

KINETICS OF ELECTRODE REACTION OF $\text{Eu}^{3+}/\text{Eu}^{2+}$ STUDIED BY CYCLIC VOLTAMMETRY AND TAST POLAROGRAPHY

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The electrochemical behaviour of europium at the dropping mercury electrode was studied in the medium of 1M- NaClO_4 , 1M- NaCl , 1M- NaNO_3 , and 1M- Na_2SO_4 . The curves obtained by Tast polarography and the kinetic parameters (k_s , α) for the $\text{Eu}^{3+}/\text{Eu}^{2+}$ system in the medium of perchlorate and chloride solutions are in accord with the results published earlier. The kinetic parameters in nitrate and sulphate media are given for the first time. In the medium of nitrates, the electrode reaction is probably accompanied by a chemical reaction.

The electrochemical behaviour of europium remains in the focus of interest of many workers in the field. The oxidation state +3 is characteristic of all earth elements. Also divalent ions of Eu, Yb, and Sm are relatively stable in aqueous solutions, where Eu(II) appears most stable of the three. This fact is utilized in the separation of Eu from mixtures of rare earth elements^{1,2}. The study of the kinetics of $\text{Eu}^{3+}/\text{Eu}^{2+}$ electrode reaction on various electrode materials and in the presence of various anions seems therefore desirable.

Of the electrode materials, mercury is most often used. The standard redox potential of the electrode process is in many supporting electrolytes close to the zero charge potential, E_z , of mercury, hence the influence of the double layer on the rate of charge transfer can be studied on both positively and negatively charged interface^{3,4}. The electrochemical behaviour of europium was studied on other electrode materials as well, namely on Pt, Cu, graphite, Au, and Ni (ref.⁵).

The values of rate constant k_s and charge transfer coefficient α of the electrode reaction on Hg electrode in the presence of Cl^- , ClO_4^- , I^- , and Br^- ions or ethylenediaminetetraacetic acid were given by many authors⁶⁻¹⁶.

We decided to study the couple $\text{Eu}^{3+}/\text{Eu}^{2+}$ by cyclic voltammetry on a hanging mercury drop electrode (HMDE) and by Tast polarography in one-molar solutions of NaCl , NaClO_4 , NaNO_3 , and Na_2SO_4 , and to compare the found values of k_s and α with those published previously.

EXPERIMENTAL

Voltammetric curves were measured at $25 \pm 1^\circ\text{C}$ with a PA-3 polarographic analyser connected with a static mercury drop electrode SMDE 1 and an X-Y 4 105 recorder (Laboratorní Přístroje,

Prague). The hanging mercury drop electrode used in cyclic voltammetry had a surface area of 0.020 cm^2 ; the dropping mercury electrode (DME) used in Tast polarography had a surface area of 0.012 cm^2 at a drop time of 1 s and rate of flow 1.75 mg s^{-1} . The reference electrode was of saturated AgCl type and the counter electrode was a Pt foil (1.5 cm^2). The potential values are given against the AgCl electrode.

The values of pH were measured with an OP 211/1 pH-meter (Radelkis, Hungary) with a combined electrode Orion 81-02.

Solutions containing $0.005 \text{ mol l}^{-1} \text{Eu}^{3+}$ and 1 mol l^{-1} of a sodium salt (chloride, perchlorate, nitrate, or sulphate) were prepared by dissolving Eu_2O_3 (99.99% purity, Johnson Matthey, U.K.) in the corresponding acid (of reagent grade); the solution was then titrated with a sodium hydroxide solution to attain pH 4.0 and the desired composition. The concentration of Eu^{3+} was checked polarographically (with differential pulse polarography) by the method of standard addition in the medium of $0.5 \text{ mol l}^{-1} \text{KCl}$ and 0.05 mol l^{-1} potassium hydrogen phthalate¹⁷. The mentioned chloride solution served as standard, whose concentration was checked complexometrically by using methylthymol blue as indicator.

RESULTS AND DISCUSSION

Whereas Tast polarography gave qualitative data about the envisaged system, cyclic voltammetry enabled us to determine the diffusion coefficient, D_0 , the charge transfer coefficient, α , and the standard rate constant of the electrode reaction, k_s .

