

## Electrochemical Studies on Interactions of $\text{Cu}^{2+}$ , $\text{Zn}^{2+}$ and $\text{Cd}^{2+}$ with Leucine and Isoleucine

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### Abstract

The interaction of some divalent metal ions with leucine (leu) and isoleucine (ile) was studied in aqueous solution. Electrochemical techniques like cyclic voltammetry, chronoamperometry and chronocoulometry were used for this study. The electrochemical study demonstrates that the maximum interaction of each metal ion occurs with two deprotonated ligand. The metal ions exchange electrons quasi-reversibly in presence of the ligands and some sort of chemical reaction may be competing with diffusion process at the electrode surface. The current-time and charge-time response accounts for the adsorption of reactant or product or both at the electrode surface.

**Keywords:** Leucine, Isoleucine, Voltammetry, Chronoamperometry, Chronocoulometry

### I. Introduction

The metal-amino acid complexes are prominently using in medication and stimulating chemical reaction. There have been many reports on such applications<sup>[1-5]</sup>. The human bodies consume leucine and isoleucine from dietary source and use them to synthesize protein and hemoglobin. These two amino acid boosts up insulin level which in turn controls blood sugar. They are also well known for healing wounds and preventing muscle protein breakdown caused by injury. These amino acid can retrieve blood loss by producing hemoglobin<sup>[6-7]</sup>. The presence of the amino and carboxylic acid group makes leucine and isoleucine a bidentate ligand to coordinate with the mentioned metal ions. Therefore, the study of interaction of transition metal ion which are biologically important with leucine and isoleucine will give information about the mode of action of these micronutrients. Electrochemical techniques are being using to analyze or modeling metal-ligand interaction due to the advantages of fast response, simple operation and high sensitivity. Some studies in metal-ligand interaction using electrochemistry are reported<sup>[8-12]</sup>. There are many electrochemical techniques among them cyclic voltammetry, however is widely used and attracted attention to the scientists, because it can provide useful information about the redox properties of the metal ions and the reversibility of the redox reaction we are studying. Redox reaction intermediates, electron transfer kinetics may also be studied using the cyclic voltammetry (CV) technique. The diffusion coefficient and the redox potential of an analyte can be determined using cyclic voltammetry. Chronoamperometry and chrono coulometry are also typical techniques used in electrochemistry for different purposes. The surface area of an electrode, diffusion coefficient, analyte concentration, electron transfer kinetics, coupled chemical reactions, nature of adsorption or adsorbed species at the electrode surface and calculation of effective time window of a cell can be measured applying these tools. This laboratory

reports some research in this field<sup>[13-17]</sup>. In this communication we report the investigation on electrochemical interaction of Cu(II), Zn(II) and Cd(II) with amino acids leucine and isoleucine in aqueous solution.

### II. Experimental

#### *Chemical items and design of instrument*

Analytical graded (E. Merck, BDH, Sigma-Aldrich) chemicals were utilized in all the experimental work. The electrochemical experiments were done with an electrochemical analyzer made by CH instrument company, USA. The instrument is computer controlled. A glassy carbon electrode plays the role of working electrode while Ag/AgCl electrode acts as reference. A Pt wire makes counter electrode. 0.1 M KCl solution was used as supporting electrolyte. The surface of the working electrode was cleaned by polishing with fine alumina powder on a wet polishing cloth and then washing with deionized water. Before the measurements were done all electrolyte solutions were spurge with  $\text{N}_2$  gas to avoid interference from dissolved  $\text{O}_2$ .

### III. Results and Discussions

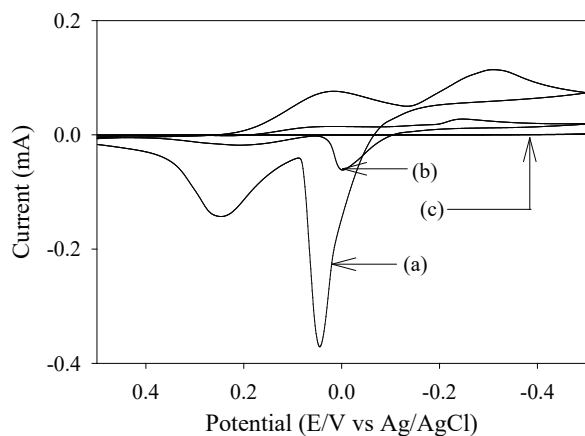
To begin with this study, the cyclic voltammogram of the free metal ions was recorded within a suitable potential window. Then the same was done in presence of the amino acids. The metal ion solution was mixed with the ligand solution in same magnitude of volume and concentration. The final mixture was subject to record the voltammogram. Background subtraction was done to eliminate capacitive current.

