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The Kinetics of the Ligand-substitution Reactions of Nitrilo(diacetic)-propionato- and Nitrilo(diacetic)isopropionatoniccolate(II) Ions with EDTA, and of Taurin-*N*-diacetatoniccolate(II) Ions with EDTA and CyDTA

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The kinetics of the reactions of nickel(II)-nitrilo(diacetic)propionate (NDAP) and nickel(II)-nitrilo(diacetic)isopropionate (NDAIP) complexes with ethylenediaminetetraacetate (EDTA) ions, and those of the nickel(II)-taurin-*N*-diacetate (TDA) complex with EDTA and *trans*-1,2-cyclohexanediaminetetraacetate (CyDTA) ions, have been studied polarographically in solutions with pH 4.8—6.0 at 25°C and at an ionic strength of 0.2. All the reactions except those with CyDTA proceeded through four reaction paths, and the rate constants for the reaction paths were determined. The reaction of the nickel(II)-TDA complex with CyDTA was found to proceed only through the complete dissociation of the Ni(II)-TDA complex. There was not a direct reaction of the complex with CyDTA. Consequently, the overall reaction with CyDTA became much slower than that of the same complex with EDTA. The rate constants obtained were compared with those of the similar reactions of the nickel(II)-nitrilotriacetate (NTA) complex with EDTA and CyTDA which had been reported previously. The rate of the dissociation reaction of nickel(II) complexes increased in the order: NDAIP$\leq$NDAP$<$NTA$<$TDA. Especially, the rate of the Ni(II)-TDA complex was about 30 times that of Ni(II)-NTA complex.

The metal-chelating tendencies of the chelating agents, nitrilo(diacetic)propionic acid (NDAP) and taurin-*N*-diacetic acid (TDA), which are resulted from the substitution of one acetate group in nitrilotriacetic acid (NTA) have been extensively investigated.[1-3] Recently, a new agent, nitrilo(diacetic)-isopropionic acid (NDAIP) was synthesized by Uehara *et al.*[3] In previous studies,[4,5] the kinetics of the reaction of the nickel(II)-NTA complex with ethylenediaminetetraacetate (EDTA) ions, *N*-hydroxyethylethylenediaminetriacetate(HEDTA) ions, and *trans*-1,2-cyclohexanediaminetetraacetate (CyDTA) ions were dealt with. Since it seems important and necessary to extend the study to the investigation of the effect of various ligands on the reaction rate and the mechanism, the reactions of several nickel(II) complexes with EDTA and/or CyDTA were carried out in the present study. The rate constants of the dissociation of the nickel(II) complexes were compared with the metal-chelating tendencies of the chelating agents.

The reaction of the nickel(II)-TDA complex with CyDTA was run for the purpose of determining the rate constant of the dissociation reaction of the nickel complex; this study aimed to determine the rate constants of the ligand-substitution reactions and also those of the dissociation reactions of the nickel complexes. In a previous paper,[4] the kinetics of the reaction of the nickel(II)-NTA complex with CyDTA were dealt with and compared with those of the reaction of the same complex with EDTA. Changes in the reaction mechanism and a large decrease in the overall rate were observed when EDTA was replaced by CyDTA. The reasons for this were discussed in the previous paper.[4]

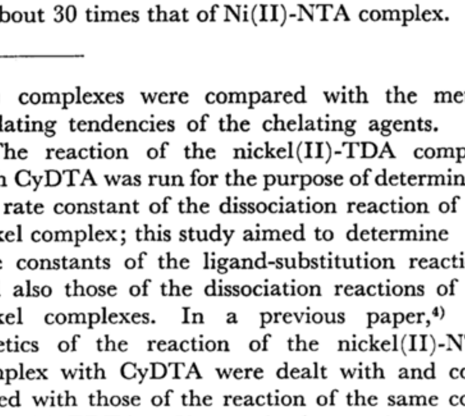

Fig. 1. Structural formulas of the chelating agents.

