Polarographic Study of the Rate of the Dissociation Reaction of the Zinc(II)-Nitrilotriacetate Complex in Ammonia-Ammonium Nitrate Buffer Solutions

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It has been known that the cadmium-nitrilotriacetate complex in ammonia-ammonium nitrate buffer solutions gives a reversible kinetic wave due to the dissociation of the complex and that the height of the limiting current of the kinetic wave increases with the concentration of ammonia[1,2]. A similar phenomena can also be observed in the case of zinc(II)-nitrilotriacetate[3]. In this study, the nature of the kinetic wave due to the dissociation of zinc(II)-nitrilotriacetate complex ions has been investigated more thoroughly from both theoretical and experimental viewpoints.

Experimental

Apparatus.—Direct current (D. C.) polarograms were measured by a manual polarograph similar to that of Kolthoff and Lingane[4]. The current was calculated from the ohmic potential drop, measured by a potentiometer, across a 10000-ohm resistance which was in series with the polarographic cell. A Yanagimoto Model GA-103 galvarecorder equipped with an automatically-scanning potentiometer was employed for the measurements of all alternating current (A. C.) polarograms.

A dropping mercury electrode, which has an m value of 1.23_7 mg./sec. and a drop time of 4.02 sec./drop in air-free 0.1 M potassium chloride solutions with an open circuit at 70 cm. of mercury column at 25.0±0.1°C, was used for all measurements. A saturated calomel electrode (S. C. E.) of a large area was used as the reference electrode and was connected to the cell solution through a Hume and Harris-type[5] salt bridge.

The dissolved oxygen in the solution was removed by bubbling pure nitrogen gas through the solution. All D. C. polarograms given in this paper were measured at 25.0±0.1°C unless otherwise stated and are corrected for residual currents. The pH value of the solution was measured with a glass electrode pH meter (Toyoroshi Kaisha Model G).

Reagent.—A standard solution of zinc(II) was prepared by dissolving pure zinc sulfate crystals in redistilled water. The concentration of zinc(II) was determined accurately by titrating it with standard nitrilotriacetate volumetrically[6]. Nitrilotriacetic acid (NTA) of an analytical reagent grade (Wako Pure Chemical Industries, Ltd.) was used without further purification. The stock solution of NTA was standardized with a standard nickel(II) solution[7]. The ammonia-ammonium nitrate buffer solutions were prepared by the method described in a previous paper[6]. All other chemicals were of an analytical reagent grade and were used without further purification. The ionic strength of the solution was adjusted to 0.4 by adding appropriate amounts of potassium nitrate.

Results and Discussion

In order to simplify the theoretical treatment, it is desirable to keep the concentration of NTA ions at the electrode surface constant during the reaction. This is ordinarily attained by adding a large excess of NTA ions. In the present case, however, it is advantegeous to keep the concentration of NTA ions fairly low, because the kinetic wave decreases with the increase in the concentration of free NTA ions. As an alternative, the above condition may be satisfied by adding a large excess of calcium ions to the solution; these ions react with free NTA ions to form stable complex ions. Therefore, all experiments were carried out in a solution containing a large excess of calcium ions, in other words, in a solution well-buffered with respect to free NTA ions.

The zinc(II)-nitrilotriacetate complex ion in a 0.1 M potassium nitrate medium does not show a reduction wave at less negative potentials than those where the supporting electrolyte is reduced. The system containing $2.11_6\times10^{-3}$ M NTA, $9.15_2\times10^{-4}$ M zinc(II) and 0.1 M calcium nitrate, however, exhibits a reduction wave in the ammonia buffer medium of a pH value of 8.25 (ionic strength 0.4), which corresponds to the reduction of zinc(II)-ammine complex.

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[1] J. Koryta, *Collection Czechoslov. Chem. Commun.*, **24**, 2903 (1959).

[2] J. Koryrta, ibid., **24**, 3057 (1956).

[3] M. Brezina, kandidatur-Dissertationsarbeit, Polarographisches Institut, Tschecholowakische Akademie der Wissenschaften, Prague 1956.

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

[5] D. N. Hume and W. E. Harris, *Ind. Eng. Chem. Anal. Ed.*, **15**, 465 (1943).

[6] G. Numaziri, M. Kodama and A. Shimizu, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 454 (1960).

[7] M. Kodama, A. Shimizu and H. Terakado, ibid., **81**, 1545 (1960).

ions (see Fig. 1). The limiting current of the polarogram is much larger than that which would be expected from the calculated concentration of the free ions which are in equilibrium with the zinc(II)-nitrilotriacetate complex at a pH value of 8.25. The numerical values for the equilibrium constants of NTA, ammonia, and their complexes, which were used for the calculation of the concentration of zinc(II)-ammine complex ions, the ZnX^-, NH_3 and X^{3-} listed in Table III, are given in Table II. These values were also used for the various calculations discussed below.