#### *Study of the redox properties of $\text{Cu}^{2+}$ in presence of leu and ile*

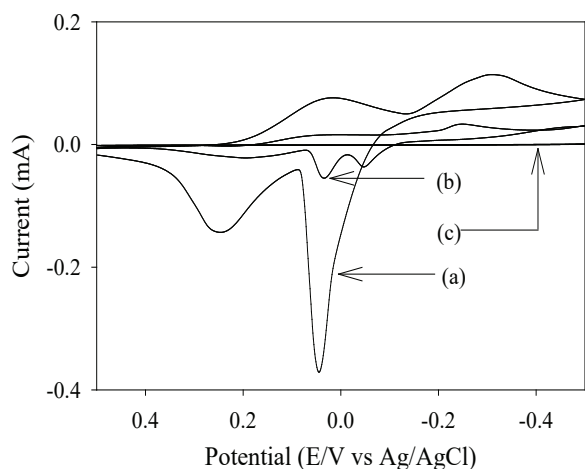
The electron transfer process of  $\text{Cu}^{2+}$  in presence of deprotonated ligands leucine leu and ile in equal mol ratio was studied separately in the potential window of 0.5 V to

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-0.5 V. The pH of the reaction mixtures was found 5.23 and 5.20 respectively. While the pH of leu, ile and  $\text{CuCl}_2$  was 9.28, 9.14 and 4.57 respectively. A notable change in pH was observed when metal ion was mixed with ligand. The voltammograms of  $\text{Cu}^{2+}$  before and after interaction with the ligands are displayed in Fig. 1 and Fig. 2. The peak position (potential) and peak current of  $\text{Cu}^{2+}$  changes due to interaction with ligand. The sharp fall of peak current and the peak potential shift confirms the interaction. The redox behavior of  $\text{Cu}^{2+}$  before and after interaction is a double one electron transfer process.

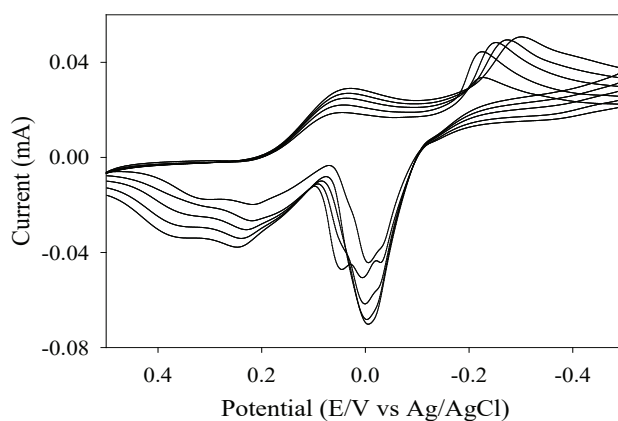


**Fig. 1.** CV's of (a) free  $\text{Cu}^{2+}$ , (b)  $\text{Cu}^{2+}$  in presence of deprotonated leucine and (c) free deprotonated leucine

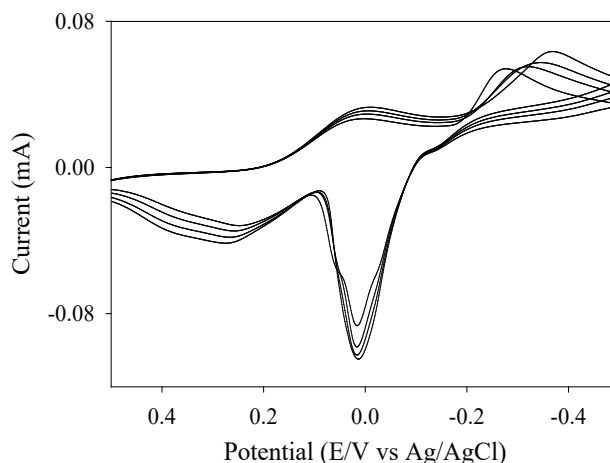


**Fig. 2.** CV's of (a) free  $\text{Cu}^{2+}$ , (b)  $\text{Cu}^{2+}$  in presence of deprotonated isoleucine and (c) free deprotonated isoleucine

The interactions of  $\text{Cu}^{2+}$  were studied at different mole ratio. The peak position has significantly changed and the current peaks at minimum value for the 1:2 reaction mixture. The utmost interaction of  $\text{Cu}^{2+}$  with the ligands occurs in 1:2 mole ratio.