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[1] G. Schwarzenbach, H. Ackermann and P. Ruckstuhl, *Helv. Chim. Acta*, **42**, 1175 (1949).

[2] S. Chaberek, Jr., and A. E. Martell, *J. Am. Chem. Soc.*, **75**, 2888 (1953).

[3] A. Uehara, E. Kyuno and R. Tsuchiya, This Bulletin, **41**, 2393 (1968).

[4] M. Kimura, *ibid.*, **42**, 2841 (1969).

[5] M. Kimura, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **89**, 1209 (1968).

Experimental

The chelating agents, NDAIP,[3] NDAP[6] and TDA,[7] were prepared by the procedures reported by Uehara *et al.* Uehara's method for the syntheses of NDAP and TDA was a modification of Schwarzenbach's.[1] All the other chemicals and the apparatus used were the same as had been described in previous papers.[4,5] The rate of the reaction was measured by a method which was, in principle, the same as that employed in previous studies.[4,5] The temperature was maintained at 25°C. The ionic strength was adjusted to 0.2 with potassium nitrate.

Results

The overall reaction of Ni(II)-NDAP, Ni(II)-NDAIP, and Ni(II)-TDA complexes with EDTA or CyDTA may be expressed as:

$$\left\{\begin{array}{c}\mathrm{NiX^-}\\ \upharpoonleft\downharpoonright\\ \mathrm{NiHX}\end{array}\right\} + \left\{\begin{array}{c}\mathrm{Y^{4-}}\\ \upharpoonleft\downharpoonright\\ \vdots\\ \upharpoonleft\downharpoonright\\ \mathrm{H_4Y}\end{array}\right\} \overset{V_i^+}{\rightleftharpoons} \left\{\begin{array}{c}\mathrm{NiY^{2-}}\\ \upharpoonleft\downharpoonright\\ \mathrm{NiHY^-}\end{array}\right\} + \left\{\begin{array}{c}\mathrm{X^{3-}}\\ \upharpoonleft\downharpoonright\\ \vdots\\ \upharpoonleft\downharpoonright\\ \mathrm{H_3X}\end{array}\right\} \qquad (1)$$

Where X^{3-} indicates $ndap^{3-}$, $ndaip^{3-}$ and tda^{3-}, which are tervalent anions of NDAP, NDAIP, and TDA respectively, and where Y^{4-} indicates $edta^{4-}$ and $cydta^{4-}$, which are tetravalent anions of EDTA and CyDTA respectively. The concentrations of EDTA and CyDTA that can be determined polarographically are those of the uncomplexed EDTA and CyDTA, which are given by the equation:

$$[\mathrm{EDTA}] = \sum_{j=0}^{4} [\mathrm{H}_j\mathrm{Y}^{(4-j)-}] \qquad (2)$$

(or [CyDTA])

Under the present experimental conditions, all the reactions of Eq. (1) except that of the Ni(II)-TDA complex with EDTA were so sluggish that the initial rate, $-\Delta[\mathrm{EDTA}]_i/\Delta t$ or $-\Delta[\mathrm{CyDTA}]_i/\Delta t$ could be measured accurately (the subscript i indicates the initial state). Two experimental examples of the current-time curve of the reaction of the Ni(II)-TDA complex with EDTA and CyDTA are given in Fig. 2. The initial rates (V_i^+) were obtained under various experimental conditions. The initial rates of the reactions of nickel(II)-NDAP and nickel(II)-NDAIP complexes with EDTA were: (1) independent of the concentration of uncomplexed NDAP or NDAIP (see Table 1); (2) proportional to the initial concentration of the complex, $[\mathrm{Ni}\,ndap^-]_i$ or $[\mathrm{Ni}\,ndaip^-]_i$; (3) linear to the initial concentration of the entering

