A Comparative Study of Electrochemical Kinetic Parameters by the Potential Step Method. Electrode Reactions of CyDTA and EDTA Complexes of Cu(II) at DME

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By using the same current-time (*I-t*) curves, electrochemical kinetic parameters are determined by two methods, (a) using the ratio of current at a given potential to the diffusion-controlled limiting current and (b) curve fitting method, for the reduction of Cu(II)–CyDTA complex. The analysis by the method (a) shows that the rate determining step involves only one electron although the overall reduction of the complex involves two electrons suggesting thereby the stepwise reduction of the complex. The nature of *I-t* curves suggests the adsorption of intermediate species at the electrode surface. Under these circumstances more reliable kinetic parameters can be obtained by the method (a) compared to that of (b). Similar observations are found in the case of reduction of Cu(II)–EDTA complex.

The determination of electrochemical kinetic parameters of metal complexes by comparative methods is not found common. Particularly, such studies are lacking for the systems involving more than one electron in the reduction process. A comparative study of kinetic parameters of such systems by different methods of analysis could verify the reliability of the results obtained by each method and also throw some light on the mechanism of reduction of the complexes at the electrode interface. With this in view, kinetic parameters of two complexes, Cu(II)-*trans*-1,2-cyclohexanediamine-*N*,*N*,*N'*,-*N'*-tetraacetic acid (Cu–CyDTA) and Cu–EDTA, were determined by the potential step method. Current-time (*I-t*) curves were analyzed by the two different methods: method (a) using the ratio of current at a given potential to the diffusion-controlled limiting current, and method (b) using the curve fitting procedure. The details of the methods employed were reported elsewhere.[1–3]

The basic equations relating the conditional rate constant, $k_c^\ominus$, with the rate constants for the oxidizing (k_{ox}) and reducing (k_{red}) reactions, $O+ne \rightleftarrows R$, can be written as follows:

$$k_{red} = k_c^\ominus \exp\left[-\frac{\alpha_c nF}{RT}(E-E^{\circ\prime})\right] \qquad (1)$$

$$k_{ox} = k_c^\ominus \exp\left[\frac{\alpha_a nF}{RT}(E-E^{\circ\prime})\right] \qquad (2)$$

where α_c and α_a are cathodic and anodic transfer coefficients respectively, $E^{\circ\prime}$ is the conditional potential, and R, T, n, F have their usual meaning. These equations can be used to determine the kinetic parameters from the current-time relationship at each potential.

Experimental

Apparatus and Chemicals. The electronic potential step generator along with a timer for dislodging the mercury drop was constructed by using operational amplifiers. The cell was of conventional type. The working electrode was a slowly dropping mercury electrode the drop time and the rate flow of mercury being 18.0 s and 0.624 mg s^{-1} respectively, measured at the height of the mercury column of 42 cm. A spiral of bright platinum was used as the counter electrode. The solution was deaerated with pure nitrogen and was kept under nitrogen atmosphere throughout the experiment. The temperature of the solution was kept constant at 25±0.2 °C. All solutions were prepared in double distilled water and all chemicals used were of analytical grade.

Cu(II)–CyDTA complex was prepared by mixing equimolar solutions of $CuCl_2$ and disodium salt of CyDTA.[4] Cu(II)–EDTA complex was prepared by mixing equimolar solutions of $CuCl_2$ and disodium salt of EDTA.[5]

Method of Measurement. The initial potential for the Cu(II)–CyDTA system was fixed at −0.200 V *vs.* SCE. The potential was stepped up at 14 s after the mercury drop starts growing. The current-time curves were photographed on a Tektronix oscilloscope, Type 564, with a Type 2A63 differential amplifier and Type 2B67 time-base unit. The difference between each potential step-up in subsequent steps was of the order of 5 mV along the rising portion of the reduction wave and 25 mV on the limiting current plateau. Enlarged prints were used for calculating the current. The calculation was programmed on a SOBAX ICC-2700 calculator.

