BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 2677—2680 (1966)

Polarographic and Potentiometric Studies of Indium(III)- and Europium(III)-Iminodiacetate Complexes

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(Received March 31, 1966)

The successive chelate formation constants for In(III)- and Eu(III)-IDA complexes were obtained by potentiometric titration and calculation by Bjerrum's method. The values of log K_1 and log K_2 for the In(III)-IDA complex are 9.54 and 8.87, and those for the Eu(III)-IDA complex are 6.22 and 4.72, respectively. The electrode reactions of these complexes were studied polarographically and found to be irreversible and diffusion-controlled. The ionic states of these complexes before reduction in the vicinity of the electrode surface were estimated to be $[InY_2(OH)]^{2-}$ or InY_2^- and $Eu(H_2O)_x^{3+}$. The rate constant, $(k_f{}^\circ)_B$, of the electron transfer for the Eu(III)-IDA complex was calculated to be 1.3×10^{-20} cm.sec^{-1}.

The polarography of complexes of some metal ions (e. g., zinc(II) and cadmium(II)[1]) with iminodiacetic acid (IDA) and the chelate formation constants of IDA complexes of rare earths[2] and some other metal ions[3] obtained by potentiometric titration have been investigated by serveral workers. In this paper, polarographic studies of indium(III)- and europium(III)-IDA complexes, of their electrode reaction, the rate constant, and the ionic state in the vicinity of electrode surface, are presented. The chelate formation constants for these complexes have also been determined by using Bjerrum's method.

Experimental

Reagents.—Stock solutions of indium(III) and europium(III) were prepared by dissolving metal perchlorates (more than 99.9% pure in distilled water; they were standardized volumetrically. The concentration of each stock solution was 0.01 M. Reagent-grade IDA (made by Wako Pure Chemical Industries) was used without any further purification.

A stock solution of monopotassium iminodiacetate (IDA-1K salt) was prepared by neutralizing IDA with a potassium hydroxide solution, and the concentration of IDA was adjusted to 0.5 M. A borate buffer (H_3BO_3-KCl-KOH) was used to adjust the pH of the solution. The ionic strength (μ) was adjusted with potassium chloride. A carbonate-free potassium hydroxide solution was prepared by the ion-exchange method.[4] All the other chemicals used were of an analytical reagent grade.

Apparatus.—A Yanagimoto PA-102 pen-recording polarograph was used to record the current-voltage curves. An H-type cell connected with a saturated calomel electrode (SCE) was used. The capillary used had a flowing weight, m, of mercury of 1.474 mg. sec^{-1} and a drop time, t_d, of 4.97 sec. drop^{-1} at the applied potential of -1.1 V. vs. SCE in an air-free 0.05 M IDA solution at a corrected height ($h_{corr.}$) of the mercury column of 68.41 cm. The measurement of the pH was made with a Hitachi pH meter, EHM-1 type. A titration apparatus consisting of a Horiba pH meter, P type, a titration vessel, and a thermostat was used. The titration vessel was a 150 ml. beaker fitted with a rubber stopper with holes for electrodes, a microburet, a thermometer, a gas inlet and outlet tubes; it was enveloped with a water jacket to maintain the solution at 25.0±0.1°C during the measurements.

Procedure. — *Potentiometric Titration.*—Solutions of 1 : 1, 1 : 2, 1 : 3 and 1 : 5 ratios of metal ion to IDA were used. A sample solution was made up to 50 ml. or 100 ml., where the ionic strength was kept at 0.3 by the addition of potassium chloride. Purified nitrogen

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[1] K. W. Bernaver, D. Walz and S. Fallab, *Helv. Chim. Acta*, **41**, 2094 (1958).

[2] L. C. Thompson, *Inorg. Chem.*, **1**, 490 (1962).

[3] S. Chaberek, Jr., and A. E. Martel, *J. Am. Chem. Soc.*, **74**, 5052 (1952).

[4] A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," Methuen and Co., Ltd., London (1962).

gas was passed through the solution; the solution was meanwhile being stirred in order to remove any carbon dioxde from the solution. Then the solution was titrated with 0.1 N potassium hydroxide, and the pH was measured. All experiments were carried out at a constant temperature of 25.0±0.1°C.

Polarography.—To a solution indium(III) or europium(III) containing an appropriate quantity of IDA, a borate buffer solution was added in order to adjust the pH to the required value. Potassium chloride was also added to keep an ionic strength of 0.3. The solution was prepared at 25.0±0.1°C, and purified nitrogen gas was passed through the solution for about 30 min. in order to remove any dissolved oxygen before a polarogram was recorded.

