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Polarographic Study of Copper(II)-*N*-(2-Hydroxyethyl)ethylenediamine-*N*,*N*′,*N*′-triacetate and -2,2′-Ethylenedioxybis[ethyliminodi(acetate)] Chelates

Mutsuo KODAMA and Yayoe TOMINAGA

Department of Chemistry, Ibaraki University, Mito, Ibaraki

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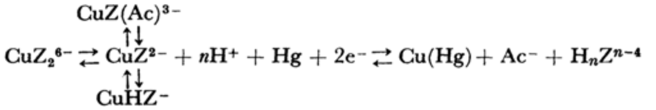
D.c. polarographic behavior of copper(II) ion in *N*-(2-hydroxyethyl)ethylenediamine-*N*,*N*′,*N*′-triacetate (EDTA-OH) and 2,2′-ehtylenedioxybis[ethyliminodi(acetate)] (GEDTA) solutions was studied systematically. In an EDTA-OH solution, copper(II) ion gave invariably a single well-defined wave corresponding to the following two-electron reduction.

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

On the other hand, in a GEDTA solution, two waves were obtained. The height of the first wave, which is reversible in nature, increases with increasing pH of the solution at the expense of the height of the irreversible second wave. From the relation between the half-wave potential and the concentrations of hydrogen ion, GEDTA and acetate ion, determined experimentally, the compositions and the stability constants of copper(II)-GEDTA chelates in solution were determined and the electrode reaction mechanism established:



$$\begin{array}{c} \mathrm{CuZ(Ac)^{3-}} \\ \uparrow\downarrow \\ \mathrm{CuZ_2^{6-}} \rightleftarrows \mathrm{CuZ^{2-}} + n\mathrm{H^+} + \mathrm{Hg} + 2e^- \rightleftarrows \mathrm{Cu(Hg)} + \mathrm{Ac^-} + \mathrm{H}_n\mathrm{Z}^{n-4} \\ \uparrow\downarrow \\ \mathrm{CuHZ^-} \end{array}$$

Copper(II) ion has been reported to form stable chelates with several polyaminocarboxylic acids.[1] Generally, copper(II) ion and its chelates behave reversibly in polarographic electrolysis. Therefore, the polarographic method is well suited to the study of copper(II) chelates.

In this paper, results of a polarographic study of copper(II) chelates of *N*-(2-hydroxyethyl)ethylenediamine-*N*,*N*′,*N*′-triacetic acid (EDTA-OH) and 2,2′-ethylenedioxybis[ethyliminodi(acetic acid)] (GEDTA) are presented.

Experimental

Reagents. Purification of EDTA-OH and GEDTA and the preparation of their solutions were as described previously.[2] Preparation and standardization of copper(II) perchlorate solution are also given is a previous paper.[3] All other chemicals were analytical reagent grade, and were used without further purification. The ionic strength of the sample solutions was adjusted to 0.30 by adding $\mathrm{NaClO_4}$ solution.

Apparatus and Experimental Procedure. All apparatus (manual and pen-recording polarographs, and the dropping mercury electrode (DME)) and experimental procedures were as employed previously.[4]

Results and Discussion

D. C. Polarographic Behavior of Copper(II)-*N*-(2-Hydroxyethyl) ethylenediamine-*N*, *N*′, *N*′-triacetate Chelate. The d. c. polarographic behavior of copper(II) ion in an EDTA-OH solution was studied systematically in the pH range 3.80 to 5.90. To maintain the pH of the solution constant, acetate buffer (total concentration of acetate = 0.10 M) was used. As illustrated by the curve in Fig. 1, copper(II) ion in an EDTA-OH solution gave invariably a single well-defined wave over the entire pH range studied. The plot of $\log(i/(i_d-i))$ *versus* potential E gave a straight line with a slope of -32 mV (Fig. 2). Here, i_d and i denote the limiting current and current at potential E, respectively.

The limiting current i_d was exactly proportional to the bulk concentration of copper(II) ion and to the square-root of the effective pressure on the dropping mercury electrode (Tables 1 and 2). These facts clearly imply that the electrode reaction of copper(II) ion in an EDTA-OH solution proceeds reversibly in the usual polarographic sense, corre-

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[1] L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London (1964).

[2] M. Kodama, C. Sasaki, and T. Noda, This Bulletin, **41**, 2033 (1968).

