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Polarographic Study of the Rates of the Dissociation Reactions of the Eu(III)-HAHA Complex and of the Eu(III)-, Gd(III)-, and Ho(III)-PAPA Complexes

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Polyaza macrocycles carrying acetate groups, HAHA and PAPA, were found to form solely 1:1 ratio complexes with Eu(III), Gd(III), or Ho(III) ions. The PAPA complexes of the Eu(III), Gd(III), and Ho(III) ions and the HAHA complex of the Eu(III) ion in acetate buffer solutions containing an excess of the Eu(III), Gd(III), or Ho(III) ion produce anodic waves, which are kinetic in nature. They can be ascribed to the free macrocycles formed upon the dissociations of the complexes preceding electron-transfer steps at the electrode surface. From an experimental examination of the nature of these kinetic waves, the reaction mechanisms and rates for the dissociation reactions were determined. The dissociation reactions for the HAHA and PAPA complexes were found to proceed through (A) and (B), respectively. The $(k_d)_o$ values for the Eu(III)-HAHA and -PAPA complexes were 5.1×10^{-1} and 3.9×10^{-2} (sec^{-1}), respectively, and those for the Gd(III)- and Ho(III)-PAPA complexes, $4.0_4\times10^{-2}$ and 1.2×10^{-2} (sec^{-1}).

$$\begin{array}{llllll} \mathrm{EuH_2L^-} & & \overset{(k_d)_o}{\rightleftharpoons} & \mathrm{Eu^{3+}} + \mathrm{H_2L^{4-}} & & \text{slow} \\ \mathrm{EuH_2L^-} & + \ \mathrm{H^+} & \overset{(k_d)_H}{\rightleftharpoons} & \mathrm{Eu^{3+}} & + \ \mathrm{H_3L^{3-}} & \text{slow} \end{array} \qquad \text{(A)}$$

where H_iL^{i-6} is the protonated HAHA anion.

$$\begin{array}{llllll} \mathrm{MX^{2-}} & & \overset{(k_d)_o}{\rightleftharpoons} & \mathrm{M^{3+}} + \mathrm{X^{5-}} & & \text{slow} \\ \mathrm{MX^{2-}} & + \ \mathrm{H^+} & \overset{(k_d)_H}{\rightleftharpoons} & \mathrm{M^{3+}} & + \ \mathrm{HX^{4-}} & \text{slow} \end{array} \qquad \text{(B)}$$

where H_jX^{j-5} is the protonated PAPA anion.

The $(k_d)_H$ values for the Eu(III)-HAHA and -PAPA complexes were $3.7_0\times10^2$ and $4.2_4\times10^5$ (mol^{-1} dm^3 s^{-1}) and those for the Gd(III)- and Ho(III)-PAPA complexes, $2.4_5\times10^5$ and $2.0_5\times10^4$ (mol^{-1} dm^3 s^{-1}).

Polarography is an efficient tool for studying the reaction rates as well as equilibria of metal complexes. If the polarographic processes for the reduction of metal complexes are partially controlled by their dissociation occurring in the immediate vicinity of the dropping mercury electrode (DME) surface, they produce kinetic waves due to their dissociation.1) In such cases, one can determine both the mechanism and the rates of the dissociation reactions by analyzing the nature of the kinetic waves.

The Eu(III) complex of 18-membered macrocyclic hexamine carrying an acetate group on each nitrogen-(HAHA)2) gives a well-defined two-step polarographic (cathodic) wave in acetate buffer solutions. The first step is of a kinetic-controlled nature and can be ascribed to a reduction of the free Eu(III) ion formed upon the dissociation of its HAHA complex. Although the polarographic wave is ill-defined, the Eu(III) complex of a newly synthesized 15-membered macrocyclic pentamine carrying five acetate groups (PAPA) also gives a similar kinetic wave. In acetate buffer solutions where excess metal(III) ions are present and hence, all PAPA anions are considered to exist as Eu(III), Gd(III), or Ho(III) complex, a well-developed anodic step having a kinetic character can be observed. This anodic step might be ascribable to uncomplexed PAPA anions formed upon the dissociation of the Eu(III), Gd(III), or Ho(III) complex.

The present findings might lead to a better understanding of the reactions of the lanthanide metal(III) ions, and also to an exploration of useful applications of the polarography to the dissociation kinetics of the complexes involving polarographically inactive metal ions.

Experimental

Reagents. Preparation of 1,4,7,10,13,16-hexakis(carboxymethyl)-1,4,7,10,13,16-hexaazacyclooctadecane([18]aneN$_6$(OAcH)$_6$·6HCl, HAHA) was described previously.2) 1,4,10,13-pentakis(carboxymethyl)-1,4,7,10,13-pentaazacyclopentadecane([15]aneN$_5$(OAcH)$_5$·5HCl, PAPA)(Fig. 1) was also synthesized according to the method employed in the preparation of HAHA.2) Europium(III), Gadolinium(III), and Holomium(III) nitrate pentahydrates of 99.9% purity were purchased from Aldrich Chemical Company, Inc. Their aqueous solutions were standardized by titrations with EDTA by the method of Schwarzenbach.3) All of the other chemicals used in this study were of analytical reagent grades and were used without further purification.