Results and Discussion

Potentiometric Titration.—The acid dissociation constant and the chelate formation constant were determined by the method outlined by Chabereck and Martel.[3)]

The Dissociation Constant of IDA. — The dissociation constant of IDA was calculated by a direct algebraic method, using a titration curve. The values obtained were pk_1=3.01 and pk_1=9.60* at 25.0±0.1°C and μ=0.3(KCl).

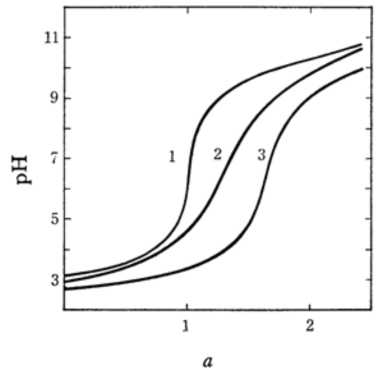

Fig. 1. Titration curves.
1) IDA, 2) [Eu^{3+}]/[IDA]=1/3,
3) [In^{3+}]/[IDA]=1/5
a=moles of base added per mole of acid.

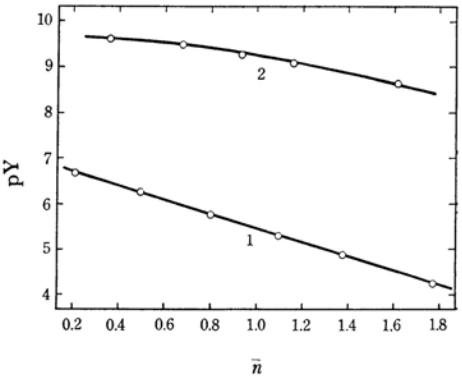

Fig. 2. Formation functions.
1) Eu(III)-IDA complex, 2) In(III)-IDA complex. $\bar{n}$=average number of donor groups bound per metal ion present. pY=negative logarithm of anion concentration, Y^{2-}.

The Chelate Formation Constant. — The chelate formation constant was calculated by using Bjerrum's method. In a solution with a 1 : 1 ratio of metal(III) to IDA, a hydrolytic buffer region appeared. However, from the solution with a 1 : 5 ratio of indium(III) to IDA or a 1 : 3 ratio of europium(III) to IDA, it disappeared, as Fig. 1 shows. The formation functions for In(III)- and Eu(III)-IDA complexes, plotted in Fig. 2, give a clear indication of the formation of the 1 : 1 and 1 : 2 complexes. The values of the successive chelate formation constants obtained are as follows:

	log K_1	log K_2
In^{3+}	9.54	8.78
Eu^{3+}**	6.22	4.72

Polarography.—Typical polarograms of In(III)- and Eu(III)-IDA complexes in borate buffer solutions are shown in Fig. 3.

Each complex ion shows a single reduction wave. The half-wave potentials for In(III)- and Eu(III)-IDA complexes shifted to the more negative side than that of the reduction wave of the corresponding metal aquo ion.

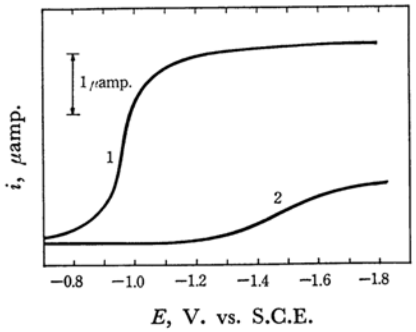

Fig. 3. Current-voltage curves of indium(III) and europium(III) in 0.05 M IDA solution.
1) [In^{3+}]=0.5 mM, pH=9.2; 2) [Eu^{3+}]=0.5 mM, pH=11.0

The Dependence of the Limiting Current on the Pressure of the Dropping Mercury Electrode.—The relation between limiting currents and various heights of the mercury column is shown in Table I.

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* L. C. Thompson reported that pk_1=2.58 and pk_2=9.33 at 25°C and that μ=0.1 (Ref. 2).

** L. C. Thompson: logK_1=6.73 and logK_2=5.38 (Ref. 2).

TABLE I. DEPENDENCE OF LIMITING CURRENT ON THE HEIGHT OF MERCURY COLUMN

a) In(III)-IDA complex

$h_{\rm corr.}$, cm.	i_l, μamp.	$i_l/\sqrt{h_{\rm corr.}}$
53.41	2.828	0.395
63.41	3.144	0.395
73.41	3.372	0.394

0.5 mM In^{3+} in 0.05 M IDA medium, pH=9.2

b) Eu(III)-IDA complex

$h_{\rm corr.}$, cm.	i_l, μamp.	$i_l/\sqrt{h_{\rm corr.}}$
58.20	0.578	0.0757
63.21	0.604	0.0759
68.21	0.626	0.0758

0.5 mM Eu^{3+} in 0.05M IDA medium, pH=11.4

The values of $i_l/\sqrt{h_{\rm corr.}}$ were found to be 0.395 ±0.001 μamp. cm$^{-1/2}$ for the In(III)-IDA complex and 0.0758±0.0001 μamp. cm$^{-1/2}$ for the Eu(III)-IDA complex. These results obviously indicate that the limiting currents for both In(III)- and Eu(III)-IDA complexes are diffusion-controlled.

