Unusual Influence of the Temperature on the Standard Rate Constants of Charge Transfer for the Eu(III)/Eu(II) Redox Couple in Chloride-Bromide Melts

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The influence of bromide ions and temperature on the standard rate constants of the Eu(III)/Eu(II) redox reaction was determined. Cyclic voltammetry was used for the calculation of the kinetic parameters. It was shown that in NaCl-KCl (equimolar mixture)-NaBr (15 wt%)-$EuCl_3$ melts increase of the temperature from 973 K up to 1023 K leads to a drastical decrease of the standard rate constant k_s for the Eu(III)/Eu(II) redox reaction. This unusual influence of the temperature on the k_s value was explained by a change of the electron transfer mechanism. It is suggested that at 1023 K another mechanism becomes dominant – the transfer of electrons through dissolved bromine in the melt. Bromine appeared in the melt due to the decomposition of chloride-bromide or bromide complexes of Eu(III), and the concentration of bromine in the melt increased with the growth of temperature.

Key words: Europium; Chloride-Bromide Melt; Electrode Reaction; Outer-Sphere Cation; Charge Transfer Mechanism.

1. Introduction

In our previous studies the standard rate constants of charge transfer for the Eu(III)/Eu(II) redox couple were determined in NaCl-KCl, KCl and CsCl melts [1, 2]. It was found that the standard rate constants of charge transfer (k_s) increase from NaCl-KCl to CsCl melt. On the base of these experimental results it was suggested that the electron transfer related to the Eu(III)/Eu(II) redox reaction may proceed over an outer-sphere cation. The highest values of k_s were observed in CsCl melt because of the large polarizability of caesium. The influence of fluoride ions on the electrochemical behaviour of NaCl-KCl-$EuCl_3$ melt was investigated in [3]. It was shown that the formation of stronger fluoride complexes reduce the diffusion coefficients, standard rate constants for charge transfer of the Eu(III)/Eu(II) redox couple and shift the formal standard redox potentials to more electronegative values. In the present study the influence of bromide ions and temperature on the standard rate constants for the Eu(III)/Eu(II) redox reaction was determined. A cyclic voltammetry was used for the calculation of the kinetic parameters.

2. Experimental Details

2.1. Chemicals; Preparation of Salts

Europium trichloride was synthesized from the oxide Eu_2O_3 (Johnson Matthey, 99.9%). Thionyl chloride (Johnson Matthey, 99%) was used as a chlorinating agent [4]. The $SOCl_2$ vapour was passed through solid Eu_2O_3 at 823 K using argon as a carrier gas during 6 h. $EuCl_3$ 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 in 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 maintained at this temperature for 3 h under static vacuum. Then the temperature was

