The Kinetics of the Complex-forming Reaction between Nickel(II) and Ethylenediaminetetraacetate

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Although there are a number of papers concerning the inorganic reactions involving metal complexes, few of them deal with the kinetics of the complex-forming reactions between metal ions and organic ligands. Several investigations in which the dissociation reactions, the substitution reactions or the exchange reactions involving metal-ethylenediaminetetraacetate complexes were dealt with have given some information of the complex-forming reactions between the metal and ethylenediaminetetraacetate (EDTA)[1-5]. Those reactions, which are reactions of copper(II)[3], cadmium II)[2], lead(II)[5], nickel (II)[4], and iron(II)[1] with EDTA, proceed so rapidly that the direct measurement of the concentration-time relation by the conventional techniques seems to be difficult.

Recently, a rotated dropping mercury electrode (RDME) has been developed, which has a current sensitivity some ten times as great as that of the conventional dropping mercury electrode[6-12]. In this investigation, the rate of the complex-forming reaction between nickel(II) and EDTA was followed by measuring the limiting current of nickel(II) at the RDME. The mechanisms of the reaction and the rate constant for each reaction path are presented in this paper.

Theoretical

Let us consider a complex-forming reaction of nickel(II) with ethylenediaminetetraacetate (EDTA) in sodium acetate-acetic acid buffers which contain 0.1 M acetate. At pH of the acetate buffer, EDTA exists mainly in the form of H_2Y^{2-} and partly in the forms of H_3Y^- and HY^{3-}, where Y^{4-} denotes the completely dissociated EDTA anion. These species are in equilibrium given in Eqs. 1 and 2.

$$H_3Y^- \rightleftarrows H_2Y^{2-} + H^+ \tag{1}$$

$$H_2Y^{2-} \rightleftarrows HY^{3-} + H^+ \tag{2}$$

Nickel(II) forms acetato complexes in a solution containing acetate ions. It has been found that the monoacetatonickel(II) ion is a predominant species of acetato complexes unless the concentration of acetate exceeds 0.2 M[13]. The monoacetatonickel(II) and the hydrated nickel ions are in equilibrium according to the equation,

$$Ni^{2+} + OAc^- \rightleftarrows NiOAc^+ \tag{3}$$

The reaction between nickel(II) and EDTA may proceed through various reaction paths. Among three ionic species of EDTA mentioned above, H_3Y^- is considered to be the least favorable to react with nickel(II). The rate of the reaction between nickel(II) and H_3Y^- seems to be much smaller than those between nickel (II) and other ionic species of EDTA. From these considerations, the following reaction paths are assumed:

$$Ni^{2+} + HY^{3-} \xrightarrow{k_{1a}} NiHY^- \tag{4}$$
$$NiHY^- \rightleftarrows NiY^{2-} + H^+$$

$$Ni^{2+} + H_2Y^{2-} \xrightarrow{k_{2a}} NiH_2Y \tag{5}$$
$$NiH_2Y \rightleftarrows NiHY^- + H^+ \rightleftarrows NiY^{2-} + 2H^+$$

$$NiOAc^+ + HY^{3-} \xrightarrow{k_{1b}} NiHY^- + OAc^- \tag{6}$$
$$NiHY^- \rightleftarrows NiY^{2-} + H^+$$

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[1] S. Jones and F. A. Long, *J. Phys. Chem.*, **56**, 25 (1952).

[2] N. Tanaka, R. Tamamushi and M. Kodama, *Z. physik. Chem.* (*Frankfurt*), **14**, 141 (1958).

[3] N. Tanaka, K. Kato and R. Tamamushi, This Bulletin, **31**, 283 (1958).

[4] C. M. Cook, Jr. and F. A. Long, *J. Am. Chem. Soc.*, **80**, 33 (1958).

[5] N. Tanaka and K. Kato, unpublished.

[6] W. Stricks and I. M. Kolthoff, *J. Am. Chem. Soc.*, **78**, 2085 (1956).

[7] N. Tanaka, *J. Japan. Chem.* (*Kagaku no Ryoiki*), **10**, 814 (1956).

[8] N. Tanaka and T. Koizumi, This Bulletin, **30**, 303 (1957).

[9] Y. Okinaka and I. M. Kolthoff, *J. Am. Chem. Soc.*, **79**, 3326 (1957).

[10] I. M. Kolthoff and Y. Okinaka, *Anal. Chim. Acta*, **18**, 83 (1958).

[11] N. Tanaka, T. Koizumi, T. Murayama, M. Kodama and Y. Sakuma, ibid., **18**, 97 (1958).

[12] I. M. Kolthoff, Y. Okinaka and T. Fujinaga, ibid., **18**, 295 (1958).

