Polarographic Study of the Rates of the Dissociation Reactions of the Nickel(II)-, Zinc(II)-, and Cadmium(II)-2,2′-Ethylenedioxybis[ethyliminodi(acetate)] (GEDTA) Complexes

Mutsuo KODAMA and Noboru OYAMA*

Department of Chemistry, Ibaraki University, Bunkyo, Mito, Ibaraki

**Chemistry Department, Faculty of Engineering, Ibaraki University, Narisawa, Hitachi, Ibaraki*

(Received January 27, 1972)

In GEDTA solutions with pH's lower than 7.0_0, the nickel(II), zinc(II), and cadmium(II) ions were found to yield the one-step, two-step, and three-step polarographic waves respectively. The polarographic wave of the nickel(II) ion, the first step of the zinc(II) ion, and the first and second steps of the cadmium(II) ion showed a kinetic-controlled nature. In this study, the polarographic wave of the nickel(II) ion, the first step of the zinc(II) ion, and the second step of cadmium(II) ion were studied systematically. From an experimental examination of the nature of the kinetic currents of these complexes, the mechanisms for the above polarographic steps were determined as:

i) $NiHY^- \rightleftharpoons Ni^{2+} + HY^{3-}$ rate-determining step
$\downarrow\uparrow$ rapid
pH<5.70 NiY^{2-}
$Ni^{2+} + 2e^- + Hg = Ni(Hg)$
$NiY^{2-} \rightleftharpoons Ni^{2+} + Y^{4-}$ rate-determining step
$\downarrow\uparrow$ rapid
pH>5.70 $NiHY^-$
$Ni^{2+} + 2e^- + Hg = Ni(Hg)$

ii) $ZnHY^- + H^+ = Zn^{2+} + H_2Y^{2-}$ rate-determining step
$\downarrow\uparrow$ rapid
ZnY^{2-}
$Zn^{2+} + 2e^- + Hg = Zn(Hg)$

iii) $Cd(HY)_2^{4-}$
$\downarrow\uparrow$ rapid
$CdHY^- = CdHY^{-*}$ rate-determining step
$\downarrow\uparrow$ rapid
CdY^{2-}
$CdHY^{-*} + 2e^- + Hg = Cd(Hg) + HY^{3-}$

where $CdHY^{-*}$ is the electroactive cadmium(II)-GEDTA complex. By comparing the dissociation rate constant of the nickel(II)-GEDTA complex with that of the nickel(II)-aspartate complex, the detailed dissociation mechanism was determined. The rates and mechanisms of the dissociations of zinc(II) and cadmium(II)-GEDTA complexes were also discussed in detail.

In a previous paper,[1] we studied the polarographic behavior of the copper(II)-2,2′-ethylenedioxybis[ethyliminodi(acetate)] (GEDTA) complex systematically. In contrast with the copper(II)-ethylenediaminetetraacetate and *N*-(2-hydroxyethyl)-ethylenediamine-*N*,*N*′,*N*′-triacetate (EDTA-OH) complexes, it has been found to give two polarographic waves, both of which are diffusion-controlled in nature. From the GEDTA concentration dependence of the half-wave potential, it was concluded that the hexadentate GEDTA anion can form a complex with a 1:2 composition with the copper(II) ion. The GEDTA complex of the zinc(II) ion also gives the two-step polarographic wave in GEDTA solutions of pH's lower than 7.00. The second polarographic step of the zinc(II)-GEDTA complex was diffusion-controlled in nature. However, the first step showed a kinetic-controlled nature. The nickel(II) and cadmium(II) ions in GEDTA solutions were also found to give kinetic waves. In this paper, we will investigate the polarographic behaviors of nickel(II), zinc(II)-, and cadmium(II)-GEDTA complexes systematically, and will determine the rate constants and the electrode reaction mechanisms by analyzing the experimental data with the aid of theoretical relations derived previously.[2] The structure of the reaction intermediate and the reaction mechanism will also be discussed in detail on the basis of a comparison of the observed rate constant with that calculated from the reaction intermediate proposed.

Experimental

Reagents. The way of preparing the standard nickel(II) nitrate solution was given previously.[2] Standard zinc(II) and cadmium(II) solutions were prepared by dissolving known amounts of pure cadmium(II) and zinc(II) sulfates in redistilled water. GEDTA (2,2′-ethylenedioxybis[ethyliminodi(acetic acid)]) was recrystallized from its aqueous solution by adding pure ethanol and hydrochloric acid. All the other chemicals used were of an analytical-reagent grade and were used without further purification.

Apparatus and Experimental Procedures. All the DC current-voltage curves were measured by using a manual polarograph similar to that of Kolthoff and Lingane or a

1) M. Kodama and Y. Tominaga, This Bulletin, **42**, 394 (1969).

2) M. Kodama, H. Nunokawa, and N. Oyama, *ibid.*, **44**, 2387 (1971).

Yanagimoto pen-recording polarograph, PA-102. The characteristic features of the dropping mercury electrode (DME) used in this study were given previously.[2] All the other apparatuses used and the experimental procedures were also described in that previous paper.[2] The ionic strength of the solution was adjusted to 0.30 by adding an appropriate amount of pure sodium perchlorate. To keep the solution's pH constant, a sodium acetate–acetic acid mixture or a potassium dihydrogen phosphate–disodium hydrogen phosphate mixture was used.

