Spectroelectrochemistry and Electrochemistry of Europium Ions in Alkali Chloride Melts

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In order to investigate the redox equilibrium of europium ions in molten NaCl-2CsCl, UV-Vis absorption spectrophotometry measurements were performed for Eu^{2+} and Eu^{3+} in molten NaCl-2CsCl at 923 K under simultaneous electrolytic control of their ratio. Molar absorptivities of $EuCl_3$ and $EuCl_2$ in NaCl-2CsCl at 923 K were determined to be (420 ± 21) $M^{-1}cm^{-1}$ at 31200 cm^{-1} and (1130 ± 56) $M^{-1}cm^{-1}$ at 30300 cm^{-1}, respectively. The formal redox potential of the Eu^{2+}/Eu^{3+} couple in NaCl-2CsCl melt at 923 K was determined to be (-0.941 ± 0.004) V vs. Cl_2/Cl^- by electromotive force measurements on varying concentration ratios of Eu^{2+} and Eu^{3+}, which were performed using a technique based on the combination of electrolysis and spectrophotometry. Cyclic voltammetry was also carried out in order to examine the characteristics of the voltammograms for the Eu^{2+}/Eu^{3+} couple in NaCl-2CsCl melt. The formal redox potential of the Eu^{2+}/Eu^{3+} couple determined by a spectroelectrochemical method agreed with that determined by cyclic voltammetry $[(-0.946 \pm 0.008)$ V vs. $Cl_2/Cl^-]$. The effects of temperature on the redox potential of the Eu^{2+}/Eu^{3+} couple in NaCl-2CsCl, NaCl-KCl, LiCl-KCl, and CsCl melts were studied by cyclic voltammetry in the range from 923 to 1123 K.

Key words: Molten Salt; NaCl-2CsCl; Europium; Spectroelectrochemistry; Cyclic Voltammetry.

1. Introduction

Recently the development of pyro-reprocessing of spent nuclear fuels, using the oxide electro-winning method, has progressed notably [1]. It has been reported that in this process the efficiency of the electrolysis is seriously affected by circulation currents caused by some fission products and the materials of construction [2]. Solute elements that have two valence states are likely to cause the so-called circulation current. This current occurs by alterenate reduction and oxidation reactions of elements at the cathode and anode. Europium has divalent and trivalent states that can exist in the electrolysis process and may contribute to the circulation current in the process.

The redox behavior of europium ions in molten alkali chlorides has been investigated [3 – 8]. Recently, Novoselova et al. [5, 6] have determined the formal re-dox potential of the Eu^{2+}/Eu^{3+} couple, $E^{o\prime}_{Eu(II)/Eu(III)}$ in alkali chloride melts such as LiCl, KCl, CsCl, and NaCl-KCl by electromotive force measurements. Kuznetsov and co-workers [7, 8] have determined the formal redox potentials of Eu^{2+}/Eu^{3+}, Eu^{3+}/Eu and Eu^{2+}/Eu couples in NaCl-KCl, KCl and CsCl by linear sweep voltammetry. Spectroelectrochemistry [9] is an effective method to determine the formal redox potential precisely. In this method, the electromotive force of the solution, which contains both the oxidant and reductant, is measured. The concentration ratio of Eu^{2+} and Eu^{3+} is controlled by electrolysis and monitored by spectrophotometry simultaneously, and $E^{o\prime}$ can be evaluated based on the Nernst equation. Smirnov [10] and Nagai et al. [11, 12] have applied this method to determine the formal redox potential of Cr^{2+}/Cr^{3+}, Ni^{2+}/Ni^{3+}, U^{3+}/U^{4+}, and UO_2^+/UO_2^{2+} in molten salts.