[13] N. Tanaka and K. Kato, This Bulletin, **32**, 516 (1959).

$$\mathrm{NiOAc^+ + H_2Y^{2-}} \xrightarrow{k_{2b}} \mathrm{NiH_2Y + OAc^-} \qquad (7)$$

$$\mathrm{NiH_2Y \rightleftarrows NiHY^- + H^+ \rightleftarrows NiY^{2-} + 2H^+}$$

From reactions 4 and 5, the rate of the decrease of $[\mathrm{Ni^{2+}}]$ is expressed as,

$$\begin{aligned}-\frac{\mathrm{d}[\mathrm{Ni^{2+}}]}{\mathrm{d}t} &= k_{1a}[\mathrm{Ni^{2+}}][\mathrm{HY^{3-}}] + k_{2a}[\mathrm{Ni^{2+}}][\mathrm{H_2Y^{2-}}] \\ &= \left\{k_{1a}\frac{K_{\mathrm{H_2Y}}}{[\mathrm{H^+}]} + k_{2a}\right\}[\mathrm{Ni^{2+}}][\mathrm{H_2Y^{2-}}] \qquad (8)\end{aligned}$$

where $K_{\mathrm{H_2Y}}$ represents the dissociation constant of $\mathrm{H_2Y^{2-}}$ $(=[\mathrm{HY^{3-}}][\mathrm{H^+}]/[\mathrm{H_2Y^{2-}}])$. From reactions 6 and 7 the rate of the decrease of $[\mathrm{NiOAc^+}]$ is expressed as,

$$\begin{aligned}-\frac{\mathrm{d}[\mathrm{NiOAc^+}]}{\mathrm{d}t} &= k_{1b}[\mathrm{NiOAc^+}][\mathrm{HY^{3-}}] \\ &\quad + k_{2b}[\mathrm{NiOAc^+}][\mathrm{H_2Y^{2-}}] \\ &= \left\{k_{1b}\frac{K_{\mathrm{H_2Y}}}{[\mathrm{H^+}]} + k_{2b}\right\}[\mathrm{NiOAc^+}][\mathrm{H_2Y^{2-}}] \qquad (9)\end{aligned}$$

The quantity of nickel(II) that is determined polarographically in acetate buffer is not the quantity of the hydrated nickel(II) ion, but the sum of those of the monoacetato- and the hydrated nickel ions[13]. If the sum is denoted by $[\mathrm{Ni^{2+}}]_{\mathrm{app.}}$,

$$[\mathrm{Ni^{2+}}]_{\mathrm{app.}} = [\mathrm{Ni^{2+}}] + [\mathrm{NiOAc^+}] \qquad (10)$$

Therefore, the rate of the decrease of nickel(II) that is followed by the polarographic method is given as,

$$\begin{aligned}-\frac{\mathrm{d}[\mathrm{Ni^{2+}}]_{\mathrm{app.}}}{\mathrm{d}t} &= -\frac{\mathrm{d}\{[\mathrm{Ni^{2+}}] + [\mathrm{NiOAc^+}]\}}{\mathrm{d}t} \\ &= -\left\{\frac{\mathrm{d}[\mathrm{Ni^{2+}}]}{\mathrm{d}t} + \frac{\mathrm{d}[\mathrm{NiOAc^+}]}{\mathrm{d}t}\right\} \qquad (11)\end{aligned}$$

As for the EDTA present in the acetate buffer, the total concentratration of uncomplexed EDTA, $[\mathrm{EDTA}]_{\mathrm{f}}$, is represented by

$$[\mathrm{EDTA}]_{\mathrm{f}} = [\mathrm{HY^{3-}}] + [\mathrm{H_2Y^{2-}}] + [\mathrm{H_3Y^-}] \qquad (12)$$

From Eq. 12, $[\mathrm{H_2Y^{2-}}]$ is given as

$$[\mathrm{H_2Y^{2-}}] = \frac{[\mathrm{EDTA}]_{\mathrm{f}}}{\dfrac{[\mathrm{H^+}]}{K_{\mathrm{H_3Y}}} + 1 + \dfrac{K_{\mathrm{H_2Y}}}{[\mathrm{H^+}]}} \qquad (13)$$

where $K_{\mathrm{H_3Y}}$ is the dissociation constant of $\mathrm{H_3Y^-}$ $(=[\mathrm{H_2Y^{2-}}][\mathrm{H^+}]/[\mathrm{H_3Y^-}])$. The concentration of $\mathrm{NiOAc^+}$ is written with the formation constant (K_{NiOAc}) and the concentrations of $\mathrm{Ni^{2+}}$ and $\mathrm{OAc^-}$,

$$[\mathrm{NiOAc^+}] = K_{\mathrm{NiOAc}}[\mathrm{Ni^{2+}}][\mathrm{OAc^-}] \qquad (14)$$