Results and Discussion

Polarographic Behavior of the Nickel(II) Ion in the GEDTA Solution. From the thermodynamic point of view,[3] all the nickel(II) ions in a 10.0 mM GEDTA solution with a pH higher than 5.0 are considered to exist as GEDTA complex. Even under these experimental conditions, the nickel(II)-GEDTA complex gives the polarographic step at the potentials where the nickel(II) aquo ions give a polarographic wave

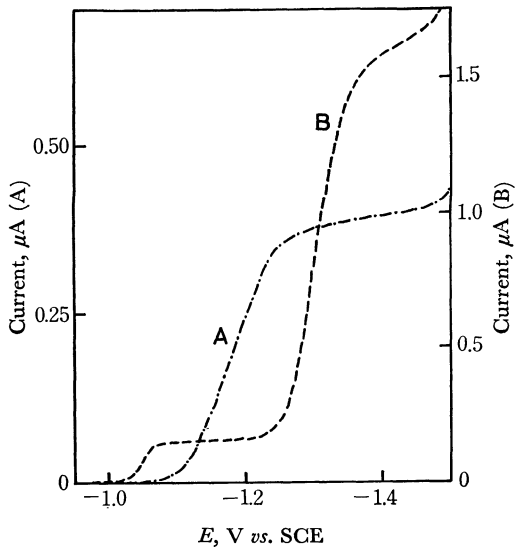

Fig. 1. Polarograms of metal(II)-GEDTA complexes.
A) Ni(II)-GEDTA system
The concentration of uncomplexed GEDTA=20.0 mM
The concentration of nickel(II) ion=1.00 mM
The total concentration of phosphate=0.12 M
pH=6.11, μ=0.30, 25°C
B) Zn(II)-GEDTA system
The concentration of uncomplexed GEDTA=10.0 mM
The concentration of zinc(II) ion=0.50$_0$ mM
The concentration of uncomplexed acetate ion=20.0 mM
pH=5.24, μ=0.30, 25°C

(Fig. 1). Although the results are not shown, its limiting current was almost independent of the effective pressure of the mercury column within the limits of experimental error. This fact clearly implies that the polarographic step of the nickel(II)-GEDTA complex is kinetic-controlled in nature. In order to maintain the solution's pH constant, an acetic acid–acetate buffer mixture (5.00<pH<5.70) or a potassium dihydrogen phosphate–disodium hydrogen phosphate mixture

3) A. Ringbom, "Complexation in Analytical Chemistry," John Wiley & Sons, New York (1963).

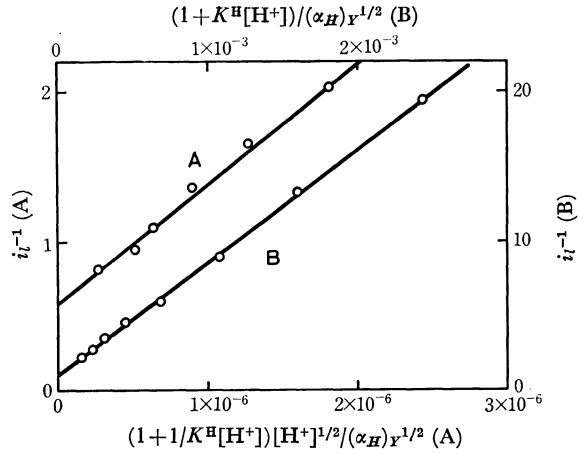

Fig. 2. The plot of i_l^{-1} against $(1+1/K^{H}[H^+])[H^+]^{1/2}/(\alpha_H)_Y^{1/2}$ or $(1+K^{H}[H^+])/(\alpha_H)_Y^{1/2}$.
The concentration of uncomplexed GEDTA=20.0 mM
The concentration of nickel(II) ion=1.00 mM
μ=0.30, 25°C
A) The plot of i_l^{-1} *vs.* $(1+1/K^{H}[H^+])[H^+]^{1/2}/(\alpha_H)_Y^{1/2}$ 5.00<pH<5.70, The total concentration of acetate=0.05M
B) The plot of i_l^{-1} *vs.* $(1+K^{H}[H^+])/(\alpha_H)_Y^{1/2}$ 5.70<pH<7.00, The total concentration of phospate=0.12M

(5.70<pH<7.00) was used in this study. However, these buffer mixtures had no effect on the wave-height and the half-wave potential of the reduction wave of the nickel(II)-GEDTA complex. In the pH range from 5.00 to 5.70, the plot of a reciprocal of the wave-height, i_l^{-1}, against the $(1+1/K^{H}\cdot[H^+])\cdot[H^+]^{1/2}/(\alpha_H)_Y^{1/2}$ or the $[Y]_f^{1/2}$ gave a straight line with an intercept nearly identical to the reciprocal of i_d (Fig. 2). Here, i_d is the limiting current when it is completely diffusion-controlled and is represented by the well-known Ilkoviç equation. K^{H} is the protonation constant of the nickel(II)-GEDTA complex (defined as $K^{H}=[NiHY^-]/[NiY^{2-}]\cdot[H^+]$); $(\alpha_H)_Y$, the (α_H) value of GEDTA, and $[Y]_f$, the concentration of uncomplexed GEDTA On the other hand, in solutions with pH