Apparatus and Experimental Procedures. The apparatus and experimental procedures for the polarographic measurements and the potentiometric study were as previously used.4,5) The pH values of the solutions were determined

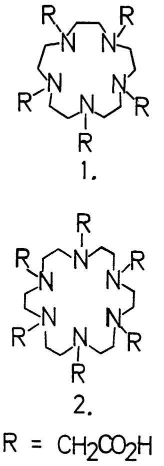

Fig. 1. Ligands. 1. [15]aneN$_5$·(OAcH)$_5$, 2. [18]aneN$_6$·(OAcH)$_6$.

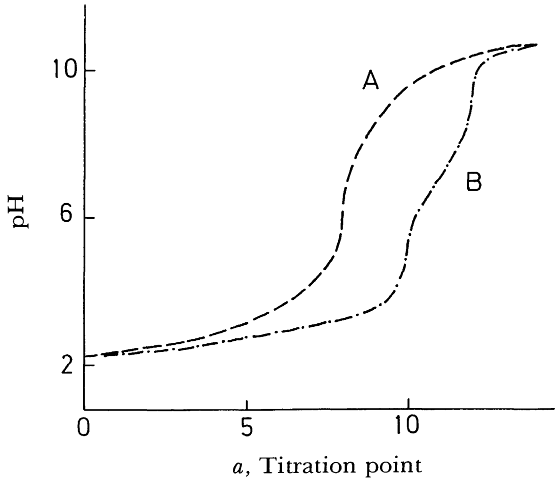

Fig. 2. Titration curves. Eu(III)—[18]aneN$_6$·(OAcH)$_6$·6HCl mixture. I=0.20 M, 25 °C. A. Ligand (0.50 mM) only, B. Ligand (0.50 mM)+Eu(III) (0.50 mM).

with a glass electrode pH-meter (a Horiba F8-AT). The values of $-\log[H^+]$ used for the calculation of the formation constants were estimated from pH readings: $-\log[H^+]=pH-0.13$.[5]

The log protonation constants for the pentavalent PAPA anion were determined potentiometrically to be 10.15, 9.41, 6.14, 4.11, and 3.19 (25 °C). Those for the hexavalent HAHA anion were 10.10, 10.01, 8.92, 8.20, 4.64, and 3.53. All of the solutions were adjusted to an ionic strength(I) of 0.20 mol dm^{-3} by adding an appropriate amount of NaClO$_4$ and maintained at 25.0±0.1 °C.

Results and Discussion

Complex Formation Equilibria. Complex formation between the Eu(III) ion and HAHA or PAPA and that between Gd(III) or the Ho(III) ion and PAPA were analysed in an identical manner as that previously applied to the macrocyclic polyamine complexes of transition metal(II) ions[6] and of histamine and its H$_2$agonists,[7] wherein the theory was described in detail. The titration curve for the equimolar mixture solution of the Eu(III) ion and HAHA in its fully protonated form ($H_{12}L^{6+}$) gave two buffer regions at titration points $10>a>0$ and $12>a>10$ (Fig. 2). Here, a indicates the number of moles of base added per mole of ligand present. Two breaks, occurring at $a=10$ and at $a=12$, suggest the formation of a doubly-protonated complex, EuH_2L^-, and the subsequent proton dissociation from it. As mentioned previosly,[6,7] the equation $(\alpha(\alpha_H)_L-\beta_H^L\cdot C_L)(10(\alpha_H)_L-\beta_H^L)=K_{EuH_2L}(10C_L-\alpha)^2\cdot(\alpha_H)_L\cdot[H^+]^2\times K_1\cdot K_2$ gives the best fit with the pH titration data for the formation of EuH_2L^-, and the relation $\log(\alpha'/2/(C_L-\alpha'/2))=\log K^{-2H}+2pH$ for the dissociation of EuH_2L^-,[8] $EuH_2L^-=EuL^{3-}+2H^+$. Here, $\alpha=aC_L+[H^+]-[OH^-]$, $(\alpha_H)_L=1+[H^+]\times K_1+[H^+]^2\times K_1\cdot K_2+\cdots+[H^+]^6\times K_1K_2\cdots K_6$, $\beta_H^L=12+11[H^+]\times K_1+10[H^+]^2\times K_1\cdot K_2+\cdots+6[H^+]^6\times K_1K_2\cdots K_6$, $\alpha'=(a-10)\cdot C_L$ and K_i denotes the protonation constant of HAHA anion. The K_{EuH_2L} (=$[EuH_2L^-]/[Eu^{3+}]\cdot[H_2L^{4-}]$) value could be determined graphically from the plots of $(\alpha(\alpha_H)_L-\beta_L^H\cdot C_L)(10(\alpha_H)_L-\beta_H^L)$ against $(10C_L-\alpha)^2\times(\alpha_H)_L\cdot[H^+]^2$ to be 1.49×10^{17} (Fig. 3) and the K^{-2H} (=$[EuL^{3-}]\cdot[H^+]^2/[EuH_2L^-]$) value from the plots of $\log(\alpha'/2/(C_L-\alpha'/2))$ against pH to be 2.5×10^{-15} (Fig. 4).

