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Polarographic Studies of Copper(II) Chelates of Ethylenediamine-*N*,*N*,*N′*,*N′*-tetrapropionic Acid and Diethylenetriamine-pentaacetic Acid

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D. c. polarographic behavior of copper(II) in ethylenediamine-*N*,*N*,*N′*,*N′*-tetrapropionate (EDTP) and diethylenetriaminepentaacetate (DTPA) solutions was studied systematically. In EDTP solution, copper(II) ion invariably gave a single well-defined wave corresponding to the following reduction.

$$\mathrm{CuX^{2-}} + n\mathrm{H^+} + \mathrm{Hg} + 2\mathrm{e^-} = \mathrm{Cu(Hg)} + \mathrm{H}_n\mathrm{X}^{n-4}$$

In the DTPA solution, copper(II) ion gave a single wave reversible in nature at pH below 5.0, corresponding to the following electrode reaction.

$$\begin{array}{l}\mathrm{CuZ^{3-}} + n\mathrm{H^+} + \mathrm{Hg} + 2\mathrm{e^-} = \mathrm{Cu(Hg)} + \mathrm{H}_n\mathrm{Z}^{n-5}\\ \upharpoonleft\!\downharpoonright \mathrm{H^+}\\ \mathrm{CuHZ^{2-}}\end{array}$$

At higher pH, however, two waves could be observed. The second step was irreversible and its wave-height increased with increasing pH at the expense of the height of the first step.

In a previous paper,1) d.c. polarographic behavior of copper(II)-*N*-(2-hydroxyethyl)-ethylenediamine *N*,*N′*,*N′*-triacetate and -2,2′-ethyldioxybis[ethyliminodi(acetato)] chelates was studied systematically. In *N*-(2-hydroxyethyl)-ethylenediamine *N*,*N′*,*N′*-triacetate (EDTA-OH) solution, copper(II) ion was found to form only a normal chelate with a 1-to-1 composition with EDTA-OH, and to give invariably a single well-defined wave over the entire pH range covered. In 2,2′-ethylenedioxybis[ethyliminodi(acetate)] (GEDTA) solution, however, copper(II) ion gave two waves. The first wave was reversible in nature, but the second irreversible. The precise nature of the first step could be satisfactorily described by assuming that a normal copper(II)-GEDTA chelate of a 1-to-1 composition, which is in equilibrium with a normal chelate of a 1-to-2 composition, a protonated chelate and a mixed ligand chelate involving an acetate ion in solution, undergoes a reversible two-electron reduction at the mercury electrode.

In the present paper, results of a d.c. polarographic study on copper(II) chelates of ethylenediamine-*N*,*N*,*N′*,*N′*-tetrapropionic acid (EDTP) and diethylenetriaminepentaacetic acid (DTPA) are presented.

Experimental

Reagents. The preparation and standardization of copper(II) perchlorate solutions were described previously.2) The purification of EDTP and DTPA and the preparation of their solutions were also described previously.3) All other chemicals were of analytical reagent grade and used without further purification. The ionic strength of the sample solution was adjusted to 0.30 by adding an appropriate volume of 1.0 M $\mathrm{NaClO_4}$ solution.

Apparatus and Experimental Procedures. All apparatus and experimental procedures were as employed

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1) M. Kodama and Y. Tominaga, This Bulletin, **42**, 721 (1969).

2) M. Kodama and H. Ebine, This Bulletin, **40**, 1857 (1967).

previously.[3,4)]

Results and Discussion

D.C. Polarographic Behavior of Copper(II) Ion in EDTP Solution. D. c. polarographic behavior of copper(II)-EDTP chelate in solutions containing an excess of un-complexed EDTP was studied systematically in the pH range 3.46 to 7.80. In the pH range from 3.46 to 5.80, an acetate buffer (total concentration of acetate, 0.10 M) was used in order to maintain the pH of the solution at a constant value. At pH above 5.80, no buffer reagent was used because in this pH region, the present system containing un-complexed EDTP is considered to have enough buffer capacity to keep the pH constant.

