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Normal Pulse Polarographic Study of the Electrode Reaction of Copper(II) Complexes with Ethylenediaminetetraacetic Acid(EDTA) and *N*-(2-Hydroxyethyl)ethylenediamine-*N*,*N*′,*N*′-triacetic Acid(HEDTA)

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The normal pulse polarographic behavior of the Cu(II)–EDTA and –HEDTA complexes was examined in a wide range of pH values to elucidate the mechanisms of their electrode reactions and to evaluate the relevant electrochemical kinetic parameters. From analysis of the dependence of the half-wave potentials on the sampling time and the hydrogen ion concentration, it was shown that the reduction wave of the Cu(II)–EDTA complexes observed in the pH range of 2.0 to 9.5 at −0.1 to −0.5 V *vs.* SCE corresponds to the simultaneous reduction of four complex species, CuH_3L^+, CuH_2L^0, $CuHL^-$, and CuL^{2-}, where $CuH_pL^{(p-2)+}$ and L^{4-} denote the protonated complex species with p protons and the unprotonated EDTA ion, respectively. The reduction wave of the Cu(II)–HEDTA complexes in the pH range of 3.0 to 9.0 at −0.25 to −0.4 V *vs.* SCE corresponds to the simultaneous reduction of two complex species, $CuHL^0$ and CuL^-, where L^{3-} denotes the unprotonated HEDTA ion. The kinetic parameters of the corresponding complex species (*i.e.* the cathodic transfer coefficient and the standard rate constant of electrode reaction) were evaluated.

In a series of papers,[1–3] we have examined the electrode reaction mechanism of the Cd(II) and Pb(II) complexes with ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (EDTA) and *N*-(2-hydroxyethyl)ethylenediamine-*N*,*N*′,*N*′-triacetic acid (HEDTA) and it has been shown that many protonated complex species of the type MH_pL ($p=1,2,3$ for the EDTA complex and $p=1,2$ for the HEDTA complex) complex species, as well as the ordinary unprotonated complex species can participate directly in the charge transfer processes. The relevant electrochemical kinetic parameters have been evaluated therein.

Our careful analysis of the d.c. polarograms for the Cu(II) complexes with EDTA and HEDTA confirmed that the electrode reactions are the quasi-reversible[4] in the range of pH=1.0 to 11.0, although their electrode processes have been considered to be reversible in the polarographic time scale.[5–8] It has been recognized that in the case of the quasi-reversible processes less reliable data regarding the electrochemical kinetic parameters are obtained from the analysis of the d.c. polarograms.

Normal pulse polarography (NPP) among the numerous pulse techniques is most suitable for the examination of the kinetics of polarographically quasi-reversibel electrode processes, because the current measuring time in NPP can be widely varied from 10^{-4} to a few seconds and the shape of normal pulse polarograms is similar to that of d.c. polarograms, so that the analysis of the normal pulse polarograms can be easily carried out by using the procedure similar to that of the analysis of the d.c. polarograms.[9] However, NPP has been ever applied to the examination of the electrode kinetics in only a few examples.[10–13] In general many pulse techniques[14] have been used for the microanalysis so far, since they were proposed by Barker[15,16] in 1957.

In this paper, we demonstrate that NPP is the powerful method to elucidate in detail the mechanism of the electrode processes of Cu(II)–EDTA and –HEDTA complexes and determine the values of the kinetic parameters of many protonated complexes and the unprotonated complexes being participating in the electrode reactions. Previously,[4] we have performed the examination of complex equilibrium of the Cu(II) aqua ion with EDTA and HEDTA by potentiometric titration measurements and reported the values of the formation constants of many protonated complexes and hydroxo complexes, being newly found.

