Studies on the Polarographic Behaviour of Bis(Ethylenediamine)-Copper(II) Ion and Bis(Glycinato)Copper(II) and the Rates of their Electro-Reduction*

D. BANERJEA

Inorganic Chemistry Laboratories,

Chemistry Department, University College of Science, Calcutta-9

&

P. BANERJEE

Department of Inorganic Chemistry,

Indian Association for the Cultivation of Science, Calcutta-32.

In aqueous KNO_3 medium (with 0.01% gelatin) bis(ethylenediamine)copper(II) ion, $Cu(en)_2^{2+}$, and bis(glycinato)copper(II), $Cu(gly)_2$, undergo one-step irreversible reduction $Cu^{II} \rightarrow Cu^0$ at the D.M.E. The effect of the salt medium on the $E_{1/2}$ of $Cu(en)_2^{2+}$ seems to suggest ion-association. The effect of 'free ligand' in solution on the nature of the wave has also been studied for both the complexes. From the characteristics of the irreversible wave the rate constant, k_r, for the electro-reduction of each complex was evaluated at a reference potential of -0.7 V vs. SCE, and from the k_r values at three different temperatures the corresponding activation energies, E_a, were also evaluated. It has been observed that $Cu(gly)_2$ with a lower wave number of the principal ligand field band is more readily reduced (as shown by less negative $E_{1/2}$, higher value of k_r and lower value of E_a) than $Cu(en)_2^{2+}$. A plausible mechanism of electron transfer from the electrode to the Cu^{II} in the complex has been suggested which explains this observation.

The polarographic behaviour of bis(ethylenediamine)copper(II) ion and bis(glycinato)-copper(II) have been studied in different media to obtain useful information including rates of electro-reduction of these complexes at the dropping mercury electrode under comparable conditions.

EXPERIMENTAL

Materials and Reagents : The complexes bis(ethylenediamine)copper(II) nitrate, $Cu(en)_2(NO_3)_2.2H_2O$, and bis(glycinato)copper(II), $Cu(gly)_2$, are too well-known and were prepared by known methods. Their purity was checked by analysis for copper (volumetrically) and nitrogen (by semi-micro combustion) as usual.

Ethylenediamine (L.R.) was purified by treatment with solid sodium hydroxide, then with sodium metal followed by distillation. An aqueous stock solution of this was prepared and standardized as usual.

All other chemicals used were of reagent quality (G.R., E. Merck or A.R., B.D.H.). Distilled water redistilled in an all-glass still with the addition of a little KMnO₄ and KOH was used to prepare all the solutions.

Freshly prepared solution of gelatin (bacteriological grade) was used as suppressor of polarographic maxima.

Jena glass vessels were used for storage of all solutions.

Electrolytic hydrogen purified by passing over a hot bed of pure copper chips was used for deaeration of the experimental solutions before recording the polarograms.

Apparatus and Procedure : A manual Polarograph (Toshniwal, India), with a sensitive galvanometer (Pye, Cambridge, England) with built-in lamp and scale was used. The unit was calibrated before use as usual. An external SCE was used which was connected to the experimental solution in the polarographic cell through appropriate agar-salt bridge. The polarographic cell with the solution and the SCE were both kept immersed in a water thermostat at the experimental temperature. All polarograms were run on freshly prepared solutions.

