September, 1971] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44. 2387—2394 (1971) 2387

Polarographic Study of the Rates of the Dissociation Reactions of the Cobalt(II)-Acetylacetonate Complex and of the Nickel(II)-Acetylacetonate, -Glutamate, -Aspartate, and -Iminodiacetate Complexes

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(Received December 22, 1970)

The cobalt(II)-acetylacetonate complex and the nickel(II)-acetylacetonate, -glutamate, -aspartate and -iminodiacetate complexes were found to give kinetic waves due to the dissociation of these complexes at the electrode surface preceding the electron-transfer step. From the experimental examination of the nature of the kinetic current and a theoretical consideration, the mechanism and the rate constants of the dissociation of these complexes at the mercury-electrode surface were determined. The dissociation reactions were found to proceed through the following mechanism:

$$\begin{array}{llll} MX_2{}^{2-2m} & \rightleftharpoons MX^{2-m} & + X^{m-} & \text{rapid} \\ MX^{2-m} & \overset{k_d}{\rightleftharpoons} M^{2+} & + X^{m-} & \text{slow} \\ M^+ + 2e^- + Hg = M(Hg) & & & \end{array}$$

The rate constants, k_d's, for the dissociation reactions of cobalt(II)-acetylacetonate complex and of nickel(II)-acetylacetonate, -glutamate, -aspartate, and -iminodiacetate complexes at 25°C were estimated to be 9.3_0, 0.56, 0.69, $1.2_1 \times 10^{-2}$, and 2.5×10^{-4} sec^{-1} respectively. From a comparison of the rate constants, the dissociation of nickel(II)-aminopolycarboxylate complexes was concluded to proceed invariably through a reaction intermediate in which the leaving aminopolycarboxylate anions is bonded to the nickel(II) ion through one nitrogen and one oxygen atoms (Glycinate intermediate). In the formation reactions of cobalt(II)- and nickel(II)-acetylacetonate complexes in a 1:1 ratio, the dissociation of coordinated water from the metal(II) ion is rate-determining (water-loss mechanism).

Previously,[1,2] we reported that the cadmium(II)-EDTA complex in an acetate buffer solution and the zinc(II)-NTA complex in an ammonia buffer solution give kinetic waves due to the dissociation of these complexes preceding the electron-transfer step at the electrode surface; we then thoroughly investigated the nature of these kinetic waves from both theoretical and experimental viewpoints and determined the rates and the mechanism of the dissociation reactions of cadmium(II)-EDTA and zinc(II)-NTA complexes. Quite similar phenomena could also be observed in the polarography of the cobalt(II)-acetylacetonate (ACAC) complex and in that of the nickel(II)-ACAC, -glutamate (Glut), -aspartate (Asp) and -iminodiacetate (IDA) complexes. In this paper, we will study systematically the nature of the kinetic waves due to the dissociation of these complexes from both theoretical and experimental viewpoints, and will determine the mechanism and the rates. From a comparison of rate constants for the dissociation of the nickel(II)-aminopolycarboxylate complexes with those estimated on the basis of the proposed reaction intermediate, the structures of the reaction intermediates will be determined in detail. The mechanism of the formation reactions of 1:1 ratio cobalt(II)- and nickel(II)-ACAC complexes will also be discussed.

Experimental

Reagents. Standard nickel(II) and cobalt(II) nitrate solutions were prepared by dissolving known amounts of metallic nickel and cobalt (99.99% pure) in dilute nitric acid (1+1), and by then removing the excess nitric acid by distillation under reduced pressure. L-Glutamic acid (Glut), L-aspartic acid (Asp) and iminodiacetic acid (IDA) were recrystallized from their aqueous solutions by adding pure ethanol and hydrochloric acid. The acetylacetone used was purified twice by distillation under reduced pressure. The standard solutions of Glut, Asp, and IDA were prepared by dissolving known amounts of recrystallized Glut, Asp, and IDA in redistilled water. All the other chemicals used were of analytical-reagent grades 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[3] or a Yanagimoto pen-recording polarograph PA-102. The characteristic feature of the dropping mercury electrode (DME) used in this study was described previously.[4] A saturated calomel electrode (SCE) with a large area was used as the reference electrode and was connected to the cell solution through a Hume and Harris-type salt bridge.[5] The pH value of the solution was measured with a glass electrode pH meter (a Hitachi-Horiba F-5). The dissolved oxygen in the solution was removed by bubbling pure nitrogen gas through the solution. The ionic strength of the solution was adjusted to 0.20 by adding an appropriate amount of pure sodium perchlorate or potassium nitrate. To keep the solution's pH constant, a sodium acetate-acetic acid mixture in the nickel-

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[1] N. Tanaka, R. Tamamushi, and M. Kodama, *Z. Phys. Chem., N. F.*, **14**, 141 (1958).

[2] M. Kodama and M. Hashimoto, This Bulletin, **35**, 1802 (1962).

[3] I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 1, Interscience Publishers, New York (1952), p. 297.

[4] Y. Fujii, T. Ueda, and M. Kodama, This Bulletin, **43**, 409 (1970).

[5] D. N. Hume and W. E. Harris, *Ind. Engng. Chem., Analyt. Edit.*, **15**, 465 (1943).

(II)-IDA system and a potassium dihydrogen phosphate-disodium hydrogen phosphate mixture in the nickel(II)-ACAC and -Asp systems were used. In the cases of the nickel(II)-Glut and cobalt(II)-ACAC systems, no buffer mixture was used, for the sample solution always contained a large excess of uncomplexed Glut or ACAC, and, hence, was considered to have a sufficient buffer capacity over the entire pH range covered ($7.80 < \text{pH} < 9.00$ in the cobalt(II)-ACAC system, $8.50 < \text{pH} < 9.30$ in the nickel(II)-Glut system).