Experimental

Instrumentation. Current-potential curves were measured by home-made instruments with multifunctions (d.c. polarography, differential pulse polarography, and normal pulse polarography). The program controlling potentials was generated by CMOS logic IC and programmable timer counter IC (Intersil ICM 7250) with a quartz oscillator, which acted through a 12-bit D/A converter driving the potentiostat. The current response, which was converted to the voltage at the current follower of the potentiostat, was fed through a sample-hold circuits (Intersil IH 5110) into two integrator-type sample-hold circuits (using Analog Devies AD515k) with very small drift rate (<1 μV s^{-1}) at the hold-mode. Individual storing information was recorded with a two-pen X-Y-Y recorder. The sampling times of normal pulse polarography can be set at two arbitrary values from 0.1 ms to 9.9 s. The magnitude of the increase in the potential pulse height, ΔE, at each mercury drop can be changed from 1 to 99 mV. As an another current sampling method, we also used the following method: the current was integrated over a time interval, which is shorter than one-tenth of the pulse width, near the end of the pulse and the average value of the integrated current was taken as the current sampled. In order to increase the signal-to-noise ratio, especially when the faradic current is small, A spike-like pulse which is generated between a dropping mercury electrode and a counter electrode at the moment of mercury drop fall is employed as a signal indicating the drop birth.[17] A chatter-free wetting mercury relay was employed to remove the counter electrode from potentiostatic control after measuring the current.

In the differential pulse polarographic mode operation, the dual slope integrating technique reported by Kalvoda and Trojanek[18,19] was employed.

Procedure. An electrolytic cell which was specially designed to be able to monitor continuously the concentration of hydrogen ion during the polarographic measurements, was a seven-neck vesel which was set with a dropping mercury electrode (DME), an 1.0 M (1 M=1 mol dm^{-3}) NaCl agar-agar bridge for connection with a saturated calomel electrode (SCE), a Pt wire counter electrode, a glass electrode, an Ag–AgCl reference electrode and two burets. A digital pH/mV meter (Orion Research, model 801) was used for pH measurements, in combination with a Beckman 40495 glass electrode and an Ag/AgCl electrode. The determination of the pH values was carried out in a similar manner as reported previously.[1,20] The flow rate of the mercury of the DME was $m=0.97$ mg s^{-1} and the drop time 6 s at the height of mercury head $h=60$ cm in 1 M $NaClO_4$ solution.

All measurements were performed in a parafine oil thermostat at (25.0±0.1) °C. The hydrogen ion concentration of the test solution was varied and measured before and after the recording of each polarogram. The difference in these pH values was within 0.01 pH unit as a rule. The composition of the test solution was 4.00×10^{-4} M of Cu(II) aqua ion, 8.00×10^{-3} M of EDTA or 2.00×10^{-2} M for HEDTA, and 1.0 M $NaClO_4$, unless otherwise noted. No buffer was added in the pH ranges 1.0—3.5 and 5.5—10.0 because the ligands are expected to have a large buffer capacity in these pH ranges. In the pH range 3.5—5.5, the acetate buffer was used at three different concentrations, 20, 40, and 80 mM CH_3COONa. The acetate ion did not show any influence on the shape and the position of the polarograms obtained. No maximum suppressor was added, since no polarographic maximum appeared in the pH range 1.0—11.5. The test solution was deaerated for 30 min with argon gas before each measurement of the polarograms.

Reagents. Ethylenediaminetetraacetic acid (disodium salt) (reagent grade, Dojindo Lab.) was recrystallized twice, dried and stored over silica gel in a desiccator. *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 a $HClO_4$ solution and purified by recrystallizing three times from distilled water. The stock solution contained a small amount of $HClO_4$ to prevent hydrolysis of Cu(II) aqua ion. The concentration of Cu(II) aqua ion in the stock solution was determined by electrogravimetry.

Sodium perchlorate, sodium hydroxide and perchloric acid stock solutions were prepared by the methods described previously.[20]

Results

The Cu(II)-EDTA Complexes. Normal pulse polarograms for the reduction of the Cu(II) complexes were measured in the pH range from 1.0 to 11.0. Typical normal pulse polarograms are shown in Fig. 1. The half-wave potential of reduction waves shifted to cathodic direction with increasing the pH value and with decreasing sampling time, θ. Their limiting current was diffusion-controlled, as proved from the fact that the product of the limiting current and $\theta^{1/2}$ is always constant.

