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The Complex Formation of the Copper(II) Ion with Ethylenediaminetetraacetic Acid and *N*-(2-Hydroxyethyl)ethylenediamine-*N*,*N'*,*N'*-triacetic Acid

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The complex formation of the Cu(II) ion with ethylenediaminetetraacetic acid (EDTA) and *N*-(2-hydroxyethyl)ethylenediamine-*N*,*N'*,*N'*-triacetic acid (HEDTA) has been studied potentiometrically and polarographically over the wide pH range from 1 to 11 in aqueous solutions containing 1.0 mol dm^{-1} $NaClO_4$ at 25.0 °C. Both the emf data obtained by potentiometric titrations and the pH-dependence of reversible half-wave potentials were explained in terms of the formation of the following complex species: for the Cu–EDTA complexes, CuL^{2-} ($\log \beta_{101}=17.28\pm0.04$), $CuHL^-$ ($\log \beta_{111}=20.15\pm0.04$), CuH_2L ($\log \beta_{121}=22.73\pm0.04$), CuH_3L^+ ($\log \beta_{131}=24.12\pm0.04$), and $CuH_{-1}L^{3-}$ ($\log \beta_{1-11}=6.83\pm0.05$); for the Cu–HEDTA complexes, CuL^- ($\log \beta_{101}=16.30\pm0.05$), CuHL ($\log \beta_{111}=18.76\pm0.04$), CuH_2L^+ ($\log \beta_{121}=19.85\pm0.04$) and $CuH_{-1}L^{2-}$ ($\log \beta_{1-11}=6.35\pm0.05$), where $\beta_{pqr}=[Cu_pH_qL_r]/[Cu^{2+}]^p[H^+]^q[L]^r$, and where L denotes the unprotonated molecule of EDTA or HEDTA.

The complex-formation reaction of the Cu(II) ion with ethylenediaminetetraacetic acid (EDTA) and *N*-(2-hydroxyethyl)ethylenediamine-*N*,*N'*,*N'*-triacetic acid (HEDTA) has been studied by a number of workers, and the formation constants of unprotonated and monoprotonated species have been reported.[1,2] The formation constants of the diprotonated Cu(II)–EDTA complex have been reported only by Gorelova *et al.*[3] Interest has also been shown in the problem of determining the protonation schemes of the coordinated ligands and structures of metal complexes by using infrared spectrometry,[4–6] NMR spectrometry[4,7–10] and other methods.[11–14] Nuttall and Stalker[15] have recently proposed, from measurements of the Raman spectra, that protons in protonated Cu(II)–EDTA complexes are located at the oxygen atoms of the ligand carboxyl groups.

In our previous papers[16,17] we have found that a number of protonated complex species of the MH_qL type ($q=1,2,3$ for the EDTA complex and $q=1,2$ for the HEDTA complex) are formed in an acidic solution containing Cd(II) and Pb(II) ions. Therefore, it seemed it would be interesting to see if Cu(II)-complexes with EDTA and HEDTA form a series of protonated species in an acidic solution. The examination of complex-formation equilibria was performed by potentiometric titration measurements, polarographic method, and visible-spectrum measurements over the wide pH range from 1.0 to 11.0.

Symbols

h	Concentration of hydrogen ions at equilibrium.
m	Concentration of metal ions at equilibrium.
H	Analytical excess of hydrogen ions in a test solution.
c_{Cu}	Total concentration of Cu(II) ions.
L	Ethylenediaminetetraacetate anion (edta^{4-}) or *N*-(2-Hydroxyethyl)ethylenediamine-*N*,*N'*,*N'*-triacetate anion (hedta^{3-}).
c_L	Total concentration of L.
l	Concentration of free L.
$\bar{X}$	Degree of neutralization of H_4L for EDTA or H_3L for HEDTA: $(-H+[H]-[OH])/c_L$.
p	Number of metal atoms bound to the complex.
q	Number of protons bound to the complex; $q<0$ corresponds to the formation of a deprotonated complex.
r	Number of ligands bound to the complex.
β_{pqr}	Equilibrium constant for the reaction: $pM+qH+rL=M_pH_qL_r$.
[ ]	Concentration.
D_{Cu}	Diffusion coefficient of the aqua Cu(II) ion.
D	Average diffusion coefficient of all complex species present.[18]
$(E_{1/2})_{Cu}$	Reversible half-wave potential of the aqua Cu(II) ion.
$(E^r_{1/2})_{rev}$	Reversible half-wave potential of the Cu(II)–EDTA or –HEDTA system.
R	Gas constant.
T	Thermodynamic temperature.
F	Faraday constant.