The relation between the limiting current of the reduction wave, i_t, and the effective pressure, H_e, was examined. The limiting current was found to be independent of H_e within the range of experimental error (Table I).

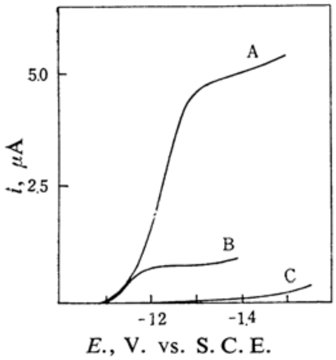

Fig. 1. The reduction wave of $9.15_2\times10^{-4}$ M Zn(II).

A: Ammonia-buffer of pH 9.2_5
B: Ammonia-buffer of pH 8.2_6 containing $2.11_6\times10^{-3}$ M NTA and 0.1 M $Ca(NO_3)_2$
C: 0.1 M KNO_3 medium containing $2.11_6\times10^{-3}$ M NTA

TABLE I. RELATION BETWEEN THE LIMITING CURRENT AND THE EFFECTIVE PRESSURE OF MERCURY ON THE DME

($9.15_2\times10^{-4}$ M Zn(II), $2.11_6\times10^{-3}$ M NTA, 0.1 M $Ca(NO_3)_2$, ionic strength 0.4, 25°C)

Height of mercury column, H cm.	Limiting current i_l, μA	$i_l/H_e^{1/2}\times10$
55	0.74_5	1.02_1
70	0.75_1	0.91_0
90	0.75_5	0.80_5

H_e: Effective pressure in cm.

TABLE II

i) Dissociation constants of NTA (hybrid constants; ionic strength: 0.4)[8]
$pK_1=1.82_1$ $pK_2=2.30_6$ $pK_3=9.44_5$
ii) Dissociation constants of zinc-ammine complex (ionic strength: 0.4)[9]
$pK_1=2.18$ $pK_2=2.25$ $pK_3=2.31$
$pK_4=1.96$
iii) Formation constant of Zn(II)-NTA (ionic strength: 0.4)[10]
$K_{ZnX}=C_{ZnX}/C_{Zn}\cdot C_X=10^{10.09}$
iv) Formation constant of Ca(II)-NTA (ionic strength: 0.4)[8]
$K_{CaX}=C_{CaX}/C_{ca}\cdot C_X=10^{5.834}$
v) Dissociation constant of ammonia (hybrid constant; ionic strength: 0.4)[11]
$pK=9.30$

In this table, the C's, represent the concentration of the corresponding ionic species.

As these values had not been determined experimentally, they were calculated from the related formation constants in the solution of an ionic strength of 0.1 at 20°C. The activity coefficients of the ions were calculated by means of the Debye-Hückel equation, using the proper values of ionic radii given in Kielland's table[12]. The temperature coefficients of these formation constants were assumed to be zero between 15° and 33°C in these calculations.

The effect of the pH value of the solution on i_l was studied over the pH range of 8.26 to 9.36 in ammonia buffer solutions containing $2.11_6\times10^{-3}$ M NTA, $9.15_2\times10^{-4}$ M zinc(II) and 0.1 M or 0.05 M calcium(II), the ionic strength of which was adjusted to 0.4. The total concentration of ammonia in the solution was 0.1 M or 0.05 M. The expeimental results show that the limiting current increases with the pH value of the solution, provided the other conditions are kept constant (Table III). The concentration of ammonia was calculated by successive approximation. Similar results were also obtained at 15 and 33°C.

The relation between $\log(i/(i_l-i))$ and E, where i_l indicates the limiting current, and i, the current at a potential of E, was analyzed with some typical examples. This relation gave a straight line with a slope of 57 mV. (Fig. 2), which is greater than the value of 45 mV. obtained for the zinc(II) ion in the ammonia buffer solution[13].

