Electrochemical and Thermodynamic Properties of $EuCl_3$ and $EuCl_2$ in an Equimolar NaCl-KCl Melt

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The electroreduction of $EuCl_3$ in an equimolar NaCl-KCl mixture was studied at 973 - 1123 K by different electrochemical methods. This reduction of Eu(III) in NaCl-KCl melt occurs via two successive reversible steps involving transfer of one and two electrons. The diffusion coefficients of Eu(III) and Eu(II) were measured by linear sweep voltammetry and chronopotentiometry. The values found by these methods are in a good agreement. The standard rate constants for the redox reaction $Eu(III) + e^- \Leftrightarrow Eu(II)$ were calculated from cyclic voltammetry data. The sluggish kinetics of this reaction is discussed in terms of substantial rearrangement of the europium coordination sphere. Special attention was paid to the choice of working electrodes for the study of electrode reactions. The formal standard potentials $E^*_{Eu(II)/Eu}$, $E^*_{Eu(III)/Eu}$ and the formal redox potentials $E^*_{Eu(III)/Eu(II)}$ were determined from open-circuit potentiometry and linear sweep voltammetry data. The free Gibbs energy changes for the reaction $EuCl_{3(sol.)} \Leftrightarrow EuCl_{2(sol.)} + 1/2\ Cl_{2(g.)}$ and the equilibrium constants of the metal-salt reaction $2Eu(III) + Eu \Leftrightarrow 3\ Eu(II)$ were calculated. The thermodynamics of the formation of dilute solutions of europium di- and trichloride in an equimolar NaCl-KCl melt were determined. It was shown that electrochemical transient techniques give the possibility of the determination of the relative partial molar mixing enthalpy of europium trichloride and dichloride in NaCl-KCl melt.

Key words: Europium; Molten Salts; Kinetics of Electrode Reaction; Formal Standard Potentials; Mixing Enthalpy.

1. Introduction

Rare-earth metals of high purity are needed in various modern techniques. Electrowinning and electrorefining in molten salts is a promising method for the production of high-purity rare-earth metals [1 - 4]. Electrochemical synthesis is an effective method for obtaining alloys of rare-earth metals in melts [5]. Rare-earth metals and molten salts are also 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 [6]. The actinides are selectively deposited at the cathodes due to the differences among the redox potentials of the elements while fission products remain in the anode and in the electrolyte [7 - 8]. Among the fission products, the lanthanides and actinides are the most difficult ones to separate. Notwithstanding the active research, especially on rare-earth metal electrowinning and electrorefining, the electrochemistry and thermodynamics of some rare-earth metals in melts have not yet been addressed in depth.

The standard redox potentials $E^*_{Eu(III)/Eu(II)}$ in a eutectic LiCl-KCl melt were determined in [9], and the formal standard potentials $E^*_{Eu(II)/Eu}$ in a eutectic NaCl-CsCl melt were obtained in [10]. In our recent investigations [11 - 12] we studied the electrochemistry of the redox process $Eu(III) + e^- \Leftrightarrow Eu(II)$ by different electrochemical techniques and determined

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the formal standard redox potentials of $E^*_{Eu(III)/Eu(II)}$ in an equimolar sodium-potassium chloride mixture. A direct potentiometric method for the determination of $E^*_{Eu(III)/Eu(II)}$ in NaCl-KCl melt was used in [13]. In [14 - 15] it is shown that linear sweep voltammetry is not only a powerful method for studying electrode kinetics, but also an effective method for the determination of thermodynamic properties.

Thus in this article the electrochemical and thermodynamic properties of $EuCl_3$ and $EuCl_2$ are determined by electrochemical transient techniques in an equimolar NaCl-KCl melt.

2. Experimental Details

2.1. Chemicals; Preparation of Salts

Europium dichloride was synthesized from Eu_2O_3 (Johnson Matthey, 99.9%). Thionyl chloride (Johnson Matthey, 99%) was used as a chlorinating agent. The $SOCl_2$ vapour was carried through solid Eu_2O_3 at 823 K by argon during 6 hours. $EuCl_3$ was obtained in the first step of this synthesis. Reduction to $EuCl_2$ was performed by zinc. Europium trichloride and zinc, in a twofold excess with respect to stoichiometry, were put into a quartz ampoule inside a silica reactor, which was evacuated to a pressure of about 1 Pa. The temperature was gradually increased up to 773 K and kept for 3 hours under static vacuum. Then the temperature was increased to 1093 K and kept during 5 hours still under static vacuum. Finally, the $EuCl_2$ compound was separated from zinc by distillation at 1193 K. Chemical analysis of the prepared $EuCl_2$ was performed by mercurimetric (chloride) and complexometric (EDTA in presence of xylenole orange - europium) methods. Results of the analysis showed that the ratio Cl/Eu was essentially two. Due to the highly hygroscopic properties of lanthanide compounds, $EuCl_3$ and $EuCl_2$ were stored in sealed glass ampoules under vacuum. All further handling of europium chlorides and filling of experimental cells were performed in a controlled purified argon atmosphere glove-box (water content less than 2 ppm).

Alkali chlorides (NaCl and KCl) were purchased from Prolabo (99.5% min.). They were dehydrated by continuous and progressive heating just above the melting point under gaseous HCl atmosphere in quartz ampoules. Excess HCl was removed from the melt by argon. The salts were handled in the glove box and stored in sealed glass ampoules, as explained above. The total concentration of europium was determined by inductively coupled plasma atomic spectroscopy (ICP-AES). Determination of Eu(II) in quenched samples was performed by potentiometric titration with potassium dichromate.