In the present study we report the formal redox potential of the Eu^{2+}/Eu^{3+} couple for NaCl-2CsCl, determined by a spectroelectrochemical method. The NaCl-2CsCl system [1] is considered as a solvent for the oxide-winning method of spent nuclear fuels. However, there is a limited number of absorption spectra of Eu^{2+} and Eu^{3+} reported for molten salts [13 – 16]. To our knowledge, no detailed spectra of Eu^{2+} and Eu^{3+} in NaCl-2CsCl molten salt have been reported before. Hence, the absorption spectra of Eu^{2+} and Eu^{3+} in a NaCl-2CsCl eutectic melt, which are a fundamental information for spectroelectrochemistry, were precisely measured, and then the formal redox potential of the Eu^{2+}/Eu^{3+} couple was determined by a spectroelectrochemical method. The redox potentials of the Eu^{2+}/Eu^{3+} couple were also determined by cyclic voltammetry for the systems NaCl-2CsCl, NaCl-KCl, LiCl-KCl, and CsCl, and their temperature dependence was carefully investigated.

2. Experimental

2.1. Chemicals

The anhydrous alkaline chlorides NaCl-2CsCl eutectic (99.99%), NaCl-KCl eutectic (99.99%), LiCl-KCl eutectic (99.99%), CsCl (99.99%) and $EuCl_3$ (99.99%) were purchased from Aldrich-APL LLC and used without further treatment. All other chemicals were of reagent grade quality.

2.2. Apparatus

The spectroelectrochemical cell used for the spectrophotometric and voltammetric studies was described in [11]. The self-registering spectrophotometer JASCO V-350 (JASCO Co.) was used for the measurements over wavenumbers from 15000 to 36000 cm^{-1}. The sample cell was a quartz tube, 35 cm in length and 13 mm in inner diameter. To the bottom of the tube a transparent optical measurement cell, having a 10 mm light path, was welded. In the cyclic voltammetry, a pyro-graphite-coated graphite rod (Tokai Carbon Co.) of 3 mm diameter was used as working and counter electrode. Instead of the pyro-graphite electrode a molybdenum rod electrode was also tested as working electrode, but it was found that it is not adoptable for repeated use because of elution. A silver|silver ion ($Ag|Ag^+$) electrode was used as a reference electrode. This electrode consisted of a closed end tube

of porous alumina (50% Al_2O_3 + 46% SiO_2; Nikkato Co.) in which alkaline chloride eutectic salt containing 4.85 mol% AgCl was placed, and an Ag wire of 1 mm diameter was immersed in the salt. In every experiment, the same salt as the bulk solution was used the reference electrode in order to eliminate the effect of a liquid junction potential. If the electromotive force of the reference electrode was not known, such as in case of NaCl-2CsCl, an experiment to calibrate it to the Cl_2/Cl^- electrode was carried out.

The temperature of the cell was controlled in the range 723 to 1123 K by an automatic temperature control system. The electrochemical measurement system Hz-3000 (Hokuto Denko Co. Ltd.) was used for the cyclic voltammetry and controlled potential electrolysis [11, 12].

All the experiments were carried out in a glove box filled with dry argon, and the humidity and oxygen impurity was continuously kept below 1 ppm.