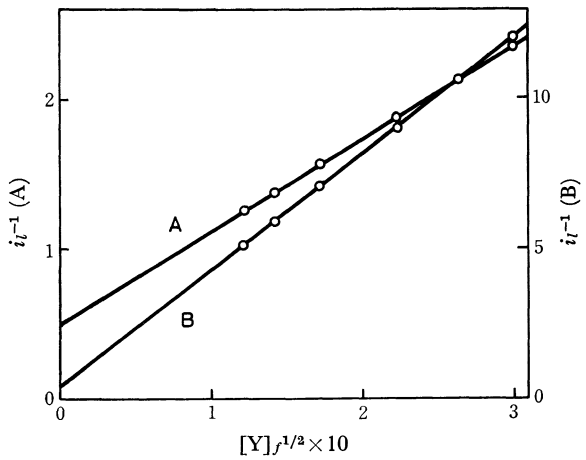

Fig. 3. The plot of i_l^{-1} against $[Y]_f^{1/2}$.
μ=0.30, 25°C
The concentration of nickel(II) ion=1.00 mM
A) pH=5.37
The total concentration of acetate=0.05M
B) pH=6.69
The total concentration of phosphate=0.12M

values from 5.70 to 7.00, the plot of i_l^{-1} *vs.* the $(1+K^H\cdot[H^+])/(\alpha_H)_Y^{1/2}$ or $[Y]_f^{1/2}$ gave a straight line (Fig. 3). As was discussed in connection with polarography of the nickel(II)-aspartate and glutamate complexes,[2] these facts evidently show that the reaction mechanism for the polarographic wave of the nickel(II)-GEDTA complex can be expressed as:

$5.00<pH<5.70$

$NiHY^- \overset{(k_d)_{NiHY}}{\rightleftharpoons} Ni^{2+}+HY^{3-}$ r.d.s.

$\downarrow\uparrow$ rapid

NiY^{2-} I

$Ni^{2+}+2e^-+Hg=Ni(Hg)$

$5.70<pH<7.00$

$NiY^{2-} \overset{(k_d)_{NiY}}{\rightleftharpoons} Ni^{2+}+Y^{4-}$ r.d.s.

$\downarrow\uparrow$ rapid

$NiHY^-$ II

$Ni^{2+}+2e^-+Hg\rightleftharpoons Ni(Hg)$

where Y^{4-} denotes the completely-deprotonated GEDTA anion. In consideration of the chemical equilibria in solution, the following two equations can be derived for the above reaction mechanisms, I and II respectively:

$$\frac{1}{i_l}=\frac{K_{NiHY}^{1/2}\left(1+\frac{1}{K^H[H^+]}\right)\cdot[Y]_f^{1/2}}{2AF\cdot D^{1/2}(k_d)_{NiHY}^{1/2}\cdot(\alpha_H)_Y^{1/2}}+\frac{1}{i_d} \quad (1)$$

$$\frac{1}{i_l}=\frac{K_{NiY}^{1/2}\,(1+K^H\cdot[H^+])\cdot[Y]_f^{1/2}}{2AF\cdot D^{1/2}\cdot(k_d)_{NiY}^{1/2}\cdot(\alpha_H)_Y^{1/2}}+\frac{1}{i_d} \quad (2)$$

All the symbols used in Eqs. (1) and (2) have their usual meanings.[2]

Table 1. Rate constants (μ=0.30, 25°C)

Elementary reaction	Rate constant
$NiHY^-=Ni^{2+}+HY^{3-}$	9.3×10^{-4} sec^{-1}
$NiY^{2-}=Ni^{2+}+Y^{4-}$	$2.5_3\times10^{-3}$ sec^{-1}
$ZnHY^-+H^+=Zn^{2+}+H_2Y^{2-}$	14.9 M^{-1} sec^{-1}

From the slopes of the linear relations in Figs. 2. and 3, the $(k_d)_{NiHY}$ and $(k_d)_{NiY}$ values were determined; they are listed in Table 1 together with other numerical values. If the electrode reaction mechanisms for the polarographic step of the nickel(II)-GEDTA complex at pH's lower than 5.70 and that at pH's higher than 5.70 are given by I and II respectively, the half-wave potentials should be given by (3) and (4) respectively:

$$E_{1/2}=\text{constant}_1+\frac{0.0591}{4\alpha}\cdot\log\frac{[Y]_f[H^+]}{(\alpha_H)_Y} \quad (3)$$

$$E_{1/2}=\text{constant}_2+\frac{0.0591}{4\alpha}\cdot\log\frac{[Y]_f}{(\alpha_H)_Y} \quad (4)$$

These relations were examined by using some typical experimental data. Typical results obtained at pH's lower than 5.70 are shown in Tables 2 and 3. The agreement between the shift of the half-wave potential obtained experimentally, $(\Delta E_{1/2})_{ob}$, and that calculated with the aid of Eq. (3), using the α value of 0.50, can be regarded as satisfactory. In solutions of pH's higher than 7.00, the nickel(II)-GEDTA complex give no polarographic wave.

Polarographic Behavior of Zinc(II) Ions in a GEDTA Solution. Reported equilibrium constants for the formation of the zinc(II)-GEDTA complex[3] show that all the zinc(II) ions in the 10.0 mM GEDTA solutions with pH's higher than 4.60 invariably exist as GEDTA complex. As is illustrated by the polarogram in Fig. 1, in the pH range from 5.0 to 6.0, the zinc(II) ions in 10.0 mM GEDTA solutions yielded two polarographic steps. Under the present experimental conditions, the total wave-height was almost constant, but was exactly proportional to the square-root of the effective pressure on the DME and zinc(II) ion concentrations. However, the wave-height of the first reduction step was

Table 2. The dependence of $E_{1/2}$ on the pH
The concentration of uncomplexed GEDTA=20.0 mM
The concentration of nickel(II) ion=1.0 mM
The total concentration of acetate=0.05 M
μ=0.30, 25°C

pH	$E_{1/2}$ V *vs.* SCE	$\Delta E_{1/2}$, mV Obsd	Calcd
5.04	−1.082	0	0
5.17	−1.087	− 5.0	− 7.8
5.35	−1.102	−20.0	−18.6
5.51	−1.107	−25.0	−28.2
5.65	−1.112	−30.0	−31.6

