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Solution Equilibria between the Nickel(II) Ion and the Ethylenediaminetetrepropionate Ion and the Substitution Kinetics of the Nickel(II)-Ethylenediaminetetrapropionate Complex with Cyclohexane-1,2-*N*,*N*,*N*′,*N*′,-tetraacetic Acid (CyDTA)

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In the polarographic determination of solution equilibria between ethylenediaminetetrapropionic acid (EDTP) and the cadmium(II) ion,[1] we have previously mentioned that the cadmium(II) ion can form 1 : 1 as well as 1 : 2 complexes with EDTP. The nickel(II) ion in the EDTP solution gives an absorption curve with two maxima at around 375 and 600 mμ. With an increase in both the pH value and the EDTP concentration, the absorbance increases remarkably and the absorption maxima shift to shorter wavelengths. These facts can be interpreted as resulting from the formation of the 1 : 2 nickel(II)-EDTP complex. Furthermore, the nickel(II) ion in solutions containing an excess amount of EDTP has been found to react with CyDTA at a measurable rate. In this paper, the author will attempt to estimate the second successive formation constant of the nickel(II)-EDTP complex by determining the change in the absorbance with an increase in the pH, and to analyze polarographically the kinetics of the nucleophilic substitution reaction between the nickel(II)-EDTP complex and CyDTA. He hopes to show that, by analyzing the formation of the 1 : 2 nickel(II)-EDTP complex, we can understand the kinetic behavior of the nickel(II)-EDTP complex in a substitution reaction.

Experimental

Reagents. The preparation of a standard nickel(II) nitrate solution had been described in a previous paper.[2] The EDTP and CyDTA were recrystallized twice from their aqueous solutions by adding an appropriate amount of pure ethanol. The other chemicals were of analytical reagent grades and were used without further purification.[2,3]

Apparatus and Experimental Procedures. All the apparatus (the penrecording spectrophotometer and polarograph, and the dropping-mercury electrode(DME) and the experimental procedures used in this study have been described previously.[2,3] The rate of the substitution reaction was determined by measuring changgs over a period of time in the diffusion current due to the presence of uncomplexed CyDTA. In this study, all the measurements were carried out in solutions with an ionic strength of 0.30 ($NaClO_4$) at 25°C. Kinetic measurements were conducted in solutions containing excess amounts of complexed and uncomplexed EDTP over CyDTA in the pH range from 8.50 to 9.50. Therefore, no buffer reagent is needed to keep the pH constant, and the substitution reaction can be treated as a pseudo first-order reaction.

Results and Discussion

Spectrophotometric Determination of Solution Equilibria between the Nickel(II) Ion and the Ethylenediaminetetrapropionate Anion. From observing the magnitude of both the stability constant of a 1 : 1 nickel(II)-EDTP complex and the p*K* values of EDTP,[4] it can safely be concluded that the complexation reaction of the nickel(II) ion in 10 mM EDTP solutions with pH's higher than 5.0 proceeds completely. As has been reported previously,[5] the nickel(II) ion in the EDTP solution gives an absorption curve with two maxima, at 375 and 600 mμ. By increasing the solution's pH value and the concentration of the uncomplexed EDTP, the absorbance in the visible region was increased remarkably and both the maxima shifted to shorter wavelengths. This fact may be interpreted as resulting from the formation of the 1 : 2 nickel(II)-EDTP complex. As has been discussed in a previous paper,[6] if the nickel(II) ion forms 1 : 1 as well as 1 : 2 complexes with EDTP, the following relation can be applied to the present system:

$$\log\frac{K_2}{(\alpha_H)_X}=\log\frac{A-A_{NiX}}{A_{NiX_2}-A}\times\frac{1}{\left([X]_t-2\cdot[Ni]_t+\dfrac{A_{NiX}-A}{\varepsilon_{NiX_2}-\varepsilon_{NiX}}\right)}\qquad(1)$$

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[1] M. Kodama and Y. Tominaga, This Bulletin, **42**, 2267 (1969).

[2] M. Kodama, *ibid.*, **42**, 2532 (1969).

