

## Electrochemical reduction of Cu(II)-CyDTA complex at dropping mercury electrode. An impedance approach

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**Abstract.** The electrochemical reduction of Cu(II)-CyDTA (CyDTA -- trans 1,2-cyclohexanediamine N, N, N', N' tetraacetic acid) by impedance method reveals the unusual behaviour of complex plane polarograms owing to potential dependence of double layer capacitance. The impedance plane plots by frequency variation method indicates the quasi-reversible nature of the system. From these plots the charge-transfer resistance at various potentials was evaluated. The standard rate constant was evaluated which complements the prediction of impedance plots for the quasi-reversible behaviour of the system.

**Keywords.** Electrochemical reduction; Cu-CyDTA system; impedance method; complex plane polarography.

### 1. Introduction

In recent years electrochemical investigations by a.c. bridge method (Sluyters and Sluyters 1963) or by phase selective recording system (Smith 1966; De Levie and Husovsky 1969) has been found to be a useful technique for fundamental research. The main advantage of this method is that information can be obtained about faradaic impedance, double layer capacitance and ohmic resistance without referring to the studies in absence of electroactive species (Sluyters-Rehbach and Sluyters 1970). There are some interesting cases that are studied employing this technique in inorganic salts, in organic systems (Bhat and Subrahmanya 1978), in metal chelates (Verkroost *et al* 1972; Bhat 1976a). The present work deals with the analysis of impedance data for Cu(II)-CyDTA system where some unusual behaviour is found.

### 2. Experimental

The measurement of cell impedance was carried out on phase sensitive a.c. polarograph (Matsuda *et al* 1970). A small amplitude of sinusoidal wave (<3 mV) was applied to the cell and the in-phase and quadrature components were recorded simultaneously as the function of d.c. potential. These curves were analysed to obtain the real and imaginary components of the cell impedance. Such analysis was carried out at several d.c. potentials and at several frequencies. The calculations were programmed on IBM-360/44 computer.

The electrolysis cell was of conventional type. The solution was deaerated with pure nitrogen and nitrogen was passed over the solution throughout the experiments. The working electrode was a dropping mercury electrode ( $m=0.925$  mg/sec) and the counter electrode was a spiral of bright platinum. Mercury drop was dislodged at 5.88 sec. The potential was applied against SCE and the temperature of the experiments was  $25^{\circ}\text{C}\pm 0.5^{\circ}\text{C}$ .

The stock solution of Cu-CyDTA was prepared by mixing equimolar solutions of disodium salt of CyDTA and  $\text{CuCl}_2$  (Schwarzenbach and Ackermann 1949). The solution was tested for free copper ion polarographically and no trace of it was found in the solution. All solutions were prepared in double distilled water and all chemicals used were of analytical grade.

### 3. Results and discussion

#### 3.1. Nature of the impedance plane plots at a fixed frequency and at different potentials

The equivalent circuit considered for this system is of Randles' type (Randles 1947) and is shown in figure 1b. The total cell impedance was calculated on the basis of this equivalent circuit from the recorded in-phase and quadrature components (figure 2) in terms of real ( $R_s$ ) and imaginary  $(\omega C_s)^{-1}$  components at different potentials and at fixed frequency. The salient features of these polarograms are mentioned below. At low frequencies the complex plane polarograms are sharp, steep and well