Results and Discussion

Polarographic Behavior of Nickel(II) and Cobalt(II) Ions in Acetylacetonate Solutions. As is shown in Fig. 1, both nickel(II) and cobalt(II) ions in acetylacetonate solutions exhibited the polarographic steps at potentials where the aquo complexes of these metal(II) ions will give polarographic waves due to their reduction even under the experimental conditions where, from the thermodynamic point of view,[6] all the metal(II) ions may be considered to exist as acetylacetonate complex. The second wave of the nickel(II)-ACAC complex may correspond to its direct reduction. Its limiting current was proportional to the square root of the effective pressure of mercury. At lower solution pH's, the polarographic step corresponding to the direct reduction of cobalt(II)-ACAC complex could also be observed, but this step merges in the base current at higher pH's. The limiting current of the reduction wave of the cobalt(II)-ACAC complex and that of the first wave of the nickel(II)-ACAC complex were almost independent of the effective pressure of the mercury column within the limits of experimental error. Some typical data are given in Table 1. This fact clearly implies that both limiting currents are kinetic-controlled in nature. The polarogram of the cobalt(II)-ACAC complex and the first wave of the nickel(II)-ACAC complex gave linear log-plots ($\log(i/(i_1-i))$ *vs.* E_{dme}) with slopes of about 54 and 57 mV respectively, thus indicating an irreversible two-electron reduction. The results are not shown here. The reduction wave-height of the cobalt(II) ion in the ACAC solution was found to decrease with an increase in the solution's pH or with the concentration of uncomplexed ACAC. In the nickel(II)-ACAC system, although the total wave-height was almost constant under the present experimental conditions, the height of the first wave also decreased with an increase in the solution's pH or in the concentration of uncomplexed ACAC. Considering that the concentration of the deprotonated ACAC anion increases with an increase in the solutions' pH all the facts given above indicate that the first wave of the nickel(II)-ACAC complex and the polarographic step of the cobalt(II)-ACAC complex can be ascribed to the reduction of the uncomplexed metal(II) ion or a lower ACAC complex liberated by the dissociation of nickel(II) and cobalt(II) complexes of ACAC at the mercury electrode surface proceding the electron-transfer step.

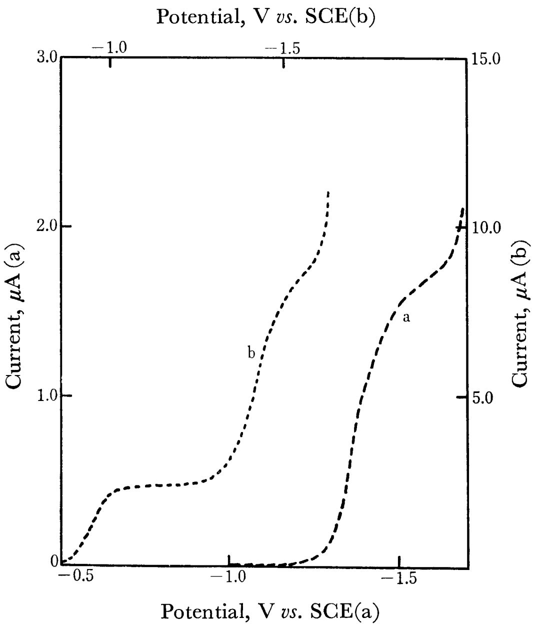

Fig. 1. Polarograms of metal(II)-ACAC complexes.
a) Co(II)-ACAC complex
The Co(II) concentration=1.0 mM
The concentration of uncomplexed ACAC=50.0 mM
pH=8.24, $\mu=0.20$
b) Ni(II)-ACAC complex
The Ni(II) concentration=2.0 mM,
Total phosphate concentration=0.10 M
The concentration of uncomplexed ACAC=25 mM
pH=7.29, $\mu=0.20$

Table 1. The relation between the limiting current and the effective pressure of mercury
$\mu=0.20$, 25°C

i) Co(II)-ACAC system
the concentration of cobalt(II) ion =2.0 mM,
pH=9.00
the concentration of uncomplexed ACAC =50.0 mM

H_c, cm	i_l, μA
55.0	0.480
65.0	0.480
75.0	0.485

ii) Ni(II)-ACAC system
the concentration of nickel(II) ion=2.0 mM,
pH=7.40
the concentration of uncomplexed ACAC=50.0 mM
the total concentration phosphate=0.10 M

H_c, cm	First wave-height i_l, μA	Second wave-height i_d, μA	$i_d/H_c^{1/2}$
55.0	1.64_0	5.71_0	0.771
65.0	1.65_1	6.22_1	0.773
75.0	1.67_3	6.69_3	0.775

Since all the systems studied in this paper contained a large excess of uncomplexed ACAC over the metal(II) ion, the dissociation of metal(II)-ACAC complexes can be treated as a psuedo-first-order reaction. Therefore, as both metal(II) ions form 1:1- and 1:2-ratio ACAC complexes under the present experimental conditions, the reaction mechanism can be written in a simpler form as (A) or (B):

$$\text{(A)}\quad\begin{cases} \mathrm{A} \underset{}{\overset{K_{1a}}{\rightleftharpoons}} \mathrm{B} & \text{rapid} \quad (1)\\ \mathrm{B} \underset{\overleftarrow{k}_{2a}}{\overset{\overrightarrow{k}_{2a}}{\rightleftharpoons}} \mathrm{O} & \text{slow} \quad (2)\\ \mathrm{O} + 2\mathrm{e}^- \underset{\overleftarrow{k}}{\overset{\overrightarrow{k}}{\rightleftharpoons}} \mathrm{R} & \quad (3) \end{cases}$$

$$\text{(B)}\quad\begin{cases} \mathrm{A} \underset{\overleftarrow{k}_{1b}}{\overset{\overrightarrow{k}_{1b}}{\rightleftharpoons}} \mathrm{O} & \text{slow} \quad (4)\\ \mathrm{O} + 2\mathrm{e}^- \underset{\overleftarrow{k}}{\overset{\overrightarrow{k}}{\rightleftharpoons}} \mathrm{R} & \quad (3') \end{cases}$$