Introducing Eq. 14 into Eq. 10, $[\mathrm{Ni^{2+}}]$ is given by

$$[\mathrm{Ni^{2+}}] = \frac{[\mathrm{Ni^{2+}}]_{\mathrm{app.}}}{1 + K_{\mathrm{NiOAc}}[\mathrm{OAc^-}]} \qquad (15)$$

Introducing Eqs. 8 and 9 into Eq. 11 and substituting Eq. 14 for $[\mathrm{NiOAc^+}]$, we obtain

$$\begin{aligned}-\frac{\mathrm{d}[\mathrm{Ni^{2+}}]_{\mathrm{app.}}}{\mathrm{d}t} &= \left[\left\{k_{1a}\frac{K_{\mathrm{H_2Y}}}{[\mathrm{H^+}]} + k_{2a}\right\} + \left\{k_{1b}\frac{K_{\mathrm{H_2Y}}}{[\mathrm{H^+}]}\right.\right. \\ &\quad \left.\left. + k_{2b}\right\}K_{\mathrm{NiOAc}}[\mathrm{OAc^-}]\right][\mathrm{Ni^{2+}}][\mathrm{H_2Y^{2-}}] \qquad (16)\end{aligned}$$

Replacing $[\mathrm{H_2Y^{2-}}]$ and $[\mathrm{Ni^{2+}}]$ by the expressions given in Eqs. 13 and 15, respectively, and rearranging the resulted equation, Eq. 17 is obtained. Eq. 17 represents the overall rate expression for the complex-forming reaction between nickel(II) and EDTA whose reaction mechanisms are given by Eqs. 4 to 7. If $[\mathrm{H^+}]$ and $[\mathrm{OAc^-}]$ are not varied while the reaction proceeds, Eq. 17 can be written as

$$-\frac{\mathrm{d}[\mathrm{Ni^{2+}}]_{\mathrm{app.}}}{\mathrm{d}t} = k_{app.}[\mathrm{Ni^{2+}}]_{\mathrm{app.}}[\mathrm{EDTA}]_{\mathrm{f}} \qquad (18)$$

where $k_{app.}$ means an apparent rate constant and corresponds to Eq. 19. The magnitude of $k_{app.}$ is dependent on both pH and the acetate concentration of the solution.

Experimental

Reagents.—A stock solution of disodium ethylenediaminetetraacetate was prepared by dissolving the commercial guaranteed reagent, and

$$-\frac{\mathrm{d}[\mathrm{Ni^{2+}}]_{\mathrm{app.}}}{\mathrm{d}t} = \frac{\{k_{1a} + k_{1b}K_{\mathrm{NiOAc}}[\mathrm{OAc^-}]\}\dfrac{K_{\mathrm{H_2Y}}}{[\mathrm{H^+}]} + \{k_{2a} + k_{2b}K_{\mathrm{NiOAc}}[\mathrm{OAc^-}]\}}{\{1 + K_{\mathrm{NiOAc}}[\mathrm{OAc^-}]\}\left\{\dfrac{[\mathrm{H^+}]}{K_{\mathrm{H_3Y}}} + 1 + \dfrac{K_{\mathrm{H_2Y}}}{[\mathrm{H^+}]}\right\}}[\mathrm{Ni^{2+}}]_{\mathrm{app.}}[\mathrm{EDTA}]_{\mathrm{f}} \qquad (17)$$

$$k_{app.} = \frac{\{k_{1a} + k_{1b}K_{\mathrm{NiOAc}}[\mathrm{OAc^-}]\}\dfrac{K_{\mathrm{H_2Y}}}{[\mathrm{H^+}]} + \{k_{2a} + k_{2b}K_{\mathrm{NiOAc}}[\mathrm{OAc^-}]\}}{\{1 + K_{\mathrm{NiOAc}}[\mathrm{OAc^-}]\}\left\{\dfrac{[\mathrm{H^+}]}{K_{\mathrm{H_3Y}}} + 1 + \dfrac{K_{\mathrm{H_2Y}}}{[\mathrm{H^+}]}\right\}} \qquad (19)$$

standardized against the standard copper(II) solution by amperometric titration using a dropping mercury electrode as an indicator electrode[14]. The copper(II) solution was prepared by dissolving recrystallized copper(II) sulfate, and its concentration was determined by electrogravimetry at constant potential by means of a Yanagimoto automatic potentiostat. The standard solution of nickel nitrate was obtained in the following way[15]. The alcoholic solution of dimethylglyoxime was added to the dilute solution of guaranteed nickel(II) nitrate. The precipitates were filtered and dissolved in guaranteed nitric acid. The nickel(II) solution obtained was made ammoniacal and subjected to the electrolysis. The nickel metal deposited was weighed accurately, dissolved in guaranteed nitric acid and diluted to the desired concentration with redistilled water. The concentration of nickel(II) of the solution was determined with the standard EDTA solution by amperometric trtration[16]. The concentration obtained was in good agreement with that determined by electrogravimetry.