[3] M. Kodama and H. Ebine, *ibid.*, **40**, 1857 (1967).

[4] L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," 2nd Ed., The Chemical Society, London (1964), p. 696.

[5] M. Kodama and K. Miyamoto, This Bulletin, **42**, 1596 (1969).

[6] M. Kodama, Y. Fujii and T. Ueda, *ibid.*, **43**, 2085 (1970).

where:

K_2 = the second successive formation constant of the nickel(II)-EDTP complex

$$(\alpha_H)_X = 1 + \frac{[H^+]}{K_4} + \frac{[H^+]^2}{K_4 \cdot K_3} + \frac{[H^+]^3}{K_4 \cdot K_3 \cdot K_2} + \frac{[H^+]^4}{K_4 \cdot K_3 \cdot K_2 \cdot K_1},$$

K's = dissociation constants of EDTP,
$[X]_t$ = the total concentration of EDTP,
$[Ni]_t$ = the total concentration of the nickel(II) ion,
A_{NiX_2} = the absorbance for the solution where all the nickel(II) ions exist in the form of NiX_2^{6-},
A_{NiX} = the absorbance for the solution where all the nickel(II) ions exist in the form of NiX^{2-},
A = the absorbance of each of the solutions ($= \varepsilon_{NiX}[NiX^{2-}] + \varepsilon_{NiX_2}[NiX_2^{6-}]$),
ε's = the molar extinction coefficients.

The molar extinction coefficient for the 1 : 2 complex, ε_{NiX_2}, is much larger than that for the 1 : 1 complex, ε_{NiX}. This fact clearly shows that the EDTP anions in the 1 : 2 complex are coordinated to the nickel(II) ion through nitrogen. Equation (1) suggests that the plot of the right-hand side against log $(\alpha_H)_X$ will give a straight line with a slope of -1.0 and that the log $(\alpha_H)_X$ value at log $[(A-A_{NiX})/[(A_{NiX_2}-A)([X]_t-2[Ni]_t+(A_{NiX}-A)/(\varepsilon_{NiX_2}-\varepsilon_{NiX}))]]$ = zero can be equated with the log K_2 value. By means of this equation, the experimental data were analyzed successfully. The results are given in Fig. 1. From the intercept of the straight line, the log K_2 value was estimated to be 3.5_2.

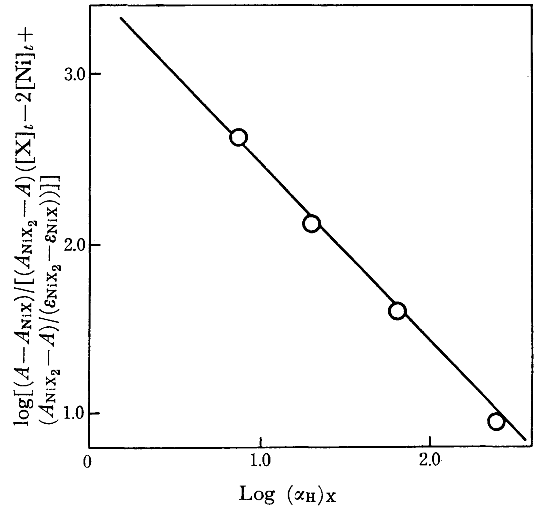

Fig. 1. The plot of $\log[(A-A_{NiX})/[(A_{NiX_2}-A)([X]_t-2[Ni]_t+(A_{NiX_2}-A)/(\varepsilon_{NiX_2}-\varepsilon_{NiX}))]]$ against log $(\alpha_H)_X$.
Total concentration of EDTP=40.0 mM
Concentration of nickel(II) ion=18.56 mM
25°C, μ=0.30