As in the EDTA-OH system,[1)] copper(II) ion in EDTP solution gave a single well-defined wave, the height of which was exactly proportional to the bulk concentration of copper(II) ion and the square-root of the effective pressure on the dropping mercury electrode (DME). The result is not shown here. A typical polarogram and the result of a log-plot are shown in Figs. 1 and 2. These results clearly indicate that the copper(II) ion in the EDTP solution undergoes a reversible, two-electron reduction at the mercury electrode. As shown in Fig. 3, the half-wave potential, $(E_{1/2})_X$, was found to shift to more negative potentials with increasing pH of the solution according to the following relation.

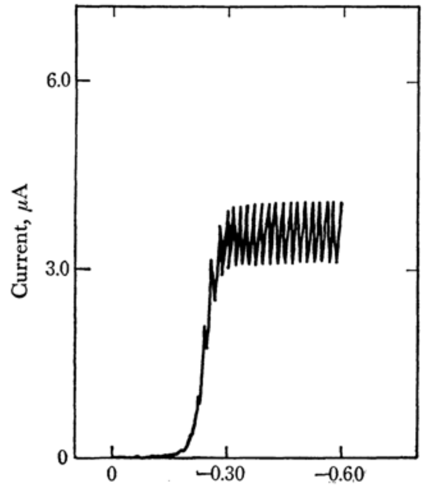

Fig. 1. D.c. polarogram of copper(II)-EDTP chelate.
pH=5.46, μ=0.30
Concentration of EDTP=20.0 mM
Concentration of copper(II)=0.682 mM

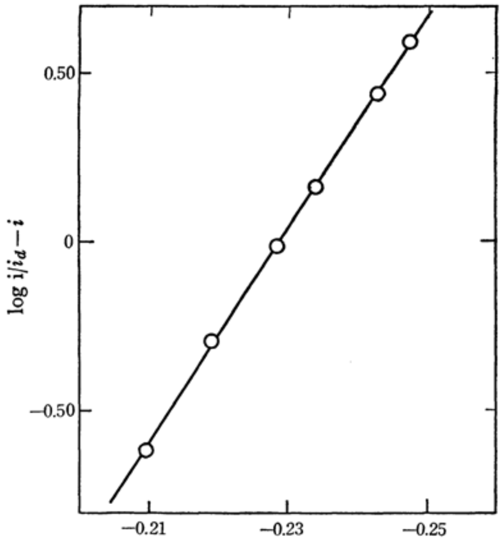

Fig. 2. The d.c. log-plot analysis.
pH=5.46, μ=0.30
Concentration of EDTP=20.0 mM
Concentration of copper(II)=0.682 mM

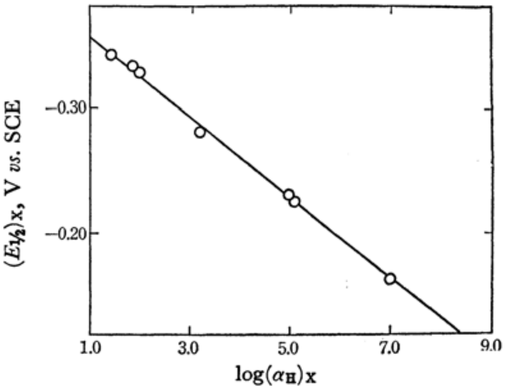

Fig. 3. The relation between the half-wave potential and the pH value.
μ=0.30
Concentration of EDTP=20.0 mM
Concentration of copper(II)=0.682 mM

$$(E_{1/2})_X = \text{constant}_1 + 0.0296 \log (\alpha_H)_X \qquad (1)$$

where $(\alpha_H)_X = 1+[H^+]/k_4+[H^+]^2/k_4 \cdot k_3+[H^+]^3/k_4 \cdot k_3 \cdot k_2+[H^+]^4/k_4 \cdot k_3 \cdot k_2 \cdot k_1$, and k's are the dissociation constants of EDTP.