All ionic charges are omitted for the sake of convenience.

Experimental

Reagents. *Disodium ethylenediaminetetraacetate* (reagent grade, Dojindo Lab.) was recrystallized twice, dried, and then stored in a desiccator over silica gel. N-*(2-Hydroxyethyl)ethylenediamine*-N,N',N'-*triacetic acid* (Dojindo Lab.) was recrystallized from distilled water and dried under a reduced pressure. *Copper(II) perchlorate* was prepared by dissolving $CuCO_3$ in an $HClO_4$ solution and purified by recrystallizing it three times from distilled water. The $CuCO_3$ used was precipitated from a $Cu(NO_3)_2$ solution with Na_2CO_3 and then thoroughly decanted. The stock solution contained a small amount of $HClO_4$ to prevent the hydrolysis of the Cu(II) ion. The concentration of excess $HClO_4$ in the solution was determined from the location of the end point of neutralization by means of a Gran-plot. The concentration of Cu(II) ions in the stock solution was determined by electrogravimetry. *Sodium perchlorate*, *sodium hydroxide*, and *perchloric acid* stock solutions were prepared by the methods described previously.[16] A copper-amalgam was prepared by the electrolysis of a copper sulfate

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solution with a Metrohm model E 211 A coulometer. The metal content of the amalgam was about 1 wt%. The oxidation of the amalgam was prevented by preparing and storing it in a nitrogen atmosphere. All the other chemicals were prepared and purified by the methods described previously.[16)]

Potentiometric Measurements. The measurements were carried out in a paraffin oil thermostat at (25.00±0.02) °C by using glass and copper-amalgam electrodes. Emf measurements of electrodes were carried out with essentially the same method as has been described previously.[16)] The potential of the amalgam electrode became constant after 5—15 min within an accuracy of ±0.02 mV in the pH range of 1.0—2.5 and within an accuracy of ±0.05 mV in that of 2.5—4.0. At pH values above 4.0 the potential was slightly unstable, and it required 1 h to attain a constant value within an accuracy of ±0.1 mV at pH values up to 10.0. The emf of the glass electrode cell became constant after about 5 min and was determined within an accuracy of 0.1 mV over the pH range of 1.0—11.0. The perchlorate concentration was kept constant at 1.0 mol dm^{-3} in all runs. The apparatus and the experimental procedures used for potentiometric titrations have been described previously.[16)]

Polarographic Measurements. The polarographic apparatus used was described previously.[18)] No buffer was added to the test solution, because the ligands present in a large excess relative to Cu(II) ions have a large buffer capacity in the pH ranges below 3.5 and from 5.5 to 10.5 for both HEDTA and EDTA, and because the polarographic wave-form may be affected by the presence of an acetate buffer in the pH range from 3.5 to 5.5. The hydrogen-ion concentration of the test solution was varied and measured before and after the recording of each polarogram.[16)] The difference between the pH values (−log h) obtained before and after recording was less than 0.01 pH unit. No maximum suppressor was added, since no polarographic maximum appeared at pH values above 1. The test solution was deaerated for at least 30 min with argon gas before each measurement.

Spectrophotometric Measurements. The ultraviolet and visible absorption spectra were measured by using a Hitachi Model 200-10 Spectrophotometer at room temperature (25±1 °C).

