Polarographic Studies on the Rare Earths. II. Europium

By Seizo MISUMI and Yasushi IDE

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Europium has the stable dipositive oxidation state similar to samarium and ytterbium among the rare earth elements. It is also clearly recognized that this intermediate dipositive oxidation state exists during the reduction process of the tripositive europium ions on dropping mercury electrode and this fact has already been studied by some investigators. Laitinen and Taebel[1], and also Noddack and Brukl[2] obtained only a single wave having the half-wave potential of −0.77 V. vs. S. C. E. in acidic solution and −0.67 V. vs. S. C. E. in neutral solution. On the other hand, Holleck[3] obtained double wave for europium. Namely, the half-wave potential of the first wave was −0.78 V. vs. S. C. E. and that of the second wave, −2.14 V. vs. S. C. E. with lithium chloride as the supporting electrolyte, and −0.82 V. and −2.14 V. vs. S. C. E. respectively when with tetramethylammonium iodide. Many other polarographic studies on the europium complexes with various complex-forming agents were reported by Holleck[4], Onstott[5] and Vlček[6].

In this paper, the authors have reported the behaviors of europium ion in the process of reduction on the dropping mercury electrode. The reduction waves were studied in detail under various conditions, especially in order to know the electrode reactions.

Experimental

All current-voltage curves were recorded by the Yanagimoto photographic polarograph PEL-Model 3 Type. All potentials were corrected and referred to saturated calomel electrode (S. C. E). The capillary used had the flowing weight of mercury, $m=0.789$ mg./sec. at the height of 58.5 cm. (corr.) Hg and the drop time, $t=5.20$ and 3.10 sec./drop at the applied potentials of −0.8 V. and −2.0 V. vs. S. C. E. respectively (the factor $m^{2/3}\,t^{1/6}$ was from 1.021 to 1.135 mg$^{2/3}$ sec$^{-1/2}$ in the same potential range). pH value of the solution was measured with the Hitachi glass electrode pH meter EHM-1 Type for micro amount. All experiments were carried out in a thermostat of 25.0±0.1°C.

Europium solution was prepared by dissolving pure europium oxide (Eu_2O_3: more than 99.9%), purified with ion exchange resin. The concentration of the stock solution was 0.01 M/l. Lithium chloride and lithium perchlorate used as supporting electrolytes were guaranteed grade pure Shikajirushi. The concentrations of these stock solutions were 1 mol./l. The gelatin solution used as maximum suppressor, was prepared freshly in every experiment.

To the sample solution of europium, certain quantities of the supporting electrolyte and of gelatin were added to be the final concentrations, 0.1 M/l. and 0.01%, respectively. And then a micro amount of 0.01 N sulfuric acid was added to prevent the hydrolysis of the aquo europium ion and to adjust pH at the same time. The total volume of the solution was made up to 5 ml. with distilled water. The concentration of europium ion was in the range from 0.5 to 1.6 mM/l. and pH of the solution was varied from 2.75 to 3.90. Dissolved oxygen was removed by passing purified nitrogen gas through the solution for at least 20 min. Then polarograms were recorded.

Results and Discussion

1) The Reduction Wave of Aquo Tripositive Europium Ion. — Typical reduction waves of aquo tripositive europium ion are shown in Fig. 1. At pH less than 3.9, three stepped waves were obtained and the first and the third waves are due to the

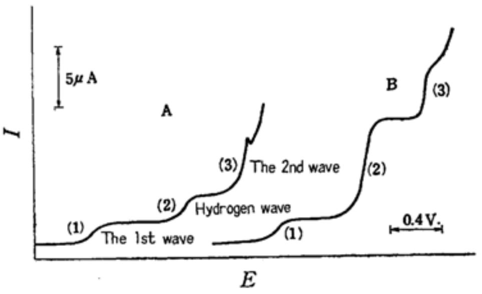

Fig. 1. The reduction waves of europium. Eu^{3+} ion: 1.104 mM in 0.1 M LiCl and 0.01% gelatin medium. pH: A=3.50, B=3.05.