The half-wave potential also shifted to more negative potentials with increasing concentration of un-complexed EDTP, $[X]_f$, according to the following relation,

$$(E_{1/2})_X = \text{constant}_2 - 0.0296 \log [X]_f \qquad (2)$$

but it is independent of the concentration of acetate and copper(II) ions. Results are given in Table 1.

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3) M. Kodama and A. Kimura, *ibid.*, **40**, 1639 (1967).

4) M. Kodama, T. Noda and M. Murata, *ibid.*, **41**, 354 (1968).

TABLE 1. DEPENDENCE OF $(E_{1/2})_X$ ON THE CONCENTRATION OF EDTP OR ACETATE ION
pH=5.33, μ=0.30
Concentration of copper(II)=0.682 mM

A) Dependence of $(E_{1/2})_X$ on the concentration of EDTP.
Total concentration of acetate=0.10 M

Concentration of EDTP mM	$(E_{1/2})_X$ V *vs.* SCE	$\Delta(E_{1/2})_X$, mV	
		Calcd	Obsd
15.0	−0.229	3.6	4.0
20.0	−0.233	0	0
40.0	−0.241	−9.0	−8.0
40.0*1	−0.242	−9.0	−9.0

*1 Concentration of copper(II)=1.364 mM

B) Dependence of $(E_{1/2})_X$ on the concentration of acetate.
Concentration of EDTP=20.0 mM

Concentration of acetate, M	$(E_{1/2})_X$ V *vs.* SCE
0.05	−0.233
0.10	−0.233
0.30	−0.231

From the above experimental results, it can be safely concluded that copper(II) ion forms only a normal 1-to-1 chelate with EDTP under the present experimental conditions and the electrode reaction can be expressed as,

$$\mathrm{CuX^{2-}} + n\mathrm{H^+} + \mathrm{Hg} + 2\mathrm{e^-} = \mathrm{Cu(Hg)} + \mathrm{H}_n\mathrm{X}^{n-4} \quad (3)$$

with the half-wave potential corresponding to:

$$(E_{1/2})_X = E^0_{\mathrm{Cu}} + 0.0296[\log f_{\mathrm{Cu}^{2+}} + \log\frac{k_{\mathrm{Cu(Hg)}}}{k_{\mathrm{CuX}}} + \log(\alpha_{\mathrm{H}})_X - \log K_{\mathrm{CuX}} - \log[\mathrm{X}]_f] \quad (4)$$

where $\mathrm{CuX^{2-}}$ and $\mathrm{H}_n\mathrm{X}^{n-4}$ refer to copper(II)-EDTP chelate and incompletely dissociated EDTP anion, respectively, and $f_{\mathrm{Cu}^{2+}}$, $k_{\mathrm{Cu(Hg)}}$, k_{CuX}, K_{CuX} and E^0_{Cu} have their usual meanings. Therefore, as discussed previously,1) the shift of the half-wave potential of copper(II), $\Delta E_{1/2}$, by complex formation with EDTP, can be given by:

$$\Delta E_{1/2} = 0.0296[\log K_{\mathrm{CuX}} + \log\frac{k_{\mathrm{CuX}}}{k_{\mathrm{Cu}^{2+}}} + \log[\mathrm{X}]_f - \log(\alpha_{\mathrm{H}})_X] \quad (5)$$

where $k_{\mathrm{Cu}^{2+}}$ has the same meaning as in a previous paper.1)

With the aid of Eq. (5), $\log K_{\mathrm{CuX}}$ value was calculated to be 15.1 from the $\Delta E_{1/2}$ value at $(\alpha_{\mathrm{H}})_X=1$. In the calculation, $k_{\mathrm{CuX}}/k_{\mathrm{Cu}^{2+}}$ determined experimentally as 1/1.20 was used. The $\log K_{\mathrm{CuX}}$ value thus obtained agreed well with the reported one (14.80 at μ=0.30).5) This agreement lends strong support to the above explanation.