2.3. Determination of the Formal Redox Potential by a Spectroelectrochemical Method

The formal redox potential of the Eu^{2+}/Eu^{3+} couple, $E^{o\prime}_{Eu(II)/Eu(III)}$, was determined by the relation between the equilibrium potential and the ratio of the concentrations of Eu^{2+} and Eu^{3+} in the melt, which was simultaneously monitored with the absorption spectra of Eu^{2+} and Eu^{3+}. The spectrum of Eu^{3+} was measured after dissolving a weighted amount of $EuCl_3$ in the melt. The spectrum of Eu^{2+} was measured after reducing Eu^{3+} completely to Eu^{2+} by controlled potential electrolysis. Equilibrium potential measurement at changed ratios of the concentration of Eu^{2+} and Eu^{3+} was performed by following procedure. As step (i) europium ions in the melt were completely reduced to Eu^{2+} by controlled potential electrolysis. As step (ii), after a portion of Eu^{2+} was oxidized to Eu^{3+} by controlled potential electrolysis for about 10 min, absorption spectra and equilibrium potentials were measured. Step (ii) was repeated until the oxidation of Eu^{2+} to Eu^{3+} was completed. The concentrations of Eu^{2+} and Eu^{3+} were monitored as the integral of the absolute band from 27027 to 23810 cm^{-1}. The logarithm of the ratio of the concentrations of Eu^{2+} to Eu^{3+} was plotted as a function of the equilibrium potential. Here, the equilibrium potential in the melt was measured as rest potential between the reference and working electrode. The potential at $\ln[Eu^{2+}]/[Eu^{3+}] = 0$ gave the formal redox potential of the Eu^{2+}/Eu^{3+} cou-
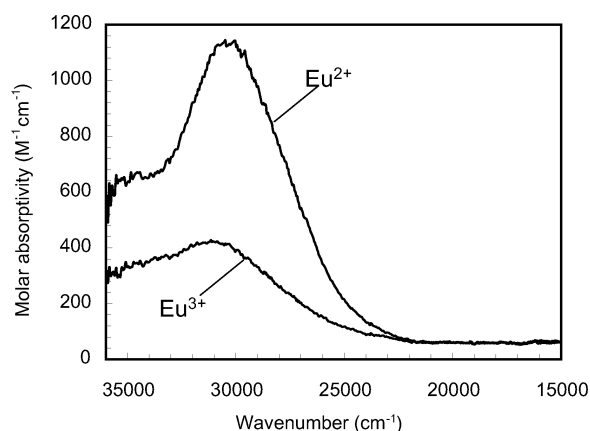
Fig. 1. Absorption spectra of Eu^{2+} and Eu^{3+} in NaCl-2CsCl melt at 923 K.

ple. In these experiments, involving electrolysis operation, a counter electrode, having a protective tube, was used. This counter electrode had the same configuration as the reference electrode, so that the counter reaction of the electrolysis occured only in the isolated area.

3. Results and Discussion

3.1. Determination of the Formal Redox Potential of the Eu^{2+}/Eu^{3+} Couple, $E^{o\prime}_{Eu(II)/Eu(III)}$, in NaCl-2CsCl Melt by Spectroelectrochemistry

The observed absorption spectrum of 8.11×10^{-4} M $EuCl_3$ in the NaCl-2CsCl melt at 923 K is shown in Figure 1. The molar absorptivity of Eu^{3+} at the maximum of the charge transfer band, 31200 cm^{-1}, was determined to be (420 ± 21) $M^{-1}cm^{-1}$. In order to measure the spectrum of $EuCl_2$, controlled potential electrolysis was carried out with -1.55 V vs. Cl_2/Cl^- for 30 min. The 30 min electrolysis was found to be sufficient for a quantitative reaction since there was no further growth of the absorption peak of Eu^{2+} after 30 min, and the equilibrium potential became by 550 mV more negative than the anticipated formal potential. The absorption intensity of Eu^{2+}, which is attributable to the $4f^7 \rightarrow 4f^6 5d^1$ transition [14], was higher than that of Eu^{3+}, and gave the molar absorptivity (1130 ± 56) $M^{-1}cm^{-1}$ at 30300 cm^{-1}. Similar spectra of Eu^{3+} and Eu^{2+} in molten salts have been reported in earlier studies [14–16].