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TABLE I. DEPENDENCE OF LIMITING CURRENTS OF THE FIRST AND THE SECOND WAVES ON THE HEIGHTS OF THE MERCURY COLUMN

h cm.	h_{corr} cm.		i_l, μA		$i_l/\sqrt{h_{corr}}$	
	$h_{1.corr}$	$h_{2.corr}$	i_{l_1}	i_{l_2}	$i_{l_1}/\sqrt{h_{1.corr}}$	$i_{l_2}/\sqrt{h_{2.corr}}$
40	38.4	38.1	1.60	3.29	0.258	0.535
50	48.4	48.1	1.79	3.62	0.257	0.522
90	58.5	58.1	1.94	3.97	0.254	0.521

(Eu^{3+} ion: 1.023 mM in 0.1 M LiCl and 0.01% gelatin medium, pH: 3.10)

reduction of aquo europium ion and the second wave is the hydrogen wave. In this paper hereafter, the first step is called "the first wave" and the third step "the second wave" of europium.

Owing to the variation in pH and the concentration of europium, the differences between the forms of the reduction waves were indicated. From the polarograms obtained, the following results were derived as the common characteristics, i.e., 1) at pH more than 3.2, independent of concentration, the second wave had a small maximum, but as the pH decreased, this maximum usually disappeared; 2) at pH less than 2.7, a well defined second wave could not be obtained. It is supposed that the large diffusion current of the hydrogen wave probably disturbed the second wave. The effect of various supporting electrolytes on the forms of the reduction waves were rather small and negligible, giving polarograms of similar types.

2) **Dependence of Limiting Current of the First and the Second Waves on the Pressure of Dropping Mercury and Influence of Temperature on the Diffusion Current.** — The relation between limiting currents and various heights of the mercury column is shown in Table I. The results obviously indicate the fact that the limiting current is proportional to the square root of the height of the mercury column, corrected for the back pressure. Accordingly, the limiting current is diffusion controlled.

The temperature coefficient of the half-wave potential of the first wave at 20~30°C, was 0.4 mV./deg. and that of the limiting current 1.9%/deg., which would be expected in the case of diffusion controlled process for the reduction of tripositive ion.

3) **Reversibility.** — The reduction waves were analyzed by logarithmic plot. The results are shown in Table II. As the reciprocal slope of the first wave was nearly constant, the average value 0.087 V., in the range of pH 3.50 to 2.75, the first reduction wave was irreversible and due to one electron transfer. The value of $\alpha_1 n_1$, was about 0.68 on the average. The transfer coefficient α was equal to 0.68 if the number of electrons associated with the electrode reaction was assumed to be one (α is a transfer coefficient in the equation of potential on irreversible wave, $E=E_{1/2}-\boldsymbol{RT}/\alpha n\boldsymbol{F}\cdot\ln(i/i_d-i)$. The plots of E against $\log(i/i_d-i)$ indicated an almost straight line. The reciprocal slope of the second wave decreased gradually with decrease of pH and approached a constant value, about 0.030 and the value of $\alpha_2 n_2$ increased reversely up to about 2.0. The plots of E against $\log(i/i_d-i)$ for the second wave indicated the slightly curved line near a pH about 3.50, but with decrease of pH it approached a straight line. Therefore, it is considered that the electrode reaction of the second wave was irreversible or quasi-reversible and according to the decrease of pH, it approached the reversible wave and the reaction was accompanied with two electron transfer. Many investigators have reported the reduction process of aquo tripositive europium ion as reversible except Vlček[6] who suggested that it was irreversible. The results in this experiment were also in good agreement with those of Vlček's report on the confirmation of irreversibility in the reduction process of the aquo europium ion.