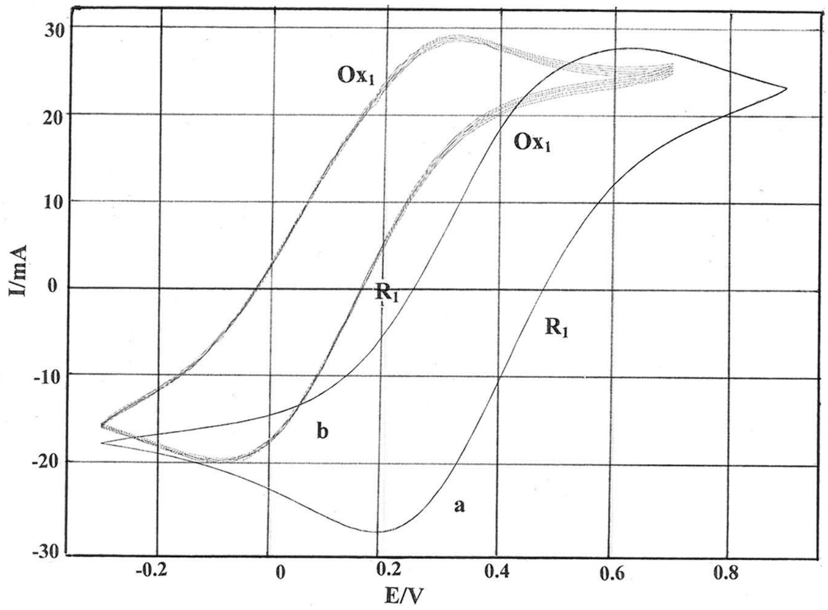

Fig. 1. Cyclic voltammetric curves obtained in NaCl-KCl-$EuCl_3$ melt: (a) before addition of NaBr; (b) after addition of 5 wt% NaBr. Sweep rate: 1.0 V s^{-1}; temperature: 973 K; concentration of $EuCl_3$: $6.71 \cdot 10^{-5}$ mol cm^{-3}; reference electrode: Ag/NaCl-KCl-AgCl (2 wt%).

increased up to 1093 K and kept during 5 h still under static vacuum. Finally, the $EuCl_2$ compound was purified from zinc by distillation at 1193 K. Chemical analysis of the prepared $EuCl_2$ was performed by use of mercurimetric (chloride) and complexometric (EDTA in presence of xylenol orange-europium) methods. The results of the analysis showed that the ratio Cl/Eu was essentially two. Because of the 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).

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 emission 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 the required ratio and placed in an ampoule made of glassy carbon (SU-2000 type) which was transferred to a hermetically sealed stainless steel retort. The latter was evacuated to a residual pressure of 0.7 Pa, first at room temperature and then at higher temperatures (473, 673 and 873 K). The retort was then filled with high purity argon and the electrolyte was melted. The experiments were performed under argon (U-grade: less than 3 ppm H_2O and 2 ppm O_2) atmosphere. The cell was heated using a programmable furnace, and the temperatures were measured using a Pt-PtRh (10%) thermocouple.

The investigations were performed employing linear sweep voltammetry (LSV) and cyclic voltammetry (CV), using a VoltaLab-40 potentiostat with packaged software "VoltaMaster 4" version 6. The potential scan rate (v) was varied between $5 \cdot 10^{-3}$ and 5.0 V s^{-1}. Experiments were carried out in the temperature range 973 – 1073 K. The electrochemical curves were recorded at a 0.8 – 2.0 mm diameter glassy carbon electrode with respect to a glassy carbon plate as a quasi-reference electrode. An Ag/NaCl-KCl-AgCl (2 wt%) reference electrode was used in this study [5].