The determination of $E^{o\prime}_{Eu(II)/Eu(III)}$ by a spectroelectrochemical method was carried out by using NaCl-
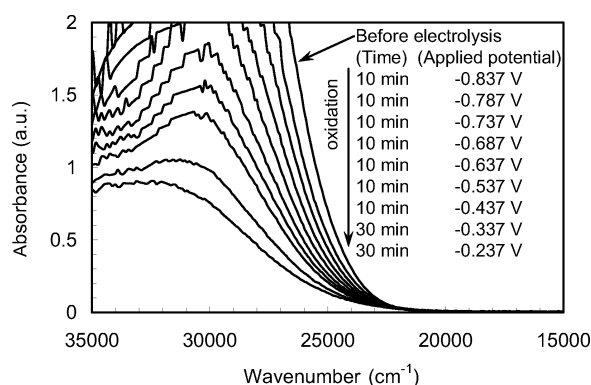

Fig. 2. Absorption spectra of europium ions in molten NaCl-2CsCl at 923 K, while oxidizing Eu^{2+} to Eu^{3+}.
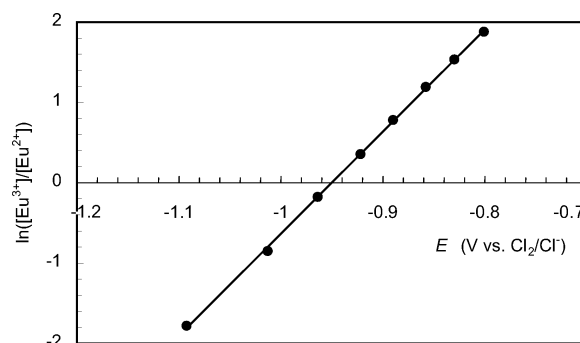

Fig. 3. Relation between the logarithm of the concentration ratio Eu^{3+}/Eu^{2+} and the rest potential in molten NaCl-2CsCl at 923 K.

2CsCl containing 2.17×10^{-4} M $EuCl_2$. In order to oxidize Eu^{2+} to Eu^{3+}, potential-controlled electrolysis was performed by applying -0.85 V vs. Cl_2/Cl^-. As the electrolysis proceeded, the absorption intensity of Eu^{2+} decreased, the trend of which is shown in Figure 2. After the electrolysis operated for 130 min, no further decrease of the absorption intensity was observed. For evaluating the concentration of Eu^{2+} and Eu^{3+}, the average absorbance over the region from 27027 to 23810 cm^{-1} was used. During the progressing electrolysis, the ratio of Eu^{2+} and Eu^{3+} was estimated from the decrease of the absorbance from the initial value, corresponding to 100% Eu^{2+}. Figure 3 shows the relation between the logarithm of the concentration ratio of Eu^{2+} to Eu^{3+} and the equilibrium potential. The slope of the straight line was 12.7, and this agreed well with the theoretical value (12.6) of the Nernst equation for one electron transfer at 923 K. The $E^{o\prime}_{Eu(II)/Eu(III)}$ was determined to be (-0.941 ± 0.004) V vs. Cl_2/Cl^-.

3.2. Cyclic Voltammetry of Eu in NaCl-2CsCl, NaCl-KCl, LiCl-KCl, and CsCl Melts

Cyclic voltammograms in NaCl-2CsCl melt containing 0.0696 M (0.724 wt%) $EuCl_3$ at 923 K were measured as shown in Figure 4. The voltammograms were measured at various concentrations of europium ion between 0.0371 M (0.387 wt%) and 0.0696 M. It was found that the peak currents were proportional to the concentration of the europium ion, and that the mid-point potentials were independent of the concentration of europium ions, as well as on the potential scanning rate, (-0.940 ± 0.005) V vs. Cl_2/Cl^-. The positive and negative peak currents were proportional to the square root of the potential scanning rate, which indicated that these currents were controlled by the diffusion of the europium ion in the melt. The potential difference between the positive and negative peak potentials at 923 K was (0.195 ± 0.010) V, which

Table 1. Comparison of formal redox potentials of the Eu^{2+}/Eu^{3+} couple, $E^{o\prime}_{Eu(II)/Eu(III)}$ (V vs. Cl_2/Cl^-), in NaCl-KCl, NaCl-2CsCl, CsCl, and KCl melts.