2.2. Procedures and Electrochemical Cell

Chlorides of sodium and potassium were mixed in required ratio, placed in an ampoule made of glassy carbon of the SU-2000 type and transferred to a hermetically sealed retort of stainless steel. The latter was evacuated to a residual pressure of $5 \cdot 10^{-3}$ Torr, first at room temperature and then at higher temperatures (473, 673 and 873 K). After this the retort was filled with high purity argon and the electrolyte was melted.

The study was performed employing linear sweep voltammetry (LSV), cyclic voltammetry (CV), chronopotentiometry (CP) and reversal chronopotentiometry (RCP) methods using a VoltaLab-40 potentiostat with packaged software "VoltaMaster 4". The potential scan rate was varied between $5 \cdot 10^{-3}$ and $5.0\ Vs^{-1}$. The experiments were carried out at 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 reference electrode, Ag/NaCl-KCl-AgCl (2 wt%). The glassy carbon ampoule served as the counter electrode. The potentials from the silver reference electrode were converted to a Cl^-/Cl_2 reference electrode.

3. Results and Discussion

3.1. Choice of Working Electrodes Materials

In our studies [11 - 12] all results for the redox process

$$Eu(III) + e^- \Leftrightarrow Eu(II) \qquad (1)$$

were obtained at a glassy carbon electrode. The cyclic voltammetric curves in the NaCl-KCl-$EuCl_3$ melt obtained at a glassy carbon electrode are presented in Figure 1. Wave 1 is observed in the cathodic-anodic region that indicates the appearance in the melt of Eu(II) due to the reaction

$$2\ EuCl_3 \Leftrightarrow 2\ EuCl_2 + Cl_2. \qquad (2)$$

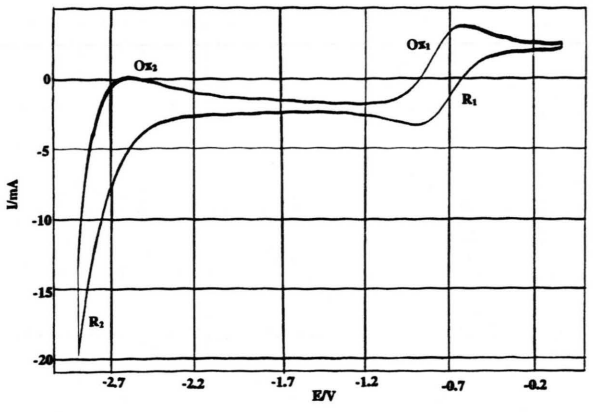

Fig. 1. Cyclic voltammograms (7 cycles) at a glassy carbon electrode in NaCl-KCl-$EuCl_3$ melt. Area: 0.18 cm^2. Sweep rate: 0.15 V s^{-1}. Temperature: 973 K. Concentration of $EuCl_3$: 6.64 · 10^{-5} mol cm^{-3}. Reference electrode: Cl_2/Cl^-.

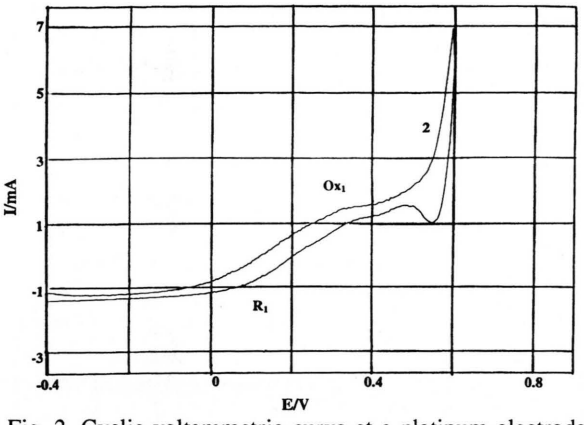

Fig. 2. Cyclic voltammetric curve at a platinum electrode in NaCl-KCl-$EuCl_3$ melt. Area: 0.16 cm^2. Sweep rate: 0.05 V s^{-1}. Temperature: 973 K. Concentration of $EuCl_3$: 9.25 · 10^{-5} mol cm^{-3}. Quasi-reference electrode: glassy carbon. 1: Eu(III)+e^- ↔ Eu(II); 2: Pt-2e ↔ Pt(II).

This result agrees with [16], where it was found that the trichloride of europium starts to decompose into dichloride and chlorine in the solid phase at temperatures above 300 °C.

For the study of the process (1) it is also possible to use a platinum electrode. As can be seen from the Fig. 2 the difference of potentials between the redox reaction (1) and dissolution of platinum Pt –2e → Pt(II) is not large, and the initial section of the wave 1 is short. Thus there are some difficulties in the peak current determination and the calculation of the diffusion coefficient when using a platinum electrode.

