

Electrochemical and calorimetric investigations of some thermodynamic properties of EuCl_3 and EuCl_2 dissolved in alkali chloride melts

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Abstract

The electroreduction of EuCl_3 in alkali chloride melts (NaCl-KCl , KCl , CsCl) was studied in the temperature range 973–1123 K by different electrochemical methods. It was determined that electrochemical reduction of Eu(III) in alkali chloride molten salts occurs via two successive reversible stages involving transfer of one and two electrons. The formal standard potentials of $E_{\text{Eu(II)/Eu}}^*$, $E_{\text{Eu(III)/Eu}}^*$ and formal redox potentials of $E_{\text{Eu(III)/Eu(II)}}^*$ were determined from open-circuit potentiometry and linear sweep voltammetry data. The thermodynamics of formation dilute solutions of europium di- and tri-chloride in alkali chloride melts was determined. The relative partial molar enthalpies of mixing EuCl_2 with alkali chloride melts when dilute solutions are formed have been measured previously by direct calorimetry in a Calvet type calorimeter using of ampoule break-off technique. It was shown that the values determined from electrochemical measurements are in a good agreement with those data obtained by calorimetric method.

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1. Introduction

Rare-earth metals and molten salts are involved in the recycling of spent nuclear fuel. The lanthanide elements, which are present in spent fuel from fast nuclear reactors, can be converted into molten salts by anodic dissolution [1]. The aim is to remove the actinides and lanthanides

from spent fuel. Lanthanides and actinides due to their physical and chemical properties, are the elements the most difficult to separate. Until now, the various elements present in nuclear wastes are separated by hydro-metallurgical processes. The Purex process is the most used technique but permits to recover only U and Pu. Thus many investigations actually focus on alternative technologies based on pyrochemical processes to obtain more compact fuel cycle, allowing the reduction of all wastes. In such techniques, molten alkali salt baths are widely used. Thus a knowledge of the europium (III, II) thermodynamics in molten salts is very useful for the understanding the recycling of spent fuel.

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Chlorides of rare-earth metals in pyrochemical processes usually formed a dilute solution in molten salt medium and in this case as was shown in our works [2,3] an electrochemical transient technique is not only a powerful method for studying electrode kinetics, but also an effective method for determination of thermodynamic properties.

Thus in this article some thermodynamic properties of EuCl_3 and EuCl_2 are determined by electrochemical methods and measured by direct calorimetry in a Calvet type calorimeter with utilization of ampoule break-off technique. Comparison between the electrochemical and calorimetric data has been performed.

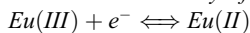
2. Experimental

The preparation of europium (II, III) chloride salts and alkali chloride melts described in detail in [2,3]. The electrochemical study was performed employing the linear sweep voltammetry, cyclic voltammetry and chronopotentiometry (CP) methods using a VoltaLab-40 potentiostat with packaged software 'VoltaMaster 4'. The potential scan rate was varied between 5×10^{-3} and 5.0 V s^{-1} . The experiments were carried out in a temperature range 973–1123 K. The cyclic voltammetric curves and chronopotentiograms were recorded at 0.8–2.0 mm diameter glassy carbon and different metallic electrodes with respect to a glassy carbon plate as a quasi-reference electrode and to a silver–silver chloride reference electrode, $\text{Ag}/\text{NaCl-KCl-AgCl}$ (2 wt.%). The glassy carbon ampoule served as the counter electrode. The potentials from silver–silver chloride reference electrode were converted to a Cl^-/Cl_2 reference electrode.

The mixing experiments were all of the simple liquid–liquid type, performed under argon at atmospheric pressure. The calorimetric apparatus, a Calvet-type high-temperature microcalorimeter, the mixing devices used and the experimental methods adopted have all been described in some details elsewhere [4].

