Spectroscopic and Electrochemical Studies of Interaction of Cu(II) Ion with Different Aliphatic and Aromatic Amine Based Ligands in Aqueous Solutions

Marjan Hossain Onik, Ahnaf Bin R. Q. Khan, Mahjabin Tarannum Nabila, Fatema and M. Q. Ehsan

Department of Chemistry, University of Dhaka, Dhaka-1000, Bangladesh

Abstract

The composition and stability constant of the complexes of copper(II) with the ligands 2,2–bipyridine, 1,10-phenanthroline, saccharin, and ethylenediamine tetraacetic acid (EDTA), were determined, as well as the effect of temperature on the thermodynamic parameters were studied. The metal-to-ligand ratio in the EDTA complex is found 1:1 and in the rest of the cases, the ratio is 1:2. The redox behavior of the Cu(II) / Cu(0) system in the Cu-ligand complex has been studied in KCl solution as a supporting electrolyte. The redox process of the Cu(II) / Cu(0) system in the Cu-sac complex is almost similar to that of the Cu(II) solution in the absence of any ligand. In other cases, the redox process is a single-step 2-electron transfer process. The electron transfer process in all the cases is diffusion-controlled. The values of peak current ratio and peak potential separation are the evidence that the redox processes are quasi-reversible.

I. Introduction

Metals are essential cellular components selected by nature to function in several indispensable biochemical processes for living organisms[1]. Transition metal complexes have significantly contributed to catalysis, materials synthesis, photochemistry[2,] and biological systemssince the last century. Bipyridine is one of the most influential ligands of the last century with a profound impact on biological, chemical, coordination, and electrochemical systems[3]. Copper is one of the earliest discovered metals which brought revolutionary changes to human civilization from infrastructure, and manufacturing industry to medicine for cancer[4]. Due to its redox nature, it's both harmful and beneficial to health[5].

The present study aims to find out the stoicheiometric composition[6] by which copper[7] forms a complex with 2,2'-bipyridine, 1,10-phenanthroline, saccharin, and EDTA, in solution and estimation of the stability constant[8] of the respective complexes to find the feasibility of the formation of the complex in various conditions. The formation of the complexeswas ensured by an electrochemical system[9] and the redox properties of the formed complexes were studied. The ligands were selected for their vast impact on the chemical and biological fields. Bipyridine is a natural ligand, it is popular due to its robust redox stability and ease of functionalization[10]. The presence of three aromatic rings provides rigidity to 1,10-phenanthroline which makes it an entropically better chelating ligand. This is a direct result of the aquaphobic character of ligands and to ensuing larger desolvation of metal cation on complex origination[11]. EDTA is a widely used chelating agent with 6 lone-pair donating capabilities. It is an excellent ligand for forming complexes with transition metals[12].Saccharin is also one of the most versatile ligands found in the world.

In this communication, we studied the interaction of four very common ligands with Cu(II) ion in the aqueous medium and determined the composition, stability constants, thermodynamic parameters, and studied the redox behaviour of Cu(II) ion in the presence of the four different ligands.

II. Experimental

Materials and Methods

Analytical grade chemicals were used in all the experimental work. (copper chloride from BDH2,2-bipyridyl from E. Merck, 1,10-phenanthroline from Smart lab, saccharine and EDTA from Sigma) The electrochemical experiments were done with a computer-controlled electrochemical analyzer made by CH Instrument Inc., USA. An electrode made of glassy carbon plays the role of a working electrode while the electrode Ag/AgCl acts as a reference. A Pt wire was used as a counter electrode. As a supporting electrolyte, We used 0.1 M KCl solution. The working electrode was cleaned by polishing on a wet polishing cloth with fine alumina powder and then washed with deionized water. Before the measurements were done all electrolyte solutions were purged with N_2 gas to avoid interference from dissolved O_2.

For finding the composition and stability constant of the complexes three well-known methods(i) Jobs method[13], (ii) the mole ratio method[14] and (iii) the slope ratio method[15] were used. For electrochemical analysis, cyclic voltammetry was employed to ensure the formation of the complex and the redox nature of the complex in solution

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*Author for correspondence. e-mail: mqehsan@du.ac.bd

Preparation

Cu–L complexes were prepared by mixing 0.01M Cu(II) solution with a 0.01M ligand solution at room temperature in an appropriate ratio found through Spectroscopic methods. The Cu(II) and ligand solutions were prepared by dissolving the appropriate amount of copper salt and the ligands in deionized water.0.1M KCl was prepared by dissolving 0.747g KCl in 100 mL deIonized water. Electrochemical solutions for Cu(II), Ligand, and Complex were prepared similarly and then an appropriate amount of KCl was added.