A Philips Conductivity Bridge (Type PR9500/90) was used for conductance measurements for evaluation of diffusion coefficient as required.
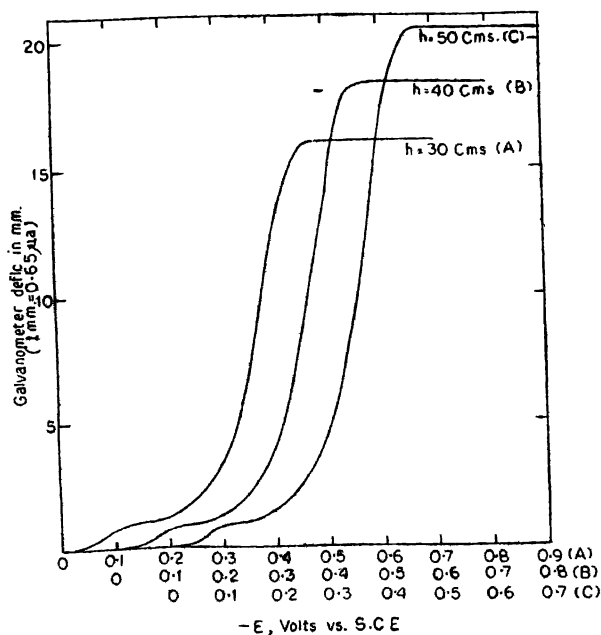

Fig. 1. Polarograms for $Cu(en)_2(NO_3)_2$ ($0.001M$) in $0.1M$ KNO₃ (aqueous solution, containing 0.01% gelatin) at 30°.

A : h, 30 cm; m, 2·104 mg/sec; t, 3·55 sec.

B : h, 40 cm; m, 3·483 mg/sec; t, 2·70 sec.

C : h, 50 cm; m, 4·961 mg/sec; t, 2·15 sec.

RESULTS AND DISCUSSION

For each of the complexes in absence of 'free' ligand in solution it has been found that the main polarographic wave is preceded by a very small pre-wave the height of which is independent of the height of the mercury column (see Fig. 1 for $Cu(en)_2^{2+}$ in KNO_3 medium; the behaviour of $Cu(gly)_2$ is similar). However, for the main wave for each complex $i_{lim}/h^{\frac{1}{2}}_{eff}$ ($h_{eff} \approx h - 3 \cdot 1/m^{1/3}t^{1/3}$) is constant indicating that this is diffusion controlled (see Table 1).

TABLE 1

Effect of mercury pressure on i_{lim} (in $0 \cdot 1M$ KNO_3 medium with $0 \cdot 01\%$ gelatin)

Temp. °C	h, cm	$i_{lim}/h^{\frac{1}{2}}_{eff}$	
		$Cu(en)_2^{2+}$	$Cu(gly)_2$
25	30	1.57	1.63
	40	1.55	1.62
	50	1.55	1.64
30	30	1.69	1.71
	40	1.69	1.69
	50	1.70	1.71
35	30	1.82	1.80
	40	1.81	1.78
	50	1.81	1.78

The diffusion current constants of $Cu(en)_2^{2+}$ and $Cu(gly)_2$ at 25° are 3·54 and 3·67 respectively. Hence, by use of the Ilkovic equation ($i_{lim} = 607\ nD^{\frac{1}{2}}\ Cm^{2/3}t^{1/6}$) it was possible to evaluate the value of n, the number of electrons involved in the electrode process. For this evaluation the value of the diffusion coefficient D for $Cu(en)_2^{2+}$ was obtained from the experimental
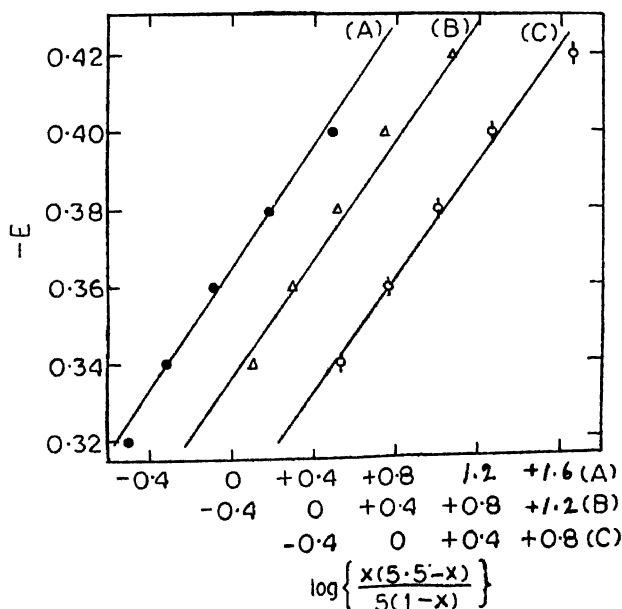