[3] M. Kodama and H. Ebine, *ibid.*, **40**, 1857 (1967).

[4] M. Kodama and A. Kimura, *ibid.*, **40**, 1637 (1967).

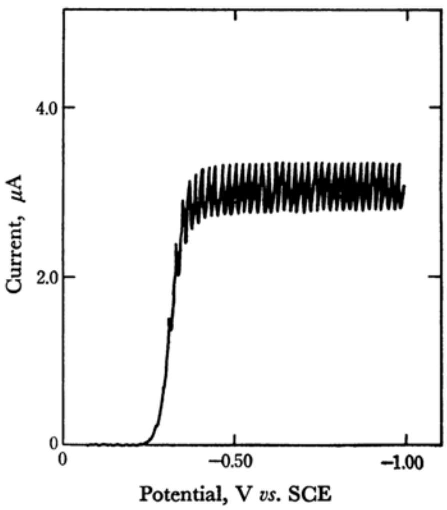

Fig. 1. D.c. polarogram of copper(II)-EDTA-OH chelate.

pH=5.62 (acetate buffer, 0.10м), μ=0.30
Concentration of EDTA-OH=20.0 mм
Concentration of copper(II)=0.682 mм

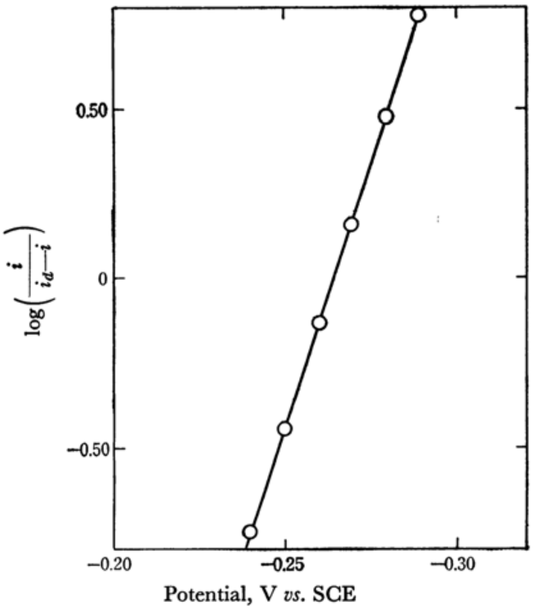

Fig. 2. The d. c. log-plot analysis.

pH=5.62 (acetate buffer, 0.10м), μ=0.30
Concentration of EDTA-OH=20.0 mм
Concentration of copper(II)=0.682 mм

sponding to a two-electron reduction.

When the bulk concentration of uncomplexed EDTA-OH is constant, the half-wave potential $(E_{1/2})_{\mathrm{CuX}}$ shifts linearly to negative potentials with decreasing $\log(\alpha_{\mathrm{H}})_x$ value of EDTA-OH, obeying the following relation (Fig. 3).

$$\frac{\Delta(E_{1/2})_{\mathrm{CuX}}}{\Delta \log(\alpha_{\mathrm{H}})_x} = 31\,\mathrm{mV} \qquad (1)$$

Here, $(\alpha_{\mathrm{H}})_x$ is given by

$$(\alpha_{\mathrm{H}})_x = 1 + \frac{[\mathrm{H}^+]}{k_3} + \frac{[\mathrm{H}^+]^2}{k_3 \cdot k_2} + \frac{[\mathrm{H}^+]^3}{k_3 \cdot k_2 \cdot k_1} \qquad (2)$$

where k's are dissociation constants of EDTA-OH.

When the hydrogen ion concentration of solution was kept constant, $(E_{1/2})_{\mathrm{CuX}}$ also shifted to negative potentials with increasing concentration of uncomplexed EDTA-OH, obeying the following relation (Table 3),

$$\frac{\Delta(E)_{1/2})_{\mathrm{CuX}}}{\Delta \log[\mathrm{X}]_f} = -\,31\,\mathrm{mV}, \qquad (3)$$

but was independent of acetate ion concentration (Table 4).

