Polarography of Europium(III) in Acetonitrile in the Presence of Thiocyanate and Halide Ions

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Studies were carried out on the polarographic behavior of europium in acetonitrile in the presence of SCN^-, Br^-, I^- and Cl^-. Two reduction waves were found in the Eu(III)–SCN^- system, one corresponding to the reduction of $[Eu(NCS)_6]^{3-}$ and the other to the reduction of $[Eu(NCS)_2]$. In the Eu(III)–Br^- system, the reduction potential of Eu(III)-bromide complex species was more positive than that of the $[HgBr_4]^{2-}/Hg$ couple. In the Eu(III)–I^- system, iodide ions were oxidized in acetonitrile by europium(III). The formation constants of Eu(III)–SCN^- system were found to be: $\log\beta_6=24.4$ for $[Eu(NCS)_6]^{3-}$ and $\log\beta_2=6.0$ for $[Eu(NCS)_2]$. The degree of complexation of europium(III) and mercury(II) with bromide ion was also determined.

Polarographic and potentiometric studies of metal(II, III)–halide and –thiocyanate complexes in acetonitrile have been reported.[1–3] The polarographic reduction of europium (III) in tetraethylammonium perchlorate in acetonitrile was studied by several authors,[4,5] the reduction process at DME in acetonitrile being Eu(III)→Eu(II) and Eu(II)→Eu(0). In a study on the influence of water on the reduction waves, the addition of small amounts of water was found to give a negative shift of the half-wave potential, which is caused by the rate of the electrode reaction being affected by the presence of water molecules adsorbed on the mercury electrode surface.[5]

The polarographic behavior of europium(III) in the presence of halide ions in non-aqueous solvents has not been studied. The waves of lanthanoids(III) in acetonitrile occur at considerably more negative potentials with tetraethylammonium bromide than with tetraethylammonium perchlorate as a supporting electrolyte.[4] This paper deals with the polarography of europium(III) in the presence of SCN^-, Br^-, I^- and Cl^-. The formation constants for Eu(III)–SCN^- and Eu(III)–Br^- systems were obtained and the electrode process of these systems was also determined.

Experimental

Materials. Commercial acetonitrile was purified by the method of Coetzee *et al.*[6] The water contant was found to be less than 0.01% by Karl Fischer titration. Tetraethylammonium halides and tetraethylammonium thiocyanate were prepared by the procedures reported.[2,3]

Apparatus. The electrolysis cell consists of three electrodes.[1] The reference electrode was an SCE with a salt bridge:

$$\left(\frac{0.5\ \mathrm{M}\ \mathrm{Et_4NClO_4}}{\mathrm{AN}}\middle|\frac{1\ \mathrm{M}\ \mathrm{NaClO_4}}{\mathrm{H_2O}}\middle|\frac{1\ \mathrm{M\ NaCl}}{\mathrm{H_2O}}\middle|\frac{1\ \mathrm{M\ KCl}}{\mathrm{H_2O}}\right)$$

Procedure. Sample solutions were prepared by dissolving 0.5 mM europium(III) perchlorate in acetonitrile with an appropriate amount each of Et_4NX(X^-: SCN^-, Cl^-, Br^- and I^-). Et_4NClO_4 was used to keep the concentration of Et_4N^+ 0.1 M. Other procedures were the same as described previously.[1]

Results and Discussion

Europium(III) Perchlorate in Acetonitrile. Europium(III) gave a two-step reduction wave corresponding to the one- and two-electron reduction. The half-wave potentials were in line with those reported by Cokal and Wise.[5] The electrode reaction of the first and second waves was found to be reversible and diffusion-controlled.

Eu(III)–SCN⁻ System. Polarograms of 0.5 mM Eu(III) in the presence of thiocyanate ions are shown

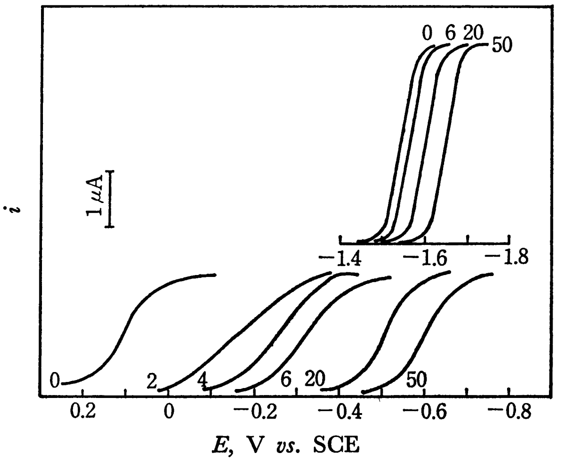

Fig. 1. DC polarograms of europium(III) in the presence of thiocyanate ion. Numbers on curves indicate mole ratio, $[SCN^-]_t/[Eu(III)]_t$.

