Redox Potentials of Samarium and Europium in Molten Lithium Chloride

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The samarium (III)/(II) and europium (III)/(II) redox potentials in molten lithium chloride were measured using the direct potentiometric method in the temperature range from 923 to 1094 K. Glassy carbon was used as the indifferent working electrode, and the standard chlorine electrode as a reference. The total concentration of rare-earth chlorides dissolved in molten lithium chloride did not exceed 4.5 mol%.

Key words: Molten Salts; Redox Potentials; Samarium Chlorides; Europium Chlorides; Lithium Chloride.

1. Introduction

The problem of co-existence of rare-earth di- and trichlorides in molten $LnCl_2$-$LnCl_3$-MCl systems (Ln = Lantanide, M = Metal) was a matter of significant scientific interest for several decades. This problem is closely connected with the determination of redox potentials of lanthanide (III)/(II) couples ($E_{Ln^{3+}/Ln^{2+}}$).

Samarium and europium exhibit only two oxidation states in molten alkali metal halides [1 - 4]. In dilute solutions they can form two- and trivalent complex ions $LnCl_4{}^{2-}$ and $LnCl_6{}^{3-}$ [3, 5]. The ratio between their concentrations is closely connected with the redox potential of the medium. According to the values of the $E_{Ln^{3+}/Ln^{2+}}$ redox potentials one can consider the relative stability of different valence states.

The value of the redox potential is determined as

$$E_{Ln^{3+}/Ln^{2+}} = E^*_{Ln^{3+}/Ln^{2+}} + \frac{RT}{F} \ln \frac{[Ln^{3+}]}{[Ln^{2+}]},$$

where $E^*_{Ln^{3+}/Ln^{2+}}$ is the formal standard redox potential which depends on the composition of the melt.

2. Experimental Details

2.1. Reagents

Chemically pure LiCl was dried and then purified by zone recrystallization. The anhydrous samarium and europium trichlorides were prepared by chlorination of their hydrates $LnCl_3 \cdot nH_2O$ by heating in a stream of carbon tetrachloride vapour. The rare-earth chloride hydrates were obtained by dissolving their oxides in hydrochloric acid and then evaporating to dryness on a water bath. To prevent the possible formation of samarium and europium oxychlorides a mixture of chlorine and carbon tetrachloride was bubbled through the melt placed in glassy carbon or pyrografite crucibles before the experiment. Weightning, grinding and storing of all the prepared salts were carried out in a dry box under nitrogen atmosphere.

2.2. Procedure

The experimental cell and procedure were described in details in [6]. The total concentration of rare-earth trichlorides dissolved in molten lithium chloride did not exceed 4.5 mol% in all experiments. Glassy carbon was chosen as an indifferent material for the working electrode. A standard chlorine electrode was used as the reference electrode. The measurements were carried out under purified argon atmosphere. All the experimental values of the electromotive force reported here are given with the thermoelectromotive force taken into account.

The trichloride of a chosen rare-earth metal dissolved in LiCl melt was electrochemically reduced to dichloride. The dichloride concentration was calculated according to the amount of electric charge (Q) passed through the system. The value of Q was controlled during the electrolysis using a copper coulometer.

After the experiments were completed, the quenched melts were analysed to determine the concentrations of the samarium or europium two- and trivalent ions. Samarium-containing melts were dissolved in a weak solution of HCl, and the content of samarium(II) was determined from the amount of the evolved hydrogen according to the reaction

$$Sm^{2+} + H^+ \rightarrow Sm^{3+} + {}^1/_2\, H_2.$$

The europium (II) concentration in the europium-containing melts was determined by potentiometric titration with potassium dichromate. The total concentration of rare-earth trivalent ions was determined complexometrically by titration with EDTA.

3. Results and Discussion

The measured redox potentials ($E_{Ln^{3+}/Ln^{2+}}$) as functions of ln $\{[Ln^{3+}]/[Ln^{2+}]\}$ are shown in Fig. 1 (for samarium) and in Fig. 2 (for europium).