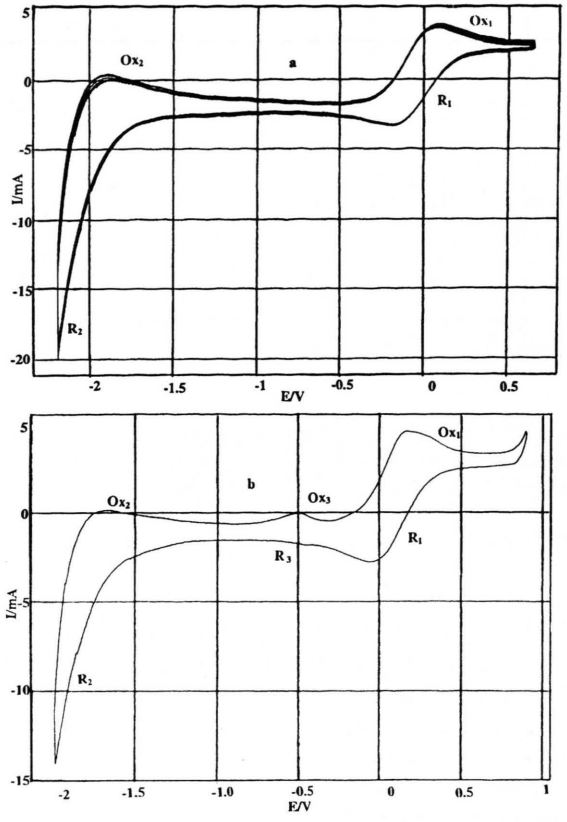

Fig. 3. Cyclic voltammograms at a glassy carbon electrode in NaCl-KCl-$EuCl_3$ melt; a: before; b: after exposure of tungsten electrode in the melt during 5 min. Sweep rate: 0.15 V s^{-1}. Temperature: 973 K. Concentration of $EuCl_3$: 6.64·10^{-5} mol cm^{-3}. Quasi-reference electrode: glassy carbon. 1: Eu(III)+e^- ↔ Eu(II); 2: Eu(II)+2e^- ↔ Eu(II); 3: W(II))+2e^- ↔ W.

In the molten NaCl-KCl-$EuCl_3$ system, molybdenum or tungsten electrodes interact with the melt due to reaction

$$2\,Eu(III) + Me \Leftrightarrow 2\,Eu(II) + Me(II), \qquad (3)$$

where Me = Mo, W.

The cyclic voltammograms of the NaCl-KCl-$EuCl_3$ melt before and after tungsten exposure are presented in the Fig. 3, where it is seen that due to reaction (3) the cathodic part (R_1) of the recharge wave is decreased and the anodic part (Ox_1) is increased. The appearance of additional redox waves (R_3, Ox_3) of tungsten cations at more negative potentials than process (1) was observed on cyclic voltammograms. So the molybdenum and tungsten electrodes have more negative potentials of dissolution than the re-

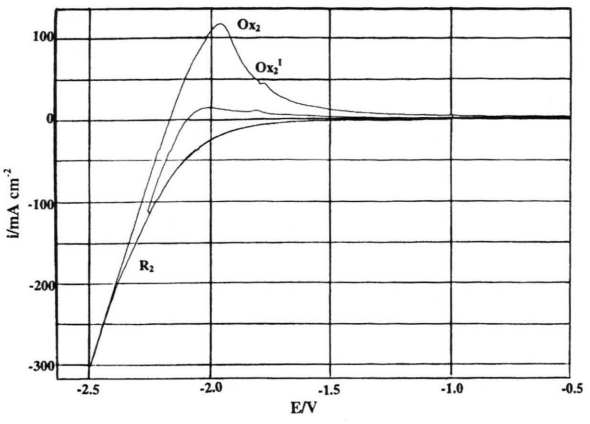

Fig. 4. Cyclic voltammograms at a glassy carbon electrode in NaCl-KCl-$EuCl_2$ melt at different values of reverse potential. Sweep rate: 0.1 V s^{-1}. Temperature: 973 K. Concentration of $EuCl_2$: $6.60 \cdot 10^{-5}$ mol cm^{-3}. Quasi-reference electrode: glassy carbon.

dox potentials of the electrode reaction (1) and it is not possible to registrate the process (1) at these electrodes. Thus the more suitable electrode for the study of redox reaction (1) is of glassy carbon.

Special attention should be paid to the choice and behavior of the working electrode for the study of the process

$$Eu(II) + 2\,e^- \Leftrightarrow Eu. \qquad (4)$$

At high temperature europium can react with many materials and to form alloys with metallic substrates and carbides with carbon electrodes [17]. At a glassy carbon electrode in the cathodic half cycle it was difficult to observe the process of europium carbide formation, but in the anodic half cycle the processes of electrooxidation of europium (wave Ox_2) and europium carbide (wave Ox_2^I) are recorded quite clearly (Fig. 4). At more negative potentials the process of europium discharge can be complicated by the electroreduction of sodium and potassium which form intercalation compounds or carbides on a glassy carbon electrode [18]. It is not the aim of the present paper to discuss the problem of using a glassy carbon electrode for investigation of the process (4). The use of glassy carbon electrodes for studying of electroreduction of refractory metal complexes was discussed in [19].

The aforementioned results indicate that for negative potentials which imply process (4) it is better to use metallic electrodes. The popular metallic electrodes are platinum, copper, silver, nickel. Voltammetric studies showed the formation of intermetallic compounds during discharge of europium on these substrates (Fig. 5). The number of waves on voltammograms due to alloy formation depends on the ex-

