A Polarographic Study of the Dissociation Reactions of the Ethylenediaminemonoacetatocobalt(II) (Co(II)-EDMA) and Ethylenediaminediacetatonickel(II) (Ni(II)-EDDA) Complexes

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The rates and the mechanisms of the dissociation reactions of the Co(II)-EDMA complex in a phosphate buffer solution and the Ni(II)-EDDA complex in an ethylenediaminediacetate solution were studied by analyzing their kinetic waves by means of conventional DC polarography. The dissociation of the Co(II)-EDMA complex gave this rate law: $-\mathrm{d}[\mathrm{Co(II)\text{-}EDMA}]/\mathrm{d}t = k_\mathrm{p}\cdot[\mathrm{Co(edma)}^+]\cdot[\mathrm{H_2PO_4}]^-$. On the other hand, the dissociation of the Ni(II)-EDDA complex was found to proceed through a reaction mechanism which involves ligandolysis, corresponding to this rate law: $-\mathrm{d}[\mathrm{Ni(edda)}^0]/\mathrm{d}t = k_0 \times [\mathrm{Ni(edda)}^0]$. On the basis of the relative rate constant, the detailed reaction mechanism was discussed. In the dissociation of the Co(II)-EDMA complex, the phosphate anion acts just as a proton donor. In the case of the Ni(II)-EDDA complex, the ligandolysis of the coordinated water has a profound effect on the dissociation rate of the edda^{2-} anion from the nickel(II) ion.

Previously,[1] the present author determined the detailed dissociation mechanisms of the aspartate, iminodiacetate, and 2,2′-ethylenedioxydi(ethylamine)-*N*,*N*,*N*′,*N*′-tetraacetate complexes of cobalt(II) by studying the nature of the kinetic waves they gave. The Co(II)-EDMA complex in a phosphate buffer solution and the Ni(II)-EDDA complex in an ethylenediaminediacetate (EDDA) solution also gave kinetic waves due to their dissociations at the electrode surface. In this paper, the present author will study their dissociation reactions by examining the nature of the kinetic waves. The effect of the phosphate anion on the dissociation of the Co(II)-EDMA complex, and that of the ligandolysis of the coordinated water on the dissociation rate of Ni(II)-EDDA complex, will also be discussed.

Experimental

Reagents. The procedure used to prepare the standard nickel(II) and cobalt(II) nitrate solutions was described previously.[2] The preparation and purification of the acid form of EDMA were also given in a previous paper.[3] All the other chemicals used were of analytical reagent-grades and were used without further purification.

Apparatus and Experimental Procedures. All the polarographs used for the measurement of the DC current-voltage curves have been described previously.[2] The characteristic feature of the DME used in this study has also been described previously.[4] All the other apparatus and the experimental procedures employed have also been described previously.[2] The ionic strength of the sample solution was adjusted to 0.30 by adding an appropriate amount of pure sodium perchlorate. For the Co(II)-EDMA system, a phosphate buffer solution was used. In the case of the Ni(II)-EDDA system, no buffer reagent was used, because the sample solutions always contained a large excess of uncomplexed EDDA and had a sufficient buffer capacity ($5.40 < \mathrm{pH} < 7.20$).

Results and Discussion

The Co(II)-EDMA complex in a phosphate buffer solution containing an excess of ethylenediaminemonoacetate (EDMA) gave a single wave which is kinetically-controlled in nature. From the effects of the solution pH and the concentration of the uncomplexed EDMA, $[\mathrm{X}]_\mathrm{f}$, on the limiting current, i_k, the kinetic wave can be ascribed to the dissociation of the Co(II)-EDMA complex at the electrode surface. As in the case of the aminopolycarboxylate complexes of cobalt(II),[1] the reaction mechanism was investigated with the aid of the relation employed by Koryta in his polarographic study of the dissociation of the nitrilotriacetate complex of cadmium(II).[5] As is shown by the results in Fig. 1, at given concentrations of uncomplexed EDMA, $[\mathrm{X}]_\mathrm{f}$, and phosphate, $[\mathrm{P}]_\mathrm{f}$, the plot of $i_\mathrm{k}/(i_\mathrm{d}-i_\mathrm{k})$ against $[\mathrm{H}^+]\cdot(\alpha_\mathrm{H})_\mathrm{X}{}^{1/2}/(\alpha_\mathrm{H})_\mathrm{P}{}^{1/2}\cdot(1+K_2\cdot[\mathrm{X}]_\mathrm{f}/(\alpha_\mathrm{H})_\mathrm{X})$ invariably gave a linear relation passing through the point of origin. Furthermore, the plot of $i_\mathrm{k}/(i_\mathrm{d}-i_\mathrm{k})$ against $[\mathrm{H}^+]\cdot(\alpha_\mathrm{H})_\mathrm{X}{}^{1/2}/(\alpha_\mathrm{H})_\mathrm{P}{}^{1/2}\cdot(1+K_2\cdot[\mathrm{X}]_\mathrm{f}/(\alpha_\mathrm{H})_\mathrm{X})\cdot[\mathrm{X}]_\mathrm{f}{}^{1/2}$ also gave a straight line passing through the point of origin (Fig. 1). Here, $(\alpha_\mathrm{H})_\mathrm{X}$ and $(\alpha_\mathrm{H})_\mathrm{P}$

