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

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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\%)-EuCl\textsubscript{3} melts increase of the temperature from 973 K up to 1023 K leads to a drastic 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.

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