Tast polarographic curves for reduction of europium are shown in Fig. 1; their half-wave potentials correspond to those published earlier. In accord with Kinard and Philp¹⁹, who studied classical polarographic curves for reduction of europium ions in the presence of various anions, the curve for reduction of Eu(III) in a sulphate solution is more irreversible in character than the curves in the media of chlorides, nitrates, and perchlorates (the half-wave potential is markedly shifted to negative values and the wave height is much smaller). In contrast to the mentioned work¹⁹, however, the wave for Eu(III) in the presence of Cl^- ions is somewhat lower than the waves in the media of perchlorates and nitrates, and the decrease of the wave in sulphate solution is considerably more pronounced. Kinard and Philp used solutions of $1.7 \cdot 10^{-3} \text{ mol l}^{-1} \text{Eu(III)}$ in one-molar supporting electrolytes of pH 2, each of them containing ClO_4^- ions. They used perchloric acid to dissolve Eu_2O_3 and to control the value of pH. We used in the present work solutions of $5 \cdot 10^{-3} \text{ M-Eu}^{3+}$ of pH 4 containing only one anion.

Test polarographic measurements (Fig. 1) together with the known values of the rate constant of the electrode reaction imply a quasireversible process in the presence of Cl^- , ClO_4^- , and NO_3^- ions and an irreversible process in the presence of SO_4^{2-} ions. Therefore, we decided to use cyclic voltammetry for the determination of the parameters of the electrode reaction in view of the possibility to use the theory of quasireversible electrode processes²⁰.

The voltammetric curves were recorded at various scan rates, v ; those obtained in nitrate solutions are shown in Fig. 2. In Tables I–IV are summarized the data

read from the voltammetric curves (anodic peak potential, $E_{p,a}$, cathodic peak potential, $E_{p,c}$, cathodic half-wave potential $E_{p/2,c}$, and $\Delta E_p = E_{p,a} - E_{p,c}$). Further included are the values of the function ψ corresponding to ΔE_p (according to Table I in ref.²⁰) and the calculated values of the transfer coefficient α and standard rate constant k_s of the electrode reaction $\text{Eu}^{3+}/\text{Eu}^{2+}$. These were calculated from the equations

$$\alpha n = 0.048 (E_{p/2,c} - E_{p,c}), \quad (1)$$

$$k_s = \psi(\pi a D_O)^{1/2} / v^\alpha \quad (2)$$

$$v = (D_O/D_R)^{1/2}, \quad a = nFv/RT. \quad (3), (4)$$

Here, the ratio of D_O/D_R was set equal to 0.73.

For the sulphate medium, the above equations could not be used to calculate k_s ; we preferred the equation published in refs^{22,23}:

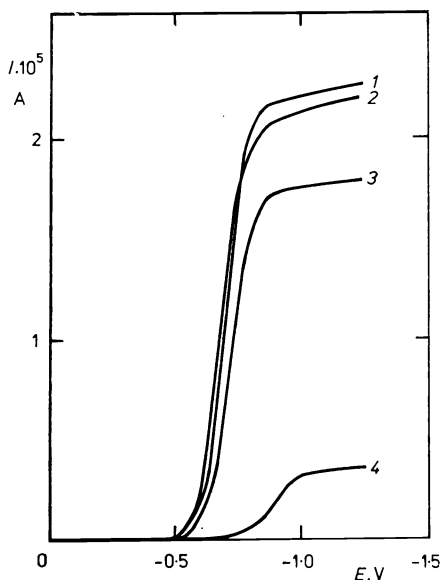


FIG. 1

Tast-polarographic curves for reduction of Eu(III) in the medium of 1 1M-NaNO_3 ; 2 1M-NaClO_4 ; 3 1M-NaCl ; 4 $1\text{M-Na}_2\text{SO}_4$ containing 0.005M-Eu^{3+} ; pH 4, drop time 1 s, scan rate 0.5 mV s^{-1} , $h = 50\text{ cm}$

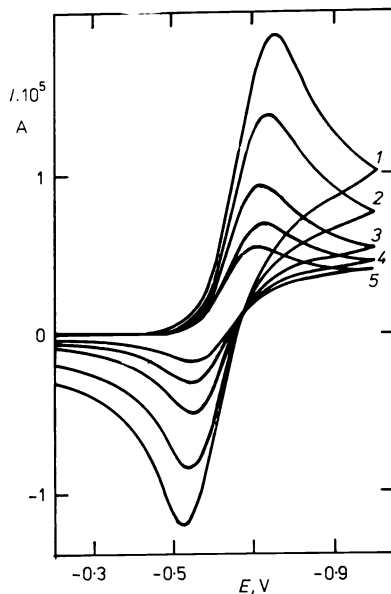


FIG. 2

Voltammetric curves for the $\text{Eu}^{3+}/\text{Eu}^{2+}$ system in 1M-NaNO_3 at various scan rates (v , mV s^{-1}): 1 100; 2 50; 3 20; 4 10; 5 5