Reversibility.—The reversibility of the electrode reaction for the In(III)- or the Eu(III)-IDA complex was verified by plotting log $i/(i_d-i)$ vs. E. As is shown in Table II, the mean values of the reciprocal slope for the In(III)-IDA complex and that for the Eu(III)-IDA complex were found to be 0.041 V. and 0.079 V. respectively. The mean values of αn were, therefore, 1.4 and 0.75 respectively, where α is the transfer coefficient and n, the number of electrons associated with the electrode reaction. Consequently, the electrode reactions for In(III)- and Eu(III)-IDA complexes were irreversible; three electrons change in the former, while one electron changes in the latter.

The Effects of the pH on Reduction Waves.—Polarograms were recorded with 0.5 mM Eu(III) or In(III) in 0.05 M IDA solutions at various pH's. The results are shown in Table II. The half-wave potential for the In(III)-IDA complex shifted to the more negative side as the pH increased from 9.2 to 10.6, whereas the half-wave potential for the Eu(III)-IDA complex was independent of the pH in the pH range from 9.2 to 12.0. The values of $d(-E_{1/2})_c/d\log C_{OH^-}$ calculated from the experimental data are as follows:

$$d(-E_{1/2})_c/d\log C_{OH^-}=0.054$$

for the In(III)-IDA complex

$$d(-E_{1/2})_c/d\log C_{OH^-}=0$$

for the En(III)-IDA complex

where $(E_{1/2})_c$ is the half-wave potential of complex ions and C_{OH^-} the concentration of hydroxyl ions.

The diffusion current for the In(III)-IDA complex decreased with an increase in the pH. It was supposed that the decrease in the diffusion current was caused by the precipitation of basic substances on the electrode. The diffusion current for the Eu(III)-IDA complex, on the other hand, was almost the same in the pH range from 10.0 to 12.0.

TABLE II. EFFECTS OF pH ON REDUCTION WAVE

a) In(III)-IDA complex

pH	$(E_{1/2})_c$ V. vs. SCE	i_d μamp.	Reciprocal slope mV.	αn
9.2	−0.977	3.244	39	1.5
9.5	−0.997	3.188	42	1.4
9.8	−1.020	3.032	42	1.4
10.2	−1.035	2.716	42	1.4
10.6	−1.057	1.744	42	1.4
		mean value	41	1.4

0.5 mM In^{3+} in 0.05 M IDA medium $\mu=0.3$

b) Eu(III)-IDA complex

pH	$(E_{1/2})_c$ V. vs. SCE	i_d μamp.	Reciprocal slope mV.	αn
9.2	−1.427	0.552	74	0.80
9.8	−1.425	0.576	70	0.84
10.0	−1.425	0.620	82	0.72
11.0	−1.424	0.614	84	0.70
12.0	−1.426	0.616	83	0.71
		mean value	79	0.75

0.5 mM Eu^{3+} in 0.05 M IDA medium $\mu=0.3$

The Effects of the Concentration of IDA on the Reduction Wave.—Polarograms were recorded in the range of the concentration of IDA from 5 mM to 50 mM at pH 9.2 for the In(III)-IDA complex and from 30 mM to 60 mM at pH 11.4 for the Eu(III)-IDA complex. The results are shown in Table III.

TABLE III. EFFECTS OF CONCENTRATION OF IDA ON REDUCTION WAVE

a) In(III)-IDA complex

Concn. of IDA mM	$(E_{1/2})_c$ V. vs. SCE	i_d μamp.	Reciprocal slope mV.	αn
5	−0.983	2.960	41	1.4
10	−0.987	3.188	42	1.4
25	−0.981	3.208	42	1.4
50	−0.980	3.224	40	1.5
		mean value	41	1.4

In^{3+}: 0.5 mM, pH=9.2 $\mu=0.3$

b) Eu(III)-IDA complex

Concn. of IDA mM	$(E_{1/2})_c$ V. vs. SCE	i_d μamp.	Reciprocal slope mV.	αn
30	−1.378	0.630	77	0.77
40	−1.393	0.628	75	0.79
50	−1.411	0.604	76	0.78
60	−1.422	0.630	79	0.75
		mean value	77	0.77

Eu^{3+}: 0.5 mM, pH=11.4. $\mu=0.3$.