For the mechanims (A), where (3) is rapid in a polarographic sense, we previously[1] derived the general relations of the limiting current and the current-voltage curve by taking into consideration the diffusion processes of A and B from the bulk of the solution to the electrode surface and that of R from the mercury surface to the inside of mercury, and by assuming the conditions of the stationary state with respect to the concentrations of A, B, O, and R at the electrode surface. Equation (25) in Ref. 1 is applicable to the present systems, in which the (3) process is irreversible, without making any modification. That is, we can use the following relation to examine the nature of the limiting current:

$$\frac{1}{i_l} = \frac{1}{2AF\cdot K_{2a}\cdot D^{1/2}\cdot \overrightarrow{k}_{2a}^{1/2}\cdot C_{\mathrm{B}}{}^0} + \frac{1}{2AF\cdot K^{\mathrm{D}}\cdot C^0} \qquad (5a)$$

where C^0 is equal to $C^0{}_{\mathrm{A}} + C^0{}_{\mathrm{B}}$ and where all the symbols used have the same meanings as in the previous paper.[1] As is clear from the log-plot slopes, the electron-transfer process (3) is assumed to be irreversible, *i.e.*, $\overrightarrow{k} \gg \overleftarrow{k}$, in the present systems. Therefore, Eq. (27) in Ref. 1 should be replaced by the (6_a) relation:

$$E = \text{constant} - \frac{0.0591}{2\alpha}\log\frac{i}{i_l - i} - \frac{0.0591}{4\alpha}\log \overleftarrow{k}_{2a} \qquad (6a)$$

For the (B) mechanism, where (3′) is irreversible in nature, we had already derived the theoretical relations for the limiting current and for the current voltage curve.[2] The relations, (16) and (18) or (20), in Ref. 2 can be used without any modification. Thus, for the (B) reaction mechanism we can derive the following two relations:

$$\frac{1}{i_l} = \frac{1}{2AF\cdot K_{1b}^{1/2}\cdot D^{1/2}\cdot \overrightarrow{k}_{1b}^{1/2}\cdot C_{\mathrm{A}}{}^0} + \frac{1}{2AF\cdot K^{\mathrm{D}}\cdot C_{\mathrm{A}}{}^0} \qquad (5b)$$

$$E = \text{constant} - \frac{0.0591}{2\alpha}\log\frac{i}{i_l - i} - \frac{0.0591}{4\alpha}\log \overleftarrow{k}_{1b} \qquad (6b)$$

Provided that the other experimental conditions are kept constant, both the polarographic wave of the cobalt(II)-ACAC complex and the first step of the nickel(II)-ACAC system gave excellent linear relations between $1/i_l$ and the $(1+K'_2[\mathrm{X}]_f)[\mathrm{X}]_f{}^{1/2}$ value or the $(1+K_2'\cdot[\mathrm{X}]_f)/(\alpha_H)_X{}^{1/2}$ value. Typical results are shown in Figs. 2, 3, and 4. Here, $(\alpha_H)_X$ denotes the apparent (α_H) value of acetylacetone, defined as $1+5\cdot[\mathrm{H}^+]/K_a$; K_a, the dissociation constant of the tautomeric enol acetylacetone; $[\mathrm{X}]_f$, the concentration of uncomplexed acetylacetone, and K_2', the conditional second successive formation constant of the acetylacetonate complex. The aqueous equilibrium keto : enol ratio was assumed to be approximately four to one.[7] The keto: enol ratio 4:1 suggests that if the ketonization rate of the

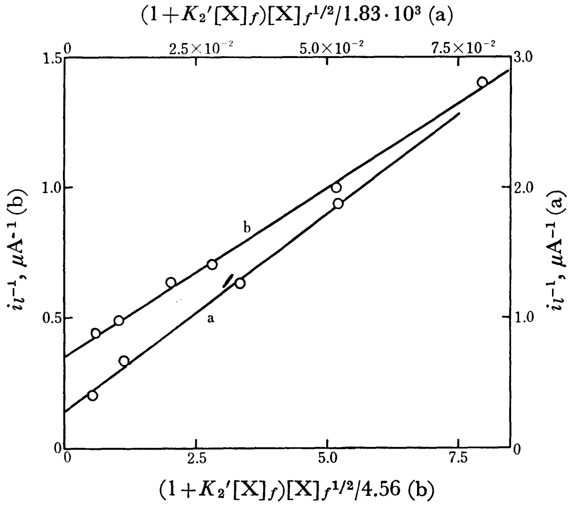

Fig. 2. The plot of $1/i_l$ against $(1+K_2'\cdot[\mathrm{X}]_f)\cdot[\mathrm{X}]_f{}^{1/2}$.
a) Co(II)-ACAC complex
The Co(II) concentration=1.0 mM
pH=8.24, μ=0.20, 25°C
The concentration of uncomplexed ACAC ranged from 30 to 150 mM
b) Ni(II)-ACAC complex
The Ni(II) concentration=2.0 mM
pH=7.40, μ=0.20, 25°C
The concentration of uncomplexed ACAC ranged from 15 to 100 mM
Total concentration of phosphate=0.10 M

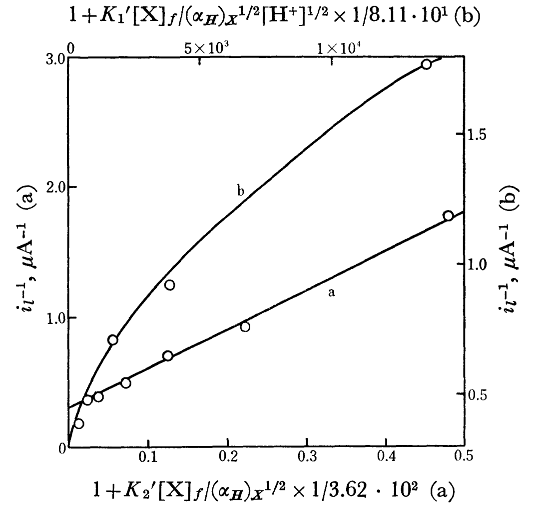

Fig. 3. The plot of $1/i_l$ against $(1+K_2'\cdot[\mathrm{X}]_f)/(\alpha_H)_X{}^1/{}^2$ or $(1+K_2'[\mathrm{X}]_f)/(\alpha_H)_X{}^1/{}^2[\mathrm{H}^+]^{1/2}$.
The Co(II) concentration=2.0 mM
The concentration uncomplexed ACAC=50.0 mM
μ=0.20, 25°C
a) $1/i_l$ *vs.* $(1+K_2'[\mathrm{X}]_f)/(\alpha_H)_X{}^{1/2}$ plot
b) $1/i_l$ *vs.* $(1+K_2'[\mathrm{X}]_f)/(\alpha_H)_X{}^{1/2}\cdot[\mathrm{H}^+]^{+1/2}$ plot

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[6] L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," 2nd Ed., The Chemical Society, London (1964). pp. 444—445.

