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CYCLIC VOLTAMMETRIC INVESTIGATION OF COPPER (II) IMIDAZOLE COMPLEXES IN AQUEOUS MEDIUM

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ABSTRACT: The electrochemical behaviour of Copper (II) imidazole complexes at (Cu²⁺) : (ImH), molar ratio (= 1:10; 1:100), 1×10^{-3} M Cu (ClO₄)₂·6H₂O in aqueous 0.2M NaClO₄, has been investigated by means of cyclic voltammetry. The cyclic voltammetric parameters were calculated. The cyclic voltammograms scanned cathodically from +0.50 to -1.10V showed two redox steps. The first step (Cu^{2+/+}) involves single electron, diffusion controlled quasi-reversible electrode process (EC mechanism), while the second step involves irreversible reduction of Cu(I) species to metallic copper at glassy carbon electrode (GCE). At 1:10 molar ratio, anodic peaks a'₁ and a''₁ appear which are absent in 1:100 molar ratio. The redox behaviour of 1:10 copper (II) imidazole system, 1×10^{-3} M CuCl₂·2H₂O also investigated at GCE and at pH 5.03, 7.4 and 8.03 shows that the electrode process seems to become irreversible with increasing pH of the medium.

INTRODUCTION

Histidine plays an important role in stabilizing the active sites of a number of metalloproteins. In particular, copper proteins are known to contain several imidazole ligands per copper center, (Chen et al 1994). The ability of range of derivatives of L-histidine, histamine and imidazole to act as inhibitors have been reported, (Field et al 1991).

Metallo-micelles and metallo-vesicles possess catalytic or redox-active centers. Examples include micelle bilayer-forming zinc and copper complexes. The spontaneous formation of vesicles by ammonium surfactants containing imidazole groups, induced by binding of copper (II) ions have been reported, (Van Esch, et al 1994).

Carnosine is the major β-alanine source in the human body. Its ability to act as a ligand in the generation of coordination complexes with different metallic ions has been established to be due to its imidazole moiety, (Baran, 2000).

A series of complexes incorporating the epoxy-imidazole adduct of phenylglycidyl ether with 2-ethyl-4-methylimidazole has been prepared with the aceto and chloro transition metals. These complexes have been characterised using spectroscopic methods and their thermal stabilities determined using elevated temperature techniques, (Brown, 2000).

A new idea of encapsulation of proton-carrier molecule-imidazole in aluminium porous coordination polymers for the creation of a hybridized proton conductor under anhydrous conditions has been proposed, (Bureekaew, et al 2009).

Mixed ligand complexes of copper (II) with imidazole as secondary ligand have been synthesized and characterized by molar conductivity, magnetic moments, electronic IR and ESR spectral data, (Babua, et al 2009). A series of new biologically active complexes of Zn(II), Cu(II), Co(II) and Ni(II) with imidazole derivative have been synthesized. These

results show that most of the metal complexes were more active than the neat ligand, (Rehman, et al 2010).

Electrochemical reactions catalyzed by metal complexes had attracted considerable attention during the past several decades. Recently, considerable efforts have been directed toward the study of Cu(II) complexes incorporating pyridine, thioether, imidazole and imine donors which not only stem from their fascinating structures but also from their potential applications as new materials.

In view of the importance of imidazole and its complexes with copper we earlier reported the electrochemical behaviour of the first reduction step $\text{Cu}^{2+/+}$ of copper (II)-imidazole complexes at various $(\text{Cu}^{2+}):(\text{ImH})$ molar ratio. In this paper, we report the result of electrochemical study extended to include the second reduction step $\text{Cu}^{+/0}$ of copper (II) imidazole complexes $(\text{Cu}^{2+}):(\text{ImH})$ molar ratio (=1:10, 1:100) in order to determine their electrode mechanism. The effect of pH on the electrode process of $(\text{Cu}^{2+}):(\text{ImH})$ molar ratio 1:10, $1 \times 10^{-3}\text{M}$ $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ has also been studied.

EXPERIMENTAL

Material

The voltammetric parameters were obtained with BAS Model CV-1B (Indiana, USA) cyclic voltammograph instrument having an electrochemical cell with a three electrode system. The working electrode was a Glassy Carbon Electrode (GCE). Platinum wire was used as an auxiliary electrode, while a Saturated Calomel Electrode (SCE) as reference electrode with $E^0 = 242\text{V}$ vs NHE. The voltammograms were recorded on a X-Y recorder. Imidazole (ImH), copper perchlorate $(\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O})$, sodium perchlorate (NaClO_4) , copper chloride, $(\text{CuCl}_2 \cdot 2\text{H}_2\text{O})$ were of analytical reagent grade.

