BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 2575—2579 (1967)

Spectrophotometric Studies of the Solution Equilibria and the Kinetics of the Substitution Reaction between Eriochrom Black T and Cobalt(II)-Ethylenediaminetetraacetate Chelate

Mutsuo KODAMA

Department of Chemistry, Ibaraki University, Mito, Ibaraki

(Received May 30, 1967)

The solution equilibria and the kinetics of the substitution reaction between Eriochrom Black T (BT) and cobalt(II)-EDTA chelate were studied spectrophotometrically. At the pH range from 8.50 to 9.50, BT was found to form only 1 to 1 normal chelate $\mathrm{CoD^-}$ with cobalt(II), the stability constant of which is $10^{20.0}(\mu=0.30)$. Kinetically, the substitution reaction was found to proceed through the following two simultaneous reaction paths,

$$\text{i)}\quad \mathrm{HD^{2-} + CoY^{2-} \overset{k_1^*}{\rightleftharpoons} CoD^- + HY^{3-}}$$

$$\text{ii)}\quad \mathrm{HD^{2-} \overset{rapid}{\rightleftharpoons} D^{3-} + H^+}$$

$$\mathrm{D^{3-} + CoY^{2-} \overset{k_2^*}{\rightleftharpoons} CoD^- + Y^{4-}}$$

and k_1^* and k_2^* were determined to be $0.23\ l\,\mathrm{mol^{-1}\,sec^{-1}}$ and $6.76\times10^2\ l\,\mathrm{mol^{-1}\,sec^{-1}}$, respectively, at 20°C.

In the previous paper,[1] the solution equilibria between Eriochrom Black T (BT) and zinc(II)-NTA or copper(II)-CyDTA chelate were studied spectrophotometrically, and the stability constants and the compositions of 1 to 1 chelates of BT with these metal ions were determined. The rate of substitution reaction between BT and zinc(II)-NTA or copper(II)-CyDTA chelates was very large and the reaction mixtures reached the equilibrium within 30 sec.

In the case of the substitution reaction of BT and cobalt(II)-EDTA chelate, however, the reaction proceeds at a considerable rate. In the present paper, spectrophotometeric studies of the solution equilibria and of the kinetics of the substitution reaction between BT and cobalt(II)-EDTA chelate are presented.

Experimental

The standard solution of cobalt(II) was prepared by the following procedure. Hot ammoniacal metal solution was treated with a 1 percent solution of dimethylglyoxime in ethanol and filtered carefully using a fritted-glass funnel. To the filterate, an excessive amount of sodium hydroxide was added and the solution was heated nearly to boiling point to precipitate cobalt(II) ions as hydroxide. The resulting precipitate was filtered off, washed thoroughly with redistilled water, and dissolved in diluted perchloric acid solution. The concentration of cobalt(II) was then determined by titration with a standard EDTA solution.[2] The solution of disodium salt of ethylenediaminetetraacetate (EDTA) was standardized against pure metallic zinc.

As was described in the previous paper,[1] BT was purified by employing the procedure described by Diehl and Lindstrom[3] and the purity was checked spectrophotometrically. All the other chemicals were of analytical reagent grade and used without further purification.

All measurements were conducted in solutions of constant ionic strength ($\mu=0.30$). In the study of the solution equilibria, the apparatus used and the experimental procedure employed were the same as described in the previous paper.[1]

In the kinetic study, the absorbance-time curves were obtained with Hitachi EPS-3 pen recording spectrophotometer and the pH of the solution was measured immediately after the measurement of absorbance-time curves. The reaction was initiated by adding a known amount of BT into the reaction mixture with the aid of 5.00 m*l* pipet within 3 sec, diluting with redistilled water to the mark and shaking the mixture vigorously for 5 sec. The resulting mixture was transferred to a 1 cm quartz cell and the change in absorbance at 620 mμ with time was measured using the solution containing the same amount of cobalt(II)-EDTA chelate as reference. With the above technique, reproducible absorbance-time curves were obtained from 20 sec after the initiation of the reaction. In this study, no other buffer reagent was

---

[1] M. Kodama and H. Ebine, This Bulletin, **40**, 1857 (1967).

[2] H. Flaschka and H. Abdine, *Chemist-Analyst*, **44**, 30 (1955).

[3] H. Diehl and F. Lindstrom, *Anal. Chem.*, **31**, 414 (1959).

used, because EDTA was considered to have the enough buffer capacity at the pH range from 8.50 to 9.50.