TABLE II. THE RECIPROCAL SLOPE OF E VS. $\log(i/i_d-i)$ AND THE VALUE OF αn

pH	Reciprocal slope, V.		$\alpha_1 n_1$	$\alpha_2 n_2$
	1st wave	2nd wave		
3.50	0.087	0.045	0.63	1.3
3.15	0.085	0.045	0.78	1.7
3.05	0.086	0.034	0.69	1.7
2.95	0.087	0.030	0.68	2.0
2.75	0.090	0.030	0.66	2.0
(Eu^{3+} ion: 1.104 mM in 0.1 M LiCl and 0.01% gelatin medium)				
2.90	0.090	0.048	0.65	1.2
2.80	0.082	0.036	0.71	1.6
(Eu^{3+} ion: 1.000 mM in 0.1 M $LiClO_4$ and 0.01% gelatin medium)				

The oxidation wave of aquo dipositive europium ions (Eu^{2+} aq.), which were obtained by the reduction of aquo tripositive europium ions (Eu^{3+} aq.) with John's reductor, was studied. The half-wave potential of the oxidation wave of aquo dipositive europium ions was -0.292 V. vs. S. C. E. at pH 2.55 and this value did not coincide with the half-wave potential of the reduction wave of aquo tripositive europium ions under the same conditions. Thus, from this fact, the electrode reaction of the first wave was shown evidently to be irreversible (the potential difference of anodic and cathodic waves was about 0.440 V.).

4) **The Effects of Variation in pH Value on the Reduction Waves.**—The results of variation in pH value are shown in Table III, by which the effects on half-wave potentials and diffusion currents were studied. Both the half-wave potential of the first wave $(E_1)_{1/2}$ and the second wave $(E_2)_{1/2}$ shifted all to the more negative side as pH values were decreased. The extent of the shift for the first wave was somewhat greater especially in the range of pH 3.50 to 3.15 than at pH less than 3.15. This fact is probably due to the existence of various hydroxo europium complex ions, produced by hydrolysis of aquo europium complex ions in each step of variation in pH of solution, owing to the basicity of europium. The diffusion currents were independent of pH, almost constant at the same concentration in the range of pH, given in Table III.

5) **The Effects of Variation in Concentration on the Reduction Wave.** — In the various concentrations of europium ion, i. e., 0.552, 1.104 and 1.656 mM/l. at the constant pH (adjusted to ca. 2.95), the reduction waves were recorded. These effects of variations in concentrations of europium ions on half-wave potentials and diffusion currents were studied. Results are shown in Table IV.

The half-wave potentials of the first and the second wave, $(E_1)_{1/2}$ and $(E_2)_{1/2}$, were constant, independent of concentrations. The diffusion current of the first wave i_d, increased proportionally to concentration and thus the ratio i_{d_1}/c (c : concentration of europium ion) indicated constant value too, i. e., there exists a linear relationship between diffusion current and concentration, which can be used for determination of europium. Especially, since in the potential range where the first wave of tripositive europium ion appears, the reduction waves of all other rare earth ions are absent, it is possible to determine polarographically the contents of europium in a mixture of several kinds of rare earth elements. The diffusion current constant of the first wave, I_{d_1}, was also constant. The diffusion current of the second wave, i_{d_2}, however, increased anomalously with the increase of the concentration and the value of the ratio i_{d_2}/c and the diffusion current constant of the second wave, I_{d_2}, decreased gradually

TABLE III. THE EFFECTS OF VARIATION IN pH ON HALF-WAVE POTENTIAL, DIFFUSION CURRENT AND DIFFUSION CURRENT CONSTANT

pH	Half-wave potential V. vs. S. C. E.		Diffusion current μA		Diffusion current constant	
	$(E_1)_{1/2}$	$(E_2)_{1/2}$	i_{d_1}	i_{d_2}	I_{d_1}	I_{d_2}
3.50	−0.731	−1.948	1.94	3.97	1.55	3.43
3.15	−0.760	−1.958	1.98	3.89	1.58	3.40
3.05	−0.762	−1.967	1.95	3.92	1.56	3.42
2.95	−0.767	−1.971	1.94	3.95	1.55	3.44
2.75	−0.771	−1.975	2.00	3.99	1.60	3.45