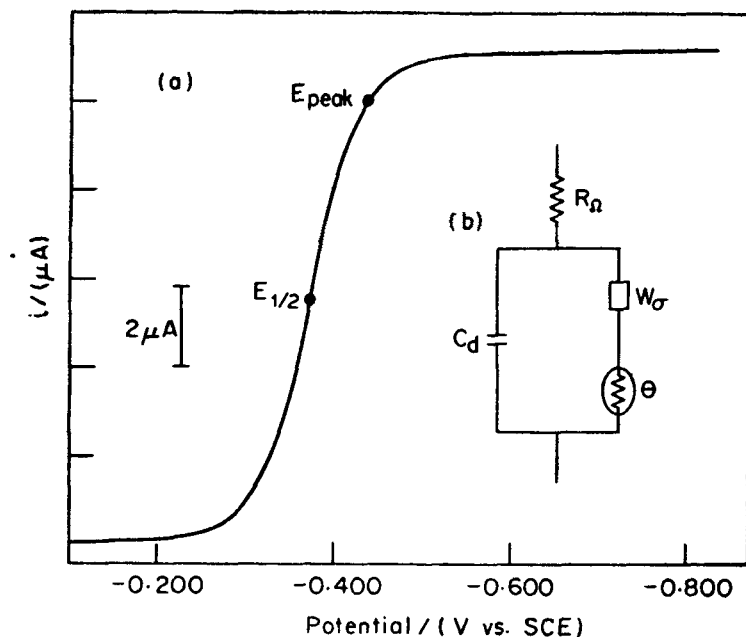
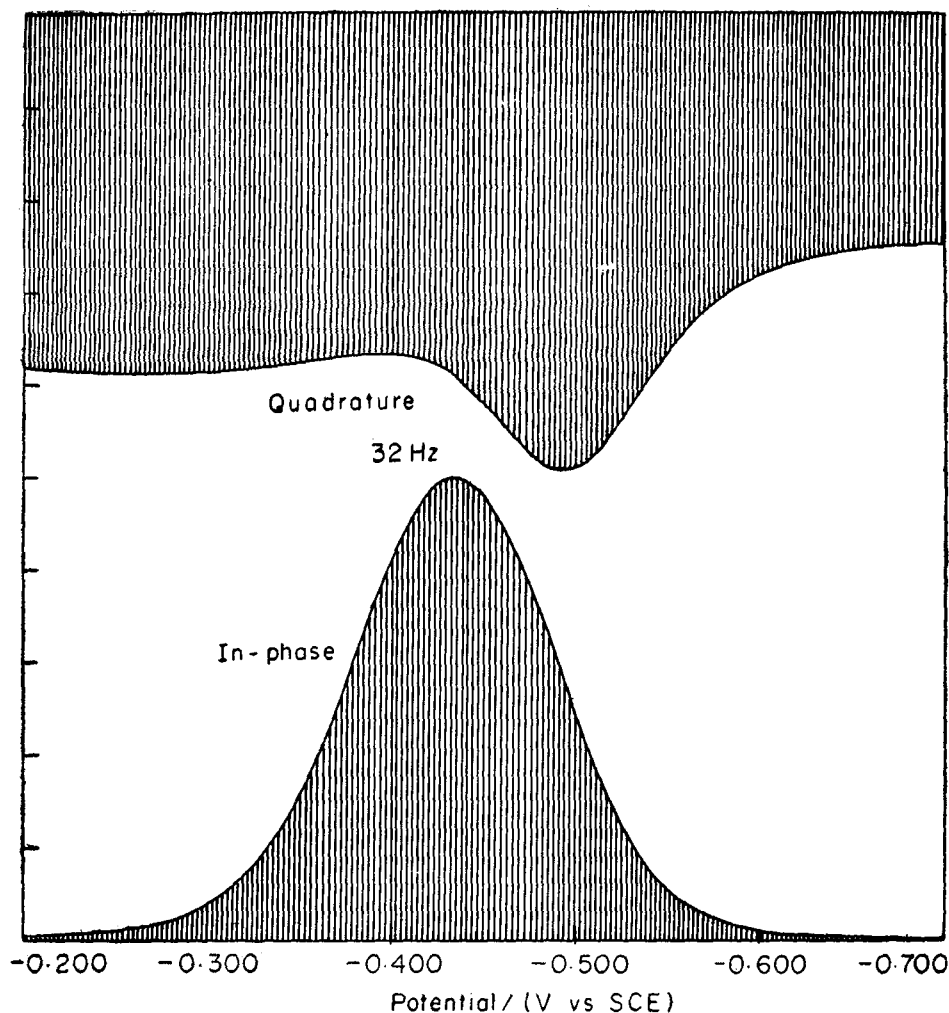