3. Results and discussion

3.1. Electrochemistry of redox process



The electrochemistry of the redox process in NaCl-KCl melt in the temperature range 973–1123 K on glassy carbon electrode was studied in detail previously [3,5]. A similar electrochemical behavior was obtained for KCl and CsCl melts. The cyclic voltammetric curves in the NaCl-KCl-EuCl_3 melt for the $\text{Eu(III)}/\text{Eu(II)}$ redox couple obtained at the glassy carbon electrode are presented in Fig. 1. Wave 1 is observed in the cathodic–anodic

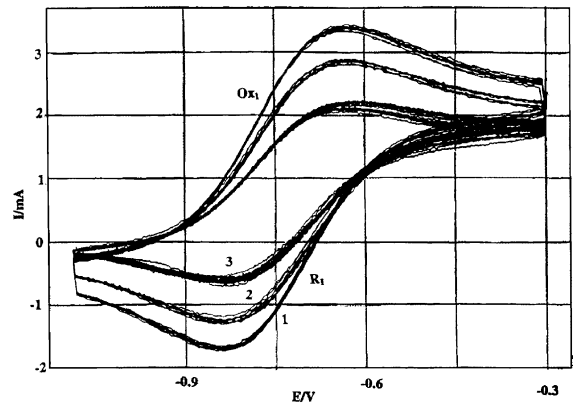
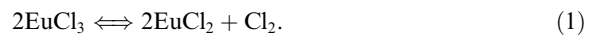


Fig. 1. A series of cyclic voltammograms at a glassy carbon electrode for various scan rates in NaCl-KCl-EuCl_3 melt. Area: 0.19 cm^2 ; temperature: 973 K; concentration of EuCl_3 : $9.0 \times 10^{-5} \text{ mol cm}^{-3}$. Reference electrode: Cl_2/Cl^- . 1– $v = 0.1 \text{ V s}^{-1}$; 2– $v = 0.075 \text{ V s}^{-1}$; 3– $v = 0.05 \text{ V s}^{-1}$.

region indicates the appearance of Eu(II) in the melt according to the reaction [5]



It was found that in alkali chloride melts the peak current of the electroreduction process is directly proportional to the square root of the polarization rate, while the peak potential does not depend on the polarization rate up to $v = 0.1 \text{ V s}^{-1}$. The peak current is a linear function on the EuCl_3 concentration, while the peak potential does not depend on the concentration of europium trichloride in the melt. The potentiostatic electrolysis at potentials of the cathodic peak did not lead to the formation of any solid phase at the electrode and no visible transformation of the electrode itself was observed. According to the theory of linear sweep voltammetry [6], up to polarization rate of 0.1 V s^{-1} , the electrode process is controlled by the rate of mass transfer and yields a reduced form soluble in the melt.

3.2. Formal standard potentials of $E_{\text{Eu(III)}/\text{Eu(II)}}^*$ in alkali chloride melts

According to the theory of linear sweep and steady state voltammetry the following relations are valid for the reversible electrochemical reduction between the cathodic and anodic peak potentials and half-wave potential [7]

$$E_p^C = E_{1/2} - 1.11(RT/F), \quad (2)$$

$$E_p^A = E_{1/2} + 1.11(RT/F), \quad (3)$$

$$(E_p^C + E_p^A)/2 = E_{1/2}, \quad (4)$$

where

$$E_{1/2} = E_{\text{Eu(III)/Eu(II)}}^0 + RT/F \ln(D_{\text{Eu(II)}}/D_{\text{Eu(III)}})^{1/2} + RT/F \ln(\gamma_{\text{Eu(III)}}/\gamma_{\text{Eu(II)}}). \quad (5)$$

In the concentration range of ions with mole fraction (N) less than $(3-5) \times 10^{-2}$ the activity coefficients in the molten salts remain constant which leads up to the values of the formal standard potentials [15]

$$E_{\text{Eu(III)/Eu(II)}}^* = E_{\text{Eu(III)/Eu(II)}}^0 + RT/F \times \ln(\gamma_{\text{Eu(III)}}/\gamma_{\text{Eu(II)}}). \quad (6)$$