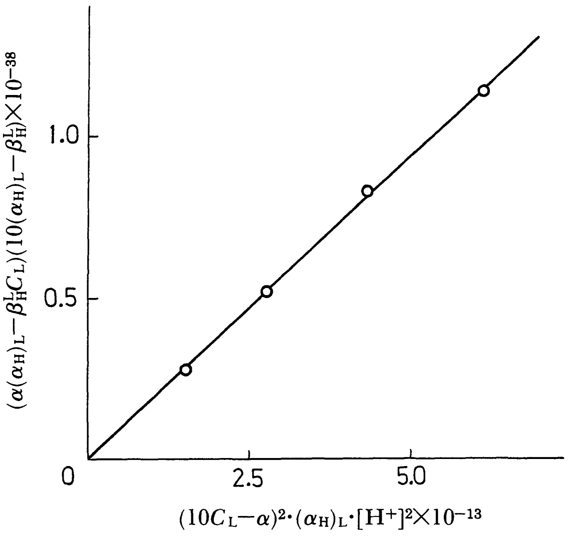

Fig. 3. Plots of $(\alpha(\alpha_H)_L-\beta_H^LC_L)\cdot(10(\alpha_H)_L-\beta_H^L)$ against $(10C_L-\alpha)^2\cdot(\alpha_H)_L\cdot[H^+]^2$. Eu(III)—[18]aneN$_6$·(OAcH)$_6$·6HCl system. I=0.20 M, 25 °C.

In the PAPA system an equimolar mixture of the metal(III) ion and the ligand in its fully-protonated form ($H_{10}X^{5+}$) gave only one buffer region at titration point $10>a>0$; a break occurred at $a=10$. This finding evidently suggests the formation of a normal complex, MX^{2-}. When the PAPA forms only 1:1 ratio complex, MX^{2-}, the relation $(\alpha(\alpha_H)_X-\beta_H^X\cdot C_X)(10(\alpha_H)_X-\beta_H^X)=K_{MX}\cdot(10C_X-\alpha)^2\cdot(\alpha_H)_X$ is expected to fit best with the pH titration data.[6,7] Here, $(\alpha_H)_X$ and β_H^X are the (α_H) and β_H values of the PAPA, respectively. The K_{MX}(=

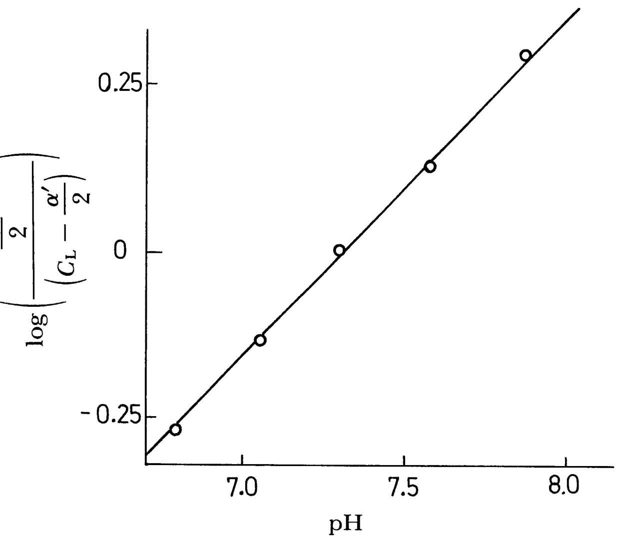

Fig. 4. Plots of $\log(\alpha'/2/(C_L-\alpha'/2))$ against pH. Eu(III)—[18]aneN$_6$·(OAcH)$_6$·6HCl system. I=0.20 M, 25 °C.

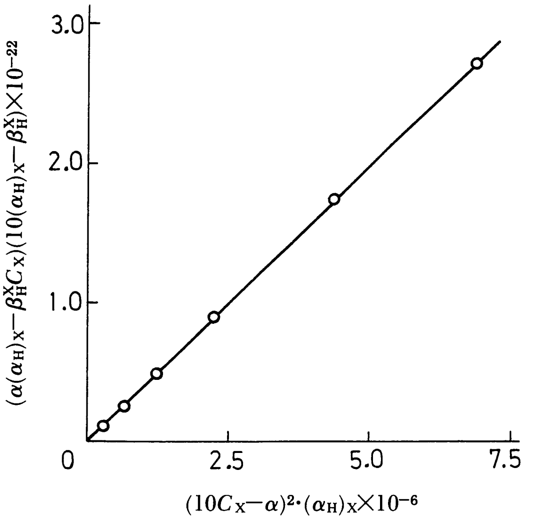

Fig. 5. Plots of $(\alpha(\alpha_H)_X-\beta_H^X C_X)\cdot(10(\alpha_H)_X-\beta_H^X)$ against $(10C_X-\alpha)^2\cdot(\alpha_H)_X$. [Eu(III)]=0.50 mM, [[15]aneN$_5$·(OAcH)$_5$·5HCl]=0.50 mM, I=0.20 M, 25 °C.

$[MX^{2-}]/[M^{3+}]\cdot[X^{5-}]$) values for the Eu(III), Gd(III), and Ho(III) complexes could be determined from the gradients of the straight lines between $(\alpha(\alpha_H)_X-\beta_H^X\cdot C_X)$-$(10(\alpha_H)_X-\beta_H^X)$ and $(10C_X-\alpha)^2\cdot(\alpha_H)_X$ to be 3.92×10^{15}, 7.51×10^{15}, and 3.00×10^{16}, respectively (Fig. 5).

Polarographic Behavior of Eu(III)-HAHA Complex. The Eu(III)-HAHA complex in an acetate buffer solution containing an excess of HAHA gave two reduction steps (Fig. 6). Judging from the reduction potential, the first step can be ascribed as being a direct one-electron reduction of uncomplexed Eu(III) to Eu(II). It showed the characteristic kinetic-controlled nature (its limiting current is almost independent of the effective mercury pressure on the DME).