Table 3. The dependence of $E_{1/2}$ on the concentration of uncomplexed GEDTA
The concentration of nickel(II) ion=1.0 mM
The total concentration of acetate=0.05 M
μ=0.30, 25°C, pH=5.35

Concentration of GEDTA, mM	$E_{1/2}$ V *vs.* SCE	$\Delta E_{1/2}$, mV Obsd	Calcd
15.0	−1.094	0	0
20.0	−1.102	− 8.0	− 7.5
30.0	−1.109	−15.0	−18.0
60.0	−1.133	−39.0	−36.1
90.0	−1.139	−45.0	−46.6

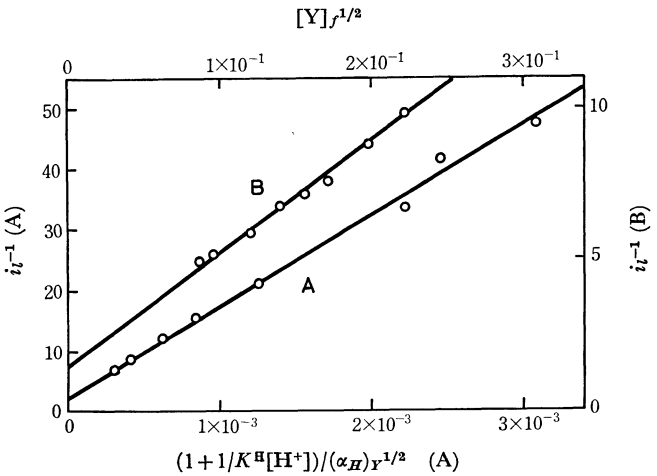

Fig. 4. The plot of i_l^{-1} against $(1+1/K^H[H^+])/(\alpha_H)_Y^{1/2}$ or $[Y]_f^{1/2}$.
The concentration of zinc(II) ion=0.50 mM
The concentration of uncomplexed acetate ion=20.0 mM
μ=0.30, 25°C
A) The plot of i_l^{-1} *vs.* $(1+1/K^H[H^+])/(\alpha_H)_Y^{1/2}$
The concentration of uncomplexed GEDTA=10.0 mM
B) The plot of i_l^{-1} *vs.* $[Y]_f^{1/2}$
pH=5.04

almost independent of the effective mercury pressure, suggesting its kinetic nature (the results are not shown here). As in the case of the polarography of the nickel(II)-GEDTA complex, the nature of the first polarographic wave of the zinc(II)-GEDTA complex was investigated thoroughly. Provided that the other experimental conditions are kept constant, the plot of the reciprocal of the limiting current, i_l^{-1}, against $[Y]_f^{1/2}$ or $(1+1/K^H\cdot[H^+])/(\alpha_H)_Y^{1/2}$ invariably gives a linear relation (Fig. 4). Considering that the first wave is located at the potentials where the zinc(II)-aquo ions will give the reduction wave, it seems that the electrode-reaction mechanism for the first step of the zinc(II)-GEDTA complex can be depicted as:

$$\begin{array}{l} ZnY^{2-} \\ \quad \downarrow \text{ rapid } (k_d)^H_{ZnHY} \\ ZnHY^- + H^+ \rightleftharpoons Zn^{2+} + H_2Y^{2-} \quad \text{r.d.s} \qquad \text{III} \\ Zn^{2+} + 2e^- + Hg = Zn(Hg) \end{array}$$

Although, in the polarographic study of the zinc(II)-GEDTA complex, an acetate buffer mixture was used to keep the solution pH constant, it has practically no effect on the polarographic behavior of the zinc(II)-GEDTA complex provided that the acetate ion concentration was lower than 0.025M. Therefore, all the kinetic measurements were carried out by using an acetate buffer mixture where the acetate-ion concentration was lower than 0.025M. If the above reaction mechanism is correct, the half-wave potential of the first wave should shift linearly to the negative potentials with an increase in the log $[Y]_f\cdot[H^+]^2/(\alpha_H)_Y$ value, giving the slope of $0.0591/4\alpha$ V. Although the experimental data are not shown here, the above linear relation could be examined successfully. From the slope of the linear relation between i_l^{-1} and $[Y]_f^{1/2}$ or $(1+1/K^H\cdot[H^+])/(\alpha_H)_Y^{1/2}$, the proton-assisted dissociation rate constant of $ZnHY^-$, $(k_d)^H_{ZnHY}$, was determined. The $(k_d)^H_{ZnHY}$ value obtained is also given in Table 1.

Polarographic Behavior of Cadmium(II) Ions in GEDTA Solutions. Previously,[4] the polarographic behavior of the cadmium(II)-GEDTA complex in acetate buffer solutions containing a large excess of calcium(II) ions, was studied by Fujisawa and Tanaka. In the presence of an excess of calcium(II) ions, the cadmium(II)-GEDTA complex gives two polarographic steps. By investigating the nature of the first reduction step systematically, they concluded that the first step can be ascribed to the reduction of the free cadmium(II) ion liberated by the dissociation of the normal cadmium(II)-GEDTA complex at the electrode surface (Reaction mechanism IV).

$$\begin{array}{l} CdY^{2-} + jH^+ \rightleftharpoons Cd^{2+} + H_jY^{j-4} \\ Cd^{2+} + 2e^- + Hg \rightleftharpoons Cd(Hg) \qquad \text{IV} \end{array}$$