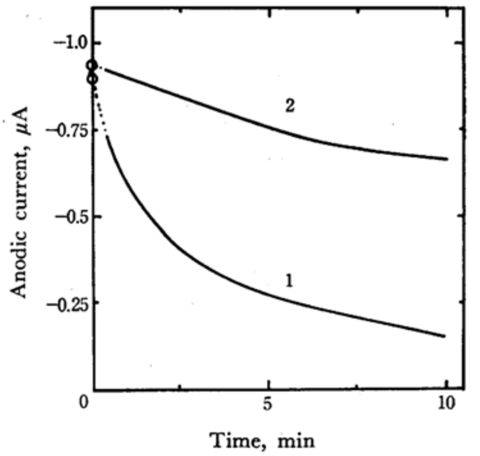

Fig. 2. Limiting current - time relation (at +0.2 V *vs.* SCE at 25°C in acetate buffer - potassium nitrate solution containing 0.04 M acetate and 0.005% gelatin).
Curve 1: the reaction of Ni(II)-TDA complex with EDTA
Curve 2: the reaction of Ni(II)-TDA complex with CyDTA
Initial concentrations are $[\mathrm{Ni}\,tda^-]_i = 2.06\times10^{-4}$ M and $[\mathrm{EDTA}]_i = 1.90\times10^{-4}$ M for curve 1, and $[\mathrm{Ni}\,tda^-]_i = 1.03\times10^{-4}$ M and $[\mathrm{CyDTA}]_i = 2.26\times10^{-4}$ M for curve 2. The pH's of the solutions are (1) pH 5.10 and (2) pH 5.14.

TABLE 1. INITIAL RATES (V_i^+) AT VARIOUS CONCENTRATIONS OF UNCOMPLEXED NDAP AND NDAIP ($\mu = 0.2$, 25°C)*

i) Ni(II)-NDAP reaction system:
Initial concentrations are $[\mathrm{Ni}\,ndap^-]_i = 3.09\times10^{-4}$ M and $[\mathrm{EDTA}]_i = 1.89\times10^{-4}$ M. pH 5.08.

$[\mathrm{NDAP}]_f\times10^4$, M	$V_i^+\times10^8$, M sec^{-1}
0.46	3.56
1.88	3.68
1.30	3.71
4.72	3.67
6.14	3.58
7.56	3.55

ii) Ni(II)-NDAIP reaction system:
Initial concentrations are $[\mathrm{Ni}\,ndaip^-]_i = 2.06\times10^{-4}$ M and $[\mathrm{EDTA}]_i = 1.89\times10^{-4}$ M. pH 5.10.

$[\mathrm{NDAIP}]_f\times10^4$, M	$V_i^+\times10^8$, M sec^{-1}
0.16	1.80
1.05	1.87
1.95	1.77
2.83	1.80
3.71	2.10
5.49	1.81
7.26	1.92

* $[\mathrm{NDAP}]_f$ and $[\mathrm{NDAIP}]_f$ mean the concentrations of uncomplexed NDAP and NDAIP, respectively.

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[6] A. Uehara, E. Kyuno and R. Tsuchiya, This Bulletin, **41**, 2385 (1968).

[7] A. Uehara, E. Kyuno and R. Tsuchiya, presented at the 18th Symposium on Coordination Compounds, Kyoto, Japan, Oct. 1968.

ligand, $[\mathrm{EDTA}]_i$ and $[edta^{4-}]_i$ (see Figs. 3,4 and 5), and (4) in a first- and second-order relation to the hydrogen-ion concentration (see Eq. (8), Figs. 6 and 7). On the basis of these results, the reaction mechanism of the ligand-substitution reactions of nickel(II)-NDAP, -NDAIP, and -TDA complexes with EDTA was assumed to be as follows:

$$\mathrm{NiX^- + HY^{3-}} \xrightleftharpoons{k_{\mathrm{NiX}}^{\mathrm{HY}}} \left\{\begin{matrix}\mathrm{NiY^{2-}}\\ \upharpoonleft\downharpoonright \\ \mathrm{NiHY^-}\end{matrix}\right\} + \mathrm{HX^{2-}} \tag{3}$$

