Polarographic and Chronopotentiometric Studies on the Dissociation Reaction of Nitrilotriacetatocadmate(II) Complexes

By Nobuyuki TANAKA, Kazuko EBATA, Tomoo TAKAHARI*
and Tsutomi KUMAGAI**

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The kinetic current due to the dissociation of nitrilotriacetatocadmate(II) complexes has been investigated by several researchers[1-4]. In early works, however, the effect of acetate ion on the kinetic current was not taken into consideration, though the measurements were made in acetic acid - sodium acetate buffer solutions. Koryta[4] was the first to consider this effect and to assume the kinetic current as due to the reduction of the free (hydrated) ions and acetato complexes of cadmium. Similar treatments of the effect of acetate and/or other coexisting ions have been approved when applied to the equilibrium and kinetic studies on the substitution or complex-forming reactions in solutions.

Since the application of the treatment to the kinetic current has not been proved, it seems worth while to investigate the dissociation reaction of nitrilotriacetatocadmate(II) in the presence and absence of acetate ions. Because of the limitations of polarographic and chronopotentiometric methods, the reaction rate was determined polarographically in the presence of acetate and chronopotentiometrically in the absence of acetate.

Experimental

Reagents. — A standard solution of cadmium nitrate was obtained by the same procedure as reported previously[5]. A stock solution of disodium nitrilotriacetate (NTA) was prepared from the commercial nitrilotriacetic acid, the concentration of which was determined against the standardized copper(II) nitrate solution by amperometric titration with a dropping mercury electrode. All chemicals used were of analytical reagent grade and all solutions were prepared with redistilled water.

Apparatus and Procedure. — Polarographic current-voltage curves were obtained with a Yanagimoto pen-recording polarograph (Polarorecorder Model PR-2 with an automatic potential scanner) and a dropping mercury electrode. The measurements were carried out in solutions containing 0.4 mM of cadmium nitrate, 0.01 M of NTA and 0.05 M of sodium acetate - acetic acid buffers. The

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* Present address: Tokyo Research Institute, Yawata Iron and Steel Co., Ltd., Ida, Kawasaki.

** Present address: Research Laboratory, Sony Corp., Fujitsuka-cho, Hodogaya, Yokohama.

[1] J. Koryta, Sbornik Mezinarod. Polarog. Sjezdu Praze, lst Congr., 1951, Part I., p. 798.

[2] K. Morinaga and T. Nomura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **79**, 200 (1958).

[3] P. Papoff, *J. Am. Chem. Soc.*, **81**, 3254 (1958).

[4] J. Koryta, *Collection Czechoslov. Chem. Communs.*, **24**, 3057 (1959).

[5] N. Tanaka, M. Kamada, H. Osawa and G. Satô, This Bulletin, **33**, 1412 (1960).

ionic strength was adjusted to be 0.2 with potassium nitrate. The pH of the solution was measured, immediately after the measurement of the current-voltage curve, with a Hitachi EHP-1 pH meter with a glass electrode.

For chronopotentiometric study, an apparatus similar to that reported in the previous paper⁽⁶⁾ was used. The hanging mercury drop electrode served as a cathode and a saturated calomel electrode with a large surface area (SCE) as an anode. Controlled electrolysis current was supplied by five 90 V. dry cells connected in series and resistors of 0.1 to 100 megohms. The electrolysis current was measured by means of a standard resistance and potentiometer. The potential difference between the working electrode and the SCE was fed to the Y-axis of a cathode-ray oscillograph (Toshiba ST-1747A) through a direct-current preamplifier. The alternating voltage of 100 to 1000 cycles/sec. from an oscillator (Yokogawa OV 21 A) was supplied for the beam modulation. Thus, chronopotentiograms were obtained as dotted curves as shown in Fig. 1, of which the transition time was determined by counting the number of dots. The measurements of chronopotentiograms were made with the solutions containing 1.04 mM of cadmium nitrate and 0.0202 M of NTA. The ionic strength was adjusted to be 0.2 with potassium nitarte and the pH, to be of an appropriate value between 2.8 and 3.4 with nitric acid. In this range of pH's, nitrilotriacetate itself served as a buffer. All chronopotentiometric measurements were carried out at 25°C.

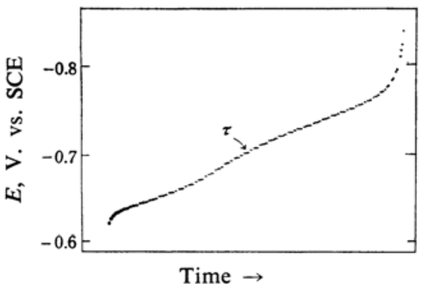

Fig. 1. Chronopotentiogram of Cd(II)-NTA complex. $[Cd^{2+}]_t$, 1.04 mM; $[NTA]_t$, 0.0202 M; pH, 3.19; μ, 0.2 (KNO_3); current density, 5.25 μamp./mm²; surface area, 3.65 mm². The interval of every two dots corresponds to 1/140 sec.