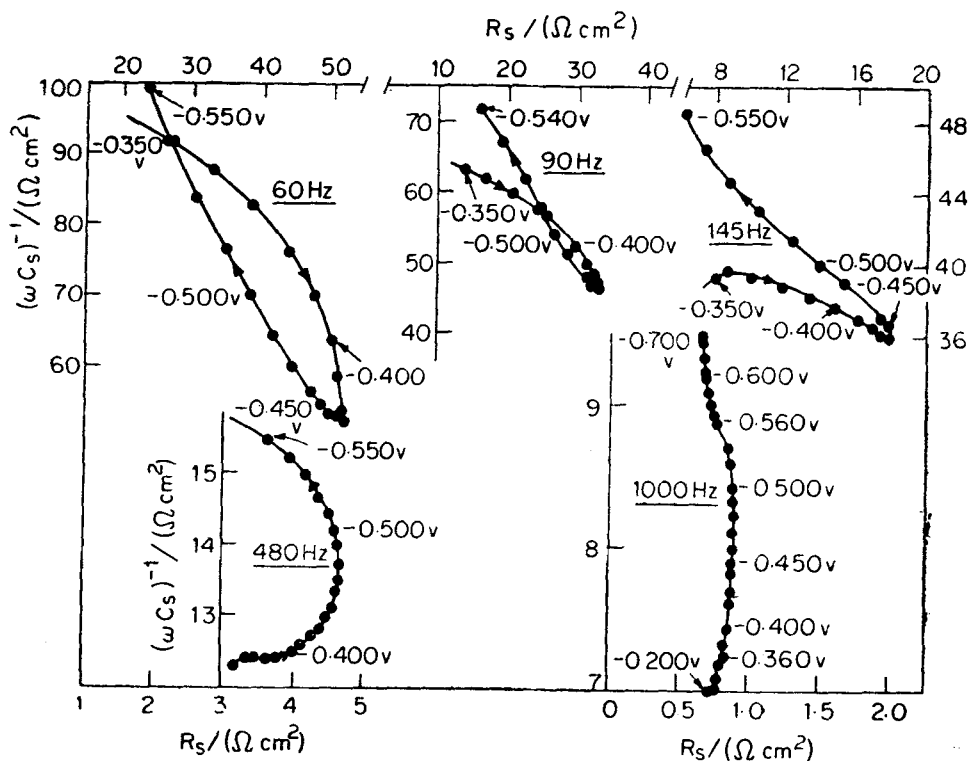
Figure 1. a. d.c. polarogram. Cu-CyDTA-2.0 mM; acetate buffer—0.1M;  $\text{KNO}_3$ —0.4 M; polyoxyethylene lauryl ether (LEO)—3  $\mu\text{M}$ . b. Randles' equivalent circuit.  $C_d$ —double layer capacitance;  $\theta$ —charge-transfer resistance;  $W_\sigma$ —warburg impedance;  $R_\Omega$ —series ohmic resistance.



**Figure 2.** In-phase and quadrature components recorded at 32 Hz. Experimental conditions are same as in figure 1a.

defined (figure 3), and exhibit peaks at about  $-0.435$  V. The descending branches (portion before the peak-potential) of the complex plane polarograms lie above the ascending branches (portion after the peak-potential). These two branches are well separated and cross each other at a point far off from the peak. As the frequency is increased these two branches come closer and cross nearer to the peak. At about 110 Hz these two branches coincide around the peak. At higher frequencies the position of these two branches gets reversed and two branches do not cross at any potential. The separation between the two also increases. At very high frequencies there are no peaks instead the curve rises upwards making a broad hump.