As has been described previously,[4] a number of protonated complex species of the MH_pL type ($p=1,2,3$) for the EDTA complex are formed in the bulk of the solution and any possibility of the formation of polynuclear or polyligand complexes can be disregarded, when the solution contains an excess of EDTA ligand relative to the Cu(II) aqua ion. Since no Cu(II) aqua ion is present above pH=1.0[4] and no its kinetic behavior was observed in the normal pulse polarograms in the pH range 1.0 to 11.0, it seems reasonable to assume that the mechanism of the electrode processes under consideration can generally be expressed by

$$\begin{array}{l}
\mathrm{CuH}_N\mathrm{L} + 2\mathrm{e} \rightleftharpoons \mathrm{Cu(Hg)} + \mathrm{H}_N\mathrm{L} \\
\updownarrow \qquad\qquad \alpha_N,\ k_N^{\circ} \\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
\updownarrow \\
\mathrm{CuH}_p\mathrm{L} + 2\mathrm{e} \rightleftharpoons \mathrm{Cu(Hg)} + \mathrm{H}_p\mathrm{L} \\
\updownarrow \qquad\qquad \alpha_p,\ k_p^{\circ} \\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
\updownarrow \\
\mathrm{CuL} + 2\mathrm{e} \rightleftharpoons \mathrm{Cu(Hg)} + \mathrm{L} \\
\qquad\quad \alpha_0,\ k_0^{\circ}
\end{array} \tag{1}$$

We have previously reported the d.c. polarographic current-potential relationship for the similar mechanism of the electrode processes and its application to the analysis of the polarograms for the reduction of the Cd(II) and Pb(II) complexes with EDTA and HEDTA.[1-3] The current-potential relationship for normal pulse polarograms of the electrode process, assuming that the CuH_pL complex predominantly participates in the charge transfer process, is given by Eq. 2 which can be derived from the modification of the general current-potential relationship for normal pulse polarograms of the simple electrode process, Ox+*n*e⇄Red.[9,13,21]

$$E = E^* - \frac{2.3RT}{2a_pF}\log\left[\frac{\sqrt{3}x}{4\sqrt{\theta}}\left\{\frac{1.75+x^2(1+\exp\zeta)^2}{1-x(1+\exp\zeta)}\right\}^{1/2}\right] \tag{2}$$

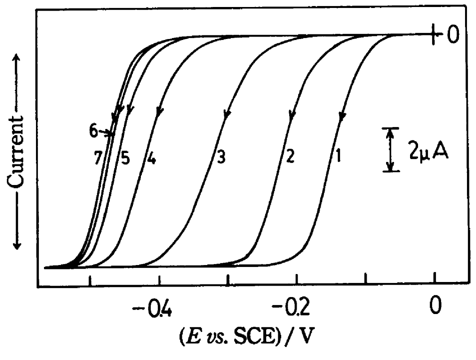

Fig. 1. Typical normal pulse polarograms for the reduction of the Cu(II)–EDTA complexes in 1.0 M $NaClO_4$ solution containing 0.4 mM Cu(II) aqua ion and 8 mM EDTA.

Sampling time $\theta=27$ ms, drop time of DME $\tau=4.0$ s and rate of the increase in potential pulse height $\Delta E=5$ mV/drop.

$-\log[H^+]$: (1) 2.12, (2) 3.06, (3) 4.02, (4) 5.85, (5) 7.36, (6) 8.59, (7) 9.37.

with

$$E^* = E^{\mathrm{r}}_{1/2,p} + \frac{2.3RT}{2\alpha_p F} \log\left[\frac{k_p^\circ(\beta_{0p1})^{\alpha_p}(\beta_{1p1})^{1-\alpha_p}[\mathrm{H}^+]^p\{F([\mathrm{H}^+])+G([\mathrm{H}^+])/C_\mathrm{L}\}^{1+\alpha_p}}{\{D_C^{1-\alpha_p}D_{\mathrm{Cu(Hg)}}^{\alpha_p}\}^{1/2}\{G([\mathrm{H}^+])/C_\mathrm{L}\}^{\alpha_p}F([\mathrm{H}^+])^2}\right], \tag{3}$$

$$X = i/(i_\mathrm{d})_\mathrm{Cott}, \tag{4}$$

$$\zeta = (2F/RT)(E-E^{r}_{1/2,\mathrm{p}}), \tag{5}$$

$$E^r_{1/2,p} = E^0_p + \frac{2.3RT}{2F} \log\left[\left(1+\frac{F([\mathrm{H}^+])}{G([\mathrm{H}^+])/C_\mathrm{L}}\right)\frac{\beta_{0p1}}{\beta_{1p1}}\right] + \frac{2.3RT}{2F}\log\frac{D_\mathrm{C}}{D_{\mathrm{Cu(Hg)}}}, \tag{6}$$