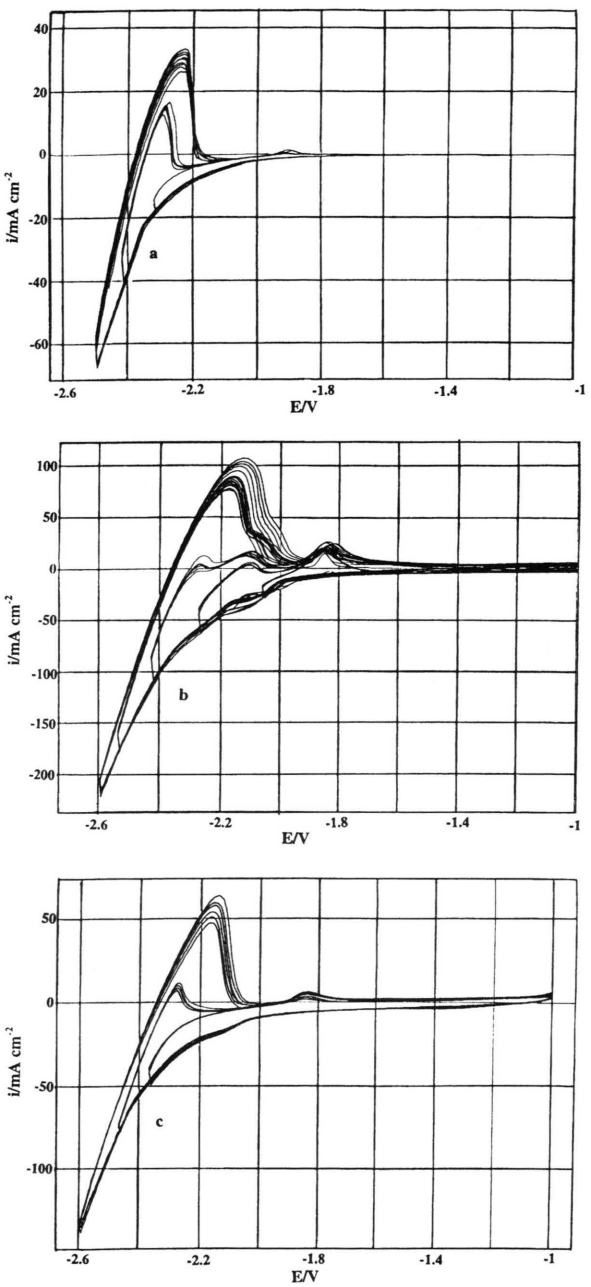

Fig. 5. Cyclic voltammograms at a platinum (a), silver (b) and khantal (c) electrode in NaCl-KCl-$EuCl_2$ melt at different values of reverse potential. Sweep rate: 0.1 V s^{-1}. Temperature: 973 K. Quasi-reference electrode: glassy carbon.

Table 1. A, B and Δ of (5) for Eu(III) complexes and activation energy ΔU for diffusion in NaCl-KCl melt.

Method	A	B	Δ	D / $cm^2s^{-1}\cdot10^5$ 1100 K	ΔU / kJ mol^{-1}
LSV[a]	2.42	2152	0.03	4.20	41.2
LSV[b]	2.33	2256	0.04	4.16	43.2
CP	2.30	2272	0.04	4.31	43.5
RCP	2.41	2171	0.03	4.13	41.6

Polarization rate: [a] 0.1 Vs^{-1}, [b] 1.0 Vs^{-1}.

Table 2. A, B and Δ of (5) for Eu(II) complexes and activation energy ΔU for diffusion in NaCl-KCl melt.

Method	A	B	Δ	D / $cm^2s^{-1}\cdot10^5$ 1100 K	ΔU / kJ mol^{-1}
LSV[a]	2.31	1983	0.03	7.71	38.0
LSV[b]	2.33	1976	0.03	7.48	37.8
CP	2.34	1956	0.02	7.62	37.5
RCP	2.36	1942	0.02	7.49	37.2

Polarization rate: [a] 0.1 Vs^{-1}, [b] 1.0 Vs^{-1}.

perimental conditions: the nature of substrate, temperature, sweep rate, reverse potential value, electrolyte composition and etc. [20]. It is necessary to note that the process of electron transfer and alloy formation is one elementary act. Alloy formation is a common process during the metal deposition from molten salts [21 - 23]. The ignorance of alloy formation has led to numerous mistakes in the interpretation of electrode reactions and the determination of kinetic parameters. The alloying can be studied by electrochemical techniques such as current reversal chronopotentiometry, which was used successfully for the determination of thermodynamic properties of intermetallic compounds [21]. The material of the working electrode is selected mainly on the base of phase equilibrium diagrams: "deposited metal-substrate" and the values of the interdiffusion coefficients in this couple. A working electrode which forms a solid solution with deposited metal with a low or insignificant solubility is preferable. From this point of view, molybdenum and tungsten are preferable working electrodes for the study of the process (4) because they don't form intermetallic compounds with europium [17], and the interdiffusion coefficients of the europium-molybdenum (tungsten) couple are small. Nevertheless, on the tungsten electrode an additional peak at more positive potentials then formation of europium on cyclic voltammograms was observed. The additional peak was obtained also during lanthanum and gadolinium deposition on a tungsten electrode in LiCl-KCl melt [24]. Probably the nature of this peak is connected with surface alloying.

3.2. Electrochemistry of the Redox Process $Eu(III) + e^- \Leftrightarrow Eu(II)$

The electrochemical redox process Eu(III) + e^- ⇔ Eu(II) in an equimolar NaCl-KCl melt at 973 - 1123 K on glassy carbon electrodes was studied by linear sweep voltammetry, cyclic voltammetry, chronopotentiometry and reversal chronopotentiometry [4]. It was found that at a sweep rate of $\nu \leq 0.1$ Vs^{-1} the electroreduction of Eu(III) to Eu(II) is reversible, at $0.1 < \nu \leq 0.3$ Vs^{-1} mixed diffusion and electron-transfer control is observed, and $\nu \geq 0.5$ Vs^{-1} results in electron-transfer control. The diffusion coefficients of Eu(III) and Eu(II) were determined by linear sweep voltammetry and chronopotentiometry.