TABLE 1. DEPENDENCE OF THE WAVE-HEIGHT ON THE CONCENTRATION OF COPPER (II)

pH = 5.86, μ = 0.30
Concentration of EDTA-OH = 20.0 mм
Height of mercury column = 60.0 cm

Concentration of Cu(II), C^0_{Cu}, mм	Limiting current i_d, μA	i_d/C^0_{Cu} μA/mм
0.682	2.94_5	4.32
1.36_4	5.88_0	4.31
2.72_8	11.78_0	4.33

TABLE 2. DEPENDENCE OF THE WAVE-HEIGHT ON THE EFFECTIVE HEIGHT OF MERCURY COLUMN

pH = 5.86, μ = 0.30
Concentration of EDTA-OH = 20.0 mм
Concentration of copper(II) = 1.36_4 mм

Effective height of mercury column h_c, cm	Limiting current id, μA	$i_d/h_c^{1/2}$
49.2	5.33_8	0.761
59.2	5.88_0	0.765
79.2	6.84_1	0.768

TABLE 3. DEPENDENCE OF THE HALF-WAVE POTEETIAL ON THE CCNCENTRATION OF EDTA-OH

pH = 5.62, μ = 0.30
Concentration of copper(II) = 0.682 mм
Concentration of acetate ion = 0.10 м

Concentration of EDTA-OH mм	Half-wave potential V vs. SCE	$\Delta E_{1/2}$, mV	
		Calcd	Obsd
10.0	−0.290	0	0
20.0	−0.300	9.0	10
40.0	−0.310	18.0	20

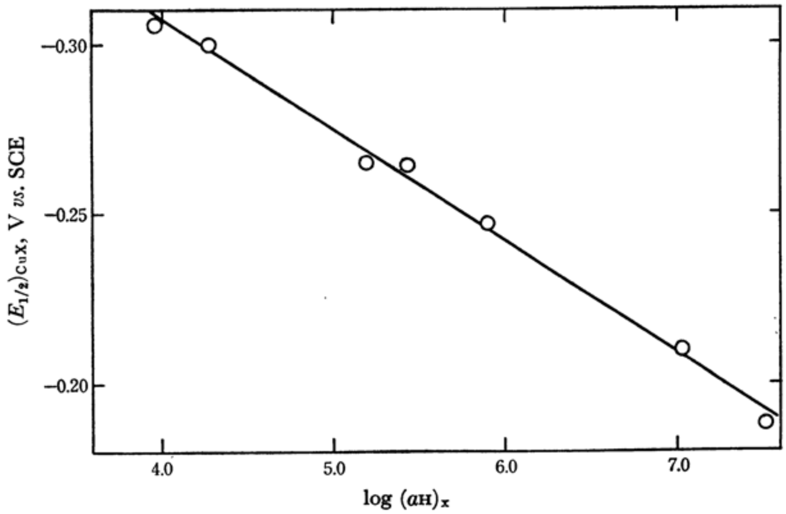

Fig. 3. The relation between the half-wave potential and the pH. $\mu=0.30$
Concentration of EDTA-OH=20.0 mM
Concentration of copper(II)=0.682 mM

TABLE 4. DEPENDENCE OF THE HALF-WAVE POTENTIAL ON THE CONCENTRATIONS OF ACETATE ION OR COPPER(II) ION

pH = 4.85, $\mu = 0.30$
Concentration of EDTA-OH = 20.0 mM

Concentration of acetation M	Concentration of copper(II) mM	Half-wave potential V *vs.* SCE
0.05	0.682	−0.265
0.10	0.682	−0.263
0.10	1.36_4	−0.264
0.20	0.682	−0.264

From the above facts, it can be safely concluded that copper(II) ion forms only a normal chelate of 1 to 1 composition with EDTA-OH under the present experimental conditions, and not a protonated chelate or mixed ligand chelate involving acetate ion. The above conclusion was also confirmed by the fact that $(E_{1/2})_{\mathrm{CuX}}$ was independent of the concentration of copper(II) ion, provided that the concentration of EDTA-OH and the pH of the solution were kept constant (Table 4).