$$F([\mathrm{H}^+]) = \sum_{p=0}^{N}\beta_{1p1}[\mathrm{H}^+]^p, \tag{7}$$

$$G([\mathrm{H}^+]) = \sum_{p=0}^{N}\beta_{0p1}[\mathrm{H}^+]^p, \tag{8}$$

$$\beta_{qpr} = [\mathrm{Cu}_q\mathrm{H}_p\mathrm{L}_r{}^{2q+p-nr}]/[\mathrm{Cu}^{2+}]^q[\mathrm{H}^+]^p[\mathrm{L}^{n-}]^r, \tag{9}$$

$$C_\mathrm{c} = \sum_{p=0}^{N}[\mathrm{CuH}_p\mathrm{L}^{2+p-n}], \tag{10}$$

$$D_\mathrm{c} = \sum_{p=0}^{N}\beta_{1p1}[\mathrm{H}^+]^pD_p/F([\mathrm{H}^+]). \tag{11}$$

In these equation, E is the electrode potential; i is the normal pulse polarographic current; θ is the sampling time; E°_p, $E^r_{1/2,p}$, k°_p, and α_p are the standard potential, the reversible half-wave potential, the standard rate constant and the cathodic transfer coefficient, respectively, of the electrode reaction: $\mathrm{CuH}_p\mathrm{L}^{2+p-n}+2\mathrm{e} \rightleftarrows \mathrm{Cu(Hg)}+\mathrm{H}_p\mathrm{L}^{p-n}$; D_p and $D_{\mathrm{Cu(Hg)}}$ are the diffusion coefficients of the complex species $\mathrm{CuH}_p\mathrm{L}^{2+p-n}$ in the solution and of the copper atoms Cu(Hg) in the amalgam, respectively; β_{qpr} which is designated by Eq. 9 is the equilibrium constant for the reaction: $q\mathrm{Cu}^{2+}+p\mathrm{H}^++r\mathrm{L}^{n-} \rightleftarrows \mathrm{Cu}_q\mathrm{H}_p\mathrm{L}_r{}^{2q+p-nr}$; C_L is the total concentration of the ligand; $[\mathrm{H}^+]$ is the concentration of hydrogen ion; $[\mathrm{Cu}^{2+}]$ and $[\mathrm{CuH}_p\mathrm{L}^{2+p-n}]$ are the concentrations of the Cu(II) aqua ion and the complex species $\mathrm{CuH}_p\mathrm{L}^{2+p-n}$, respectively; $[\mathrm{L}^{n-}]$ is the concentration of the free ligand; $(i_\mathrm{d})_\mathrm{Cott}$ denotes the diffusion current expressed by the Cottrell equation.[22]

D.c. polarograms of Cu(II)–EDTA complexes were measured in the same solutions as used in NPP. The reversible half-wave potentials, $E^r_{1/2,p}$, were evaluated from these d.c. polarograms by means of extrapolation method.[23] Thus, the values of the logarithmic term of r.h.s. of Eq. 2 and ζ can be calculated by using Eqs. 2 and 5, respectively, at any electrode potential. The modified log-plots of the normal pulse polarograms, in which the log-term on r.h.s. of Eq. 2 is plotted against E, gave straight lines for the reduction of the Cu(II)–EDTA complexes over the whole pH range examined (Fig. 2). These straight lines have constant slopes, the values of which are equal to $-2\alpha_pF/2.3RT$, in the range of pH 1.0—2.5, 3.0—4.5, 5.5—7.5, and 8.0—10.0 within experimental errors. The cathodic transfer coefficients were evaluated from their reciprocal slopes. The values obtained are given in Table 1. The constant value of α_p obtained in each pH range seems to permit us to assume that only one species predominantly participates in the charge transfer process in limited pH ranges. Thus we can apply Eq. 3 to the determination of the composition of the discharging species.

