A Polarographic Study of the Zinc(II)-Ethylenediamine-*N*,*N'*-diacetate (EDDA) and -Triethylenetetraamine (Trien) Complexes

Mutsuo Kodama

Department of Chemistry, College of General Education, Hirosaki University, Bunkyo, Hirosaki, Aomori 036

(Received November 26, 1973)

Zinc(II)-EDDA and -Trien complexes produced kinetic waves. By conducting a systematic examination of the nature of the kinetic waves, the reaction mechanisms and the rates of the rate-determining step were determined. The kinetic wave of the zinc(II)-EDDA complex could be ascribed to the reduction of the zinc(II) aquo ion formed upon its slow dissociation at the electrode surface. From a comparison of the observed rate constant with that estimated on the basis of the proposed reaction intermediate, the dissociation of the zinc(II)-EDDA complex was found to proceed through a reaction intermediate in which the leaving EDDA anion is bonded to the zinc(II) ion through the ethylenediamine chelate ring. In the case of the Trien complex, the kinetic wave could be ascribed to the reduction of the zinc(II)-Trien complex formed upon the slow configurational change of the tetrahedral zinc(II)-Trien complex at the electrode surface.

Previously,[1)] the present author studied the dissociation reactions of zinc(II)-, lead(II)-, and cadmium(II)-aminopolycarboxylate complexes by examining the nature of the kinetic waves they gave. The zinc(II)-EDDA and -Trien complexes also produced kinetic waves. In this paper, the author will describe a systematic study of the nature of the above kinetic waves and will determine the reaction mechanism and reaction rates. The effect of the thiocyanate anion on the polarographic behavior of the zinc(II)-EDDA and -Trien complexes will also be investigated.

Experimental

Reagents. The previous paper[2)] explained the preparation of a standard zinc(II) solution. An EDDA was recrystallized from its aqueous solution. Its standard solution was prepared by dissolving a known amount of recrystallized EDDA in redistilled water. The Trien was redistilled under reduced pressure. All the other chemicals were of an analytical reagent-grade and were used without further purification.

Apparatus and Experimental Procedures. The polarographs used for the measurement of the dc current-voltage cuvres were given previously.[2)] The rate of the flow of mercury, m, and the drop time, t_d, of the dropping mercury electrode (DME) used in this study were 0.836 mg/s and 4.30 s respectively at a mercury height of 58.0 cm in an air-free 0.10 M sodium perchlorate solution at 0.0 V *vs.* SCE. All the other pieces of the apparatus and all the experimental procedures employed in this study were the same as those described in the previous paper.[2)] For the EDDA system, an acetate buffer solution was used. In the case of the Trien system, no buffer reagent was used, because the sample solutions always contained a large excess of uncomplexed Trien and had a sufficient buffer capacity over the entire pH range covered ($6.00 < \mathrm{pH} < 7.50$).

Results and Discussion

Under the experimental conditions where all the zinc(II) ions exist as complexes, the zinc(II) ions in EDDA and Trien solutions gave two- and one-step polarographic waves respectively. The first wave of the EDDA complex and the reduction step of the Trien complex showed a characteristic kinetic-controlled nature, while the second wave of the EDDA complex showed a diffusion-controlled nature. From the effects of the mercury pressure, the solution pH, and the uncomplexed ligand concentration on the limiting current, the second step of the EDDA complex could be ascribed to its direct reduction at the electrode surface.