In these coordinates the results can be approximated by the linear equations (T = 923 K)

$$E_{Sm^{3+}/Sm^{2+}} = \{-(1.634 \pm 0.002) + (0.085 \pm 0.002) \cdot \ln([Sm^{3+}]/[Sm^{2+}]) \pm 0.003\}\ \text{V},$$

$$E_{Eu^{3+}/Eu^{2+}} = \{-(0.403 \pm 0.001) + (0.081 \pm 0.001) \cdot \ln([Eu^{3+}]/[Eu^{2+}]) \pm 0.002\}\ \text{V}.$$

Here $[Sm^{3+}]$, $[Sm^{2+}]$ and $[Eu^{3+}]$, $[Eu^{2+}]$ are concentrations in mole fractions of samarium and europium ions, respectively.

The number of electrons (n) taking part in the process of electrochemical reduction of rare-earth trichloride was determined from the slopes of the straight lines. For samarium the n values are 0.93 ± 0.02, and for europium they are 0.98 ± 0.02. The chemical analysis of the solidified samarium or europium chloride melts performed after the experiments confirmed the results of the electrochemical measurements. The difference between the concentrations of the rare-earth dichlorides determined coulometrically (i. e., calculated from the amount of electric charge passed through the melt for the reduction of Ln(III)) and analytically did not exceed 2.5%.

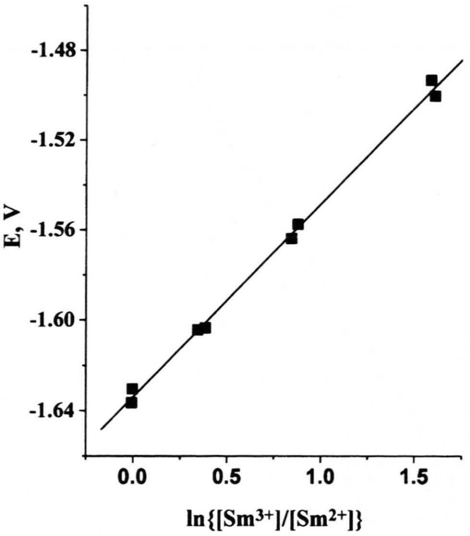

Fig. 1. Redox potentials of samarium at various ratio of Sm(III)/Sm(II) concentrations in molten LiCl at 923 K, measured at a glassy carbon electrode against a standard chlorine reference electrode.

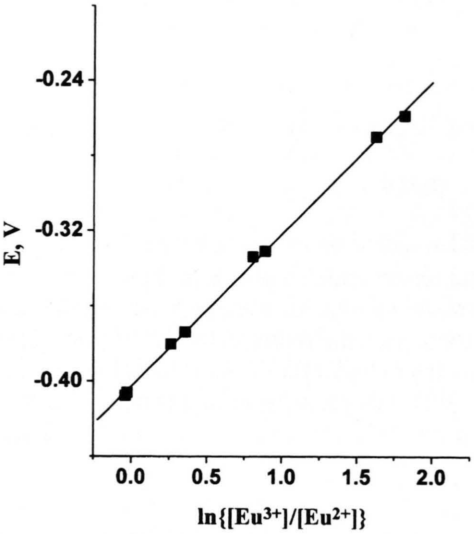

Fig. 2. Redox potentials of europium at various ratio of Eu(III)/Eu(II) concentrations in molten LiCl at 923 K, measured at a glassy carbon electrode against a standard chlorine reference electrode.