For the Cu(II)–EDTA system the initial potential was fixed at −0.130 V *vs.* SCE and the rest of the measurement was the same as in the case of the Cu(II)–CyDTA system.

The ohmic resistance of the system was about 50Ω, and the effect of the ohmic drop was neglected in the present analysis. The uncertainty of the electrode potential due to the ohmic drop was estimated to be of the order of several millivolts at potentials near $E^{\circ\prime}$. However, this uncertainty will not affect the following discussion on the kinetic parameters of the systems or on the mechanism of reduction of the complexes.

Results and Discussion

Electrode Reaction of Cu(II)–CyDTA System. Analysis by the Method (a)[1,3]: Under the conditions where the current corresponds to a large value of t ($t=t_\infty$), and the potential is sufficiently negative so as to satisfy the conditions, $Q\sqrt{t}>5$ and $k_{red} \gg k_{ox}$, the following relationships can be obtained**

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** The symbols and terminology are according to IUPAC recommendations.[6]

$$\frac{I(t)I_d(t_\infty)}{I(t_\infty)I_d(t)} = \sqrt{\pi}Q\sqrt{t}\exp(Q^2t)\operatorname{erfc}(Q\sqrt{t}) \tag{3}$$

$$k_{\rm red} = Q\frac{I(t_\infty)}{I_d(t_\infty)}\sqrt{D_{\rm O}} \tag{4}$$

$$k_{\rm ox} = Q\left[1-\frac{I(t_\infty)}{I_d(t_\infty)}\right]\sqrt{D_{\rm R}} \tag{5}$$

where $I_d(t)$ and $I_d(t_\infty)$ are the currents at far negative potentials and Q is the parameter at a given electrode potential E at which $I(t)$ and $I(t_\infty)$ were measured. For this system, t=400 μs and t_∞=1.0 s were used. The currents $I(t)$ and $I(t_\infty)$ were measured at several potentials in the neighbourhood of $E^{\circ\prime}$. Also, the diffusion-controlled currents, $I_d(t)$ and $I_d(t_\infty)$, were measured at several potentials on the diffusion current plateau. These values were substituted into Eq. 3 to get Q. By using these Q-values $k_{\rm red}$ and $k_{\rm ox}$ were obtained from Eqs. 4 and 5 assuming $D_{\rm O}=D_{\rm R}=6.8\times10^{-6}$ cm² s⁻¹, estimated from the polarographic diffusion current by the Ilkovic equation.

Figure 1 gives the typical plots of log $k_{\rm red}$ and log $k_{\rm ox}$ *vs.* potential for one value of I_d measured at a potential on the diffusion current plateau. The conditional rate constant $k_c^\ominus$ was obtained from the intersection of two straight lines and α_c and α_a were obtained from the slopes. In a similar way, by using other values of I_d's several $k_c^\ominus$-values were obtained and were plotted against the electrode potential, E_d, where the I_d-values were measured (Fig. 2).

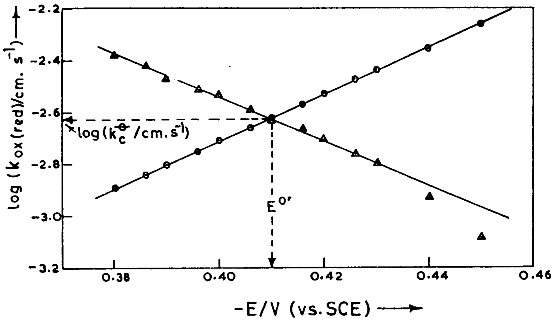

Fig. 1. Plots of log ($k_{\rm red}$/cm s⁻¹) and log ($k_{\rm ox}$/cm s⁻¹) *vs.* E; the rate constant obtained by the method (a) using diffusion-controlled limiting current. System: 6.0 mM Cu(II)-CyDTA complex in a 0.4 M KNO_3 solution containing 0.1 M acetate buffer and 3 μM polyoxyethylene lauryl ether (LEO).

