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A Polarographic Study of the Rates of the Dissociation Reactions of Nickel(II)-Ethylenediaminemonoacetate and -*N*-(2-Hydroxyethyl)ethylenediamine Complexes

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In a previous paper,[1] we studied the dissociation reactions of nickel(II)- and cobalt(II)-acetylacetonate complexes and of nickel(II)-glutamate, -aspartate, and -iminodiacetate complexes by investigating systematically the nature of the kinetic currents due to their dissociation at the electrode surface; we also determined their rate constants. The nickel(II) ions in ethylenediaminemonoacetate (EDMA) and *N*-(2-hydroxyethyl)ethylenediamine (EtEN) solutions also gave the kinetic waves due to the dissociation of the nickel(II)-EDMA and -EtEN complexes at the electrode surface preceding the electron-transfer step. In this investigation, we also studied thoroughly the nature of the kinetic waves of nickel(II)-EDMA and -EtEN complexes and determined the dissociation mechanism and their dissociation rate constants. The detailed structure of reaction intermediate was also determined.

Experimental

Reagents. The EDMA was prepared by the method of Fujii, Kyuno, and Tsuchiya.[2] The way of preparing the standard nickel(II) nitrate solution was also described in a previous paper.[3] The EtEN was purified by distillation under reduced pressure. The other chemicals used were of analytical reagent grade and were used without further purification.

Apparatus and Experimental Procedures. All the apparatus and the experimental procedures employed in this study were the same as those described in the previous paper.[1] In the present study, no buffer reagent was used, because all the sample solutions always contained an appreciable amount of uncomplexed EDMA or EtEN.

Results and Discussion

As in the cases of nickel(II) ions in acetylacetonate, glutamate, aspartate, and iminodiacetate solutions,[1] the nickel(II) ions in EDMA and EtEN solutions also exhibited the reduction waves corresponding to the reduction of the nickel(II) ion, which are kinetic-controlled in nature (the first waves). The second waves can be ascribed to the direct reduction of the nickel(II) complexes of EDMA and EtEN. In both EDMA and EtEN systems, the total wave-height was almost constant under the present experimental conditions. The log-plot examination for the first waves of nickel(II)-EDMA and -EtEN complexes gave straight lines with reciprocal slopes of about 60 and 72 mV respectively, corresponding to the two-electron irreversible reduction. Provided that the other experimental conditions are kept constant, the plot of the reciprocal of the limiting current for the first wave, i_l^{-1}, against the $(1+K_2'[X]_f)[X]_f^{1/2}$ or $(1+K_2'[X]_f)/(\alpha_H)_x^{1/2}$ value invariably gave the linear relation. However, the plot of i_l^{-1} against $(1+K_2'[X]_f)/(\alpha_H)_x^{1/2}[H^+]^{1/2}$ did not give a straight line in either system. Typical examples are shown in Fig. 1. Here, K_2' denotes the conditional

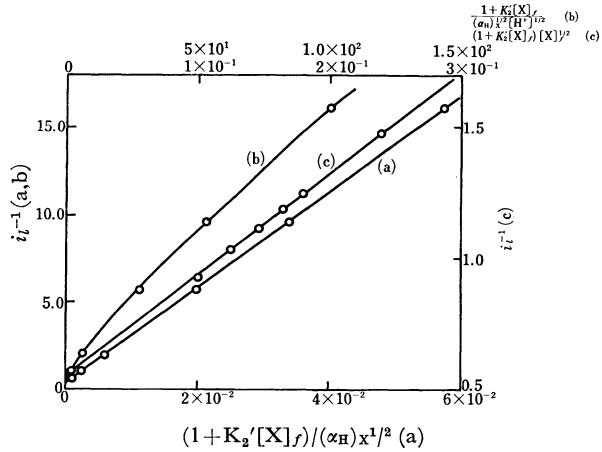

Fig. 1. The plot of $1/i_l$ against $(1+K_2'[X]_f)/(\alpha_H)x^{1/2}$, $(1+K_2'[X]_f)/(\alpha_H)x^{1/2}\cdot[H^+]^{1/2}$, or $(1+K_2'[X]_f)[X]_f^{1/2}$
The concentration of nickel(II) ion=1.0 mM 25.0°C
a) i_l^{-1} *vs.* $(1+K_2'[X]_f)/(\alpha_H)x^{1/2}$ plot
The concentration of uncomplexed EDMA=25.0 mM
b) i_l^{-1} *vs.* $(1+K_2'[X]_f)/(\alpha_H)x^{1/2}\cdot[H^+]^{1/2}$ plot
The concentration of uncomplexed EDMA=25.0 mM
c) i_l^{-1} *vs.* $(1+K_2'[X]_f)\cdot[X]_f^{1/2}$ plot
pH=5.40

second formation constant of the nickel(II)-EDMA or -EtEN complex; $[X]_f$, the concentration of uncomplexed EDMA or EtEN, and $(\alpha_H)_x$, the (α_H) value of EDMA or EtEN, defined as $1+[H^+]/K_n+[H^+]^2/K_nK_{n-1}+\cdots$. Furthermore, in both EDMA and EtEN systems, the plots of the half-wave potential against-log $[X]_f$ or log $(\alpha_H)_x$ gave straight lines, the slopes of which were 30 and 37 mV respectively. As was discussed previously,[1] these facts indicate that the electrode reaction for the first waves observed in nickel(II)-EDMA and -EtEN complexes can be expressed as:

$$NiX_2^{2-2m} \rightleftharpoons NiX^{2-m} + X^{m-} \quad \text{rapid}$$

$$NiX^{2-m} \underset{k_d}{\rightleftharpoons} Ni^{2+} + X^{m-} \quad \text{slow}$$