**Fig. 3.** CV's of  $\text{Cu}^{2+}$  in presence of deprotonated leucine at different scan rate



**Fig. 4.** CV's of reaction mixture of  $\text{Cu}^{2+}$  and deprotonated isoleucine at different scan rate

Fig. 3 and Fig. 4 respectively represent the interaction of  $\text{Cu}^{2+}$  with the two ligands leu and ile at several scan rates. The data for peak current and potential is listed in Table 1. Some pictorial analysis was done in conformity with these data and are arrayed in Fig. 5 to Fig. 10. The analyses show that the cathodic and anodic peak current grows as the scan rate is step up. The peak currents climb up almost linearly with square root of scan rate, which indicates that the systems may be diffusion controlled. A large gap in peak potential and increment of this gap at faster scan rates claims an ohmic resistance between the electrodes. The current function changes inconsistently as the scan rate is varied. The anodic to cathodic peak current ratio is greater than unity, indicating a quasi-reversible electron transfer process at the electrode surface and the process is not truly diffusion controlled. Some chemical reaction may be taking place at the electrode surface [18-25].

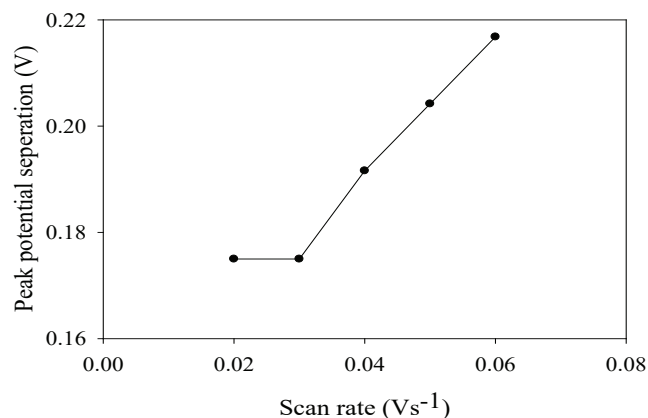


Fig. 5. Change of peak position separation with scan rate for  $Cu^{2+}$  in presence of deprotonated leucine

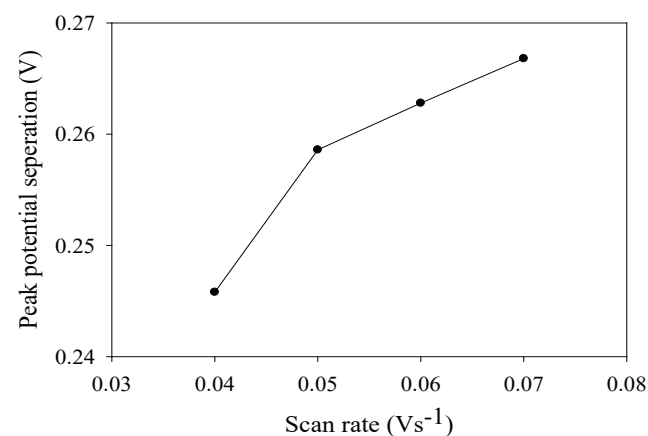


Fig. 6. Change of peak position separation with scan rate for  $Cu^{2+}$  in presence of deprotonated isoleucine

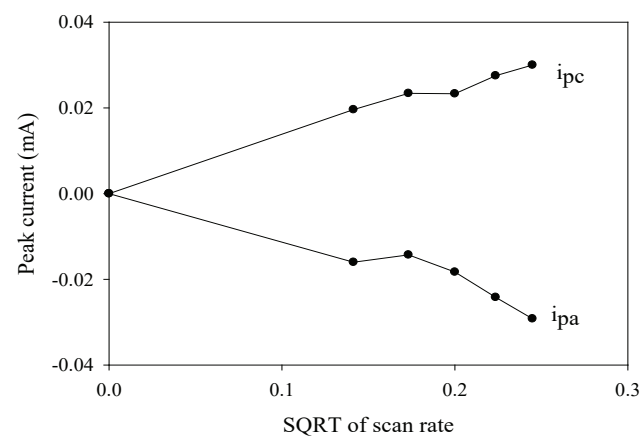


Fig. 7. Change of peak current with SQRT of scan rate for  $Cu^{2+}$  in presence of deprotonated leucine