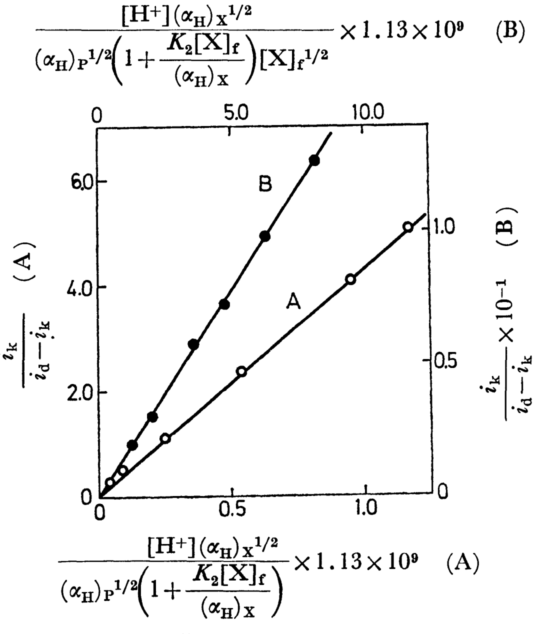

Fig. 1. The plot diagrams of $i_\mathrm{k}/(i_\mathrm{d}-i_\mathrm{k})$ against $[\mathrm{H}^+]\cdot(\alpha_\mathrm{H})_\mathrm{X}{}^{1/2}/(\alpha_\mathrm{H})_\mathrm{P}{}^{1/2}\cdot(1+K_2\cdot[\mathrm{X}]_\mathrm{f}/(\alpha_\mathrm{H})_\mathrm{X})$ (A) and of that against $[\mathrm{H}^+]\cdot(\alpha_\mathrm{H})_\mathrm{X}{}^{1/2}/(\alpha_\mathrm{H})_\mathrm{P}{}^{1/2}\cdot(1+K_2\cdot[\mathrm{X}]_\mathrm{f}/(\alpha_\mathrm{H})_\mathrm{X})\cdot[\mathrm{X}]_\mathrm{f}{}^{1/2}$ (B)

$\mu = 0.3$, 25 °C

$[\mathrm{Co(II)}] = 0.74\ \mathrm{mM}$, $[\mathrm{P}]_\mathrm{f} = 47.3\ \mathrm{M}$

(A) $[\mathrm{edma}]_\mathrm{f} = 46.3\ \mathrm{mM}$

The pH ranged from 7.00 to 8.00.

(B) $[\mathrm{edma}]_\mathrm{f}$ ranged from 15 to 6.0 mM

Table 1. The phosphate anion effect on the $i_k/(i_d-i_k)$ ratio

$\mu=0.30$, 25 °C, pH=7.38

$[\text{edma}]_f=46.3$ mM, $[\text{Co(II)}]=0.74$ mM

$[\text{P}]_f$, mM	$\dfrac{i_k}{i_d-i_k}$	$\dfrac{i_k}{i_d-i_k}\cdot\dfrac{1}{[\text{P}]_f^{1/2}}$
46.3	2.36	11.0
92.6	3.35	10.9
138.9	4.10	11.0

are the (α_H) values of EDMA[6] and phosphoric acid respectively, and K_2, the second successive formation constant of the Co(II)-EDMA complex. When the other experimental conditions are kept constant, the $i_k/(i_d-i_k)$ value divided by $[\text{P}]_f^{1/2}$ was almost independent of the concentration of phosphate, $[\text{P}]_f$, (Table 1). Taking into consideration the fact that the cobalt(II) ions do not form a stable complex with the phosphate anion under the usual experimental conditions, the above facts suggest that the following reaction mechanism may operate for the kinetic wave of the Co(II)-EDMA system:

$CoX_2^0 = CoX^+ + X^-$ in a rapid equilibrium

$CoX^+ + H_2PO_4^- \overset{k_p}{=} Co^{2+} + HX^0 + HPO_4^{2-}$ rate-determining step

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

$X^- = \text{edma}^-$

corresponding to Relation (1):

$$\frac{i_k}{i_d-i_k}=0.886\cdot\sqrt{\frac{k_p\cdot t\cdot[\text{H}^+]^2\cdot(\alpha_H)_X\cdot[\text{P}]_f}{K_{CoX}\cdot(\alpha_H)_P\cdot K_2{}^P\cdot K_3{}^P\cdot[\text{X}]_f}}\;\frac{1}{1+\dfrac{K_2\cdot[\text{X}]_f}{(\alpha_H)_X}} \tag{1}$$

where K_{CoX} ($10^{8.30}$) is the formation constant of the 1 : 1-ratio Co(II)-EDMA complex and $K_2{}^P$ and $K_3{}^P$, the second and third dissociation constants of phosphoric acid.[7] The k_p value was determined from the slope of straight line (A) given in Fig. 1; it is listed in Table 2. This value agreed well with that determined from the slope of the straight line (B) in Fig. 1, lending strong support to the above explanation.

Table 2. Dissociation rate constants

$\mu=0.30$, 25 °C

System	Rata constant
Co(II)-EDMA	$k_p=10^{8.33}$ ($M^{-1}s^{-1}$)
Ni(II)-EDDA	$k_0=10^{9.0}$ (s^{-1})

In the case of the Ni(II)-EDDA complex, the plot of $i_k/(i_d-i_k)$ against $(\alpha_H)_X{}^{1/2}$ $[\text{H}^+]^{-1/2}$ (at a given concentration of uncomplexed EDDA, $[\text{X}]_f$) or $(\alpha_H)_X{}^{1/2}/[\text{H}^+]^{1/2}\cdot[\text{X}]_f^{1/2}$ yielded a straight line passing through the point of origin (Fig. 2). Here, $(\alpha_H)_X$ means the (α_H) value of EDDA. Since the edda^{2-} anion forms only a 1 : 1-ratio complex with the nickel(II) ion, the above finding evidently implies that the reaction mechanism for the kinetic wave of the Ni(II)-EDDA system can be formulated as,

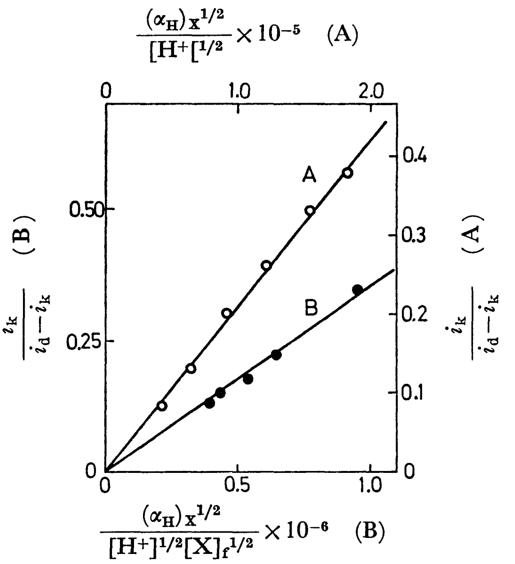

Fig. 2. The plot diagrams of $i_k/(i_d-i_k)$ against $(\alpha_H)_X{}^{1/2}/[\text{H}^+]^{1/2}$ (A) and of that against $(\alpha_H)_X{}^{1/2}/[\text{H}^+]^{1/2}\cdot[\text{X}]_f^{1/2}$ (B)
$\mu=0.30$, 25 °C
$[\text{Ni(II)}]=1.0$ mM
(A) $[\text{edda}]_f=30$ mM
The pH ranged from 5.20 to 6.50.
(B) $[\text{edda}]_f$ ranged from 10 to 50 mM.