3. Results and Discussion

3.1. Diffusion Coefficients of Eu(III) and Eu(II) in Chloride-Bromide Melts

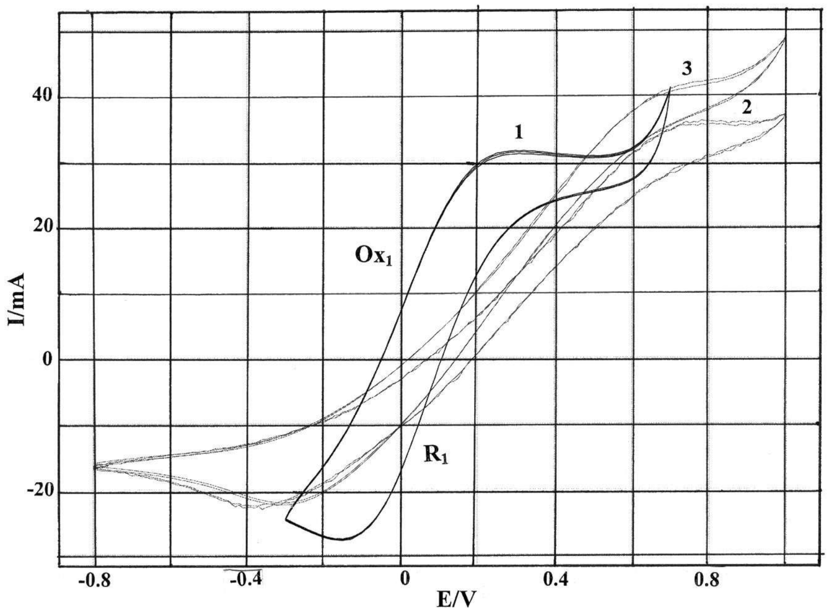

Fig. 2. Cyclic voltammograms for the redox reaction Eu(III) + $e^- \leftrightarrow$ Eu(II) in NaCl-KCl-NaBr (15 wt%)-$EuCl_3$ melt; 1, 973 K; 2, 1023 K; 3, 1073 K. Sweep rate: 1.0 V s^{-1}; concentration of $EuCl_3$: $8.62 \cdot 10^{-5}$ mol cm^{-3}; reference electrode: Ag/NaCl-KCl-AgCl (2 wt%).

The cyclic voltammetric curves of the process

$$\mathrm{Eu(III)} + e^- \leftrightarrow \mathrm{Eu(II)} \tag{1}$$

in the NaCl-KCl-$EuCl_3$ melt obtained at the glassy carbon electrode are presented in Fig. 1, curve a. Wave 1 is observed in the cathodic-anodic region, indicating the appearance of Eu(II) in the melt apparently due to the reaction [5, 6]

$$2\mathrm{EuCl_3} \leftrightarrow 2\mathrm{EuCl_2} + \mathrm{Cl_2}. \tag{2}$$

Introducing bromide ions (5 wt% NaBr) into the melt resulted in a significant shift of cathodic and anodic potential peaks to the negative region and decreasing of voltammetric curve currents (Fig. 1, curve b). At the same time the difference between the potential of the cathodic (E_p^C) and anodic (E_p^A) peaks decrease a little bit. Addition of bromide ions up to the content 10 wt% NaBr in the melt led to a slight shift of the cathodic peak potential and an insignificant diminution of current on the voltammograms. Further addition of NaBr up to 15 wt% did not lead to any changes in the voltammograms (Fig. 2, curve 1). Such a transformation of voltammetric curves is related to the formation of mixed chloride-bromide or bromide complexes according to the reactions

$$[\mathrm{EuCl_6}]^{3-} + x\mathrm{Br}^- \leftrightarrow [\mathrm{EuCl}_{6-x}\mathrm{Br}_x]^{3-} + x\mathrm{Cl}^-, \tag{3}$$

$$[\mathrm{EuCl_6}]^{3-} + 6\mathrm{Br}^- \leftrightarrow [\mathrm{EuBr_6}]^{3-} + 6\mathrm{Cl}^-. \tag{4}$$

Analogous reactions occur for Eu(II) with the formation of the complexes $[\mathrm{EuCl}_{4-x}\mathrm{Br}_x]^{2-}$ or $[\mathrm{EuBr_4}]^{2-}$. The significant shift of the peak potentials after addition of 5 wt% NaBr (Fig. 1, curve b) is caused by the formation of chloride-bromide or pure bromide complexes of europium, which are stronger than chloride complexes. Increasing the content of bromide ions from 10 up to 15 wt% NaBr did not change the composition of chloride-bromide or bromide complexes. Because of the identical composition in this concentration range, no transformation of the voltammograms was observed.

It is a matter of fact that a certain shift of a potential can be caused by a junction potential on the interface reference electrode/melt due to different anionic compositions, but this value usually does not exceed 10 mV [7].