The coefficients A, B and Δ of the equation

$$\log D = -A - B/T \pm \Delta, \tag{5}$$

the diffusion coefficient D at 1100 K, and the activation energy ΔU for diffusion of Eu(III) and Eu(II) in NaCl-KCl are given in Tables 1 and 2. ΔU was calculated from the equation

$$-\Delta U/2.303\,R = \partial \log D/\partial(1/T). \tag{6}$$

As can be seen from the Tables 1 and 2, the diffusion coefficients of Eu(III) and Eu(II) obtained by linear sweep voltammetry at the polarization rates 0.1 and 1.0 Vs^{-1} agree well and are close to the values determined from chronopotentiometry and reversal chronopotentiometry methods. The diffusion coefficients decrease when the europium oxidation state increases, while the activation energies for diffusion increase. So D decreases and ΔU increases with increasing ionicity of the diffusing species. These results agree well with numerous data on the influence of oxidation state of central atoms on diffusion coefficients and activation energies for diffusion of complexes [25]. The decrease in D is related to the increased strength of the complexes, and this in turn leads to a decrease in the contribution to the diffusion coefficient from the "hopping" mechanism as discussed in [26].

Table 3. Influence of the temperature on the standard rate constant k_s for the redox reaction Eu(III) + e^- ⇔ Eu(II) in equimolar NaCl-KCl melt.

Temperature / K	973	1023	1073
k_s / cm s^{-1}	$0.80 \cdot 10^{-2}$	$1.25 \cdot 10^{-2}$	$2.27 \cdot 10^{-2}$

Knowing the value of $D_{Eu(III)}$, it is possible to determine the diffusion layer thickness (δ) from the cathodic plateau of the steady-state voltammetric curve, which is described by

$$i_d = nFCD/\delta. \tag{7}$$

The diffusion limited current density i_d was 10.2 mA cm^{-2} at 1073 K, and the concentration C of $EuCl_3$ $8.21 \cdot 10^{-5}$ mol cm^{-3}, and hence $\delta = 2.9 \cdot 10^{-2}$ cm.

The problem of determining kinetic parameters on the basis of cyclic voltammetry was considered by Nicholson [27]. The standard rate constant of the electrode process is related to the function ψ as

$$\psi = \frac{k_s \left(D_{ox}/D_{red}\right)^{\alpha/2}}{\pi^{1/2} D_{ox}^{1/2} \left(nF/RT\right)^{1/2} \nu^{1/2}}. \tag{8}$$

Here ψ is a function related to the difference between the peaks potentials $E_p^A - E_p^C$ (mV), k_s is the standard rate constant of the electrode process (cm s^{-1}), and $\alpha = 0.5$ is the transfer coefficient.

The dependencies $E_p^A - E_p^C$ on the function ψ reported in [27] for 298 K must be recalculated for the present working temperatures. The recalculation was performed using the equations [28]

$$(\Delta E_p)_{298} = (\Delta E_p)_T 298/T \tag{9}$$

$$\psi_T = \psi_{298}(T/298)^{1/2} \tag{10}$$

The values of the ψ_T function, obtained by means of (9) and (10), and used in conjunction with (8) made it possible to calculate the standard rate for charge transfer. The influence of the temperature on the standard rate constant k_s of the electrode reaction (1) is presented in the Table 3.

According to the classification in [29, 30], the values of these constants confirm that at $\nu = 0.2$ V s^{-1}, the process (1) proceeds quasi-reversibly mostly under diffusion control.

3.3. Formal Standard Redox Rotentials $E^*_{Eu(III)/Eu(II)}$

According to the theory of linear sweep and steady state voltammetry the following relations are valid for the reversible electrochemical reduction (1) between the cathodic and anodic peak potentials and half-wave potential [31]

$$E_p^C = E_{1/2} - 1.11(RT/F), \tag{11}$$

$$E_p^A = E_{1/2} + 1.11(RT/F), \tag{12}$$

$$(E_p^C + E_p^A)/2 = E_{1/2}, \tag{13}$$

where

$$E_{1/2} = E^0_{Eu(III)/Eu(II)} + RT/F \ln(D_{red}/D_{ox})^{1/2} + RT/F \ln(\gamma_{ox}/\gamma_{red}) \tag{14}$$

In the concentration range of ions with mole fraction (N) less than $(3 - 5) \cdot 10^{-2}$, the coefficients of activity in molten salts remain constant leads up to the values of the formal standard potentials [32]

$$E^*_{Eu(III)/Eu(II)} = E^0_{Eu(III)/Eu(II)} + RT/F \ln(\gamma_{ox}/\gamma_{red}). \tag{15}$$

The formal standard redox potentials of $E^*_{Eu(III)/Eu(II)}$ were calculated from the equations

$$E^*_{Eu(III)/Eu(II)} = E_p^C + 1.11(RT/F) + RT/F \ln(D_{ox}/D_{red})^{1/2}, \tag{16}$$

$$E^*_{Eu(III)/Eu(II)} = E_p^A - 1.11(RT/F) + RT/F \ln(D_{ox}/D_{red})^{1/2}, \tag{17}$$

$$E^*_{Eu(III)/Eu(II)} = (E_p^C + E_p^A)/2 + RT/F \ln(D_{ox}/D_{red})^{1/2}. \tag{18}$$

Thus using the values for the potential peaks of process (1) and the coefficients of diffusion of Eu(III) and Eu(II), it was found that the formal standard redox potentials are described by the empirical relation [11 - 12]

$$E^*_{Eu(III)/Eu(II)}/\mathrm{V} = -(0.971 \pm 0.006) + (1.9 \pm 0.2) \cdot 10^{-4} T/\mathrm{K} \tag{19}$$

Table 4. The free Gibbs energy changes for the reaction $EuCl_{3(sol.)} \Leftrightarrow EuCl_{2(sol.)} + 1/2\ Cl_{2(g.)}$.