D. C. Polargraphic Behavior of Copper(II) Ion in Diethylenetriaminepentaacetate Solution. Polarographic behavior of copper(II)-DTPA chelates was also studied under experimental conditions similar to those in the EDTP system. At pH below 5.0, copper(II) ion in DTPA solutions invariably gave a single well-defined wave, the height of which was exactly proportional to the concentration of copper(II) ion and the square-root of the effective mercury pressure on the DME. The plot of $\log(i/(i_d-i))$ against applied d. c. potential, E, gave a linear relation with a slope of −31 mV, suggesting a reversible two-electron reduction. The results are not shown here. As shown by the curve in Fig. 4, at pH above 5.0, however, copper(II) ion gave two waves. The first wave is reversible to such an extent that a log-plot gave a linear relation with a slope of −45 mV, and the wave-height increases with increase in hydrogen ion concentration at the expense of the second wave height. The second wave was irreversible in nature. Therefore, in the present study, results obtained mainly at pH below 5.0 will be given. At pH below 3.50, no buffer reagent was used because a system containing a large excess of un-complexed DTPA has enough buffer capacity to maintain the pH value of the solution constant.

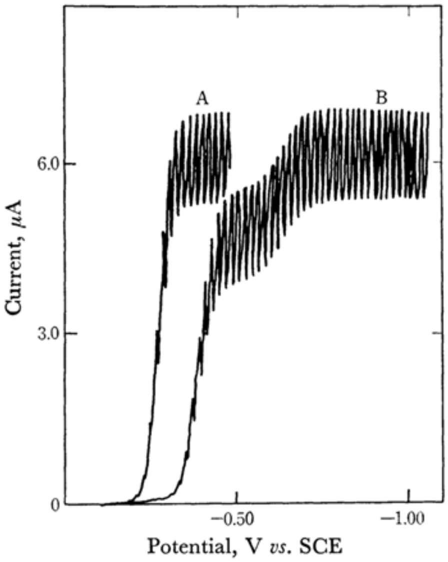

Fig. 4. D.c. polarogram of copper(II)-DTPA chelate.
μ=0.30
Concentration of DTPA=20.0 mM
Concentration of copper(II)=1.364 mM
A: pH=4.15 B: pH=6.01

As in the EDTP system, at a given pH, the half-wave potential of copper(II)-DTPA chelate, $(E_{1/2})_Z$, shifted to more negative potentials with increase in the bulk concentration of DTPA, $[\mathrm{Z}]_f$ according to the following relation:

$$(E_{1/2})_Z = \mathrm{constant}_3 - 0.0296 \log[\mathrm{Z}]_f \quad (6)$$

but, it is independent of the concentrations of acetate and copper(II) ions. The results are shown in Table 2. These facts clearly indicate that copper(II) ion forms only a normal chelate of a 1-to-1 composition with DTPA under the present experimental conditions. The half-wave potential also shifted to more negative potentials with increasing pH of the solution. But, in contrast with findings in the EDPT system, the plot of $(E_{1/2})_Z$ *vs.* $\log(\alpha_H)_Z$ did not give a linear relation with a slope of +30 mV. Here, $(\alpha_H)_Z$ is the (α_H) value of DTPA.

As discussed previously on the polarography of thallium(I)-DTPA chelate,[4] when copper(II) ion forms both normal and mono-protonated chelates with DTPA, and when the electrode reaction can be expressed as,

$$\begin{array}{l} CuZ^{3-} + nH^+ + Hg + 2e^- = Cu(Hg) + H_nZ^{n-5} \\ \quad \uparrow\downarrow H^+ \\ CuHZ^{2-} \end{array} \qquad (7)$$

the following relation can be expected thermodynamically.

$$K_{CuZ}(1+K^{H}_{CuZ}\cdot[H^+]) = \text{antilog}\left[\frac{\varDelta(E_{1/2})_Z}{0.0296} + \log(\alpha_H)_Z - \log[Z]_f + \log\frac{k_{Cu^{+2}}}{k_{CuZ}}\right] \qquad (8)$$

where $\varDelta(E_{1/2})_Z$ is the shift of the half-wave potential due to chelate formation with DTPA, K_{CuZ} the formation constant of copper(II)-DTPA chelate and $K^{H}_{CuZ}=[CuHZ^{2-}]/[CuZ^{3-}]\cdot[H^+]$. This relation was examined using some experimental data. The result shown in Fig. 5 clearly confirms the above explanation given by the present authors. From the slope and intercept of the linear relation between the right-hand side of Eq. (8) and $[H^+]$, K_{CuZ} and K^{H}_{CuZ} were estimated and given in Table 3 along with the reported value and the pK values of DTPA. The agreement between observed and reported values can be regarded as satisfactory.

