherginetz, 2004].

All reagents were handled in a glove box to avoid contamination of moisture. The experiments were performed under an inert argon atmosphere.

The potentiometric study was performed with Autolab PGSTAT302 potentiostat/galvanostat (Eco-Chimie) with specific GPES electrochemical software (version 4.9.006).

2.3 Transient electrochemical technique

The experiments were carried out under inert argon atmosphere using a standard electrochemical quartz sealed cell using a three electrodes setup. Different transient electrochemical techniques were used such as linear sweep, cyclic, square wave, differential and semi-integral voltammetry, as well as potentiometry at zero current. The electrochemical measurements were carried out using an Autolab PGSTAT302 potentiostat-galvanostat (Eco-Chimie) with specific GPES electrochemical software (version 4.9.006).

The inert working electrode was prepared using a 1.8 mm metallic W wire (Goodfellow, 99.9%). It was immersed into the molten bath between 3 - 7 mm. The active surface area was determined after each experiment by measuring the immersion depth of the electrode. The counter electrode consisted of a vitreous carbon crucible (SU - 2000). The Cl⁻/Cl₂ or Ag/Ag⁺ (0.75 mol·kg⁻¹ 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). The total curium concentrations were determined by taking samples from the melt and then analyzed by ICP-MS.

3. Results and discussion

3.1 Potentiometric investigations

The preliminary investigations of fused 3LiCl-2KCl eutectic and equimolar NaCl-KCl by of O²⁻ ions are present in Table 1. In this case, the potential of the pO²⁻ indicator electrode vs. the concentrations of added O²⁻ ions follows a Nernst behavior (eq. 5). The experiment slope is closed to its theoretical value for a two-electron process, which shows the Nernstian behavior of the system.

To identify curium oxide species and to determine their stability, the titration of Cm³⁺ by O²⁻ ions was performed. To estimate stoichiometric coefficients of reactions that involve initial components, the ligand number “α” was used.
Molten solvent | Temperature, K | $E_{\text{O}_2/\text{O}^-}$ (in V vs. Cl/Cl$_2$) | $RT/2F$ (exp.) | $RT/2F$ (theor.)
---|---|---|---|---
3LiCl-2KCl | 723 | -1.087±0.001 | 0.072±0.001 | 0.072
 | 823 | -1.102±0.001 | 0.082±0.001 | 0.082
 | 923 | -1.275±0.004 | 0.091±0.001 | 0.0911
NaCl-KCl | 1023 | -1.351±0.001 | 0.101±0.001 | 0.101
 | 1073 | -1.448±0.003 | 0.134±0.002 | 0.106
 | 1123 | -1.374±0.001 | 0.111±0.001 | 0.111
NaCl-2CsCl | 823 | -0.751±0.001 | 0.083±0.001 | 0.083
 | 923 | -0.771±0.001 | 0.092±0.001 | 0.092
 | 1023 | -0.985±0.001 | 0.113±0.009 | 0.102

Table 1. The parameters of calibration curve for 3LiCl-2KCl, NaCl-KCl and NaCl-2CsCl melts, (molality scale)

$$\alpha = \frac{[O^{2-}]_{\text{added}}}{[\text{Cm}^{3+}]_{\text{initial}}}$$

(6)

where $[O^{2-}]_{\text{added}}$ is the added concentration of oxide ions in the melt, (in mol·kg$^{-1}$); $[\text{Cm}^{3+}]_{\text{initial}}$ is the initial Cm$^{3+}$ concentration, (in mol·kg$^{-1}$).

Fig. 1. Potentiometric titration of Cm$^{3+}$ solution by O$^{2-}$ ions in NaCl-2CsCl at 1023 K. $[\text{Cm}^{3+}] = 1.2 \times 10^{-3}$ mol·kg$^{-1}$
The potentiometric titration curve $p\text{O}^2-$ versus $\alpha$ in the NaCl-2CsCl-CmCl$_3$ melt shows one equivalent point for $\alpha$ equal to 1, Fig. 1. This can be assigned to the production of solid oxoclride, CmOCl. The shape of an experimental curve shows the possibility of formation of soluble product CmO$^+$ in the beginning of titration [Cherginetz, 2004]. The precipitation of Cm$_2$O$_3$ did not fixed on experimental curves. One of the reasons of these phenomena may be the kinetic predicaments in formation of insoluble compound Cm$_2$O$_3$.