	This study	[5]	[8]
NaCl-KCl	-0.748	-0.742	-0.767
(1073 K)	$\pm 0.005^{a,d}$	$\pm 0.0006^c$	$\pm 0.006^a$
NaCl-2CsCl	-0.946 ± 0.008^a	–	–
(923 K)	-0.941 ± 0.004^b		
CsCl (1073 K)	$-0.977 \pm 0.005^{a,d}$	-0.981 ± 0.003^c	-0.967 ± 0.005^a
KCl (1073 K)	–	-0.844 ± 0.004^c	-0.783 ± 0.008^a

[a] Cyclic voltammetry.
[b] Spectroelectrochemical method.
[c] Electromotive force.
[d] Diffusion coefficients were taken from the literature [7].

agreed with the fact that the reaction was reversible with one electron transfer. The diffusion coefficient of Eu^{3+} at 923 K was calculated from the peak currents to be 2.61×10^{-5} $cm^2 s^{-1}$. In order to determine the diffusion coefficient of Eu^{2+}, cyclic voltammograms were also recorded for the solution of Eu^{2+}, which was prepared by quantitative electrolytic reduction. The diffusion coefficient of Eu^{2+} in the molten salt at 923 K was estimated from the peak currents to be 3.78×10^{-5} $cm^2 s^{-1}$. The mid-point potential was determined to be (-0.922 ± 0.005) V vs. Cl_2/Cl^-. $E^{o\prime}_{Eu(II)/Eu(III)}$ was determined to be (-0.946 ± 0.008) V vs. Cl_2/Cl^- by using the above determined diffusion coefficients. $E^{o\prime}_{Eu(II)/Eu(III)}$ determined by cyclic voltammetry agreed well with that determined by the spectroelectrochemical method within errors. The effect of the diffusion coefficient term to $E^{o\prime}_{Eu(II)/Eu(III)}$ was less than 0.015 V.

Generally, the standard potential is determined by cyclic voltammetry, using molybdenum or tungsten as a working electrode, because of their faster kinetics than glassy carbon electrodes. However, in this study the reversibility of Eu^{2+}/Eu^{3+} was confirmed to be high even with pyro-graphite carbon electrodes, and this proved the agreement between the spectroelectrochemical measurement and cyclic voltammetry. The advantage of the spectroelectrochemical measurement is that it does not depend on electrochemical dynamics, but is based on the snapshot observation of the equilibrium. In the case of Eu, which has a rather high molar absorptivity, the spectroelectrochemical technique gives a better detection limit.

Table 1 compares our results with the literature [5, 8] values in NaCl-KCl and CsCl melts at 1073 K. The literature values in Table 1 for various melt compositions at 1073 K were calculated from the equations reported by Novoselova et al. [5] and Kuznetsov et
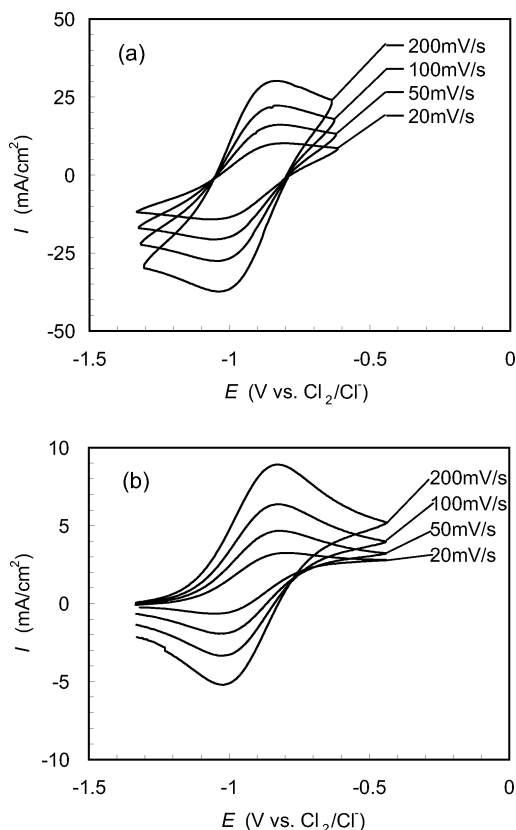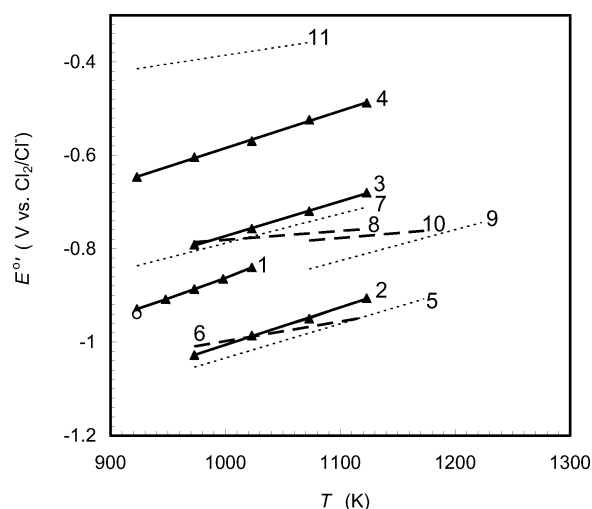