Determination of Molar Absorption Coefficient of the Cu(II)-ligand complex

To determine an accurate value of the molar absorption coefficient calibration curve was used, the absorbance vs concentration plot gives a straight line whose slope gives the value of the molar absorption coefficient.

The slope of the straight line is 0.125. The absorbance of the complex at 680 nm was A= 0.498. The molar absorption coefficient of the complex is 125 L mol^{-1}cm^{-1} [13].

III. Results and Discussion

Cu(II) as a transition metal absorbs light in the visible region. When a ligand interacts with Cu(II) the peak shifts from its original position or there are other kinds of changes in peak shape. Different aspects of the interaction between Cu(II) and ligands and their electrochemical behavior are explained.

Spectroscopic Study of Interaction of Cu(II) with Ligands

The UV-visible spectrum of Cu(II) and ligands was taken using deionized water as a reference. Dilute solutions of very low concentrations of metal and ligands were used for this purpose.

From the graphs in Fig 1, it is seen that ligands do not absorb in the 800-400 nm region but both copper and Cu-ligand complexes (of bipy-680 nm, phen-740 nm, saccharin-233 nm, and EDTA-770 nm) absorb in that region which indicates that the ligands react to form a complex with Cu(II). For the Cu-ligand complex, the absorption maximum was obtained in the 600-800 nm region.
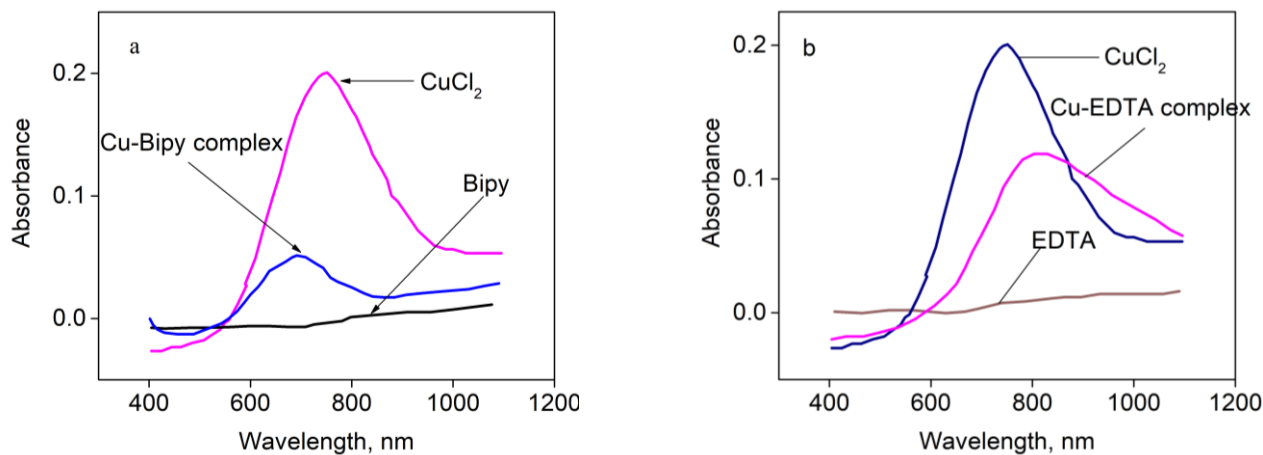

Fig. 1. UV-Visible spectra of a) Cu-bipy and b) Cu-EDTA complex in aqueous system

Determination of the Composition of the Cu(II) Complexes

The ligand-to-metal ratio was determined using three different methods –continuous variation method, mole ratio method, and slope ratio method.

Continuous Variation Method

The absorbance of the Cu-ligand complex at different ratios was measured using a UV-visible spectrophotometer at a