The formal standard redox potentials of $E_{\text{Eu(III)/Eu(II)}}^*$ were calculated from the following equations

$$E_{\text{Eu(III)/Eu(II)}}^* = E_p^C + 1.11(RT/F) + RT/F \times \ln(D_{\text{Eu(III)}}/D_{\text{Eu(II)}})^{1/2}, \quad (7)$$

$$E_{\text{Eu(III)/Eu(II)}}^* = E_p^A - 1.11(RT/F) + RT/F \times \ln(D_{\text{Eu(III)}}/D_{\text{Eu(II)}})^{1/2}, \quad (8)$$

$$E_{\text{Eu(III)/Eu(II)}}^* = (E_p^C + E_p^A)/2 + RT/F \times \ln(D_{\text{Eu(III)}}/D_{\text{Eu(II)}})^{1/2}. \quad (9)$$

The diffusion coefficients $D_{\text{Eu(III)}}$ and $D_{\text{Eu(II)}}$ were taken from our study [9]. Thus using the values of potential peaks of the redox process and the diffusion coefficients of Eu(III) and Eu(II) it was found that the formal standard redox potentials are described by the following empirical dependencies:

$$E_{\text{Eu(III)/Eu(II)}}^*/V = -(0.971 \pm 0.006) + (1.9 \pm 0.2) \times 10^{-4} T/K \quad (\text{NaCl-KCl}), \quad (10)$$

$$E_{\text{Eu(III)/Eu(II)}}^*/V = -(1.008 \pm 0.008) + (2.1 \pm 0.3) \times 10^{-4} T/K \quad (\text{KCl}), \quad (11)$$

$$E_{\text{Eu(III)/Eu(II)}}^*/V = -(1.418 \pm 0.005) + (4.2 \pm 0.2) \times 10^{-4} T/K \quad (\text{CsCl}). \quad (12)$$

3.3. Formal standard potentials of $E_{\text{Eu(II)/Eu}}^*$ in alkali chloride melts

It is not possible to use cyclic voltammetry to determine peak of electroreduction of Eu(II) to Eu, because the potentials of europium discharge process and cations of alkali metals are very similar. In the cathodic cycle of the voltammograms, the ascending sections at highly negative potentials resulted in simultaneous electroreduction of europium and alkali metals. Thus cyclic voltammetry does not provide information on determination of formal standard potentials of $E_{\text{Eu(II)/Eu}}^*$. Therefore for these

determinations an open-circuit potentiometry method was used.

Pure europium deposits are formed on a molybdenum electrode in alkali chloride melts by constant current electrolysis with current densities 50–600 mA cm⁻² during 5–120 s. The length of the potential plateau associated with dissolution of europium increased with increasing current densities and time of electrolysis. In some cases the potential plateau remained stable for more than 2–3 min, then slowly shifted toward the positive potential and finally arrived at the rest potential of molybdenum in the melt (Fig. 2). Plots of the plateau potential against log N give linear relationships with slopes, which are very close to the Nernst slope $2.3RT/2F$ for a reversible transfer of two electrons. A least squares calculation yields values of the formal standard potentials $E_{\text{Eu(II)/Eu}}^*$ (referred to Cl⁻/Cl₂ reference electrode) at each temperature. The dependence on temperature is accurately represented by the following empirical relations:

$$E_{\text{Eu(II)/Eu}}^*/V = -(4.08 \pm 0.01) + (8.2 \pm 0.2) \times 10^{-4} T/K \quad \text{NaCl-KCl}, \quad (13)$$

$$E_{\text{Eu(II)/Eu}}^*/V = -(4.17 \pm 0.01) + (8.9 \pm 0.2) \times 10^{-4} T/K \quad \text{KCl}, \quad (14)$$

$$E_{\text{Eu(II)/Eu}}^*/V = -(4.23 \pm 0.01) + (9.3 \pm 0.2) \times 10^{-4} T/K \quad \text{CsCl}. \quad (15)$$

3.4. Formal standard potentials of $E_{\text{Eu(III)/Eu}}^*$ in alkali chloride melts

The formal standard potential $E_{\text{Eu(III)/Eu}}^*$ was calculated from Luter's equation