Acetic acid-sodium acetate buffers were prepared with guaranteed sodium carbonate and acetic acid. Polyoxyethylene lauryl ether (LEO) with a mean molecular weight of 862 was used for a maximum suppressor. Other chemicals used were of guaranteed reagent grade.

Apparatus and Procedure.—The rate of the reaction between nickel(II) and EDTA was followed by measuring the change of the polarographic diffusion current of the nickel(II) with time. The current-time curves were recorded with a Yanagimoto Model PB-4 pen-recording polarograph using a rotated dropping mercury electrode (RDME)[6-12].

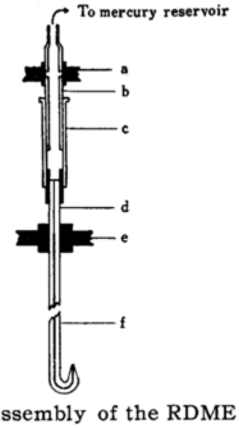

Fig. 1. Assembly of the RDME: a, fixed holder; b and c, inner and outer tubes of a 2 ml. syringe; d, capillary; e, holder of rotating apparatus; f, end tube.

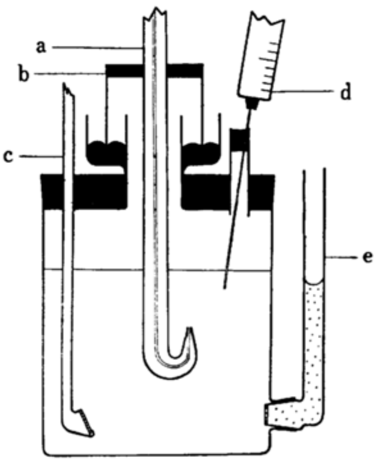

Fig. 2. Electrolysis cell: a, RDME; b, mercury seal; c, N_2 gas disperser; d, syringe; e, KNO_3-agar bridge.

In Fig. 1 is shown the RDME used in this study, which was similar to that reported by Okinaka and Kolthoft[9], being driven by means of a synchronous motor (Type A, provided with gears for speeds of 100, 150, 200 and 300 r.p.m., constructed by Yanagimoto Co., Ltd.). The electrode had an m value of 25.43 mg./sec. and a drop time of 2.95 sec. at 100 r.p.m., being measured at -0.60 volt vs. S.C.E. in air-free 0.2 M potassium nitrate solution containing 5×10^{-6} M LEO at 51.2 cm. of mercury head at 25°C.

The electrolysis cell in which the reaction took place was of a beaker-type of 100 ml. capacity as shown in Fig. 2. The cell was connected to a saturated calomel electrode through a potassium nitrate agar bridge. Special precautions were taken against the intrusion of atmospheric oxygen into the electrolysis cell during the measurement. A mercury seal was attached for this purpose. (See Fig. 2). The nitrogen gas was introduced into the solution through a gas disperser before and also during the measurement. The current measurement with the RDME was not disturbed by bubbling the gas through the solution. The rate of the flow of nitrogen gas was kept constant, being controlled by means of a flow-meter. The fluctuation of the residual current due to the change of the oxygen concentration was controlled within 0.05 microampere.

All kinetic measurements were made in acetate buffers of pH 3.8 to 5.2 at 0°C. The acetate concentrations were varied from 0.02 M to 0.1 M. The ionic strength was adjusted to be 0.2 with potassium nitrate. LEO was added as a maximum suppressor by 5×10^{-6} M in concentration. The pH of the solution was measured with a Hitachi Model EHP-1 pH meter, immediately after the measurements of current-time curves, within the accuracy of 0.02 pH unit.

The reaction was initiated by adding the air-free solution of the equivalent EDTA into the deaerated nickel(II) solution in the electrolysis

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[14] N. Tanaka, M. Kodama, M. Sasaki and M. Sugino, *Japan Analyst* (*Bunseki Kagaku*), **6**, 86 (1957).

[15] F. P. Treadwell and W. T. Hall, "Analytical Chemistry", Vol. 2, 9th ed., John Wiley and Sons, Inc., New York (1952), p. 193.

[16] R. Přibil and B. Matyska, *Collection Czechoslov. Chem. Communs.*, **16**, 139 (1951).

cell with the aid of a calibrated 1 ml. syringe. Since the RDME was driven and the nitrogen gas was bubbled throughout the measurement, reproducible current-time curves were able to be obtained immediately after the injection of the EDTA solution.