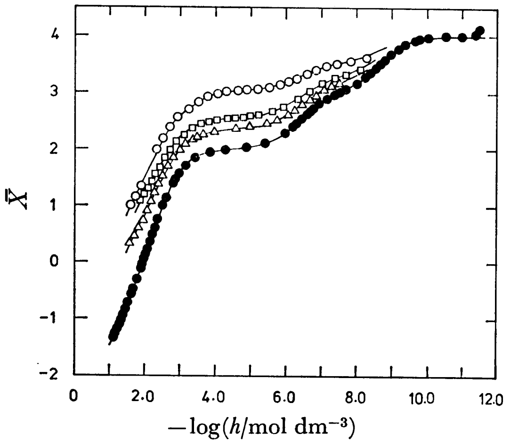


Fig. 1. Degrees of neutralization, $\bar{X}$, of EDTA solutions for the Cu(II)-EDTA system.
●: c_{Cu}=0.0 mol dm^{-3}, c_L=0.02500 mol dm^{-3}, ○: c_{Cu}=0.006221 mol dm^{-3}, c_L=0.011985 mol dm^{-3}, □: c_{Cu}=0.001107 mol dm^{-3}, c_L=0.003987 mol dm^{-3}, △: c_{Cu}=0.001075 mol dm^{-3}, c_L=0.005998 mol dm^{-3}. Solid lines are the values of $\bar{X}$ calculated by the use of the formation constants given in Table 1.

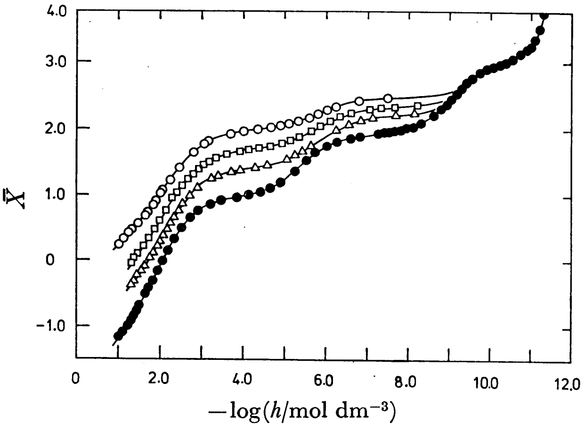


Fig. 2. Degrees of neutralization, $\bar{X}$, of HEDTA solutions for the Cu(II)-HEDTA system.
●: c_{Cu}=0.0 mol dm^{-3}, c_L=0.02500 mol dm^{-3}, ○: c_{Cu}=0.01010 mol dm^{-3}, c_L=0.02020 mol dm^{-3}, □: c_{Cu}=0.004970 mol dm^{-3}, c_L=0.02000 mol dm^{-3}, △: c_{Cu}=0.002500 mol dm^{-3}, c_L=0.02000 mol dm^{-3}. Solid lines are the values of $\bar{X}$ calculated by the use of the formation constants given in Table 1.

Results

Determination of the Composition and the Formation Constants of Cu(II)-EDTA and -HEDTA Complexes by Potentiometric Titrations. The titration curves shown in Figs. 1 and 2 result when the experiments were carried out under the conditions where the c_{Cu}/c_L ratio was 1/2, 1/4, 1/6, or 1/8 and where c_{Cu} was changed from 1 to 10 mmol dm^{-3}. Both c_{Cu} and c_L were kept practically constant for each run. The difference in neutralization degree between EDTA or HEDTA solutions with and without Cu(II) ions reveals that protons were released from the ligand by the complex formation, even at pH 1.3.

As has been described previously,[16,17)] since any possibility of the formation of polynuclear or polyligand complexes may be disregarded when the solution contains an excess of EDTA and HEDTA ligands relative to the Cu(II) ion, we can use the same procedure for data analysis as that employed for Cd(II)- and Pb(II)-complexes with EDTA and HEDTA.[16,17)] We assume that the complex formation proceeds:

$$Cu^{2+} + qH^+ + L^{z-} = CuH_qL^{(2+q-z)+} \tag{1}$$

from which the following relationships are obtained:

$$c_{Cu} = m + \sum_{q=-1}^{Q} [CuH_qL] \tag{2}$$

$$c_L = l + \sum_{n=1}^{N} [H_nL] + \sum_{q=-1}^{Q} [CuH_qL]. \tag{3}$$

The combination of Eqs. 2 and 3 leads to:

$$l = (c_L - c_{Cu} + m)/(1 + \sum_{n=1}^{N} \beta_{0n1}h^n), \tag{4}$$

where l can be calculated by using the protonation constants of the ligands obtained previously.[16,17)] A function, $F_0(h)$, is defined as:

$$F_0(h) = (c_{Cu}-m)/ml = \sum_{q=-1}^{Q} [CuH_qL]/ml = \sum_{q=-1}^{Q} \beta_{1q1}h^q \tag{5}$$