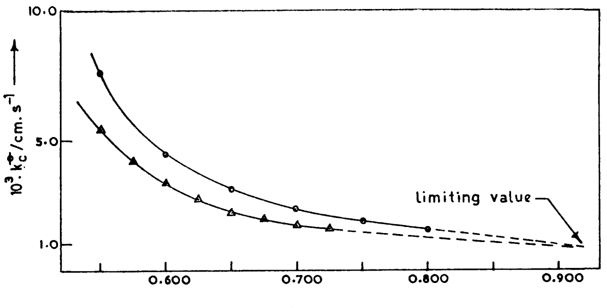

Fig. 2. Variation of $k_c^\ominus$ with potentials, E_d, at which I_d's are measured; analysis by the method (a). System: 4 mM (△) and 6 mM (○) Cu(II)-CyDTA in 0.4 M KNO_3 solutions containing 0.1 M acetate buffer and 3 μM LEO.

It is obvious from Fig. 2 that the rate constant decreases as the potential becomes more and more negative and finally comes to a limiting value. However, at far negative potentials the distortion of *I-t* curves was noticed (broken lines in Fig. 2 correspond to the potentials where the distortion was observed). The curve, $k_c^\ominus$ *vs.* E_d, was extrapolated in this region to obtain the limiting value of $k_c^\ominus$ which is in reasonably good agreement with that obtained by other methods[7] (see, Table 1).

Table 1. Kinetic parameters obtained by different methods of analysis for Cu(II)-CyDTA and Cu(II)-EDTA complexes

System	Method	$n\alpha_c$	$n\alpha_a$	$\frac{k_c^\ominus\times10^3}{\text{cm s}^{-1}}$
Cu(II)-CyDTA	Potential-step; method (a)	0.52	0.48	0.8
	Potential-step; method (b)	0.5	—	1.4
	Faradaic impedance method	—	—	0.63[a]
Cu(II)-EDTA	Potential-step; method (a)	0.53	0.48	1.7
	Potential-step; method[10]	0.54	0.46	4.0
	Faradaic impedance method	—	—	0.85[a]

a) To be published.

At all potentials of the I_d-measurement $n\alpha_c$ and $n\alpha_a$ obtained as slopes add up to one unlike in the case of Zn(II) system.[1] This suggests that the number of electrons involved in the rate determining step is only one although the overall reduction of the complex involves two electrons.[8] Therefore, the mechanism of reduction of the complex at DME can be written as follows.

$$\text{Cu(II)-CyDTA} + \text{e} \xrightarrow{\text{slow}} \text{Cu(I)-CyDTA}$$

$$\text{Cu(I)-CyDTA} + \text{e} \overset{\text{fast}}{\rightleftarrows} \text{Cu}^\circ\text{(Hg)} + \text{CyDTA}$$

Analysis by the Curve Fitting Method (b)[1,2]: At any given potential the best values of $I(t=0)$ and Q were calculated by the trial-and-error method using Eq. 6:

$$I(t)/I(t=0) = \exp(Q^2t)\operatorname{erfc}(Q\sqrt{t}) \tag{6}$$

where

$$I(t=0) = -nFAk_{\rm red}c_{\rm O} \tag{7}$$

$$Q = k_{\rm red}/\sqrt{D_{\rm O}} + k_{\rm ox}/\sqrt{D_{\rm R}} \tag{8}$$

By knowing the concentration $c_{\rm O}$, of the complex, and surface area, A, of the mercury drop and by using Eq. 7, the values of $k_{\rm red}$ were calculated at several potentials in the neighborhood of $E^{\circ\prime}$ from the best values of $I(t=0)$, and were plotted against E. From the resulting straight line graph $k_c^\ominus$ was read at $E^{\circ\prime}$ obtained by the method (a). From the slope α_c was calculated. These values agree well with the values obtained by the method (a) (see Table 1). However, the values of $k_{\rm ox}$ obtained by using appropriate Q values employing expression (8) were found to be much higher than expected (of the order of 10^{-2} cm s⁻¹).