(Eu^{3+} ion: 1.104 mM in 0.1 M LiCl and 0.01% gelatin medium)

TABLE IV. THE EFFECTS OF VARIATION IN CONCENTRATION OF EUROPIUM ION ON HALF-WAVE POTENTIALS AND DIFFUSION CURRENTS

Concn. of Eu^{3+} ion mM	Half-wave potential V. vs. S. C. E.		Diffusion current μA		i_d/c		Diffusion current constant	
	$(E_1)_{1/2}$	$(E_2)_{1/2}$	i_{d_1}	i_{d_2}	i_{d_1}/c	i_{d_2}/c	I_{d_1}	I_{d_2}
0.552	−0.761	−1.972	0.99	2.33	1.79	4.22	1.59	4.10
1.104	−0.767	−1.971	1.94	3.99	1.76	3.58	1.55	3.44
1.659	−0.764	−1.976	2.94	5.07	1.78	3.42	1.58	3.55

(pH: 2.95, 0.1 M LiCl, 0.01% gelatin)

with rise of concentration. These anomalies may be attributed to precipitation or adsorption of the basic substances of europium on the electrode surfaces.

6) The Effects by the Kinds of Anions Contained in the Supporting Electrolytes.—The reduction process of aquo europium ion on dropping mercury electrode, often depends on its ionic states. These ionic states show considerably different dependence upon the kinds of electrolytes dissolved in the solution. Therefore, the kinds of supporting electrolytes added, are frequently able to cause remarkably different results to the reduction wave. Particularly, by the anion species of supporting electrolytes and further by the differences of their concentrations, the reversibility of the electrode reaction and the rate-determining step are influenced. From this standpoint, under the same conditions, by varying the anion species of the supporting electrolytes, the effects on the reduction waves were studied. The results are shown in Table V.

At the same concentration, somewhat large effects by the species of anions in the supporting electrolytes on the reduction wave could be seen as shown in Table V. Although pH was not kept strictly the same, the trend of the effects on the reduction wave could be seen. The half-wave potential of the second wave shifted to the more negative side in the order of $I^- < Cl^- < ClO_4^-$. Since the ionic strength was kept always constant, the half-wave potential should have the same value under the same conditions, but owing to the kinds of the anion species the different values were indicated. It is considered that the aquo europium ion forms the halogeno aquo complex ion with halogen ion, which takes part in the electrode reaction. However, as the perchlorate ion is the anion which does not form complex generally with the metal ions, it is also considered that the aquo europium ion exists in the same ionic state (single ion) in the solution with lithium perchlorate as the supporting electrolyte. If the halogeno aquo europium complex ion exists in the solution with the halides as the supporting electrolytes, it is known that this complex ion becomes more reducible than the aquo europium ion (single ion) and as the results of the electrode reaction approaches the reversible one from the irreversible. These facts were recognized from the reciprocal slope and the half-wave potential in this experiment. That is to say, in the presence of the halogen ions, the half-wave potential of the second wave shifted to the positive side and the reversibility increased at the same time. The value of the diffusion current constant of the first wave, I_{d_1}, was nearly constant in the case of the halide ions, but in the case of the perchlorate ions, the diffusion current constant of the second wave, I_{d_2}, was greater, which means the irreversible reaction. Thus, the aquo complex ion (single ion) is more difficult to be reduced than the halogeno aquo complex ion. This fact

TABLE V. EFFECTS OF THE VARIOUS ANION SPECIES OF THE SUPPORTING ELECTROLYTES ON THE REDUCTION WAVES

Supporting electrolytes 0.1 M	Concn. of Eu^{3+} ion mM	pH	Half-wave potential V. vs. S. C. E.		Diffusion current constant		Reciprocal slope, V.	
			$(E_1)_{1/2}$	$(E_2)_{1/2}$	I_{d_1}	I_{d_2}	1st wave	2nd wave
LiI	1.000	3.15	−0.635	−1.965	1.56	3.44	0.089	0.034
LiCl	1.023	3.10	−0.766	−1.967	1.55	3.47	0.082	0.030
$LiClO_4$	1.000	2.90	−0.733	−2.048	1.58	4.18	0.090	0.048