Results

A typical polarogram of nickel(II) which was obtained with 2×10^{-4} M Ni(II) in acetate buffer of pH 4.6 with the RDME is shown in Fig. 3. Although the limiting current plateau of the polarogram is not well-defined, the proportionality was found between the concentration of nickel(II) and the current that was measured at -1.35 V. vs. S.C.E. and corrected for the residual current, unless the concentration of nickel(II) exceeded 5×10^{-4} M. Therefore, current-time curves of the reaction mixtures were recorded at this potential. Typical examples of the current-time curves are reproduced in Fig. 4. Those curves were recorded at varied pH's with reaction mixtures in which the initial concentrations of nickel(II) and EDTA were each 1.00×10^{-4} M and the concentration of acetate was 0.1 M. It is expected from Eq. 18 that a plot of the reciprocal of $[\mathrm{Ni}^{2+}]_{\mathrm{app.}}$ against time gives a straight line with a slope of k_{app}. Some of the plots are given in Fig. 5, from which the values of $k_{app.}$ were determined.

The current-time curves were obtained

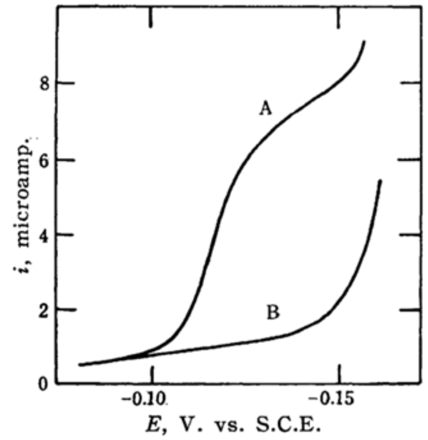

Fig. 3. Current-voltage curves of 2×10^{-4} M Ni(II) (curve A) and Ni(II)-EDTA (curve B) obtained at 0°C in acetate buffer-potassium nitrate solution of pH 4.6 and ionic strength 0.2 containing 0.1 M acetate and 5×10^{-6} M LEO.

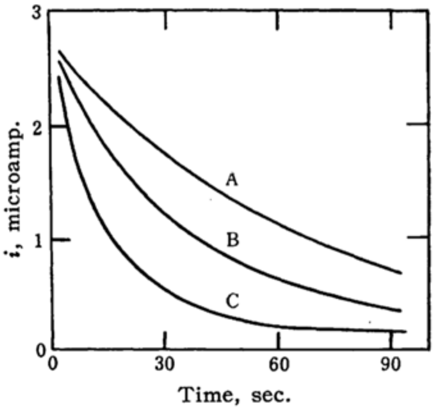

Fig. 4. Limiting current-time relation of the reaction between nickel(II) and EDTA, measured at -1.35 V. vs. S.C.E. at 0°C in acetate buffer-potassium nitrate solution of ionic strength 0.2 containing 0.1 M acetate and 5×10^{-6} M LEO, at pH 3.9 (curve A), pH 4.4 (curve B) and pH 5.0 (curve C). Initial concentrations of nickel(II) and EDTA are each 1.00×10^{-4} M.

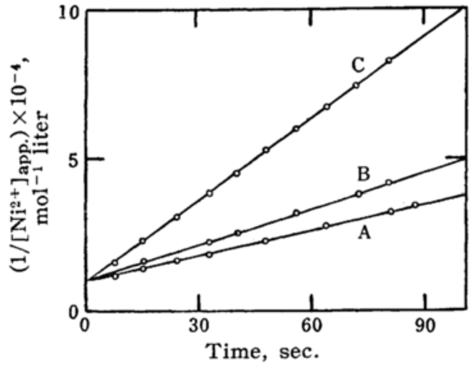

Fig. 5. Relation between the reciprocal nickel concentration and the time. Plots A, B and C are obtained from curves A, B and C in Fig. 4, respectively.

TABLE I. TYPICAL EXAMPLES OF THE RATE MEASUREMENT*

pH(0°C)	$[\mathrm{H}^+]\times10^4$, mol./l.	$\frac{[\mathrm{H}^+]}{K_{\mathrm{H_3Y}}}$	$\frac{K_{\mathrm{H_2Y}}}{[\mathrm{H}^+]}$	$k_{app.}\times10^{-2}$, (mol./l.)$^{-1}$ sec^{-1}
4.03	1.197	0.06	0.00	3.02
4.09	1.044	0.05	0.00	3.18
4.14	0.928	0.04	0.01	3.26
4.55	0.361	0.02	0.01	4.54
4.72	0.244	0.01	0.02	5.43
4.94	0.148	0.01	0.03	6.70
5.01	0.125	0.01	0.04	7.60
5.16	0.089	0.00	0.06	10.0_0
5.21	0.079	0.00	0.07	10.3_3
5.26	0.071	0.00	0.08	11.2_5

* The solutions contain 0.05 M acetate. The initial concentrations of nickel(II) and EDTA are each 1.00×10^{-4} M.

at varied pH's in the range of pH 3.8 to 5.2 and at three different concentrations of acetate. It was found that the analysis of the current-time curves which were obtained with different initial concentrations of the reactants but at the same pH and acetate concentration gave the same $k_{app.}$ This fact confirmed that the reaction in question is of second order.