$NiX^0 \overset{k_0}{=} Ni(OH)^+ + HX^-$ rate-determining step

$Ni(OH)^+ + Hg + 2e^- = Ni(Hg) + OH^-$

corresponding to Relation (2):

$$\frac{i_k}{i_d-i_k}=0.886\cdot\sqrt{\frac{k_0\cdot t\cdot(\alpha_H)_X\cdot K_{Ni(OH)}\cdot K_W}{K_{NiX}\cdot[\text{H}^+]\cdot[\text{X}]_f}} \tag{2}$$

where $K_{Ni(OH)}$ and K_{NiX}[7] are, respectively, the formation constants of the 1 : 1-ratio Ni(II)-OH and -EDDA complexes and K_w,[7] the ion product of water. The k_0 values estimated from the slopes of the straight lines, (A) and (B), in Fig. 2 agreed well with each other. This aggrement also supports the reaction mechanism proposed above. The $K_{Ni(OH)}$ value used in the estimation of k_0 was evaluated with the aid of this relation: $\log K_{Ni(OH)}=pK_w-pK^*$.[7]

Previously,[6] the present author reported that the Ni(II)-EDMA complex dissociates through the ethylenediamine-reaction intermediate. Since the cobalt(II) complex shows a kinetic behavior similar to that of the nickel(II) complex, it is not unreasonable to consider that the cobalt(II)-EDMA complex also dissociates through the ethylenediamine-reaction intermediate, by analogy with this. If the cobalt(II)-EDMA complex dissociates through the ethylenediamine-recation intermediate, the dissociation rate constant should be 10.0. This value was calculated by using the relation: $k=k_{rds}\cdot K_{Co\text{-}En}\cdot K_{st}\cdot K_{elec}/K_{CoX}$[6] and the k_{rds} estimated from the dissociation rate constant of a 1 : 1-ratio cobalt(II)-ammine complex[8] by making the correction for the rotational barrier around to C–N or C–C bond.[9] Here, $K_{Co\text{-}En}$ means the formation constant of a 1 : 1-ratio cobalt(II)-ethylenediamine complex. The observed rate constant, k_p, was $10^{7.30}$ times larger than that calculated. Previously,[10] Tanaka *et al.* determined the rate constants of direct and proton-assisted dissociations of the cobalt(II)-EDTA complex. The rate constant for the proton-assisted dissociation is about $10^{7.0}$ times larger than that for the direct dissociation. Therefore, in view of the fact that the pK_2 value of EDMA is nearly identical with the pK_3 value of EDTA,7) the fact that the k_0 value is $10^{7.30}$ times larger than the rate constant calculated on the basis of a simple ethylenediamine mechanism means that the $H_2PO_4^-$ anion acts just as a proton donor in the dissociation of the cobalt(II)-EDMA complex. This is also in full accord with the fact that the cobalt(II) ions do not form a stable complex with a phosphate anion.

The formation rate constant, k_f, of the 1 : 1-ratio Ni(II)-EDDA complex from $Ni(OH)^+$ and the $Hedda^-$ anion was estimated to be $10^{3.84}$ by employing the $k_f/k_0=K_{NiX}\cdot K_2/K_w\cdot K_{Ni(OH)}$ relation, and the k_0 value of $10.^{9.0}$ This value is nearly identical with the characteristic water-exchange rate of the aquo nickel(II) ion.11) Since the outer-sphere association constant for the $Ni(OH)^+$—$Hedda^-$ system approximated by the Fuoss equation12) is nearly equal to unity, the above fact means that the formation reaction of the 1 : 1-ratio complex, $Ni(edda)^0$, from $Ni(OH)^+$ and the $Hedda^-$ anion proceeds through a reaction mechanism in which the outer-sphere association between $Ni(OH)^+$ and $Hedda^-$ and the proton transfer from $Hedda^-$ to $Ni(OH)^+$ to give Ni^{2+} proceed verys rapidly; then, the slow dissociation of the coordinated water molecule from the nickel(II) ion is followed by the rapid formation of the Ni(II)-EDDA bond. The k_0 value determined in this study is much larger than the rate constant estimated on the basis of a simple ethylenediamine-reaction intermediate. This suggests that the ligandolysis of the coordinated water plays an important role in determining the dissociation rate of the nickel(II)-EDDA complex. That is to say, the hydroxide anion and the proton formed upon the dissociation of the coordinated water will effectively assist the dissociation of the $edda^{2-}$ anion from the nickel(II).

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