$$\mathrm{NiX^- + H_2Y^{2-}} \xrightleftharpoons{k_{\mathrm{NiX}}^{\mathrm{H_2Y}}} \left\{\begin{matrix}\mathrm{NiY^{2-}}\\ \upharpoonleft\downharpoonright \\ \mathrm{NiHY^-}\end{matrix}\right\} + \mathrm{H_2X^-} \tag{4}$$

$$\mathrm{NiX^-} \xrightleftharpoons[k_a^-]{k_{\mathrm{NiX}}} \mathrm{Ni^{2+} + X^{3-}} \tag{5}$$

$$\mathrm{NiX^- + H^+} \xrightleftharpoons[k_b^-]{k_{\mathrm{NiX}}^{\mathrm{H}}} \mathrm{Ni^{2+} + HX^{2-}} \tag{6}$$

$$\mathrm{Ni^{2+}} + \left\{\begin{matrix}\mathrm{Y^{4-}}\\ \upharpoonleft\downharpoonright \\ \vdots \\ \upharpoonleft\downharpoonright \\ \mathrm{H_4Y}\end{matrix}\right\} \xrightleftharpoons{k_j^+} \left\{\begin{matrix}\mathrm{NiY^{2-}}\\ \upharpoonleft\downharpoonright \\ \mathrm{NiHY^-}\end{matrix}\right\} + j\mathrm{H^+} \tag{7}$$

On the other hand, the initial rate of the reaction of the nickel(II)-TDA complex with CyDTA was: (1) independent of the concentration of uncomplexed TDA and also of the initial concentration of CyDTA (see Fig. 3); (2) proportional to the initial concentration of the Ni(II)-TDA complex, and (3) linear to the hydrogen-ion concentration (see Fig. 8). These results indicate that the reaction of the nickel(II)-TDA complex with CyDTA proceeds only through the complete dissociation of the Ni(II)-TDA complex, as is shown in Eqs. (5)—(7). The relation of $\sum_{j=0}^{4} k_j^+[\mathrm{H}_j\mathrm{Y}^{(4-j)-}] \gg k_a^-[\mathrm{X}^{3-}]+k_b^-[\mathrm{HX}^{2-}]$, was fulfilled because the initial rate was independent of the concentrations of uncomplexed NDAP, NDAIP, and TDA. Judging from the equilibrium constant,[8] the protonated complex, NiHX, in Eq. (1) was not expected to be present in any appreciable concentration under the present experimental conditions.

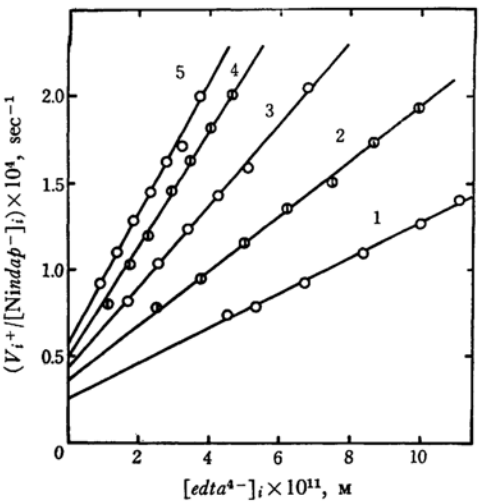

Fig. 4. $V_i^+/[\mathrm{Ni}\,ndap^-]_i$ as a function of $[edta^{4-}]_i$ in acetate buffer-potassium nitrate solutions of ionic strength 0.2 at 25°C. Initial concentration of Ni(II)-NDAP complex is 6.18×10^{-4} M. The pH's of the solutions are (1) pH 5.17, (2) pH 5.04, (3) pH 4.95, (4) pH 4.88 and (5) pH 4.82.