The magnitudes of $k_{app.}$ were determined at varied pH's and at three different concentrations of acetate. Examples of the experimental results which were obtained at 0.05 M acetate are given in Tabele I. From Eq. 19,

$$\alpha\beta k_{app.} = \{k_{1a} + k_{1b}K_{\mathrm{NiOAc}}[\mathrm{OAc}^-]\}\frac{K_{\mathrm{H_2Y}}}{[\mathrm{H}^+]} + \{k_{2a} + k_{2b}K_{\mathrm{NiOAc}}[\mathrm{OAc}^-]\}$$

$$= k_1\frac{K_{\mathrm{H_2Y}}}{[\mathrm{H}^+]} + k_2 \qquad (20)$$

$$\alpha = \frac{[\mathrm{H}^+]}{K_{\mathrm{H_3Y}}} + 1 + \frac{K_{\mathrm{H_2Y}}}{[\mathrm{H}^+]}$$

$$\beta = 1 + K_{\mathrm{NiOAc}}[\mathrm{OAc}^-]$$

$$k_1 = k_{1a} + k_{1b}K_{\mathrm{NiOAc}}[\mathrm{OAc}^-]$$

$$k_2 = k_{2a} + k_{2b}K_{\mathrm{NiOAc}}[\mathrm{OAc}^-]$$

are obtained. Eq. 20 indicates that a plot of the values of $\alpha\beta k_{app.}$ against the reciprocal of the hydrogen ion concentration should give a straight line, if $k_{app.}$'s were determined at the same concentration of acetate. The plots with the observed values of $k_{app.}$ gave the straight lines as shown in Fig. 6. The slope gave the value of $k_1K_{\mathrm{H_2Y}}$ in Eq. 20 and the intercept at $1/[\mathrm{H}^+]=0$, that of k_2. The relation between $\alpha\beta k_{app.}$ and the reciprocal of the hydrogen ion concentration was also treated by the method of least squares. The mean values and the probable errors of k_1 and k_2 were calculated as given in Table II.

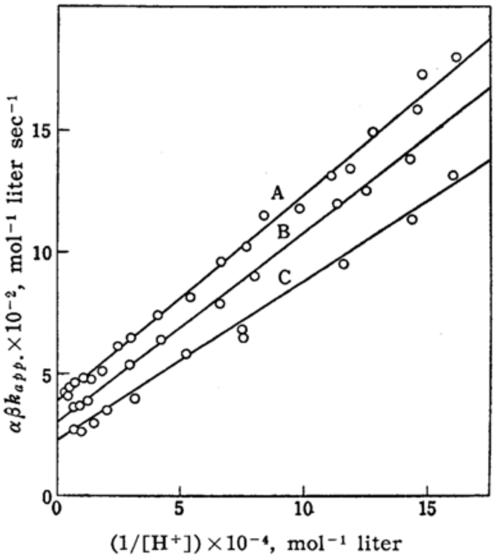

Fig. 6. Relations between $\alpha\beta k_{app.}$ and $1/[\mathrm{H}^+]$ obtained at 0°C in acetate buffer-potassium nitrate solution of ionic strength 0.2 at acetate concentrations 0.10 M (curve A), 0.05 M (curve B) and 0.02 M (curve C).

TABLE II. OBSERVED VALUES OF k_1 AND k_2

Concn. of acetate, M	$k_1\times10^{-4}$, mol^{-1} liter sec^{-1}	$k_2\times10^{-2}$, mol^{-1} liter sec^{-1}
0.10	$1.73\pm0.01_6$	$3.89\pm0.06_7$
0.05	$1.41\pm0.01_8$	$2.95\pm0.15_3$
0.02	$1.18\pm0.00_9$	$2.42\pm0.07_6$