corresponding λ_{max} of the complexes. In this method molar concentration of Cu(II) and ligand was kept constant while their ratio of volume was varied. The absorbance data was taken and plotted against the mole fraction of Cu(II) in the solutions. Fig 2 shows the absorbance vs mole fraction plot of (a) copper bipyridine and (b) copper-EDTA solution mixture.
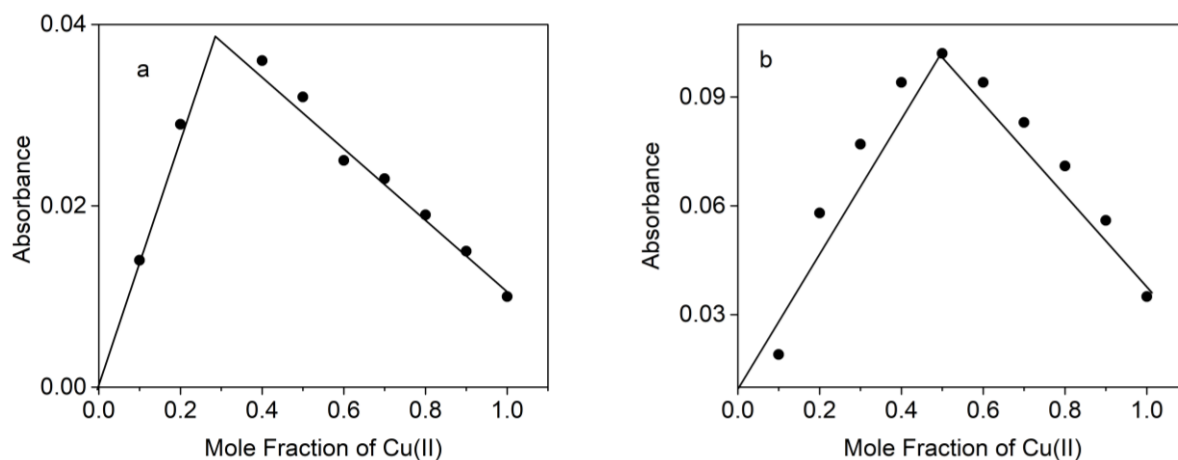
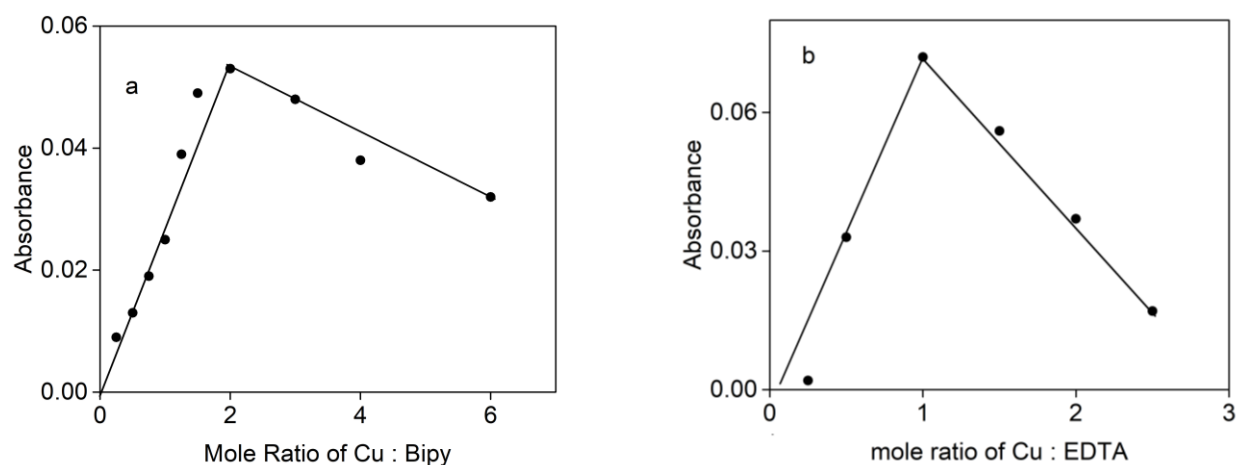**Fig. 2.** Variation of absorbance with mole fraction of Cu(II) a) Cu-Bipy complex b) Cu-EDTA complex

Fig. 3. Variation of absorbance with different mole ratios of a) bipyridine b) EDTA to Cu(II)

It is found that absorbance is highest at 0.3-mole fraction of Cu(II) for bipyridine, phenanthroline, and saccharin but 0.5 for EDTA. The ratio of moles of Cu(II) with 2,2-bipyridine, 1,10-phenanthroline, and saccharin was obtained~1:2 and with EDTA 1:1.

Mole Ratio Method

The absorbance of 0.01M Cu(II) solution with various volumes (4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24 mL) of ligand solution were measured at the room temperature and at 680 nm.

From Fig 3 it is found that the absorbance was maximum when the mole ratio of metal to ligand (bipyridine, phenanthroline, and saccharin) was 1:2 and decreased when the mole ratio of ligand to Cu(II) decreased or increased. This indicates that maximum interaction occurs at a 1:2 ratio. Similarly, for Cu-EDTA it is 1:1.

Slope Ratio Method

In the slope ratio method, two series of solutions are prepared in which varying amounts of one component in the complex are added to a large excess of the other component. The absorbance of the metal-ligandsolution mixture was measured at a constant volume of ligand and a variable volume of metal ion solution. Again, the absorbance was measured at a constant volume of metal ion solution and a variable volume of ligand solution. The absorbance was measured by spectrophotometer at 680 nm wavelength and room temperature.