Results

a) Polarographic Study. — In acetate buffer solution of an appropriate pH containing NTA in excess, cadmium(II) gave a doublet wave. As has been reported previously⁽¹⁻⁴⁾, the first wave is kinetic in nature and considered as due to the reduction of cadmium(II) which is dissociated from Cd(II)-NTA complex. The over-all electrode reaction at the dropping mercury electrode is written as

$$CdX^- + jH^+ \overset{k_j}{\rightleftharpoons} Cd^{2+} + H_jX^{(3-j)-} \qquad (j=0,1,\cdots\cdots,n) \tag{1}$$

$$Cd^{2+} + OAc^- \rightleftharpoons CdOAc^+ \tag{2}$$

$$\left\{\begin{matrix} Cd^{2+} \\ \upharpoonleft\downharpoonright \\ CdOAc^+ \end{matrix}\right\} + 2e + Hg \rightleftharpoons \left\{\begin{matrix} Cd(Hg) \\ Cd(Hg) + OAc^- \end{matrix}\right\} \tag{3}$$

where X^{3-} denotes a tervalent NTA anion and k_j the rate constant of the dissociation reaction given by Eq. 1. Assuming that reactions 2 and 3 are rapid enough to attain the equilibria and that the hydrated ions and the acetato complex ions of cadmium are both reduced at the potentials under consideration where the Cd(II)-NTA complexes are not reduced, the following equation is derived according to Koryta⁽⁴⁾,

$$\frac{\bar{i}_l}{\bar{i}_d - \bar{i}_l} = 0.886\sqrt{\frac{kK_{CdX}[X^{3-}]t_d}{1+K_{CdOAc}[OAc^-]}} \tag{4}$$

$$k = \sum_{j=0}^{n} k_j [H^+]^j$$

where $\bar{i}_l$ and $\bar{i}_d$ mean the kinetic current and the hypothetical diffusion current of total electro-inactive species respectively, K_{CdOAc} and K_{CdX} the formation constants of $CdOAc^+$ and CdX^- respectively, and t_d the drop time. Equation 4 holds only when NTA exists in a large excess over cadmium(II) in the solution.

The rate constants were calculated with the observed values of $\bar{i}_l$ at various pH's using Eq. 4. The concentration of X^{3-} at the given hydrogen ion concentration was calculated with the total concentration ($[NTA]_t$) and the dissociation constants of NTA. The values of $10^{-1.89}$, $10^{-2.49}$ and $10^{-9.73}$ were used for the first, second and third dissociation constants, respectively, which were determined by Schwarzenbach et al.⁽⁷⁾ at 20°C and 0.1 ionic strength. For the formation constants of CdX^- and $CdOAc^+$, $10^{9.83}$ (K_{CdX}) obtained by Schwarzenbach et al.⁽⁷⁾ and 16 (K_{CdOAc}) determined in this laboratory⁽⁵⁾ were used, respectively.

In Fig. 2, the rate constants at 5, 15 and 25°C are plotted against hydrogen ion concentration. Those linear plots clearly indicate that the rate constants can be expressed as linear functions of hydrogen ion concentration as shown in Table I, where the rate constants obtained by other researchers are also given. Our values at 25°C may be compared with those by Koryta, though the experimental

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6) T. Murayama, *Sci. Repts. Tohoku Univ. Ser. I*, **45**, 84 (1961).

7) G. Schwarzenbach, H. Anderegg, W. Schneider and H. Senn, *Helv. Chim. Acta*, **38**, 1147 (1955).

TABLE I. THE DISSOCIATION RATE CONSTANTS OF Cd(II)-NTA COMPLEX OBTAINED POLAROGRAPHICALLY IN ACETATE BUFFER SOLUTIONS

Conditions for measurement			Rate constants sec^{-1}	Investigators
Temp., °C	pH range	Ionic strength		
25	5.3~5.9	0.2	$3.4+2.5\times10^5[\mathrm{H}^+]$	The present authors
15	5.2~5.8	0.2	$1.5+0.4\times10^5[\mathrm{H}^+]$	
5	5.2~5.8	0.2	$0.64+0.2\times10^5[\mathrm{H}^+]$	
25	4.5~6.0	0.1	$1.6+3.0\times10^5[\mathrm{H}^+]$	Koryta[4]
25	4.6~5.7	3	$(1.5\pm0.3)\times10^6[\mathrm{H}^+]$	Papoff[3]
25		0.3	$(1.3\pm0.3)\times10^6[\mathrm{H}^+]$	
25	4.2~4.9	0.1	$(6.5\pm1.7)\times10^4[\mathrm{H}^+]$	Morinaga et al.[2]