T / K	973	1023	1073	1123
ΔG^* / kJ mol^{-1}	75.8	75.0	74.0	73.1

In [13] the standard formal redox potentials $E^*_{Eu(III)/Eu(II)}$ were measured by direct potentiometry versus a chlorine electrode. These data agree well with our determinations. The difference between our data and study [13] in the temperature range 973 - 1123 K is 4 - 48 mV. In our opinion this difference can be explained by some experimental disadvantages of the investigation [13]. A beryllium oxide crucible was used as a container for the NaCl-KCl-$EuCl_3$-$EuCl_2$ melt that does not exclude the interaction of oxide material with the melt due to the reaction

$$3\ EuCl_4^{2-} + 2\ O^{2-} \Leftrightarrow EuOCl + Eu + 10\ Cl^- . \quad (20)$$

The occurrence of this reaction changes the ratio of Eu(III)/Eu(II) in the melt. The mistake can be obtained from the results of chemical analyses on the concentration of Eu(III) and Eu(II) in the electrolyte, especially due to the change of temperature from 1233 K to room temperature. In [13], despite on many hours of experimental determination of redox potentials the authors did not observe decomposition of $EuCl_3$. At the same time in our investigation we registrated a decomposition of $EuCl_3$, because the ratio of the anodic to the cathodic current (wave 1, Fig. 1) of redox reaction (1) grew with increasing experimental time.

From the redox potentials (19) it is possible to calculate the free Gibbs energy for the reaction

$$EuCl_{3(sol.)} \Leftrightarrow EuCl_{2(sol.)} + 1/2\ Cl_{2(g.)}. \quad (21)$$

The data obtained for different temperatures are summarized in the Table 4.

3.4. *Cyclic Voltammetry of the Process* $Eu(II) + 2e^- \Leftrightarrow Eu$

Cyclic voltammetric curves recorded at a molybdenum electrode for different values of decay and different values of reverse potential are shown in Figs. 6a,b. In the cathodic half cycle of the voltammograms, the ascending sections at highly negative potentials resulted in the simultaneous electroreduction of europium and alkali metals ions. In the anodic half cycle

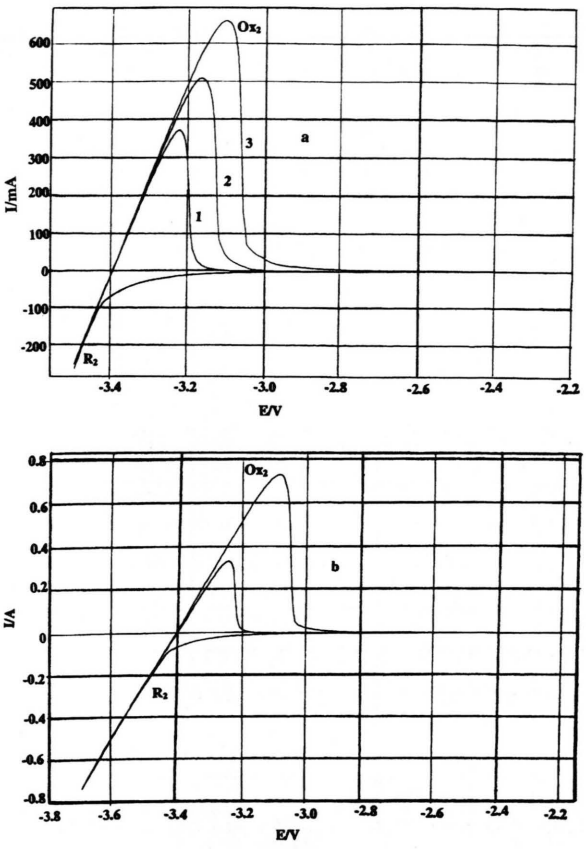

Fig. 6. Cyclic voltammetric curves recorded at a molybdenum electrode in NaCl-KCl-$EuCl_2$ melt; a: for different times of decay at reverse potential, 1: 0 sec, 2: 1 sec, 3: 2 sec; b: for different values of reverse potential. Sweep rate: 0.10 V s^{-1}. Temperature: 1000 K. Concentration of $EuCl_2$: $8.61 \cdot 10^{-5}$ mol cm^{-3}. Reference electrode: Cl_2/Cl^-.

the height of the stripping wave of europium dissolution increased with increasing of time decay (Fig. 6a) and negative values of the reverse potential (Fig. 6b).