[7] F. C. Nachod, *Z. Physik. Chem.*, **A182**, 193 (1938).

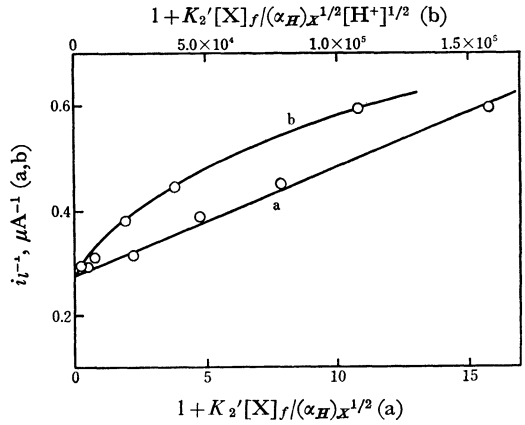

Fig. 4. The plot of $1/i_l$ against $(1+K_2'[X]_f)/(\alpha_H)_X^{1/2}$ or $(1+K_2'[X]_f)/(\alpha_H)_X^{1/2}\cdot[X]^{+1/2}$.
The Ni(II) concentration=2.0 mM
The concentration of uncomplexed ACAC=25.0 mM
Total concentration of phosphate=0.10 M
μ=0.20, 25°C
a) $1/i_l$ *vs.* $(1+K_2'[X]_f)/(\alpha_H)_X^{1/2}\cdot$plot
b) $1/i_l$ *vs.* $(1+K_2'[X]_f)/(\alpha_H)_X^{1/2}\cdot[H^+]^{1/2}$ plot

enol ACAC, which is the initial product of the protonization of the ACAC anion, is slow, the ACAC anion concentration at the electrode surface will increase with an increase in the current, especially at lower ACAC concentrations. The rapid ketonization was confirmed by following the change in the absorbance at 270 mμ (the absorption maximum of the enol form). When perchloric acid was added to an ACAC solution of pH 10.5, the absorbance decreased so rapidly that we could not determine the ketonization rate exactly by using a conventional method. Since the $[X]_f/(\alpha_H)_X$ and $[M]_t/(1+K_2'\cdot[X]_f)$ values correspond to the concentration of uncomplexed ACAC anion and the bulk concentration of a 1:1 ratio metal(II)-ACAC complex, the above findings evidently show that the reaction mechanism for the first wave of the nickel(II)-ACAC complex can be expressed as:

$$\mathrm{I_a}\begin{cases}\mathrm{MX_2}^{2-2m} \overset{K_1}{\rightleftharpoons} \mathrm{MX}^{2-m} + \mathrm{X}^{m-} & \text{rapid} \qquad (7)\\ \mathrm{MX}^{2-m} \underset{k_f}{\overset{k_d}{\rightleftharpoons}} \mathrm{M}^{2+} + \mathrm{X}^{m-} & \text{slow} \qquad (8a)\\ \mathrm{M}^{2+} + 2e^- + \mathrm{Hg} = \mathrm{M(Hg)} & \qquad (9)\end{cases}$$

where X^{m-} means the ACAC anion. For the above reaction mechanism, Eqs. (5a) and (6a) can be rewritten as:

$$\frac{1}{i_l}=\frac{K_1^{1/2}\cdot(1+K_2'\cdot[X]_f)\cdot[X]_f^{1/2}}{2AF\cdot D^{1/2}\cdot k_d^{1/2}\cdot[M]_t\cdot(\alpha_H)_X^{1/2}}+\frac{1}{2AF\cdot K^{D}\cdot[M]_t} \tag{10a}$$

$$E_{1/2}=\text{constant}-\frac{0.0591}{4\alpha}\log\frac{[X]_f}{(\alpha_H)_X} \tag{10b}$$

As was discussed in the previous paper,[1)] theoretically the $2AF\cdot D^{1/2}$ and $2AF\cdot K_d$ values in Eq. (10_a) are identical to $2.51\times10^5\cdot m^{2/3}\cdot t^{2/3}$ and $2\times6.07\times10^4\cdot m^{2/3}\cdot t^{1/6}\cdot D^{1/2}$ respectively. $[M]_t$ in Eq. (10a) signifies the total concentration of the metal(II)-ACAC complex and K_1, the formation constant of a 1:1 ratio metal(II)-ACAC

TABLE 2. THE EFFECTS OF pH AND ACAC CONCENTRATION ON THE HALF-WAVE POTENTIAL
μ=0.20, 25°C

i) pH effect

System	pH	$E_{1/2}$ V *vs.* SCE	$\Delta E_{1/2}$, mV calcd	$\Delta E_{1/2}$, mV obsd	
Co(II)	7.81	−1.327	0	0	ACAC concentration=50.0 mM Cobalt(II) concentration=1.0 mM
	8.02	−1.332	−4.9	−5	
	8.24	−1.336	−9.3	−9	
	8.49	−1.338	−14.3	−11	
	8.90	−1.352	−20.2	−25	
Ni(II)	6.66	−0.954	0	0	ACAC concentration=25.0 mM Nickel(II) concentration=2.0 mM Total concentration of phosphate=0.10 M
	7.09	−0.964	−12.0	−10	
	7.29	−0.967	−17.7	−16	
	7.40	−0.974	−20.6	−20	
	7.68	−0.980	−28.0	−26	

ii) ACAC concentration effect

System	Concentration of uncomplexed ACAC mM	$E_{1/2}$ V *vs.* SCE	$\Delta E_{1/2}$, mV calcd	$\Delta E_{1/2}$, mV obsd	
Co(II)	30.0	−1.330	0	0	Cobalt concentration=1.0 mM, pH=8.24
	50.0	−1.336	−6.0	−6	
	100.0	−1.346	−12.0	−16	
Ni(II)	15.0	−0.966	0	0	Nickel(II) concentration=2.0 mM, pH=7.40 Total concentration of phosphate=0.10 M
	25.0	−0.974	−6.3	−7	
	40.0	−0.979	−11.9	−12	
	50.0	−0.982	−14.7	−16	
	75.0	−0.987	−19.6	−20	
	100.0	−0.991	−23.1	−24	