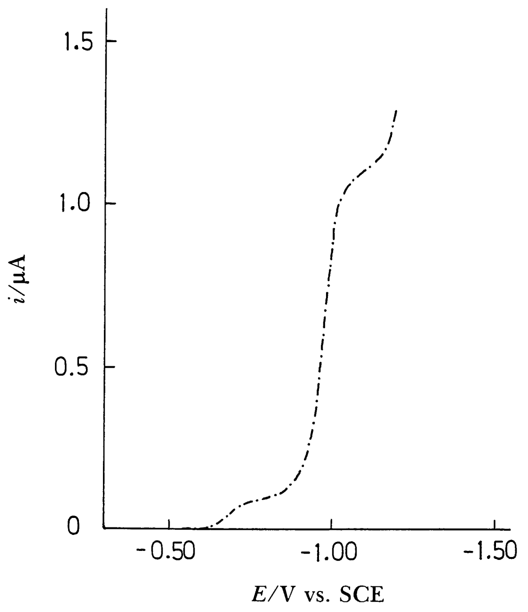

Fig. 6. Dc polarogram of Eu(III)—[18]aneN$_6$·(OAcH)$_6$ complex. [complex]=0.40 mM, [L]$_f$=4.00 mM, [OAc$^-$]=0.10 M, pH=3.89, I=0.20 M, 25 °C.

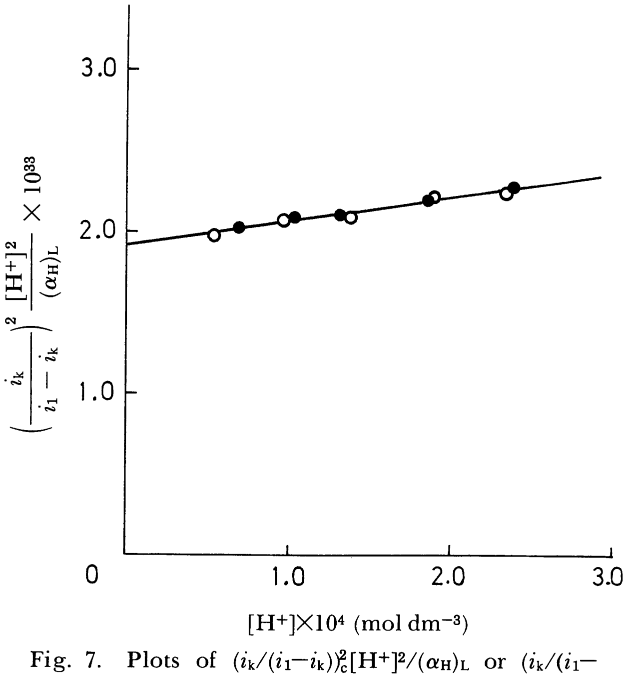

Fig. 7. Plots of $(i_k/(i_l-i_k))_c^2[H^+]^2/(\alpha_H)_L$ or $(i_k/(i_l-i_k))_a^2[H^+]^2/(\alpha_H)_L$ against [H$^+$]. Eu(III)—[18]aneN$_6$·(OAcH)$_6$ complex=0.40 mM, [OAc$^+$]=0.10 M, I=0.20 M, 25 °C. ○ [L]$_f$=4.00 mM, ● [Eu(III)]$_f$=4.00 mM.

The limiting current of the first step decreased with increases in the solution pH (Fig. 7) and in the concentration of uncomplexed HAHA (Table 1), but increased with an increase in the concentration of the acetate anion (Table 2), obeying the following relations:

Table 1. The Effect of HAHA Concentration, $[\mathrm{L}]_\mathrm{f}$, on the Height of Kinetic Wave. $[\mathrm{Eu(III)}]=0.40$ mM, pH=3.73, 25 °C, $[\mathrm{OAc}^-]=0.10$ M, $I=0.20$ M, $i_\mathrm{l}=1.140$ μA

$[\mathrm{L}]_\mathrm{f}$ / mM	i_k / μA	$\left(\frac{i_\mathrm{k}}{i_\mathrm{l}-i_\mathrm{k}}\right)^2\cdot[\mathrm{L}]_\mathrm{f}$
4.00	0.137	7.46×10^{-5}
8.00	0.100	7.40×10^{-5}
12.00	0.083	7.40×10^{-5}

Table 2. The Effect of Acetate Anion Concentration, $[\mathrm{OAc}^-]$, on the Height of Kinetic Wave. $[\mathrm{Eu(III)}]=0.40$ mM, pH=3.73, 25 °C, HAHA concentration, $[\mathrm{L}]_\mathrm{f}=4.00$ mM, $I=0.20$ M, $i_\mathrm{l}=1.140$ μA

$[\mathrm{OAc}^-]$ / M	i_k / μA	$\beta_\mathrm{OAc}^{\mathrm{a)}}$	$\left(\frac{i_\mathrm{k}}{i_\mathrm{l}-i_\mathrm{k}}\right)^2/\beta_\mathrm{OAc}$
0.050	0.081	2.50×10^{1}	2.33×10^{-4}
0.100	0.137	7.85×10^{1}	2.37×10^{-4}
0.200	0.231	2.74×10^{2}	2.37×10^{-4}

a) $\beta_\mathrm{OAc}=1+\beta_1\cdot[\mathrm{OAc}^-]+\beta_2\cdot[\mathrm{OAc}^-]^2$.