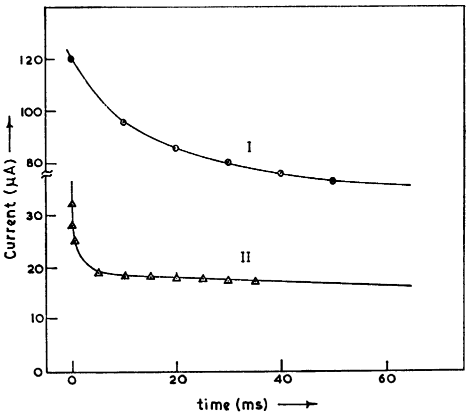

Fig. 3. (I) *I-t* curve for the reduction of zinc(II) at −0.994 V *vs.* SCE. 8.0 mM $Zn(NO_3)_2$ in a 0.5 M KNO_3 solution containing 0.2 mM HNO_3.
(II) *I-t* curve for the reduction of Cu(II)–CyDTA at −0.410 V *vs.* SCE. 6.0 mM Cu(II)–CyDTA in a 0.4 M KNO_3 solution containing 0.1 M acetate buffer and 3.0 μM LEO.

Figure 3 gives the *I-t* curves for the Cu(II)–CyDTA system and for the Zn(II) system near to their respective $E^{\circ\prime}$. A comparison of the *I-t* curves for these two systems shows that the decay of current with time is much faster in the case of the Cu–CyDTA complex than in the case of the Zn(II) system. According to Eqs. 6 and 7 the decay of current with time should be comparable for two systems if their conditional rate constants, α's and *D*'s are comparable. However, in the above two cases their *I-t* curves are found to be quite different though their kinetic parameters are comparable. Because of this the curve fitting in the case of the Cu(II)–CyDTA system had to be carried out between 600 μs and 900 μs where exists a perceptible difference in the current with time. Such a behavior of the system is probably due to the adsorption of the short-lived intermediate species during reduction. This adsorption of intermediate species could act as a capacitance in parallel to the faradaic impedance and thereby shunts the latter to make the current decay more rapidly.[9]

Electrode Reaction of Cu(II)–EDTA System. Analysis by the Method (a): The procedure adopted in this case is the same as in the previous case. The two time limits chosen were, $t=350$ μs and $t_\infty=1.0$ s. The limiting value, $k_c^\ominus$, obtained by extrapolating $k_c^\ominus$ *vs.* E_d curve is given in Table 1. In this case also, the distortion of *I-t* curve was found at far negative potentials. The values of $n\alpha_c$ and $n\alpha_a$ add up to make one suggesting that the number of electrons involved in the rate determining step is one only. Therefore, the mechanism of the reduction process can be written as follows:

$$\text{Cu(II)-EDTA} + \text{e} \xrightarrow{\text{slow}} \text{Cu(I)-EDTA}$$

$$\text{Cu(I)-EDTA} + \text{e} \xrightleftharpoons{\text{fast}} \text{Cu}^\circ\text{(Hg)} + \text{EDTA}$$

The nature of *I-t* curves in this case, *i.e.*, the decay of current with time is similar to that of the Cu(II)–CyDTA system indicating the adsorption of intermediate species.

Conclusion. The reduction of Cu(II)–CyDTA and Cu(II)–EDTA complexes occurs at DME in two steps and each step involves one electron in the reduction process. When the reduction is further complicated by the adsorption of intermediate species the analysis of *I-t* curves by the curve fitting method introduces some uncertainty in the results. On the other hand, the analysis by the method (a) can be adopted to obtain more reliable kinetic parameters.

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