

REDUCTION OF Eu(III) ON ROTATING DISC Pt AND Cu ELECTRODES

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The reduction of Eu(III) on rotating disc Pt and Cu electrodes was studied in the medium of chlorides containing some other rare earth elements. The rate constants of the electrode reaction $\text{Eu}^{3+} \rightleftharpoons \text{Eu}^{2+}$ were determined and compared with the values obtained earlier by cyclic voltammetry.

The reduction of trivalent europium to divalent is one of the steps used usually in industrial separation of europium from rare earth elements mixtures. Reduction with powdered zinc is usually preferred, although electrochemical reduction has the advantage that it does not result in contamination with an additional species. The latter process was studied mainly on mercury cathodes¹; solid cathodes have been used only recently to this purpose². The aim of the present work was to compare the reduction rates of Eu³⁺ both in the presence and in the absence of other rare earth elements.

EXPERIMENTAL

A mixture of oxides of all rare earth elements was used as starting material; the content of Ce was lowered by fractional precipitation and that of La by fractional crystallization. An amount of 30.23 g of the oxide mixture was dissolved in hydrochloric acid of reagent grade; the final concentration was 0.09M Eu³⁺, the volume of the solution was 100 ml and pH 4.2. The solution contained further $6.96 \cdot 10^{-2}$ M Ce³⁺, $1.61 \cdot 10^{-2}$ M La³⁺, $7.71 \cdot 10^{-2}$ M Pr³⁺, and 0.66M Nd³⁺, as determined by atomic absorption spectrophotometry and X-ray fluorescence analysis in the original mixture of oxides (other rare earth elements were not determined).

A three-electrode system was used: the rotation disc electrode (Laboratorní Přístroje, Prague) had an active surface area of 0.0314 cm² (Pt) or 0.0073 cm² (Cu); the reference was a saturated calomel electrode, and the auxiliary electrode was a Pt foil (2 cm²). The potential values are given against SCE; the temperature of measurement was $25 \pm 1^\circ\text{C}$. The measured solution was deaerated by bubbling with spectrally pure nitrogen for 5 min.

The potential of the indicator electrode was controlled by a PA 2 type polarograph (Laboratorní Přístroje, Prague), which served also for the current measurement. The current was recorded on an XY-4103 recorder of the same manufacturer.

RESULTS AND DISCUSSION

The current-potential curve for reduction of Eu^{3+} on the Pt electrode is shown in Fig. 1. The region of the limiting current is not distinct owing to interference with the current due to hydrogen evolution. To distinguish the two processes, the method according to Pleskov³ was used. The current due to reduction of Eu^{3+} (after correction for the hydrogen evolution) is indicated by the dashed line. The curve thus obtained has the shape expected. The curves for reduction of Eu^{3+} on the copper electrode were treated analogously. In this case, however, the corrected curves did not show a constant limiting current, but rather a slightly decreasing one (about 2% per 0.1 V). Therefore, the diffusion coefficient of Eu^{3+} ions was calculated from the data obtained with the Pt electrode.

The dependence of the limiting current density for reduction of Eu^{3+} on the rotating Pt electrode on the square root of the angular frequency is linear and its slope enabled us to calculate the diffusion coefficient as $D(\text{Eu}^{3+}) = 1.46 \cdot 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$. The kinematic viscosity of the solution was determined as $0.0214 \text{ cm}^2 \text{ s}^{-1}$ by using the Ubbelohde viscosimeter. The published values of $D(\text{Eu}^{3+})$ are, e.g., $8.5 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ in 1M KCl (ref.⁴), $6.3 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ in 1M KI (ref.⁴), and $5.6 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ in 1M KSCN (ref.⁵).

The measured dependences of the current density on the potential were evaluated by means of the equation⁶

$$1/i = 1/i_k + (1.61v^{1/6}/i_k) [(k^+/D_{\text{Eu}^{3+}}^{2/3}) + (k^-/D_{\text{Eu}^{3+}}^{2/3})]/\omega^{1/2} \quad (1)$$

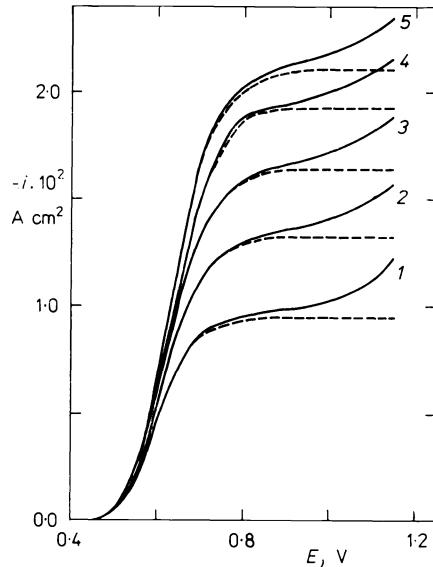


FIG. 1

Dependence of the reduction current for Eu^{3+} on the potential of rotating Pt disc electrode. Angular velocity, s^{-1} : 1 52.36; 2 104.72; 3 157.08; 4 209.44; 5 261.80. Solution concentration 0.09M Eu^{3+} . Dashed line indicates current corrected for the evolution of hydrogen

valid at constant potential. Here,

$$k^+ = k_0^+ \exp(\alpha nF/RT), \quad (2)$$

$$k^- = k_0^- \exp[-(1 - \alpha) nF/RT], \quad (3)$$

$$i_k = -nFk^-c^0(\text{Eu}^{3+}). \quad (4)$$

The last symbol in Eq. (4) denotes the bulk concentration of Eu^{3+} (that of Eu^{2+} is in our case negligible or zero), k_0^+ and k_0^- are rate constants for oxidation and reduction, respectively, at the standard potential, and other symbols have their usual significance.

The linear dependences of $1/i$ on $1/\omega$ at various potentials were correlated with Eq. (1) to give the current density i_k , which, according to Eq. (4), has the meaning of current density for reduction of Eu^{3+} controlled by charge transfer only. The charge transfer coefficient, α , was calculated as 0.47 for Pt and 0.49 for Cu electrode from the slope of the linear dependences of $\log i_k$ on the potential.

To measure the equilibrium potential, we prepared by reduction a solution with the concentration ratio of $\text{Eu}^{3+} : \text{Eu}^{2+} = 0.68 : 0.32$ at the same pH. The measured equilibrium potential was -0.545 V compared to the calculated (thermodynamic) value of -0.564 V. The rate constant k_0^- at this potential is $5.12 \cdot 10^{-4} \text{ cm s}^{-1}$ on Pt and $6.23 \cdot 10^{-4} \text{ cm s}^{-1}$ on Cu electrode. The published values² are in a KCl solution $0.9 - 1.2 \cdot 10^{-4} \text{ cm s}^{-1}$ on Pt and $1.4 - 1.9 \cdot 10^{-4} \text{ cm s}^{-1}$ on Cu electrode, as determined by cyclic voltammetry. Based on the mentioned values of the rate constants it can be assumed that the reduction rate of europium at the electrode materials used will not be lowered by the presence of other rare earth elements in the chloride solution.

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