Therefore, the titration reactions can be written as:

$$\text{Cm}^{3+}(l) + \text{O}^2-(l) \leftrightarrow \text{CmO}^+(l) \quad (0 < \alpha < 0.5) \quad (7)$$

$$\text{Cm}^{3+}(l) + \text{O}^2-(l) + \text{Cl}^-(l) \leftrightarrow \text{CmOCl}(s) \quad (0.5 < \alpha < 1.0) \quad (8)$$

$$2\text{CmOCl}(s) + \text{O}^2-(l) \leftrightarrow \text{Cm}_2\text{O}_3(s) + 2\text{Cl}^-(l) \quad (1.0 < \alpha < 1.5) \quad (9)$$

Combine expressions (8) and (9), Cm$_2$O$_3$ formation is described by (10):

$$2\text{Cm}^{3+}(l) + 3\text{O}^2-(l) \leftrightarrow \text{Cm}_2\text{O}_3(s)$$

The chloride ions activity in the melt is one. By applying mass balance equations (11, 12) and the expressions of the equilibrium constant of the reaction (7) and the solubility constants of the reactions (8, 10) it is possible to calculate the concentration of CmO$^+$ ions and the solubility of CmOCl and Cm$_2$O$_3$ in the melt:

$$\left[\text{O}^2-\right]_{\text{bulk}} = \left[\text{O}^2-\right]_{\text{added}} - \left[\text{CmO}^+\right]_{\text{bulk}} - \left[\text{CmOCl}\right]_{\text{precipitated}} - 3\left[\text{Cm}_2\text{O}_3\right]_{\text{precipitated}} \quad (11)$$

$$\left[\text{Cm}^{3+}\right]_{\text{bulk}} = \left[\text{Cm}^{3+}\right]_{\text{initial}} - \left[\text{CmO}^+\right]_{\text{bulk}} - \left[\text{CmOCl}\right]_{\text{precipitated}} - 2\left[\text{Cm}_2\text{O}_3\right]_{\text{precipitated}} \quad (12)$$

where $\left[\text{O}^2-\right]_{\text{bulk}}$ is the equilibrium concentration of oxide ions in the melt, (in mol·kg$^{-1}$); $\left[\text{Cm}^{3+}\right]_{\text{bulk}}$ is the equilibrium concentration of curium ions in the melt, (in mol·kg$^{-1}$); $\left[\text{CmO}^+\right]_{\text{bulk}}$ is the equilibrium concentration of curium oxide ions in the melt, (in mol·kg$^{-1}$).

$$K_{\text{eff}}^{\text{CmO}^+} = \frac{\left[\text{CmO}^+\right]}{\left[\text{Cm}^{3+}\right]\cdot\left[\text{O}^2-\right]} \quad (13)$$

$$K_s^{\text{CmOCl}} = \left[\text{Cm}^{3+}\right]\cdot\left[\text{O}^2-\right]\cdot\left[\text{Cl}^-\right] \quad (14)$$

$$K_s^{\text{Cm}_2\text{O}_3} = \left[\text{Cm}^{3+}\right]^2\cdot\left[\text{O}^2-\right]^3 \quad (15)$$

The formation of CmO$^+$ ions in the range $(0 < \alpha < 0.5)$ is described by the following theoretical titration curve:
\[ \alpha = \frac{[O^{2-}]_{bulk}}{[Cm^{3+}]_{initial} + [O^{2-}]_{bulk}} \times \frac{K_{eq} - K_{eq}}{[Cm^{3+}]_{initial} + 1} \]

(16)

When CmOCl is precipitating (0.5 < \( \alpha < 1.0 \)), the theoretical titration curve can be written as:

\[ \alpha = 1 + \frac{1}{[Cm^{3+}]_{initial}} \left( [O^{2-}]_{bulk} - \frac{K_{eq}}{[O^{2-}]_{bulk}} \right) \]

(17)