Table 1. Polarographic data for europium(III)-thiocyanate system

$[Eu(III)]=0.5$ mM

$[SCN]_t/[Eu(III)]_t$	1st Wave			2nd Wave		
	$E_{1/2}$ V *vs.* SCE	i_d μA	Slope mV	$E_{1/2}$ V *vs.* SCE	i_d μA	Slope mV
0	0.113	1.80	58	−1.624	3.40	28
6	−0.318	1.87	—	−1.650	3.40	30
10	−0.407	1.87	61	−1.660	3.32	30
20	−0.493	1.80	60	−1.687	3.44	31
30	−0.541	1.79	58	−1.696	3.18	34
40	−0.571	1.80	60	−1.714	3.15	35
50	−0.590	1.84	58	−1.725	3.60	34

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in Fig. 1. The first wave was shifted towards more negative potentials with increasing concentration of thiocyanate ions. The log-plot was found to be nonlinear for $[SCN^-]_t/[Eu(III)]_t<10$. Above this ratio, the electrode reaction of the first wave was found to be a reversible, one electron reduction and diffusion-controlled. The polarographic data are shown in Table 1. The second wave was also shifted towards more negative potentials with increasing concentration of thiocyanate ions. The electrode reaction of the second wave was found to be a reversible, two-electron reduction and diffusion-controlled.

Assuming that Eu^{3+}, $EuX_p{}^{3-p}$, Eu^{2+} and $EuX_q{}^{2-q}$ are reduced reversibly, the electrode reactions are given by

$$Eu^{3+} + e \rightleftharpoons Eu^{2+} \qquad (1)$$

$$EuX_p{}^{3-p} + e \rightleftharpoons EuX_q{}^{2-q} + (p-q)X^- \qquad (2)$$

$$Eu^{2+} + 2e \rightleftharpoons Eu(0) \qquad (3)$$

$$EuX_q{}^{2-q} + 2e \rightleftharpoons Eu(0) + qX^- \qquad (4)$$

where X^- is SCN^- or halide ion. The difference of the half-wave potentials for Eqs. (1) and (2), $(E_{1/2})_c-(E_{1/2})_s$, is given by

$$\Delta E = 0.0591 \log (\beta_{EuX_q}/\beta_{EuX_p}) - 0.0591(p-q) \log [X]_0 - 0.0591 \log (I_{EuX_p}\cdot I_{Eu^{2+}}/I_{EuX_q}\cdot I_{Eu^{3+}}) \qquad (5)$$

where β is overall formation constant for the complex species, I the diffusion current constant for each species and $[X]_0$ the concentration of the ligand species $[SCN^-]$, at the electrode surface; $[X]_0=(C_x-PC_M/2)/(1+K_A[Et_4N^+])$.[1] The value of $p-q$ can be obtained by

$$p - q = \frac{d(\Delta E)}{d \log[SCN^-]_0}/0.0591 \qquad (6)$$

From the plot of ΔE *vs.* $\log[SCN^-]_0$ for the first wave, $(p-q)$ and $\log(\beta_{Eu(NCS)_p}/\beta_{Eu(NCS)_q})$ were obtained to be 4.0 and 18.4, respectively. From the same plot for the second wave, q and $\log \beta_{Eu(NCS)_q}$ were found to be 1.9 and 6.0, respectively. Thus, the electrode reactions are presumed to be as follows.

$$Eu(NCS)_6{}^{3-} + e \rightleftharpoons Eu(NCS)_2 + 4SCN^- \qquad (7)$$

$$Eu(NCS)_2 + 2e \rightleftharpoons Eu(0) + 2SCN^- \qquad (8)$$

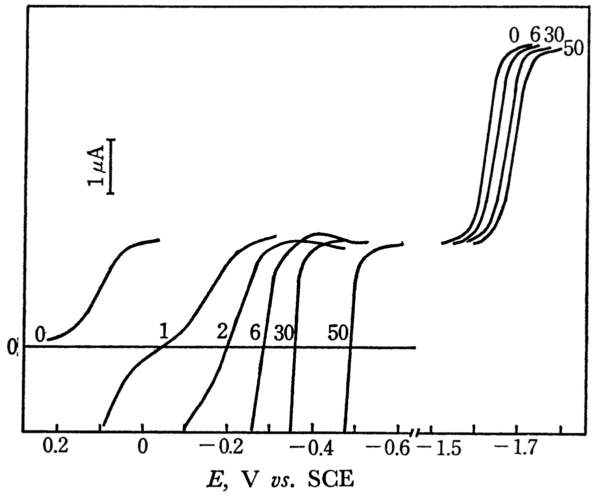

Fig. 2. DC polarograms of europium(III) in the presence of bromide ion. Numbers on curves indicate mole ratio, $[Br^-]_t/[Eu(III)]_t$.