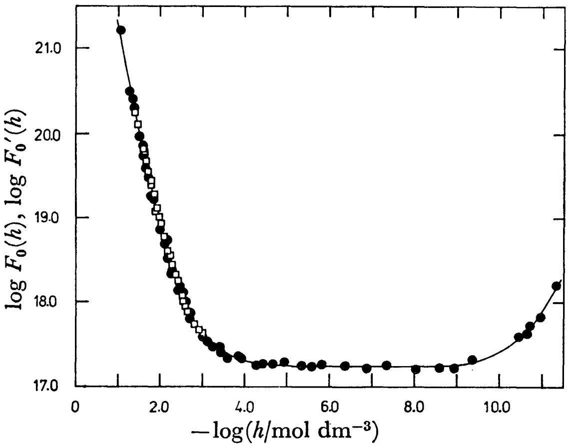


Fig. 3. Plots of log $F_0(h)$ and log $F_0'(h)$ against $-\log h$ for Cu(II)-EDTA system. Solid line is the best fit curve calculated by Eqs. 5 and 9.
□: log $F_0(h)$, ●: log $F_0'(h)$.

The plots of log $F_0(h)$ against $-\log h$ for the EDTA system fall into a single curve regardless of the variations in c_{Cu} and c_L (Fig. 3), and the assumption that no polynuclear and polyligand complexes are formed in an acidic solution is confirmed to be reasonable. The formation constant, β_{1q1}, was calculated from the $F_0(h)$ *vs.* h curve by means of a generalized least-squares method.[16] The method was applied to make the error-squares sum, $\sum\{\log F_0 - \log F_{0,\text{calcd}}\}^2$, a minimum for the set of the formation constants over the pH range of 1.0—7.0, where $F_{0,\text{calcd}}$ denotes the value of F_0 calculated for a particular set of formation constants. The values of the formation constants of all the complex species present are given in Table 1. In addition to the normal complex, CuL^{2-}, a series of protonated complexes, such as $CuHL^-$, CuH_2L^0, and CuH_3L^+, were detected. No information has yet been published on the formation of the triprotonated species.

Table 1. Formation constants of Cu(II)-EDTA and-HEDTA complexes in 1.0 mol dm^{-3} $NaClO_4$ solution at 25 °C

	Potentiometry	Polarography	Spectrophotometry
Cu(II)-EDTA system			
log β_{1-11}	—	6.83±0.05	5.5±0.1
log β_{101}	17.22±0.10	17.28±0.04	—
log β_{111}	20.15±0.04	20.13±0.06	—
log β_{121}	22.73±0.04	22.88±0.04	—
log β_{131}	24.12±0.04	24.15±0.04	—
Cu(II)-HEDTA system			
log β_{1-11}	—	6.35±0.05	5.2±0.1
log β_{101}	16.12±0.10	16.30±0.05	—
log β_{111}	18.85±0.05	18.76±0.04	—
log β_{121}	19.86±0.04	19.85±0.04	—

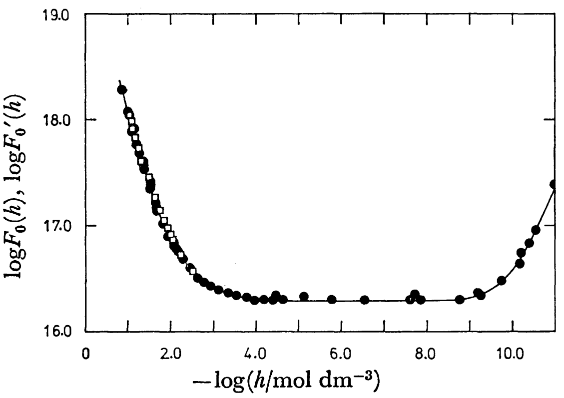


Fig. 4. Plots of log $F_0(h)$ and log $F_0'(h)$ against $-\log h$ for Cu(II)-HEDTA system. Solid line is the best fit curve calculated by Eqs. 5 and 9.
□: log $F_0(h)$, ●: log $F_0'(h)$.