The value for the degree of reversibility, K, defined by Eq. 1, was 0.03 for the reduction of the zinc(II) ions in the ammonia buffer solution. This value is much smaller than that for the reduction of cadmium(II) in a potassium nitrate medium.

$$K=I/n\cdot t_d^{1/2}\cdot i_d \qquad (1)$$

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[8] G. Schwarzenbach, H. Ackermann and P. Ruckstuhl, *Helv. Chim. Acta*, **32**, 1175 (1949).
[9] J. Bjerrum, *Chem. Revs*, **46**, 681 (1950).
[10] E. J. Wheelwright, F. H. Spedding and G. Schwarzenbach, *J. Am. Chem. Soc.*, **75**, 4196 (1953).
[11] R. G. Bates and G. D. Pinchirg, ibid., **72**, 1393 (1950).
[12] J. Kielland, ibid., **59**, 1675 (1937).
[13] M. Senda M Senda and I. Tachi, *J. Electrochem. Soc. Japan* (*Denki Kagaku*), **27**, 83 (1959).

TABLE III. EFFECT OF pH ON THE REDUCTION WAVE (IONIC STRENGTH 0.4)

pH	C°_{ZnX} M×10^4	C°_X M×10^7	$C^\circ_{NH_3}$ M×10^2	i_l μA	$E_{1/2}$ V. vs. S. C. E.
8.26[a,b]	9.15_2	39.8_3	0.83_5	0.76	−1.155
8.56[a,d]	9.15_2	52.0_1	0.76_8	0.77	−1.152
8.60[c,d]	9.15_2	20.5_6	0.83_1	0.60	−1.165
8.68[a,b]	9.15_2	23.5_6	1.93	1.99	−1.156
8.76[a,d]	9.15_2	36.5_3	1.11	1.24	−1.154
8.82[b,c]	9.15_2	10.3_9	2.46	2.04	
8.94[c,d]	9.15_2	17.5_6	1.51	1.24	−1.166
9.05[a,b]	9.15_2	6.19_1	3.50	3.77	
9.16[b,c]	9.15_2	2.03_3	2.05	2.75	
9.21[a,d]	9.15_2	2.69_6	4.36	4.15	
9.36[c,d]	9.15_2	9.74_0	2.60	2.77	−1.168

a) Total concentration of Ca(II), 0.1 M
b) Total concentration of NH_3, 0.1 M
c) Total concentration of Ca(II), 0.05 M
d) Total concentration of NH_3, 0.05 M

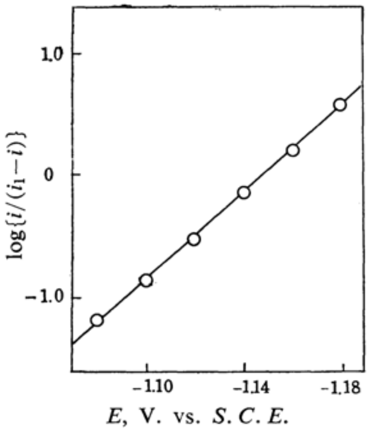

Fig. 2. Log-plot analysis of the reduction wave of Zn(II)-NTA complex in an ammonia buffer of pH 8.2_6 containing 0.1 M $Ca(NO_3)_2$ (Zn(II), $9.15_2\times10^{-4}$ M; NTA, $2.11_6\times10^{-3}$ M; $\mu=0.4$).

In Eq. 1, I indicates the A. C. peak current and t_d, the drop time.

In view of the experimental facts that K for the reduction of zinc(II) ions in the ammonia buffer solution corresponds to the value of the irreversible electrode reaction and that the slope of the log-plots for the reduction wave of the zinc(II)-NTA system is greater than that of the zinc(II) ions in the ammonia buffer solution, we can conclude that the electrode reaction of the zinc(II)-NTA system proceeds irreversibly in a usual polarographic sense.

The effect of temperature on the limiting current was also examined. The results show that the i_l increases in an appreciable degree with the temperature and that the value of the temperature coefficient was 5%, which is larger than that expected for the diffusion-controlled case (Table IV).

TABLE IV. THE RELATION BETWEEN THE LIMITING CURRENT AND THE TEMPERATURE OF THE SOLUTION

($9.15_2\times10^{-4}$ M Zn(II), $2.11_6\times10^{-3}$ M NTA 0.1 M $Ca(NO_3)_2$, ionic strength 0.4)

Temp. T, °C	Limiting current i_l, μA	$\Delta i_l/\Delta T$ %
15	0.38_2	4.8
25	0.75_1	5.8
33	1.10_1	

The experimental results on the relation between the limiting current and the effective pressure of mercury on the DME clearly indicate that the limiting current is kinetic in nature. This explanation is also supported by the experimental finding on the relation between the limiting current and the temperature of the solution.