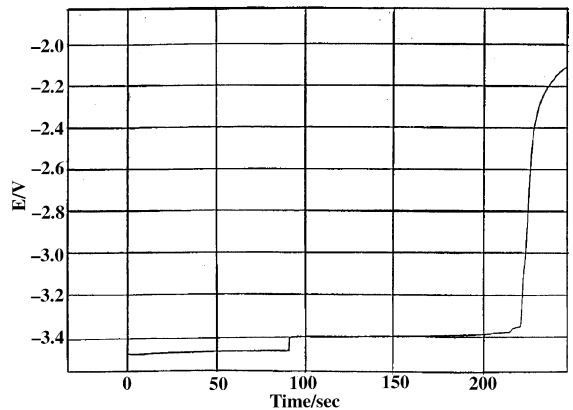


Fig. 2. Open-circuit potential decay of molybdenum electrode after polarization. Time of polarization: 90 s; current density: 360 mA cm⁻²; temperature: 1000 K; concentration of EuCl₂: 8.61×10^{-5} mol cm⁻³. Reference electrode: Cl₂/Cl⁻.

$$3E_{\text{Eu(III)/Eu}}^* = E_{\text{Eu(III)/Eu(II)}}^* + 2E_{\text{Eu(II)/Eu}}^* \quad (16)$$

and its temperature dependencies are described by equations

$$E_{\text{Eu(III)/Eu}}^*/V = -(3.044 \pm 0.009) + (6.1 \pm 0.2) \times 10^{-4} T/K \quad \text{NaCl–KCl}, \quad (17)$$

$$E_{\text{Eu(III)/Eu}}^*/V = -(3.166 \pm 0.009) + (6.6 \pm 0.2) \times 10^{-4} T/K \quad \text{KCl}, \quad (18)$$

$$E_{\text{Eu(III)/Eu}}^*/V = -(3.293 \pm 0.008) + (7.6 \pm 0.2) \times 10^{-4} T/K \quad \text{CsCl}. \quad (19)$$

3.5. Calorimetric data

Experimental results were reported in the following and indicated that for all the systems the mixing enthalpies are negative over the whole composition range (Fig. 3) [10]. For all systems the interaction parameter $\lambda = \Delta_{\text{mix}}H_m/x_{\text{EuCl}_2}(1 - x_{\text{EuCl}_2})$ was obtained from the experimental enthalpies. This parameter is representative for the energetic asymmetry in molten salt systems, and its composition dependence may be indicative of complex formation in the melt. The mixing enthalpies become more negative with increasing radius of the alkali ion. The composition dependence of the interaction parameter (Fig. 4) shows the same trend: for each system the values at $x = 0$ and $x = 1$, which correspond to the partial enthalpies at infinite dilution, become more negative when the size of alkali cation increases. A least-squares treatment of the experimental data yields [10]

$$\begin{aligned} \lambda_0(x_{\text{EuCl}_2} \rightarrow 0) &= 52.433 - 7436.2 \times (2/r_{\text{Eu}^{2+}} - 1/r_{M^+}) \\ &\pm 0.5 \text{ kJmol}^{-1}. \end{aligned} \quad (20)$$

The ionic radii were taken as 117, 102, 138, and 152 pm for Eu^{2+} , Na^+ , K^+ , and Rb^+ [11], respectively.

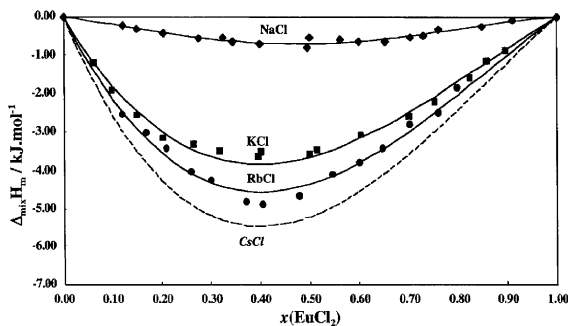


Fig. 3. Molar enthalpies of mixing $\Delta_{\text{mix}}H_m$ of MCl– EuCl_2 liquid binary systems at 1138 K. Dashed line: calculated.