On the other hand, the cadmium(II) ions in GEDTA solutions not containing calcium(II) ions give three polarographic steps at pH's lower than 3.50. With an increase in the solution's pH, the first wave-height decreased, and it disappeared completely at pH's higher than 3.50. Thus, the cadmium(II)-GEDTA complex

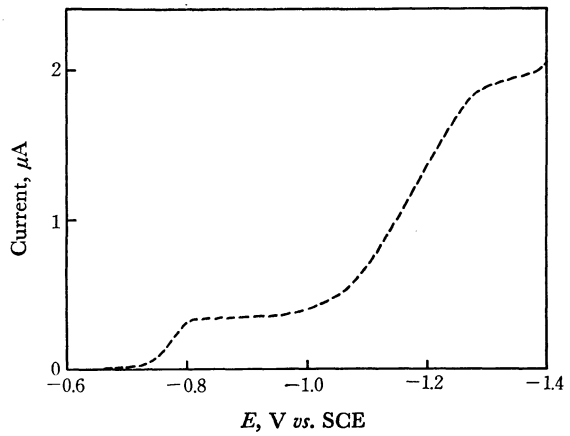

Fig. 5. Polarogram of cadmium(II)-GEDTA complex.
The concentration of cadmium(II) ion=1.00 mM
The concentration of uncomplexed GEDTA=14.0 mM
The total concentration of acetate=0.05 M
μ=0.30, 25°C, pH=4.00

in GEDTA solutions of pH's higher than 3.50 yields the two-step polarographic wave (Fig. 5). In view of the reduction potential of the first wave at pH's lower than 3.50, and in view of the effect of the GEDTA concentration on the limiting current, the first polarographic step of the cadmium(II)-GEDTA complex at pH's lower than 3.50 may be considered to correspond to the first polarographic wave reported by Fujisawa and Tanaka. In this investigation, we studied the polarographic behavior of the cadmium(II)-GEDTA complex in GEDTA solutions not containing calcium(II) ions at pH's higher than 3.50. The positive polarographic step observed in solutions containing an excess of GEDTA salt showed the characteristic kinetic-controlled nature (its limiting current is independent of the effective mercury pressure on the DME). The limiting current was decreased remarkably by increasing the solution's pH. However, the GEDTA concentration had little effect on it. By rearranging Eq. (5_a) in Ref. 2, one can easily derive the following relation:

$$\frac{i_l}{i_d - i_l} = \text{constant}_3 \times \frac{t^{1/2}k_2^{1/2}}{K_{1a}^{-1}K_{2a}^{-1/2}} \qquad (5)$$

This relation is the same as that derived by Koryta[5] for the kinetic current. With the aid of this relation, we analyzed the experimental data. Provided that the other experimental conditions are kept constant, the plot of $(i_d-i_l)/i_l$ against the reciprocal of the hydrogen-ion concentration or the GEDTA concentration, $[Y]_f$, invariably gives a linear relation. The results are reproduced in Figs. 6 and 7.

Under the present experimental conditions, the total wave-height of the cadmium(II)-GEDTA complex was exactly proportional to the square-root of the effective mercury pressure on the DME. However, it decreased appreciably with an increase in the concentration of uncomplexed GEDTA. If this can be ascribed to the formation of the cadmium(II)-GEDTA complex with a 1:2 composition, one can determine the second successive formation constant by examining the effect

4) T. Fujisawa and N. Tanaka, *Nippon Kagaku Zasshi*, **89**, 1206 (1968).

5) J. Koryta, *Collect. Czech. Chem. Commun.*, **23**, 1408 (1958).

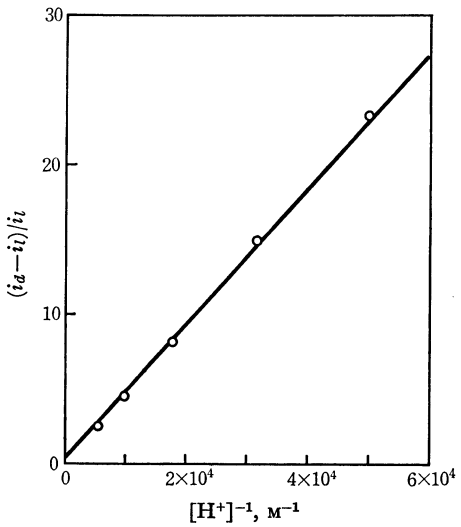

Fig. 6. The plot of $(i_d-i_l)/i_l$ against the reciprocal of hydrogen ion concentration.
The concentration of cadmium(II) ion=1.00 mM
The concentration of uncomplexed GEDTA=14.0 mM
The total concentration of acetate=0.05M
μ=0.30, 25°C

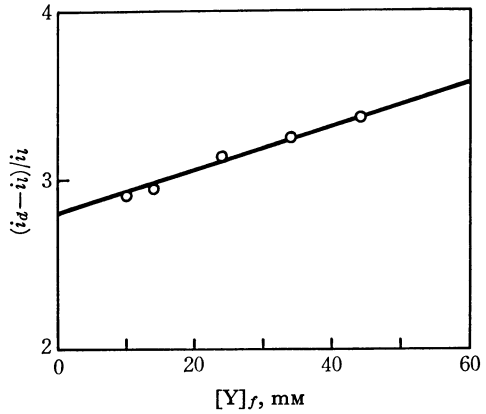

Fig. 7. The plot of $(i_d-i_l)/i_l$ against the concentration of uncomplexed GEDTA.
The concentration of cadmium(II) ion=1.00 mM
The total concentration of acetate=0.05 M
pH=4.00, μ=0.30, 25°C