As in the case of chloride complexes in an equimolar NaCl-KCl melt [5] three types of electrode process (1) were determined depending on the scan rate. It was found that the peak current is directly proportional to the square root of the polarization rate (Fig. 3a), while the peak potential does not depend on the polarization rate up to $v = 0.2$ V s^{-1} (Fig. 3b). The potentiostatic electrolysis at potentials of the cathodic peak does not lead to the formation of a solid phase at the electrode, and the electrode itself undergoes no visible transformation. This means that the product of this stage is soluble in the melt. According to the theory of lin-

v (V s^{-1})	E_p^C (V)	$E_{p/2}^C$ (V)	$E_{p/2}^C - E_p^C$ (V)	E_p^A (V)	$E_p^A - E_p^C$ (V)	Eq. (5)	Eq. (6)
0.02	0.036	0.224	0.188	0.158	0.194	0.98	0.96
0.05	0.037	0.227	0.190	0.161	0.198	0.97	0.94
0.10	0.036	0.224	0.188	0.162	0.198	0.98	0.94
0.15	0.034	0.226	0.192	0.170	0.204	0.96	0.91
0.20	0.034	0.226	0.192	0.172	0.206	0.96	0.90

Table 1. Experimental and calculated data for the determination of the number of electrons for the redox reaction (1).

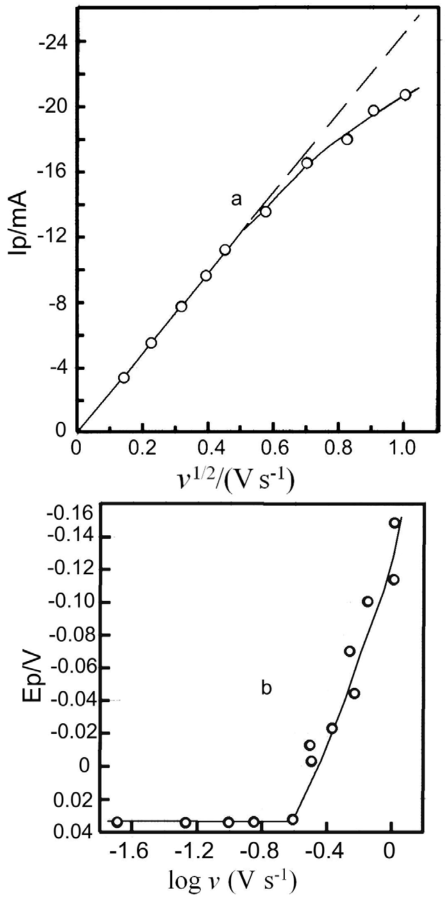

Fig. 3. Dependencies of peak currents (a) and peak potentials (b) of the redox process on the sweep rate. Area: 0.298 cm^2; temperature: 973 K; concentration: $8.21 \cdot 10^{-5}$ mol cm^{-3}; reference electrode: Ag/NaCl-KCl-AgCl (2 wt%).

ear sweep voltammetry [8], up to a polarization rate of 0.2 V s^{-1} the electrode process is controlled by the rate of mass transfer and yields a reduced form soluble in the melt. The number of electrons for the redox process was calculated by means of the equations [9]

$$E_{p/2}^C - E_p^C = 2.2\,RT/nF, \tag{5}$$

and

$$E_p^A - E_p^C = 2.22\,RT/nF, \tag{6}$$

where $E_{p/2}^C$ is the potential of the half-peak, n the number of electrons, and E_p^A the potential of the anodic peak.

The calculation of the number of electrons (Table 1) reveals, as was expected, that one electron is transferred in the redox process.

The diffusion coefficients (D) for the chloride complexes of Eu(III) were determined at $v = 0.1$ V s^{-1} using the Randles-Shevchik equation [10]

$$I_p^C = 0.4463 F^{3/2} R^{-1/2} T^{-1/2} n^{3/2} A C D^{1/2} v^{1/2}, \tag{7}$$

where I_p^C is the peak cathodic current (A), A the electrode area (cm^2), C the bulk concentration of active species (mol cm^{-3}), D the diffusion coefficient (cm^2 s^{-1}), v the potential sweep rate (V s^{-1}), and n the number of electrons involved in the reaction.

The diffusion coefficient of Eu(III) at 973 K was found to be $1.97 \cdot 10^{-5}$ cm^2 s^{-1}.