The values of $\log \beta_{Eu(NCS)_6{}^{3-}}$ and $\log \beta_{Eu(NCS)_2}$ were found to be 24.4 and 6.0, respectively. Formation of $Eu(NCS)_6{}^{3-}$ in acetonitrile has also been confirmed by Burmeister *et al.*[7]

With increasing concentration of SCN^-, the reciprocal slope of the second wave deviated from the theoretical one. The standard rate constant of reduction ($[SCN_t/[Eu(III)]_t=50$) was determined to be 1.7×10^{-4} cm/s by cyclic voltammetry, indicating that the electrode reaction was quasi-reversible at high concentrations of SCN^-.

Eu(III)-Br⁻ System. Polarograms of 0.5 mM Eu (III) in the presence of bromide ion are shown in Fig. 2. The solution containing Eu(III) and bromide ions was pale yellow, the coloration disappearing on addition of water. The formation of Eu(III)–bromide complex in acetonitrile was assumed. The first wave may be a composite wave of $EuBr_p{}^{3-p}\rightleftharpoons EuBr_q{}^{2-q}$ and $Hg\rightleftharpoons HgBr_x{}^{2-x}$ couples. Thus, the electrode reactions are given by

$$EuBr_p{}^{3-p} + e \rightleftharpoons EuBr_q{}^{2-q} + (p-q)Br^- \qquad (9)$$

$$HgBr_x{}^{2-x} + 2e \rightleftharpoons Hg + XBr^- \qquad (10)$$

The half-wave potentials for the reduction of $EuBr_p{}^{3-p}$ and $HgBr_x{}^{2-x}$ are as follows.

$$(E_{1/2})_c{}^{Eu} = (E_{1/2})_s{}^{Eu} - 0.0591 \log K - 0.0591(p-q) \log [Br^-]_0 \qquad (11)$$

$$(E_{1/2})_c{}^{Hg} = (E_{1/2})_s{}^{Hg} - 0.0295 \log \beta_{HgBr_x}{}^{2-x} - 0.0295 \log [Br^-]_0 \qquad (12)$$

where $K=\beta_{EuBr_p}{}^{3-p}/\beta_{EuBr_q}{}^{2-q}$. In the case of Eu(III)–Br⁻ system, the half-wave potential of mercury(II) bromide complex is more negative than that of Eu(III) bromide complex; $(E_{1/2})_c{}^{Hg}<(E_{1/2})_c{}^{Eu}$. From Eqs. (11) and (12), the following relationship can be obtained at $[Br^-]_0=1$ M.

$$(E_{1/2})_s{}^{Hg} - 0.0295 \log \beta_{HgBr_x}{}^{2-x}<(E_{1/2})_s{}^{Eu} - 0.0591 \log K \qquad (13)$$

Since $(E_{1/2})_s{}^{Hg}=0.557$ and $(E_{1/2})_s{}^{Eu}=0.113$ V *vs.* SCE in acetonitrile, Eq. (13) is reduced to

$$\log \beta_{HgBr_x}{}^{2-x}>2 \log K + 15 \qquad (14)$$

The value of $\log \beta_{HgBr_4}{}^{2-}$ was calculated to be *ca.* 38 by the plot of $\Delta E_{1/2}$ *vs.* $\log [Br^-]_0$. From Eq. (14), we obtain $\log K <$ *ca.* 12. On the other hand, the value of $2 \log K+15$ for Eu(III)–SCE⁻ system is 52. Thus $2 \log K+15\gg\log \beta_{Hg(SCN)_4}{}^{2-}$ (≈38). This indicates that the wave of Eu(III)–SCN⁻ complex was completely separated from the wave of Hg(II)–SCN⁻ complex (Fig. 1).

The second wave was found to be a reversible, two-electron reduction and diffusion-controlled. The values of q and $\log \beta_{EuBr_2}$ were calculated to be 1.8 and 5.31, respectively.