The absorbance of different solutions of varying amounts of Cu(II) and 2,2-bipyridine are plotted in Fig 4a. The slope of the lines was 0.261 and 0.125 respectively. The ratio of the slope is $2.09 \approx 2$ which means metal and ligand react at the ratio, of 1:2. Similarly, the ratio for Cu-phen and Cu-sac is 1:2 and Cu-EDTA is 1:1.
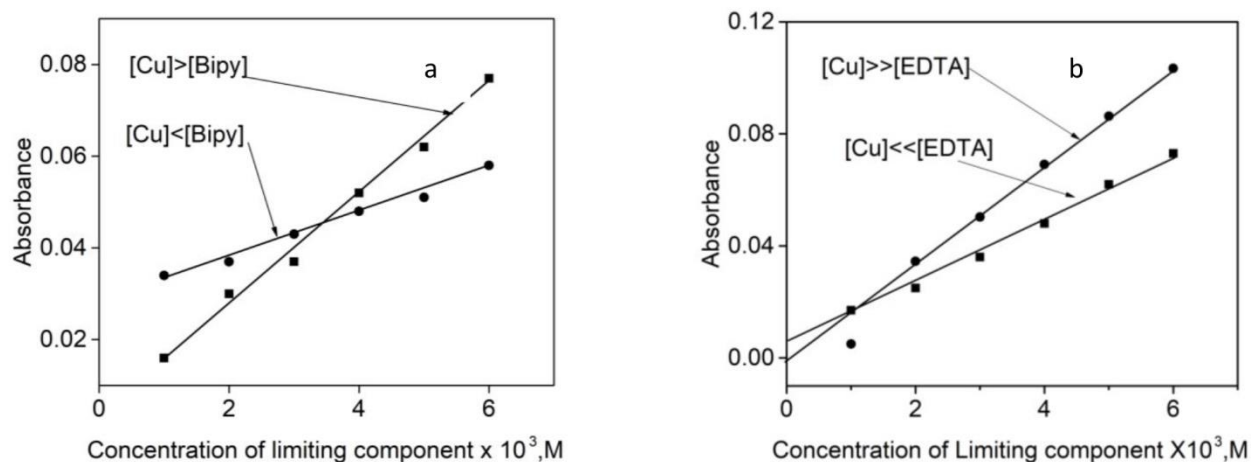
Fig. 4. Variation of absorbance with constant Cu(II) conc. vs variable a) bipy conc. and constant Bipy conc. vs variable Cu(II) concentration, b) EDTA conc. and constant EDTA conc. vs variable Cu(II) concentration

Determination of stability constant of Cu-ligand complex in aqueous solution

The stability constant can be determined by a spectrophotometric method widely. For a reaction,

$$Cu^{2+}+ \text{n-Ligand} \rightarrow [Cu\text{-Ligand}_n]^{n+} \quad (1)$$
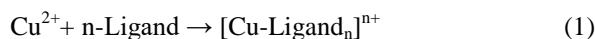
The corresponding equation for calculating the stability constant using Irving and Rossotti's spectrophotometric method is-

$$K_f = \frac{[(Cu - ligand_n)^{n+}]}{\{[Cu^{2+}]-[(Cu - ligand_n)^{n+}]\} \times \{[ligand]-[(Cu - ligand_n)^{n+}\}^n} \quad (2)$$

The concentration of the metal can be obtained by dividing the maximum absorbance by the molar absorption coefficient. The concentration of both Cu(II) and 2,2-bipyridine solution used for spectroscopic detection was 0.001M.Similarly, the active concentrations of the reactants and products at equilibrium for the other three complexes

were calculated and the calculated values of equilibrium constants are presented in Table 1.

As free energy is negative, the process of complex formation is exergonic and the formation of the complex is spontaneous at 298K or room temperature. The positive value of the stability constant indicates that the ease of complex formation and the stability of the complex at room temperature is very high.

Electrochemical study of the interaction of Cu (II) with bipyridine, phenanthroline, saccharin, and EDTA

The redox behaviour of Cu(II) ions in the presence of the ligands was studied using cyclic voltammetry. The voltammograms of Cu(II) solution, ligand solution, and Cu(II) in the presence of ligand solution shown in Fig 5 were recorded using 0.1M KCl as a supporting electrolyte in a 3-electrode system electrochemical cell. The CVs were recorded at room temperature within a potential window from 800 mV to -800 mV at a glassy carbon electrode.

