

INFLUENCE OF THE FIRST AND SECOND COORDINATION SPHERES ON ELECTROCHEMICAL AND THERMODYNAMICAL PROPERTIES OF EUROPIUM IN ALKALI CHLORIDE MELTS

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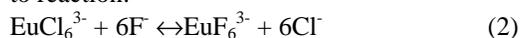
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The electroreduction of EuCl_3 in NaCl-KCl without and with additions of fluoride ions (NaF), and in KCl , CsCl melts in the temperature range 973-1123 K was studied by different electrochemical methods. It was determined that electrochemical reduction of Eu(III) in these melts occurs via two successive reversible stages involving transfer of the one and two electrons. In pure chloride melts the process:



is reversible at a polarization rate of $v \leq 0.1 \text{ V s}^{-1}$, but at a sweep rate $0.1 < v \leq 0.3 \text{ V s}^{-1}$ a mixed diffusion and electron-transfer control was observed. A further increase of polarization rate, $v \geq 0.5 \text{ V s}^{-1}$ results in the electron-transfer control.

In NaCl-KCl melt with the ratio $\text{Eu/F} = 1:6$ at the polarization rate of 0.1 V s^{-1} the redox process became quasi-reversible. The diffusion coefficients (D) of Eu(III) and Eu(II) in chloride-fluoride melt were lower in comparison with NaCl-KCl melt [1]. The decreasing of D is connected with the formation of fluoride complexes due to reaction:



Fluoride complexes are stronger than chloride ones, and this in turn leads to decrease in the contribution to the diffusion coefficients from the “hopping” mechanism.

Standard rate constants (κ_s) of the redox process (1) for fluoride complexes were determined using linear sweep voltammetry, cyclic voltammetry and impedance-spectroscopy data. The values of κ_s in chloride-fluoride melts in the temperature range 973-1023 K were 3.2-4.5 times less in comparison with pure NaCl-KCl melt [2]. This result is in accordance with the theory of elementary charge transfer, because the smaller and stronger bond complexes need a high rearrangement time, and in consequence the process (1) proceeds at a slower rate.

The formation of a stronger fluoride complexes led to significant shift to the region of negative potentials of the process (1). It is known [3] that addition of fluoride ions to chloride melts often causes stabilization of higher oxidation states of metals. In the NaCl-KCl melt with molar ratio $\text{Eu/F} = 1:6$ both complexes Eu(III) and Eu(II) were stable.

At the same time for the NaCl-KCl melt containing samarium at molar ratio $\text{Sm/F} = 1:6$ only complexes Sm(III) were thermodynamically stable. Introducing of fluoride ions to the NaCl-KCl melt containing Sm(II) is accompanied by reaction of disproportionation:



Thus complexes of Eu(II) are more stable in comparison with Sm(II) complexes.

A decrease of D is found when the cation composition of the second coordination sphere changes from Na to Cs . Similar changes in D values are well known. They are due to the decrease of the counter-polarizing effect of cations from Na to Cs , resulting in a decrease of metal-ligand bond length. The diffusion coefficients decrease when the europium oxidation state increases while the activation energies for diffusion increase. The standard rate constants of redox reaction (1) increased when going from NaCl-KCl to CsCl melt. Our experimental results suggest that electron transfer related to reaction (1) may proceed over outer-sphere cation. The highest value for κ_s was observed in CsCl melt because of the larger polarizability of caesium.

The formal standard potentials of $E^*_{\text{Eu(II)/Eu}}$, $E^*_{\text{Eu(III)/Eu}}$ and formal standard redox potentials of $E^*_{\text{Eu(III)/Eu(II)}}$ were determined from open-circuit potentiometry and cyclic voltammetry data. The thermodynamics of dilute solutions formation of europium di- and trichloride, and equilibrium constants of metal-salt reaction in alkali chloride melts were calculated.

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References

1. S.A. Kuznetsov and M. Gaune-Escard, *J. Electrochim. Acta*, **46**, 1101 (2001).
2. S.A. Kuznetsov, L. Rycerz and M. Gaune-Escard, *Z. Naturforsch.*, **56a**, 741 (2001).
3. S.A. Kuznetsov, P.T. Stangrit, *Russ. J. Appl. Chem.*, **66**, 2702 (1993).