The hydrogen ion concentration used in this calculation was derived from the pH observed and the activity coefficient of the hydrogen ion. The pH of the solution was measured at 25°C and corrected for temperature to be reduced to the value at 0°C. The activity coefficient of the hydrogen ion was calculated to be 0.78 at 0°C and ionic strength 0.2 according to Kielland[17]. The third dissociation constant of EDTA, $K_{\mathrm{H_2Y}}$, which was determined by Schwarzenbach and Ackermann[18] at 20°C and $\mu=0.1$, was used after correction for ionic strength and temperature. The ion size parameters of $\mathrm{H_2Y^{2-}}$ and $\mathrm{HY^{3-}}$ were assumed to be the same as that of suberic acid given by Kielland[17]. The temperature correction for $K_{\mathrm{H_2Y}}$ was made with the aid of the ΔH value reported by Carini and Martell[19]. The resulted value of $K_{\mathrm{H_2Y}}$ was $10^{-6.27}$. On the other hand, there has been no publication concerning the temperature coefficient of $K_{\mathrm{H_3Y}}$. In this calculation, therefore, the value of $10^{-2.67}$, which was obtained by Schwarzenbach and Ackermann[18] at 20°C and $\mu=0.1$, was used without further correction. Since this constant is concerned only with the calculation of α, in which the contribution of the term $[\mathrm{H}^+]/K_{\mathrm{H_3Y}}$ does not exceed 10% under the present condition, the use of $K_{\mathrm{H_3Y}}$ without correction seems to introduce no significant error into the calculation of the rate constant.

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[17] J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).

[18] G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **30**, 1798 (1947).

[19] F. F. Carini and A. E. Martell, *J. Am. Chem. Soc.*, **75**, 4810 (1953).

The formation constant of the monoacetatonickel(II) complex, K_{NiOAc}, was determined to be 3.0 at 0°C, by extrapolating the values obtained at 15°, 25° and 35°C in the solution of ionic strength 0.2[13].

From k_1 and k_2 in Table II, the values of k_{1a}, k_{1b}, k_{2a} and k_{2b} were calculated as given in Table III.

TABLE III. RATE CONSTANTS OF VARIOUS NICKEL(II)-EDTA REACTIONS

Reaction	Rate constant, mol^{-1} liter sec^{-1}
$Ni^{2+}+HY^{3-}\xrightarrow{k_{1a}}NiHY^-$	$1.0_6\times10^4$
$NiOAc^+ +HY^{3-}\xrightarrow{k_{1b}}NiHY^- +OAc^-$	$2.2_5\times10^4$
$Ni^{2+}+H_2Y^{2-}\xrightarrow{k_{2a}}NiH_2Y$	$2.0_4\times10^2$
$NiOAc^+ +H_2Y^{2-}\xrightarrow{k_{2b}}NiH_2Y+OAc^-$	$6.0_4\times10^2$

Discussion

The complex-forming reaction of nickel with ethylenediaminetetraacetate was found to proceed through four different reaction paths given in Eqs. 4 to 7 in acetate buffers of pH 3.8 to 5.2. The rate constants of those four elementary reactions were determined. It seems reasonable that the reactions involving HY^{3-} species are much faster than those involving H_2Y^{2-}.

On the other hand, the effect of acetate ions on the reaction rate was rather unexpected. The previous studies on the displacement reactions involving metal-EDTA complexes indicated that the reaction rate decreased with increasing concentration of acetate[20,21]. The rate of the complex-forming reaction between nickel (II) and EDTA, however, was found to decrease with decreasing concentration of acetate. The rate constants of the reactions involving the monoacetatonickel(II) ions were nearly twice as great as those of the corresponding reactions involving the hydrated nickel ions. A similar phenomenon was reported by Wilkins[22], who studied the exchange reaction involving the nickel(II)-2,3-diamino-2,3-dimethylbutane complex and observed the faster reaction rate in the presence of ammonium acetate. Although the effect of acetate on the nickel-EDTA reaction is not completely solved at the present moment, it may not be unreasonable to consider the decrease of the activation energy of the reaction as being due to the acetate co-ordinated.

It seems interesting to compare the rate constants obtained in this study with those obtained by Cook and Long[4]. They studied the exchange reaction between nickel(II) and nickel(II)-EDTA complexes with the aid of the radioactive isotope at 25°C and ionic strength 0.1, and determined the rate constants of several reaction paths including the following:

$$NiY^{2-}+H^+ \rightleftarrows Ni^{2+}+HY^{3-} \qquad (21)$$

$$NiHY^- +H^+ \rightleftarrows Ni^{2+}+H_2Y^{2-} \qquad (22)$$

The reactions given by Eqs. 21 and 22 correspond to the reverse of those given by Eqs. 4 and 5, respectively. The equilibrium constants of reactions 21 and 22,

$$K(\text{Eq. }21)=[Ni^{2+}]\,[HY^{3-}]/[NiY^{2-}]\,[H^+] =1/K_{\mathrm{NiY}}K_{\mathrm{HY}}$$

$$K(\text{Eq. }22)=[Ni^{2+}]\,[H_2Y^{2-}]/[NiHY^-]\,[H^+] =1/K_{\mathrm{NiY}}K^{\mathrm{H}}_{\mathrm{NiHY}}K_{\mathrm{HY}}K_{\mathrm{H_2Y}}$$

were calculated, where K_{NiY} represents the formation constant of NiY^{2-}, K_{HY} and $K_{\mathrm{H_2Y}}$ the dissociation constants of HY^{3-} and H_2Y^{2-}, respectively, and $K^{\mathrm{H}}_{\mathrm{NiHY}}$ the equilibrium constant of the reaction,