Results and Discussion

Determination of the Composition and the Stability Constant of Cobalt(II)-BT Chelate. As shown in Fig. 1, the absorption curve of cobalt(II)-BT chelate is quite similar to that of copper(II)-BT chelate,[1] and the ε_{max} is small, as compared with that for uncomplexed BT. Therefore, the concentration ratio between cobalt(II)-BT chelate and free BT is expected to be determined successfully by using the absorbance observed at the wavelength where the maximum for the uncomplexed BT is located.

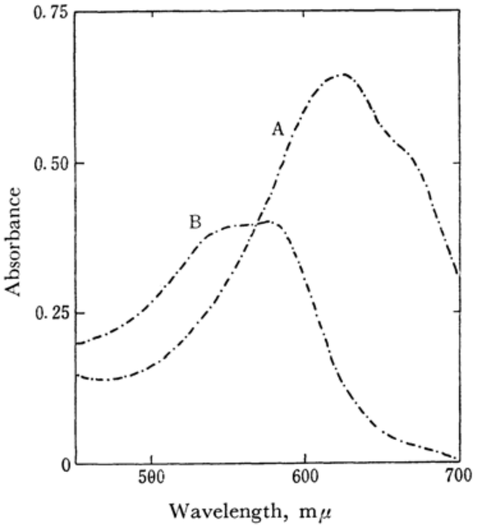

Fig. 1. Absorption curves.
A. 2.00×10^{-5} M BT, 1.00×10^{-2} M EDTA, $\mu=0.30$, pH=9.50
B. 2.00×10^{-5} M BT, 1.00×10^{-2} M EDTA, 4.00×10^{-3} M cobalt(II), $\mu=0.30$, pH=9.00

Under the given pH conditions (from 8.50 to 9.50), the concentrations of $CoHY^-$ and $CoY(OH)^{3-}$ are considered to be negligibly small as compared with that of CoY^{2-}. Consequently, if BT forms only a normal chelate CoD^-, the following exchange reaction can be assumed,

$$\left.\begin{array}{c} D^{3-} \\ \downarrow\uparrow \\ HD^{2-} \\ \downarrow\uparrow \\ H_2D^- \\ \downarrow\uparrow \\ H_3D \end{array}\right\} + CoY^{2-} = CoD^- + \left\{\begin{array}{c} Y^{4-} \\ \uparrow\downarrow \\ HY^{3-} \\ \uparrow\downarrow \\ H_2Y^{2-} \\ \uparrow\downarrow \\ H_3Y^- \\ \uparrow\downarrow \\ H_4Y \end{array}\right. \tag{1}$$

where D^{3-} and Y^{4-} refer to completely deprotonated BT and EDTA respectively, and H_iD^{i-3} and H_iY^{i-4} represent protonated BT and EDTA species respectively. For this reaction, the apparent equilibrium constant (2) can be introduced, as in the case of BT-copper(II)-CyDTA system.[1]

$$K_e = \frac{[CoD]\cdot[EDTA]_f}{[BT]_f\cdot[CoY]} = \frac{K_{CoD}\cdot(\alpha_H)_Y}{K_{CoY}\cdot(\alpha_H)_{BT}} \tag{2}$$

where $[BT]_f$ and $[EDTA]_f$ refer to the concentrations of uncomplexed BT and EDTA, and (α_H)'s have thier usual meanings.

Under the conditions that the total concentration of BT is kept constant and free EDTA is present in a large excess over BT and cobalt(II)-EDTA chelate, $[EDTA]_f$ in Eq. (2) can be practically equated with the difference in the total concentrations between EDTA and Co(II).

By rearranging the relation (2), using the relationship between the absorption data and the concentrations of colored species developed previously,[1] and casting the resulting equation into logarithmic form, the relation (3) can be obtained

$$\log K_e\cdot[BT]_t - \log[EDTA]_f = \log\frac{A_{HD}-A}{A-A_{CoD}}\cdot\frac{1}{m-\dfrac{A_{HD}-A}{A_{HD}-A_{CoD}}} \tag{3}$$

where $[BT]_t$ is the total concentration of BT added, and A's have the same meanings as in the previous paper.[1]

If a mixed chelate $CoDY^{5-}$ were formed among cobalt(II), BT and EDTA, the relation (3) should be replaced by (4).

$$\log K'_e[BT]_t = \log\frac{A_{HD}-A}{A-A'_{CoD}}\cdot\frac{1}{m-\dfrac{A_{HD}-A}{A_{HD}-A'_{CoD}}} \tag{4}$$

As is clear from Eq. (3), if cobalt(II)-BT chelate is present only in the form CoD^-, the plot of $\log 1/[EDTA]_f$ against $\log\{(A_{HD}-A)/(A-A_{CoD})\cdot[m-(A_{HD}-A)/(A_{HD}-A_{CoD})]^{-1}\}$ should give a straight line with a slope of unity.