Eu (III)-I⁻ System. Figure 3 shows the polarograms of 0.5 mM Eu (III) in the presence of iodide ions. By addition of iodide ions, the first wave was shifted towards more negative potentials, the height of the second wave becoming smaller. Limiting currents *vs.* $[I]_t/[Eu(III)]_t$ $(=x)$ are shown in Fig. 4. The height of the first wave in the presence of iodide ions was nearly equal to that in the absence of iodide ions until $x=2$ and the height of the first wave started

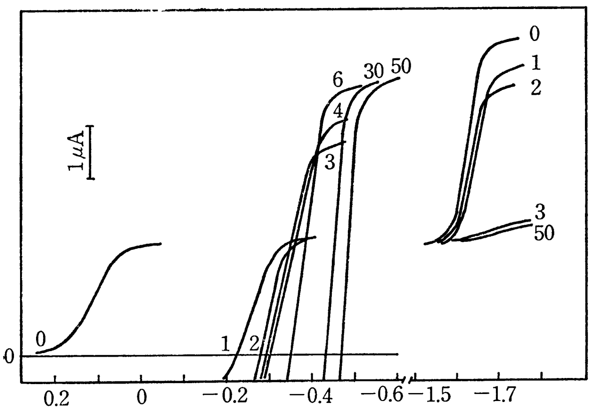

Fig. 3. DC polarograms of acetonitrile solutions containing europium(III) and iodide ion. Number on curves indicates mole ratio, $[I^-]_t/[Eu(III)]_t$.

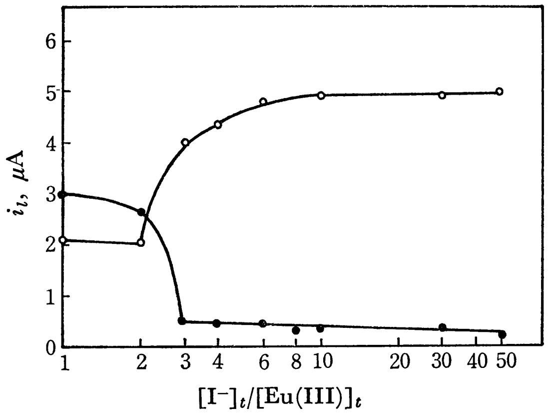

Fig. 4. Limiting currents vs. $[I^-]_t/[Eu(III)]_t$ for europium(III)-iodide system.
○: 1st wave, ●: 2nd wave.

to increase at *ca.* $x=2$. The solution containing Eu (III) and iodide ions was yellowish brown, the coloration became stronger with increasing concentration of iodide ions, finally becoming the same as that of iodine in acetonitrile. A polarogram of the solution containing I_2 and Et_4NI was similar to that of the first wave in the presence of excess of iodide ions. This indicates that Et_4NI is oxidized in acetonitrile by europium(III). The reaction product, I_2, is known to form triiodide ion (I_3^-) in the presence of iodide ions.

Since iodine and triiodide ions react rapidly with mercury of the electrode,[8] the mechanisms of chemical and electrochemical processes are given as follows.

chemical processes

$$Eu^{3+} + I^- \longrightarrow Eu^{2+} + \frac{1}{2}I_2 \tag{15}$$

$$I_2 + I^- \rightleftharpoons I_3^- \tag{16}$$

$$I_2 + Hg \rightleftharpoons HgI_2 \tag{17}$$

$$I_3^- + Hg \rightleftharpoons HgI_3^- \tag{18}$$

electrode processes

1st wave

$$Eu^{3+} + e \rightleftharpoons Eu^{2+} \tag{19}$$

$$3HgI_2 + 2e \rightleftharpoons Hg + 2HgI_3^- \tag{20}$$

$$2HgI_3^- + 4e \rightleftharpoons 2Hg + 6I^- \tag{21}$$

2nd wave

$$Eu^{2+} + 2e \rightleftharpoons Eu(0) \tag{22}$$

At $x \leq 2$, the oxidation of iodide ion by europium(III) is not complete.

The first wave might correspond to the reduction of Eqs. (19) and (20).[9] For $x \geq 3$, the reaction of Eq. (21)[9] was predominant, the height of the wave becoming large. The second wave disappeared. This may be caused by the formation of EuI_q^{2-q} which is electroinactive in this potential region.

Eu(III)-Cl⁻ System. For $x<10$, several waves appeared. But a polarogram gave a single reduction wave with a minimum in the diffusion plateau at around −1.0 V *vs.* SCE at $x \geq 10$. The electrocapillary curve of Eu(III)-Cl⁻ system showed a depression in the cathodic range (−0.8—−1.0 V *vs.* SCE). The depression was observed at potentials at which a minimum appeared. The hexachloroplatimum(IV) ion[10] produced a minimum similar to that of the complex ion. The minimum may be attributed to the formation of a film of reduction product.

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