complex. Equation (10a) suggests that $\Delta E_{1/2}/\Delta \log [\mathrm{X}]_f$ and $\Delta E_{1/2}/\Delta \log (\alpha_H)_X$ should be $-0.0591/4\alpha$ and $0.0591/4\alpha$ V respectively. These relations were also examined by using some typical data. The results are shown in Table 2. The agreement between the observed value and that calculated with the aid of Eq. (10b) can be regarded as satisfactory. On the other hand, if the reaction mechanism is written as:

$$\mathrm{I_b}\begin{cases}\mathrm{MX_2}^{2-2m} + \mathrm{H}^+ \rightleftharpoons \mathrm{MX}^{2-m} + \mathrm{HX}^{1-m} & \text{rapid}\\ \mathrm{MX}^{2-m} + \mathrm{H}^+ \rightleftharpoons \mathrm{M}^{2+} + \mathrm{HX}^{1-m} & \text{slow}\\ \mathrm{M}^{2+} + 2e^- + \mathrm{Hg} = \mathrm{M(Hg)} & \end{cases}$$

the plot of $1/i_l$ agaist the $(1+K_2'\cdot[\mathrm{X}]_f)/(\alpha_H)_X{}^{1/2}\cdot[\mathrm{H}^+]^{1/2}$ value should yield a straight line at a constant $[\mathrm{X}]_f$. The curves given in Figs. 3 and 4 completely eliminated the above reaction mechanism. By using the D value of 7.4×10^{-6}, the k_d values for the cobalt(II) and nickel(II)-ACAC complexes were estimated from the slopes of the linear relations shown in Figs. 2, 3, and 4 and listed in Table 3. In both systems, the k_d value determined from the slopes of the linear relation between $1/i_l$ and $(1+K_2'\cdot[\mathrm{X}]_f)/(\alpha_H)_X{}^{1/2}$ agreed well with that determined from the slope of the linear relation between $1/i_l$ and $(1+K_2'\cdot[\mathrm{X}]_f)\,[\mathrm{X}]_f{}^{1/2}$. A phosphate buffer used in the nickel(II)-ACAC system to keep the solution pH constant had no effect on the rate of dissociation of the nickel(II)-ACAC complex. Although the K_3 value for the nickel(II)-ACAC complex has been reported by Izatt *et al.*,[8] the possibility of the formation of a 1:3 ratio nickel(II)-ACAC complex could be eliminated by the ion-exchanger test. Under the present experimental conditions, no nickel(II) ion was adsorbed at either the cation or anion exchanger.

TABLE 3. RATE CONSTANTS

System	k_d, sec^{-1}		k_f, M^{-1} sec^{-1}
	25°C	30°C	
Co(II)-ACAC	9.3		6.4×10^5
Ni(II)-ACAC	0.56		1.7×10^5
Ni(II)-Gult	0.69	1.2_1	
Ni(II)-Asp	$1.2_1\times10^{-2}$		
Ni(II)-IDA	2.5×10^{-4}	3.6×10^{-4}	
	2.8×10^{-4} [10]		

Polarographic Behavior of Nickel(II) Ions in Glutamate, Aspartate, and Iminodiacetate Solutions. As in the cases of the metal(II)-ACAC complexes studied in this paper, the nickel(II) ions in glutamate, aspartate, and iminodiacetate solutions also gave kinetic waves as a result of their dissociation at the electrode surface. Some typical polarograms of the nickel(II)-Asp and -IDA complexes are shown in Fig. 5. Although the polarogram is not shown here, the nickel(II)-Glut complex also gave the two polarographic steps. The limiting currents of the first waves of the nickel(II)-Glut and -Asp complexes and the reduction step of the nickel(II)-IDA complex were almost independent of the effective pressure on the DME, indicating their kinetic nature (the results are not shown). The second step observed in the nickel(II)-Glut and-Asp systems may be ascribed to the direct reduction of the nickel(II)-Glut and -Asp complexes. In both systems, the total wave-height was almost constant under the present experimental conditions and was exactly proportional to the square root of the effective pressure on the DME. In the case of the nickel(II)-IDA complex, however, the polarographic step corresponding to the direct reduction of the nickel(II)-IDA complex could not be observed (Fig. 5). This

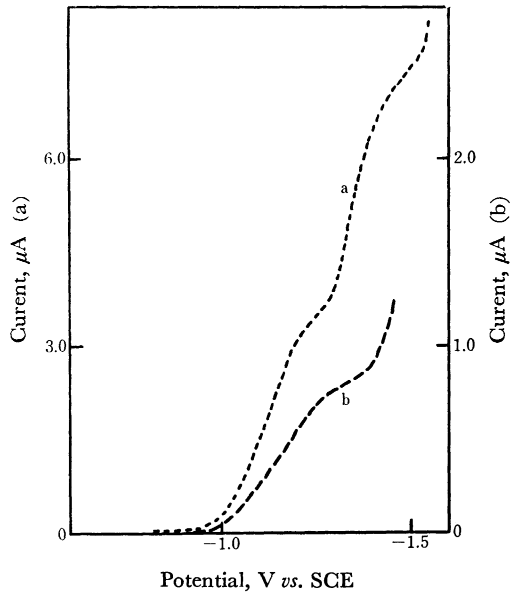

Fig. 5. Polarograms of nickel(II)-Asp and -IDA complexes.
a) Ni(II)-Asp complex
The Ni(II) concentration=2.0 mM
The concentration of uncomplexed Asp=20.0 mM
Total concentration of phosphate=0.10 M
pH=6.49, 25°C
b) Ni(II)-IDA complex
The Ni(II) concentration=2.0 mM
The concentration of uncomplexed IDA=40.0 mM
The acetate ion concentration=0.10 M
pH=5.50, 30°C