Fig. 4. Cyclic voltammograms of (a) $EuCl_3$ and (b) $EuCl_2$ in molten NaCl-CsCl at 923 K. Working electrode: graphite electrode; potential scanning rate: 20, 50, 100, and 200 mV s^{-1}, respectively.

Fig. 5. Relations between the redox potential of the Eu^{2+}/Eu^{3+} couple in various molten salts. Lines $1-4$ are the results in NaCl-2CsCl, CsCl, NaCl-KCl, and LiCl-KCl, respectively, determined in this study. Lines 5, 7, 9, and 11 are results in CsCl, NaCl-KCl, KCl, and LiCl, respectively, reported by Novoselova et al. [5], and lines 6, 8, and 10 are results in CsCl, NaCl-KCl, and KCl, respectively, reported by Kuznetsov et al. [8]. The closed plots (open circle) are results determined by spectroelectrochemistry. Diffusion coefficients of lines $1-4$ are not taken into consideration.

al. [8]. The difference of the $E^{o\prime}_{Eu(II)/Eu(III)}$ values between our study and the literature is 5 to 20 mV.

3.3. Temperature Dependence of the Redox Potential of the Eu^{2+}/Eu^{3+} Couple in Various Alkali Chloride Molten Salts

In order to evaluate the temperature dependence of the redox potential of an Eu couple, cyclic voltammograms were measured in NaCl-2CsCl, NaCl-KCl, LiCl-KCl, and CsCl, respectively, at various temperatures between 723 and 1123 K. The variation of the mid-point potential of the anodic and cathodic peak, $E_{Eu(II)/Eu(III)}$, in the NaCl-2CsCl melt along with temperature can be expressed as a function of temperature between 923 and 1023 K as

$$E_{Eu(II)/Eu(III)} = 8.862 \times 10^{-4} T - 1.748 \quad (1)$$
$$(\text{V vs. Cl}_2/\text{Cl}^- \text{ in NaCl-2CsCl}, 923 \leq T \leq 1023).$$

This is shown as line 1 in Fig. 5, and agrees well with the dot determined by the spectroelectrochemical method plotted as open circle.

Temperature dependence of $E_{Eu(II)/Eu(III)}$ in NaCl-KCl, LiCl-KCl, and CsCl melts was also determined

by cyclic voltammetry, as shown as lines $2-4$ in Figure 5. Similarly to the above-mentioned analyses, $E_{Eu(II)/Eu(III)}$ in NaCl-KCl, LiCl-KCl, and CsCl were expressed as functions by the following equations:

$$E_{Eu(II)/Eu(III)} = 7.440 \times 10^{-4} T - 1.517 \quad (2)$$
$$(\text{V vs. Cl}_2/\text{Cl}^- \text{ in NaCl-KCl}, 923 \leq T \leq 1123),$$

$$E_{Eu(II)/Eu(III)} = 7.947 \times 10^{-4} T - 1.380 \quad (3)$$
$$(\text{V vs. Cl}_2/\text{Cl}^- \text{ in LiCl-KCl}, 723 \leq T \leq 1123),$$

$$E_{Eu(II)/Eu(III)} = 8.032 \times 10^{-4} T - 1.809 \quad (4)$$
$$(\text{V vs. Cl}_2/\text{Cl}^- \text{ in CsCl}, 923 \leq T \leq 1123).$$