On the other hand, if a mixed chelate $CoDY^{5-}$ is formed, $\log\{(A_{HD}-A)/(A-A_{CoD})\cdot[m-(A_{HD}-A)/(A_{HD}-A_{CoD})]^{-1}\}$ is expected to be independent of the total concentration of EDTA.

From the observations that BT can form a chelate with cobalt(II) in a mixture of 10 mM cobalt(II)-EDTA chelate and 20 mM EDTA, and that the presence of cobalt(II) ions interferes with the color change of BT in the EDTA-Mg(II) or EDTA-Zn(II) titration,[4] the stability constant of cobalt(II)-BT chelate is expected to be much greater than that of cobalt(II)-EDTA chelate. Considering this and the observation that the apparent

---

[4] K. Ueno, "Kireto Tekiteiho (Chelatometric Titration)," Nankodo, Tokyo (1961).

rate of the substitution reaction increases with increasing the pH value of solution, as the ratio of the concentration of cobalt(II)-EDTA chelate to that of BT, *m*, was made 5.0 and all absorption measurements were conducted in solutions of constant pH of 9.50.

The substitution reaction between BT and cobalt(II)-EDTA chelate proceeds at a measurable rate. Hence, the reaction mixtures were warmed at 50°C in a water bath for 45 min, set aside in the dark for 30 min, and the absorbance of the solution was measured at 630 mμ. Absorbance of the mixture thus treated was reproducible and its variation with the time up to 5.0 hr was negligible.

Experimental data were analyzed by using Eqs. (3) and (4). A straight line with a slope of unity in Fig. 2 clearly shows that BT forms only normal chelate CoD^- with cobalt(II) under the experimental conditions. With the aid of relation (2), the stability constant for CoD^- was calculated to be $10^{20.0}$ by using the $\log\{(A_{HD}-A)/(A-A_{CoD})\cdot[m-(A_{HD}-A)/(A_{HD}-A_{CoD})]^{-1}\}$ value, -1.42 obtained when $\log 1/[EDTA]_t$ is zero, $[BT]_t$ and $\log K_{CoY}$ value of 15.71 ($\mu=0.30$).

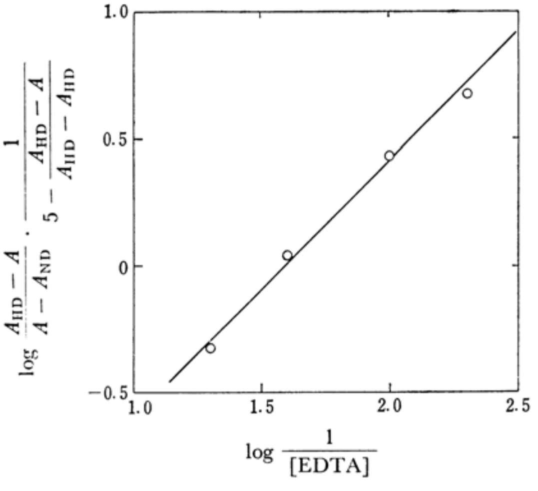

Fig. 2. Log ratio plot for determining the equilibrium constant.
1.50×10^{-5} M BT, 7.50×10^{-5} M cobalt(II), $\mu=0.30$, pH=9.50, $\lambda=630$ mμ
The concentration of EDTA ranges from 5.0×10^{-3} M to 5.0×10^{-2} M

The numerical values used for the calculation are listed in Table 1. As described previously,[1)] those were calculated from the related dissociation constants[5,6)] and stability constant[5)] in the solution of ionic strength 0.10 at 20°C and the activity constants of the ions calculated by means of Davies equation.[7)]

TABLE 1

i) Dissociation constants of EDTA and BT (mixed constant, $\mu=0.30$)
  a) EDTA[5)]
    $pK_1=1.96$, $pK_2=2.56$, $pK_3=5.97$, $pK_4=10.00$
  b) BT[6)]
    $pK_1=6.80$, $pK_2=11.31$
ii) Formation constants of chelates ($\mu=0.30$)
  $\log K_{CoY}$[5)]$=15.71$
  $\log K^*_{CoD}=20.0$

* Obtained by the present author

Kinetic study of the Substitution Reaction of BT and Cobalt(II)-EDTA Chelate. The kinetic measurements were carried out in solutions containing cobalt(II)-EDTA chelate and uncomplexed EDTA in a large excess over BT at a pH range from 8.50 to 9.50.