TABLE I

Evaluation of the cyclic voltammetric curve for system $\text{Eu}^{3+}/\text{Eu}^{2+}$ in 1M-NaClO_4

ν V s^{-1}	$E_{p,a}$ V	$E_{p,c}$ V	$E_{p/2,c}$ V	ΔE_p V	ψ	α	$k_s \cdot 10^4$ cm s^{-1}
0.005	-0.550	-0.685	-0.615	0.135	0.27	0.686	2.7
0.010	-0.545	-0.695	-0.635	0.150	0.21	0.686	3.0
0.020	-0.530	-0.710	-0.640	0.180	0.16	0.686	3.2
0.050	-0.500	-0.730	-0.650	0.230	0.09	0.600	2.8
0.100	-0.470	-0.750	-0.670	0.280	0.06	0.600	2.7

TABLE II

Evaluation of the cyclic voltammetric curve for $\text{Eu}^{3+}/\text{Eu}^{2+}$ system in 1M-NaNO_3

ν V s^{-1}	$E_{p,a}$ V	$E_{p,c}$ V	$E_{p/2,c}$ V	ΔE_p V	ψ	α	$k_s \cdot 10^4$ cm s^{-1}
0.005	-0.545	-0.710	-0.620	0.165	0.18	0.533	1.3
0.010	-0.540	-0.720	-0.630	0.180	0.16	0.533	2.1
0.020	-0.545	-0.720	-0.630	0.175	0.16	0.533	2.9
0.050	-0.535	-0.735	-0.640	0.200	0.12	0.505	3.5
0.100	-0.525	-0.750	-0.650	0.225	0.09	0.480	3.7

TABLE III

Evaluation of the cyclic voltammetric curve for $\text{Eu}^{3+}/\text{Eu}^{2+}$ system in 1M-NaCl

ν V s^{-1}	$E_{p,a}$ V	$E_{p,c}$ V	$E_{p/2,c}$ V	ΔE_p V	ψ	α	$k_s \cdot 10^4$ cm s^{-1}
0.002	-0.560	-0.695	-0.620	0.135	0.26	0.640	0.9
0.005	-0.555	-0.700	-0.625	0.145	0.22	0.640	1.2
0.010	-0.545	-0.715	-0.635	0.170	0.17	0.600	1.3
0.020	-0.535	-0.730	-0.645	0.195	0.13	0.565	1.4
0.050	-0.515	-0.750	-0.660	0.235	0.08	0.533	1.4

TABLE IV
Evaluation of the cyclic voltammetric curve for $\text{Eu}^{3+}/\text{Eu}^{2+}$ system in $1\text{M-Na}_2\text{SO}_4$

ν V s^{-1}	$E_{p,a}$ V	$E_{p,c}$ V	$E_{p/2,c}$ V	ΔE_p V	ψ	α	k_s cm s^{-1}
0.005	-0.550	-0.865	-0.765	0.315	0.02	0.480	$3.6 \cdot 10^{-6}$
0.010	-0.550	-0.890	-0.785	0.385	—	0.457	—
0.020	-0.480	-0.910	-0.805	0.430	—	0.457	—
0.050	-0.445	-0.935	-0.835	0.490	—	0.480	—

TABLE V
Evaluation of the cyclic voltammetric curve for $\text{Eu}^{3+}/\text{Eu}^{2+}$ system in $1\text{M-Na}_2\text{SO}_4$ according to Eq. (5)

ν V s^{-1}	$E_{p,c}$ V	$E^0 - E_{p,c}$ V	α	$k_s \cdot 10^6$ cm s^{-1}
0.005	-0.865	0.213	0.480	6.0
0.010	-0.890	0.238	0.457	6.4
0.020	-0.910	0.258	0.457	6.3
0.050	-0.935	0.283	0.480	5.1

TABLE VI
Summary of measured diffusion coefficients, D_O , mean charge transfer coefficients, α , and standard rate constants of the $\text{Eu}^{3+}/\text{Eu}^{2+}$ electrode reaction, k_s

Base electrolyte	D_O (Eq. (7)) $\text{cm}^2 \text{s}^{-1}$	D_O (Eq. (6)) $\text{cm}^2 \text{s}^{-1}$	α	k_s cm s^{-1}
1M-NaCl	$2.1 \cdot 10^{-6b}$	$4.3 \cdot 10^{-6}$	0.596	$1.2 \cdot 10^{-4}$
1M-NaClO ₄	$7.1 \cdot 10^{-6b}$	$15.5 \cdot 10^{-6}$	0.652	$2.9 \cdot 10^{-4}$
1M-NaNO ₃	$6.2 \cdot 10^{-6b}$	$10.7 \cdot 10^{-6}$	0.517	$2.7 \cdot 10^{-4}$
1M-Na ₂ SO ₄	$2.4 \cdot 10^{-7a}$	$3.8 \cdot 10^{-7}$	0.467	$6.0 \cdot 10^{-6}$