(Concn. of gelatin: 0.01%)

TABLE VI. EFFECTS OF THE CONCENTRATION OF THE SUPPORTING ELECTROLYTES ON THE REDUCTION WAVE

Concn. of LiCl M	Half-wave potential V. vs. S. C. E.		Diffusion current constant, μA		Reciprocal slope, V.	
	$(E_1)_{1/2}$	$(E_2)_{1/2}$	I_{d_1}	I_{d_2}	1st wave	2nd wave
0.1	−0.766	−1.967	1.55	3.47	0.092	0.035
0.2	−0.768	−1.960	1.48	3.42	0.088	0.037
0.5	−0.767	−1.953	1.57	3.51	0.096	0.034
0.7	−0.750	−1.954	1.52	3.30	0.103	0.037

(Concn. of the gelatin: 0.01%, concn. of Eu^{3+} ion: 1.000 mM, pH: 3.10) was in good agreement with the values of the reciprocal slopes for the second waves.

The results concerning the variation in the concentration of lithium chloride as supporting electrolyte are given in Table VI, in which effects of the chloride ion on the reduction wave are shown.

The half-wave potential of polarography is generally represented by the term containing activity coefficients and diffusion coefficients. If either the activity coefficient or the diffusion coefficient is varied, the half-wave potential will probably indicate a different value. With increasing ocncentratoins of total electrolytes the activity coefficient tends to decrease and as the result, the half-wave potential is likely to shift to the more negative potential. Moreover the stability of halogeno aquo europium complex ion is thermodynamically greater than the aquo europium ion and the negative shift will probably take place.

But, on the contrary, as shown in the results of Table VI, there can be seen a tendency for the half-wave potential to shift apparently to the more positive side according to the increase of the concentration of lithium chloride as the supporting electrolyte. At the concentration of 0.5 to 0.7 mmol., the extent of the shift was considerably great. With the increase of chloride ions, the increased chloro aquo complex ions caused the overpotentials to decrease and this large decrease in this overpotential, i. e., the easiness of reduction, outweighed the shift in the equilibrium relation. Thus the half-wave potential seems to shift apparently to the more positive side. In spite of these facts, the value of the reciprocal slope increased with the increase of the concentration of lithium chloride, that is, the irreversibility in the electrode reaction increased too.

7) The Effects of Concentration of Gelatin as Maximum Suppressor, on the Reduction Wave. — By the variation in concentration of gelatin from 0 to 0.05%, the effects on the reduction waves were studied. With the increase of the concentration of gelatin, the half-wave potentials of both the first and the second waves shifted to the more negative side respectively and the values of the reciprocal slopes increased. At pH less than 3.2, without gelatin, a large maximum appeared in the second wave, but with the increase of concentration of gelatin added as maximum suppressor, the maximum decreased gradually and, when 0.01% concentration of gelatin was added, it disappeared completely. At pH more than 3.2, even at concentration of gelatin 0.01%, the maximum could be seen slightly.

8) The Electrode Reduction and the Relation between Reduction Process and Electronic Structure of Aquo Europium Ion.—The reduction of aquo europium ion on dropping mercury electrode, proceeds irreversibly or quasi reversible as described in section 3. In the equation of the current-voltage curve for the irreversible reaction, $E=E_{1/2}-0.0591/\alpha n\cdot\log(i/i_{\mathrm{d}}-i)$ $(0<\alpha<1)$, it was derived that n_1 was equal to 1 and n_2 to 2, by using the results given in Table II. Consequently, the electrode reaction for the first wave was one electron change and that for the second wave two electrons. As the limiting current was diffusion controlled, with Ilkovic's equation, the following relation could be held theoretically between diffusion currents of the first wave and of the second wave, i. e., $i_{\mathrm{d}_1} : i_{\mathrm{d}_2}=1:2$. Therefore, the ratio of the diffusion current constants for the first and the second wave, $I_{\mathrm{d}_1} : I_{\mathrm{d}_2}=1:2$ is obtained.