METHOD

All the cyclic voltammetric experiments scanned cathodically from +0.50 to -1.10V and +0.60 to -0.35V were done in an inert atmosphere achieved by purging the cell solutions with nitrogen gas for about 20 minutes and maintained over the cell solution during the recording of the voltammograms. The nitrogen gas was purified by bubbling through alkaline vanadous sulphate solution and passing through a calcium sulphate drying tube before bubbling through the cell solution. The experiments were carried out at $20 \pm 1^\circ\text{C}$ in 0.2M NaClO_4 supporting electrolyte. The experiments were carried out with freshly prepared solutions.

A stock solution of $1 \times 10^{-2}\text{M}$ in 100 cm^3 water was prepared for $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. For a working volume of 20cm^3 , 2.0cm^3 was used for $1 \times 10^{-3}\text{M}$ of each copper salt. $1 \times 10^{-2}\text{M}$ and 0.1M ImH was prepared by placing 0.136g and 1.361g with respective 2.0 cm^3 copper salt solution, in a clean dry beaker and made up to 20 cm and stirred for clear solution. This is specified as 1:10 and 1:100 copper: ligand molar ratio respectively. All solutions were prepared in double distilled water.

RESULTS AND DISCUSSION

Tables 1 and 2 show the voltammetric data for the electrochemistry of 1:10 and 1:100 Cu(II): imidazole systems, $1 \times 10^{-3} \text{ M}$ $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ respectively. A single quasi-reversible, (Nicholson, 1964) redox couple $\text{Cu}^{2+/+}$ ($c_1 a_1$) was observed for both the systems with formal electrode potentials, $E^0 \cong +40$ and -80 mV vs SCE respectively at $\nu = 25\text{mVs}^{-1}$ in the potential range + 0.50 to -0.45V.

Table 1: Cyclic voltammetric parameters for 1:10 Cu (II)- ImH, 1×10^{-3} M Cu (ClO₄)₂ · 6H₂O in Aqueous 0.2M NaClO₄.

Scan rate	First step					Second step			
	Epc ₁ /mV	Epa ₁ /mV	IPc ₁ /μA	Ipa ₁ /μA	E ⁰ /mV	ΔEp/mV	Ipa ₁ /Ipc ₁	Epc ₂ /mV (Ipc ₂ /μA)	Epa ₂ /mV (Ipa ₂ /μA)
10	-30	+120	6.0	4.5	+45	150	0.75	-800 (6.0)	-250 (6.0)
25	-40	+120	9.5	7.0	+40	160	0.74	-950 ^b (10.0)	-250 (10.0)
50	-70	+130	12.0	9.5	+30	200	0.79	-1050 (11.5)	-200 (13.5)
100	-100	+150	17.0	12.0	+25	250	0.71		
150	-120	+170	20.0	14.0	+25	290	0.70		
200	-130	+190	23.0	16.5	+30	320	0.71		
250	-155	+190	25.0	18.5	+18	345	0.74		

Table 2: Cyclic voltammetric parameters for 1:100 Cu (II) ImH, 1×10^{-3} M ImM Cu (ClO₄)₂ · 6H₂O in Aqueous 0.2M NaClO₄.

Scan rate	First step					Second step			
	Epc ₁ /mV	Epa ₁ /mV	IPc ₁ /μA	Ipa ₁ /μA	E ⁰ /mV	ΔEp/mV	Ipa ₁ /Ipc ₁	Epc ₂ /mV (Ipc ₂ /μA)	Epa ₂ /mV (Ipa ₂ /μA)
10	-150	-15	6.0	4.5	-82	135	0.75	-880 (7.5)	-250 (15.0)
25	-155	-10	9.5	7.0	-82	145	0.74	-1000 (9.5)	-250 (17.0)
50	-200	-25	12.0	8.5	-87	225	0.71	-1120 (11.5)	-180 (18.0)
100	-250	-60	17.0	12.0	-95	310	0.71		

On extending the scan limit to - 1.10V, a second broad cathodic peak, c₂ at -0.95V attributed to Cu(I) – Cu(O), was observed which masks other contributions. The reverse positive scan also showed a well-defined anodic peak, a₂ at -0.25V and is related to the electro-oxidation of Cu(O) into Cu(I) species, probably Cu₂O, (Sanchez, et al 1990), and a more complicated and overlapping waves marked as a₁ at +0.11, a'₁, at + 0.24 and a''₁ at + 0.37V vs SCE, are observed at $\nu = 25 \text{ mVs}^{-1}$ for Cu (II): ImH = 1:10 molar ratio, (Fig. 1A). The anodic peaks a'₁ and a''₁ may be attributed to electrochemical transformation of Cu (O) / Cu (I) species into Cu (II) species.