$$NiY^{2-}+H^+ \rightleftarrows NiHY^-$$

The values of K_{HY}, $K_{\mathrm{H_2Y}}$, K_{NiY} and $K^{\mathrm{H}}_{\mathrm{NiHY}}$ which were determined by Schwarzenbach and his co-workers[18,23] at 20°C and $\mu=0.1$ were used without further correction. With the equilibrium constants obtained and the rate constants given by Cook and Long, the rate constants for the reverse reactions of Eqs. 21 and 22 were calculated and compared with k_{1a} and k_{2a} as shown in Table IV.

Unfortunately, Cook and Long did not take into account the effect of the acetate

TABLE IV. COMPARISON OF THE RATE CONSTANTS

Reaction	Rate constant, mol^{-1} liter sec^{-1}	
	Calculated from data at 25°C given by Cook and Long[4]	Observed at 0°C in this study
$Ni^{2+}+HY^{3-}\longrightarrow NiHY^-$	3.0×10^5	$1.0_6\times10^4$
$Ni^{2+}+H_2Y^{2-}\longrightarrow NiH_2Y$	8.1×10^2	$2.0_4\times10^2$

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[20] H. Ackermann and G. Schwarzenbach, *Helv. Chim. Acta*, **35**, 485 (1952).

[21] N. Tanaka and K. Kato, unpublished.

[22] R. G. Wilkins, *J. Chem. Soc.*, **1957**, 4521.

[23] G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954).

on the reaction mechanisms and gave no information of the concentration of acetate present in their reaction mixtures. Therefore, the rate constants given by those authors do not exactly correspond to those given in this study. Nevertheless, it may be concluded that the results obtained in both investigations are in reasonable agreement.

Bjerrum and Poulsen[24] studied the kinetics of the formation of nickel(II) and copper(II) complexes of ethylenediamine in methanol at 0°C. They found that copper(II) complexes are more labile than the corresonding nickel(II) compounds. The rate constants of the formation of $\mathrm{Ni(en)^{2+}}$ was $2.5\times10^4\ \mathrm{mol^{-1}\ liter\ sec^{-1}}$ and that of $\mathrm{Cu(en)^{2+}}$, $5\times10^{11}\ \mathrm{mol^{-1}\ liter\ sec^{-1}}$, where en denotes ethylenediamine.

Recent studies[3,5] in this laboratory revealed that the rate constants of the formation of copper(II) and lead(II) complexes of EDTA through the reaction

$$\mathrm{M^{2+}+HY^{3-} \rightleftharpoons MY^{2-}+H^+} \qquad (\mathrm{M=Cu\ or\ Pb})$$

range from 10^9 to $10^{11}\ \mathrm{mol^{-1}\ liter\ sec^{-1}}$ at room temperature. The slower rate of the formation of nickel(II)-EDTA complexes is apparent as in the case of the formation of nickel-ethylenediamine complexes.

Summary

The complex-forming reaction of nickel (II) with ethylenediaminetetraacetate (EDTA) was found to proceed in acetate buffers of pH 3.8 to 5.2 through four different reaction paths,

$$\mathrm{Ni^{2+}+HY^{3-} \xrightarrow{k_{1a}} NiHY^-}$$

$$\mathrm{NiOAc^{+}+HY^{3-} \xrightarrow{k_{1b}} NiHY^-+OAc^-}$$

$$\mathrm{NiHY^- \rightleftharpoons NiY^{2-}+H^+}$$

$$\mathrm{Ni^{2+}+H_2Y^{2-} \xrightarrow{k_{2a}} NiH_2Y}$$

$$\mathrm{NiOAc^{+}+H_2Y^{2-} \xrightarrow{k_{2b}} NiH_2Y+OAc^-}$$

$$\mathrm{NiH_2Y \rightleftharpoons NiHY^-+H^+ \rightleftharpoons NiY^{2-}+2H^+}$$

The change in the polarographic diffusion current of nickel(II) at the rotated dropping mercury electrode was utilized to follow the decrease of the nickel(II) concentration in the reaction mixture after the initiation of the reaction. The rate constants of the reaction paths were determined at 0°C and ionic strength 0.2, with the results:

$k_{1a}=1.0_6\times10^4\quad \mathrm{mol^{-1}\ liter\ sec^{-1}}$

$k_{1b}=2.2_5\times10^4$ 〃

$k_{2a}=2.0_4\times10^2$ 〃

$k_{2b}=6.0_4\times10^2$ 〃

These constants are much smaller than those of the corresponding reactions between copper(II) and EDTA.

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[24] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", John Wiley & Sons, Inc., New York (1958), p. 204.