From the above experimental results and discussion, it is evident that the electrode reaction of copper(II) ion in EDTA-OH solution can be expressed as

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

with the half-wave potential $(E_{1/2})_{\mathrm{CuX}}$, corresponding to:

$$(E_{1/2})_{\mathrm{CuX}} = E^0_{\mathrm{Cu}} + 0.0296[\log f_{\mathrm{Cu}^{2+}} + \log \frac{k_{\mathrm{Cu(Hg)}}}{k_{\mathrm{CuX}}} + \log(a_{\mathrm{H}})_x - \log K_{\mathrm{CuX}} - \log[\mathrm{X}]_f], \quad (5)$$

where $E^0{}_{\mathrm{Cu}}$ denotes the standard potential, K_{CuX} the stability constant of copper(II) - EDTA-OH chelate, k's the diffusion current constants, $f_{\mathrm{Cu}^{2+}}$ the activity coefficient of copper(II) ion at $\mu=0.30$ and $[\mathrm{X}]_f$ the bulk concentration of uncomplexed EDTA-OH.

As stated already, the relations between the half-wave potential and the concentrations of acetate ion, EDTA-OH and hydrogen ion, predicted from Eq. (5), were verified satisfactorily by the experimental results.

For the reversible two-electron reduction of copper(II) ion at the mercury electrode, the half-wave potential can be derived as

$$(E_{1/2})_{\mathrm{Cu}^{2+}} = E^0_{\mathrm{Cu}} + 0.0296\left[\log \frac{k_{\mathrm{Cu(Hg)}}}{k_{\mathrm{Cu}^{2+}}} + \log f_{\mathrm{Cu}^{2+}}\right] \quad (6)$$

Therefore, the shift of the half-wave potential of copper(II) due to the chelate formation with EDTA-OH becomes

$$\Delta(E_{1/2}) = (E_{1/2})_{\mathrm{Cu}^{2+}} - (E_{1/2})_{\mathrm{CuX}} = 0.0296\Big[\log K_{\mathrm{CuX}} + \log \frac{k_{\mathrm{CuX}}}{k_{\mathrm{Cu}^{2+}}} + \log[\mathrm{X}]_f - \log(a_{\mathrm{H}})_x\Big] \quad (7)$$

Using the $\Delta(E_{1/2})$ value at $(a_{\mathrm{H}})x=1$, log K_{CuX} was calculated to be 16.96*[1] with the aid of Eq. (7). This agrees well with the value reported by Moeller and Ferrus,[5] and confirms the above explanation.

D. C. Polarographic Behavior of Copper(II)-

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*[1] This value corresponds to 17.41 at ionic strength 0.10.

[5] T. Moeller and R. Ferrus, *J. Inorg. Nuclear Chem.*, **11**, 261 (1961).

2,2′-Ethylenedioxybis[ethyliminodi(acetate)] Chelate. The polarographic behavior of copper(II) ions in a GEDTA solution was studied under experimental conditions similar to those employed in the EDTA-OH system. Copper(II) ion in EDTA-OH solutions gave invariably a well-defined single wave over the entire pH range studied. However, copper(II) ion in a GEDTA solution gave two waves, the heights of which were exactly proportional to the bulk concentration of copper(II) ion and to the square-root of the effective mercury pressure on DME at a given pH (Fig. 4).

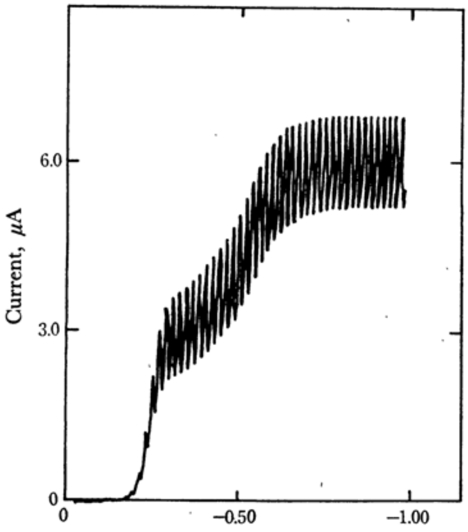


Fig. 4. D. c. polarogram of copper(II)-GEDTA chelate.

pH=5.54 (acetate bufier, 0.10M), μ=0.30
Concentration of GEDTA=18.6 mM
Concentration of copper(II)=1.36_4 mM

The height of the first wave, which is reversible in nature, increases with increasing concentration of hydrogen ion at the expense of the height of the irreversible second wave. The sum of two wave heights is almost constant under the experimental conditions employed ($3.30<\mathrm{pH}<6.00$, acetate buffer). When the pH value of the solution is kept constant, with increasing concentration of acetate ion or of GEDTA, the first wave height also increases and the half-wave potential shifts to more negative potentials.