of the GEDTA concentration on the limiting current with the aid of the following well-known relation (6):

$$D_{ob}=\frac{D_1+D_2\cdot K'_2[Y]_f}{1+K'_2\cdot[Y]_f} \quad (6)$$

If the composition of a 1:2 ratio complex is given by $Cd(HY)_2^{4-}$, K'_2 in Eq. (6) should be given by $K_2^{HY}\cdot[H^+]/(1+K^{H-1}\cdot[H^+]^{-1})\cdot K_4\cdot(\alpha_H)_Y$. On the other hand, if the composition of the 1:2 ratio complex is given by CdY_2^{6-}, K_2 will be given by $K_2^Y/(1+K^H\cdot[H^+])\cdot(\alpha_H)_Y$. Here, $K_2^{HY}=[Cd(HY)_2^{4-}]/[CdHY^-]\cdot[HY^{3-}]$, $K_2^Y=[CdY_2^{6-}]/[CdY^{2-}][Y^{4-}]$, and K_4 is the fourth dissociation constant of GEDTA. By introducing the Ilkoviç equation into Eq. (6) and by rearranging the resulted equation, we can obtain the following relation:

$$(i_d)_{ob}^2=\frac{(i_d)_0^2-(i_d)_{ob}^2}{[Y]_f}\times\frac{1}{K_2}+(i_d)_i^2 \quad (7)$$

where $(i_d)_{ob}$ is the diffusion current of the cadmium(II)-

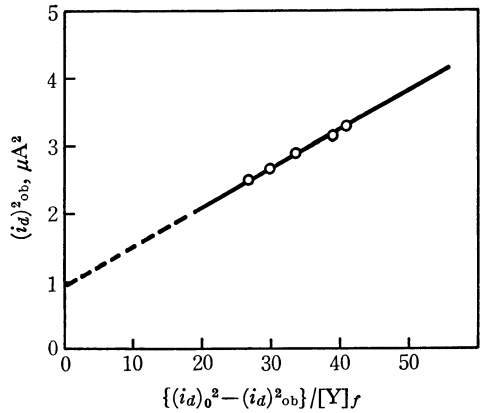

Fig. 8. The plot of $(i_d)^2_{ob}$ against $[(i_d)_0^2-(i_d)^2_{ob}]/[Y]_f$.
The concentration of cadmium(II) ion=1.00 mM
The total concentration of acetate=0.05M
μ=0.30, 25°C, pH=4.00
The concentration of uncomplexed GEDTA ranged from 10.0 to 44.0 mM

GEDTA complex in a solution where 1:1 and 1:2 complexes coexist; $(i_d)_o$, the diffusion current in a solution where all the complex ions have the 1:1 composition, and $(i_d)_i$, the diffusion current in a solution where all the complex ions have the 1:2 composition. The above relation was examined by using some typical experimental data. A typical result is shown in Fig. 8. From the slope of the straight line in Fig. 8, the K_2^{HY} or K_2^Y value was determined to be $10^{6.34}$ or $10^{11.34}$. The latter value is too large to be understood, disproving the formation of CdY_2^{6-}. It was also found that the solution's pH and the concentration of free GEDTA had practically no effect on the half-wave potential. All the above findings evidently indicate that the electrode reaction mechanism for the second step of the cadmium(II)-GEDTA complex can be expressed as:

$$\begin{array}{l} CdY^{2-} \\ \quad\downarrow\uparrow \text{ rapid} \\ CdHY^- \underset{K}{\overset{k_f}{\rightleftharpoons}} CdHY^{-*} \quad \text{r.d.s.} \qquad \text{V} \\ \quad\downarrow\uparrow \text{ rapid} \\ Cd(HY)_2^{4-} \\ CdHY^{-*}+2e^-+Hg=Cd(Hg)+HY^{3-} \end{array}$$

Here, $CdHY^{-*}$ means the electroactive protonated-cadmium(II)-GEDTA complex. For the above reaction mechanism, the (5) relation can be rewritten as:

$$\frac{i_l}{i_d-i_l}=\text{constant}_4\times\frac{t^{1/2}\cdot k_f^{1/2}}{\left(1+\dfrac{1}{K^H\cdot[H^+]}+\dfrac{K_2^{HY}\cdot K_3\cdot[H_2Y^{2-}]}{[H^+]}\right)} \quad (8)$$

where K_3 is the third dissociation constant of GEDTA and K, $[CdHY^{-*}]/[CdHY^-]$. We can mention here that, under the present experimental conditions, $[H_2Y^{2-}]$ is practically equal to the $[Y]_f$ value. Equation (8) evidently indicates that, from the slope of linear relations shown in Figs. 6 and 7, the k_f value can be estimated. However, the lack of data on the K value prevents us from calculating the k_f value from

the slope of linear relations shown in Figs. 6 and 7.

The formation constant of the protonated nickel(II)-GEDTA complex, $NiHY^-$, $K_{NiHY}=[NiHY^-]/[Ni^{2+}]\cdot[HY^{3-}]$, can be calculated to be $10^{7.94}$ ($\mu=0.30$) from the relation $K_{NiHY}=K_{NiY}\cdot K^H K_4$. This value is in good agreement with the formation constant of the 1 : 1 ratio nickel(II)-iminodiacetate complex. This agreement suggests that the tervalent GEDTA anion in the protonated nickel(II)-GEDTA complex is coordinated to the nickel(II) ion through an iminodiacetate chelate ring. Therefore, it is reasonable to believe that the protonated nickel(II)-GEDTA complex can be depicted by (A) in Fig. 9. If the structure proposed above is reasonable, the reaction intermediate in the dissociation reaction of $NiHY^-$ must be given by (B) in Fig. 9.