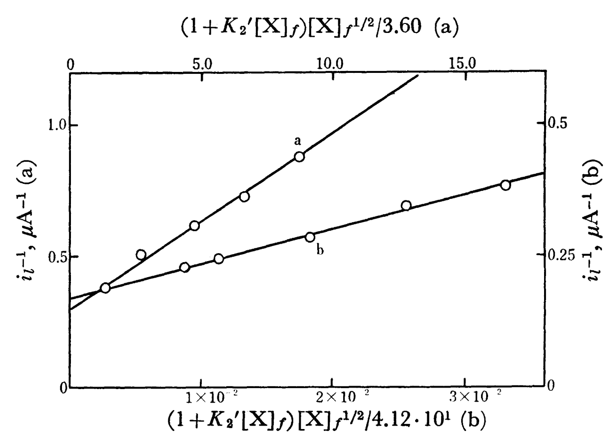

Fig. 6. The plot of $1/i_l$ against $(1+K_2'[\mathrm{X}]_f)[\mathrm{X}]_f{}^{1/2}$.
The Ni(II) concentration=2.0 mM
a) Ni(II)-Glut system
pH=8.50, 30°C
b) Ni(II)-Asp system
pH=6.25, 25°C
Total phosphate concentration=0.10 M

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[8] R. M. Izatt, W. C. Fernelius, C. G. Haas, Jr., and B. P. Block, *J. Phys. Chem.*, **59**, 170 (1955).

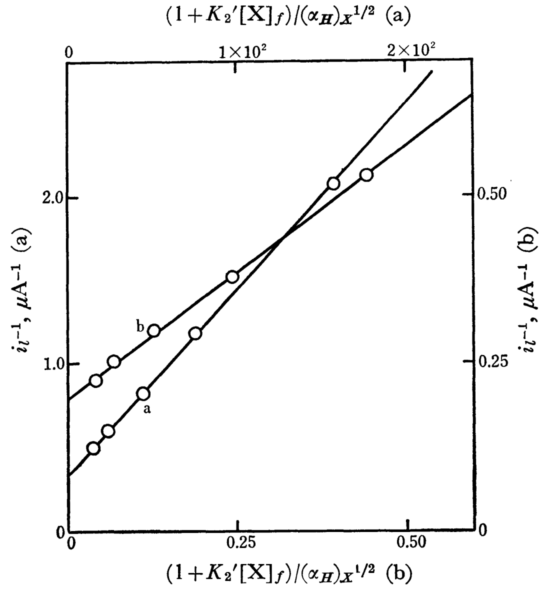

Fig. 7. The plot of $1/i_l$ against $(1+K_2'[X]_f)/(\alpha_H)_X{}^{1/2}$.
The Ni(II) concentration=2.0 mM
a) Ni(II)-Glut system
The concentration of uncomplexed Glut=30.0 mM, 30°C
b) Ni(II)-Asp system
The concentration of uncomplexed Asp=20.0 mM, 25°C
Total concentration of phosphate=0.10 M

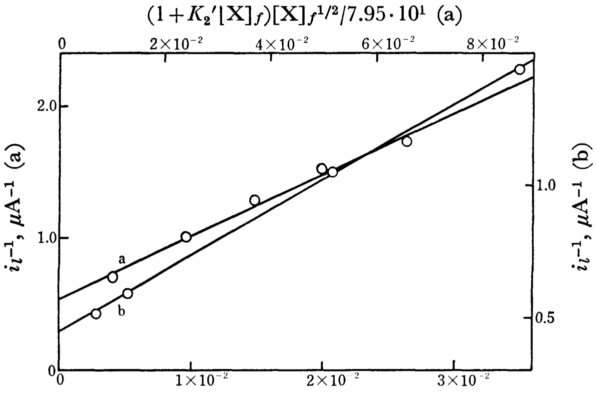

Fig. 8. The plot of $1/i_l$ against $(1+K_2'\cdot[X]_f)[X]_f{}^{1/2}$ or $(1+K_2'\cdot[X]_f)/(\alpha_H)_X{}^{1/2}$
The Ni(II) concentration=2.0 mM, 30°C
The concentration of acetate ion=0.10 M
a) $1/i_l$ vs. $(1+K_2'[X]_f)[X]_f{}^{1/2}$ plot
pH=5.50
b) $1/i_l$ vs. $(1+K_2'[X]_f)/(\alpha_H)_X{}^{1/2}$ plot
The concentration of uncomplexed IDA=20.0 mM

can be ascribed to the inertness of the nickel(II)-iminodiacetate complex. The first waves of the nickel(II)-Glut and -Asp complexes and the reduction wave of the nickel(II)-IDA complex gave linear log-plots with slopes falling in the range from 65 to 75 mV. As in the cases of the cobalt(II)- and nickel(II)-ACAC complexes, all three waves invariably gave linear relations between $1/i_l$ and $(1+K_2'\cdot[X]_f)\cdot[X]_f{}^{1/2}$ or $(1+K_2'\cdot[X]_f)/(\alpha_H)_X{}^{1/2}$, with intercepts corresponding to the reciprocal of the total wave-height. Here, K'_2 means the conditional second successive formation constant; $[X]_f$, the concentration of uncomplexed Glut, Asp, or IDA, and $(\alpha_H)_X$, the (α_H) value of Glut, Asp, or IDA. The results are shown in Figs. 6, 7, and 8. The linear relations found in the nickel(II)-Glut and -Asp systems evidently imply that the electrode reaction mechanism for the first waves of these complexes is also given by (I_a), and that the concentration dependence of the half-wave potential is also given by Eq. (10b). Some typical results obtained in the nickel(II)-Asp system are given in Table 4. The shifts of the half-wave potential, as calculated with the acid of Eq. (10b) agreed well with those determined experimentally. As we observed in the acetylacetonate system, curves obtained by plotting the $1/i_l$ against the $(1+K_2'\cdot[X]_f)/(\alpha_H)^{1/2}\cdot[H^+]_X{}^{1/2}$ also eliminate the proton-assisted reaction mechanism. From the slopes of the linear relations shown in Fig. 6 and 7, the k_d values for the dissociation of the 1 : 1 ratio nickel(II)-Glut and -Asp complexes were determined to be 1.2_0 (30°C) and $1.2_1\times10^{-2}$ sec⁻¹ (25°C) respectively.