In the range (1.0 < \( \alpha < 1.5 \)), where Cm\(_2\)O\(_3\) is precipitating, the theoretical titration curve is:

\[ \alpha = 1.5 + \frac{1}{[Cm^{3+}]_{initial}} \left( [O^{2-}]_{bulk} - \frac{1.5 \cdot (K_{eq})^{1/2}}{[O^{2-}]_{bulk}^{3/2}} \right) \]

(18)

<table>
<thead>
<tr>
<th>Molten solvent</th>
<th>Temperature, K</th>
<th>( pK_{CmO^+} )</th>
<th>( pK_{CmOCl} )</th>
<th>( pK_{Cm_2O_3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3LiCl-2KCl</td>
<td>723</td>
<td>2.5±0.2</td>
<td>7.5±0.2</td>
<td>15.5±0.5</td>
</tr>
<tr>
<td></td>
<td>823</td>
<td>2.4±0.2</td>
<td>5.7±0.2</td>
<td>12.7±0.5</td>
</tr>
<tr>
<td></td>
<td>923</td>
<td>0.8±0.1</td>
<td>5.2±0.2</td>
<td>12.5±0.5</td>
</tr>
<tr>
<td>NaCl-KCl</td>
<td>1023</td>
<td>2.6±0.2</td>
<td>5.9±0.2</td>
<td>12.9±0.4</td>
</tr>
<tr>
<td></td>
<td>1073</td>
<td>2.4±0.2</td>
<td>5.8±0.2</td>
<td>12.6±0.4</td>
</tr>
<tr>
<td></td>
<td>1123</td>
<td>1.3±0.1</td>
<td>5.6±0.2</td>
<td>12.1±0.4</td>
</tr>
<tr>
<td>NaCl-2CsCl</td>
<td>829</td>
<td>4.2±0.2</td>
<td>7.9±0.2</td>
<td>20.1±0.3</td>
</tr>
<tr>
<td></td>
<td>923</td>
<td>3.4±0.2</td>
<td>7.5±0.2</td>
<td>18.5±0.3</td>
</tr>
<tr>
<td></td>
<td>1023</td>
<td>3.7±0.2</td>
<td>6.7±0.2</td>
<td>16.8±0.3</td>
</tr>
</tbody>
</table>

Table 2. The experimental values of dissociation constants of CmO\(^+\), CmOCl and Cm\(_2\)O\(_3\) in fused solvents at different temperatures, (molality scale)

The best conformity of the experimental and theoretical titration curves at different temperatures is obtained with the constants, offers in Table 2. All results are presented in Tables 3-5. Thermodynamic data allowed us to draw the potential-pO\(_2\)-diagrams, Fig. 2-4, which summarized the stability areas of curium compounds in different solvents at various temperatures.

The decreasing of the temperature and the shift of the ionic radius of the solvent (in \( z/r, \) nm) [Lebedev, 1993] from LiCl up to CsCl mixtures show regular decreasing of the solubility of curium in the solvents [Yamana, 2003].
### System Expression for equilibrium potential

<table>
<thead>
<tr>
<th>SystemExpression</th>
<th>Expression for equilibrium potential</th>
<th>Apparent standard potential (V vs. Cl⁻/Cl₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Cm³⁺ + 3e⁻ ↔ Cm</td>
<td>( E_1 = E_1^* + \frac{2.3RT}{3F} \log [Cm^{3+}] )</td>
<td>( E^* (1) = -2.924 )</td>
</tr>
<tr>
<td>2. CmO⁺ + 3e⁻ ↔ Cm + O²⁻</td>
<td>( E_2 = E_1^* - \frac{2.3RT}{3F} pK_{eq(CmO^+)} + \frac{2.3RT}{3F} \log [CmO^+] + \frac{2.3RT}{3F} )</td>
<td>( E^* (2) = -3.055 )</td>
</tr>
<tr>
<td>3. CmOCl + 3e⁻ ↔ Cm + O²⁻ + Cl⁻</td>
<td>( E_3 = E_1^* - \frac{2.3RT}{3F} pK_{S(CmOCl)} + \frac{2.3RT}{3F} pO^2^- )</td>
<td>( E^* (3) = -3.220 )</td>
</tr>
<tr>
<td>4. Cm₂O₃ + 6e⁻ ↔ 2Cm + 3O²⁻</td>
<td>( E_4 = E_1^* - \frac{2.3RT}{6F} pK_{S(Cm_2O_3)} + \frac{2.3RT}{2F} pO^2^- )</td>
<td>( E^* (4) = -3.286 )</td>
</tr>
<tr>
<td>5. Cm³⁺ + O²⁻ ↔ CmO⁺</td>
<td>( pK_{eq} = -4.7455 + 5426/T )</td>
<td>( pK_{eq} = 2.5 )</td>
</tr>
<tr>
<td>6. Cm³⁺ + O²⁻ + Cl⁻ ↔ CmOCl</td>
<td>( pK_s = 1.5132 + 3394/T )</td>
<td>( pK_s = 7.5 )</td>
</tr>
<tr>
<td>7. 2Cm³⁺ + 3O²⁻ ↔ Cm₂O₃</td>
<td>( pK_s = 0.779 + 10407.5/T )</td>
<td>( pK_s = 15.5 )</td>
</tr>
</tbody>
</table>