The temperature dependencies of the formal standard redox potentials of the samarium- and europium-containing electrolytes (obtained at a glassy carbon electrode) were linear in the whole temperature range studied. The experimental data were least-squares fitted to the equations

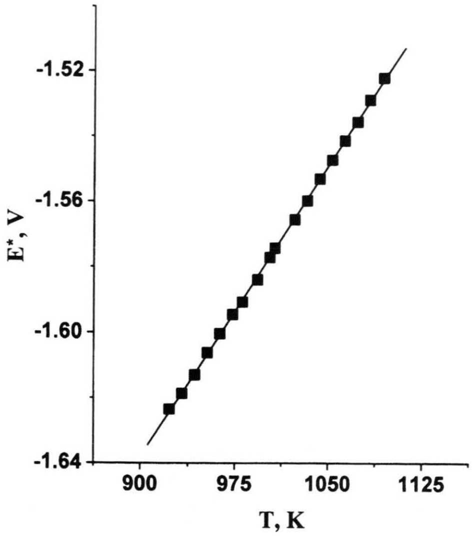

Fig. 3. Effect of temperature on the Sm(III)/Sm(II) formal standard redox potential in molten LiCl. Working electrode: glassy carbon, reference electrode: chlorine.

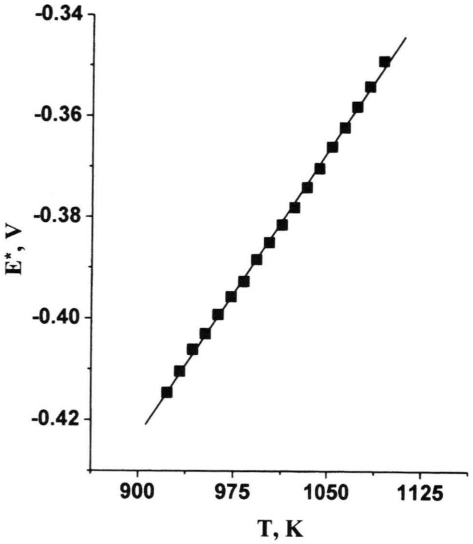

Fig. 4. Effect of temperature on the Eu(III)/Eu(II) formal standard redox potential in molten LiCl. Working electrode: glassy carbon, reference electrode: chlorine.

$$E^*_{\mathrm{Sm}^{3+}/\mathrm{Sm}^{2+}} = \{-(2.173 \pm 0.003) + (59.4 \pm 0.3) \cdot 10^{-5}\, T \pm 0.0006\}\ \mathrm{V},$$

$$E^*_{\mathrm{Eu}^{3+}/\mathrm{Eu}^{2+}} = \{-(0.761 \pm 0.003) + (37.5 \pm 0.3) \cdot 10^{-5}\, T \pm 0.0007\}\ \mathrm{V}.$$

(T = 923 - 1094 K)

The formal standard redox potentials ($E^*_{\mathrm{Ln}^{3+}/\mathrm{Ln}^{2+}}$) increase with temperature as shown in Figs. 3 and 4.

The results of our investigation show that at equal temperatures the redox potential of samarium ($E_{\mathrm{Sm}^{3+}/\mathrm{Sm}^{2+}}$) is more negative than that of europium ($E_{\mathrm{Eu}^{3+}/\mathrm{Eu}^{2+}}$). This fact is in a good agreement with data reported previously for the solutions of samarium and europium chlorides in other alkali metal chloride melts [4, 6].

4. Conclusions

- The $\mathrm{Ln}^{3+}/\mathrm{Ln}^{2+}$ redox potentials depend linearly on $\ln\{[\mathrm{Ln}^{3+}]/[\mathrm{Ln}^{2+}]\}$. The results obtained are described by the Nernst equation. The number of electrons is close to one, indicating that the reaction $\mathrm{Ln}^{3+} + \mathrm{e} \Leftrightarrow \mathrm{Ln}^{2+}$ takes place in the systems studied.
- The formal standard redox potentials ($E^*_{\mathrm{Ln}^{3+}/\mathrm{Ln}^{2+}}$) in LiCl-based melts increase with temperature.
- The redox potential $E_{\mathrm{Sm}^{3+}/\mathrm{Sm}^{2+}}$ was found to be more negative than $E_{\mathrm{Eu}^{3+}/\mathrm{Eu}^{2+}}$ at the same temperature and the same ratio of Ln(III)/Ln(II) concentrations in the systems investigated.

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