The cyclic voltammetric features of the Cu (II): imidazole complex at 1:100 molar ratio (Fig. 1B) differ from that of 1:10 molar ratio with respect to:

- (i) the cathodic peak c₂ is sharp,
- (ii) the position of anodic peak a₂ remains the same but appears as stripping peak and may be attributed to copper (O) electro-dissolution into Cu (I) species,
- (iii) the anodic peak, a₁ is free from any complication and is assigned to reoxidation of electro-chemically degenerated Cu (I)- imidazole complex species into Cu (II)- imidazole complex, and
- (iv) the reduction potentials (Epc₁ and Epc₂) are shifted in a negative direction (Table 2).

The plots of Ipc₁ vs $\nu^{1/2}$, for both 1:10 and 1:100 Cu (II): imidazole systems, gave straight lines with positive intercepts (Fig. 2).

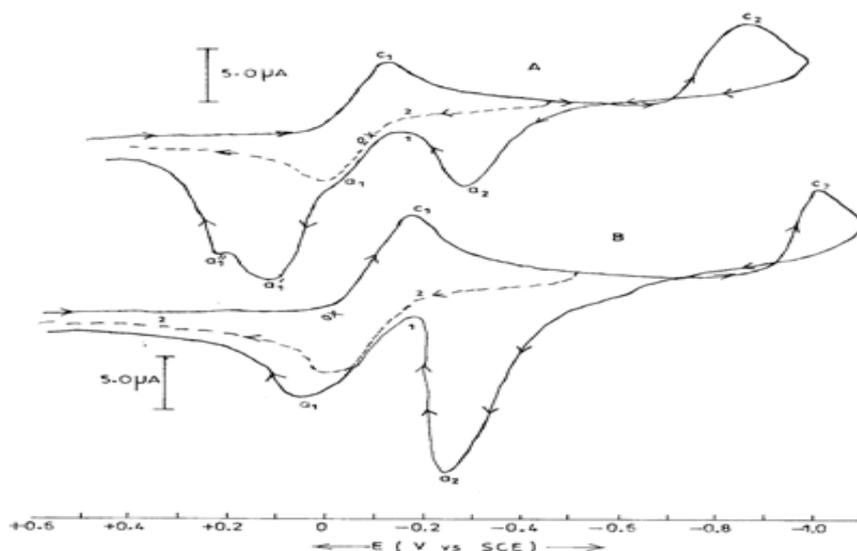


Fig. 1: CV for (Cu^{2+}) , (1mH) system, A = 1:10, B = 1:100 molar ratio at $v = 25\text{mv/s}$, $1\text{mM}\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in aqueous $0.2\text{M}\text{NaClO}_4$.

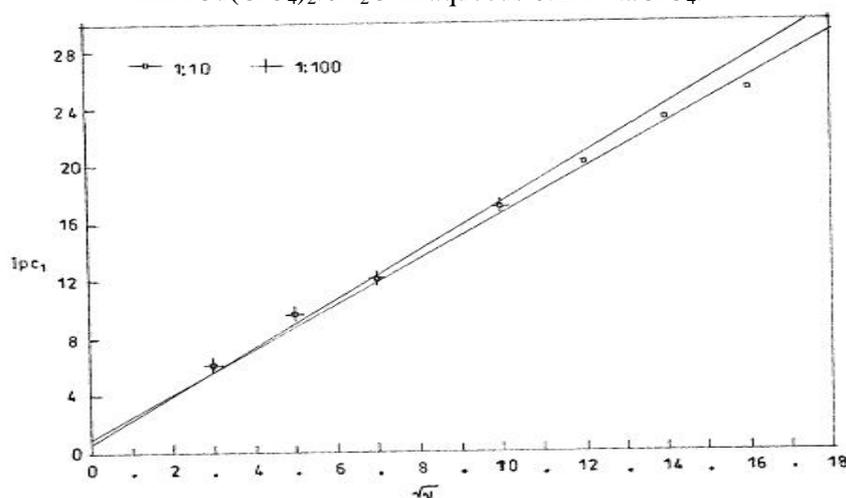
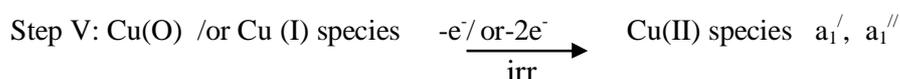
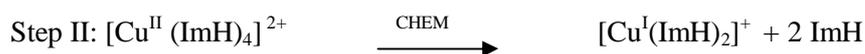
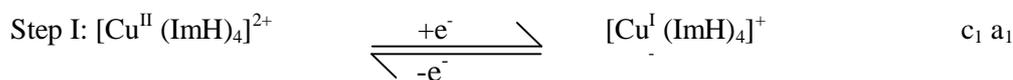


Fig. 2: Ipc_1 vs $v^{1/2}$ for (Cu^{2+}) :(1mH) molar ratios, $1 \times 10^{-3}\text{M}\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$.