$$\left(\frac{i_\mathrm{k}}{i_\mathrm{l}-i_\mathrm{k}}\right)_\mathrm{c}^2\times\frac{[\mathrm{H}^+]^2}{(\alpha_\mathrm{H})_\mathrm{L}}=a+b\cdot[\mathrm{H}^+], \tag{1}$$

where a and b are constants
(at given HAHA and acetate concentrations),

$$\left(\frac{i_\mathrm{k}}{i_\mathrm{l}-i_\mathrm{k}}\right)_\mathrm{c}^2\times[\mathrm{L}]_\mathrm{f}=\text{constant} \tag{2}$$

(at given pH and acetate concentration),

$$\left(\frac{i_\mathrm{k}}{i_\mathrm{l}-i_\mathrm{k}}\right)_\mathrm{c}^2\times\frac{1}{\beta_\mathrm{OAc}}=\text{constant} \tag{3}$$

(at given pH and HAHA concentration).

Here, $[\mathrm{L}]_\mathrm{f}$ indicates the concentration of uncomplexed HAHA, i_k the limiting current of the first step, i_l the hypothetical diffusion current which can be approximated to the sum of the first and second wave heights, $(\alpha_\mathrm{H})_\mathrm{L}$, $1+[\mathrm{H}]\times K_1+[\mathrm{H}^+]^2\times K_1\cdot K_2+\cdots,Ki$, the protonation constant of the hexavalent HAHA anion, $\beta_\mathrm{OAc}=1+\beta_1\cdot[\mathrm{OAc}^-]+\beta_2\cdot[\mathrm{OAc}^-]^2$, and β_j the overall formation constant of the Eu(III)-acetato complex. β_1 and β_2 used were $10^{2.27}$ and $10^{3.77}$, respectively.

As was discussed in connection with the polarography of aminopolycarboxylato complexes of Zn(II), Pb(II), and Cd(II) ions,[9] the reaction mechanism and the dissociation rates were determined from the i_k and i_l values using the treatment by Koryta.[10] In view of the above findings, the Koryta equation for the kinetic wave of the Eu(III)-HAHA complex under the present experimental conditions can be formulated as

$$\left(\frac{i_\mathrm{k}}{i_\mathrm{l}-i_\mathrm{k}}\right)_\mathrm{c}=0.886\sqrt{\frac{((k_\mathrm{d})_\mathrm{O}+(k_\mathrm{d})_\mathrm{H}\cdot[\mathrm{H}^+])\beta_\mathrm{OAc}\cdot(\alpha_\mathrm{H})_\mathrm{L}\cdot t_\mathrm{d}}{(\mathrm{K}_\mathrm{EuL}/\mathrm{K}^{-2\mathrm{H}})\cdot[\mathrm{L}]_\mathrm{f}\cdot[\mathrm{H}^+]^2}}, \tag{4}$$

corresponding to the following reaction mechanism:

$$\left.\begin{array}{llllll}
\mathrm{EuH_2L^-} & & \overset{(k_\mathrm{d})_\mathrm{O}}{\rightleftharpoons} & \mathrm{Eu^{3+}} + \mathrm{H_2L^{4-}} & (5)_\mathrm{a} & \text{slow} \\
\mathrm{EuH_2L^-} & + \ \mathrm{H^+} & \overset{(k_\mathrm{d})_\mathrm{H}}{\rightleftharpoons} & \mathrm{Eu^{3+}} + \mathrm{H_3L^{3-}} & (5)_\mathrm{b} & \text{slow} \\
\mathrm{Eu^{3+}} & + \ i\mathrm{OAc^-} & \rightleftharpoons & \mathrm{Eu(OAc)}_i^{3-i} & (5)_\mathrm{c} & \text{rapid}
\end{array}\right\} \quad (\mathrm{A})$$

$$\underbrace{\mathrm{Eu^{3+}} + i\mathrm{OAc^-} \rightleftharpoons \mathrm{Eu(OAc)}_i^{3-i}}\ \Big\Downarrow\ \mathrm{e}^- \quad \mathrm{Eu^{2+}} + i\mathrm{OAc^-}$$

The rate constants, $(k_\mathrm{d})_\mathrm{O}$ and $(k_\mathrm{d})_\mathrm{H}$, were determind to be 5.1×10^{-1} (s^{-1}) and 3.7×10^{2} ($\mathrm{mol}^{-1}\,\mathrm{dm}^3\,\mathrm{s}^{-1}$), respectively, from the intercept and the gradient of the straight line in Fig. 7. The drop time, t_d, used in an estimation of the rate constants were 5.10 sec/drop. The $K_\mathrm{EuL}/K^{-2\mathrm{H}}$ in Eq. 4 is equal to $K_{\mathrm{EuH_2L}}\times K_1K_2$.