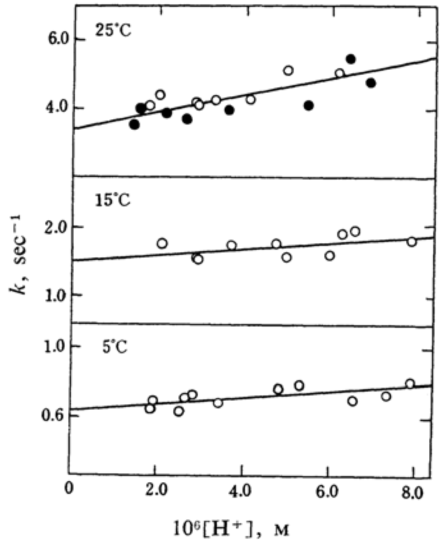

Fig. 2. Dissociation rate constants as a function of hydrogen ion concentration at various temperatures. $[\mathrm{Cd}^{2+}]_t$, 0.4 mM; $[\mathrm{NTA}]_t$, 0.01 M; $[\mathrm{OAc}^-]$, 0.05 M; μ, 0.2 ($\mathrm{KNO_3}$). ○ 1st run, ● 2nd run.

conditions and the values of various constants used in the calculation are not the same.

b) Chronopotentiometric Study. — Chronopotentiometric potential-time curves were obtained with the solutions of pH 2.8 to 3.4 in the absence of acetate. An example of those curves is given in Fig. 1, which shows the separation of two steps to be ambiguous. Therefore, the transition time was determined by measuring the time that was required for the given change in potential from the beginning of electrolysis. Such a potential change was not the same at different pH's and, consequently, was determined preliminarily at every pH with the chronopotentiogram which is relatively well-defined. Examples of the transition times obtained at varied current densities are given in Table II.

TABLE II. EXAMPLES OF CHRONOPOTENTIOMETRIC MEASUREMENTS

$\mathrm{Cd(NO_3)_2}$ 1.04 mM; NTA 0.0202 M; pH 3.12; ionic strength 0.2; 25°C

i_0, μ amp./mm²	τ, sec.	$i_0\tau^{1/2}$
4.06	0.68_0	3.3_5
5.23	0.36_5	3.1_6
5.74	0.25_5	2.9_0
7.02	0.15_2	2.7_4
8.65	0.09_0	2.6_0
9.30	0.07_3	2.5_1

The relation between the transition time and the current density for the electrochemical reaction which is preceded by a first order chemical reaction was derived first by Delahay and Berzins[8] for a linear diffusion and later by Murayama[6] for a spherical diffusion. Although the measurements were made with the hanging mercury drop electrode, the observed values of transition time were not accurate enough for the Murayama's rigorous treatment. In this study, therefore, the equation derived by Delahay and Berzins for a linear diffusion was employed.

When NTA is present in the solution in a large excess over cadmium(II), the relation,

$$i_0\tau^{1/2}=\pi^{1/2}\boldsymbol{F}D^{1/2}[\mathrm{Cd}^{2+}]_t-\frac{\pi^{1/2}K_{\mathrm{CdX}}[\mathrm{X}^{3-}]}{2k^{1/2}(1+K_{\mathrm{CdX}}[\mathrm{X}^{3-}])^{1/2}}i_0 \qquad (5)$$

holds, where i_0 is the current density, τ the transition time for the reduction of free cadmium ion, $\boldsymbol{F}$ the Faraday, D the common value of the diffusion coefficients of various species which are assumed to be equal, and $[\mathrm{Cd}^{2+}]_t$ the total concentration of cadmium. Equation 5 indicates that the plot of $i_0\tau^{1/2}$ against i_0 should give a straight line with a negative slope. In Fig. 3, the values of $i_0\tau^{1/2}$ calculated with the observed transition times at pH 2.99 and 3.35 are plotted against current

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[8] P. Delahay and T. Berzins, *J. Am. Chem. Soc.*, **75**, 2486 (1953).

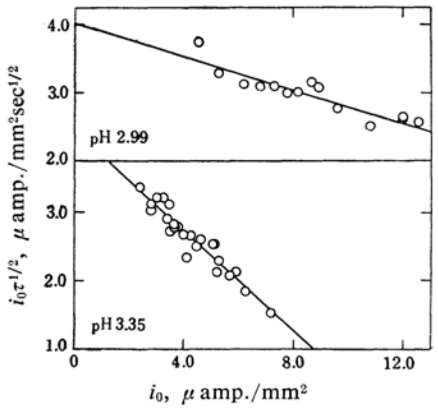

Fig. 3. $i_0\tau^{1/2}$ as a function of i_0 at various pH's.