The positions of ascending and descending branches at low frequencies are peculiar and could be attributed to the potential dependence of the double layer capacitance (Sluyters 1978). The detailed theory and explanations for this effect are being worked out and will be published later. Since the system is quasi-reversible it does not



**Figure 3.** Complex plane polarograms. Potential variation at a single frequency. The direction of arrow shows the cathodic increase in potential applied. Experimental conditions are same as in figure 1a.

respond well to the alternation of high frequencies ( $>700$  Hz) and the main contribution to the complex plane polarograms, which are having hump-like shape and rising upwards, comes from the double layer capacitance.

### 3.2. Nature of the complex impedance plane plots with varying frequency and at fixed potential

At a fixed potential near about the peak of the complex plane polarogram the in-phase and quadrature components are analysed at various frequencies ranging from 22 Hz to 1000 Hz. The real and imaginary components obtained are plotted on a complex impedance plane as a function of frequency (figures 4 and 5). The complex plane plots form semicircles and points below 60 Hz deviate from semicircles owing to diffusion polarisation. The semicircles suggest that the rate of electrochemical reduction of this complex is charge-transfer controlled. The semicircles are according to equation (1) (Sluyters and Sluyters 1963).

$$(R_s - R_\Omega - \theta/2)^2 - [(\omega C_s)^{-1}]^2 = \theta^2/4. \quad (1)$$

where  $R_\Omega$  is the ohmic resistance of the cell,  $\theta$  is the charge-transfer resistance,  $R_s$  is the series resistance,  $C_s$  is the series capacitance and  $\omega = 2\pi f$ ,  $f$  is the frequency in Hz.

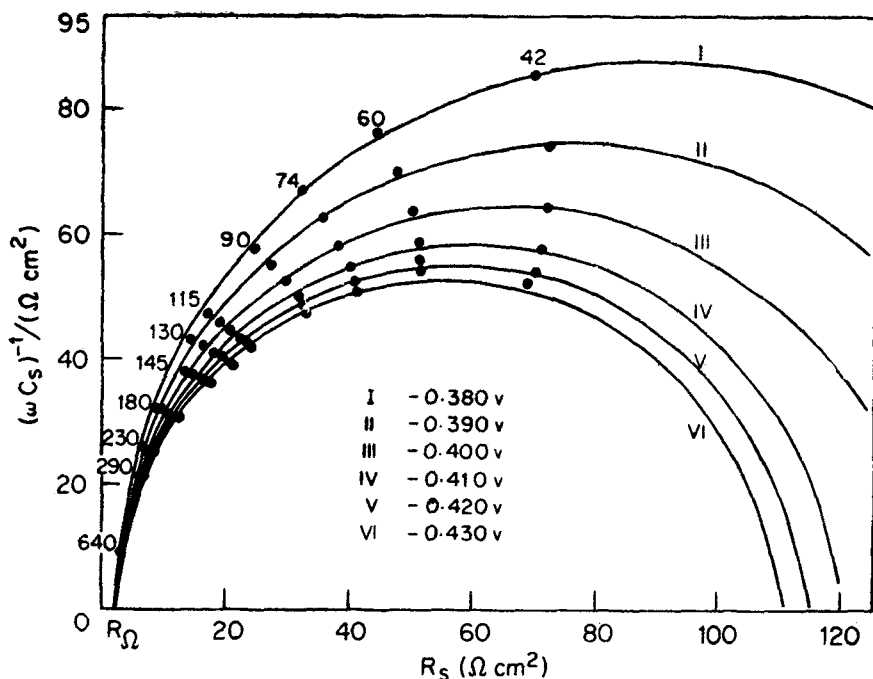


Figure 4. Complex plane plots. Frequency variation at a fixed potential. The numbers on the semicircles indicate the frequency in Hz. Experimental conditions are same as in figure 1a.