Table 3. Equilibrium potentials and values of apparent standard potentials of redox system in 3LiCl-2KCl at 723 K. \([\text{Cm}^{3+}] = 1 \text{ mol·kg}^{-1}\). Potentials are given vs. Cl⁻/Cl₂ reference electrode.
Recent Trend in Electrochemical Science and Technology

Fig. 2. Potential–pO$_2^-$ diagram for curium in 3LiCl-2KCl eutectic at 723 K. [Cm$^{3+}$] = 1 mol·kg$^{-1}$. Potentials are given vs. Cl$^-$/Cl$_2$ reference electrode.

Fig. 3. Potential–pO$_2^-$ diagram for curium in equimolar NaCl-KCl at 1023 K. [Cm$^{3+}$] = 1 mol·kg$^{-1}$. Potentials are given vs. Cl$^-$/Cl$_2$ reference electrode.
**System Expression for equilibrium potential**

<table>
<thead>
<tr>
<th>System</th>
<th>Expression for equilibrium potential</th>
<th>Apparent standard potential (V vs. Cl⁻/Cl₂) [Cm³⁺] = 1 mol·kg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Cm³⁺ + 3e⁻ ↔ Cm</td>
<td>[ E_1 = E_1^* + \frac{2.3RT}{3F} \log \left[ Cm^{3+} \right] ]</td>
<td>[ E'(1) = -2.727 ]</td>
</tr>
<tr>
<td>2. CmO⁺ + 3e⁻ ↔ Cm + O²⁻</td>
<td>[ E_2 = E_1^* - \frac{2.3RT}{3F} pK_{eq(CmO^+)} + \frac{2.3RT}{3F} \log \left[ CmO^+ \right] + \frac{2.3RT}{3F} pO_2^- ]</td>
<td>[ E'(2) = -2.915 ]</td>
</tr>
<tr>
<td>3. CmOCl + 3e⁻ ↔ Cm + O²⁻ + Cl⁻</td>
<td>[ E_3 = E_1^* - \frac{2.3RT}{3F} pK_{S(CmOCl)} + \frac{2.3RT}{3F} pO_2^- ]</td>
<td>[ E'(3) = -3.128 ]</td>
</tr>
<tr>
<td>4. Cm₂O₃ + 6e⁻ ↔ 2Cm + 3O²⁻</td>
<td>[ E_4 = E_1^* - \frac{2.3RT}{6F} pK_{S(Cm_2O_3)} + \frac{2.3RT}{2F} pO_2^- ]</td>
<td>[ E'(4) = -3.165 ]</td>
</tr>
<tr>
<td>5. Cm³⁺ + O²⁻ ↔ CmO⁺</td>
<td>[ pK_{eq} = -4.7455 + 5426/T ]</td>
<td>[ pK_{eq} = 2.6 ]</td>
</tr>
<tr>
<td>6. Cm³⁺ + O²⁻ + Cl⁻ ↔ CmOCl</td>
<td>[ pK_s = 1.5132 + 3394/T ]</td>
<td>[ pK_s = 5.9 ]</td>
</tr>
<tr>
<td>7. 2Cm³⁺ + 3O²⁻ ↔ Cm₂O₃</td>
<td>[ pK_s = 0.779 + 10407.5/T ]</td>
<td>[ pK_s = 12.9 ]</td>
</tr>
</tbody>
</table>