Equation (7) was employed for the calculation of $D_{\mathrm{Eu(II)}}$ in the chloride-bromide melt on the basis of the peak current determined for the process

$$\mathrm{Eu(II)} - e^- \rightarrow \mathrm{Eu(III)}, \tag{8}$$

and $D_{\mathrm{Eu(II)}}$ was equal to $4.08 \cdot 10^{-5}$ cm^2 s^{-1}.

The process (1) in the chloride-bromide melt was classified as quasi-reversible at a scan rate $0.2 < v \le 1.0$ V s^{-1}. A mixed diffusion and electron transfer rate controlled process (1) at $v > 0.2$ V s^{-1} is indicated by the deviation of experimental points from linearity in the I_p^C vs. $v^{1/2}$ plot, by the dependence E_p^C on v (Fig. 3), and by the magnitude of the difference between E_p^A and E_p^C, which is larger than required for a reversible process (Fig. 2, curve 1).

Increasing the sweep polarization rate from 1.2 V s^{-1} to 4.0 V s^{-1} results in irreversible electroreduction, because the peak current is directly proportional to $v^{1/2}$ (Fig. 4a), while the peak potentials shift in the cathodic direction with increasing scan rate (Fig. 4b).

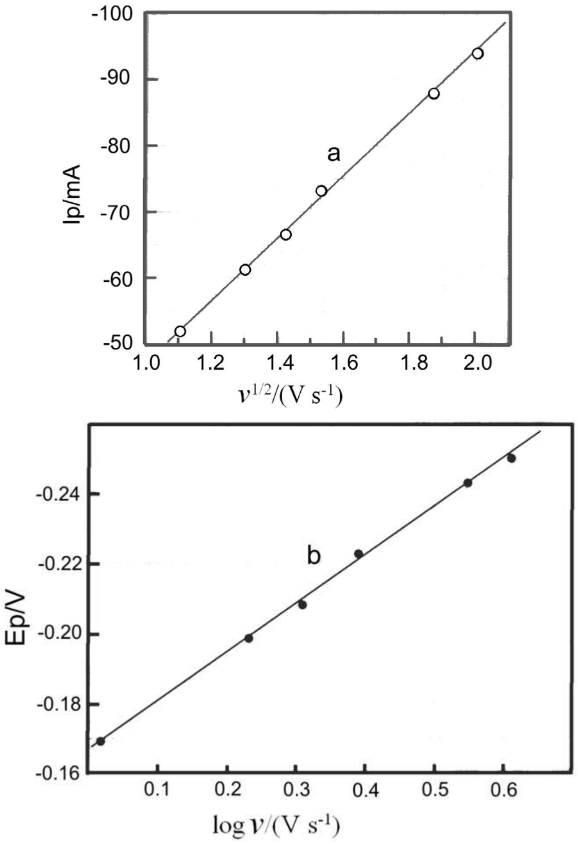

Fig. 4. Dependencies of peak currents (a) and peak potentials (b) of the redox reaction (1) on the sweep rate $\nu > 1.0$ V s^{-1}. Area: 0.308 cm^2; temperature: 973 K; concentration: $2.64 \cdot 10^{-4}$ mol cm^{-3}; reference electrode: Ag/NaCl-KCl-AgCl (2 wt%).

In the coordinates $E_\mathrm{P} - \log \nu$ (Fig. 4b) the following slope was found [9] at 973 K:

$$K = 2.303RT/2\alpha n_\alpha F = 0.142 \text{ V}, \tag{9}$$

where α is the electrochemical transfer coefficient and n_α the number of transferred electrons. So the product αn_α can be calculated by the expression

$$\alpha n_\alpha = 2.303RT/2KF = 0.68. \tag{10}$$

This value, also at the same temperature 973 K, is very close to those αn_α, which were found from the expressions described in [9, 11]:

$$E_\mathrm{p} - E_{\mathrm{p}/2} = -1.857RT/\alpha n_\alpha F, \tag{11}$$

$$E_\mathrm{p}^2 - E_\mathrm{p}^1 = (RT/\alpha n_\alpha F) \cdot \ln(\nu^1/\nu^2). \tag{12}$$

Equation	α
(10)	0.68
(11)	0.72
(12)	0.67

Table 2. Values of the charge transfer coefficient α for the Eu(III)/Eu(II) redox couple obtained by different equations.