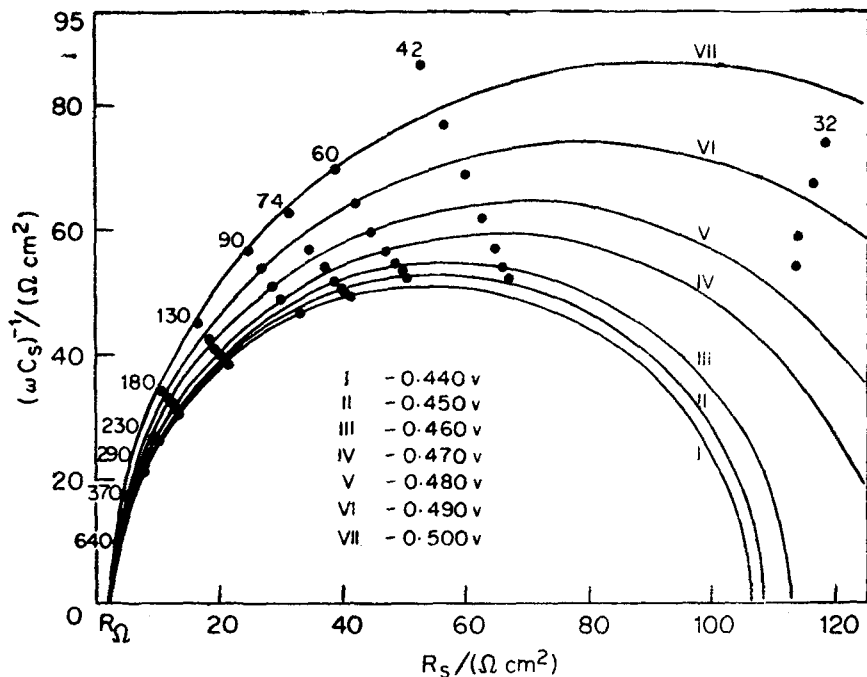


Figure 5. Complex plane plots. Frequency variation at a fixed potential. The numbers on the semicircles indicate the frequency in Hz. Experimental conditions are same as in figure 1a.

The above equation suggests that the diameter of the semicircle should give the value of charge-transfer resistance at that potential and intercept on  $R_s$  axis at infinite frequency would give the ohmic resistance  $R_\Omega$ . From the complex plane plots at several potentials the charge-transfer resistances were calculated and were plotted against potential (figure 6b). As seen from figure 6b, the variation of charge-transfer resistance with potential is hyperbolic in nature and the minimum of this curve occurs at  $-0.435$  V for this system.

The exact evaluation of the standard rate constant at this minimum potential for quasi-reversible systems involves the use of complicated expression (Sluyters and Sluyters 1970) and needs lot of computation. In order to get the qualitative value of the standard rate constant a simpler expression derived for d.c. reversible systems is used. The expression is

$$K_s = \frac{RT}{n^2 F^2 \theta_{\min} C} \times \frac{d^{1/2(1-a)}}{a^a(1-a)^{(1-a)}} \quad (2)$$

where  $d = D_R/D_O$ ,  $D_R$  and  $D_O$  are diffusion coefficients of the reduced and oxidised species respectively,  $a$  is the cathodic transfer coefficient,  $C$  is the concentration of the depolariser,  $R$ ,  $T$ ,  $n$  and  $F$  have their usual meaning: The value of  $a$  is taken as 0.52