Table 4. Equilibrium potentials and values of apparent standard potentials of redox system in equimolar NaCl-KCl at 1023 K. [Cm³⁺] = 1 mol·kg⁻¹. Potentials are given vs. Cl⁻/Cl₂ reference electrode.
System | Expression for equilibrium potential | Apparent standard potential (V vs. Cl⁻/Cl₂)
--- | --- | ---
1. Cm³⁺ + 3e⁻ ↔ Cm | 
 \[ E_1 = E_1^* + \frac{2.3RT}{3F} \log \left[ \text{Cm}^{3+} \right] \] | \( E^* (1) = -2.996 \)
2. CmO⁺ + 3e⁻ ↔ Cm + O²⁻ | 
 \[ E_2 = E_2^* - \frac{2.3RT}{3F} pK_{eq(CmO^+)} + \frac{2.3RT}{3F} \log [\text{CmO}^+] + \frac{2.3RT}{3F} pO^{2-} \] | \( E^* (2) = -3.220 \)
3. CmOCl + 3e⁻ ↔ Cm + O²⁻ + Cl⁻ | 
 \[ E_3 = E_3^* - \frac{2.3RT}{3F} pK_{S(CmOCl)} + \frac{2.3RT}{3F} pO^{2-} \] | \( E^* (3) = -3.430 \)
4. Cm₂O₃ + 6e⁻ ↔ 2Cm + 3O²⁻ | 
 \[ E_4 = E_4^* - \frac{2.3RT}{6F} pK_{S(Cm_2O_3)} + \frac{2.3RT}{2F} pO^{2-} \] | \( E^* (4) = -3.546 \)
5. Cm³⁺ + O²⁻ ↔ CmO⁺ | 
 \( pK_{eq} = -4.7455 + 5426/T \) | \( pK_{eq} = 4.2 \)
6. Cm³⁺ + O²⁻ + Cl⁻ ↔ CmOCl | 
 \( pK_s = 1.5132 + 3394/T \) | \( pK_s = 7.9 \)
7. 2Cm³⁺ + 3O²⁻ ↔ Cm₂O₃ | 
 \( pK_s = 0.779 + 10407.5/T \) | \( pK_s = 20.1 \)

Table 5. Equilibrium potentials and values of apparent standard potentials of redox system in NaCl-2CsCl eutectic at 829 K. [Cm³⁺] = 1 mol·kg⁻¹. Potentials are given vs. Cl⁻/Cl₂ reference electrode.
3.2 Transient electrochemical technique

3.2.1 Voltammetric studies on inert electrodes

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. 5, 6. It shows that the cathodic peak potential ($E_p$) is constant from 0.04 V/s up to 0.1 V/s and independent of the potential sweep rate, Fig. 7. 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 sweep rate. So in this case (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 ($\nu$). According to the theory of the linear sweep voltammetry technique [Bard & Folkner, 1980] 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 at scan rates from 0.04 up to 0.1 V/s:

$$E_p - E_{p/2} = -0.77 \frac{RT}{nF}$$

where $E_p$ is a peak potential (V), $E_{p/2}$ is a half-peak potential (V), $F$ is the Faraday constant (96500 C·mol⁻¹), $R$ is the ideal gas constant (J·K⁻¹·mol⁻¹) and $T$ is the absolute temperature (K), $n$ is the number of exchanged electrons. The results are 3.01±0.04.
Fig. 5. Cyclic voltammograms of fused 2LiCl-3KCl-CmCl$_3$ salt at different sweep potential rates at 723 K. Working electrode: W (S = 0.36 cm$^2$). [Cm(III)] = 5.0·10$^{-2}$ mol·kg$^{-1}$