Under the experimental conditions employed, ZnX^-, zinc ammine complex ions and zinc(II) ions coexist in the bulk of the solution; their concentrations are determined according to the following chemical equilibria:

$$ZnX^- + m\,NH_3 \rightleftharpoons Zn(NH_3)_m{}^{2+} + X^{3-} \quad (2)$$

$$Zn(NH_3)^{2+} \rightleftharpoons Zn^{2+} + NH_3 \quad (3)$$

$$Zn(NH_3)_2{}^{2+} \rightleftharpoons Zn(NH_3)^{2+} + NH_3 \quad (4)$$

$$Zn(NH_3)_3{}^{2+} \rightleftharpoons Zn(NH_3)_2{}^{2+} + NH_3 \quad (5)$$

$$Zn(NH_3)_4{}^{2+} \rightleftharpoons Zn(NH_3)_3{}^{2+} + NH_3 \quad (6)$$

In an ammonia buffer of a value from pH 8.3 to 9.5 and containing a large excess of calcium(II) ions with respect to the total concentration of NTA, the equilibrium between ZnX^- and zinc ammine-complex ions is greatly in favor of ZnX^-; i. e., the concentration of

ZnX^- is virtually equal to the total concentration of zinc in the bulk of the solution.

It is a well-known fact that the electrode reaction of zinc ions at mercury electrodes in ammonia buffer solutions corresponds to the direct reduction of zinc ammine complex ions[14]. From the above consideration, and from the fact that the limiting current increases with the concentration of ammonia in the solution provided that the other conditions are kept constant (Table III), it is very reasonable to conclude that the reaction at the electrode surface proceeds according to the following equations:

$$(\mathrm{I_a})\quad \left\{\begin{aligned} &\mathrm{ZnX^-} + m\,\mathrm{NH_3} \rightleftharpoons \mathrm{Zn(NH_3)}_m{}^{2+} \\ &\qquad + \mathrm{X^{3-}}\ \text{(slow)} && (2) \\ &\mathrm{Zn(NH_3)}_m{}^{2+} + 2\,\mathrm{e^-} + \mathrm{Hg} \\ &\qquad \rightleftharpoons \mathrm{Zn(Hg)} + m\,\mathrm{NH_3} && (7) \end{aligned}\right.$$

where the forward reaction rate of process 2 is assumed to be nearly equal to or smaller than the rate of the diffusion process of the ordinary ionic species and where the electron transfer reaction 7 proceeds irreversibly.

The theoretical equation of the kinetic current derived for the simple electrode reaction by Delahay[15] can not be applied without modification to the kinetic current obtained in the electrode reaction, where the complicated chemical reaction precedes the irreversible electron-transfer process. Therefore, we tried to derive a theoretical equation of the current-voltage curve obtained under such a mechanism as Ia by using the concept of the reaction layer[17], as in the case of cadmium(II)-EDTA complex ions[16].

When the concentrations of hydrogen ions, ammonia and X^{3-} ions at the electrode surface are kept constant by using buffer solutions containing a large excess of calcium ions which readily react with X^{3-} ions and form stable complex ions, reaction (I_a) can be written in a simpler form:

$$(\mathrm{II})\quad \left\{\begin{aligned} &\mathrm{Y} \underset{\overrightarrow{k}_8}{\overset{\overrightarrow{k}_8}{\rightleftharpoons}} \mathrm{O} && \text{slow}\ (8) \\ &\mathrm{O} + 2\,\mathrm{e} \underset{\overrightarrow{\kappa}}{\overset{\overrightarrow{\kappa}}{\rightleftharpoons}} \mathrm{R} && (9) \end{aligned}\right.$$

where the $(m+1)$-th order reaction 2 is replaced by the pseudo-first order reaction 8. O represents the oxidized form, and R, the reduced form, both of which concern the electron-transfer process. The terms k and κ are the reaction rate constants corresponding to each process, the former of which is a usual rate constant of the first order homogeneous reaction expressed in sec^{-1}, while the latter is a rate constant of an electron-transfer process expressed in cm. sec^{-1}. In the present case, $\overrightarrow{\kappa}$ and $\overleftarrow{\kappa}$ are represented by the following relations:

$$\overrightarrow{\kappa} = \overrightarrow{\kappa}_0 \exp\left(\frac{-2\,\alpha EF}{\boldsymbol{R}T}\right)$$

$$\overleftarrow{\kappa} = \overleftarrow{\kappa}_0 \exp\left(\frac{+2(1-\alpha)EF}{\boldsymbol{R}T}\right) \qquad (10)$$

where E is the electrode potential, α, the transfer coefficient, F, the Faraday constant, $\boldsymbol{R}$, the gas constant, T, the absolute temperature, and κ_0, the value of κ at $E=0$.