Table 3. Diffusion coefficients of Eu(III) and Eu(II) complexes obtained at different scan rates ν.

ν (V s^{-1})	$D_{\mathrm{Eu(III)}}$ (10^{-5} cm^2 s^{-1})	$D_{\mathrm{Eu(II)}}$ (10^{-5} cm^2 s^{-1})
0.1, Eq. (7)	1.97	4.08
1.0, Eq. (13)	2.03	4.20

Scan rates 1.2 V s^{-1} and 2.5 V s^{-1} were used for the determination of αn_α from (12). The αn_α values obtained from (10) – (12) are given in Table 2.

The diffusion coefficients for the Eu(III) complexes were determined at 973 K, at a polarization rate $\nu = 1.5$ V s^{-1} (at this rate, the double layer charging current was virtually insignificant relative to the Faradayic current), using the Delahay equation for irreversible electrochemical processes [10]

$$I_\mathrm{p}^\mathrm{C} = 0.496nFCAD^{1/2}(\alpha n_\alpha F\nu/RT)^{1/2}. \tag{13}$$

Equation (13) was employed for calculating of the diffusion coefficients of Eu(II) on the basis of the peak current determined for oxidation of Eu(II) to Eu(III).

The diffusion coefficients of Eu(III) and Eu(II) at different polarization rates are presented in Table 3.

As can be seen from Table 3, the diffusion coefficients decrease when the oxidation state increases. The diffusion coefficients of Eu(III) and Eu(II) in a chloride-bromide melt a smaller than in a NaCl-KCl equimolar mixture [2, 5]. The decrease in D is related to the increased strength of the chlroride-bromide or bromide complexes, and this in turn leads to a decrease in the contribution of the diffusion coefficient from the "hopping" mechanism as discussed in [12].

3.2. *Standard Rate Constants of the Electrode Reaction Eu(III) + e$^-$ $\leftrightarrow$ Eu(II) in Chloride-Bromide Melt*

A mixed diffusion and electron transfer control for process (1) was observed in the potential sweep rate range $0.2 < \nu \leq 1.0$ V s^{-1} (Fig. 3).

The problem of determining kinetic parameters on the basis of cyclic voltammetry was addressed by Nicholson [13]. The standard rate constant of the electrode process is related to the function ψ as follows:

$$\psi = \frac{k_\mathrm{s}\left(\frac{D_\mathrm{ox}}{D_\mathrm{red}}\right)^{a/2}}{\pi^{1/2} D_\mathrm{ox}^{1/2}\left(\frac{nF}{RT}\right)^{1/2} \nu^{1/2}}. \tag{14}$$

Here ψ is a function related to the difference between the peak potentials $E_\mathrm{p}^\mathrm{A} - E_\mathrm{p}^\mathrm{C}$ (Fig. 2, curve 1, mV), k_s is the standard rate constant of the electrode process (cm s^{-1}), $\alpha = 0.5$ is the charge transfer coefficient.

The value α was taken as 0.5, because in the original paper [13] the function ψ is related to the difference between the peak potentials $E_\mathrm{p}^\mathrm{A} - E_\mathrm{p}^\mathrm{C}$ at the value $\alpha = 0.5$. Utilization of this value instead of that determined experimentally (Table 2) has no influence on the value k_s, because the difference between the peak potentials is almost the same for $0.3 \le \alpha \le 0.7$ [9].