Fig. 6. 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)] = 4.4·10$^{-2}$ mol·kg$^{-1}$
Fig. 7. Variation of the cathodic peak potential as a function Naperian logarithm of the sweep rate in fused NaCl-2CsCl-CmCl$_3$ at 823 K. Working electrode: W ($S$ = 0.59 cm$^2$). [Cm(III)] = $4.4 \cdot 10^{-2}$ mol·kg$^{-1}$

Fig. 8. Square wave voltammogram of NaCl-2CsCl-CmCl$_3$ at 25 Hz at 823 K. Working electrode: W ($S$ = 0.29 cm$^2$). [Cm(III)] = $9.7 \cdot 10^{-3}$ mol·kg$^{-1}$

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. 8 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 [Bard & Folkner, 1980]:

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

(20)
where $T$ is the temperature (in K), $R$ is the ideal gas constant (in J K$^{-1}$ mol$^{-1}$), $n$ is the number of electrons exchanged and $F$ is the Faraday constant (in C·mol$^{-1}$).

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 ($n = 2.99 \pm 0.15$).

The same results were found in the system $3\text{LiCl-2KCl-CmCl}_3$ [Osipenko, 2011].

On differential pulse voltammetry only one peak was fixed at potential range from -1.5 up to -2.2 V vs. Ag/Ag$^+$ reference electrode, Fig. 9. It means that the curium ions reduction process at the electrode is a single step process.

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 curves was obtained, Fig. 10.

So the mechanism of the cathodic reduction of curium (III) ions is the following:

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

(21)

![Differential pulse voltammogram of NaCl-2CsCl-CmCl$_3$ melt at 923 K. [Cm(III)] = 4.4·10$^{-2}$ mol·kg$^{-1}$](image)

Fig. 9. Differential pulse voltammmogram of NaCl-2CsCl-CmCl$_3$ melt at 923 K. [Cm(III)] = 4.4·10$^{-2}$ mol·kg$^{-1}$

### 3.2.2 Diffusion coefficient of Cm (III) ions

The diffusion coefficient of Cm(III) ions in molten chloride media was determined using the cyclic voltammetry technique and applying Berzins-Delahay equation, valid for reversible soluble-insoluble system at the scan rates 0.04-0.1 V/s [Bard & Faulkner, 1980]:

$$I_p = 0.61 \left( nF \right)^{3/2} C_0 S \left( \frac{Dv}{RT} \right)^{1/2}$$

(22)
where $S$ is the electrode surface area (in cm$^2$), $C_0$ is the solute concentration (in mol cm$^{-3}$), $D$ is the diffusion coefficient (in cm$^2$ s$^{-1}$), $F$ is the Faraday constant (in 96500 C mol$^{-1}$), $R$ is the ideal gas constant (in J K$^{-1}$ mol$^{-1}$), $n$ is the number of exchanged electrons, $v$ is the potential sweep rate (in V/s) and $T$ is the absolute temperature (in K).

The values obtained for the different molten chlorides tested at several temperatures are quoted in Table 6.

The diffusion coefficient values have been used to calculate the activation energy for the diffusion process. The influence of the temperature on the diffusion coefficient obeys the Arrhenius’s law through the following equation:

$$D = D_0 \exp \left( -\frac{E_A}{RT} \right) \pm \Delta$$

$$E_A$$

<table>
<thead>
<tr>
<th>Solvent</th>
<th>T/K</th>
<th>D/cm$^2$.s$^{-1}$</th>
<th>-E$_A$/kJ·mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl-KCl</td>
<td>723</td>
<td>9.27·10$^{-6}$</td>
<td>28.2</td>
</tr>
<tr>
<td></td>
<td>823</td>
<td>1.62·10$^{-5}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>923</td>
<td>2.57·10$^{-5}$</td>
<td></td>
</tr>
<tr>
<td>NaCl-2CsCl</td>
<td>873</td>
<td>6.97·10$^{-6}$</td>
<td>44.5</td>
</tr>
<tr>
<td></td>
<td>973</td>
<td>1.33·10$^{-5}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1023</td>
<td>2.49·10$^{-5}$</td>
<td></td>
</tr>
</tbody>
</table>

Table 6. Diffusion coefficient of Cm(III) ions in molten alkali metal chlorides at several temperatures. Activation energy for the curium ions diffusion process.
where $E_A$ is the activation energy for the diffusion process (in kJ·mol$^{-1}$), $D_0$ is the pre-exponential term (in cm$^2$·s$^{-1}$) and $\Delta$ is the experimental error.

