Electrochemical and Thermodynamic Properties of EuCl$_3$ and EuCl$_2$ in an Equimolar NaCl-KCl Melt

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The electroreduction of EuCl$_3$ in an equimolar NaCl-KCl mixture was studied at 973 - 1123 K by different electrochemical methods. This reduction of Eu(III) in NaCl-KCl melt occurs via two successive reversible steps involving transfer of one and two electrons. The diffusion coefficients of Eu(III) and Eu(II) were measured by linear sweep voltammetry and chronopotentiometry. The values found by these methods are in a good agreement. The standard rate constants for the redox reaction $Eu(III) + e^- \Leftrightarrow Eu(II)$ were calculated from cyclic voltammetry data. The sluggish kinetics of this reaction is discussed in terms of substantial rearrangement of the europium coordination sphere. Special attention was paid to the choice of working electrodes for the study of electrode reactions. The formal standard potentials $E^*_{Eu(II)/Eu}$, $E^*_{Eu(III)/Eu}$ and the formal redox potentials $E^*_{Eu(III)/Eu(II)}$ were determined from open-circuit potentiometry and linear sweep voltammetry data. The free Gibbs energy changes for the reaction $EuCl_{3(sol.)} \Leftrightarrow EuCl_{2(sol.)} + 1/2\ Cl_{2(g.)}$ and the equilibrium constants of the metal-salt reaction $2Eu(III) + Eu \Leftrightarrow 3\ Eu(II)$ were calculated. The thermodynamics of the formation of dilute solutions of europium di- and trichloride in an equimolar NaCl-KCl melt were determined. It was shown that electrochemical transient techniques give the possibility of the determination of the relative partial molar mixing enthalpy of europium trichloride and dichloride in NaCl-KCl melt.

Key words: Europium; Molten Salts; Kinetics of Electrode Reaction; Formal Standard Potentials; Mixing Enthalpy.