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

where X^{m-} means the completely-deprotonated EDMA

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2) Y. Fujii, E. Kyuno, and R. Tsuchiya, *ibid.*, **43**, 786 (1970).
3) M. Kodama, *ibid.*, **42**, 2532 (1969).

Table 1. Dissociation rate constants (μ=0.20, 25°C) and formation constants

i) Dissociation rate constants	
System	k_d, sec^{-1}
Nickel(II)-*N*-(2-hydroxyethyl)-ethylenediamine complex	0.20
Nickesl(II)-ethyleledíaminemono-acetate complex	$2.4_4\times10^{-4}$
ii) Formation constants (μ=0.20)	
System	log K_{MX}
Nickel(II)-*N*-(2-hydroxyethyl)-ethylenediamine complex	6.66[9]
Nickel(II)-ethylenediaminemono-acetate complex	10.40[8]

anion or EtEN. From the slopes of the linear relation between the i_l^{-1} value and the $(1+K_2'[X]_f)[X]_f^{1/2}$ or $(1+K_2'[X]_f)/(\alpha_H)_x^{1/2}$ value obtained by using Eq. (10_a) in Ref. 1, the dissociation rate constants, k_d's, were determined (Table 1).

The k_d value for the nickel(II)-EtEN complex is nearly equal to the rate constant for the breakage of a nickel(II)-nitrogen bond, which forms part of a five-membered chelate ring in which both ends of the chelate are amino nitrogen atoms.[4] This fact evidently implies that, in the dissociation of a 1:1 nickel-(II)-EtEN complex, the bond breakage of the first nitrogen is the rate-determining step, and that the hydroxyethyl group in the EtEN has little effect on the rate of dissociation of the nickel(II)-EtEN complex.

In the dissociation of the nickel(II)-EDMA complex, it is very hard to believe that all three nickel(II)-EDMA bond breakages are involved in the rate-determining step. Therefore, the dissociation may proceed through one of the three reaction intermediates shown in Fig. 2. The reaction intermediate where the leaving EDMA anion is bonded to the nickel(II) ion through an acetate group can be eliminated, because the nickel-oxygen bond rupture is much faster than the nickel-nitrogen bond rupture.[5] As was discussed in the previous paper,[1] by relating the observed rate constant to the rate constant calculated on the basis of the proposed reaction intermediate, we determined the correct reaction intermediate. The rate constants calculated on the basis of the reaction intermediates in Fig. 2 by using the following relation are given in Table 2. Here, K_{MX} is the formation constant of the nickel(II)-EDMA complex with a 1:1 ratio; k_{rds},[4,6,7] the rate constant for

$$k_d = \frac{K_{int}}{K_{MX}} k_{rds}$$

the rate-determining step, and $K_{int.}$, the stability constant of the reaction intermediate prior to the rate-determining step. In the calculation, the electrostatic contribution to the stability of the reaction intermediate was also taken into consideration. The rate constant calculated on the basis of the reaction intermediate I agreed best with the observed one. We have already mentioned that the substitution reaction of the nickel-(II)-EDMA complex with cyclohexane-1,2-diamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (CyDTA) proceeds through the reaction intermediate in which the displaced EDMA anion is bonded to the nickel(II) ion through an ethylenediamine five-membered chelate ring.[8] Therefore, the finding that the dissociation of the nickel(II)-EDMA complex proceeds through the reaction intermediate with an ethylenediamine five-membered chelate ring suggests that, in the nucleophilic substitution reaction involving the nickel(II)-EDMA complex, the attacking group just assists the dissociation of the EDMA anion from the nickel(II) ion, without effecting any change in the detailed dissociation mechanism of the nickel(II)-EDMA complex.

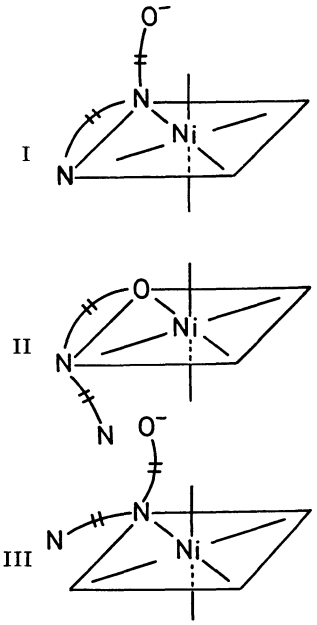

Fig. 2. Reaction intermediates for the dissociation of nickel (II)-EDMA complex

Table 2. The k_d values calculated

Reaction intermediate	k_d
I	4.5×10^{-4}
II	3.7×10^{-6}
III	1.3×10^{-6}

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