The same analytical method as was used for the EDTA system was used to determine the formation constants for the HEDTA system. Figure 4 demonstrates that the plots of log $F_0(h)$ against $-\log h$ in the HEDTA system give a single curve. From the analysis of the curve, we found that the normal complex, CuL^-, as well as two protonated complexes, CuHL and CuH_2L^+, are formed. The formation constant of the diprotonated species was obtained for the first time in the Cu–HEDTA system. The solid curve in Fig. 4 represents the curve calculated from the final values of the formation constants which are summarized in Table 1.

Above pH 4.0, the emf's of the amalgam electrodes became unstable for both systems, and the values of log $F_0(h)$ in Figs. 3 and 4 were somewhat scattered around the best-fit curve. This may be due to the contamination of amalgam surfaces by a small amount of oxygen dissolved in solution. Thus, we may expect to obtain correct information on complex-formation reactions above pH 4 by means of polarographic measurements.

Determination of the Formation Constants by Polarography. Single well-defined waves with diffusion-controlled limiting currents were observed for the Cu(II)-EDTA and -HEDTA systems in the pH range from 1.0 to

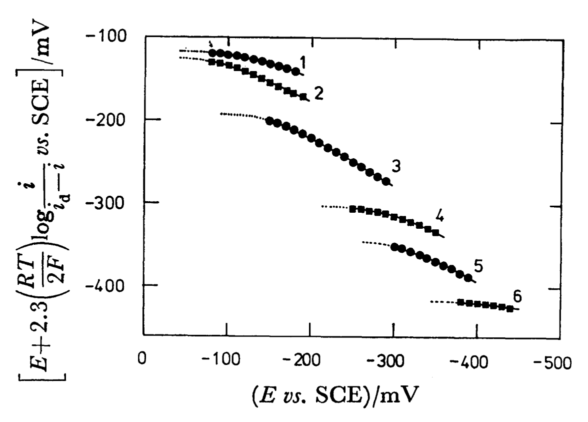


Fig. 5. Typical examples of the plots of $E+2.3\,(RT/2F)\cdot\log[i/(i_d-i)]$ *vs.* E for determination of reversible half-wave potentials. $c_{Cu}=0.00040$ mol dm^{-3}.
●: Cu(II)-EDTA system. $c_L=0.0080$ mol dm^{-3}. Values of $-\log(h/\text{mol dm}^{-3})$: (1) 2.12, (3) 3.73, (5) 6.11.
■: Cu(II)-HEDTA system. $c_L=0.0200$ mol dm^{-3}. Values of $-\log(h/\text{mol dm}^{-3})$: (2) 2.70, (4) 6.05, (6) 10.19.

11.0. The log-plot analysis of the current-potential curves demonstrates that the waves correspond to the quasi-reversible, two-electron reduction. For the quasi-reversible wave we can determine the reversible half-wave potential by using the extrapolation methods.[19,20] Figure 5 shows typical examples of the $[E+2.3(RT/2F)\times \log\{i/(i_d-i)\}]$ *vs.* E plots, where E denotes the potential of the dropping mercury electrode, i the current corresponding to E, and i_d the limiting diffusion current. The reversible half-wave potentials were determined as the limiting constant values of $[E+2.3(RT/2F)\log\{i/(i_d-i)\}]$ at sufficiently positive potentials.[19]

Consider the electrode reaction, symbolically designated by:

$$\left\{\begin{array}{l} \mathrm{CuH}_Q\mathrm{L}^{(2+Q-z)+} \\ \vdots \\ \downarrow\uparrow \\ \vdots \\ \mathrm{CuH}_q\mathrm{L}^{(2+q-z)+} \\ \vdots \\ \downarrow\uparrow \\ \vdots \\ \mathrm{CuL}^{(2-z)+} \\ \downarrow\uparrow \\ \mathrm{CuH}_{-1}\mathrm{L}^{(1-z)+} \end{array}\right\} + 2\mathrm{e(Hg)} \rightleftharpoons \mathrm{Cu(Hg)} + \left\{\begin{array}{l} \mathrm{H}_N\mathrm{L}^{(N-z)+} \\ \vdots \\ \downarrow\uparrow \\ \vdots \\ \mathrm{H}_n\mathrm{L}^{(n-z)+} \\ \vdots \\ \downarrow\uparrow \\ \vdots \\ \mathrm{L}^{-z} \end{array}\right\}. \tag{6}$$