After some rearrangements of Eq. 3, we obtain

$$Z_p \equiv \frac{2\alpha_pF}{2.3RT}(E^*-E^r_{1/2,p}) + \log\left[\frac{\{G([\mathrm{H}^+])/C_\mathrm{L}\}^{\alpha_p}F([\mathrm{H}^+])^2}{\{F([\mathrm{H}^+])+G([\mathrm{H}^+])/C_\mathrm{L}\}^{1+\alpha_p}}\right], \tag{12}$$

$$= \log[k^\circ_p(\beta_{0p1})^{\alpha_p}(\beta_{1p1})^{1-\alpha_p}] - \frac{1}{2}\log[D_\mathrm{c}^{1-\alpha_p}D_{\mathrm{Cu(Hg)}}{}^{\alpha_p}]+p\log[\mathrm{H}^+]. \tag{13}$$

The values of the function Z_p, defined by Eq. 12, were calculated as a function of $[\mathrm{H}^+]$ for each pH range. Hence, the composition of the discharging complex species, *i.e.*, p can be determined from the dependence of the function, $-Z_p$, upon $-\log[\mathrm{H}^+]$. In Fig. 3, the values of $-Z_p$ are plotted against $-\log[\mathrm{H}^+]$. As can readily be seen from Fig. 3, a linear relationship is obtained with $p=3$ in the pH range 1.0—2.5, indicating that the discharging species is the species $\mathrm{CuH_3L^+}$. Similarly, the discharging species is primarily $\mathrm{CuH_2L^0}$ in the pH range 3.0—4.5, $\mathrm{CuHL^-}$ in 5.5—7.5 and $\mathrm{CuL^{2-}}$ in pH 8.0—10.0, respectively. Thus, it can be concluded

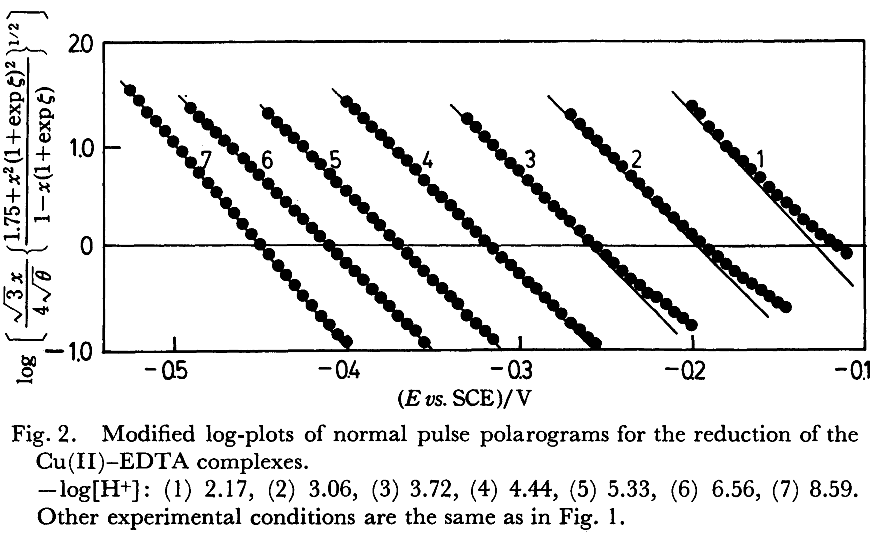

Fig. 2. Modified log-plots of normal pulse polarograms for the reduction of the Cu(II)–EDTA complexes.
$-\log[\mathrm{H}^+]$: (1) 2.17, (2) 3.06, (3) 3.72, (4) 4.44, (5) 5.33, (6) 6.56, (7) 8.59. Other experimental conditions are the same as in Fig. 1.

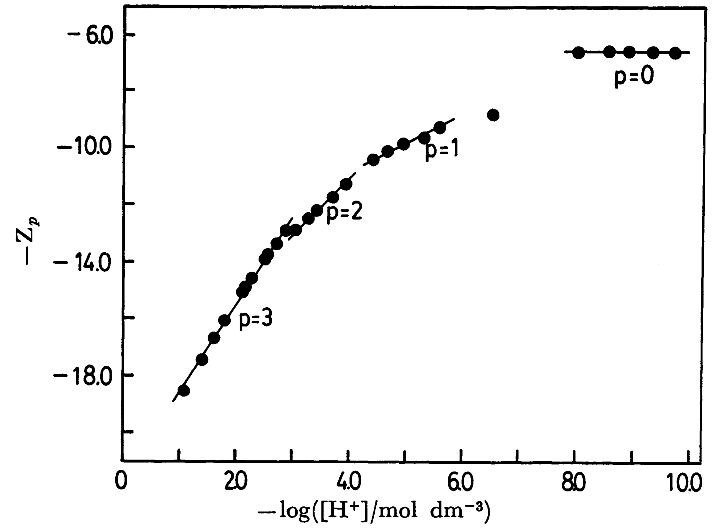

Fig. 3. Dependence of the function, $-Z_p$, upon $-\log[H^+]$ for the Cu(II)–EDTA complexes.
Experimental conditions are the same as in Fig. 1.