The Kinetic Study of the Substitution Reaction of the Nickel(II)-EDTP Complex with CyDTA. The CyDTA anion can displace the EDTP anion from its nickel(II) complex at a measurable rate. The present substitution reaction showed just the same kinetic behavior as that observed in the reaction of the nickel(II)-nitrilotriacetate complex with diethylenetriaminepentaacetic acid (DTPA).$^{2)}$ The plot of log (i_0/i_t) against the time, t, invariably gave a straight line passing through the point of origin. Here, i_0 and i_t denote the wave heights of CyDTA at time $t=0$ and $t=t$ respectively. The slope of the above log-plot was independent of the initial concentration of CyDTA and was not influenced by the addition of the nickel(II)-CyDTA complex (the results are not shown). These facts clearly indicate that: (i) The rate of the backward reaction is negligibly small as compared with that of the forward reaction; (ii) the log-plot slope multiplied by 2.303 is equal to the apparent rate constant for the forward reaction, k_{ap}^{+},$^{2)}$ and (iii) the present reaction does not involve the dissociation of the nickel(II)-EDTP complex. In the solutions with constant pH's, the log-plot slope was exactly proportional to the concentration of the 1 : 1 complex, $[Ni]_t/(1+K_2 \cdot [X]_f/(\alpha_H)_X)$ (Table 1). This means that the nickel(II) ion forms 1 : 1 as well as 1 : 2 complexes with an EDTP, and that the reaction proceeds exclusively through the 1 : 1 complex. Furthermore, provided that the other experimental conditions are kept constant, the product of the log-plot slope and $2.303\times(\alpha_H)_Z$

Table 1. The relation between the log-plot slope and the concentration of nickel(II)-DETP complex with a 1-to-1 composition
25°C, μ=0.30, pH=9.00
Initial cocentration of CyDTA=0.50 mM

Ni(II) ion concentration mM	EDTP concentration mM	Concentration of 1-to-1 ratio Ni(II)-EDTP complex, C_{NiX} mM	Log-plot slope, S sec^{-1}	S/C_{NiX}
5.00	35.0	1.87×10^{-1}	1.91×10^{-4}	1.02×10^{-3}
8.00	25.0	7.00×10^{-1}	7.00×10^{-4}	1.00×10^{-3}
10.00	40.0	4.38×10^{-1}	4.67×10^{-4}	1.07×10^{-3}
14.00	35.0	1.35	1.40×10^{-3}	1.04×10^{-3}

$(1+K_2\cdot[\mathrm{X}]_f/(\alpha_{\mathrm{H}})_{\mathrm{X}})/[\mathrm{Ni}]_t$ is a linear function of the hydrogen-ion concentration and can be given by:

$$\frac{k_{ap}^{+}\cdot(\alpha_{\mathrm{H}})_{\mathrm{Z}}(1+K_2\cdot[\mathrm{X}]_f/(\alpha_{\mathrm{H}})_{\mathrm{X}})}{[\mathrm{Ni}]_t} = k_{\alpha}^{+} + k_{\beta}^{+}\cdot[\mathrm{H}^+] \qquad (2)$$

were $(\alpha_{\mathrm{H}})_{\mathrm{Z}}$ is the (α_{H}) value of CyDTA. Therefore, the present reaction can be concluded to proceed through the following two simultaneous reaction pathways:

$$\begin{tikzcd} \text{i)}\quad \mathrm{NiX^{2-}} + \mathrm{Z^{4-}} \arrow[r, shift left, "k_1^+"] \arrow[d, shift left, "\text{rapid}"] & \mathrm{NiZ^{2-}} + \mathrm{X^{4-}} \arrow[l, shift left] \\ \mathrm{NiX_2^{6-}} \arrow[u, shift left] & \end{tikzcd}$$

$$\begin{tikzcd} \text{ii)}\quad \mathrm{NiX^{2-}} + \mathrm{HZ^{3-}} \arrow[r, shift left, "k_2^+"] \arrow[d, shift left, "\text{rapid}"] & \mathrm{NiZ^{2-}} + \mathrm{HX^{3-}} \arrow[l, shift left] \\ \mathrm{NiX_2^{6-}} \arrow[u, shift left] & \end{tikzcd}$$