As shown in Fig. 5, a plot of $\log[i/(i_l-i)]$ *vs.* E for the first wave gave a straight line with a slope of −31 mV, corresponding to the two-electron reversible reduction. Here i_l means the limiting current.

These facts may suggest that the first wave corresponds to a two-electron reduction involving copper(II)-GEDTA chelates and the electrode reaction can be expressed as

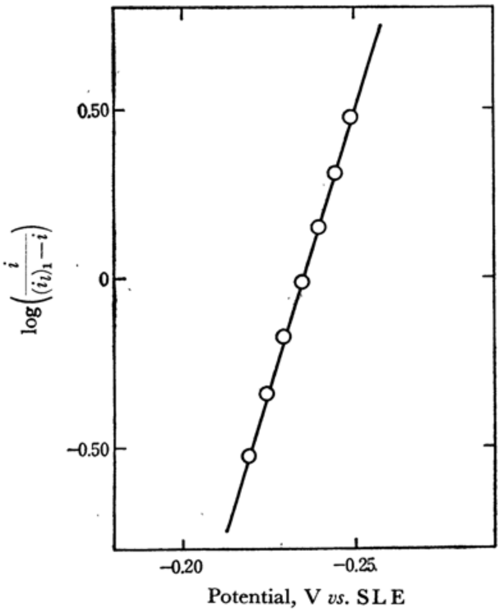
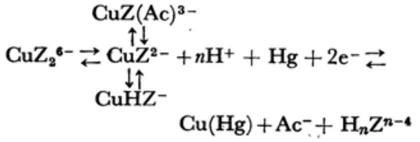


Fig. 5. The d. c. log-plot analysis of the first wave.

pH=5.54 (acetate buffer, 0.10M), μ=0.30
Concentration of GEDTA =18.6 mM
Concentration of copper(II)=1.36_4 mM



$$\begin{array}{l} \qquad\qquad \mathrm{CuZ(Ac)^{3-}} \\ \qquad\qquad\quad \uparrow\downarrow \\ \mathrm{CuZ_2{}^{6-}} \rightleftarrows \mathrm{CuZ^{2-}} + n\mathrm{H^+} + \mathrm{Hg} + 2\mathrm{e^-} \rightleftarrows \\ \qquad\qquad\quad \downarrow\uparrow \\ \qquad\qquad \mathrm{CuHZ^-} \\ \qquad\qquad\qquad\qquad \mathrm{Cu(Hg)} + \mathrm{Ac^-} + \mathrm{H}_n\mathrm{Z}^{n-4} \end{array} \tag{8}$$

where $\mathrm{CuHZ^-}$ denotes the protonated chelate, $\mathrm{CuZ(Ac)^{3-}}$ the mixed chelate involving acetate ion, $\mathrm{CuZ^{2-}}$ and $\mathrm{CuZ_2{}^{6-}}$, normal chelates of 1 to 1 and 1 to 2 compositions and $\mathrm{Z^{4-}}$ completely de-protonated GEDTA anion.

For the above electrode reaction, one can derive the following relation thermodynamically by assuming that all diffusion current constants of copper(II) GEDTA chelates are the same.

$$\begin{aligned}(E_{1/2})_{\mathrm{CuZ}} = E^0_{\mathrm{Cu}} - 0.0296\Big[\log K_{\mathrm{CuZ}}\Big(1+K^{\mathrm{H}}_{\mathrm{CuZ}}[\mathrm{H^+}] \\ + K^{\mathrm{Ac}}_{\mathrm{CuZ}}[\mathrm{Ac^-}] + K^{\mathrm{Z}}_{\mathrm{CuZ}}\frac{[\mathrm{Z}]_f}{(\alpha_{\mathrm{H}})_z}\Big) - \log(\alpha_{\mathrm{H}})_z \\ + \log[\mathrm{Z}]_f + \log\frac{k_{\mathrm{CuZ}}}{k_{\mathrm{Cu(Hg)}}} + \log f_{\mathrm{Cu^{2+}}}\Big],\end{aligned} \tag{9}$$

where $(\alpha_{\mathrm{H}})_z$ is the (α_{H}) value of GEDTA and other notations used are defined as follows.