In solutions of the given pH and the given concentrations of EDTA and cobalt(II)-EDTA chelate, the apparent initial reaction rate $-\Delta[BT]_f/\Delta t$ was found to be proportional to the initial concentration of BT, $[BT]_0$, and is given by $-\Delta[BT]_f/\Delta t=k_r\cdot[BT]_0$. With reference to the relation given by Tanaka *et al.*[8)] for the apparent initial rate of the substitution reaction between lead(II) and cobalt(II)-EDTA chelate, the above finding clearly indicates that the substitution reaction between BT and cobalt(II)-EDTA chelate does not include the reaction path where the dissociation of cobalt(II)-EDTA chelate acts as a rate-determining reaction.

Since the kinetic measurements were carried out in solutions containing EDTA and cobalt(II)-EDTA chelate in an excess over BT, the overall exchange reaction of BT and cobalt(II)-EDTA system (1) can be simplified to,

$$\left\{\begin{matrix} D^{3-} \\ \upharpoonleft\downharpoonright \\ HD^{2-} \end{matrix}\right. \quad \underset{k^-}{\overset{k^+}{\rightleftharpoons}} \quad CoD^- \qquad (5)$$

whose reaction rate is given by

$$-\frac{d[BT]_f}{dt}=k^+\cdot[BT]_f-k^-\cdot[CoD] \qquad (6)$$

where *k*'s mean the apparent rate constants.

Integrating Eq. (6), one can obtain

$$\ln\left(\frac{[BT]_0-[BT]_e}{[BT]_f-[BT]_e}\right)=(k^+ + k^-)\cdot t \qquad (7)$$

where $[BT]_e$ means the concentration of uncomplexed BT at equilibrium.

---

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

6) G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, **31**, 678 (1948).

7) J. N. Butler, "Ionic Equilibrium," Addison-Wesley Publishing Co., Inc., Reading, Massachusetts (1964), p. 437.

8) N. Tanaka, H. Osawa and M. Kamada, This Bulletin, **36**, 67 (1963).

At the equilibrium of the reaction, the relation

$$\frac{k^+}{k^-} = \frac{[\mathrm{CoD}]_e}{[\mathrm{BT}]_e} = K_e \cdot \frac{[\mathrm{CoY}]_e}{[\mathrm{EDTA}]_e} \tag{8}$$

also should be satisfied.

Considering that K_e value can be calculated to be about $10^{3.0}$ at a pH range from 8.50 to 9.50, k^+ in Eq. (7) must be much greater than k^-, and $[\mathrm{BT}]_0$ and $[\mathrm{BT}]_f$, than $[\mathrm{BT}]_e$, under the conditions where $[\mathrm{CoY}]_e$ is nearly equal to $[\mathrm{EDTA}]_e$. Therefore, Eq. (7) can be simplified to,

$$\ln\left(\frac{[\mathrm{BT}]_0}{[\mathrm{BT}]_f}\right) = k^+ \cdot t \tag{9}$$

Here, $[\mathrm{BT}]_0/[\mathrm{BT}]_f$ can be given by

$$\frac{[\mathrm{BT}]_0}{[\mathrm{BT}]_f} = \frac{A_{\mathrm{HD}}}{A - A_{\mathrm{CoD}}} \cdot \frac{\varepsilon_{\mathrm{HD}} - \varepsilon_{\mathrm{CoD}}}{\varepsilon_{\mathrm{HD}}} \tag{10}$$

Accordingly, by plot $\log\,[A_{\mathrm{HD}}/(A-A_{\mathrm{CoD}}) \times (\varepsilon_{\mathrm{HD}}-\varepsilon_{\mathrm{CoD}})/\varepsilon_{\mathrm{HD}}]$ against t, the straight line with a slope of k^+ can be obtained.

In the preliminary experiments, the followings were also found out.

1) In solutions of the given pH and the given concentrations of cobalt(II)-EDTA chelate and EDTA, k^+ is constant and is independent of the initial concentration of BT, $[\mathrm{BT}]_0$ (Fig. 3).