The effect of the temperature on $E_{Eu(II)/Eu(III)}$ in CsCl, KCl and NaCl-KCl melts was reported by Kuznetsov et al. [8], and that in LiCl, NaCl-KCl, KCl, and CsCl melts by Novoselova et al. [5]. These reported functions are shown as lines $5-11$, respectively, in Figure 5. $E_{Eu(II)/Eu(III)}$ in NaCl-KCl determined in this study (line 3) shows good agreement with the lines 7 and 8, reported by Novoselova et al. [5] and Kuznetsov et al. [8]. $E_{Eu(II)/Eu(III)}$ in CsCl, determined in this study (line 2), is close to line 6 [8], whereas it is about 30 mV more positive than line 5 [5]. The slopes of the lines $1-4$, which are obtained by the present study, are similar to those of lines 5, 7, 9, 11 reported by Novoselova et al. [5], but they are distinctly different from those of lines 6, 8, 10 reported by Kuznetsov et al. [8]. The difference of these slopes by Kuznetsov et al. could not be explained by us.

4. Conclusion

The redox equilibrium of europium ions was studied for molten NaCl-2CsCl. The $E^{o\prime}_{Eu(II)/Eu(III)}$ in NaCl-2CsCl at 923 K was determined to be (-0.941 ± 0.004) V vs. Cl_2/Cl^- by using the spectroelectrochemical method. This value agreed with that determined by cyclic voltammetry, (-0.946 ± 0.008) V vs. Cl_2/Cl^-. The temperature dependence of $E_{Eu(II)/Eu(III)}$ was investigated for various molten chlorides, which showed the following relations:

$$E_{Eu(II)/Eu(III)} = 8.862 \times 10^{-4} T - 1.748$$
$$(\text{V vs. Cl}_2/\text{Cl}^- \text{ in NaCl-2CsCl}, 923 \leq T \leq 1023),$$

$$E_{Eu(II)/Eu(III)} = 7.440 \times 10^{-4} T - 1.517$$
$$(\text{V vs. Cl}_2/\text{Cl}^- \text{ in NaCl-KCl}, 923 \leq T \leq 1123),$$

$$E_{\mathrm{Eu(II)/Eu(III)}} = 7.947 \times 10^{-4}\, T - 1.380$$
(V vs. $\mathrm{Cl_2/Cl^-}$ in LiCl-KCl, $723 \leq T \leq 1123$),

$$E_{\mathrm{Eu(II)/Eu(III)}} = 8.032 \times 10^{-4}\, T - 1.809$$
(V vs. $\mathrm{Cl_2/Cl^-}$ in CsCl, $923 \leq T \leq 1123$).

$E_{\mathrm{Eu(II)/Eu(III)}}$ and its temperature dependence, precisely determined in the present study, can help to understand the coordination change of europium complexes.

UV/Vis absorption spectra of $\mathrm{Eu^{3+}}$ and $\mathrm{Eu^{2+}}$ were quantitatively prepared by electrolysis in NaCl-2CsCl at 923 K, and their spectra were measured. Their molar absorptivities were determined to be (420 ± 21) $\mathrm{M^{-1}\,cm^{-1}}$ at 31200 $\mathrm{cm^{-1}}$ and (1130 ± 56) $\mathrm{M^{-1}\,cm^{-1}}$ at $30300\ \mathrm{cm^{-1}}$.

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