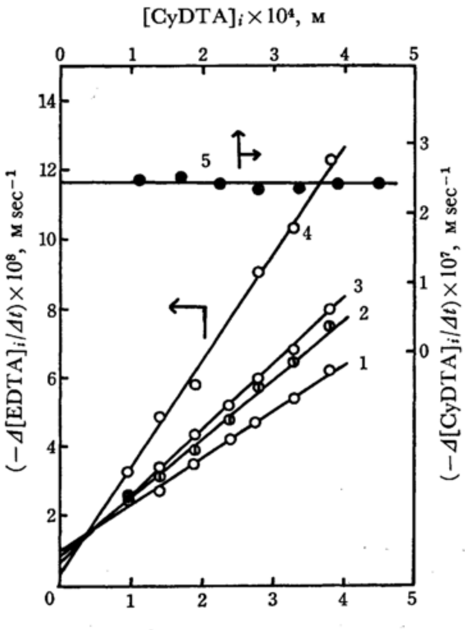

Fig. 3. Initial rates (V_i^+) as a function of the concentrations of entering ligands ($[\mathrm{EDTA}]_i$ and $[\mathrm{CyDTA}]_i$) in acetate buffer-potassium nitrate solutions of ionic strength 0.2 at 25°C. Initial concentrations of Ni(II)-NDAP and Ni(II)-TDA complexes are 3.09×10^{-4} M (curves 1, 2, 3 and 4) and 2.06×10^{-4} M (curve 5) respectively. The pH's of the solutions are (1) pH 5.08, (2) pH 5.30, (3) pH 5.46, (4) pH 5.81 and (5) pH 5.52.

From the reaction mechanism, the expressions for the rates of decrease from the initial concentration, $[\mathrm{EDTA}]_i$ and $[\mathrm{CyDTA}]_i$, can be derived as:

$$-\Delta[\mathrm{EDTA}]_i/\Delta t = [\mathrm{NiX^-}]_i\{k_{\mathrm{NiX}} + k_{\mathrm{NiX}}^{\mathrm{H}}[\mathrm{H^+}] + (k_1[\mathrm{H^+}]+k_2[\mathrm{H^+}]^2)[\mathrm{Y^{4-}}]_i\} \tag{8}$$

where

$$k_1 = k_{\mathrm{NiX}}^{\mathrm{HY}}/K_{\mathrm{HY}},\ k_2 = k_{\mathrm{NiX}}^{\mathrm{H_2Y}}/(K_{\mathrm{HY}}K_{\mathrm{H_2Y}}),$$

$$[\mathrm{Y^{4-}}]_i = [\mathrm{EDTA}]_i/\alpha_{\mathrm{H}}$$

$$\alpha_{\mathrm{H}} = 1 + [\mathrm{H^+}]/K_{\mathrm{HY}} + [\mathrm{H^+}]^2/(K_{\mathrm{HX}}K_{\mathrm{H_2Y}}) + [\mathrm{H^+}]^3/(K_{\mathrm{HY}}K_{\mathrm{H_2Y}}K_{\mathrm{H_3Y}}) + [\mathrm{H^+}]^4/(K_{\mathrm{HY}}K_{\mathrm{H_2Y}}K_{\mathrm{H_3Y}}K_{\mathrm{H_4Y}}) \tag{8'}$$

and

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[8] N. Tanaka and M. Kimura, *Sci. Repts. Tohoku Univ. Ser. I*, **50**, 203 (1967).

$$-\Delta[\mathrm{CyDTA}]_i/\Delta t = [\mathrm{NiX}^-]_i(k_{\mathrm{NiX}} + k^{\mathrm{H}}_{\mathrm{NiX}}[\mathrm{H}^+]) \tag{9}$$