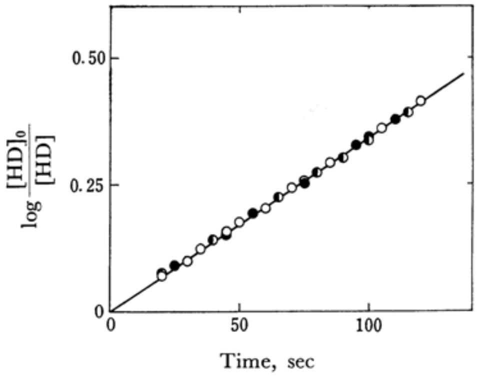

Fig. 3. The plot of $\log\,[A_{\mathrm{HD}}/(A-A_{\mathrm{CoD}})\times(\varepsilon_{\mathrm{HD}}-\varepsilon_{\mathrm{CoD}})/\varepsilon_{\mathrm{HD}}]$ against t.
3.0×10^{-3} M cobalt(II)-EDTA chelate,
1.70×10^{-2} M EDTA, $\mu=0.30$, pH=8.85
○ 1.0×10^{-5} M BT, ◑ 2.0×10^{-5} M BT
● 3.0×10^{-5} M BT

2) In solutions of the given pH and the given concentrations of BT and EDTA, k^+ is proportional to the initial concentration of cobalt(II)-EDTA chelate, $[\mathrm{CoY}]_0$(Fig. 4).

3) In solutions of the given pH and the given concentrations of BT and cobalt(II)-EDTA chelate, k^+ is independent of the concentration of EDTA (Fig. 5).

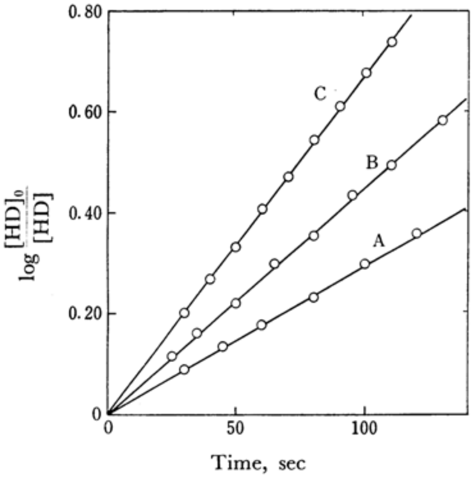

Fig. 4. The plot of $\log\,[A_{\mathrm{HD}}/(A-A_{\mathrm{CoD}})\times(\varepsilon_{\mathrm{HD}}-\varepsilon_{\mathrm{CoD}})/\varepsilon_{\mathrm{HD}}]$ against t.
2.0×10^{-5} M BT, 1.20×10^{-2} M EDTA
$\mu=0.30$, pH=9.00
A 2.0×10^{-3} M cobalt(II)-EDTA chelate
B 3.0×10^{-3} M cobalt(II)-EDTA chelate
C 4.5×10^{-3} M cobalt(II)-EDTA chelate

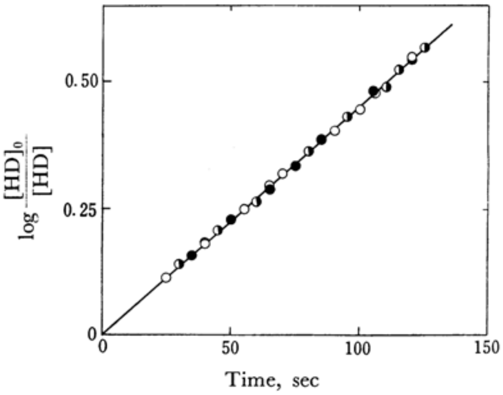

Fig. 5. The plot of $\log\,[A_{\mathrm{HD}}/(A-A_{\mathrm{CoD}})\times(\varepsilon_{\mathrm{HD}}-\varepsilon_{\mathrm{CoD}})/\varepsilon_{\mathrm{HD}}]$ against t.
3.0×10^{-5} M BT, 3.0×10^{-3} M cobalt(II)-EDTA chelate $\mu=0.30$, pH=9.00
○ 1.20×10^{-2} M EDTA
◐ 1.70×10^{-2} M EDTA
● 2.70×10^{-2} M EDTA