The half-wave potentials for the In(III)-IDA complex were independent of the IDA concentration, but that for the Eu(III)-IDA complex shifted to the more negative side with an increase in the IDA concentration. Thus:

$$d(-E_{1/2})_c/d\log C_{IDA}=0 \text{ for the In(III)-IDA complex at pH 9.2}$$

and:

$$d(-E_{1/2})_c/d\log C_{IDA}=0.150 \text{ for the Eu(III)-IDA complex at pH 11.4,}$$

where C_{IDA} was the concentration of the complexing agent, IDA. The diffusion current for the In(III)-IDA complex increased with increasing IDA concentrations, while that for the Eu(III)-IDA complex was almost constant.

The Electrode Process and the Species of Complex in the Vicinity of the Electrode Surface. — If an irreversible electrode process for the metal M(III) complex takes place according to the following scheme:

$$\begin{aligned} &MX_p{}^{3-pb} \rightleftarrows MX_q{}^{3-qb} + (p-q)X^{b-} \\ &MX_q{}^{3-qb} + ne \rightarrow MX_q{}^{(3-qb-n)} \end{aligned} \qquad (1)$$

where p is the maximum number of ligands (X^{b-}) attached to a metal ion in the bulk solution; q, the number of ligands attached to a metal ion in the vicinity of the electrode surface, and n, the number of electrons associated with the electrode reaction, an equation derived by Matsuda and Ayabe[5] for the current-voltage curve due to an irreversible electrode reaction of a complex ion is applicable. Therefore, as the electrode reaction of In(III)- or Eu(III)-IDA complex is irreversible and diffusion-controlled, the half-wave potential, $(E_{1/2})_c$, is given by Eq. 2[5]:

$$(E_{1/2})_c=2.3\frac{\boldsymbol{RT}}{\alpha n\boldsymbol{F}}[\log(k_f^\circ)_B f_{MX_p}/\sqrt{D_{MX_p}} + 0.5\log t_d - 0.053 - (p-q)\log(f_X D_X)] \qquad (2)$$

where $(k_f^\circ)_B$ is the forward reduction rate constant of the electron transfer process at the potential of the normal hydrogen potential; D_{MX_p}, the diffusion coefficient of the complex metal ion, $MX_p{}^{3-pb}$; t_d, the drop time; C_X, the concentration of the complexing agent, and f_{MX_p} and f_X, the activity coefficients of the complex metal ion and the complexing agent respectively. From Eq. 2, a plot of $-(E_{1/2})_c$ vs. $\log(f_X C_X)$ should produce a straight line with a slope equal to $(p-q)$ $2.3\,\boldsymbol{R}T/\alpha n\,\boldsymbol{F}$; the value of the tangent for $-(E_{1/2})_c$ vs. $\log f_X C_X$ is given by:

$$d(-E_{1/2})_c/d\log f_X C_X=(p-q)\ 0.0591/\alpha n$$

As the electrode reaction for the In(III)-IDA complex is an irreversible three-electron change ($n=3$) and is independent of the IDA concentration between 5 mM to 50 mM, the value of $(p-q)$ for OH in the case of the In(III)-IDA complex was calculated to be about 1, by using the observed value, 1.4, of αn in the pH range from 9.2 to 10.6. On the assumption that $p=2$ or $p=1$ for OH, for example, the $[InY_2(OH)]^{2-}$ or $InY_2{}^-$ species would participate in the electron transfer process, where H_2Y indicates IDA. On the other hand, as the electrode reaction for the Eu(III)-IDA complex is irreversible, of a one-electron change ($n=1$), and independent of pH values from 9.2 to 12.0, the value of $(p-q)$ for IDA was calculated to be about 2, by using the observed value, 0.77, of αn in the range of the IDA concentration from 30 mM to 60 mM. Therefore, if it is assumed that $p=2$ for IDA, for example, the $Eu(H_2O)_x{}^{3+}$ species would participate in the electron transfer process, the transfer coefficient, α, being equal to 0.77.

The value of the forward rate constant, $(k_f^\circ)_B$, of the electron transfer process for the Eu(III)-IDA complex was calculated for the IDA concentration of 0.05 M with the value of the half-wave potential of -1.178 V. vs. NHE; a diffusion coefficient of the Eu(III)-IDA complex, D_{MX_p}, of 1.16×10^{-6} cm² sec⁻¹, and a drop time of 3.91 sec., provided that $f_{MX_p}=f_X=1$. The value obtained was:

$$\log(k_f^\circ)_B=-19.9\ (k_f^\circ \text{ cm. sec}^{-1})$$

In conclusion, the above results indicate that the species which participate directly in the electron transfer process are mainly $[InY_2(OH)]^{2-}$ or $InY_2{}^-$ and $Eu(H_2O)_x{}^{3+}$.

The authors wish to thank the Ministry of Education for the financial support granted this research.

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[5] H. Matsuda and Y. Ayabe, *Z. Elektrochem.*, **63**, 1164 (1959).