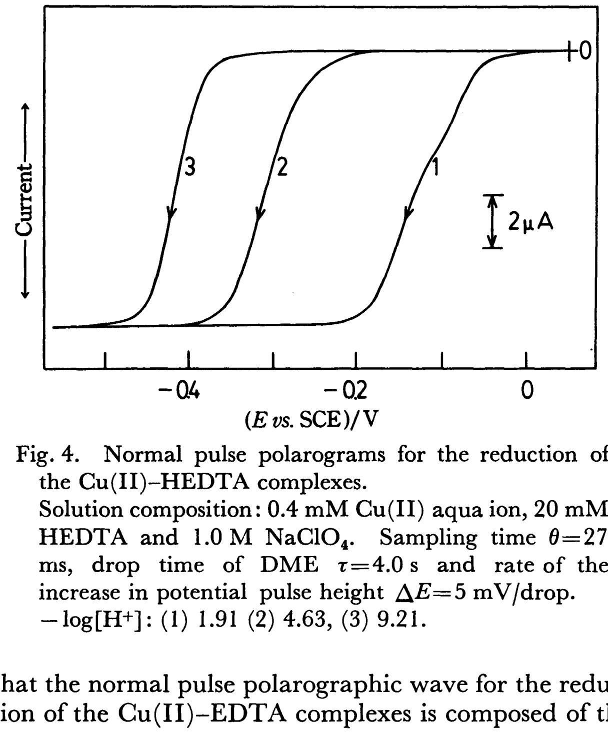

Fig. 4. Normal pulse polarograms for the reduction of the Cu(II)–HEDTA complexes.
Solution composition: 0.4 mM Cu(II) aqua ion, 20 mM HEDTA and 1.0 M $NaClO_4$. Sampling time θ=27 ms, drop time of DME τ=4.0 s and rate of the increase in potential pulse height ΔE=5 mV/drop.
$-\log[H^+]$: (1) 1.91 (2) 4.63, (3) 9.21.

that the normal pulse polarographic wave for the reduction of the Cu(II)–EDTA complexes is composed of the four charge transfer processes, $CuH_pL^{p-2}+2e\rightleftarrows Cu(Hg)+H_pL^{p-4}$ (p=3, 2, 1, 0). The standard rate constant, k_p°, of each charge transfer process can be evaluated from the value of the intercept of the plots shown in Fig. 3 and by introducing the experimental data into Eq. 13, where the values of D_p and $D_{Cu(Hg)}$ were 5.4×10^{-6} cm^2 s^{-1} and 1.06×10^{-5} cm^2 s^{-1},[24] respectively. The above value of D_p was obtained from the cathodic limiting currents of d.c. polarograms by using the Ilkovic equation.[14] The kinetic parameters obtained are given in Table 1.

The Cu(II)–HEDTA Complexes. Figure 4 shows a set of normal pulse polarograms for the reduction of the system of the Cu(II)–HEDTA complexes in the solution of various pH. Figure 5 shows the modified log-plots of the normal pulse polarograms. These log-plots satisfied the straight lines and their slopes were constants in the range of pH 3.0—6.0 and 7.5—9.5, respectively. The cathodic transfer coefficients were evaluated from their reciprocal slopes. In Fig. 6, the values of $-Z_p$, calculated from Eq. 12, are plotted against $-\log[H^+]$. It is apparent from this figure that the discharging species is primarily $CuHL'^0$ and CuL'^- (L'=hedta^{3-}) in the pH range 3.0—6.0 and 7.5—9.5, respectively. The standard rate constants for these discharging species were evaluated by means of the same method as described in the previous section. The values obtained are summarized in Table 1.