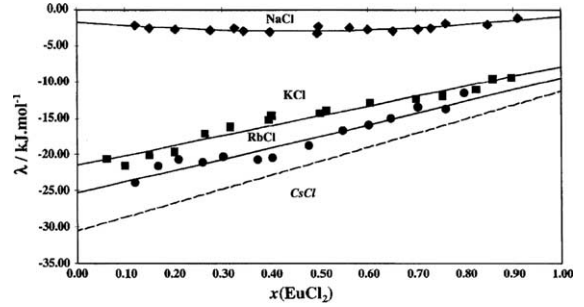


Fig. 4. Variation of the interaction parameter λ with the composition of the MCl– EuCl_2 liquid binary systems. Dashed line: calculated.

3.6. Comparison between the electrochemical and calorimetric data

The change in the partial Gibbs energies for the formation of europium dichloride from the elements in alkali chloride melts was calculated using Eqs. (13)–(15). For the formation of europium dichloride in alkali chloride melts, the following changes in the partial Gibbs energies were obtained

$$\begin{aligned} \Delta \bar{G}_{\text{EuCl}_2}^*/\text{kJ mol}^{-1} &= -(787 \pm 2) + (158 \pm 4) \\ &\times 10^{-3} T/K \quad \text{NaCl–KCl}, \end{aligned} \quad (21)$$

$$\begin{aligned} \Delta \bar{G}_{\text{EuCl}_2}^*/\text{kJ mol}^{-1} &= -(805 \pm 2) + (172 \pm 6) \\ &\times 10^{-3} T/K \quad \text{KCl}, \end{aligned} \quad (22)$$

$$\begin{aligned} \Delta \bar{G}_{\text{EuCl}_2}^*/\text{kJ mol}^{-1} &= -(816 \pm 2) + (180 \pm 4) \\ &\times 10^{-3} T/K \quad \text{CsCl}. \end{aligned} \quad (23)$$

The change in the partial Gibbs energies for the formation of europium trichloride from the elements in alkali chloride melts was calculated using Eqs. (17)–(19).

$$\begin{aligned} \Delta \bar{G}_{\text{EuCl}_3}^*/\text{kJ mol}^{-1} &= -(881 \pm 3) + (176 \pm 6) \\ &\times 10^{-3} T/K \quad \text{NaCl–KCl}, \end{aligned} \quad (24)$$

$$\begin{aligned} \Delta \bar{G}_{\text{EuCl}_3}^*/\text{kJ mol}^{-1} &= -(916 \pm 3) + (191 \pm 6) \\ &\times 10^{-3} T/K \quad \text{KCl}, \end{aligned} \quad (25)$$

$$\begin{aligned} \Delta \bar{G}_{\text{EuCl}_3}^*/\text{kJ mol}^{-1} &= -(953 \pm 2) + (220 \pm 6) \\ &\times 10^{-3} T/K \quad \text{CsCl}. \end{aligned} \quad (26)$$

The first terms in these Eqs. (21)–(26) represent the enthalpy of the reaction, the exothermicity of which increase with increasing stability of the europium chloride complexes. The temperature coefficient, taken with their signs reversed, give the formal standard values of partial entropy of the reactions. The increase of the formal standard partial entropy of the reactions from

Table 1

The relative partial enthalpy of mixing EuCl_2 with alkali chloride melts

System	NaCl	NaCl–KCl	KCl	RbCl	CsCl
Electrochemical	–	+2	–16	–	–27
Calorimetry	–1.6	–	–21.4	–25.3	–30.2

NaCl–KCl to CsCl is due both to a higher degree of order of the reaction products as the result of complex formation and to changes in their natural frequency with increasing stability [8].

The literature thermodynamic data [12] on the reaction of europium with chlorine with formation of liquid dichloride allow us to calculate the change in standard enthalpy, which at 1138 K is -789 kJ mol^{-1} for EuCl_2 . The data of the relative partial molar enthalpy of mixing EuCl_2 with alkali chlorides melts when dilute solution are formed obtained by electrochemical and calorimetric methods are presented in Table 1.