where $\mathrm{NiX_2^{6-}}$ means the 1 : 2 nickel(II)-EDTP complex, and $\mathrm{Z^{4-}}$, the completelydeprotonated CyDTA anion. Here, k_1^+ can be equated with k_α^+ and k_2^+, with the product of k_β^+ and the fourth dissociation constant of CyDTA, k_4. As was discussed with reference to the reaction of the nickel(II)-nitrilotriacetate complex with DTPA,[2] the k_1^+ and k_2^+ values in the above reaction mechanism can be determined from the intercept and the slope respectively of the straight line in Fig. 2. The k_1^+ and k_2^+ values obtained are listed in Table 2, together with the K_2 value determined spectrophotometrically. In the kinetic study of the substitution reactions of the nickel(II)-aspartate complex with CyDTA and DTPA,[7] we have previously mentioned that the six-membered ring in the nickel(II)-aspartate complex is much more substitutionlabile than the five-membered ring. Generally, the nickel(II)-oxygen bond rupture is much faster than the nickel(II)-nitrogen bond rupture. Therefore, in the substitution reaction of the nickel(II)-EDTP complex, a reaction intermediate (activated complex) having a propionate group bonded to the nickel(II) ion seems unlikely. If the present reaction proceeds through a reaction intermediate similar to that of the reaction of the nickel(II)-ethylenediamine complex with CyDTA,[6] a comparison of the rate constants for the two elementary reactions, i) and ii), with those of the reaction of the nickel(II)-ethylenediamine complex is possible. On the basis of the reaction intermediate having two nitrogen groups of EDTP or of ethylenediamine bonded to the nickel(II) ion, the k_1^+ and k_2^+ ratios between the reactions of EDTP and ethylenediamine complexes can be estimated to be $1/53._6$. When the additional stability of the reaction intermediate due to the electrostatic attraction between the nickel(II) ion and the propionate group is taken into consideration, the rate constant ratios should be larger than $1/53._6$. The observed ratios for the two elementary reactions, i) and ii), were $1/3.3\times10^2$ and $1/1.1\times10^4$ respectively. This disagreement may imply that the reaction of the nickel(II)-EDTP complex proceeds through a reaction intermediate quite different from that of the nickel(II)-ethylenediamine complex or that, although both reactions have the same reaction intermediate, the electrostatic repulsion between the nickel(II)-EDTP complex anion and the CyDTA anion makes the reaction more sluggish.

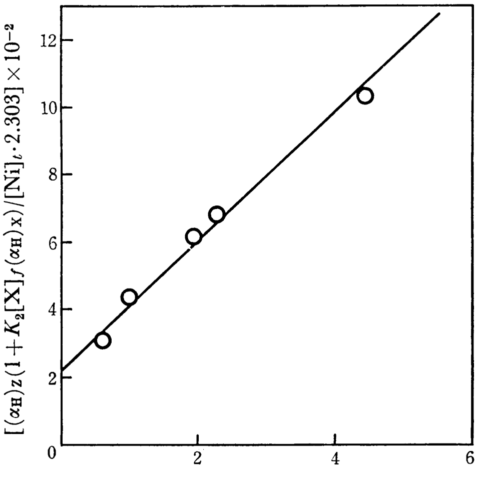

Fig. 2. The plot of k_{ap}^{+} $(\alpha_{\mathrm{H}})_{\mathrm{Z}}(1+K_2[\mathrm{X}]_f/(\alpha_{\mathrm{H}})_{\mathrm{X}})/2.303[\mathrm{Ni}]_t$ against the hydrogen ion concentration.
Total concentration of EDTP=25.0 mM
Concentration of nickel(II) ion=8.00 mM
Initial concentration of CyDTA=0.50 mM
25°C, μ=0.30

Table 2. Formation constant and rate constans
25°C, μ=0.30

i) Second successive formation constant of the nickel(II)-EDTP compelx, K_2
$K_2 = 3.31\times10^3$

ii) Rate constants ($\mathrm{M^{-1}\cdot sec^{-1}}$)
Reaction pathway i): $k_1^+ = 2.2\times10^2$
Reaction pathway ii): $k_2^+ = 9.45\times10^{-1}$

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[7] M. Kodama and T. Ueda, This Bulletin, **43**, 419 (1970).