Taking into consideration the diffusion process of Y from the bulk of the solution to the electrode surface and assuming the condition of the stationary state with respect to the concentrations of Y, O and R at the electrode surface, the following equations are obtained:

$$\mathrm{d}C_\mathrm{Y}/\mathrm{d}t = K^\mathrm{D}{}_\mathrm{Y}(C^\circ{}_\mathrm{Y} - C_\mathrm{Y}) - (\overrightarrow{k}_8{}' C_\mathrm{Y} - \overleftarrow{k}_8{}' C_\mathrm{O}) = 0 \qquad (11)$$

$$\mathrm{d}C_\mathrm{O}/\mathrm{d}t = (\overrightarrow{k}_8{}' C_\mathrm{Y} - \overleftarrow{k}_8{}' C_\mathrm{O}) - (\overrightarrow{\kappa} C_\mathrm{O} - \overleftarrow{\kappa} C_\mathrm{R}) = 0 \qquad (12)$$

$$\mathrm{d}C_\mathrm{R}/\mathrm{d}t = (\overrightarrow{\kappa} C_0 - \overleftarrow{\kappa} C_\mathrm{R}) - K^\mathrm{D}{}_\mathrm{R} C_\mathrm{R} = 0 \qquad (13)$$

$$\overrightarrow{k}_8{}' = \mu_8 \overrightarrow{k}_8$$

$$\overleftarrow{k}_8{}' = \mu_8 \overleftarrow{k}_8$$

where the C°'s represent the concentrations in the bulk of the solution, the C's, the concentrations at the electrode surface, the K's, the rate constants corresponding to the diffusion processes, and the μ's, the thicknesses of the reaction layer of the corresponding chemical reactions expressed in cm^{-1}. In the above equations, the diffusion process of O is neglected, because, in the present case, the concentration of O in the bulk of the solution can be assumed to be negligibly small.

The average current, i, can be represented by the equation:

$$i = 2\,AF(\overrightarrow{\kappa} C_\mathrm{O} - \overleftarrow{\kappa} C_\mathrm{R}) \qquad (14)$$

where A is the mean surface area of DME. From Eqs. 11, 12, 13 and 14, we can obtain the following equation for the limiting current, i_1:

$$i_1 = 2\,AF\left\{\frac{\overrightarrow{k}_8{}' \cdot C^\circ{}_\mathrm{Y}}{1 + \overrightarrow{k}_8{}'/K^\mathrm{D}}\right\} \qquad (15)$$

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

[15] P. Delahay, "New Instrumental Methods in Electrochemistry", Interscience Publishers, New York (1954), p. 87.

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

[17] For example, see Ref. 15, p. 94.

under the assumption that $K_Y{}^D$ and $K_R{}^D$ are the same ($=K^D$).

By introducing the relation $\mu_8=K_8{}^{1/2}\cdot D^{1/2}\cdot(\overrightarrow{k_8})^{-1/2}$ 17), Eq. 15 can be rearranged to:

$$\frac{1}{i_l}=\frac{1}{2AFK_8{}^{1/2}\,D^{1/2}\,\overrightarrow{k_8}{}^{1/2}\,C^\circ}+\frac{1}{2AFK^D\,C^\circ{}_Y}\tag{16}$$

where D is the diffusion coefficient of Y and O, and $K_8=C^\circ{}_O/C^\circ{}_Y$. On the right-hand side of Eq. 16, the first and the second terms represent the contribution of the kinetic and the diffusion currents respectively to the limiting current. If $K^{1/2}\,D^{1/2}\,\overrightarrow{k_8}{}^{1/2}\,C^\circ{}_Y$ is much larger than $K^D\,C^\circ{}_Y$, the limiting current comes to be completely diffusion-controlled, which state is represented by the well-known Ilkovic equation.

If the electron-transfer process is assumed to be irreversible, i. e., $\overrightarrow{\kappa}\gg\overleftarrow{\kappa}$, as in the present case of the zinc(II)-NTA system, we can obtain the following equation, which represents the current-voltage relation of the so-called irreversible reduction wave corresponding to reaction II by combining Eqs. 11, 12, 13 and 14.

$$i=\frac{\overrightarrow{\kappa}}{\overleftarrow{k_8}}(i_l-i)\left(1+\frac{\overrightarrow{k_8}'}{K^D}\right)\tag{17}$$

When the limiting current is kinetic in nature, as in the case of the zinc(II)-NTA system, $\overrightarrow{k_8}'$ is assumed to be much smaller than K^D. For this reason, the term $\overrightarrow{k_8}'/K^D$ is negligibly small in comparison with 1 and Eq. 17 can be simplified as follows at 25°C:

$$E=\frac{0.0591}{2}\left\{\log\overrightarrow{\kappa_0}-\log\left(\frac{i}{i_l-i}\right)-\log\overleftarrow{k_8}'\right\}\tag{18}$$