TABLE 4. THE EFFECTS OF pH AND THE CONCENTRATION OF UNCOMPLEXED ASPARTATE ON THE HALF-WAVE POTENTIAL

$\mu=0.20$, 25°C, phosphate concentration=0.10 M

i) pH effect

The concentration of uncomplexed Asp=30.0 mM

pH	$E_{1/2}$ V vs. SCE	$\Delta E_{1/2}$, mV calcd	$\Delta E_{1/2}$, mV obsd
6.05	−1.083	0	0
6.28	−1.093	−10.5	−10
6.46	−1.106	−18.9	−23
6.68	−1.115	−29.0	−32
6.87	−1.120	−37.7	−37

ii) Asp concentration effect

pH=6.28

Concentration of uncomplexed Asp (mM)	$E_{1/2}$ V vs. SCE	$\Delta E_{1/2}$, mV calcd	$\Delta E_{1/2}$, mV obsd
15.0	−1.089	0	0
20.0	−1.096	−5.7	−7
30.0	−1.103	−15.7	−14
40.0	−1.113	−20.0	−24
50.0	−1.118	−24.1	−29

As in the case of the nickel(II)-ACAC system, a phosphate buffer mixture had no effect on the wave-height of the nickel(II)-Asp complex. An acetate buffer, however, had a remarkable effect on the wave-height of the nickel(II)-IDA complex. The wave-height was increased remarkably by increasing the concentration of an acetate ion. This indicates that the acetate anion effectively assists the dissociation of the nickel(II)-IDA complex at the electrode surface. Judging from the magnitude of the formation constant of the nickel(II)-acetate complex,[9] an acetate anion can not participate in the formation of a mixed ligand complex of the nickel(II) ion involving an IDA anion under the present experimental conditions. Therefore, the ace-

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[9] N. Tanaka and K. Kato, This Bulletin, **32**, 516 (1959).

tate ion will help only the dissociation of a 1:1 nickel(II)-IDA complex at the electrode surface. If the dissociation of a 1:1 nickel(II)-IDA complex proceeds through both the (8b) and (8a) reaction pathways, one can derive Eq. (11) for the limiting current:

$$\mathrm{NiX^0} + \mathrm{Ac^-} \underset{}{\overset{(k_d)_{\mathrm{Ac}}}{\rightleftharpoons}} \mathrm{Ni(Ac)^+} + \mathrm{X^{2-}} \tag{8b}$$

$$\frac{1}{i_l} = \frac{K_1{}^{1/2}\cdot(1+K_2{}'\cdot[\mathrm{X}]_f)\cdot[\mathrm{X}]_f{}^{1/2}}{2AF\cdot D^{1/2}\cdot(k_d{}^{1/2}+(k_d)_{\mathrm{Ac}}^{1/2}\cdot K_{\mathrm{NiAc}}^{1/2}\cdot[\mathrm{Ac^-}])(\alpha_H)_X{}^{1/2}\cdot[\mathrm{Ni}]_t} + \frac{1}{i_d} \tag{11}$$

where K_{NiAc} denotes the first formation constant of the nickel(II)-acetate complex; $[\mathrm{Ac^-}]$, the concentration of the uncomplexed acetate ion, and $[\mathrm{Ni}]_t$, the total concentration of the nickel(II)-IDA complex, and where i_d corresponds to the $2AF\cdot \mathrm{K^D}\cdot[\mathrm{M}]_t$ value in Eq. (10a). From Eq. (11), one can easily derive the following relation.

$$\frac{i_d i_l}{i_d-i}\times\frac{(1+K_2{}'\cdot[\mathrm{X}]_f)\cdot[\mathrm{X}]_f{}^{1/2}}{(\alpha_H)_X{}^{1/2}} = 2AF\cdot D^{1/2}\cdot[\mathrm{Ni}]_t(k_d{}^{1/2}+(k_d)_{\mathrm{Ac}}^{1/2}\cdot K_{\mathrm{NiAc}}^{1/2}\cdot[\mathrm{Ac^-}]) \tag{12}$$

This relation indicates that the plot of the left-hand side of Eq. (12) against $[\mathrm{Ac^-}]$ will give a linear relation, the slope and intercept of which correspond to $2AF\cdot D^{1/2}\cdot[\mathrm{Ni}]_t\cdot(k_d)_{\mathrm{Ac}}{}^{1/2}\cdot K_{\mathrm{NiAc}}{}^{1/2}$ and $2AF\cdot D^{1/2}\cdot[\mathrm{Ni}]_t\cdot k_d{}^{1/2}$ respectively, if the dissociation of a 1:1 ratio nickel(II)-IDA complex at the electrode surface proceeds through the two reaction pathways, (8a) and (8b). The above relation was examined by using some typical experimental data. As is shown in Fig. 9, a fairly good linear relation could be obtained. From the slope and intercept of the linear relation in Fig. 9, the $(k_d)_{\mathrm{Ac}}$ and k_d values at 30°C were determined to be 3.8×10^{-4} and $3._9\times10^{-4}$ respectively. In a similar way, the k_d value of the nickel(II)-Asp and Glut complexes at 15°C were also determined (Table 3). The k_d value for the nickel(II)-IDA complex determined in this study agrees well with that reported by Bydalek and Constant.[10] This agreement also supports the present author's explanation.

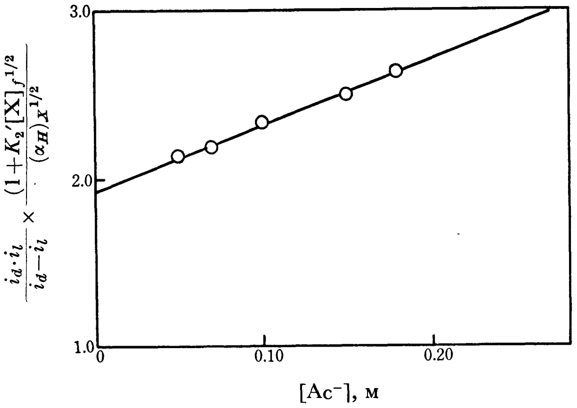

Fig. 9. The plot of $i_d\times i_l$ $(1+K_2{}'[\mathrm{X}]_f)[\mathrm{X}]_f{}^{1/2}/(i_d-i_l)\cdot(\alpha_H)_X{}^{1/2}$ against the acetate ion concentration
The Ni(II) concentration=2.0 mM, 30°C, pH=5.40
The concentration of uncomplexed IDA=20.0 mM