The reversible half-wave potential can then be expressed by:[18]

$$(E_{1/2})_{\mathrm{rev}} = (E^{\mathrm{r}}_{1/2})_{\mathrm{Cu}} - \frac{RT}{2F}\ln\sqrt{\frac{D}{D_{\mathrm{Cu}}}} - \frac{RT}{2F}\ln[1+(\sum_{q=-1}^{Q}\beta_{1q1}h^q)l]. \tag{7}$$

Equation 7 can be rewritten as:

$$\left\{\sqrt{\frac{D_{\mathrm{Cu}}}{D}}\exp\left\{\left(\frac{2F}{RT}\right)[(E^{\mathrm{r}}_{1/2})_{\mathrm{Cu}} - (E_{1/2})_{\mathrm{rev}}]\right\} - 1\right\}/l = \sum_{q=-1}^{Q}\beta_{1q1}h^q. \tag{8}$$

The left-hand side of Eq. 8 is the experimentally accessible quantity and is here written as $F_0'(h)$. Thus,

$$F_0'(h) = \sum_{q=-1}^{Q}\beta_{1q1}h^q, \tag{9}$$

which is identical to the $F_0(h)$ function defined by Eq. 5.

The plots of $\log F_0'(h)$ against $-\log h$ are shown in Figs. 3 and 4 for the systems of EDTA and HEDTA respectively. In each system, a single curve was obtained for both functions, $F_0(h)$ and $F_0'(h)$, and only small differences between the formation constants determined from these two functions were observed.

In the EDTA system, the triprotonated complex, $\mathrm{CuH_3L^+}$, was also detected by polarography. In the pH range of 4.0—9.5, the values of the $\log F_0'(h)$ function were constant, and we can consider that the Cu(II) ion is present predominantly as the normal complex, $\mathrm{CuL^{2-}}$, in a solution containing an excess EDTA. The values of the $\log F_0'(h)$ function begin to increase above pH 10.0 (Fig. 3), indicating the formation of hydroxo complexes. The $F_0'(h)$ function is proportional to h^{-1} in the range above pH 10.0, and the product $[F_0'(h)-\beta_{101}]\times h$ yields a constant value. This behavior of $F_0'(h)$ can be understood in terms of the formation of only one deprotonated complex, $\mathrm{CuH_{-1}L^{3-}}$, which is probably the same as the hydroxo complex $\mathrm{Cu(OH)L^{3-}}$, reported previously.[3] The formation constant of the hydroxo complex was determined by the curve-fitting method; it is given in Table 1.

In the HEDTA system, all of the complex species, $\mathrm{CuL^-}$, $\mathrm{CuHL^0}$, and $\mathrm{CuH_2L^+}$, being found potentiometrically, were also detected by the polarographic method. Above pH 9.0, the values of the $\log F_0'(h)$ function began to increase, indicating the formation of deprotonated species, $\mathrm{CuH_{-1}L^{2-}}$. The formation constants of these four species were determined by the analysis of the $F_0'(h)$ *vs.* h curve; they are given in Table 1.