$$K^{\mathrm{AC}}_{\mathrm{CuZ}} = \frac{[\mathrm{CuZ(Ac)^{3-}}]}{[\mathrm{CuZ^{2-}}]\cdot[\mathrm{Ac^-}]},\quad K^{\mathrm{H}}_{\mathrm{CuZ}} = \frac{[\mathrm{CuHZ^-}]}{[\mathrm{CuZ^{2-}}]\cdot[\mathrm{H^+}]}$$

$$K^{\mathrm{Z}}_{\mathrm{CuZ}} = \frac{[\mathrm{CuZ_2{}^{6-}}]}{[\mathrm{CuZ^{2-}}]\cdot[\mathrm{Z^{4-}}]}$$

Equation (9) indicates that if the above electrode reaction mechanism proposed is correct, it would be possible to calculate $K^{\mathrm{H}}_{\mathrm{CuZ}}$, $K^{\mathrm{Ac}}_{\mathrm{CuZ}}$ and $K^{\mathrm{Z}}_{\mathrm{CuZ}}$ values, at least from six $(E_{1/2})_{\mathrm{CuZ}}$ values observed at various concentrations of three species, namely, hydrogen ion, acetate ion and GEDTA. The three K values thus estimated should explain satisfactorily the change in height of the first wave with change in concentrations of the above three species.

$K^{\mathrm{H}}_{\mathrm{CuZ}}$, $K^{\mathrm{Ac}}_{\mathrm{CuZ}}$ and $K^{\mathrm{Z}}_{\mathrm{CuZ}}$ values were calculated using the half-wave potentials given in Tables 5, 6 and 7, and are listed in Table 8.

TABLE 5. DEPENDENCE OF THE HALF-WAVE POTENTIAL AND THE WAVE-HEIGHT ON pH

$\mu = 030$, Concentration of GEDTA = 18.6 mM
Totoal concentration of acetate = 0.10 M
Concentration of copper(II) = 1.36_4 mM

pH	$E_{1/2}$ of the first wave, V *vs.* SCE	Wave-height, μA		$(i_l)_1/(i_l)_2$ ratio	
		$(i_l)_1$	$(i_l)_2$	Calcd	Obsd
3.80	-0.160_5	5.67_5	0.54_0	13.0	12.1
4.80	-0.200	3.66_0	2.54_0	1.61	1.64
5.54	-0.235	2.75_2	3.17_1	1.00	1.00

TABLE 6. DEPENDENCE OF THE HALF-WAVE POTENTIAL AND THE WAVE-HEIGHT ON THE CONCENTRATION OF ACETATE ION

pH = 5.54, $\mu = 0.30$
Concentration of GEDTA = 18.6 mM
Concentration of copper(II) = 1.36_4 mM

Total concn. of acetate, M	$E_{1/2}$ of the first wave V *vs.* SCE	Wave-height μA		$(i_l)_1/(i_l)_2$ ratio	
		$(i_l)_1$	$(i_l)_2$	Calcd	Obsd
0.10	-0.235	2.75_2	3.17_1	1.00	1.00
0.30	-0.245	3.24_5	2.64_7	1.40	1.40

TABLE 7. DEPENDENCE OF THE HALF-WAVE POTENTIAL AND THE WAVE-HEIGHT ON THE CONCENTRATION OF GEDTA

pH = 5.54, $\mu = 0.30$
Total concentration of acetate = 0.10 M
Concentration of copper(II) = 1.36_4 mM

Concn. of GEDTA mM	$E_{1/2}$ of the first wave V *vs.* SCE	Wave-height, μA		$(i_l)_1/(i_l)_2$ ratio	
		$(i_l)_1$	$(i_l)_2$	Calcd	Obsd
13.6	-0.228	2.41_1	3.41_0	1.00	1.00
18.6	-0.235	2.75_2	3.17_1	1.12	1.22
38.6	-0.249	3.11_5	2.85_7	1.53	1.54