This suggests that the electrode process is not completely diffusion-controlled. The measurements of peak current ratio, Ipa/Ipc , (<1.0) showed that electron transfer is followed by a chemical reaction (EC) mechanism, (Nicholson, 1964 and Prasad, et al 1994). A tentative interpretation of these experimental results is based on the assumption of the following sequence of events, (Sanchez, et al 1990 and (Li, et al 1954).



It has been shown that at a high concentration of imidazole (1.835M), each polarographic wave consists of two waves of approximately equal height and each wave is due to a one-electron change with $E_{1/2}$ (first wave) = 0.205 and $E_{1/2}$ (second wave) = -0.582 V vs SCE, 5×10^{-4} M $\text{Cu}(\text{NO}_3)_2$ in aqueous 0.158M KNO_3 . The formation constants for $\text{Cu}(\text{ImH})_4^{2+}$ and $\text{Cu}(\text{ImH})_2^+$ have been found to be $\log K_f = 12.6$ and $\log K_f = 10.8$ respectively, (Li, et al 1954).

Table 3: Cyclic voltammetric parameters for 1:10 Cu (II)- ImH System, 1×10^{-3} M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in aqueous 0.2M NaClO_4 .

Scan rate mVS^{-1}	E_{pc_1} /mV	E_{pa_1} /mV	IP_{c_1} / μA	I_{pa_1} / μA	E^0 /mV	ΔE_p /mV	$\frac{I_{pa_1}}{I_{pc_1}}$
<u>at pH=5.03</u>							
10	+15	+120	6.0	5.5	+68	105	0.91
25	+10	+130	10.0	7.0	+70	120	0.70
50	-5	+130	14.0	9.0	+63	135	0.64
100	-20	+140	18.5	11.0	+60	160	0.59
150	-25	+145	22.0	14.0	+60	170	0.64
200	-35	+150	25.0	15.5	+58	185	0.62
250	-40	+160	27.5	17.0	+60	200	0.62
<u>at pH=7.4</u>							
10	+10	+130	7.0	6.0	+70	120	0.86
25	-10	+140	10.5	8.5	+65	150	0.81
50	-20	+155	14.5	11.0	+68	175	0.76
100	-50	+165	20.0	15.0	+58	215	0.75
150	-60	+180	24.0	18.0	+60	240	0.75
200	-80	+180	27.5	20.5	+50	260	0.75
250	-90	+195	30.0	22.5	+53	285	0.75
<u>at pH=8.03</u>							
10	-15	+135	7.5	6.0	+60	150	0.80
25	-30	+150	11.0	8.0	+60	180	0.72
50	-55	+170	14.5	10.0	+58	225	0.68
100	-80	+200	20.0	13.0	+60	280	0.65
150	-105	+215	23.5	15.0	+53	315	0.63
200	-130	+220	27.0	17.5	+45	350	0.65
250	-140	+230	29.5	19.0	+45	370	0.64

The redox behaviour of 1:10 copper (II): imidazole system, 1×10^{-3} M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in aqueous 0.2M NaClO_4 was also investigated at GCE at pH values 5.03, 7.4 and 8.03. The CV parameters listed in Table 3 show that a quasi-reversible, (Nicholson, 1964 and Prasad, et al 1994) one electron transfer reaction is observed in the potential region from + 0.60 to -0.35V vs SCE due to $\text{Cu}^{2+/+}$ couple at these pH values. Table 3 also shows that the cathodic peak c_1 is shifted in a negative potential direction with increasing pH of the medium at a given scan rate in agreement with the thermodynamic predictions of the different $\text{Cu}^{2+/0}$ and $\text{Cu}^{+/0}$ electrode reactions, (Sanchez, et al 1990). However, opposite trend is noticed for the anodic peak a_1 . Also the difference in anodic to cathodic peak potential (ΔE_p) increases with increasing scan rate as well as pH.

Copper (II)- imidazole complexes with different copper to imidazole ratios have been crystallized from chloride medium. $\text{Cu}(\text{ImH})_4 \text{Cl}_2$ was obtained at a ratio Cu(II): ImH of about 1:10 and pH 8.0. At the same ratio but slightly lower pH (7.5-8.0) $\text{Cu}(\text{ImH})_2(\text{Im}^-)\text{Cl}$ were obtained. At Cu(II): ImH =1:2 and pH 5.0 crystals of $\text{Cu}(\text{ImH})_2\text{Cl}_2$ can be obtained by almost complete evaporation, (Lundbery, 1972).

CONCLUSION

The electrode process for $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ system expectedly involves a one electron charge transfer. Where the electron transfer is followed by a chemical reaction is an observation. The appearance of oxidation peaks a_1'/a_1'' is interesting and needs coulometric results for clear characterisation. It can be concluded that for the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ system, the electrode process is subject to the pH of the medium.

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