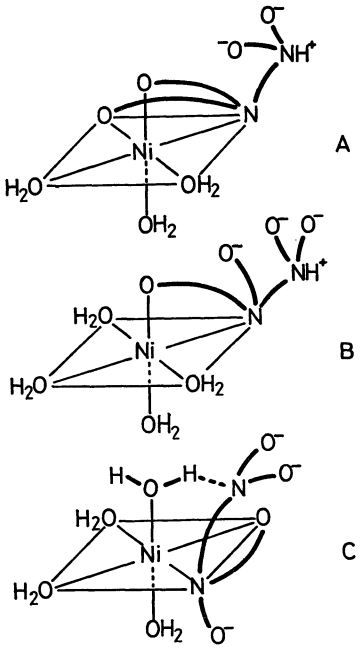

Fig. 9. Reaction intermediates.

As has been reported previously,[2] the nickel(II)-aspartate complex dissociates through the glycinate reaction intermediate, in which the leaving aspartate anion is bonded to the nickel(II) ion through a glycinate chelate ring. When the structure of the reaction intermediate in the dissociation of $NiHY^-$ is depicted by (B), and when the dissociations of aspartate and GEDTA anions from the glycinate reaction intermediates are rate-determining steps, the dissociation-rate-constant ratio between the aspartate and GEDTA systems should be given by $K_{NiHY}/K_{Ni(II)-Asp}\times 2=7.0$. Here, 2 is the statistical factor for the reaction intermediate (B). The observed ratio was 13.0. The agreement between the observed ratio and that calculated on the basis of the glycinate reaction intermediates can be regarded as satisfactory. Furthermore, the rate constant for the formation of the protonated nickel(II)-EDTA complex has been reported to be $10^{5.30}$ by Margerum and Zabin.[6] This corresponds to the dissociation constant of $2.4\times10^{-6}\,sec^{-1}$. The dissociation rate constant ratio between the protonated GEDTA and EDTA complexes, calculated by using the above rate constant, was found to be nearly equal to the ratio of the reciprocals of the K_{NiHY} value between the GEDTA and EDTA complexes of the nickel(II) ion. This suggests that the protonated nickel(II)-EDTA complex also dissociates through the reaction intermidiate in which the leaving tervalent EDTA anion is bonded to the nickel(II) ion through the glycinate chelate ring. The formation rate constant of the protonated nickel(II)-GEDTA complex, k_f, from Ni^{2+} and HY^{3-} was claculated to be $8.1\times10^4\,M^{-1}sec^{-1}$ from the relation $K_{NiHY}=k_f/k_d$. This value is slightly larger than the reported rate constant for the water loss from the aquated nickel(II) ion.[7] Considering that the association constant of the outer-sphere complex between the nickel(II) ion and the HY^{3-} anion is expected to be larger than unity from the Fuoss equation,[8] the k_f value thus estimated suggests that the rate-determining step in the formation of $NiHY^-$ is the water loss from the nickel(II)-aquo ion. As is shown in Table 1, the k_d value for the dissociation of the normal nickel(II)-GEDTA complex, NiY^{2-}, was $2.5_3\times10^{-3}\,sec^{-1}$. As has been discussed in the dissociation of $NiHY^-$ with reference to the dissociation of the nickel(II)-aspartate complex, if the normal complex, NiY^{2-}, also dissociates through the glycinate reaction intermediate, the dissociation-rate-constant ratio between the protonated and normal nickel(II)-GEDTA complexes should be approximately 1.4×10^2. Here, the electrostatic contribution to the stability of the reaction intermediate and the statistical factor are also taken into account. The observed ratio was 0.36. This is approximately 360 times smaller than that calculated on the basis of the simple glycinate reaction intermediate. The larger discrepancy between the observed and calculated ratios evidently implies that the stability of the reaction intermediate in the dissociation of NiY^{2-} is much greater than that of the simple glycinate reaction intermediate. Here, we can mention that the second protonation constant of the GEDTA anion ($pK_{a_3}=8.74$) is nearly identical to the protonation constants of $Ni(OH_2)_5(OH)^+$ ($\log K^{Ni-H}=9.0$).[9] This similarity in the two protonation constants strongly suggests the possibility of a hydrogen-bond formation between the water molecule coordinated to the nickel(II) ion and the free nitrogen donor atom of the GEDTA anion in the reaction intermediate. This internal hydrogen-bond formation within the reaction intermediate will effectively increase its stability and, thus, will give an enhanced rate constant. Therefore, it is reasonable to assume the following reaction intermediate (C) for the dissociation of NiY^{2-}. On the other hand, the tervalent GEDTA anion in the reaction intermediate of the dissociation of $NiHY^-$ has no such nitrogen donor atom available for the formation of a hydrogen bond with the coordinated water molecule. For this reason, the observed dissociation rate constant of $NiHY^-$ agrees well with

6) D. W. Margerum and B. A. Zabin, *J. Phys. Chem.*, **66**, 2214 (1962).

7) M. Eigen, *Ber. Bunsenges. Phys. Chem.*, **67**, 753 (1963).

8) R. M. Fuoss, *J. Amer. Chem. Soc.*, **80**, 5059 (1958).

9) D. B. Rorabacher, *Inorg. Chem.*, **5**, 1891 (1966).

that calculated on the basis of a simple glycinate reaction intermediate.