Table 1. Stability constant of Cu-ligand complexes at 298K

| Complex	Cu-Bipy	Cu-Phen	Cu-EDTA	Cu-Sac
Molar extinction coefficient L mol^{-1} cm^{-1}	125	825	1730	3250
Concentration of complex	3.98×10^{-3}	2.061×10^{-5}	1.098×10^{-5}	1.526×10^{-4}
Concentration of Cu(II)	2.0×10^{-5}	8.78×10^{-6}	1.098×10^{-5}	2.474×10^{-4}
Concentration of ligand	4.0×10^{-5}	1.939×10^{-5}	3.902×10^{-5}	4.95×10^{-4}
$K_f = \dfrac{[(Cu - ligand_n)^{n+}]}{[Cu^{2+}]^* \times [ligand]^{*n}}$	1.24×10^{11}	9.096×10^9	2.562×10^5	1.758×10^8
Log K_f	11.14	9.958	5.4087	8.24
$\Delta G = -RTlnK_f$	- 63586.7	-56818.837	-30861.29	- 46788
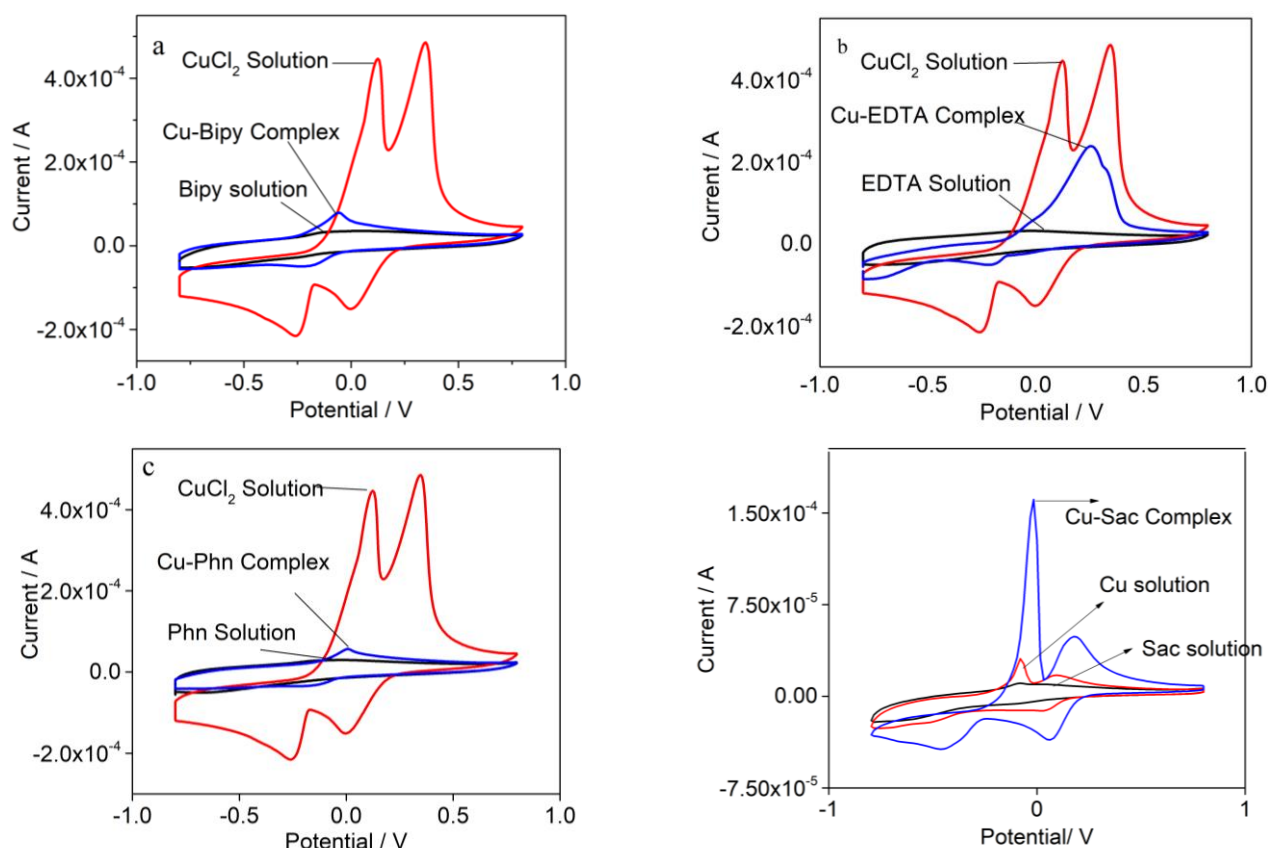
Fig 5. The CVs of complex formation of a) Cu-bipy b) Cu-phen c) Cu-EDTA and d) Cu-sac complex. The CVs of metal, ligand, and metal-ligand interaction are overlayed in the same figure.

The CVs of the Cu(II) solution and Cu-ligand complex system are distinct in peak position, peak intensity, and shape. Cu(II) solution shows two distinct peaks in CVs due to two one-electron transfer processes[16].