From this expression, the value of the activation energy for the Cm(III) ions diffusion process was calculated in the different melts tested (Table 6).

The average value of the radius of molten mixtures ($r_{R^*}$) was calculated by using the following equation [Lebedev, 1993]:

$$ r_{R^*} = \sum_{i=1}^{N} c_i r_i $$  \hspace{1cm} (24)

where $c_i$ is the mole fraction of $i$ cations; $r_i$ is the radius of $i$ cations in molten mixture, consist of $N$ different alkali chlorides, nm.

The diffusion coefficient of curium (III) ions becomes smaller with the increase of the radius of the cation of alkali metal in the line from Li to Cs (Table 6). Such behaviour takes place due to an increasing on the strength of complex ions and the decrease in contribution of $D$ to the “hopping” mechanism. The increase of temperature leads to the increase of the diffusion coefficients in all the solvents.

### 3.2.3 Apparent standard potentials of the redox couple 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$_3$ was used (e.g. Fig. 10). A short cathodic polarisation was applied, 5-15 seconds, 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. 10). 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:

$$ E_{\text{Cm(III)/Cm(0)}} = E_{\text{Cm(III)/Cm(0)}}^* + \frac{RT}{nF} \ln X_{\text{CmCl}_3} $$  \hspace{1cm} (25)

being,

$$ E_{\text{Cm(III)/Cm(0)}}^* = E_{\text{Cm(III)/Cm(0)}}^0 + \frac{RT}{nF} \ln \gamma_{\text{CmCl}_3} $$  \hspace{1cm} (26)

The apparent standard potential is obtained in the mole fraction scale versus the Ag/AgCl (0.75 mol kg$^{-1}$) reference electrode and then transformed into values of potential versus the Cl$^-$/Cl$_2$ reference electrode scale or direct versus Cl$^-$/Cl$_2$ reference electrode. For this purpose the special measurements were carried out for building the temperature dependence between Ag/AgCl (0.75 mol kg$^{-1}$) and Cl$^-$/Cl$_2$ reference electrodes. From the experimental data obtained in this work the following empirical equation for the apparent standard potential of the Cm(III)/Cm(0) system versus the Cl$^-$/Cl$_2$ reference electrode was obtained using:
\[ E^\ast_{\text{Cm(III)/Cm(0)}} = -(3.285 \pm 0.004) + (5.48 \pm 0.15) \times 10^{-4}T + 0.002 \text{ V} \ [3\text{LiCl-2KCl, 723-923 K}] \] (27)

\[ E^\ast_{\text{Cm(III)/Cm(0)}} = -(3.750 \pm 0.006) + (9.98 \pm 0.16) \times 10^{-4}T + 0.003 \text{ V} \ [\text{NaCl-KCl, 1023-1123 K}] \] (28)

\[ E^\ast_{\text{Cm(III)/Cm(0)}} = -(3.407 \pm 0.005) + (5.42 \pm 0.14) \times 10^{-4}T + 0.002 \text{ V} \ [\text{NaCl-2CsCl, 823-1023 K}] \] (29)

The relative stability of complex actinides ions increases with the increase of the solvent cation radius, and the apparent standard redox potential shifts to more negative values [Barbanel, 1985]. Our results are in a good agreement with the literature ones [Smirnov, 1973].

### 3.2.4 Thermodynamics properties

The apparent standard Gibbs energy of formation \( \Delta G^\ast_{\text{CmCl}_3} \) was calculated according by the following expression:

\[ \Delta G^\ast_{\text{CmCl}_3} = nFE^\ast_{\text{Cm(III)/Cm(0)}} \] (30)

The least square fit of the standard Gibbs energy versus the temperature allowed us to determine the values of \( \Delta H^\ast \) and \( \Delta S^\ast \) more precisely by the following equation:

\[ \Delta G^\ast_{\text{CmCl}_3} = \Delta H^\ast_{\text{CmCl}_3} - T \Delta S^\ast_{\text{CmCl}_3} \] (31)