As in the cases of the cobalt(II)-iminodiacetate (IDA) and -aspartate (Asp) complexes,[3)] the first step of the zinc(II)-EDDA complex invariably gave a linear relation passing through the point of origin between $i_k/(i_d - i_k)$ and $(\alpha_H)_X^{1/2}$ (at a given EDDA concentration, $[X]_f$) or $[X]_f^{-1/2}$ (at a given solution pH) (Fig. 1). Here, $(\alpha_H)_x$ and i_k are, respectively, the (α_H) value of EDDA and the kinetic wave height. Provided that the other experimental conditions are kept constant, the plot of $i_k/(i_d - i_k)$ against $\beta_{Ac}^{1/2}$ $(= 1 + K_1{}^{Ac}\cdot[Ac^-] + K_1{}^{Ac}\cdot K_2{}^{Ac}\cdot[Ac^-]^2 + \cdots]^{1/2})$[1)] also gave a straght line which passes through the point of origin. Since the zinc(II) ion forms only a 1 : 1-ratio complex with EDDA[4)], the above facts suggest that the following

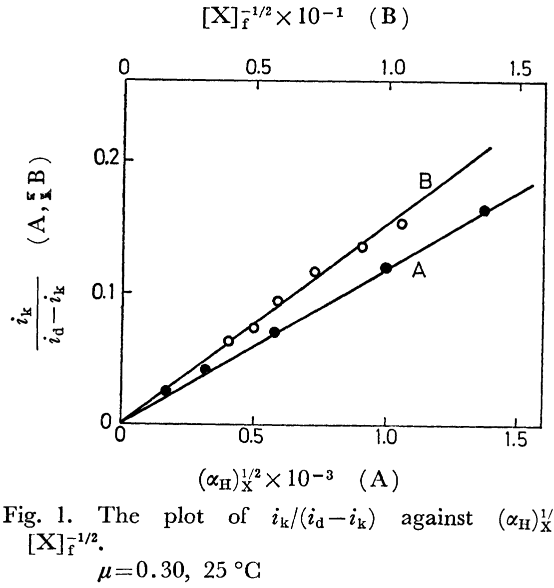

Fig. 1. The plot of $i_k/(i_d - i_k)$ against $(\alpha_H)_X^{1/2}$ or $[X]_f^{-1/2}$.
$\mu = 0.30$, 25 °C
$[Zn(II)] = 0.60$ mM, $]Ac]_f = 0.060$ M
A) The plot of $i_k/(i_d - i_k)$ against $(\alpha)_X^{1/2}$
$[EDDA]_f = 14.0$ mM
pH ranged from 4.60 to 5.90
B) The plot of $i_k/(i_d - i_k)$ against $[X]_f^{-1/2}$
$[EDDA]_f$ ranged from 9.0 to 40.0 M
pH = 5.00

reaction mechanism can be assumed for the kinetic wave of the zinc(II)-EDDA complex:

$$\mathrm{ZnX^0} \overset{k_d}{\rightleftharpoons} \mathrm{Zn^{2+} + X^{2-}} \qquad (1)\ \text{rds}$$

$$\underbrace{\mathrm{Zn^{2+}} + i\mathrm{Ac^-} \rightleftharpoons \mathrm{Zn(Ac)}_i{}^{2-i}}_{\mathrm{Hg}\ \Downarrow\ 2\mathrm{e}^-} \qquad \text{in a rapid equil.}$$

$$\mathrm{Zn(Hg)}$$

The k_d value was determined from the slope of the linear relation in Fig. 1; it is listed in Table 1, together with other numerical data. In the presence of the thiocyanate anion, the plot of $((i_d-i_k)/i_k)\cdot\beta_{\mathrm{NCS}}^{1/2}$ against $[\mathrm{NCS^-}]$ gave a linear relation with an intercept of a finite value (Fig. 2). Here, β_{NCS} is defined as $1+K_1{}^{\mathrm{NCS}}\cdot[\mathrm{NCS^-}]+K_1{}^{\mathrm{NCS}}\cdot K_2{}^{\mathrm{NCS}}\cdot[\mathrm{NCS^-}]^2+\cdots$, and $[\mathrm{NCS^-}]$ is the concentration of the uncomplexed thiocyanate anion. The above facts evidently suggest the formation of a mixed-ligand complex, $\mathrm{ZnX(NCS)^-}$. Therefore, in view of the fact that the zinc(II)–thiocyanate complex is much more stable than the corresponding acetate complex, one can assume the following reaction mechanism for the kinetic wave of the zinc(II)–EDDA complex in solutions containing thiocyanate anions:

$$\mathrm{ZnX(NCS)^-} \rightleftharpoons \mathrm{ZnX^0 + NCS^-} \qquad (2)\ \text{in a rapid equil.}$$

$$\mathrm{ZnX^0} \overset{k_d}{\rightleftharpoons} \mathrm{Zn^{2+} + X^{2-}} \qquad (1)\ \text{rds}$$

$$\underbrace{\mathrm{Zn^{2+}} + j\mathrm{NCS^-} \rightleftharpoons \mathrm{Zn(NCS)}_j{}^{2-j}}_{\mathrm{Hg}\ \Downarrow\ 2\mathrm{e}^-} \qquad \text{in a rapid equil.}$$

$$\mathrm{Zn(Hg)}$$

corresponding to Relation (1):

$$\frac{i_k}{i_d-i_k} = 0.886\cdot\sqrt{\frac{k_d\cdot t\cdot(\alpha_{\mathrm{H}})_{\mathrm{X}}\cdot\beta_{\mathrm{NCS}}}{K_{\mathrm{ZnX}}\cdot[\mathrm{X}]_f}}\cdot\frac{1}{1+K_{\mathrm{ZnX(NCS)}}^{\mathrm{NCS}}\cdot[\mathrm{NCS^-}]} \qquad (1)$$

Relation (1) was examined successfully by using some typical experimental data and the $K_{\mathrm{ZnX(NCS)}}^{\mathrm{NCS}}$ $(=[\mathrm{ZnX(NCS)^-}]/[\mathrm{ZnX^0}]\cdot[\mathrm{NCS^-}])$ value of 2.24 determined from the ratio between the intercept and the slope of the straight line (A) in Fig. 2. The good agreement of the k_d value estimated from the slope of the linear relation (B) in Fig. 2 with that determined from the slope of the straight line in Fig. 1 also supports the above explanation.

In the zinc(II)–Trien system, i_k also decreased with an increase in the solution pH, and the plot of $i_k/(i_d-i_k)$ against $K^{\mathrm{H}}\cdot[\mathrm{H^+}]^{1/2}/(1+K^{\mathrm{H}}\cdot[\mathrm{H^+}])$ gave a linear relation passing through the point of origin (Fig. 3). However, the $i_k/(i_d-i_k)$ ratio was almost independent of the concentration of the uncomplexed Trien, $[\mathrm{X}]_f$. These facts suggest the following reaction mechanism for the kinetic wave of the zinc(II)–Trien complex:

$$\mathrm{ZnX^{2+} + H^+} \rightleftharpoons \mathrm{ZnHX^{3+}} \qquad \text{in a rapid equilibrium}$$

$$\mathrm{ZnHX^{3+}} \overset{k}{\rightleftharpoons} \mathrm{ZnX^{2+}{*} + H^+} \qquad \text{rds}$$

$$\mathrm{ZnX^{2+}{*} + 2e^- + Hg} \rightleftharpoons \mathrm{Zn(Hg) + X^0}$$

corresponding to Relation (2):

$$\frac{i_k}{i_d-i_k} = 0.886\cdot\sqrt{\frac{k\cdot t}{K\cdot[\mathrm{H^+}]}}\cdot\frac{K^{\mathrm{H}}\cdot[\mathrm{H^+}]}{1+K^{\mathrm{H}}\cdot[\mathrm{H^+}]} \qquad (2)$$

where K^{H} is the protonation constant of $\mathrm{ZnX^0}$, K, $[\mathrm{ZnHX^{3+}}]/[\mathrm{ZnX^{2+}{*}}]\cdot[\mathrm{H^+}]$, and $\mathrm{ZnX^{2+}{*}}$, the electroactive zinc(II)–Trien complex. If the above reaction mech-