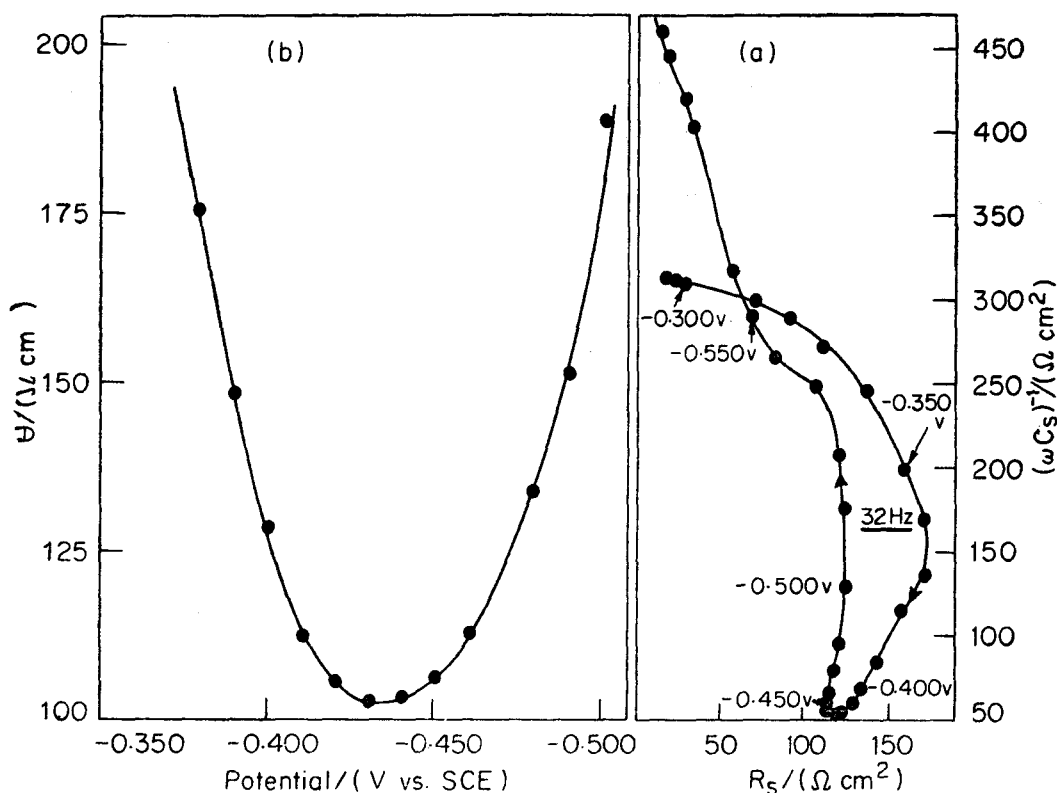


Figure 6. a. Complex plane polarogram covering wide range of potential. b. Charge-transfer resistance as a function of potential.

**Table 1.** Shift in the peak potentials of in-phase and quadrature components with varying frequency. All potential refer with respect to SCE.  $E_{1/2} = -0.385 \pm 0.003$  V

Frequency (Hz)	$-E_{\text{peak}}$ (V) (in-phase)	$-E_{\text{peak}}$ (V) (quadrature)
22	0.435	0.485
28	0.435	0.490
32	0.435	0.495
35	0.437	0.495
42	0.437	0.495
60	0.437	0.502
74	0.445	0.505
90	0.445	0.507
115	0.445	0.507
145	0.447	0.507
180	0.447	—
230	0.450	—
290	0.445	—
370	0.445	—
480	0.430	—
600	0.420	—
740	0.405	—

(Bhat 1976 b). The  $\theta$  value at the minimum potential is  $210 \Omega \text{ cm}^2 \text{ mole/cc}$  and the standard rate constant thus calculated is  $6.4 \times 10^{-4} \text{ cm. sec}^{-1}$ . The intercept on  $R_s$ -axis at infinite frequency,  $R_\Omega = 2.76 \Omega \text{ cm}^2$  and is in agreement with  $R_\Omega = 2.79 \Omega \text{ cm}^2$  obtained from the blank solution.

It is noted from the in-phase and quadrature components that their maxima do not lie at the same potential at all frequencies. Table 1 gives the magnitudes of deviation with frequencies. Both for in-phase and quadrature components there is a small shift of potential of maximum towards more negative potential as the frequencies increase and attains a steady value at some frequency range and shifts back as frequency is further increased. This sort of behaviour is yet to be explained on theoretical grounds.

Another interesting feature is that the potential where the minimum of the complex plane polarogram occurs does not coincide with the  $E_{1/2}$  of the d.c. polarogram (figure 1a). The difference between  $E_{1/2}$  and  $E_{\text{peak}}$  is of the order of 0.050 V. This difference is due to the irreversible nature of the system. Quantitative treatment to explain this behaviour is in progress.

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