Though the Eu(III)-PAPA complex in an acetate buffer solution containing an excess of uncomplexed PAPA seemingly gave an ill-defined one-step dc polarogram, its ac polarogram showed two peaks, the first of which evidently corresponds to the uncomplexed Eu(III) ions. These findings can be explained in terms of the poor potential separation between the dc reduction steps of free and complexed Eu(III) ions. It is therefore practically impossible to investigate the cathodic polarography of the Eu(III)-PAPA complex. On the other hand, in an acetate buffer solution containing excess uncomplexed Eu(III) ions, where all the PAPA or HAHA anions are considered to exist as Eu(III)-PAPA or -HAHA complex, the Eu(III) complex gave a well-defined anodic step due to the oxidation of mercury (Fig. 8). This anodic step shows a kinetic character and might be ascribed to the uncomplexed PAPA or HAHA anions supplied by the slow dissociation of the Eu(III) complex at the electrode surface. A rigorous theoretical equation for

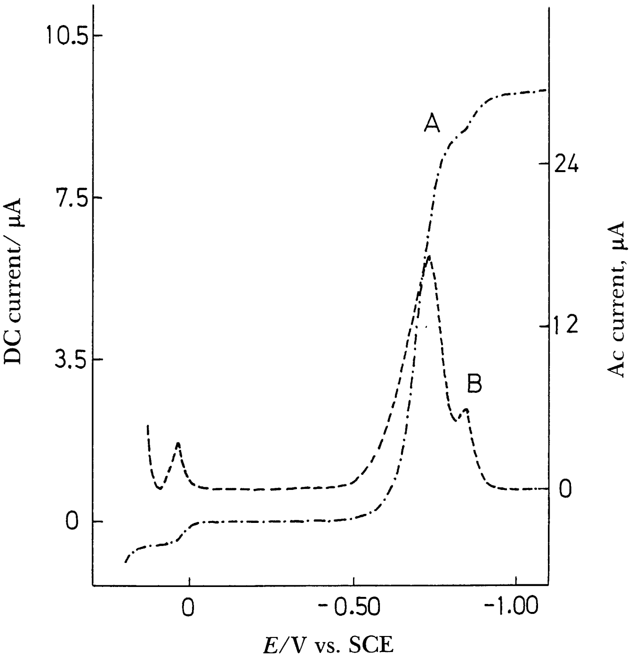

Fig. 8. Dc and ac polarogram of Eu(III)—[15]aneN$_5$$\cdot$(OAcH)$_5$ complex. [complex]=0.384 mM, [Eu(III)]$_f$= 4.38 mM, [OAc$^-$]=0.10 M, I=0.20 M, 25 °C. A. dc polarogram, B. ac polarogram.

the kinetic waves was originally derived for an electrode process in which the electron-transfer step is preceded by a first-order chemical reaction.[10,11] In this connection the theoretical equation for the kinetic current usually applied to a cathodic wave can be safely applied to the anodic waves observed in buffered Eu(III)-PAPA or -HAHA complex solutions containing excess Eu(III) ions.

The above-mentioned anodic waves were characterized by studying the effects of the solution pH and the concentrations of uncomplexed Eu(III) and acetate ions on their limiting currents. Provided that the other experimental conditions are kept constant, $(i_k/(i_l-i_k))_a^2/\beta_{OAc}$ and $(i_k(i_l-i_k))_a^2 \times [\mathrm{Eu(III)}]_f$ values were constant, but the $(i_k/(i_l-i_k))_a^2/(\alpha_H)_X$ for the PAPA system and the $(i_k/(i_l-i_k))_a^2 \cdot [\mathrm{H}^+]^2/(\alpha_H)_L$ values for the HAHA system were found to increase on increasing the hydrogen ion concentration obeying the following equation:

$$\left(\frac{i_k}{i_1 - i_k}\right)_a^2 \times \frac{1}{(\alpha_H)_X} = a' + b'[\mathrm{H}^+] \qquad (6)$$

(PAPA system)

$$\left(\frac{i_k}{i_1 - i_k}\right)_a^2 \times \frac{[\mathrm{H}^+]^2}{(\alpha_H)_L} = a + b[\mathrm{H}^+] \qquad (1')$$

(HAHA system)

Here, the $(i_k/(i_l-i_k))_a$ ratio means the $(i_k/(i_l-i_k))$ value for the anodic polarogram, $(\alpha_H)_X$ the (α_H) value for the PAPA system, and $[\mathrm{Eu(III)}]_f$ the concentration of uncomplexed Eu(III) ion. The other symbols used have the same meanings as in the HAHA system. The i_l value can be equated with the anodic wave height in the absence of Eu(III) ions.

The above-mentioned evidence collected in the anodic polarogram of Eu(III)-PAPA and -HAHA complexes made it possible to safely conclude that the Koryta equation for the anodic waves of the Eu(III)-PAPA and -HAHA complexes can be formulated by (7) and (4′), respectively, corresponding to reaction mechanisms (B) and (C).