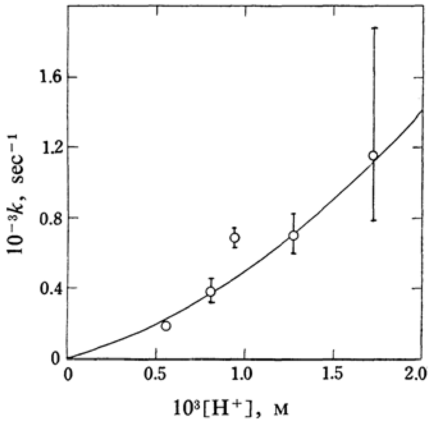

Fig. 4. Dependence of the dissociation rate constant on the hydrogen ion concentration. The solid curve represents the relation, $k=3\times10^5[H^+]+2\times10^8[H^+]^2$.

density. The negative slopes of those plots clearly indicate that the electrode processes are kinetic in nature. The rate constants at various pH's were calculated from the slopes, and are plotted against hydrogen ion concentration with the standard deviation (Fig. 4). The solid curve in Fig. 4 represents a relation given by the equation,

$$k=3\times10^5[H^+]+2\times10^8[H^+]^2 \tag{6}$$

At lower pH's the contribution of the term independent of the hydrogen ion concentration is so small compared to other terms that it can be hardly determined.

Discussions

Inaccuracy of the present chronopotentiometric measurement is due to mainly the fact that the reduction potentials for hydrated ion and NTA complex of cadmium are not sufficiently separated. In addition, the chronopotentiogram of cadmium is considerably affected by the presence of surface-active substance, and this may be another cause of the inaccuracy of the measurement. Murayama⁶⁾ reported that the presence of 0.001% gelatin decreased the transition time and deteriorated the shape of the chronopotentiogram of hydrated cadmium ion. In the present experiment, redistilled water was used and no surface-active substance was added, but an effect of aging of the hanging mercury drop electrode was clearly observed. Transition time was measured as a function of time after the formation of a mercury drop (θ) and the values of $i_0\tau^{1/2}$ were plotted against θ (Fig. 5). Those linear plots in Fig. 5 suggest that an abrupt decrease in $i_0\tau^{1/2}$ in the region of small values of θ would be most unlikely.

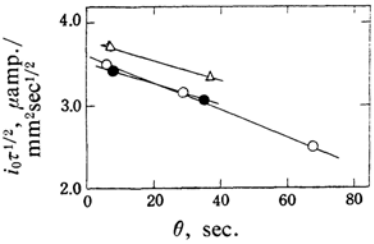

Fig. 5. Variations of $i_0\tau^{1/2}$ with θ.
-△-△-, pH 3.19 and i_0 3.64 μamp./mm²;
-○-○-, pH 3.12 and i_0 4.06 μamp./mm²;
-●-●-, pH 2.86 and i_0 5.87 μamp./mm².

The over-all rate constant k obtained from the kinetic current was a linear function of the hydrogen ion concentration. The chronopotentiometric study, on the other hand, showed that at lower pH's the over-all rate involves a second-order term with respect to the hydrogen ion concentration. The first-term of Eq. 6 obtained by the chronopotentiometric method, $3\times10^{-5}[H^+]$, is in good agreement with the values obtained polarographically by the authors and by Koryta (see Table I). This proves clearly that the Koryta's treatment of the effect of acetate ion on the kinetic current is appropriate.

In conclusion, the rate constant of the dissociation of Cd(II)-NTA complex is a function of hydrogen ion concentration, and expressed as

$$k=3.4+2.5\times10^5[H^+]+2\times10^8[H^+]^2$$

at 25°C, from the results obtained polarographically and those obtained chronopotentiometrically. The dissociation reaction, therefore, is considered to proceed through three simultaneous reaction paths,

$$CdX^- \rightarrow Cd^{2+}+X^{3-}$$
$$CdX^-+H^+ \rightarrow Cd^{2+}+HX^{2-}$$
$$CdX^-+2H^+ \rightarrow Cd^{2+}+H_2X^-$$

Summary

The dissociation reaction of nitrilotriacetatocadmate(II) complexes has been investigated polarographically and chronopotentiometrically in the presence and the absence of acetate ions. The results indicate that the treatment reported by Koryta for the effect of acetate ion on the kinetic current is appropriate.

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at 25°C.

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Department of Chemistry
Faculty of Science
Tohoku University
Katahira-cho, Sendai