TABLE 2. DEPENDENCE OF $(E_{1/2})_Z$ ON THE CONCENTRATION OF DTPA OR ACETATE ION
pH = 3.80, μ = 0.30
Concentration of copper (II) = 0.682 mM

A) Dependence of $(E_{1/2})_Z$ on the concentration of DTPA.

Total concentration of acetate = 0.10 M

Concentration of DTPA, mM	$(E_{1/2})_Z$ V *vs.* SCE	$\varDelta(E_{1/2})_Z$, mV	
		Calcd	Obsd
10.0	−0.229	5.6	5.0
15.0	−0.234	0	0
20.0	−0.239	−3.9	−5.0
20.0*1	−0.239	−3.9	−5.0
40.0	−0.245	−9.1	−11.0

*1 Concentration of copper (II) = 1.364 mM

B) Dependence of $(E_{1/2})_Z$ on the concentration of acetate.

Concentration of DTPA = 20.0 mM

Concentration of acetate, M	$(E_{1/2})_Z$, V *vs.* SCE
0.05	−0.244
0.10	−0.245
0.30	−0.243

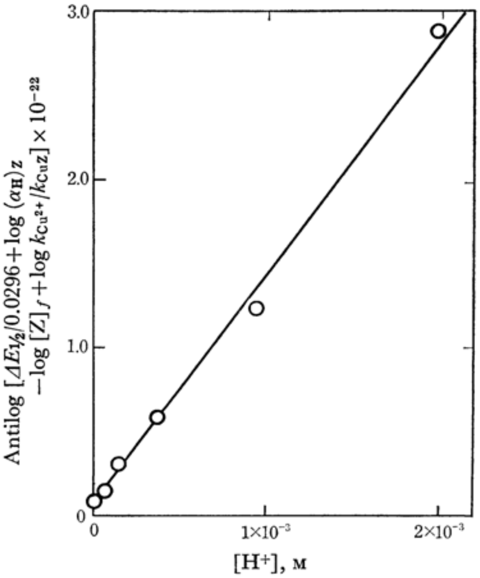

Fig. 5. The relation between antilog $[\varDelta(E_{1/2})/0.0296 + \log(\alpha_H)_Z - \log[Z]_f + \log(k_{Cu^{2+}}/k_{CuZ})]$ and the concentration of hydrogen ion.
μ=0.30
Concentration of copper(II) = 0.683 mM

TABLE 3. EQUILIBRIUM CONSTANTS (μ=0.30)

i) Dissocidation constants (mixed constants)

	pK_1	pK_2	pK_3	pK_4	pK_5
EDTP[5]**	2.96	3.32	6.58	9.33	—
DTPA[6]**	1.82	2.68	4.10	7.74	10.14

ii) Stability constants

	log K_{CuZ}	
Copper(II)-EDTP chelate	15.10*	14.80[5]**
Copper(II)-DTPA chelate	21.00*	20.78[7]**

iii) Equilibrium constant (mixed constant)

Cu(II)-DTPA chelate:	$\log K^{H}_{CuZ}(=[CuHZ^{2-}]/[CuZ^{3-}]\cdot[H^+])$	
	4.12*	4.45[7]**

* These values were obtained by the present authors.
** Those values were calculated from the related constants in solutions of ionic strength 0.10 and the activity coefficients of the ions calculated by means of Davies equation.[8]

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6) E. Wanninen, *Suomen Kem.*, **28B**, 146 (1955).

7) G. Anderegg, P. Nageli, F. Muller and G. Schwarzenbach, *Helv. Chim. Acta*, **42**, 827 (1959).

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