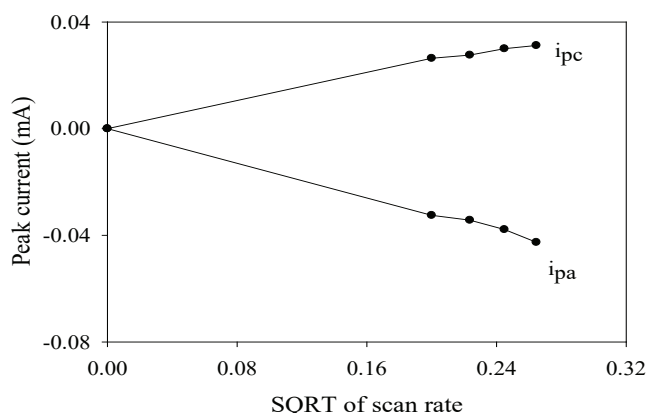


Fig. 8. Change of peak current for  $Cu^{2+}$  in presence of deprotonated isoleucine with SQRT of scan rate

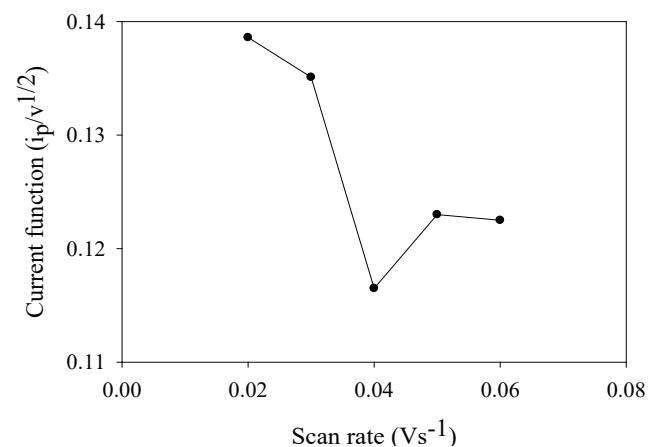


Fig. 9. Change of current function with scan rate for  $Cu^{2+}$  in presence of deprotonated leucine

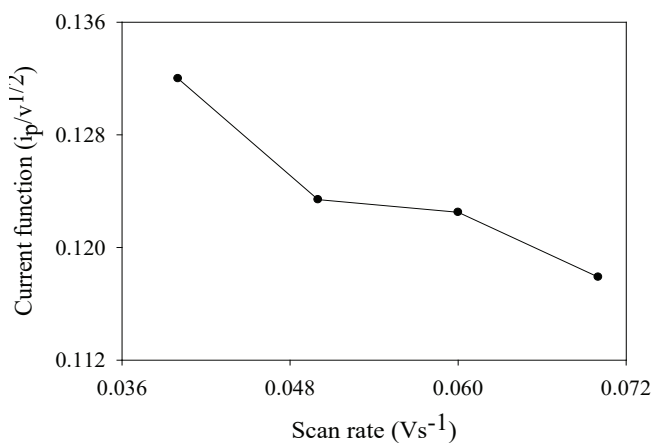


Fig. 10. Change of current function for  $Cu^{2+}$  in presence of deprotonated isoleucine at different scan rate