TABLE 8. NUMERICAL VALUES

A) Dissociation constants (μ=0.30, mixed constants)
  i) EDTA-OH*
    $pK_1 = 2.35$, $pK_2 = 5.26$, $pK_3 = 9.74$
  ii) GEDTA*
    $pK_1 = 1.96$, $pK_2 = 2.57$, $pK_3 = 8.66$, $pK_4 = 9.19$
  iii) Acetic acid
    $pK_a = 4.75$
B) Stability constants (μ=0.30)
  i) Copper(II) - EDTA-OH chelate
    $\log K_{\mathrm{CuX}} = 16.96$**, 16.95[5],*
  ii) Copper(II)-GEDTA chelate
    $\log K_{\mathrm{CuZ}} = 16.77$**, 16.73[6],*
C) Equilibrium constants (μ=0.30)**

$$K^{\mathrm{H}}_{\mathrm{CuZ}} = \frac{[\mathrm{CuHZ}^-]}{[\mathrm{CuZ}^{2-}]\cdot[\mathrm{H}^+]} = 3.87 \times 10^5$$

$$K^{\mathrm{Ac}}_{\mathrm{CuZ}} = \frac{[\mathrm{CuZ(Ac)}^{3-}}{\mathrm{CuZ}^{2-}]\cdot[\mathrm{Ac}^-]} = 11.5$$

$$K^{\mathrm{Z}}_{\mathrm{CuZ}} = \frac{[\mathrm{CuZ_2}^{6-}}{[\mathrm{CuZ}^{6-}]\cdot[\mathrm{Z}^{4-}]} = 4.34 \times 10^8$$

* Those values were calculated from the related constants in solutions of ionic strength 0.10 and the activity constants of the ions calculated by means of Davies equation.[7]

** These values were obtained by the present authors.

Since the half-wave potential of the second wave also shifts to more negative potentials with increasing concentration of GEDTA and pH, this step also corresponds to the reduction of copper(II)-GEDTA chelate. If two species of copper(II)-GEDTA chelates, which show different polarographic behavior, co-exist in equilibrium in solution, the following relation would be expected on the assumption of equal diffusion current constants.

$$\frac{(i_l)_1}{(i_l)_2} = \frac{[\mathrm{CuZ}^{2-}]+[\mathrm{CuHZ}^-]+[\mathrm{CuZ(Ac)}^{3-}]+[\mathrm{CuZ_2}^{6-}]}{[\mathrm{Cu(II)\text{-}GEDTA^*}]}$$
$$= \frac{1+K^{\mathrm{H}}_{\mathrm{CuZ}}[\mathrm{H}^+]+K^{\mathrm{Ac}}_{\mathrm{CuZ}}[\mathrm{Ac}^-]+K^{\mathrm{Z}}_{\mathrm{CuZ}}[\mathrm{Z}]_f/(a_{\mathrm{H}})_z}{K}, \tag{10}$$

where $(i_l)_1$ and $(i_l)_2$ denotes the limiting currents of the first and second steps, respectively, and K the equilibrium constant defined as $K=[\mathrm{Cu(II)\text{-}GEDTA^*}]/[\mathrm{CuZ}^{2-}]$. Here, Cu(II)-GEDTA* means the species which corresponds to the second step.

The ratios $(i_l)_1/(i_l)_2$'s, calculated using $K^{\mathrm{H}}_{\mathrm{CuZ}}$, $K^{\mathrm{Ac}}_{\mathrm{CuZ}}$ and $K^{\mathrm{Z}}_{\mathrm{CuZ}}$ are listed in Tables 5, 6 and 7 together with observed values. The calculated values agree well with those observed. Although there may be some small doubt about the presence of normal copper(II)-GEDTA chelate of a 1 to 2 composition, this agreement supports the above explanation.

With the aid of Eqs. (6) and (9), log K_{CuZ} was also calculated to be 17.44 (μ=0.10) using the $K^{\mathrm{H}}_{\mathrm{CuZ}}$, $K^{\mathrm{Ac}}_{\mathrm{CuZ}}$ and $K^{\mathrm{Z}}_{\mathrm{CuZ}}$ values. This also agrees well with the reported value,[6] giving further confirmation to the above explanation.

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[6] J. H. Holloway and C. N. Reilley, *Anal. Chem.*, **32**, 249 (1960).

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

Since there is little reason to believe that the two ether oxygens in GEDTA can not partake in the chelate formation of GEDTA, it can not rule out the possibility that there exist two species of copper(II)-GEDTA chelates. Because of its irreversibility, further systematic studies on the nature of the second step were not conducted in this investigation, but to get an insight into the precise nature of the chelate corresponding to the second wave, further systematic investigations by the methods other than polarography should be carried out.