The experimental results on the zinc(II)-NTA system were analyzed with the aid of Eqs. 16 and 18. When these equations are applied to the electrode Eq. Ia, Y and O correspond to ZnX^- and $Zn(NH_3)_m{}^{2+}$ respectively, and the rate constants and equilibrium constants in these equations must be replaced by the corresponding terms, as in the following way:

$$\overrightarrow{k_8}=\overrightarrow{k_2}(C^\circ{}_{NH_3})^m$$

$$\overleftarrow{k_8}=\overleftarrow{k_2}C^\circ{}_X$$

$$K_8=\frac{C^\circ{}_{Zn(NH_3)m}}{C^\circ{}_{ZnX}}=K\times\frac{(C^\circ{}_{NH_3})^m}{C^\circ{}_X}$$

$$K=K_{Zn(NH_3)m}/K_{ZnX}$$

$$K_{Zn(NH_3)m}=\frac{C^\circ{}_{Zn(NH_3)m}}{(C^\circ{}_{NH_3})^m C^\circ{}_X}$$

$$K_{ZnX}=\frac{C^\circ{}_{ZnX}}{C^\circ{}_{Zn}\cdot C^\circ{}_X}$$

Therefore, Eq. 16 can be written as

$$\frac{1}{i_l}=\frac{1}{2\,AFD^{1/2}\,K^{1/2}\,\overrightarrow{k_2}{}^{1/2}}\cdot\frac{(C^\circ{}_X)^{1/2}}{C^\circ{}_{ZnX}\cdot(C^\circ{}_{NH_3})^m}+\frac{1}{2\,AFK^D\cdot C^\circ{}_{ZnX}}\tag{19}$$

This equation indicates that, if the electrode reaction proceeds according to the Ia mechanism, the relation between $1/i_l$ and $(C^\circ{}_X)^{1/2}/C^\circ{}_{ZnX}\cdot(C^\circ{}_{NN_3})^m$ must be linear. The above relations were examined in connection with the experimental data in Table III. Linear relations were found between $1/i_l$ and $(C^\circ{}_X)^{1/2}/C^\circ{}_{ZnX}\cdot(C^\circ{}_{NN_3})^2$, but not between $1/i_l$ and $(C^\circ{}_X)^{1/2}/C^\circ{}_{ZnX}$, $(C^\circ{}_X)^{1/2}/C^\circ{}_{ZnX}\cdot C^\circ{}_{NN_3}$ or $(C^\circ{}_X)^{1/2}/C^\circ{}_{ZnX}\cdot(C^\circ{}_{NN_3})^3$ (Figs. 3, 4, 5 and 6). Similar results were also obtained at 15 and 33°C. Therefore, it can be concluded that the electrode reaction

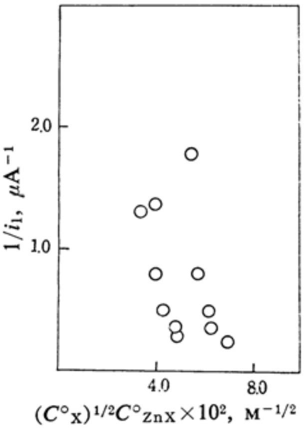

Fig. 3. Relation between $1/i_l$ and $(C^\circ{}_X)^{1/2}/C^\circ{}_{ZnX}$.

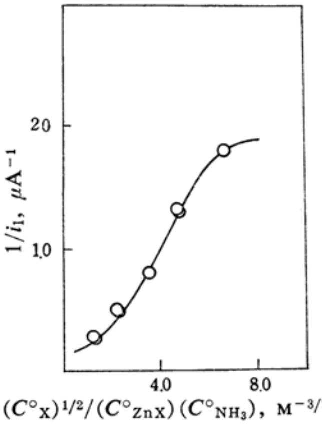

Fig. 4. Relation between $1/i_l$ and $(C^\circ{}_X)^{1/2}/(C^\circ{}_{ZnX}\cdot C^\circ{}_{NH_3})$.

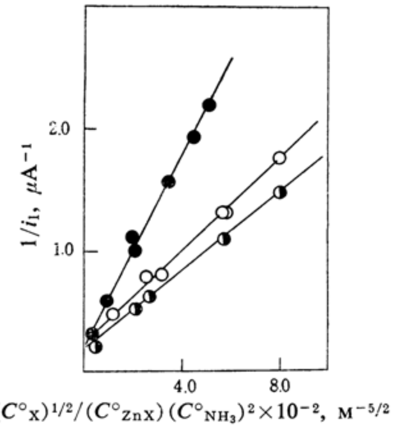

Fig. 5. Relation between $1/i_l$ and $(C^\circ_X)^{1/2}/(C^\circ_{ZnX})(C^\circ_{NH_3})^2$.