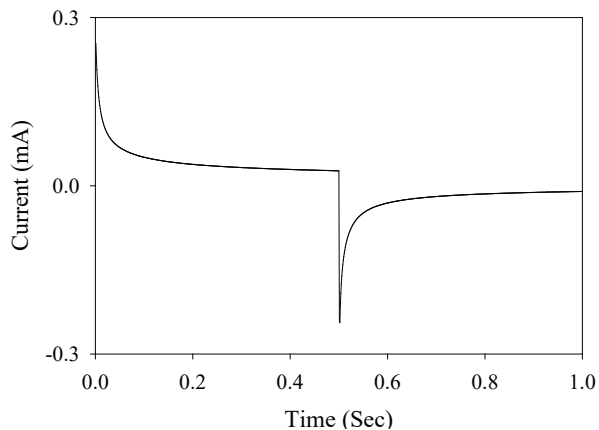
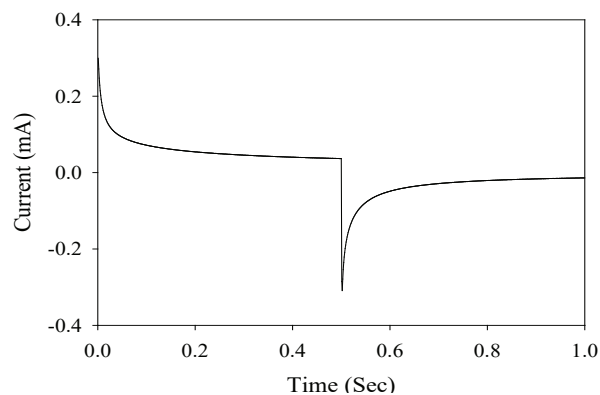
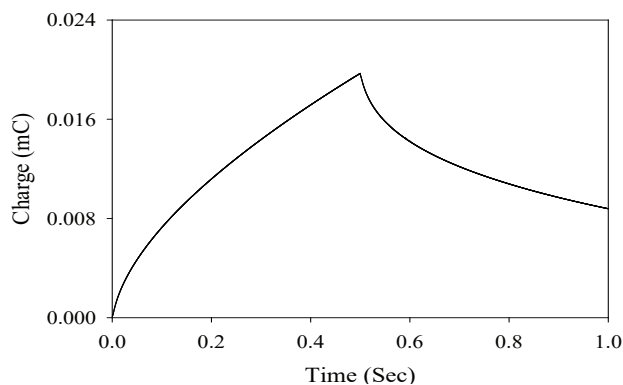
**Table 1. Parameters of the 1<sup>st</sup> peak pair of the  $\text{Cu}^{2+}$  voltammogram in presence of deprotonated ligand at variable scan rate**

$v$	$v^{1/2}$	$+E_{pc}$	$+E_{pa}$	$+i_{pc}$	$-i_{pa}$	$\Delta E_p$	$i_{pa}/i_{pc}$
$\text{Vs}^{-1}$	$\text{Vs}^{-1}$	Volt	Volt	mA	mA	Volt	
<b>in presence of deprotonated leucine</b>							
0.02	0.1414	0.0416	0.2166	0.0196	0.0160	0.1750	1.225
0.03	0.1732	0.0416	0.2166	0.0234	0.0143	0.1750	1.636
0.04	0.2000	0.0376	0.2292	0.0233	0.0183	0.1916	1.273
0.05	0.2236	0.0334	0.2376	0.0275	0.0242	0.2042	1.136
0.06	0.2449	0.0292	0.2460	0.0300	0.0292	0.2168	1.027
<b>in presence of deprotonated isoleucine</b>							
0.04	0.2000	0.0042	0.2500	0.0264	0.0325	0.2458	1.23
0.05	0.2236	0.0040	0.2626	0.0276	0.0343	0.2586	1.24
0.06	0.2449	0.0040	0.2668	0.0300	0.0378	0.2628	1.26
0.07	0.2646	0.0082	0.2750	0.0312	0.0426	0.2668	1.36

$v$  = scan rate,  $v^{1/2}$  = SQRT of scan rate,  $E_{pc}$  = cathodic peak potential,  $E_{pa}$  = anodic peak potential,  $i_{pc}$  = cathodic peak current,  $i_{pa}$  = anodic peak current,  $\Delta E_p$  = peak potential separation,  $i_{pa}/i_{pc}$  = peak current ratio

*Chronoamperometric (CA) and chronocoulometric (CC) study of  $\text{Cu}^{2+}$  in presence of leu and ile*

CA and CC study of  $\text{Cu}^{2+}$  and deprotonated ligand reaction mixture were executed. The amperograms are shown in Fig. 11 and Fig. 12 respectively. The analogous charge vs. time plots are shown in Fig. 13 and Fig. 14. The feedback shows that the charges at first step time ( $\tau$ ) is about 19.71  $\mu\text{C}$  and 28.24  $\mu\text{C}$  for  $\text{Cu}^{2+}$ -deprotonated leucine and  $\text{Cu}^{2+}$ -deprotonated isoleucine system respectively. For free  $\text{Cu}^{2+}$  ion the value is 130.25  $\mu\text{C}$ . Metal-ligand interaction declines the charge. The Anson plots in Fig. 15 and Fig. 16 proclaim that at the zero line the two straight lines do not intersect each other. They do not have also equal gradients; these facts indicate that reactant or products are adsorbed on the electrode during electrolysis<sup>[18-26]</sup>.