Fig. 2. Graphical evaluation of $E_{\frac{1}{2}}$ and $2 \cdot 303RT/\alpha nF$ for $Cu(en)_2^{2+}$ in $0 \cdot 1M$ KNO_3 (A, 25°; B, 30°; C, 35°).

value of the equivalent conductance of the ion at infinite dilution from the following relation : $D = (RT/ZF^2)\lambda_0$. For the non-ionic $Cu(gly)_2$ the value of D for $Cu(en)_2{}^{2+}$ was used as a reasonable approximation. The value of n thus obtained was very nearly equal to 2 for each of the complexes.

The usual 'log plot' of $-E$ vs. $\log\{i/(i_{ltm}-i)\}$ was used for evaluation of $E_{\frac{1}{2}}$. But the slopes of the log plots were very much higher than the theoretical value of $2\cdot303RT/nF$ for each of the complexes indicating irreversible nature of the waves.

To infer about any possible ion-pairing (outer sphere association) in the $Cu(en)_2{}^{2+}$ system its polarograms were recorded in different salt media and the results are shown in Table 2 which do indicate weak ion-association.

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TABLE 2

Polarographic characteristics of $Cu(en)_2{}^{2+}$ in different media

$Cu(en)_2{}^{2+}$, $0\cdot001M$; gelatin, $0\cdot01\%$; $25°$

h, 50 cm; m, $4\cdot961$ mg/sec.; t, $2\cdot15$ sec.

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Medium :	NaOAc	KNO$_3$	KNO$_3$	KCl	Na$_2$SO$_4$
	$0\cdot01M$	$0\cdot1M$	$1M$	$0\cdot1M$	$0\cdot05M$
$E_{\frac{1}{2}}$, Volt vs SCE :	-0.357	-0.366	-0.415	-0.362	-0.372
Slope of 'log plot' :	0.079	0.076	0.088	0.080	0.081

The polarographic behaviour of $Cu(en)_2{}^{2+}$ has been found to undergo a profound change in presence of free ethylenediamine in the solution. In presence of free ethylenediamine the pre-wave disappears completely. On gradually increasing the concentration of ethylenediamine the $E_{\frac{1}{2}}$ shifts to more negative values (*see* Table 3) but i_{ltm} is not very much affected. The slope of the log plot also diminishes and even in presence of a moderate concentration of ethylenediamine attains a value very near the theoretical value for a truly reversible wave. Similar but much less pronounced effects have been observed in the case of $Cu(gly)_2$ (*see* Table 3).

From the characteristics of the irreversible waves of the two complexes in $0.1M$ KNO$_3$, the rate constants for the electrode reactions were evaluated at a reference potential of -0.7 volt vs. SCE (which is within the diffusion current plateau for both the systems) making use of Oldham and Parry's method[1]. According to these authors the equation for an irreversible diffusion controlled wave is,

$$-E = -E_{\frac{1}{2}}+(2\cdot303RT/\alpha nF)\times \log\{X(5\cdot5-X)/5(1-X)\}$$

where, $X = i_E/i_{ltm}$ ($i_E =$ current at potential E) which is valid in the entire region where $0 \leqslant X \leqslant 1$. From the plot of $-E$ vs. $\log\{X(5\cdot5-X)/5(1-X)\}$ (*see* Figs. 2 & 3), the values of $2\cdot303RT/\alpha nF$ and $E_{\frac{1}{2}}$ could be evaluated from the slope and intercept respectively. Again, for an irreversible wave the half-wave potential is related to the rate constant for the electrode reaction as follows :

$$E_{\frac{1}{2}} = E_r+(2\cdot303RT/\alpha nF)\times \log\left\{0\cdot89k_r\sqrt{\frac{t}{D}}\right\}$$

TABLE 3

Polarographic characteristics of $Cu(en)_2{}^{2+}$ and $Cu(gly)_2$ in presence of 'free' ligand in solution (25°)

(A) $Cu(en)_2{}^{2+}$, $0.001M$; KNO_3, $0.1M$; gelatin, 0.01%;
h, 40 cm; m, 3.483 mg/sec; t, 2.70 sec.