$$\left(\frac{i_k}{i_1 - i_k}\right)_a = 0.886\sqrt{\frac{((k_d)_O + (k_d)_H \cdot [\mathrm{H}^+])\beta_{OAc} \cdot (\alpha_H)_X \cdot t_d}{K_{EuX} \cdot [\mathrm{Eu(III)}]_f}}, \qquad (7)$$

$$\left(\frac{i_k}{i_1 - i_k}\right)_a = 0.886\sqrt{\frac{((k_d)_O + (k_d)_H \cdot [\mathrm{H}^+])\beta_{OAc} \cdot (\alpha_H)_L \cdot t_d}{(K_{EuL}/K^{-2H}) \cdot [\mathrm{Eu(III)}]_f \cdot [\mathrm{H}^+]^2}}, \qquad (4')$$

$$\left.\begin{array}{llllllll}
\mathrm{EuX^{2-}} & & \overset{(k_d)_O}{\rightleftharpoons} & \mathrm{Eu^{3+}} + \mathrm{X^{5-}} & & (8)_a & \text{slow} \\
\mathrm{EuX^{2-}} & + \mathrm{H^+} & \overset{(k_d)_H}{\rightleftharpoons} & \mathrm{Eu^{3+}} + \mathrm{HX^{4-}} & & (8)_b & \text{slow} \\
\mathrm{Eu^{3+}} & + i\mathrm{OAc^-} & \rightleftharpoons & \mathrm{Eu(OAc)}_i^{3-i} & & & \text{rapid} \\
\mathrm{Hg} & + \mathrm{H}_j\mathrm{X}^{j-5} & \rightleftharpoons & \mathrm{HgHX^{2-}} + (j-1)\mathrm{H^+} + 2e^- & & (8)_c &
\end{array}\right\} \quad (\mathrm{B})$$

where $\mathrm{H}_j\mathrm{X}^{j-5}$ means the protonated PAPA anion.

$$\left.\begin{array}{lll}
\mathrm{EuH_2L^-} \xrightleftharpoons{(k_d)_O} \mathrm{Eu^{3+}} + \mathrm{H_2L^{4-}} & (5)_a & \text{slow} \\
\mathrm{EuH_2L^-} + \mathrm{H^+} \xrightleftharpoons{(k_d)_H} \mathrm{Eu^{3+}} + \mathrm{H_3L^{3-}} & (5)_b & \text{slow} \\
\mathrm{Eu^{3+}} + i\mathrm{OAc^-} \rightleftharpoons \mathrm{Eu(OAc)}_i^{3-i} & & \text{rapid} \\
\mathrm{Hg} + \mathrm{H}_k\mathrm{L}^{k-6} \rightleftharpoons \mathrm{HgH_3L^-} + (k-3)\mathrm{H^+} & & \\
\qquad + 2e^- & (5)_d &
\end{array}\right\} \quad (C)$$

The $(k_d)_o$ and $(k_d)_H$ values were estimated from the intercepts and gradients of the straight lines in Figs. 9 and 7, and are listed together in Table 3. The t_d value used in the calculation was 4.70 sec/drop. The straight line obtained by plotting the $(i_k(i_l-i_k)^2{}_a\cdot[\mathrm{H^+}]^2/(\alpha_H)_L$ against $[\mathrm{H^+}]$ gave the same intercept and gradient as those obtained in its cathodic polarography (Fig. 7). This agreement suggests that the above-mentioned theoretical treatment in the anodic polarography is absolutely reasonable.

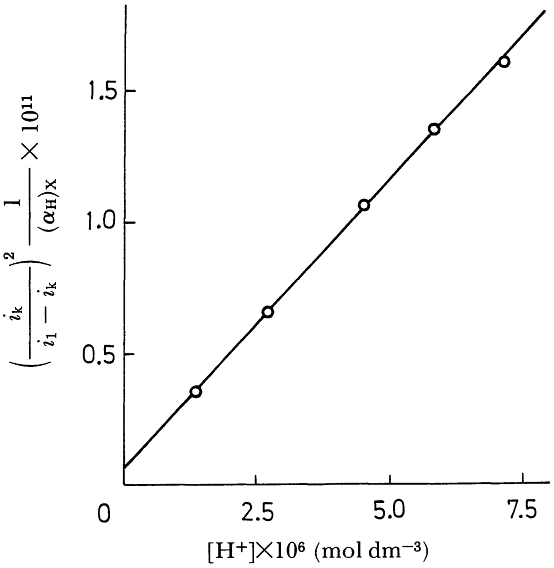

Fig. 9. Plots of $(i_k/(i_1-i_k))_a^2/(\alpha_H)_X$ against $[\mathrm{H^+}]$. Eu(III)—[15]aneN$_5\cdot$(OAcH)$_5$ complex]=0.384 mM, $[\mathrm{Eu(III)}]_f$=4.38 mM, $[\mathrm{OAc^-}]$=0.050 M, I=0.20 M, 25 °C.

The Gd(III)- and Ho(III)-PAPA complexes in acetate buffer solutions containing excess metal(III) ions showed similar polarographic behaviors. As in the case of the Eu(III) complex, the $(k_d)_O$ and $(k_d)_H$ values for the Gd(III)- and Ho(III)-PAPA complexes were also graphically determined from plots of $(i_k/(i_l-i_k))^2{}_a/(\alpha_H)_X$ with $[\mathrm{H^+}]$ (Table 3). The $\log\beta_1$ values used in the calculation of β_{OAc} for the Gd(III) and Ho(III) systems are 2.12 and 2.01, and $\log\beta_2$ used are 3.62 and 3.55.

The rate constants, $(k_f)_{HX}$ and $(k_f)_X$, for the formation of PAPA complexes from the singly-protonated PAPA anion, $\mathrm{HX^{4-}}$, and completely-deprotonated PAPA anion, $\mathrm{X^{5-}}$, were calculated from the relations of $(k_f)_{HX}=(k_d)_H\cdot K_{MX}\times K_1$ and $(k_f)_X=(k_d)_O\times K_{MX}$. In a similar way the $(k_f)_{H2L}$ and $(k_f)_{H3L}$ values of the Eu(III)-HAHA complex were estimated from the $(k_d)_O$ and $(k_d)_H$ values. They are listed in Table 2. All the formation rate constants calculated are larger than the characteristic water exchange rate constants of the aquo lanthanide metal(III) ions, $k_M{}^{-H_2O}$[12] (Table 4).