Alkali metals (Me-Na, K) which are formed during electroreduction can interact in the vicinity of the electrode with europium dichloride according to the reaction

$$2\ Me + EuCl_2 \Leftrightarrow 2\ MeCl + Eu. \quad (22)$$

Reaction (22) leads to a decrease of the europium concentration in the vicinity of the electrode in comparison with its concentration in the bulk of the melt. On the other hand, formation of alkali metals or europium solutions results in the appearance of electronic conductivity in the melt, which brings about the shift of the electrochemical interface into the bulk

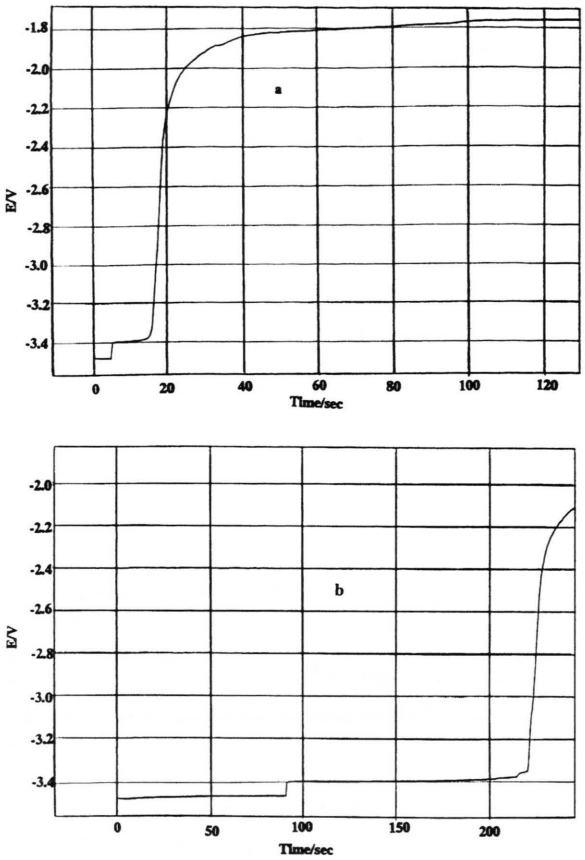

Fig. 7. Open-circuit potential decay of molybdenum electrode after polarization. Time of polarization: a: 5 sec, b: 90 sec; Current density: 360 mA cm^{-2}. Temperature: 1000 K. Concentration of $EuCl_2$: 8.61 · 10^{-5} mol cm^{-3}. Reference electrode: Cl_2/Cl^-.

of the melt. Probably this shift is quite large, because the diffusion coefficients of alkali metals have values of 10^{-3} - 10^{-2} cm^2s^{-1} [33], that is at least two orders of magnitude higher than diffusion coefficients of europium ions. So the process of electroreduction occurs not only on the surface substrate, but in the bulk of the melt also. The appearance of electronic conductivity in the melt leads to the uncertain values in the electrode area of the reactant concentration. For the melts with electronic conductivity the usual equations of voltammetry and other methods are not applicable.

As can be seen from Fig. 6 by using cyclic voltammetry it is not possible to determine the electroreduction peak value for the process (4) and to use the procedure of formal standard potential determination of $E^*_{Eu(II)/Eu}$ from the magnitude of the peak potential [14 - 15]. Thus cyclic voltammetry does not provide information on determination of formal standard potentials of $E^*_{Eu(II)/Eu}$. Therefore for these determinations we used an open-circuit potentiometry method.

3.5. Open-circuit Potentiometry

Pure europium deposits are formed on a molybdenum electrode in the NaCl-KCl-$EuCl_2$ melt by constant current electrolysis with current densities of 50 - 600 mA/cm^2 during 5 - 120 sec. Typical potential decays obtained after electrolysis are shown in Figs. 7a,b. 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 (Fig. 7b), then slowly shifted toward the positive potential and finally arrived at the rest potential of molybdenum in the melt. As can be

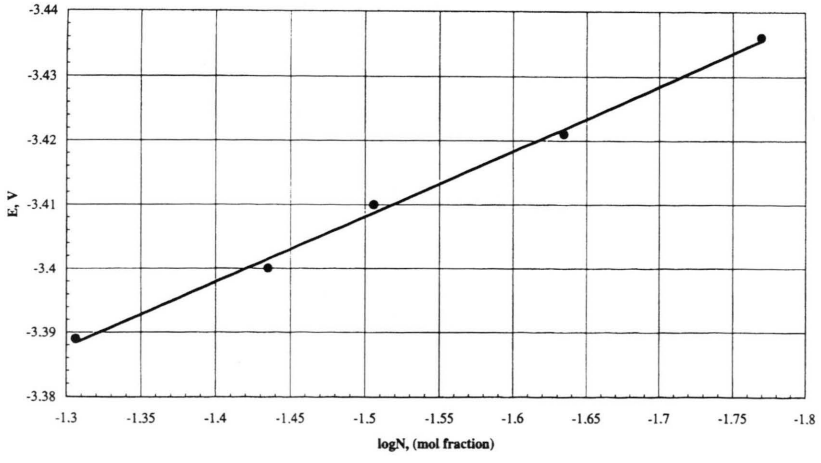

Fig. 8. A plot of the plateau potential against log N (mole fraction) of $EuCl_2$. Temperature: 1000 K.