^a Used in calculating k_s in $1\text{M-Na}_2\text{SO}_4$ (Table V); ^b used in calculating k_s in other electrolytes (Tables I—III).

$$\log k_s = 1.13 - \frac{\alpha n}{0.059} (E^0 - E_{p,c}) + \log D_O + 0.5 \log nv. \quad (5)$$

The calculated values of k_s are given in Table V; these are based on the standard electrode potential $E^0 = -0.652$ V.

The slope of the dependence of $i_{p,c}$ on $v^{1/2}$ was calculated by the least squares method; the diffusion coefficient D_O (Table VI) was calculated from Eq. (6) or (7) for the reversible and irreversible process, respectively:

$$i_p = 2.74 \cdot 10^5 n^{3/2} D_O^{1/2} c^0 v^{1/2}, \quad (6)$$

$$i_p = 3.01 \cdot 10^5 n^{3/2} \alpha^{1/2} D_O^{1/2} c^0 v^{1/2}. \quad (7)$$

The results are summarized in Table VI, while the published data about the behaviour of europium at the DME are given in Table VII. The calculated standard rate constants in the media used are proportional to the wave heights in Fig. 1; in chloride

TABLE VII

Survey of published values of diffusion coefficients (D_O , D_R), standard rate constants (k_s), and charge transfer coefficients (α) for the $\text{Eu}^{3+}/\text{Eu}^{2+}$ electrode reaction

Base electrolyte	$D_O \cdot 10^{-6}$ $\text{cm}^2 \text{ s}^{-1}$	$D_R \cdot 10^{-6}$ $\text{cm}^2 \text{ s}^{-1}$	k_s cm s^{-1}	α	T $^{\circ}\text{C}$	Ref.
1M-KCl	—	—	$4.6 \cdot 10^{-4}$	0.53	30	10
	8.5	11.7	$(3.2-4.9) \cdot 10^{-4}$	0.59	—	8
	—	—	$2.1 \cdot 10^{-4}$	—	20	6
	—	—	$1.7 \cdot 10^{-4}$	0.53	—	18
0.5M-NaClO ₄	—	—	$(5.8 \pm 0.3) \cdot 10^{-4}$	0.66	25	11
1M-NaClO ₄	—	—	$(5.0 \pm 0.3) \cdot 10^{-4}$	0.58	25	11
	—	—	$(4.3 \pm 0.3) \cdot 10^{-4}$	0.60	20	11
1M-KBr	—	—	$1.5 \cdot 10^{-3}$	0.55	30	10
1M-HBr	6.8	8.6	—	—	—	13
1M-KI	—	—	$4.0 \cdot 10^{-3}$	0.61	30	10
	6.3	8.3	$(2.8-4) \cdot 10^{-3}$	0.5-0.6	—	8
1M-KSCN	—	—	$2.4 \cdot 10^{-2}$	0.64	30	10
	5.6	7.3	$(2.6-3.3) \cdot 10^{-2}$	—	—	6
	—	—	$1.5 \cdot 10^{-2}$	—	—	9
0.1M-EDTA	4.3	—	$1.4 \cdot 10^{-2}$	0.68	—	10

and perchlorate solutions they are in satisfactory agreement with the published data. The values of k_s in the medium of nitrates and sulphates are not known from the literature.

The ratio of the anodic and cathodic peak heights, $i_{p,a}/i_{p,c}$, at different scan rates shows whether the use of the method of Nicholson²⁰ for the calculation of k_s is justified: this ratio can be used as a diagnostic criterion to detect any preceding, parallel, or follow-up reaction in the overall electrode process. Since divalent europium is very easily oxidized with nitrate ions and it is rapidly precipitated with sulphate ions as EuSO_4 , it can be expected that these reactions will influence the course of the voltammetric curves and thus the ratio of $i_{p,a}/i_{p,c}$. In reality, this ratio was found to increase with the scan rate in the nitrate medium only. According to ref.²¹, the dependence found by us corresponds to a chemical reaction preceding the reversible charge transfer. On the other hand, in the case of a follow-up chemical reaction, i.e. oxidation of Eu(II) , the ratio of $i_{p,a}/i_{p,c}$ should decrease with increasing scan rate.

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