From the $K_1=k_f/k_d$ relation, the formation rate constant, k_f, of the 1:1 ratio cobalt(II)-ACAC complex and that of the 1:1 ratio nickel(II)-ACAC complex were determined to be 6.4×10^5 and 1.7×10^5 M$^{-1}\cdot$sec^{-1} respectively. These values are nearly identical with the characteristic water exchange rate constants of these metal(II) ions.[11] This fact indicates that, in the formation reaction of both cobalt(II)- and nickel(II)-ACAC complexes with a 1:1 ratio, the dissociation of water from the metal(II) aquo ion is the rate-determining step. The finding that, in the formation of the 1:1 cobalt(II)-ACAC complex, the dissociation of water from the cobalt(II) ion is the rate-determining step is contrary to the prediction of Pearson and Anderson[12] that the steric rearrangement of the ligand will provide the main activation energy barrier (sterically controlled substitution, SCS mechanism) in the formation of a six-membered chelate ring of the cobalt(II) complex. The k_f value for the 1:1 nickel(II)-ACAC complex is slightly larger than the characteristic water-exchange rate constant of the nickel(II) ion. However, this value can also be taken as evidence for the usual water exchange mechanism. Although Pearson and Moor[13] mentioned that the complexation reaction of neutral enol ACAC with the nickel(II) ion is very slow, and explained this slow reaction in terms of the SCS mechanism, there is, as yet, no satisfactory explanation for the distinct difference in the reaction rate between enol ACAC and its anion.

Generally, it is very hard to believe that, in the dissociation of nickel(II)-aminopolycarboxylate complexes, all three bond breakages are involved in the rate-determining step. Furthermore, as the nickel(II)-oxygen bond (carboxylate) breakage is much faster than

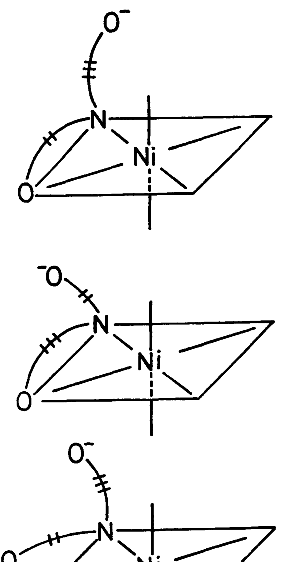

Fig. 10. Reaction intermediates for the dissociation of nickel(II)-aspartate complex.

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[10] T. J. Bydalek and A. H. Constant, *Inorg. Chem.*, **4**, 833 (1965).

[11] M. Eigen, *Ber. Bunsenges. Physik. Chem.*, **67**, 753 (1963).

[12] R. G. Pearson and O. P. Anderson, *Inorg. Chem.*, **9**, 39 (1970).

[13] R. G. Pearson and J. W. More, *ibid.*, **5**, 1523 (1966).

the nickel(II)-nitrogen bond (amine) breakage,[14] at least the nickel(II)-nitrogen bond breakage should be involved in the rate-determining step. Therefore, in the case of the nickel(II)-Asp complex, the dissociation can be expected to proceed through one of the following three reaction intermediates (Fig. 10). Here, one can eliminate the I_b reaction intermediate because the six-membered chelate ring is much more labile than the five-membered chelate ring in the substitution reaction of the nickel(II) ion complex. As was discussed by Rorabacher and Margerum,[15] the observed rate constant for the dissociation of the nickel(II)-aspartate complex can be related to the rate constant of the rate-determining step, k_{rds}, and the stability constant of the reaction intermediate prior to the rate-determining step, K_{int}, in the following manner:

$$k_d = \frac{k_{rds}\cdot K_{int}}{K_{MX}} \qquad (13)$$

Here, K_{MX} is the formation constant of the nickel(II)-Asp complex with a 1:1 ratio. With the aid of the above relation, we calculated the k_d values for two reaction intermediates, I_a and I_c. The k_d values calculated for these two reaction intermediates were $1.1_4\times10^{-2}$ and 4.5×10^{-3} sec^{-1} respectively. The k_d value estimated on the basis of I_a agrees better with the observed rate constant. In the calculation, the *N*-ethylglycinate and ammine complexes were used as models, and the electrostatic contribution was taken into consideration. The k_{rds} values[16] reported by Hammes and Steinfeld and by Margerum *et al.* were used.

Equation (13) also suggests that, if the dissociation of the nickel(II)-Glut and -IDA complexes proceeds through the glycinate reaction intermediate, as in the case of nickel(II)-Asp complex, the dissociation rate constant should be inversely proportional to the stability constant. The ratio of k_d was compared with that of the reciprocal of the stability constant, K_{MX}^{-1}. The results are shown in Table 5. In the case of the nickel(II)-IDA system, the statistical factor was also taken into account. The agreement between the k_d ratio and the K_{MX}^{-1} ratio can be regraded as satisfactory. This agreement evidently implies that all three nickel(II)-aminopolycarboxylate complexes studied in this paper dissociate invariably through the reaction intermediate in which the leaving aminopolycarboxylate anion is bonded to the nickel(II) ion through the five-membered glycinate chelate ring, and that, in the dissociation of the nickel(II) ion complex, the six- and seven-membered chelate rings are much more labile than the corresponding five-membered chelate ring.

Table 5. Ratios of k_d and K_{MX}^{-1}

System	k_d ratio	K_{MX}^{-1} ratio	log K_{MX} (μ=0.20)
Ni(II)-Gult	2.7×10^3	5.6×10^3	5.30
Ni(II)-Asp	4.8×10^1	1.4×10^1	6.91
Ni(II)-IDA	1.0	1.0	8.05

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[14] T. J. Bydalek and D. W. Margerum, *Inorg. Chem.*, **2**, 678 (1963).

[15] D. B. Rorabacher and D. W. Margerum, *ibid.*, **3**, 382 (1964).

[16] a) G. G. Hammes and J. I. Steinfeld, *J. Amer. Chem. Soc.*, **84**, 4639 (1962). b) D. W. Margerum, D. B. Rorabacher, and J. F. G. Clarke, Jr., *Inorg. Chem.*, **2**, 667 (1963).