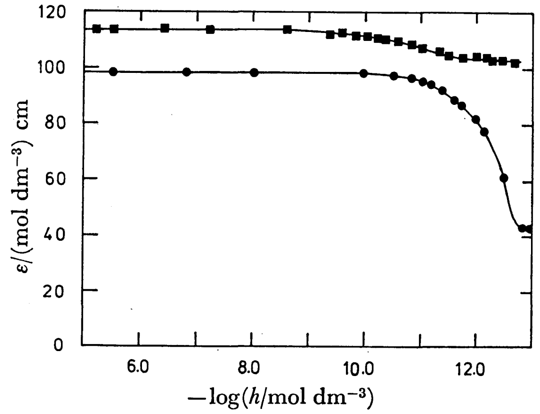


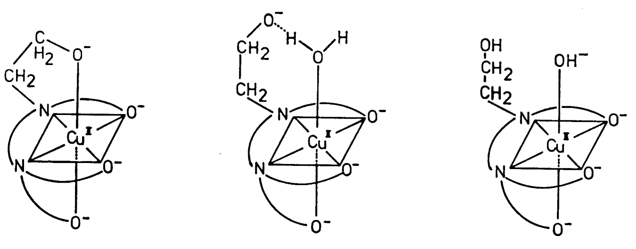
Fig. 6. Variations of the molar absorbances with $-\log h$ at the absorption maxima of Cu(II)–EDTA (●) and Cu(II)–HEDTA (■) solutions.

Spectrophotometric Measurements. In order to obtain further information on the formation of deprotonated species, measurements of the absorption spectra were carried out in the alkaline region. For the EDTA system, the hydroxo complex formation was also observed by spectrophotometry. Figure 6 demonstrates the intensity change in the absorption maximum (at 740 nm) with $-\log h$, from which the formation of the $\mathrm{Cu(OH)L^{3-}}$ species was confirmed to be as previously reported by Bhat and Krishnamurthy.[13] On the other hand, the intensity change in the absorption maximum (at 710 nm) with $-\log h$ for the HEDTA system in the pH range of 9.5—12 is not so large (Fig. 6), though two isosbestic points were observed at 600 and 835 nm. This fact proves that two species, the normal complex, $\mathrm{CuL^-}$ and only one deprotonated complex, $\mathrm{CuH_{-1}L^{-2}}$, are formed in the pH range from 9.5 to 12.

As can be seen from Table 1, the values of the formation constants obtained by spectrophotometry are different from those obtained by polarography. The reason for this discrepancy is not clear at present.

Discussion

The step-by-step protonation constants for protonated complexes of the $CuH_{q-1}L$ type may be defined as $K_{H}^{CuH_qL}=[CuH_qL]/[CuH_{q-1}L][H]=\beta_{1q1}/\beta_{1(q-1)1}$. The values of $\log K_{H}^{CuH_qL}$ for the EDTA complexes are 2.87, 2.58, and 1.39 for $q=1,2$, and 3 respectively, while those of the HEDTA complexes are 2.46 and 1.09 for $q=1$ and 2 respectively. These values are close to the values of $\log K_{H}^{H_nL}=\log\{[H_nL]/[H_{n-1}L][H]\}$ with $n=3,4$, and 5 of the corresponding ligands,[17] which are the step-by-step protonation constants for the carboxyl groups of the EDTA and HEDTA ligands. Thus, as has been reported previously[16,17] for the systems of the Cd(II)- and Pd(II)-HEDTA and -EDTA complexes, we may conclude that the protonation of the complexes occurs on the carboxyl groups with the cleavage of Cu(II)-oxygen bonds within the complexes, while the strong Cu(II)-nitrogen bonds remain unaltered.



1 2 3

Fig. 7. Possible structures for the deprotonated species of Cu(II)-HEDTA complex.

We define the deprotonation constant of the $CuH_{-1}L$ species as $K_{H_{-1}}^{CuH_{-1}L}=\{[CuH_{-1}L][H]/[CuL]\}$. Then, we obtain $\log K_{H_{-1}}^{CuH_{-1}L}=-10.45$ and -9.95 for the EDTA and HEDTA systems respectively. Thus, the values of the deprotonation constant are shown to be almost the same for the EDTA and HEDTA systems. However, Fig. 6 indicates that the intensity changes in the absorption maxima with $-\log h$ in the pH range from 10 to 11.5 are large for the EDTA system, but not for the HEDTA system. The observed result may be attributable to the difference between the deprotonation reaction schemes of the EDTA and HEDTA complexes. The large intensity change in the absorption maximum for the EDTA complex is possibly caused by the deprotonation of the water molecule coordinated to the Cu(II) ion, and the resulting species is a hydroxo complex. On the other hand, three possible reaction schemes for the HEDTA complex may be considered on the basis of the pentadentate coordination of the HEDTA ligand to the Cu(II) ion at the state of the normal complex, as is shown in Fig. 7: (1) the hydroxyethyl group in the ligand releases a proton, and the resulting ethyl alcoholate coordinates to the Cu(II) ion directly; (2) the hydroxyethyl group releases a proton to form a hydrogen bond with the water molecule coordinated to the Cu(II) ion, or (3) the deprotonation occurs from the water molecule coordinated to Cu(II), and the hydroxyethyl group gives no interaction for the hydrolysis reaction. The observed absorption spectra seem to support the reaction scheme (2), since the Cu(II) ion was not subjected to any strong interaction with the deprotonation of the complex.