4) In solutions of the given concentrations of BT, EDTA and cobalt(II)-EDTA chelate, k^+ is a function of the hydrogen ion concentration and given by the relation

$$k^+ = k_{\mathrm{i}} + k_{\mathrm{ii}}/[\mathrm{H}^+] \tag{11}$$

By analogy of the reaction between copper(II) and cobalt(II)-EDTA chelate,⁹⁾ the above facts clearly show that the substitution reaction between BT and cobalt(II)-EDTA chelate proceeds through two simultaneous reaction paths (i) and (ii), but, not through (iii).

$$\text{(i)}\quad \mathrm{HD}^{2-} + \mathrm{CoY}^{2-} \underset{k_1^-}{\overset{k_1^+}{\rightleftharpoons}} \mathrm{CoD}^- + \mathrm{HY}^{3-} \tag{12}$$

---

9) N. Tanaka, H. Osawa and M. Kamada, This Bulletin, **36**, 530 (1963).

$$\text{(ii)}\quad \mathrm{HD^{2-}} \xrightleftharpoons{\text{rapid}} \mathrm{H^+} + \mathrm{D^{3-}} \tag{13a}$$

$$\mathrm{D^{3-}} + \mathrm{CoY^{2-}} \xrightleftharpoons[k_2^-]{k_2^+} \mathrm{CoD^-} + \mathrm{Y^{4-}} \tag{13b}$$

(rate determining step)

$$\begin{tikzcd} \text{(iii)}\quad \mathrm{CoY^{2-}} \arrow[r, shift left, "\text{rapid}"] \arrow[d, shift left, "\mathrm{H^+}"] & \mathrm{Co^{2+}} + \mathrm{Y^{4-}} \arrow[l, shift left] \\ \mathrm{CoHY^-} \arrow[u, shift left, "-\mathrm{H^+}"] & \end{tikzcd} \tag{14a}$$

$$\mathrm{Co^{2+}} + \left\{ \begin{array}{l} \mathrm{HD^{2-}} \\ \mathrm{D^{3-}} \end{array} \right. \xrightleftharpoons{\text{slow}} \mathrm{CoD^-} \tag{14b}$$

As the concentration of free cobalt(II) ion can be evaluted to be very small under the present experimental conditions where the pH ranges from 8.50 to 9.50, and EDTA is present in an excess over cobalt(II), the rate of the reaction (14b) must be very small. Therefore, the conclusion that the percentage of the contribution of the reaction path (iii) to the whole reaction can be neglected as compared with those of (i) and (ii) must be plausible.

Assuming the reaction paths (i) and (ii) for the reaction (1), k^+ in Eq. (9) is considered to be given by

$$k^+ = [\mathrm{CoY}]_0 \cdot \left(k_1^+ + k_2^+ \frac{10^{-\mathrm{p}K_2}}{[\mathrm{H^+}]} \right) \tag{15}$$

where $\mathrm{p}K_2$ corresponds to the pK value of the dissociation of the second phenolic group of BT.[6]

k_1^+ and k_2^+ were determined to be 0.23 $l\,\mathrm{mol^{-1}\cdot sec^{-1}}$ and $6.76 \times 10^2\ l\,\mathrm{mol^{-1}sec^{-1}}$ from the linear relation between $1/[\mathrm{H^+}]$ and the value of $k^+/[\mathrm{CoY}]_0$ which were obtained at various pH's at three different concentrations of cobalt(II)-EDTA chelate (Fig. 6).

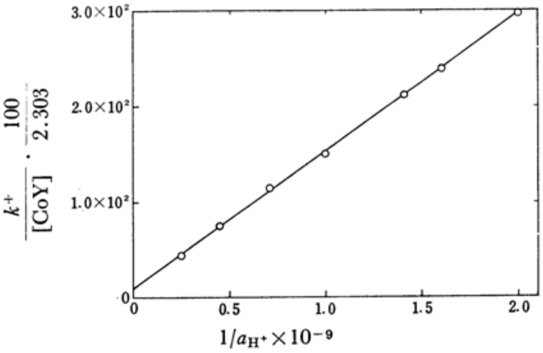

Fig. 6. The plot of $k^+/[\mathrm{CoY}]_0$ against $1/[\mathrm{H^+}]$ $\mu = 0.30$, 20°C.

The kinetic study of the substitution reaction of BT and cobalt(II)-EDTA chelate at the temperature other than 20°C is now in progress.

The present author is indebted to Mr. Hide Ebine for his assistance in the experimental work, and also thanks the Ministry of Education for the financial support granted for this research.