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

\[ \Delta G^\ast_{\text{CmCl}_3} = -950.5 + 0.182 \cdot T \pm 0.6 \text{ kJ mol}^{-1} \ \text{3LiCl-2KCl} \] (32)

\[ \Delta G^\ast_{\text{CmCl}_3} = -1085.3 + 0.312 \cdot T \pm 0.8 \text{ kJ mol}^{-1} \ \text{NaCl-KCl} \] (33)

\[ \Delta G^\ast_{\text{CmCl}_3} = -986.4 + 0.174 \cdot T \pm 0.6 \text{ kJ mol}^{-1} \ \text{NaCl-2CsCl} \] (34)

The calculated values are summarized in Table 7. The average value of the radius of these molten mixtures in this line, pro tanto, is 0.094 nm for fused 3LiCl-2KCl eutectic; 0.1155 nm for fused equimolar NaCl-KCl and 0.143 nm for fused NaCl-2CsCl eutectic [Lebedev, 1993]. From the data given in Table 7 one can see that the relative stability of curium (III) complexes ions is naturally increased in the line (3LiCl-2KCl)\text{eut.} - (NaCl-2CsCl)\text{eut.}.

<table>
<thead>
<tr>
<th>Thermodynamic properties</th>
<th>3LiCl-2KCl</th>
<th>NaCl-KCl</th>
<th>NaCl-2CsCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E^\ast / \text{V} )</td>
<td>-2.752</td>
<td>-2.779</td>
<td>-2.880</td>
</tr>
<tr>
<td>( \Delta G^\ast / (\text{kJ mol}^{-1}) )</td>
<td>-773.4</td>
<td>-781.7</td>
<td>817.1</td>
</tr>
<tr>
<td>( \Delta H^\ast / (\text{kJ mol}^{-1}) )</td>
<td>-950.5</td>
<td>-1085.3</td>
<td>-986.4</td>
</tr>
<tr>
<td>( \Delta S^\ast / (\text{J K}^{-1} \text{mol}^{-1}) )</td>
<td>0.182</td>
<td>0.312</td>
<td>0.174</td>
</tr>
</tbody>
</table>

Table 7. The comparison of the base thermodynamic properties of Cm in molten alkali metal chlorides at 973 K. Apparent standard redox potentials are given in the molar fraction scale.
The changes of the thermodynamic parameters of curium versus the radius of the solvent cation show the increasing in strength of the Cm-Cl bond in the complex ions $\left[\text{CmCl}_6\right]^{3-}$ in the line from LiCl to CsCl [Barbanel, 1985].

4. Conclusion

The electrochemical behaviour of CmCl$_3$ in molten alkali metal chlorides has been investigated using inert (W) electrode at the temperatures range 723-1123 K. Different behaviour was found for the reduction process. At low scan rates (< 0.1 V/s) Cm(III) ions are reversible 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 temperature dependence according to the Arrhenius law. The activation energy for diffusion process was found.

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 influence of the nature of the solvent (ionic radius) on the thermodynamic properties of curium compound was assessed. It was found that the strength of the Cm-Cl bond increases in the line from Li to Cs cation.

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

5. Acknowledgement

This work was carried out with the financial support of ISTC project # 3261.

6. References


Korshunov, B.G.; Safonov, V.V. & Drobot, D.V. (1979). Phase equilibriums in halide systems, Metallurgiya, Moscow, USSR


Smirnov, M.V. (1973). Electrode Potentials in Molten Chlorides, Nauka, Moscow, USSR


This book titled "Recent Trend in Electrochemical Science and Technology" contains a selection of chapters focused on advanced methods used in the research area of electrochemical science and technologies; descriptions of electrochemical systems; processing of novel materials and mechanisms relevant for their operation. This book provides an overview on some of the recent development in electrochemical science and technology. Particular emphasis is given both to the theoretical and the experimental aspect of modern electrochemistry. Since it was impossible to cover the rich diversity of electrochemical techniques and applications in a single issue, the focus is on the recent trends and achievements related to electrochemical science and technology.

How to reference
In order to correctly reference this scholarly work, feel free to copy and paste the following:
