Thermodynamic Characteristics of Samarium and Europium Chlorides in Molten Alkali Metal Chlorides

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Z. Naturforsch. **56 a,** 837–840 (2001); received August 20, 2001

Presented at the NATO Advanced Study Institute, Kas, Turkey, May 4 - 14, 2001.

The formal standard redox potentials of samarium (III)/(II) ($E^{*}_{\mathrm{Sm}^{3+}/\mathrm{Sm}^{2+}}$) and europium (III)/(II) ($E^{*}_{\mathrm{Eu}^{3+}/\mathrm{Eu}^{2+}}$) in molten alkali metal chlorides were measured potentiometrically against a reference chlorine electrode. The Gibbs energy changes and equilibrium constants for the reaction $\mathrm{LnCl}_{2(\mathrm{l})} + {}^{1}/_{2}\,\mathrm{Cl}_{2(\mathrm{g})} \Leftrightarrow \mathrm{LnCl}_{3(\mathrm{l})}$ were calculated for the salt systems studied. The effect of the cationic composition of the melt-solvent on the above thermodynamic characteristics is also reported.

Key words: Thermodynamic Stability; Rare Earth Chlorides; Molten Alkali Metal Chlorides; Redox Potentials; Gibbs Energy Changes

1. Introduction

The existence of various valencies of rare-earth metal chlorides in molten Ln-LnCl_3 systems (where Ln is any lanthanide from lanthanum to lutetium) is a matter of significant scientific interest. For the lanthanides of cerium group neodymium, samarium and europium dichlorides have been obtained [1 - 4]. The existence of praseodymium dichloride is also possible. Preparation of cerium and lanthanum dichlorides is unlikely to be successful. This problem is closely connected to the values of the corresponding redox potentials ($E_{\mathrm{Ln}^{3+}/\mathrm{Ln}^{2+}}$).

The role of the electrochemical methods of processing rare-earth raw materials in molten salts is currently becoming more important because of growing use of rare-earth metals, their alloys and compounds in modern technologies. In the electrochemical systems based on molten alkali metal halides, rare-earth metals can be present in a variety of oxidation states. The information available on the oxidation-reduction processes in fused salt electrolytes containing halides of rare-earth metals is scarce [5]. The values of the thermodynamic characteristics are often presented only as estimates obtained from either indirect methods for the determination of electrochemical parameters [6] or linear sweep voltammetry [7]. Application of techniques allowing direct determination of decomposition potentials or redox potentials of halide systems containing rare-earth metals are connected with significant experimental difficulties. At the potentials of lanthanide chloride decomposition, alkali metals are also deposited to a considerable extent, and, on the other hand, the high affinity of lanthanides to oxygen requires extreme care in carrying out the experiments. All these points were clearly addressed in previous works [7 - 8].

We would like to point out the following important problems of the electrochemistry of molten alkali metal halides containing rare-earth metals which are insufficiently elucidated in the existing literature. First, the stability of rare-earth ions containing Ln in various oxidation states in these systems. Second, the quantitative characteristics of oxidation-reduction reactions, particularly the calculation of the number of electrons taking place in the reaction, the equilibrium constants as well as their dependence on the ionic composition of the melt, rare-earth halide concentration and temperature. The critical analysis of the available data [7, 9 - 11] as well as our studies clearly show that samarium and europium exhibit only two stable oxidation states Ln^{3+} and Ln^{2+}, which can participate in to the reversible one-electron oxidation-reduction reaction [12].

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In this paper, the results of studying the equilibrium of the oxidation-reduction reactions

$$SmCl_{2(l)} + {}^{1}/_{2}\, Cl_{2(g)} \Leftrightarrow SmCl_{3(l)} \qquad (1)$$

and

$$EuCl_{2(l)} + {}^{1}/_{2}Cl_{2(g)} \Leftrightarrow EuCl_{3(l)} \qquad (2)$$

in molten alkali metal chlorides are discussed.

2. Experimental Details

The potentiometric technique used in the present work was described in [12]. The anhydrous samarium and europium trichlorides were prepared from their hydrates by heating with carbon tetrachloride vapour. The melts investigated were prepared in situ during the experiment. The total concentration of rare-earth trichlorides dissolved in molten alkali metal chloride did not exceed 4.5 mol.% in all experiments. Glassy carbon was used as the indifferent working electrode, and a standard chlorine electrode was used as the reference one. The measurements were carried out under purified argon.

The trichloride of the selected rare-earth metal added to the corresponding salt-solvent was electrochemically reduced to dichloride. The concentration of the dichloride was calculated from the quantity of electricity passed through the system during the reduction. After the experiments, the quenched melts were analysed to determine the concentrations of two- and trivalent ions of samarium or europium. The content of europium dichloride in the solidified melt was determined by potentiometric titration with potassium dichromate, and the content of samarium dichloride was determined by a volumometric method, by dissoluting the melt in a weak solution of HCl and measuring the volume of hydrogen evolved. The total content of rare-earth trivalent ions was determined complexometrically using EDTA.

3. Results and Discussion

The redox potential ($E_{Ln^{3+}/Ln^{2+}}$) depends linearly on the logarithm of the ratio of the trichloride-to-dichloride concentrations ($\ln\{[Ln^{3+}]/[Ln^{2+}]\}$). The number of electrons (n) taking part in the electrochemical reduction of rare-earth trichloride was determined from the slope of the isotherms. The values obtained are shown in Table 1.

Table 1. The experimental formal standard redox potentials ($E^{*}_{Ln^{3+}/Ln^{2+}}$) in molten alkali metal chlorides.

Solvent	R_{Me}, Å	$E^{*}_{Sm^{3+}/Sm^{2+}}$ n	$E^{*}_{Sm^{3+}/Sm^{2+}}$ 1073 K	$E^{*}_{Eu^{3+}/Eu^{2+}}$ n	$E^{*}_{Eu^{3+}/Eu^{2+}}$ 1073 K
LiCl	0.78	0.93 ± 0.02	–1.536 V	0.98 ± 0.02	–0.358 V
NaCl-KCl	1.155	0.90 ± 0.01	–1.880 V	1.02 ± 0.03	–0.742 V
KCl	1.33	0.96 ± 0.01	–1.966 V	0.95 ± 0.01	–0.844 V
CsCl	1.65	1.01 ± 0.01	–2.087 V	1.02 ± 0.03	–0.981 V

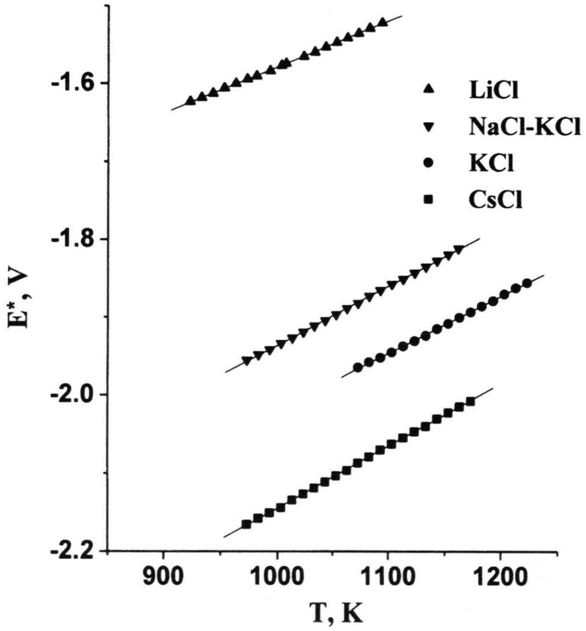

Fig. 1. Redox potentials of samarium at various Sm(III)/Sm(II) concentrations, measured on a glassy carbon electrode against a standard chlorine reference electrode in molten alkali metal chlorides.

The chemical analysis of quenched melts carried out after the experiments confirmed the results of the electrochemical measurements. The concentrations of samarium and europium dichlorides in the solidified melts were determined using two independent methods. The differences between the results of the coulometric (first method) and analytical (second method) determinations did not exceed 2.5%. The results thus obtained confirm the conclusions made from the results of potentiometric investigations.

The formal standard redox potentials of the samarium and europium systems (obtained on the glassy carbon electrode) show a linear temperature dependence in the temperature range investigated, as illustrated in Figs. 1 and 2.

The results of the investigations show that the $E_{Sm^{3+}/Sm^{2+}}$ redox potential is more negative than

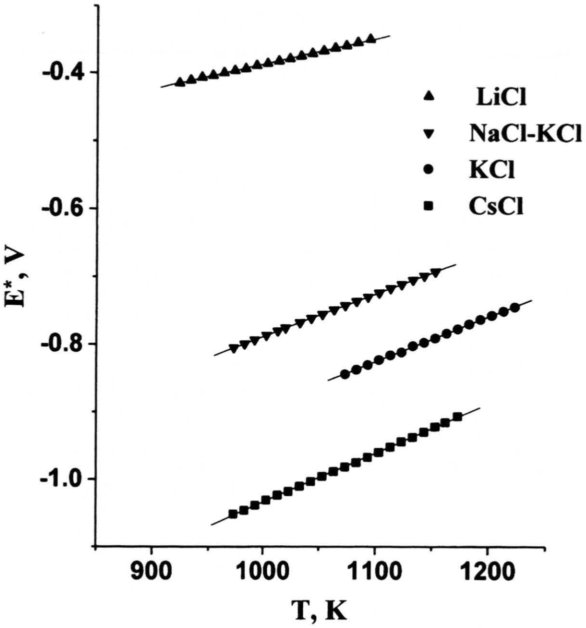

Fig. 2. Redox potentials of europium at various Eu(III)/ Eu(II) concentrations, measured on a glassy carbon electrode against a standard chlorine reference electrode in molten alkali metal chlorides.

Table 2. The calculated formal standard redox potentials ($E^*_{\mathrm{Ln^{3+}/Ln^{2+}}}$) for several molten alkali metal chlorides at different temperatures.

	$E^*_{\mathrm{Sm^{3+}/Sm^{2+}}}$, V			$E^*_{\mathrm{Eu^{3+}/Eu^{2+}}}$, V		
Melt	1073 K	1123 K	1173 K	1073 K	1123 K	1173 K
NaCl	–	−1.720	−1.683	–	−0.572	−0.542
RbCl	−2.033	−1.995	−1.956	−0.923	−0.885	−0.850
LiCl-KCl	−1.719	−1.686	−1.649	−0.561	−0.533	−0.504

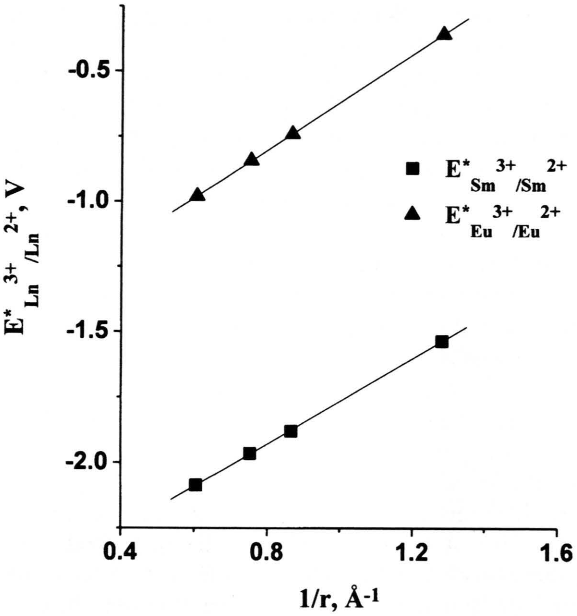

Fig. 3. Dependences of the formal standard redox potentials of $E^*_{\mathrm{Ln^{3+}/Ln^{2+}}}$ on the reciprocal radius of the cation of the solvent at 1073 K in molten alkali metal chlorides.

$E_{\mathrm{Eu^{3+}/Eu^{2+}}}$ one at the same temperatures and the concentration ratio of the electroactive species for all the salt systems studied.

It is interesting to note that changing the salt-solvent, results in a shift of the formal standard redox potentials of samarium and europium ($E^*_{\mathrm{Ln^{3+}/Ln^{2+}}}$). The values of $E^*_{\mathrm{Ln^{3+}/Ln^{2+}}}$ measured in different salt-solvents are presented in Table 1.

Figure 3 shows that the dependence of the formal standard redox potentials of $E^*_{\mathrm{Ln^{3+}/Ln^{2+}}}$ on the reciprocal radius of the cation of the salt-solvent was also linear for pure molten alkali metal chlorides and their mixtures. These plots allow to estimate the values of $E^*_{\mathrm{Ln^{3+}/Ln^{2+}}}$ for unstudied chlorides or their mixtures for alkali metals in the sequence from $\mathrm{Li^+}$ to $\mathrm{Cs^+}$. The estimated values of the formal standard redox potentials of $E^*_{\mathrm{Sm^{3+}/Sm^{2+}}}$ and $E^*_{\mathrm{Eu^{3+}/Eu^{2+}}}$ at different temperatures for molten NaCl, RbCl, and LiCl-KCl eutectic mixtures are summarized in Table 2.