In these equations, the initial concentrations, $[\mathrm{EDTA}]_i$, $[\mathrm{NiX}^-]_i$ and $[\mathrm{CyDTA}]_i$, are substituted for [EDTA], $[\mathrm{NiX}^-]$, and [CyDTA] respectively. The changes in their concentrations during the period of the measurement of the initial rate of the reaction were considered to be negligibly small under the present conditions. Equation (8) indicates that if the values of $V_i{}^+/[\mathrm{NiX}^-]_i$ are plotted against $[\mathrm{Y}^{4-}]_i$ (or $[\mathrm{EDTA}]_i$) when all quantities but $[\mathrm{EDTA}]_i$ are kept constant, a straight line should be obtained with an intercept at $[\mathrm{Y}^{4-}]_i=0$ given by:

$$(\text{Intercept}) = k_{\mathrm{NiX}} + k^{\mathrm{H}}_{\mathrm{NiX}}[\mathrm{H}^+] \tag{10}$$

and a slope given by:

$$(\text{Slope}) = k_1[\mathrm{H}^+] + k_2[\mathrm{H}^+]^2 \tag{11}$$

Therefore, if the values of the intercept and the slope obtained at various concentrations of hydrogen ion are plotted against the hydrogen-ion concentrations, the values of the rate constants in Eq. (8) can be determined. In the case of the reaction of the nickel(II)-TDA complex with CyDTA, the $V_i{}^+/[\mathrm{NiX}^-]_i$ obtained from Eq. (9) corresponds to Eq. (10) itself.

Determination of the Rate Constants of the Reactions of Ni(II)-NDAP and Ni(II)-NDAIP Complexes with EDTA. The initial rate ($V_i{}^+$) was measured for the reactions of nickel(II)-NDAP and -NDAIP complexes with varied concentrations of EDTA, but a constant concentration of other species present and at constant pH. Several examples of the plots of $V_i{}^+$ *vs.* $[\mathrm{EDTA}]_i$ and $V_i{}^+/[\mathrm{NiX}^-]_i$ *vs.* $[\mathrm{Y}^{4-}]_i$ are given in Figs. 3, 4, and 5 (Fig. 3 shows one example of V^+ *vs.* $[\mathrm{CyDTA}]_i$ together with the plots of $V_i{}^+$ *vs.* $[\mathrm{EDTA}]_i$).

The intercepts and the slopes of the plots, $V_i{}^+/[\mathrm{NiX}^-]_i$ *vs.* $[\mathrm{Y}^{4-}]_i$, correspond to Eqs. (10) and (11) respectively. The intercepts and the slopes were also plotted against the hydrogen-ion concentrations according to Eqs. (10) and (11). These plots are shown in Figs. 6 and 7, from which the values of the rate constants in Eq. (8) were determined.

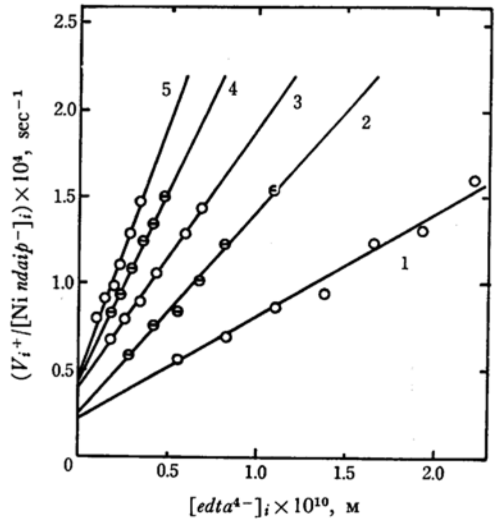


Fig. 5. $V_i{}^+/[\mathrm{Ni}\ ndaip^-]_i$ as a function of $[edta^{4-}]_i$ in acetate buffer-potassium nitrate solutions of ionic strength 0.2 at 25°C. Initial concentration of Ni(II)-NDAIP complex is 6.18×10^{-4} M. The pH's of the solutions are (1) pH 5.22, (2) pH 5.08, (3) pH 4.94, (4) pH 4.86 and (5) pH 4.82.

The rate constants for reactions (3) and (4) were calculated from the relations given in Eq. (8′). The results are shown in Table 2.