In the presence of a ligand, the redox behavior of the Cu(II) / Cu(0) system has been changed considerably. In the case of bipyridine, phenanthroline, and EDTA. Only one pair of redox peaks was found in the voltammogram (Fig 6). The cathodic peaks move towards the right and the intensity of both cathodic and anodic peaks have been reduced considerably.
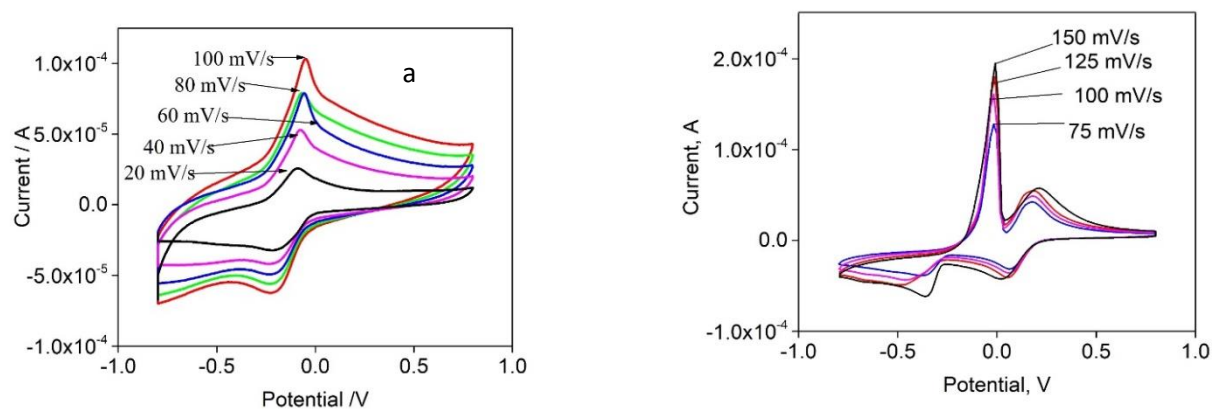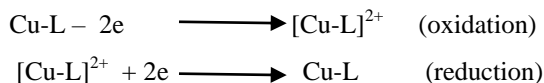

Fig. 6. Cyclic voltammogram of Cu-ligand reaction mixture. a) Cu-bipy b) Cu-sac solution at the different scan rate

The slight difference in voltammogram might be due to the different compositions of copper and ligand in the Cu-phen, Cu-bipy, and Cu-EDTA complexes. The possible reactions are

$$Cu\text{-}L - 2e \longrightarrow [Cu\text{-}L]^{2+} \quad (oxidation)$$

$$[Cu\text{-}L]^{2+} + 2e \longrightarrow Cu\text{-}L \quad (reduction)$$

But in the case of the Cu-sac complex, the voltammogram is more or less the same as that of the Cu(II) solution which consists of two one-electron transfer processes. Another distinguishing property of the Cu-sac complex is that the peak current of the complex has increased compared to the Cu(II) solution. In the rest of the complexes, it was the opposite. The possible reactions in Cu-sac are
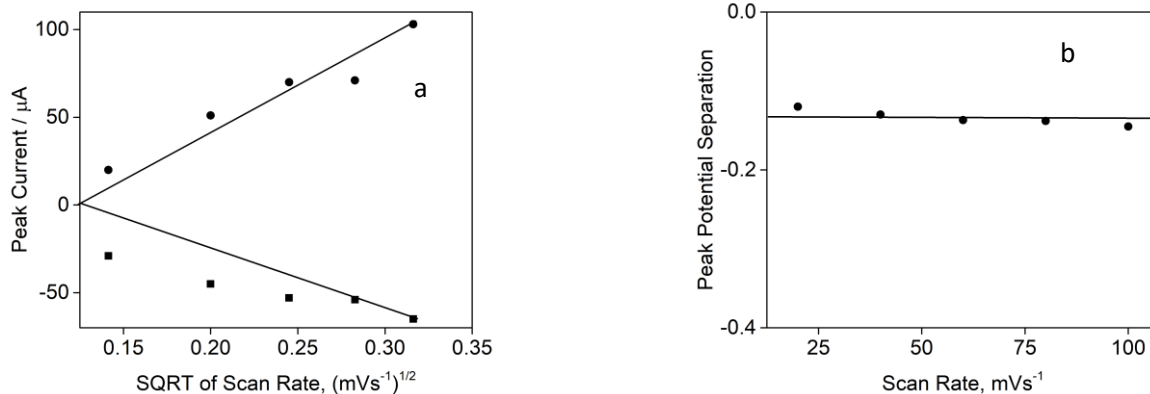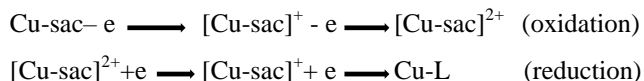
$$Cu\text{-}sac - e \longrightarrow [Cu\text{-}sac]^+ - e \longrightarrow [Cu\text{-}sac]^{2+} \quad (oxidation)$$

$$[Cu\text{-}sac]^{2+} + e \longrightarrow [Cu\text{-}sac]^+ + e \longrightarrow Cu\text{-}L \quad (reduction)$$