As can be seen from Table 1 the difference between electrochemical and calorimetric data is $3\text{--}5 \text{ kJ mol}^{-1}$. Let us try to discuss lacks and advantages of both methods.

The error in determination of enthalpy mixing by calorimetric method when $x_{\text{EuCl}_2} \rightarrow 0$ is higher than for middle concentration range due to small value of function $x_{\text{EuCl}_2}/(1 - x_{\text{EuCl}_2})$. In this study enthalpy of mixing for dilute solutions was determined by extrapolation of experimental values (straight lines) from relatively high concentration to $x_{\text{EuCl}_2} \rightarrow 0$ (Fig. 4). But usually the enthalpy interaction parameter at small concentration of rare-earth compound change sharply a slope to the region more positive values [13].

Data obtained from electrochemical measurements beside experimental errors, which are indicated in Eqs. (21)–(23) include original thermodynamic data for pure europium dichloride. Thus the accuracy of enthalpy mixing determination by electrochemical method depends on correctness of EuCl_2 standard enthalpy.

Above-mentioned discussion of both methods allow us to conclude that the results obtained by electrochemical and calorimetric methods are in a good agreement.

The change in the relative partial molar enthalpy of mixing EuCl_2 with NaCl and NaCl–KCl melts when dilute solutions are formed is, within experimental error, close to zero. So probably europium dichloride does not form chloride complexes in NaCl– EuCl_2 and NaCl–KCl– EuCl_2 melts. At the same time the values of relative partial molar enthalpy of mixing EuCl_2 with KCl, and CsCl melts at the temperature 1138 K have a negative values due to the complex formation reaction (Table 1).

It is not possible to determine relative partial enthalpy of mixing EuCl_3 with alkali chloride melts using calorimetric method due to decomposition of EuCl_3 [14]. So

Table 2

Activity coefficients of EuCl_3 in alkali chloride melts at temperature 1138 K

Melt	NaCl–KCl	KCl	CsCl
γ_{EuCl_3}	7.2×10^{-2}	1.1×10^{-2}	7.1×10^{-3}

in the case of EuCl_3 electrochemical method has a certain advantage in comparison with calorimetry.

The standard enthalpy of liquid europium trichloride formation from the elements at temperature 1138 K is -865 kJ mol^{-1} [15]. Recently [14] it was determined standard enthalpy of EuCl_3 , which is equal to -873 kJ mol^{-1} . Thus the relative partial enthalpy of mixing EuCl_3 with NaCl–KCl, KCl and CsCl with formation of dilute solutions is -16 , -41 and -88 kJ mol^{-1} if to use data [15], and -8 , -33 and -80 kJ mol^{-1} according to study [14].

The larger values of relative partial enthalpy of mixing EuCl_3 with alkali chloride melts in comparison with EuCl_2 are in agreement with data [16] on the influence of rare-earth metal oxidation state on the enthalpy of mixing.

The activity coefficients (γ) of EuCl_3 were calculated at temperature 1138 K using the change in the partial Gibbs energies for the formation of europium trichloride from the elements in alkali chloride melts (24)–(26) with the reference free energy of formation $\text{EuCl}_3(\text{liq.})$ [14], by means of the equation

$$RT \ln \gamma = \Delta \bar{G}_{\text{EuCl}_3}^* - \Delta G_{\text{EuCl}_3(\text{liq.})}^0 \quad (27)$$

The data on activity coefficients of EuCl_3 are given in Table 2. It is known that complexation power depends on the nature of second coordination sphere. As can be seen from Table 2, the Eu(III) ions are more complexed by the chloride ions in KCl and CsCl melts than in equimolar mixture NaCl–KCl.

4. Conclusion

The thermodynamics of dilute solutions formation of europium di- and tri-chloride in alkali chloride melts have been measured using transient electrochemical techniques. The relative molar enthalpy of mixing EuCl_2 with alkali chloride melts was measured also by direct calorimetry in a Calvet type calorimeter. The values for the relative partial molar enthalpy of mixing EuCl_2 in alkali chloride melts from electrochemical measurements are in a good agreement with data obtaining by calorimetric method.

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