The acid dissociation constants of EDTA, K_{HY}, $K_{\mathrm{H_2Y}}$, $K_{\mathrm{H_3Y}}$, and $K_{\mathrm{H_4Y}}$, which were used in the calculation of $k^{\mathrm{HY}}_{\mathrm{NiX}}$, $k^{\mathrm{H_2Y}}_{\mathrm{NiX}}$, and α_{H} are the same values as those employed in a previous study.[5)]

Determination of the Rate Constants of the Reaction of the Ni(II)-TDA Complex with CyDTA. The initial rate, $-\Delta[\mathrm{CyDTA}]_i/\Delta t$, was measured at varied concentrations of hydrogen ion and at two different concentrations of $[\mathrm{Ni}\ tda^-]_i$ and $[\mathrm{CyDTA}]_i$. The values of $(-\Delta[\mathrm{CyDTA}]_i/\Delta t)/[\mathrm{Ni}\ tda^-]_i$ were then plotted against the hydrogen-ion concentrations. The results are given in Fig. 8. The rate constants of the dissociation reactions, (5) and (6), were obtained from the intercept and the slope in Fig. 8. The results are given in Table 2, together with the rate constants obtained from the other reaction systems.

TABLE 2. RATE CONSTANTS AT IONIC STRENGTH 0.2 AND 25°C

Reaction system	Rate constants*						Ref.
	k_{NiX}	$k^{\mathrm{H}}_{\mathrm{NiX}}$	$k^{\mathrm{HY}}_{\mathrm{NiX}}$	$k^{\mathrm{H_2Y}}_{\mathrm{NiX}}$	k_1	k_2	
Ni(*nta*)-HEDTA	3.4×10^{-5}	3.7	1.96	4.27×10^{-1}	1.45×10^{10}	6.3×10^{14}	5)
Ni(*nta*)-EDTA	3.0×10^{-5}	3.7	4.14	4.43×10^{-1}	6.7×10^{10}	1.2×10^{16}	5)
Ni(*nta*)-CyDTA	2.0×10^{-5}	3.8					4)
Ni(*ndap*)-EDTA	1.0×10^{-5}	2.4	3.27	3.89×10^{-1}	5.3×10^{10}	7.9×10^{15}	Thit study
Ni(*ndaip*)-EDTA	0.4×10^{-5}	2.5	1.73	2.84×10^{-1}	2.8×10^{10}	5.5×10^{15}	This study
Ni(*tda*)-CyDTA	8×10^{-4}	8.8×10					This study

* Units of rate constants: sec^{-1} for k_{NiX}; l mol^{-1} sec^{-1} for $k^{\mathrm{H}}_{\mathrm{NiX}}$, $k^{\mathrm{HY}}_{\mathrm{NiX}}$ and $k^{\mathrm{H_2Y}}_{\mathrm{NiX}}$; l^2 mol^{-2} sec^{-1} for k_1; l^3 mol^{-3} sec^{-1} for k_2.

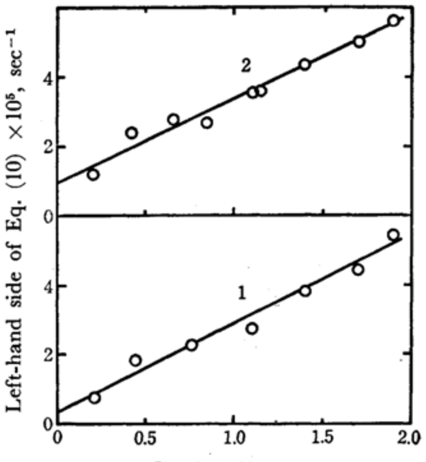


Fig. 6. Eq. (10) as a function of the hydrogen ion concentrations. Reaction systems are Ni *ndaip*-EDTA (curve 1) and Ni *ndap*-EDTA (curve 2). The conditions are the same as for Figs. 3, 4 and 5.