Fig. 7. Plot of a) peak current vs SQRT of scan rate b) peak potential separation vs scan rate for Cu-bipy complex

For the case of reversible electron transfer by the Randles-Sevcik equation (at 25ºC)

$$i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} C \, v^{1/2}$$

Thus, peak currents will increase linearly as a function of the square root of the scan rate for reversible electron transfer. Plots of i_p vs. $v^{1/2}$ are useful in the characterization of electrochemically reversible redox systems. Deviations from linearity are indicative either of complications in the kinetics of the observed electron transfer or the result of chemical changes that occur as a result of the electron transfer (homogeneous reactions). From Fig 7a, it can be inferred that the process was reversible and diffusion-controlled as a peak current vs sqrt of scan rate plot passing through origin indicates peak current is directly proportional to sqrt of scan rate[17]. From 7b it can be ensured that the process is linear and precise. The rate of redox reaction increases linearly with increasing scan rate.
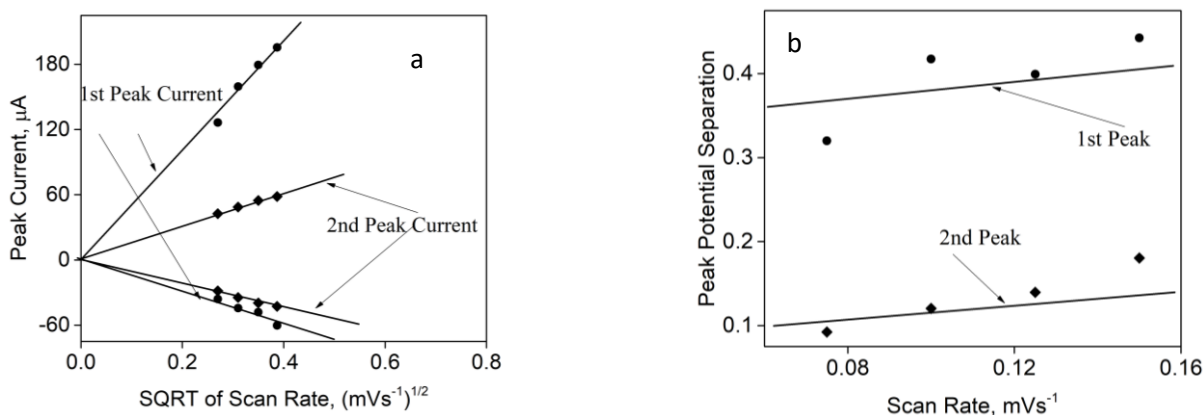

Fig. 8. Plot of a) peak current vs SQRT of scan rate and b) peak potential separation vs scan rate for Cu-sac complex

For the Cu-sac complex, (plot 8a) it can be inferred that the electrochemical processes involved are diffusion-controlled. It can be ensured that both processes are linear and precise. The rate of redox reaction increases linearly for increasing scan rate.

From the electrochemical analysis, it is clear that the complex of copper with EDTA, bipyridine, and phenanthroline is less electroactive than the Cu(II) ion but the Cu-sac complex is more electroactive than the Cu(II) ion[18].

IV Conclusion

The reaction between Cu(II) and the ligands, 2,2 – bipyridine, 1,10 phenanthroline, and saccharin produces 1:2 complexes in the aqueous medium, with EDTA copper produces complex in 1:1 ratio. The spectrophotometric

method was used to determine the stability constant of the reaction between Cu(II) and the four ligands. The value of stability constant of the Cu – bipy complex at 298K is, $K_f=$ 1.24×10^{11}, $\log K_f=$ 11.14, which indicates the complex is very stable at room temperature. The value of the stability constant of the Cu-phen complex $K_f= 9.096 \times 10^9$ $\log K_f=$ 9.96 for Cu-sac complex $K_f = 1.758 \times 108$, $\log K_f = 8.24$ and for Cu –EDTA complex, $K_f= 2.56 \times 10^5$ and $\log K_f = 5.41$ at 298K. The value of free energy change of complex formation is negative for all complexes implying that the formation of the complex is exergonic and spontaneous. The redox process of the Cu(II) / Cu(0) system in the Cu – ligand complex is diffusion-controlled. The peak current ratio and peak potential separation values are the evidence that the redox processes are quasi-reversible. The formed complexes are electro active and the Cu-sac complex has more reactivity than the Cu(II) ion.