In general, the complexation reactions of multidentate ligands can be broken down into many reaction steps including a diffusion-controlled outer-sphere association of the metal ion with a ligand anion. If the reaction mechanism involves several rapid equilibria followed by a rate-determining step, the experimentally observed rate constant should be given by the relation $(k_f)=k_{rds}\,|K_1\cdot|K_2\cdot|K_3\cdots$. Here, k_{rds} indicates the rate constant for the rate-determining step and $|K_1$, $|K_2$, $|K_3,\cdots$ are the equilibrium constants of the precedent rapid reaction steps. When the complexation reaction involves the formation of an equilibrated outer-sphere complex, preceding the loss of a coordinated water molecule as the rate-determining step, the

Table 3. The (k_d) Values Observed. I=0.20 M, 25 °C

System		$(k_d)_O$	$(k_d)_H$
		sec^{-1}	M^{-1} sec^{-1}
PAPA	Eu(III)	$3.9_1\times10^{-2}$	4.24×10^5
	Gd(III)	$4.0_4\times10^{-2}$	2.45×10^5
	Ho(III)	$1.2\ \times10^{-2}$	2.05×10^4
HAHA	Eu(III)	$5.1\ \times10^{-1}$	$3.7_0\times10^2$

Table 4. Reported $k_M^{-H_2O}$ Values (25 °C)[12]

Metal(III)	$k_M^{-H_2O}$
	sec^{-1}
Eu(III)	4.9×10^{8}[a]—1.0×10^{9}[b]
Gd(III)	6.3×10^{7}[c]—1.3×10^{9}[b]
Ho(III)	$9\ \times10^{6}$[c]—2.5×10^{8}[a]

a) Ref. 12a). b) Ref. 12b). c) Ref. 12c).

Table 5. Estimated (k_f) and $K_{os}\cdot k_M^{-H_2O}$ Values. I=0.20 M, 25 °C

System		$(k_f)_{HX}$ $M^{-1}\,sec^{-1}$	$K_{os}\cdot k_M^{-H_2O}$	$(k_f)_X$ $M^{-1}\,sec^{-1}$	$K_{os}\cdot k_M^{-H_2O}$
PAPA	Eu(III)	1.2×10^{11}	2.5×10^{12}—$5\ \times10^{12}$	1.5×10^{14}	3.3×10^{13}—6.5×10^{13}
	Gd(III)	1.3×10^{12}	3.2×10^{11}—6.5×10^{12}	3.0×10^{14}	4.0×10^{12}—8.2×10^{13}
	Ho(III)	4.4×10^{10}	$5\ \times10^{10}$—1.3×10^{12}	3.7×10^{14}	5.7×10^{11}—1.7×10^{13}
HAHA	Eu(III)	6.6×10^{10}[a)]	2.5×10^{11}—5.0×10^{11}	7.6×10^{16}[b)]	2.5×10^{12}—5.0×10^{12}

a) $(k_f)_{H_3L}$ value. b) $(k_f)_{H_2L}$ value.

rate constant can be written as the product of the outer-sphere association constant, K_{os}, and $k_M^{-H_2O}$. As predicted by the Fuoss equation[13)] the K_{os} values for the outer-sphere association of M^{3+} with highly charged ligand anions are expected to be much larger than unity. The calculated $\log K_{os}$ values for the +3—−3, +3—−4, and +3—−5 systems at I=0.20, using the center to center distance, a, of 5.0 Å are 2.7, 3.7, and 4.8, respectively. The rate constant reported for the water-exchange of aquated Gd^{3+} ion falls between 6.3×10^7 and 1.3×10^9 sec^{-1}[12)] (Table 4). Therefore, the $K_{os}\cdot k_M^{-H_2O}$ value for the reactions of Gd^{3+} ion with tetravalent and pentavalent PAPA anions would lie in the ranges from 3.2×10^{11} to 6.5×10^{12} and from 4.2×10^{12} to 8.5×10^{13} $mol^{-1}\,dm^3\,s^{-1}$, respectively (Table 5). Considering the limitation of the Fuoss's theoretical treatment, an agreement between the observed and calculated rate constants for the reaction of Gd^{3+} ion with singly-protonated PAPA anion can be regarded as good, suggesting a water-exchange mechanism. The same comparisons were made for the other reactions studied. The rate constants observed in the reactions of HX^{4-} and H_3L^{3-} showed satisfactory agreement with the product, $K_{os}\cdot k_M^{-H_2O}$. Thus, these reactions are accounted for by the same water-exchange mechanism. However, the reactions of X^{5-} and H_2L^{4-} studied gave rate constants much larger than the $K_{os}\cdot k_M^{-H_2O}$ values (Table 5). At present, though we have no immediate explanation for these large rate constants, they may be explained in terms of a reaction mechanism which involves several (intermediate formation) equilibria preceding the rate-determining step.

Applications of anodic polarography to a kinetic study of the PAPA complexes of the rare earth metal(III) ions other than Eu(III), Gd(III), and Ho(III) ions are now underway in our laboratory.

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