The experimental average values of diffusion current constants were as follows, namely, $(I_{\mathrm{d}_1})_{\mathrm{av}}=1.57$ and $(I_{\mathrm{d}_2})_{\mathrm{av}}=3.46$. Hence, the ratio $(I_{\mathrm{d}_1})_{\mathrm{av}} : (I_{\mathrm{d}_2})_{\mathrm{av}}=1:2.2$ was obtained, which was in fairly good agreement with the value of the theoretical ratio. Thus, it is considered that the electrode reaction in the reduction of aquo tripositive europium ion proceeds as follows:

The first wave,

$$\mathrm{Eu^{3+}\,aq.} + \mathrm{e^-} \rightarrow \mathrm{Eu^{2+}aq.}$$

The second wave,

$$\mathrm{Eu^{2+}\,aq.} + 2\mathrm{e^-} \rightarrow \mathrm{Eu^0}$$

For the rate determining steps of the irreversible electrode reaction, the following main factors are supposedly considered.

a) The overpotential required for dehydration of the coordinated water molecules.

b) The stepwise dissociation of the aquo complex ion.

c) The overpotential required for the changes of the inner electronic configuration (in some $(n-2)f$ orbitals).

d) The stability in the oxidation state of the aquo complex ion.

e) The others.

The results of the irreversible reduction process of the aquo europium complex ion at the dropping mercury electrode, was

TABLE VII. POLAROGRAPHIC REDUCTION (ELECTRON TRANSFER AND ELECTRONIC CONFIGURATION)

Electrode reaction		Electronic configuration (Oxidized form) 1st wave	Electronic configuration (Reduced form) 2nd wave	
Eu^{3+} aq. → Eu^{2+} aq.	Irreversible	$f^6s^2p^6d^0d^0d^0[d^2sp^3]+e^-$		
			$\rightarrow f^6s^2p^6d^1d^0d^0[d^2sp^3]$	(2 step electron transfer)
			$\rightarrow f^7s^2p^6d^0d^0d^0[d^2sp^3]+2e^-$	
Eu^{2+} aq. → Eu^0	Irreversible			$\rightarrow f^7s^2p^6d^1d^1d^0[d^2sp^3]$
				$\rightarrow f^7s^2p^6s^2$—ligand

(Eu: $4f^75s^25p^66s^2$)

in good agreement with the conclusions of Vlček's rule⁷⁾, concerning the mechanism of the electron transfer by polarographic reduction. The dipositive stable oxidation state of europium is already known in solution. As Vlček pointed out, the true two step reduction wave as *f*-transition element was seen for the aquo europium complex ion. Generally, the rate of the electrode reaction is determined always by the slowest of the processes and the change by the electron transfer in reduction processes may always have a tendency to produce the most stable electronic configuration. The aquo europium complex ion is assumed to have simply the coordination number 6 and to be $Eu(H_2O)_6{}^{3+}$ complex ions. The probable relation between electron transfer and electronic configuration is shown in Table VII.

Summary

The double reduction waves of pure aquo tripositive europium ion, under various conditions, at dropping mercury electrode were studied. The effects of the variations in pH, the concentration of europium ion, the anion species of supporting electrolytes, and the concentration of gelatin as maximum suppressor, etc. were examined. The electrode reaction of the first wave was irreversible and one electron reduction, and that of the second wave was the irreversible or quasi reversible two electrons reduction. The half-wave potentials of the first wave and the second wave at pH 2.95 were as follows.

$$(E_1)_{1/2}:\ -0.767\ \text{V. vs. S. C. E.}$$

$$(E_2)_{1/2}:\ -1.971\ \text{V. vs. S. C. E.}$$

where concentration of Eu^{3+} ion: 1.104 mM in 0.1 M LiCl and 0.01% gelatin medium.

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Department of Chemistry
Faculty of Science
Kyushu University
Hakozaki, Fukuoka

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