● 15°C ○ 25°C
◐ 33°C

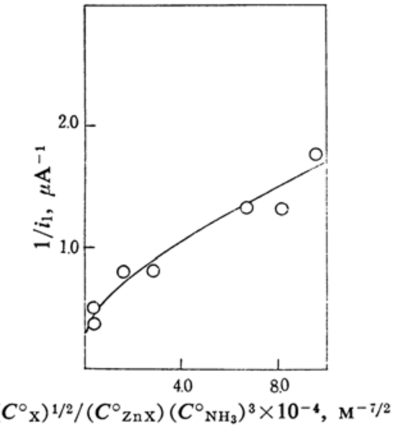

Fig. 6. Relation between $1/i_l$ and $(C^\circ_X)^{1/2}/(C^\circ_{ZnX})(C^\circ_{NH_3})^3$.

of the zinc(II)-NTA system proceeds according to the following mechanism:

$$
\text{(Ib)}\begin{cases}
ZnX^- + 2\,NH_3 \rightleftharpoons Zn(NH_3)_2{}^{2+} + X^{3-} & (2)\\
Zn(NH_3)_2{}^{2+} + 2\,e + Hg \rightleftharpoons Zn(Hg) + 2NH_3 & (7)
\end{cases}
$$

By remembering the fact, mentioned by Matsuda and Ayabe[14)], that the reduction wave of zinc-ammine complex ions at the dropping mercury electrode is due to the direct reduction of $Zn(NH_3)_2{}^{2+}$, it is very plausible to propose the I_b electrode reaction mechanism, where the dissociation reaction of ZnX^- precedes the electron transfer process.

The fact that linear relations between $1/i_l$ and $(C^\circ_X)^{1/2}/C^\circ_{ZnX}(C^\circ_{NN_3})^2$ were found at 15, 25 and 33°C clearly show that the concentration of calcium(II) employed was high enough to keep the concentration of X^{3-} constant at the electrode surface.

Figure 5 clearly shows the existence of a small contribution of the diffusion-controlled current to the total limiting current, which must be equal to $(2\,AFK^D C^\circ_{ZnX})^{-1}$, according to Eq. 19. Theretically, this term must be equal to $(2\times 6.07\times 10^4\times m^{2/3}\,t^{1/6}\,D^{1/2}\,C^\circ)^{-1}$ in comparison with the Ilkovic equation, where m is expressed in g./sec. and t_d, in sec., and where D is the deffusion coefficient of Zn^{2+}, ZnX^- or $Zn(NH_3)_m{}^{2+}$ expressed in cm. sec^{-2}[18)]. The current is expressed in ampere and the concentration, in mol./cc. The observed value of $(2\,AFK^D C^\circ_{ZnX})^{-1}$ was 1.8×10^3 amp^{-1}, whereas the calculated value is 2×10^3 amp^{-1}. It could be said that the observed value agrees with the calculated value.

The tangent of the relation of $1/i_l$ vs. $(C^\circ_X)^{1/2}/C^\circ_{ZnX}(C^\circ_{NN_3})^2$ was found to be 2.4 $\times 10^{-3}$. According to Eq. 22, this value must be equal to $(2\,AFK^{1/2}\,D^{1/2}\,\overrightarrow{k}_2{}^{1/2})^{-1}$, which can be written as $(2.51+10^5\,m^{2/3}\,t^{2/3}\,D^{1/2}\,K^{1/2}\,k_2{}^{1/2})^{-1}$. If we use the values of $10^{10.09}$ for K_{ZnX} and $10^{4.43}$ for $K_{Zn(NH_3)_2}$, $\overrightarrow{k}_2$ in Eq. 22 is calculated to be 0.85_0 (mol./l.)$^{-2}$ sec^{-1}, which corresponds to the rate constant of the forward reaction of $ZnX^- + 2\,NH_3 = Zn(NH_3)_2{}^{2+} + X^{3-}$ at 25°C in the medium with the ionic strength of 0.4 containing a large excess of calcium(II) ions. The rate constant of the backward reaction, $\overleftarrow{k}_2$, is also found to be equal to 2.42×10^5 (mol./l.)$^{-1}$ sec^{-1} from the $K=\overrightarrow{k}_2/\overleftarrow{k}_2$ relation.