In the acidic solution below pH 3.0, the modified log-plots of the normal pulse polarograms deviated from the straight line, as shown in Fig. 5, when the value of the logarithmic term of r.h.s. of Eq. 2 is below zero. The deviation seems to result from that the

TABLE 1. ELECTROCHEMICAL KINETIC PARAMETERS OF THE Cu(II)–EDTA AND -HEDTA COMPLEXES IN 1.0 M $NaClO_4$ AT 25 °C (L=edta^{4-} AND L′=hedta^{3-})

Discharging species	Cu(II)–EDTA complex				Cu(II)–HEDTA complex	
	CuL^{2-}	$CuHL^-$	CuH_2L^0	CuH_3L^+	CuL'^-	$CuHL'^0$
k_p°/cm s^{-1}	9.3×10^{-4}	8.7×10^{-3}	1.6×10^{-2}	3.6×10^{-3}	2.7×10^{-2}	1.5×10^{-1}
α_p	0.59	0.50	0.48	0.52	0.58	0.47
(E_p° vs. SCE)/mV	−488	−321	−205	−171	−460	−266
$\Delta\phi_2$/mV	−6.0	13	25	29	−3.7	20
$(k_p^\circ)_{corr}$/cm s^{-1}	4.4×10^{-4}	2.4×10^{-2}	9.2×10^{-3}	1.7×10^{-2}	2.0×10^{-2}	3.0×10^{-1}

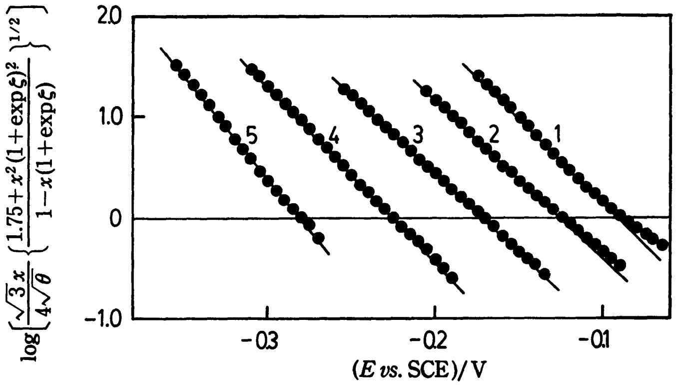

Fig. 5. Modified log-plots of normal pulse polarograms for the reduction of the Cu(II)-HEDTA complexes.
Total concentration of HEDTA=20 mM and concentration of Cu(II) aqua ion=0.4 mM. Sampling time θ=6 ms, drop time of DME τ=4.0 s and rate of the increase in potential pulse height ΔE=10 mV/drop.
$-\log[H^+]$: (1) 2.96, (2) 3.62, (3) 4.40, (4) 6.07, (5) 8.89.

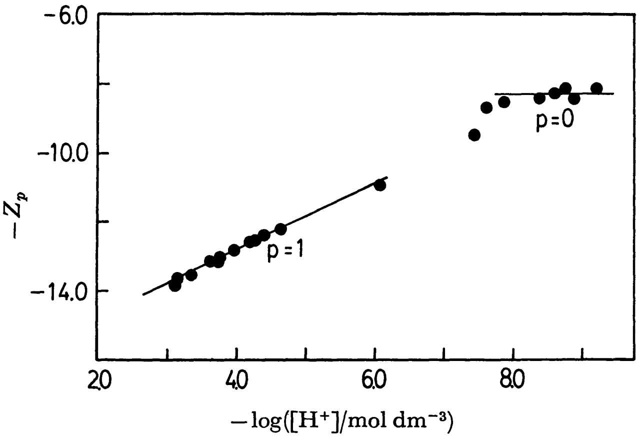

Fig. 6. Dependence of the function, $-Z_p$, upon $-\log[H^+]$ for the Cu(II)-HEDTA complexes.
Experimental conditions are the same as in Fig. 4.