seen from the Figs. 6 and 7, the values of potential plateau and the potential which intersects cyclic voltammograms at zero current are identical. Thus in some cases the rough determination of formal standard potentials can be obtained by extrapolation of the ascending section of the voltammetric curve to the potential axis. A plot of the plateau potential E against log N gives a linear relationship with a slope which is very close to the Nernst slope 2.3 RT/2F for a reversible transfer of two electrons (Fig. 8). A least squares calculation gives values of formal standard potentials $E^*_{Eu(II)/Eu}$ (referred to a Cl^-/Cl_2 reference electrode) at each temperature, and the dependence on temperature is accurately represented by the empirical relation

$$E^*_{Eu(II)/Eu}/V = -(4.08\pm0.01) + (8.2\pm0.2)\cdot10^{-4}T/K. \quad (23)$$

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

$$3\,E^*_{Eu(III)/Eu} = E^*_{Eu(III)/Eu(II)} + 2\,E^*_{Eu(II)/Eu}, \quad (24)$$

and its temperature dependence is described by the equation

$$E_{Eu(III)/Eu}/V = -(3.044\pm0.009) + (6.1\pm0.2)\cdot10^{-4}T/K. \quad (25)$$

3.6. *The Equilibrium Constant of the Metal-salt Reaction 2 Eu(III) + Eu ⇔ 3Eu(II)*

The values of the formal standard potentials of $E^*_{Eu(III)/Eu}$ and $E^*_{Eu(II)/Eu}$ were used for the calculation of the equilibrium constants of the metal-salt reaction

$$2\,Eu(III) + Eu\;3 \Leftrightarrow Eu(II), \quad (26)$$

employing the equation [32]

$$\log K^* = nm\cdot10^4\,[E^*_{Eu(III)/Eu} - E^*_{Eu(II)/Eu}]/1.984\,T \quad (27)$$

where $n = 3$ and $m = 2$ in our case.

The calculated values of the equilibrium constants logarithm depend linearly upon the reciprocal of temperature in the NaCl-KCl melt:

$$\log K^* = -6.351 + 31331/T \pm 0.2. \quad (28)$$

Since $\Delta G^* = -2.303\,RT \log K^*$, thus for the metal-salt reaction in the melt NaCl-KCl

$$\Delta G^*/kJmol^{-1} = -600 + 0.122\,T/K \quad (29)$$

As can be seen from (28) and (29), on contact with metallic europium in a NaCl-KCl-$EuCl_3$ melt, only the species Eu^{2+} exists in the melt.

3.7. *Comparison between the Present Results and Calorimetric Data*

The changes in the partial Gibbs energies for the formation of europium chlorides from the elements in NaCl-KCl were calculated using (23) and (25). For the formation of europium chlorides in molten NaCl-KCl, the following changes were obtained:

$$\Delta\overline{G}^*\,EuCl_2/kJ\,mol^{-1} = -(787\pm2) + (158\pm4)\cdot10^{-3}\,T/K, \quad (30)$$

$$\Delta\overline{G}^*\,EuCl_3/kJ\,mol^{-1} = -(881\pm3) + (176\pm6)\cdot10^{-3}\,T/K. \quad (31)$$

The literature data [34, 35] on the thermodynamics of the reaction of liquid europium with chlorine with formation of dichloride and trichloride europium allows us to calculate the changes in standard enthalpy, which at 1133 K are –789 $kJmol^{-1}$ for $EuCl_2$ and –865 $kJmol^{-1}$ for $EuCl_3$. Thus the change in the relative partial molar enthalpy of mixing $EuCl_2$ with an equimolar mixture NaCl-KCl, when dilute solutions are formed, is, within experimental error, close to zero. This value agrees well with the partial molar enthalpy derived from the integral mixing enthalpy for the system $EuCl_2$-NaCl obtained by a calorimetric method [36]. So probably europium dichloride does not form chloride complexes in the melt. At the same time the relative partial enthalpy of mixing $EuCl_3$ with NaCl-KCl melt at 1133 K is –16 kJ mol^{-1} due to the complex formation reaction

$$Eu^{3+} + 6\,Cl^- \Leftrightarrow EuCl_6^{3-}. \quad (32)$$

3.8. *Peculiarity of Intervalence Charge Transfer of the Couple Eu(III)/Eu(II)*

The peculiarity of redox electrochemistry of the couple Eu(III)/Eu(II) is a sluggish kinetics of reaction (1). The electron transfer itself, which in the condensed phase may occur on a time scale of 10^{-15} s, is preceded by the slower step of complex rearrangement [37]. The energy and the time required for the complex rearrangement decreases as the scale of chemical bond rearrangement decreases. Related with this is the fact that a redox electrochemical reaction

usually is a reversible process (even at high polarization rates up 5 - 10 Vs^{-1}) [38], because these reactions can in principle occur only with a change of charge and without a change in the composition of the complexes. The sluggish kinetics of the reaction

$$EuCl_6^{3-} + e^- \rightarrow Eu^{2+} + 6Cl^- \qquad (33)$$

is connected with substantial rearrangement of the europium coordination sphere (probably the loss of six ligands) which occurs during the electrode reaction.

4. Conclusion

The electrochemical reduction of Eu(III) in a NaCl-KCl equimolar mixture occurs via two successive reversible stages involving transfer of one and two electrons. The diffusion coefficients of Eu(III) and Eu(II) were determined by linear sweep voltammetry and chronopotentiometry. The standard rate constants for the reaction of the intervalence charge transfer were calculated on the basis of cyclic voltammetry data. The formal standard potentials $E^*_{Eu(II)/Eu}$, $E^*_{Eu(III)/Eu}$ and formal redox potentials $E^*_{Eu(III)/Eu(II)}$ were determined from open-circuit potentiometry and linear sweep voltammetry data. The thermodynamics of dilute solution formation of europium di- and trichloride, and equilibrium constants of metal-salt reactions in NaCl-KCl melt were calculated. The value for the relative partial molar enthalpy of mixing $EuCl_2$ in NaCl-KCl from electrochemical measurements agrees well with data obtained by calorimetry.

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