The rate constant, $(k_d)^{H}_{ZnHY}$, for the proton-assisted dissociation of the protonated zinc(II)-GEDTA complex was determined to be 13.0 sec^{-1} from the slope of the linear relation between i_l^{-1} and $(1+1/K^{H}\cdot[H^+])/(\alpha_H)_Y^{1/2}$. By using the $(k_d)^{H}_{ZnHY}$ value thus determined, the rate constant for the formation of $ZnHY^-$ from Zn^{2+} and H_2Y^{2-}, $(k_f)_{ZnHY}$, was calculated to be $2.5 M^{-1}sec^{-1}$ with the aid of the relation $(k_f)_{ZnHY}=(k_d)_{ZnHY}\cdot K_{ZnY}\cdot K^{H}_{ZnY}\cdot K_3\cdot K_4$. The estimated $(k_f)_{ZnHY}$ value is very small as compared with the reported water exchange rate of the zinc(II) aquo complex, $k_{Zn}^{-H_2O}$, $5\times10^7\ sec^{-1}$.[10] Genearlly, it is assumed that, in the formation of a metal complex in an aqueous solution, the metal ion and the ligand first diffuse together to form an outer-sphere complex, and that then a water molecule dissociates from the aquated metal ion and a donor group of the ligand coordinates with the metal ion. If the dissociation of the proton from the ligand is rapid enough, and if the water loss from the aquated metal ion is the rate-determining step, the formation-rate constant should be given by $K_{as}k_M^{-H_2O}$. Here, K_{as} means the association constant for the formation of an outer-sphere complex. Since the K_{as} value for the formation of the outer-sphere complex between Zn^{2+} and H_2Y^{2-} is considered to be larger than unity, if the formation of $ZnHY^-$ from Zn^{2+} and H_2Y^{2-} has a water-loss mechanism, the $(k_f)_{ZnHY}$ value should be larger than $5\times10^7 M^{-1}sec^{-1}$. Sudmeier and Reilley have reported in their NMR study of the protonation of the GEDTA anion in an aqueous solution[11] that two nitrogen atoms of the divalent GEDTA anion, H_2Y^{2-}, are completely protonated. Although the small $(k_f)_{ZnHY}$ value obtained may be explained by assuming an alternative mechanism, it is also possible to interpret it by assuming that the reactive species in the complex formation of the divalent GEDTA anion with the zinc(II) ion is not the nitrogen-protonated GEDTA due to the blocking of the nitrogen atoms by the proton, but is the carboxylate-protonated H_2Y^{2-} isomer with a small equilibrium concentration, in which at least one of the two nitrogen atoms is deprotonated. Similar reactive species has been proposed for the reaction of the diprotonated EDTA anion with the nickel(II) ion.[12] As was suggested by Rabenstein,[10] the relative amount of the carboxylate-protonated H_2Y^{2-} species is calculated from the relative basicity of the nitrogen atom and that of the carboxylate oxygen group of GEDTA. Since the K_4 and K_1 values approximate the basicity of the nitrogen and carboxylate oxygen groups of the GEDTA anion, the relative amount of carboxylate-protonated species is approximated as 1×10^{-7}. This estimated value will explain satisfactorily the discrepancy between the observed $(k_f)_{ZnHY}$ value and the value calculated on the basis of the simple water-loss mechanism.

Equation (8) indicates that, at a constant pH, the slope and the intercept of the linear relation between the $(i_d-i_l)/i_l$ value and the concentration of uncomplexed GEDTA $[Y]_f$, should be $K_2^{HY}\cdot K_3/K^{1/2}\cdot t^{1/2}\cdot k_f^{1/2}\cdot[H^+]$ $constant_4$ and $1/K^{1/2}\cdot t^{1/2}\cdot k_f^{1/2}\cdot K^{H}_{CdY}\cdot[H^+]$ $constant_4$ respectively. By using the $1/K^{1/2}\cdot t^{1/2}\cdot k_f^{1/2}$ $constant_4$ value determined from the slope of the linear relation between the $(i_d-i_l)/i_l$ value and $1/[H^+]$, the slope and intercept were calculated as 9.6 and 4.0 respectively. The observed slope and intercept were 12.6 and 3.0. The agreement between the observed value and the calculated one can be regarded as satisfactory. This agreement also gives strong support to the reaction mechanism (V) proposed by the present authors. The formation constant of $CdHY^-$, K_{CdHY}, was estimated to be $10^{10.23}$ from the relation $K_{CdHY}(=[CdHY^-]/[Cd^{2+}][HY^{3-}])=K_{CdY}K^{H}_{CdY}K_4$. In sharp contrast to the finding observed in the nickel(II)-GEDTA system, this value is much greater than the first successive formation constant of the cadmium(II)-iminodiacetate ($10^{5.35}$) or -*N*-2-hydroxyethyliminodiacetate complex ($10^{7.21}$). This fact suggests that two iminodiacetate groups of the GEDTA anion are involved in the complex formation of $CdHY^-$. Therefore, it is reasonable to believe that the electroactive form, $CdHY^{-*}$, proposed in the dissociation reaction of the cadmium(II)-GEDTA complex is that resulting from the partial rupture of the cadmium(II)-GEDTA bonds in the $CdHY^-$. To describe the detailed structure of $CdHY^{-*}$ precisely, further systematic investigations will be necessary.

10) D. L. Rabenstein, *J. Amer. Chem. Soc.*, **91**, 2501 (1969).
11) J. L. Sudmeier and C. N. Reilley, *Anal. Chem.*, **36**, 1698 (1964).
12) J. C. Cassatt and R. G. Wilkins, *J. Amer. Chem. Soc.*, **90**, 6045 (1968).