Free en, Molar	Pre-wave	$-E_{\frac{1}{2}}$, V vs. SCE	Slope of 'log plot'
0	Present	0.366	0.076
0.002	Not present	0.413	0.048
0.03	-Do-	0.484	0.042
0.2	-Do-	0.528	0.036

(B) $Cu(gly)_2$, $0.001M$; KNO_3, $0.1M$; gelatin, 0.01%;
h, 30 cm; m, 2.104 mg/sec; t, 3.55 sec.

Free glyH, Molar	Pre-wave	$-E_{\frac{1}{2}}$, V vs. SCE	Slope of 'log plot'
0	Present	0.230	0.080
0.01	-Do-	0.255	0.062
0.03	Not present	0.255	0.060
0.4	-Do-	0.255	0.058
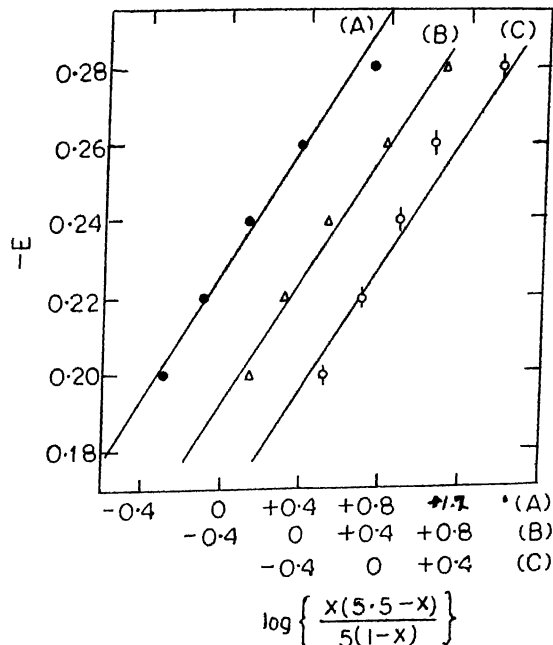
Fig. 3. Graphical evaluation of $E_{\frac{1}{2}}$ and $2.303RT/\alpha nF$ for $Cu(gly)_2$ in $0.1M$ KNO_3 (A, 25°; B, 30°; C, 35°).

wheie, k_r is the rate constant at the reference potential E_r and D and t have their usual significance. Hence, k_r could be evaluated from the experimental data. From Arrhenius plot of the type $-\log k_r$ vs. $1/T$ (see Fig. 4) the activation energy value, E_a, could also be evaluated. The results are given in Table 4.

TABLE 4

A comparison of the characteristics of $Cu(en)_2{}^{2+}$ and $Cu(gly)_2$ (in $0.1M$ KNO_3).