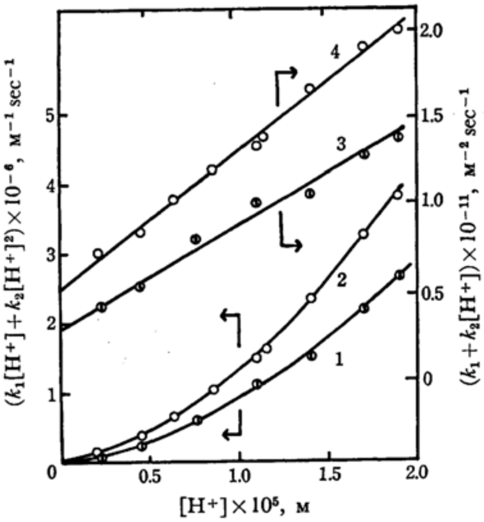


Fig. 7. Eq. (11) and Eq. (11)/[H$^+$] as the functions of the hydrogen ion concentrations. Reaction systems are Ni *ndaip*-EDTA (curves 1 and 3) and Ni *ndap*-EDTA (curves 2 and 4). The conditions are the same as for Figs. 3, 4 and 5.

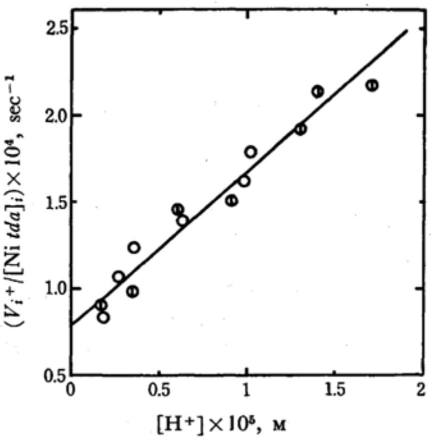
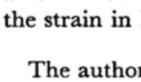


Fig. 8. $(-\Delta[\mathrm{CyDTA}]_i/\Delta t)/[\mathrm{Ni}\ tda^-]_i$ as a function of the hydrogen ion concentrations in acetate solutions of ionic strength 0.2 at 25°C. Initical oncentrations are $[\mathrm{Ni}\ tda^-]_i=2.06\times10^{-4}$ M (○) and 1.03×10^{-4} M (⦶), and $[\mathrm{CyDTA}]_i=4.49\times10^{-4}$ M (○) and 2.25×10^{-4} M (⦶). The concentrations of uncompleyed TDA are $[\mathrm{TDA}]_f=2\times10^{-5}$ M (○) and 1×10^{-5} M (⦶).

Discussion

Eigen[9,10] reported that, with most of the divalent transition metal ions in the first series, the rate of a complex-forming reaction of a metal ion with a ligand is independent of the nature of the ligand. If this assumption is satisfied, the rate of the dissociation reaction of a metal complex is expected to be dependent on the stability of the complex. The rate constants of the dissociation reactions of nickel complexes in Table 2 indicate that the reaction becomes fast in the order of: NDAIP≤NDAP<NTA<TDA, which seems to be opposite to the order of the stability of the complex. Schwarzenbach *et al.*[1] reported that the third acid dissociation constant of TDA ($pK_{Htda}=8.16$) was larger than that of NTA ($pK_{Hnta}=9.73$), and that the formation constants of the alkaline earth metal complexes with TDA were smaller than those of the corresponding complexes with NTA. These facts are consistent with the fact that the dissociation reaction of the TDA complex is faster than that of the NTA complex. The segment groups,  $-\overset{\displaystyle CH_3}{\overset{|}{C}}HCOOH$ in NDAIP and $-CH_2CH_2COOH$ in NDAP, seem to bond more strongly than any acetate group in NTA. This fact may be consistent with the statements by Chaberek and Martell,[2] and by Uehara *et al.*[3,6] that there is a considerable strain on the nitrogen atom in NTA coordinated with three five-membered rings, while a formation with one six-membered ring reduces the strain in NDAP, giving a more stable complex.

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[9] M. Eigen, "Advances in the Chemistry of Coordination Compounds," ed. by S. Kirschner, Macmillan, New York (1961), p. 371.

[10] M. Eigen, *Pure Appl. Chem.*, **6**, 97 (1963).