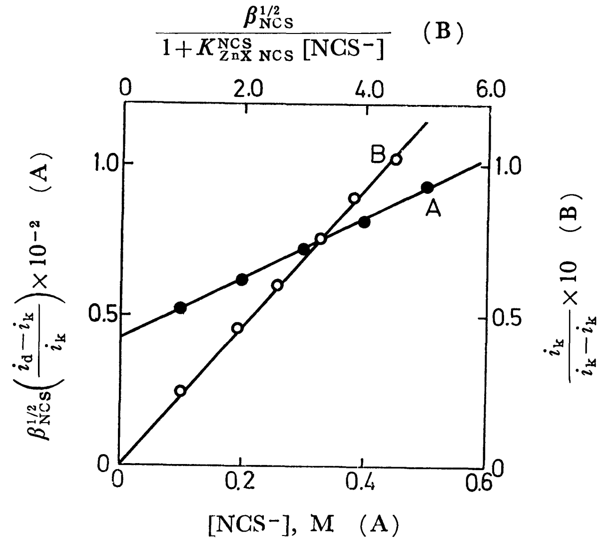

Fig. 2. The effect of NCS⁻ on the kinetic wave of the zinc(II)-EDDA complex.
$\mu=0.50$, 25 °C
$[\mathrm{EDDA}]_f=20.0$ mM, $[\mathrm{Zn(II)}]=1.0$ mM
$[\mathrm{Ac}]_f=0.06$ M, pH $=5.50$
$[\mathrm{NCS^-}]$ ranged from 0.10 to 0.50 M
A) The plot of $((i_d-i_k)/i_k)\ \beta_{\mathrm{NCS}}^{1/2}$ against $[\mathrm{NCS^-}]$
B) The plot of $i_k/(i_d-i_k)$ against $\beta_{\mathrm{NCS}}^{1/2}/(1+K_{\mathrm{ZnX(NCS)}}^{\mathrm{NCS}}[\mathrm{NCS^-}])$

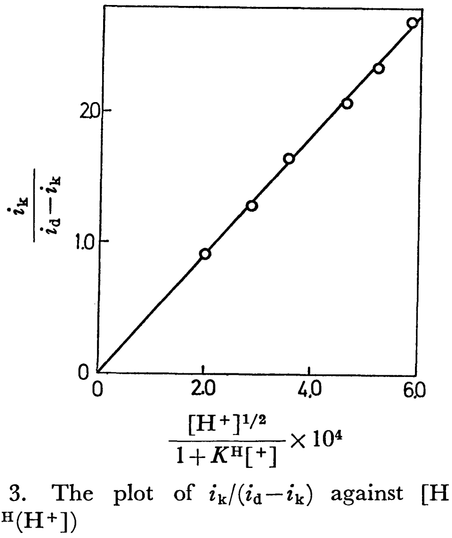

Fig. 3. The plot of $i_k/(i_d-i_k)$ against $[\mathrm{H^+}]^{1/2}/(1+K^{\mathrm{H}}(\mathrm{H^+}])$
$\mu=0.30$, 25 °C
$[\mathrm{Trien}]_f=24{\cdot}0$ mM, $[\mathrm{Zn(II)}]=1.0$ mM
pH ranged from 6.00 to 7.30.

TABLE 1. RATE CONSTANTS ($\mu=0.30$, 25 °C)

Dissociation rate constant, k_d ($\mathrm{s^{-1}}$), of Zn(II)-EDDA complex

Obsd	Calcd	
	En mechanism	Gly mechanism
3.5	1.0	7.7×10^{-3}

TABLE 2. THE EFFECT OF pH ON THE HALF-WAVE POTENTIAL OF THE Zn(II)-Trien COMPLEX

$[\mathrm{Trien}]_f=24.0$ mM, $[\mathrm{Zn(II)}]=1.0$ mM
$\mu=0.30$, 25 °C

pH	$E_{1/2}$ V *vs.* SCE	$\Delta E_{1/2}$, mV	
		Obsd	Calcd
6.24	-1.120	$+5$	$+4.7$
6.40	-1.125	0	0
6.58	-1.130	-5	-5.3
6.62	-1.133	-8	-6.5
6.88	-1.145	-15	-14.2
7.28	-1.165	-25	-26.0

anism is assumed for the zinc(II)–Trien system, the half-wave potential of the kinetic wave, $(E_{1/2})_k$, should be given by:[5]

$$(E_{1/2})_k = \text{constant} + \frac{0.0591}{4\alpha}\log\,[\mathrm{H}^+] \tag{3}$$