The experimental data on the limiting current obtained at 15 and 33°C at various pH values were analyzed by using Eq. 22. The linearity between $1/i_l$ and $(C^\circ_X)^{1/2}/C^\circ_{ZnX}(C^\circ_{NH_3})^2$ was satisfied also in these cases. If we assume that the value of the equilibrium constant, K, is independent of the temperature, the values of $\overrightarrow{k}_2$ are calculated as 0.22 (mol./l.)$^{-2}$ sec^{-1} and 5.52 (mol./l.)$^{-2}$ sec^{-1} for 15 and 33°C respectively. From the values of $\overrightarrow{k}_2$ at 15, 25 and 33°C, the heat of activation, ΔH^*, and the entropy of activation, ΔS^*, of the forward reaction of $ZnX^- + 2NH_3 = Zn(NH_3)_2{}^{2+} + X^{3-}$, are obtained as 31.1 kcal. and -25.4 e. u. respectively. These thermodynamic values, however, are not so accurate partly because of the approximate estimation of the equilibrium constants, K_{ZnX} and $K_{Zn(NH_3)_2}$.

When the mechanism of the electrode reaction is represented by Ib, the natures of the current-voltage curve must satisfy Eq. 18. This equation predicts that the log-plot analysis will give a straight line with a slope of 57 mV. at

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18) In this calculation, the diffusion coefficients of Zn^{2+}, ZnX^- and $Zn(NH_3)_2{}^{2+}$ were assumed to be the same, 8.40×10^{-6} cm. sec^{-2}.

25°C; this is in agreement with the experimental results when we employ the value of 0.53_0 for (see Fig. 2).

The expression of the half-wave potential, $E_{1/2}$, is obtained from Eqs. 10 and 18 as:

$$E_{1/2}=\frac{0.0591}{2\,\alpha}\left\{\log \overrightarrow{\kappa_0}-\log \overleftarrow{k_2'}\right\} \tag{20}$$

By remembering the nature of $\overleftarrow{k_2'}$, Eq. 20 can be written as

$$E_{1/2}=\text{const}-\frac{0.0591}{4\alpha}\log C^{\circ} \tag{21}$$

This relation was examined by using some typical data from Table III, the results of which are shown in Fig. 6. The tangent of the relation between $E_{1/2}$ and $C^{\circ}{}_{\mathrm{X}}$ is 35 mV. and is in agreement with the theoretical prediction of 29 mV.

It can be concluded from the results of the theoretical analysis of the experimental data that the reduction wave of the zinc(II)-NTA system under the presence of an excess of calcium ions is of a kinetic nature, the mechanism of which is represented by the $\mathrm{I_b}$ reaction.

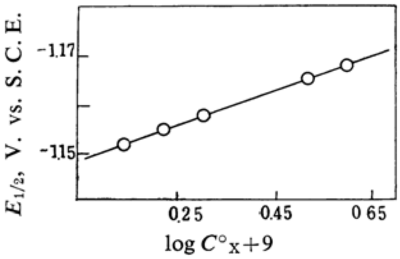

Fig. 7. Relation between $E_{1/2}$ ang $\log C^{\circ}{}_{\mathrm{X}}$.

Summary

The kinetic current due to the dissociation of zinc-nitrilotriacetate complexes has been investigated in buffers with pH values from 8.3 to 9.5 and containing a large excess of calcium ions with respect to the total concentration of nitrilotriacetate. The ionic strength was kept at 0.4.

It was confirmed that the electrode reaction at the surface of the dropping mercury electrode proceeds according to the mechanism:

$$\mathrm{ZnX^- + 2\,NH_3 \rightleftharpoons Zn(NH_3)_2{}^{2+} + X^{3-}} \qquad \text{(slow)}$$

$$\mathrm{Zn(NH_3)_2{}^{2+} + 2\,e + Hg \rightleftharpoons Zn(Hg) + 2\,NH_3} \qquad \text{(fast)}$$

The rate constants were calculated as 0.85_0 (mol./1.)$^{-2}$ sec^{-1} for the dissociation reaction of $\mathrm{ZnX^- + 2\,NH_3 = Zn(NH_3)_2{}^{2+} + X^{3-}}$ and 2.42×10^5(mol./1.)$^{-1}$ sec^{-1} for the association reaction at 25°C. in buffer solutions of pH values from 8.3 to 9.5 with an ionic strength of 0.4 and containg 0.1 M calcium nitrate. The heat of activation and the entropy of activation of the dissociation reaction were calculated as 31.1 kcal. and −25.4 e. u. respectively.

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