Anomalous Polarographic Behaviour of Some Mixed Ligand Complexes of Copper(II)

P K CHITALE, S N MANDLOI, M S VERMA* & H L NIGAM†
School of Studies in Chemistry, Vikram University, Ujjain 456010

Received 15 May 1982; revised and accepted 5 July 1982

In aqueous sodium perchlorate the complexes copper(II) LL' (L = 2, 2'-bipyridyl and L' = succinic acid residue or phthalic acid residue) have been observed to undergo two-step one-electron irreversible reduction at d.m.e. The electro-reduction of these complexes is different at different temperatures. The first half wave potential shifts towards more negative values while the second half-wave potential shifts to more positive values with the rise in temperature. The reduction of second step is facile at higher temperature. This behaviour has been explained on the basis of adsorption effects. A correlation between electrode behaviour, spectral parameter and stability constants has been explained. That the polarographic reduction of [copper(II) (bipy) (succ)] over that of [copper(II) (bipy) (Pht)] should be facile as predicted by spectral characteristics, is found to be incorrect. This anomalous behaviour has been explained on the basis of adsorption effects and delocalized π-electrons in phthalate ion.

Thermodynamic and spectroscopic studies of [Cu(bipy) (succ)] and [Cu(bipy) (Pht)] (where bipy = 2, 2'-bipyridyl, succ = succinic acid residue and Pht = phthalic acid residue) reveal that the former complex has square pyramidal structure while the latter has square planar or tetragonally distorted octahedral structure in the solid state as well as in aqueous solutions. As an extension of our earlier work on the polarographic behaviour of mixed ligand complexes, presently the mixed ligand complexes [Cu(bipy) (succ)] and [Cu(bipy) (Pht)] have been studied at the dropping mercury electrode, kinetic parameters calculated, and a mechanism of the reduction process has been proposed. Furthermore, an attempt has been made to correlate the polarographic behaviour and spectral parameters.

The complexes [Cu(bipy) (succ)] and [Cu(bipy) (Pht)] were prepared by known methods, and their purities checked by IR spectra. Sodium perchlorate (A R) was used as supporting electrolyte and Triton X-100 as a maximum suppressor.

The polarograms of the thoroughly deaerated solutions at the desired temperature were recorded with the help of a manual polarographic circuit. All the potentials were measured against a Hume and Harris saturated calomel electrode (SCE). The resistance of the polarographic cell was measured by an usual type of a.c. wheatstone bridge. The resistance was found to be 1000 ± 100 Ohms, hence no iR correction was needed. The mercury used was of A R grade. The capillary had the following characteristics (open circuit).

\[ h_{corr} = 73.5 \text{ cm}, \ t = 4.5 \text{ sec}, \ m = 1.01 \text{ mg/sec} \]

In aqueous 0.1 M sodium perchlorate, both the complexes undergo a two-step reduction at 20°, 30°, 40°, and 50° C (± 0.1° C). Plots of \( i_d \) versus \( h_{corr} \) are linear, indicating that one of the electro-active species is adsorbing reversibly. The electrocapillary curves also indicate the adsorption of the depolarizers (Fig. 1).

The values of \( (i_d)_{1} \) (diffusion current for the first wave) increase with the rise of temperature but those of \( (i_d)_{2} \) (diffusion current for second wave) decrease. The values of first half-wave potential \( (E_{1/2})_{1} \) shift towards more negative potentials while those \( (E_{1/2})_{2} \) of the second wave shift towards more positive potentials (see Table 1).

The half-wave potentials and slope values have been calculated from the plot of \(-E\) versus log \( (i_d - h/i) \). Slope values show that electro-reduction of both the complexes at all temperatures is irreversible. The plot of half-wave potential against temperature is nonlinear indicating a change of mechanism of the reduction process with the change of temperature for a particular depolarizer. The values of the number of electrons transferred, \( n_d \), obtained from Ilkovic equation are nearly equal to one for the first and second waves of each complex. The values of transfer coefficient \( a \), and those of reference rate constant, \( k_r \), have been determined by Oldham and Parry’s method, using the equation,

\[ E_{1/2} = E_r + \frac{0.0592}{zn} \log \left( \frac{0.89K_r}{\sqrt{D}} \right) \]

where \( E_r \) = reference potential; \( t \) = drop time; and \( D \) = diffusion coefficient.

![Fig. 1—Electro-capillary curves for copper(II) (bipy) (succ) & Cu(II) (bipy) (Pht)](image-url)

† Present address: Department of Chemistry, University of Allahabad, Allahabad
A perusal of the data in Table 1 reveals the following significant trends: (i) \((i_0)_1\) increases while \((i_0)_2\) decreases with the rise of temperature; (ii) \((E_{1/2})_2\), less negative as the temperature is increased; and (iii) the values of \(K_f\) and \(K_r\) do not follow the expected trend. These conflicting observations may be rationalized by proposing the existence of the following equilibria:

First step reduction:

\[
\text{Copper(II)-LL'} \rightarrow \text{Copper(I)-LL'} + e^- \]  \hspace{1cm} (1)\]

adsorbed at electrode.

Second step reduction:

\[
\text{Copper(I)-LL'} \rightarrow \text{Copper(0)} \]  \hspace{1cm} (2)\]

(\(L = 2, 2'\) bipyridyl and \(L' = \text{succinic or phthalic acid residue.}

Perhaps, in the first step of reduction depolarizer \(\text{Cu(II)-LL'}\) reaches near the electrode and gets reduced to \(\text{Cu(I)-LL'}\) which is of adsorbing nature. As the temperature rises, more of the species \(\text{Cu(II)-LL'}\) reach the electrode surface resulting in an increase in \((i_0)_1\), but on the other hand rise of temperature decreases the extent of adsorption of \(\text{Cu(I)-LL'}\) species and consequently there is decrease of \((i_0)_2\) with the rise of temperature. The decrease in \((E_{1/2})_2\) may also be explained on the basis of adsorption effects and the change of over-voltage both of which decrease with the rise of temperature. Electrons may be raised to Fermi level due to rise of temperature which may also contribute to the easier reduction. The increase in \((E_{1/2})_1\) values with increase in temperature, may be due to the lesser adsorption of \(\text{Cu(I)-LL'}\) species at higher temperature, i.e. the number of \(\text{Cu(I)-LL'}\) species increases in the inner layer which hinders the reduction of \(\text{Cu(II)-LL'}\).

The values of \(K_f\) and \(K_r\) (Table 1) do not support the trend observed for any of these parameters. At present it is very difficult to provide any satisfactory explanation for the trends in \(K_f\) and \(K_r\) values but due to increase in concentration of \(\text{Cu(II)-LL'}\) and decrease in that of \(\text{Cu(I)-LL'}\) at higher temperature.

On the basis of values of \(\lambda_{max}\) (15830 cm\(^{-1}\)) and stability constant (Log \(B = 11.10\) taken from literature, one would expect that the reduction of \([\text{Cu(bipy)(succ)}]\) complex should be easier than that of \([\text{Cu(bipy)(Ph)}]\) as the values of \(\lambda_{max}\) and stability constant for this complex are 15870 cm\(^{-1}\) and 11.86 respectively, but the polarographic studies show a reverse trend. This is probably due to site of adsorption. It seems that succinic acid or phthalic acid sites of the complexes adsorb at the electrode surface, but due to the presence of delocalized \(n\)-electrons in phthalic acid the electron transfer is easier in this case.

The authors are thankful to the U G C, New Delhi, for the award of teacher research fellowships to (P K C) and (S N M).

### References