

Unusual Influence of the Temperature on the Standard Rate Constants of Charge Transfer for the Eu(III)/Eu(II) Redox Couple in Chloride-Bromide Melts

Sergey A. Kuznetsov^{a,b} and Marcelle Gaune-Escard^b

^a Institute of Chemistry, Kola Science Centre RAS, 14 Fersman Str., 184209 Apatity, Murmansk Region, Russia

^b École Polytechnique, Département Mécanique Énergetique, Technôpole de Château Gombert, 5 rue Enrico Fermi, 13453 Marseille Cedex 13, France

Reprint requests to Prof. M. G.-E.; Fax: +33(0)4 91 11 74 39; E-mail: mge@polytech.univ-mrs.fr

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The influence of bromide ions and temperature on the standard rate constants of the Eu(III)/Eu(II) redox reaction was determined. Cyclic voltammetry was used for the calculation of the kinetic parameters. It was shown that in NaCl-KCl (equimolar mixture)-NaBr (15 wt%)-EuCl₃ melts increase of the temperature from 973 K up to 1023 K leads to a drastical decrease of the standard rate constant k_s for the Eu(III)/Eu(II) redox reaction. This unusual influence of the temperature on the k_s value was explained by a change of the electron transfer mechanism. It is suggested that at 1023 K another mechanism becomes dominant – the transfer of electrons through dissolved bromine in the melt. Bromine appeared in the melt due to the decomposition of chloride-bromide or bromide complexes of Eu(III), and the concentration of bromine in the melt increased with the growth of temperature.

Key words: Europium; Chloride-Bromide Melt; Electrode Reaction; Outer-Sphere Cation; Charge Transfer Mechanism.