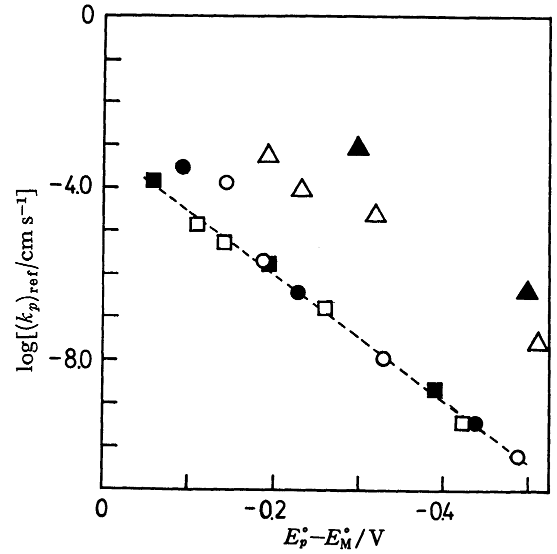

Fig. 7. Plots of $\log(k_p^\circ)_{\text{ref}}$ against $E_p^\circ - E_M^\circ$ $(=-(2.3\,RT/2F)\times\log(\beta_{1p1}/\beta_{0p1}))$ for the M(II)-EDTA complexes and the M(II)-HEDTA complexes.
(▲): Cu(II)-HEDTA complexes, (△): Cu(II)-EDTA complexes, (●): Pb(II)-HEDTA complexes, (○): Pb(II)-EDTA complexes, (■): Cd(II)-HEDTA complexes, (□): Cd(II)-EDTA complexes.

polarogram probably consists of the overlap of two waves for the reduction of Cu(II) aqua ion and the protonated Cu(II) complexes, as seen from polarogram 1 in Fig. 4. By the differential pulse polarography the two humps in polarogram were observed. However, since two waves closely overlapped, the waves could not be satisfctorily separated by using the non-linear least-squares method.[25]

Discussion

The results obtained above demonstrate that normal pulse polarography is one of the most useful pulse techniques for the examination of the electrode kinetics in d.c. polarographically quasi-reversible electrode processes. The kinetic parameters obtained are summarized in Table 1 together with the values of the standard rate constants, $(k_p^\circ)_{\text{corr}}$, corrected for the double layer effect by means of the Frumkin theory,[26] in which the values of ϕ_2 were taken from Russell's tables.[27] The values of the standard rate constants, $(k_p^\circ)_{\text{corr}}$ increase in the following order: $CuL^{2-} \ll CuH_2L^0 < CuHL^- < CuH_3L^+$ (L=edta^{4-}) for the Cu(II)-EDTA complexes and $CuL'^- < CuHL'^0$ (L'=hedta^{3-}) for the Cu(II)-HEDTA complexes. In both systems, the values of k_p° ($p \geq 1$) for the protonated complex species are larger than those for the ordinary unprotonated complex species. The corrected rate constant, $(k_p^\circ)_{\text{corr}}$, of the Cu(II)-EDTA and -HEDTA complexes except CuH(hedta)^0 and Cu(edta)$^{2-}$ were almost the same order of magnitude ($\approx 10^{-2}$ cm s^{-1}) as that of the Cu(II) aqua ion.[28] The values of the cathodic transfer coefficients for the species under consideration were in the range of 0.47 to 0.59, as summarized in Table 1.

Previously[1-3] we have found that the linear relation between the cathodic rate constants at some reference potential and the corresponding standard potentials holds for the Cd(II) and Pb(II) complexes with EDTA and related compounds and further suggested that the protonation of acetate groups of these ligands, leading to the cleavage of the metal-oxygen bonds within the complex species, accelerates the rate of charge transfer process. We examined whether such a correlation prevails for the present series of the Cu(II) complexes. In Fig. 7 the logarithms of $(k_p^\circ)_{\mathrm{ref}}$'s are plotted against $E_p^\circ - E_{\mathrm{Cu}}^\circ (= -2.3(RT/2F)\log(\beta_{1p1}/\beta_{0p1}))$, where E_p° is the standard potential of the couple $\mathrm{CuH}_p\mathrm{L/Cu(Hg)}$ or $\mathrm{CuH}_p\mathrm{L'/Cu(Hg)}$ and E_{Cu}° is the standard potential of Cu(II) aqua ion. As can readily be seen from this figure, a linear relationship between the cathodic rate constants and the corresponding standard potentials could not be obtained. We have no idea to explain such a different behavior at present, but this may probably be associated with the difference between the ordinary octahedral structure of the Cd(II) and Pb(II) complexes and the pseudo octahedral structure of the Cu(II) complex.[29-31]

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