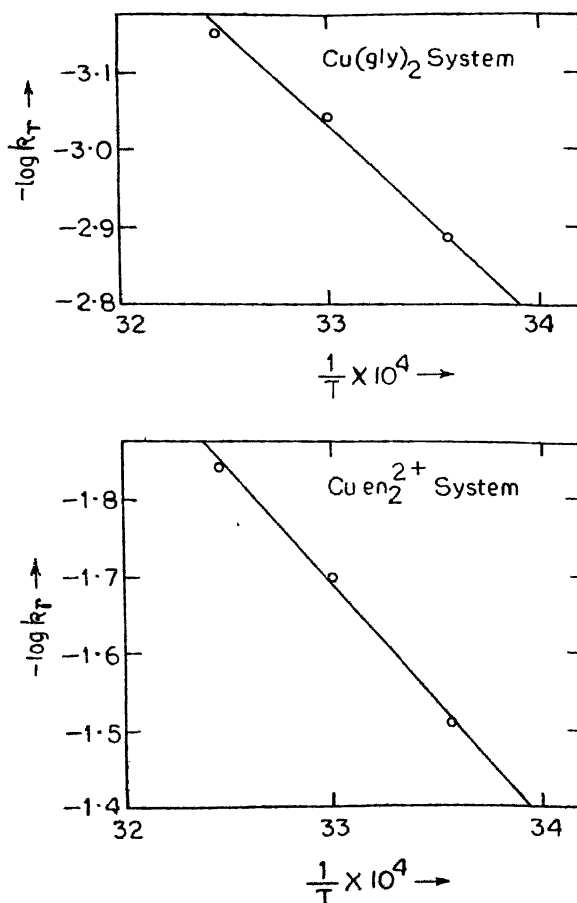| Complex	Wavenumber of principal ligand field band, cm^{-1} (ref. 2)	$E_{\frac{1}{2}}$ vs. SCE, Volt	$10^{-2}k_r$ (at -0.7 V vs. SCE, at 25°)	E_a (kcal/mole)
$Cu(gly)_2$	15,800	-0.230	7.68	11.7
$Cu(en)_2{}^{2+}$	18,200	-0.368	0.32	14.2

Fig. 4. Arrhenius plots : Evaluation of E_a values.

The molecular orbital energy level diagram for a CuL_4 type complex is shown in Fig. 5. The wavenumber of the principal ligand field band of the copper(II) complex is clearly a measure of the energy separation between the E_g and $B_{1g}*$ levels. The data in Table 4 indicate that a smaller energy difference leads to easier reduction (less negative $E_{\frac{1}{2}}$, higher value of k_r and lower value of E_a). This observation can be rationalised if we consider that the complex species undergoing reduction is oriented on the electrode surface in a manner such that the square plane containing the Cu(II) and the four primary ligand donors is
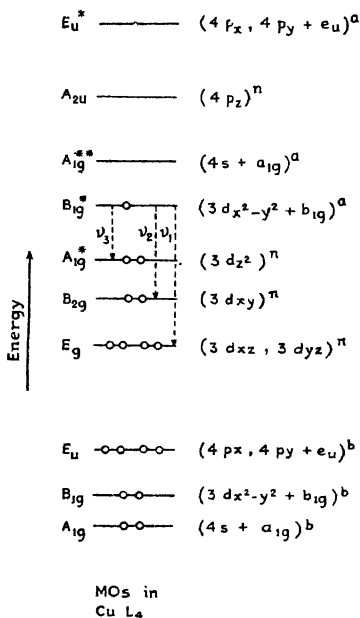

Fig. 5. Molecular orbital energy level diagram for a CuL_4 complex of Cu(II). (Metal and composite ligand orbitals are indicated in parentheses).

parallel to the electrode surface so that the Cu(II) is closer to the electrode surface to facilitate electron transfer. In this orientation the $3d_{xz}$ and $3d_{yz}$ orbitals of copper (E_g MOs in CuL_4) would point towards the electrode surface. Hence, two electrons will be transferred easily from the electrode to these oribitals leading to the process Cu(II) $\xrightarrow{2e}$ Cu provided these orbitals are duly vacated by promotion of an electron from each of these orbitals to the $3d_{x^2-y^2}$ and 4s orbitals of copper ($B_{1g}*$ and $A_{1g}**$ MOs in CuL_4). Thus, smaller the excitation energy the easier it would be for the reduction to occur as has actually been observed.

REFERENCES

1. K. B. Oldham and E. P. Parry, *Anal. Chem.*, 1968, **40**, 65.

2. cf. C. K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes", Pergamon Press, London, 1962.