The dependencies $E_\mathrm{p}^\mathrm{A} - E_\mathrm{p}^\mathrm{C}$ on the function ψ reported in [13] at 298 K must be recalculated for the present working temperature (973 K), and the following equations [14] were used:

$$(\Delta E_\mathrm{p})_\mathrm{T} = (\Delta E_\mathrm{p})_{298} T/298, \tag{15}$$

$$\psi_T = \psi_{298}(T/298)^{1/2}. \tag{16}$$

The values of the ψ_T function obtained from (15) and (16) and used in conjunction with expression (14) made it possible to calculate the standard rate constant for charge transfer, which was found to be $2.06 \cdot 10^{-2}$ cm s^{-1}.

According to Matsuda and Ayabe [11], the electrochemical process is quasi-reversible if

$$10^{-2(1+\alpha)} < k_\mathrm{s}/(Dn\nu F/RT)^{1/2} < 15. \tag{17}$$

In our case, for a chloride-bromide melt at 973 K, $6.8 \cdot 10^{-6} < k_\mathrm{s} < 0.233$ cm s^{-1}. Thus intervalence charge transfer of the Eu(III)/Eu(II) couple proceeds quasi-reversibly, mostly under diffusion control.

The value of the standard rate constant at 973 K in a chloride-bromide melt is higher than in an NaCl-KCl melt. The explanation of this fact is as follows: The size of europium complexes increase from chloride to chloride-bromide melts. According to the theory of elementary charge transfer, the larger complexes require lower rearrangement energy, and in consequence the electrode process proceeds at a faster rate [15].

The increase of the temperature from 973 K up to 1023 K leading to drastical changes of the voltammograms, resulted in larger electroreduction-electrooxidation waves along the potential axis and a sharply increased difference between cathodic and anodic peaks (Fig. 2, curve 2). All these changes in the shape of cyclic voltammograms indicated that the rate of electron transfer for redox process (1) with increasing of the temperature was decreased. Indeed at the polarization rate 1.0 V s^{-1} and at 973 K, process (1) was a quasi-reversible (i. e. the diffusion rate approached the rate of electron transfer), but at 1023 K, the difference between anodic and cathodic peaks at this rate reached the value 1.156 V (Fig. 2, curve 2), and due to this large value, the function ψ could not be determined. This indicated that the redox process (1) became irreversible (controlled by charge transfer). So, as can be seen from (17), the standard rate constant at 1023 K is approximately by four orders of magnitude smaller than at 973 K.

Such unusual behaviour can be explained by a change of the electron transfer mechanism. It was shown in [2] that in alkali chloride melts containing Eu(III) and Eu(II) complexes the mechanism of electron transfer is the transfer via the outer-sphere cation. Probably the main mechanism of electron transfer in a chloride-bromide melt at 973 K is the transfer via outer-sphere cations too. It was suggested that at 1023 K another mechanism became dominant: the transfer of electrons through dissolved bromine in the melt. Bromine appeared in the melt due to the decomposition of chloride-bromide or bromide complexes of Eu(III). Two questions can arise from the above proposed suggestion concerning the change of mechanism transfer:

1. Why was the transfer of electron through dissolved chlorine not determined in an NaCl-KCl-$\mathrm{EuCl_3}$-$\mathrm{EuCl_2}$ melt?
1. Why did the increase of the temperature lead to the change of the transfer mechanism?

The answer on these questions is connected with the solubility or concentration of dissolved bromine in the melt. The solubility of bromine is approximately by two orders of magnitude higher than that of chlorine at the same temperature, and the concentration of bromine in the melt increases with the growth of the temperature [16].

The further increase of the temperature from 1023 K up to 1123 K led to the growth of k_s (the difference between cathodic and anodic peaks decreased a little bit, Fig. 2, curve 3), but the standard rate constant of charge transfer was significantly smaller than at 973 K. Decrease of the temperature to 973 K caused the increase of the standard rate constant, and the voltammogram acquired the similar look as before the heating-cooling cycle. So, playing with the temperature, the mechanism of charge transfer can be changed.

Indeed the preliminary experiments showed that in chloride-iodide melt containing $EuCl_3$ the same transformations of voltammograms and change of charge transfer mechanism with increasing of temperature from 973 – 1023 K were observed.

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