References

1   Adimule V., B. C. Yallur, V. Kamat and P. M. Krishna, 2021, Characterization studies of novel series of cobalt(II), nickel(II) and copper(II) complexes: DNA binding and antibacterial activity, *Journal of Pharmaceutical Investigation,* **51**, 347–359.

2   Nunes B. N., C. L. de Barros, D. W. Bahnemann and A. O. T. Patrocinio, Historical 2019, Development of Inorganic Photochemistry, in *Springer Handbook of Inorganic Photochemistry*, Springer, 2022, 3–25.

3   Constable E. C. and C. E. Housecroft, 2019 The early years of 2, 2′-bipyridine—A ligand in its own lifetime, *Molecules,* **24**, 3951.

4   Ge E. J., A. I. Bush, A. Casini, P. A. Cobine, J. R. Cross, G. M. DeNicola, Q. P. Dou, K. J. Franz, V. M. Gohil, S. Gupta, 2022, Connecting copper and cancer: from transition metal signaling to metalloplasia, *Nature Reviews Cancer,* **22**, 102–113.

5   da Silva D. A., A. De Luca, R. Squitti, M. Rongioletti, L. Rossi, C. M. L. Machado, and G. Cerchiaro, 2022, Copper in tumors and the use of copper-based compounds in cancer treatment, *Journal of inorganic biochemistry,* **226**, 111634.

6   Kargar H., F. Aghaei-Meybodi, R. Behjatmanesh-Ardakani, M. R. Elahifard, V. Torabi, M. Fallah-Mehrjardi, M. N. Tahir, M. Ashfaq and K. S. Munawar, 2021, Synthesis, crystal structure, theoretical calculation, spectroscopic and antibacterial activity studies of copper(II) complexes bearing bidentate Schiff base ligands derived from 4-aminoantipyrine: Influence of substitutions on antibacterial activity, *Journal of Molecular Structure,* **1230**, 129908.

7   DiMucci I. M, J. T. Lukens, S. Chatterjee, K. M. Carsch, C. J. Titus, S. J. Lee, D. Nordlund, T. A. Betley, S. N. MacMillan and K. M. Lancaster, 2019, The myth of d8 copper(III), *Journal of the American Chemical Society,* **141**, 18508–18520.

8   Irving H. M. N. H. and R. Williams, 1953, 637. The stability of transition-metal complexes, *Journal of the Chemical Society (Resumed),* 3192–3210.

9   Schindler S. and T. Bechtold, 2019, Mechanistic insights into the electrochemical oxidation of dopamine by cyclic voltammetry, *Journal of Electroanalytical Chemistry,* **836**, 94–101.

10   Romo A. I. B., M. P. dos Reis, O. R. Nascimento, P. V. Bernhardt, J. Rodríguez-López and I. C. N. Diógenes, 2023, Interplay of electronic and geometric structure on Cu phenanthroline, bipyridine and derivative complexes, synthesis, characterization, and reactivity towards oxygen, *Coordination Chemistry Reviews,* **477**, 214943.

11   Masuri S., P. Vaňhara, M. G. Cabiddu, L. Moráň, J. Havel, E. Cadoni and T. Pivetta, 2021, Copper(II) phenanthroline-based complexes as potential anticancer drugs: a walkthrough on the mechanisms of action, *Molecules,* **27**, 49.

12   Zhang K., Z. Dai, W. Zhang, Q. Gao, Y. Dai, F. Xia and X. Zhang, 2021, EDTA-based adsorbents for the removal of metal ions in wastewater, *Coordination Chemistry Reviews,* **434**, 213809.

13   Job P., 1928, Formation and stability of inorganic complexes in solution, *Ann. chim,* **9**, 113–134.

14   Yoe J. H. and A. L. Jones, 1944, Colorimetric determination of iron with disodium-1, 2-dihydroxybenzene-3, 5-disulfonate, *Industrial & Engineering Chemistry Analytical Edition,* **16**, 111–115.

15   El-Dessouky M. N., 2021, A Modified Procedure for Slope Ratio Method in Analysis of 1: 1 Complex Compounds., *MEJ. Mansoura Engineering Journal,* **16**, 1–7.

16   Kandahari E., E. J. Smith and J. C. Goeltz, 2021, Beyond the Textbook: Introducing Undergraduates to Practical Electrochemistry, *Journal of Chemical Education,* **98**, 3263–3268.

17   Mabbott G. A., 1983, An introduction to cyclic voltammetry, *Journal of Chemical Education,* **60**, 697.

18   Wang Q., Y. Zhang, Y. Li, J. Ren, G. Qu, T. Wang, and H. Jia, 2022 Simultaneous Cu-EDTA oxidation decomplexation and Cr(VI) reduction in water by persulfate/formate system: Reaction process and mechanisms, *Chemical Engineering Journal,* **427**, 131584.