Using the formal standard redox potentials, the free Gibbs energy changes and the equilibrium constants for the reduction-oxidation reactions in all the salt systems studied can be calculated using the classical equations:

$$\Delta G^* = -nFE^*$$

and

$$\Delta G^* = -RT \ln K^*.$$

These thermodynamic parameters depend on the cation radius of the salt-solvent and the temperature. The values obtained for different temperatures of all the salt-solvents investigated are presented in Tables 3 and 4.

The shift of the formal standard redox potentials of samarium and europium towards negative values and the observed Gibbs energy changes for the oxidation-reduction reactions in the various melts in the sequence from LiCl to CsCl can be explained by the complexing processes in the melts. It is well

Table 3. The effect of temperature on the formal standard Gibbs energy changes in alkali metal chloride melts.

	$LnCl_{2(l)} + {}^1/_2\,Cl_{2(g)} \Leftrightarrow LnCl_{3(l)}$					
Solvent	Ln = Sm, ΔG^* kJ·mol^{-1}			Ln = Eu, ΔG^* kJ·mol^{-1}		
	1073 K	1123 K	1173 K	1073 K	1123 K	1173 K
LiCl	–148.2	–145.3	–142.4	–34.6	–32.8	–31.0
NaCl-KCl	–181.5	–177.8	–174.1	–71.6	–68.6	–65.6
KCl	–189.8	–186.2	–182.7	–81.4	–78.2	–74.9
CsCl	–201.3	–197.5	–193.6	–94.7	–91.1	–87.6

Table 4. The equilibrium constants (K^*) between di- and trichlorides of samarium and europium in molten alkali metal chlorides at different temperatures.

	$LnCl_{2(l)} + {}^1/_2\,Cl_{2(g)} \Leftrightarrow LnCl_{3(l)}$					
Solvent	Ln = Sm, K^*			Ln = Eu, K^*		
	1073 K	1123 K	1173 K	1073 K	1123 K	1173 K
LiCl	$1.64 \cdot 10^7$	$5.75 \cdot 10^6$	$2.21 \cdot 10^6$	48.3	33.5	23.9
NaCl-KCl	$6.81 \cdot 10^8$	$1.86 \cdot 10^8$	$5.67 \cdot 10^7$	$3.07 \cdot 10^3$	$1.55 \cdot 10^3$	$8.31 \cdot 10^2$
KCl	$1.73 \cdot 10^9$	$4.60 \cdot 10^8$	$1.37 \cdot 10^8$	$9.13 \cdot 10^3$	$4.32 \cdot 10^3$	$2.17 \cdot 10^3$
CsCl	$6.33 \cdot 10^9$	$1.53 \cdot 10^9$	$4.20 \cdot 10^8$	$4.06 \cdot 10^4$	$1.74 \cdot 10^4$	$7.98 \cdot 10^3$

known that in dilute solutions of rare-earth metals in molten alkali metal chlorides lanthanide ions form the hexachloro- and tetrachlorocoordinated complex ions $LnCl_6{}^{3-}$ and $LnCl_4{}^{2-}$. Their relative stability increases with increasing radius of the cation of the solvent in the sequence $Li^+ \rightarrow (Na\text{-}K)^+ \rightarrow K^+ \rightarrow Cs^+$ (see Table 1). As a result the redox potentials are shifted to more negative values. This is in good agreement with the modern views on the influence of the effective radius of cations of the salt-solvent on the redox potentials of many salt systems containing multiple-charged cations [13].

4. Conclusions

- The Ln^{3+}/Ln^{2+} redox potentials depend linearly on ln $\{[Ln^{3+}]/[Ln^{2+}]\}$.
- The data obtained are described by the Nernst equation, and the number of electrons is close to one, indicating the single-electron electrochemical reaction $Ln^{3+} + e^- \Leftrightarrow Ln^{2+}$ in all the systems studied.
- The formal standard redox potentials ($E^*_{Ln^{3+}/Ln^{2+}}$) in molten alkali chlorides increase with increasing temperature.
- The formal standard redox potentials of both $E^*_{Sm^{3+}/Sm^{2+}}$ and $E^*_{Eu^{3+}/Eu^{2+}}$ become more negative with increase of the cation radius of the solvent.
- The redox potential of samarium is more negative than that of europium at the same temperature and the same ratio of concentrations of electroactive species (Ln (III) and Ln (II)) for all the systems studied.
- It has been established that the stability of both samarium and europium trichloride increases with the increasing radius of the cation of the salt-solvent and/or with decreasing temperature. The highest stability of lanthanide trichlorides was observed in CsCl-based melts. Moreover, the relative stability of lanthanide (III) complexes is higher than that of lanthanide (II) ones.

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