The degree of neutralization, $\bar{X}$, of H_3hedta exceeds 3.0 at pH values above 11.0, but that of H_4edta remains constant (4.0), although the emf of the glass electrode cell becomes uncertain in such a high pH region. Therefore, it may be considered that the reaction of the hydroxyethyl group of HEDTA to ethylalcolate starts at this pH in the HEDTA solution containing no Cu(II) ion. The adoption of the reaction scheme (2) depicted in Fig. 7 means that the coordination of HEDTA to the Cu(II) ion accelerates the deprotonation of the hydroxyethyl group, since the deprotonation reaction of the Cu(II)-HEDTA complex starts at pH 9.5. The acceleration of the deprotonation process of 2-aminoethanol by its coordination to the metal ion has been reported for the $[Co(NH_2CH_2CH_2NH_2)_2(NH_2CH_2CH_2OH)]^{3+}$ complex.[21]

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References

1) L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Chemical Society, London (1964), Supplement No. 1, (1971).

2) D. D. Perrin, "Stability Constants of Metal-Ion Complexes, Part B, Organic Ligands," IUPAC Chemical Data Series No. 22, Pergamon Press, Oxford (1979).

3) R. I. Gorelova, V. A. Babich, and I. P. Gorelov, *Zh. Neorg. Khim.*, **16**, 1873 (1971).

4) D. Chapman, D. R. Lloyd, and R. H. Prince, *J. Chem. Soc.*, **1963**, 3645.

5) N. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Am. Chem. Soc.*, **85**, 309 (1963).

6) D. T. Sawyer and J. E. Tackett, *J. Am. Chem. Soc.*, **85**, 314 (1963).

7) R. J. Kula, D. T. Sawyer, S. I. Chan, and C. M. Finley, *J. Am. Chem. Soc.*, **85**, 2930 (1963).

8) J. L. Sudmeier and C. N. Reilley, *Anal. Chem.*, **36**, 1698 (1964).

9) L. E. Erickson, D. C. Young, F. F. L. Ho, S. R. Watkins, J. B. Terrill, and C. N. Reilley, *Inorg. Chem.*, **10**, 441 (1971).

10) D. S. Everhast and R. F. Evilia, *Inorg. Chem.*, **14**, 2755 (1975).

11) W. C. E. Higginson, *J. Chem. Soc.*, **1962**, 2761.

12) A. P. Brunetti, G. H. Nancollas, and P. N. Smigh, *J. Am. Chem. Soc.*, **91**, 4680 (1969).

13) T. R. Bhat and M. Krishnamurthy, *J. Inorg. Nucl. Chem.*, **25**, 1147 (1963).

14) R. G. Wilkins and R. E. Yellin, *J. Am. Chem. Soc.*, **89**, 5946 (1967).

15) R. H. Nuttall and D. M. Stalker, *Inorg. Nucl. Chem. Lett.*, **12**, 639 (1976).

16) N. Oyama, T. Shirato, H. Matsuda, and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **49**, 3047 (1976).

17) N. Oyama, H. Matsuda, and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **50**, 409 (1977).

18) N. Oyama and H. Matsuda, *J. Electroanal. Chem.*, **78** 89 (1977).

19) H. Matsuda, Y. Ayabe, and K. Adachi, *Ber. Bunsenges. Phys. Chem.*, **67**, 593 (1963); H. Matsuda, *Tokyo Kogyo Shikensho Hokoku*, **61**, 315 (1966).

20) R. Tamamushi and N. Tanaka, *Z. Phys. Chem. (Frankfurt)*, **39**, 117 (1963).

21) K. Ogino and H. Seki, *Bull. Chem. Soc. Jpn.*, **54**, 719 (1981).