By using the α value of 0.51, the effect of the solution pH on the half-wave potential was examined with the aid of Eq. (3). The result is given in Table 2. The shifts of the half-wave potential observed agreed well with those calculated.

As was discussed in connection with the dissociation mechanism of the zinc(II)–aminopolycarboxylate complex, the structure of the reaction intermediate in the dissociation of the zinc(II)–EDDA complex was determined by comparing the observed k_d value with that calculated on the basis of the proposed reaction intermediate. The k_d value calculated with the aid of the well-known relation; $k=k_{\mathrm{rds}}\cdot K_{\mathrm{inter}}\cdot K_{\mathrm{st}}\cdot K_{\mathrm{elec}}/K_{\mathrm{MX}}$,[3] on the basis of the ethylenediamine reaction intermediate was 1.0. Here, $K_{\mathrm{inter}}=10^{6.15}$, $K_{\mathrm{st}}=1.0\times10^2$, $k_{\mathrm{rds}}=3.1\times10^2$, and $K_{\mathrm{MX}}=10.^{10.79}$ The k_{rds} value used in the above calculation was estimated from the dissociation rate constant of the 1 : 1-ratio zinc(II)–ammine complex by making a correction for the rotational barrier around the C–N bond.[6] The agreement between the calculated and observed rate constants can be regarded as satisfactory. The rate constants calculated on the basis of the other reaction intermediates showed no satisfactory agreement with the observed one.

In the case of the zinc(II)–Trien complex, one can not determine the k value from the slope of the linear relation in Fig. 3, because the K value is unknown. With regard to the nature of the electroactive zinc(II)–Trien complex, two explanations are possible. One is that electroactive zinc(II)–Trien complex, ZnX^{2+*}, is the species produced upon the partial dissociation of the original complex, ZnX^{2+}. The other is that ZnX^{2+*} is the Trien complex formed upon the configurational change of the original complex. Generally, protonation of a metal complex always involves a partial dissociation of the metal complex. Therefore, the fact that the rate-determining step includes the deprotonation of the protonated zinc(II)–Trien complex eliminates the former explanation. On the basis of the ΔS value of the formation reaction, Sacconi *et al.*[7] concluded that the zinc(II)–Trien complex in a solution is tetrahedral. This could be confirmed by the finding that the thiocyanate anion had practically no effect on the polarographic behavior of the zinc(II)–Trien complex. If the zinc(II)–Trien complex in solution is octahedral, the thiocyanate anion will form a mixed ligand complex with ZnX^{2+} and will have a remarkable effect on the kinetic wave. Therefore, it must be reasonable to believe that the rate-determining step in the zinc(II)–Trien system is the configurational change of the zinc(II)–Trien complex from tetrahedral to octahedral or square pyramid. In order to describe the nature of the above configurational change more precisely, a further systematic investigation should be conducted.

References

1) M. Kodama, K. Namekawa, and T. Horiuchi, This Bulletin, in press.

2) M. Kodama and N. Oyama, This Bulletin, **45**, 2169 (1972).

3) M. Kodama, *ibid.*, **46**, 3422 (1973).

4) L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," 2nd ed., The Chemical Society, London (1964), p. 519.

5) M. Kodama, H. Nunokawa, and N. Oyama, This Bulletin, **44**, 2387 (1971).

6) D. W. Margerum, D. B. Rorabacher, and J. F. Clarke, Jr., *Inorg. Chem.*, **2**, 667 (1963).

7) L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Chem. Soc.*, **1961**, 5515.