**Fig. 11.** Current and time plot for  $\text{Cu}^{2+}$  in presence of deprotonated leucine**Fig. 12.** Current vs time plot for  $\text{Cu}^{2+}$  in presence of deprotonated isoleucine**Fig. 13.** Charge vs time plot for  $\text{Cu}^{2+}$  in presence of deprotonated leucine

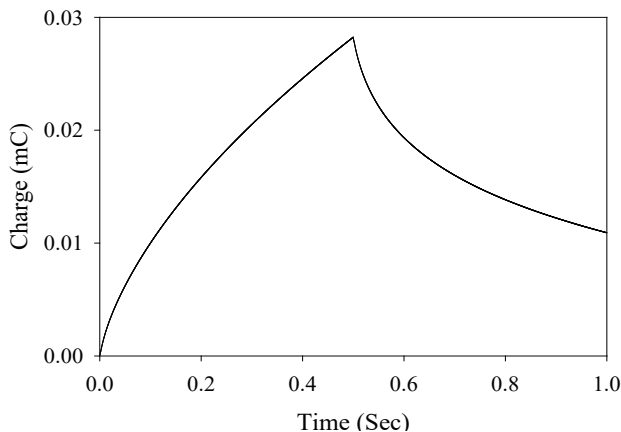


Fig. 14. Charge and time plot for  $\text{Cu}^{2+}$  in presence of deprotonated isoleucine

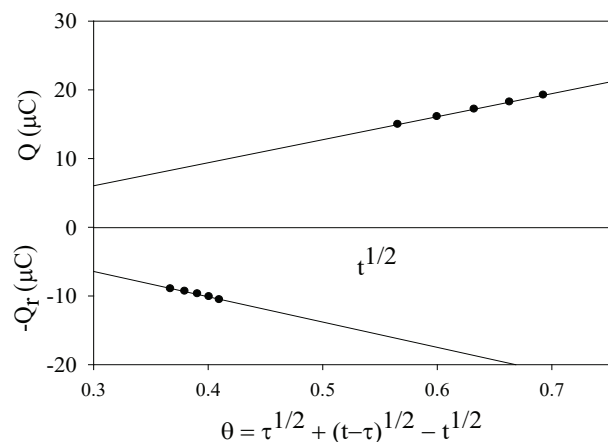


Fig. 15. Plots of  $Q$  vs  $t^{1/2}$  and  $-Q_r$  vs  $\theta$  for  $\text{Cu}^{2+}$  in presence of deprotonated leucine

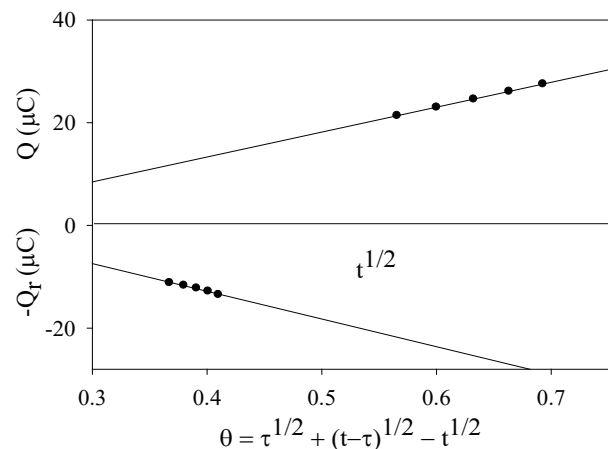


Fig. 16. Plots of  $Q$  vs  $t^{1/2}$  and  $-Q_r$  vs  $\theta$  for  $\text{Cu}^{2+}$  in presence of deprotonated isoleucine

*Cyclic voltammetric study of the interaction of  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  with leu and ile*

The oxidation reduction behavior of  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  in presence of deprotonated leu and deprotonated ile in 1:1 mol ratio was studied separately. The voltammogram of  $\text{Zn}^{2+}$  (Fig.17) and  $\text{Cd}^{2+}$  (Fig. 18) (before and after interaction) show that the peak position and amount of peak current changed significantly after mixing ligand and the metal ion. Interaction of the metal ion with the ligands the peak potential and peak current changes. The interaction is a single two electron transfer process. The maximum interaction of the metal ions with the ligand occurs in 1:2 mole ratios.

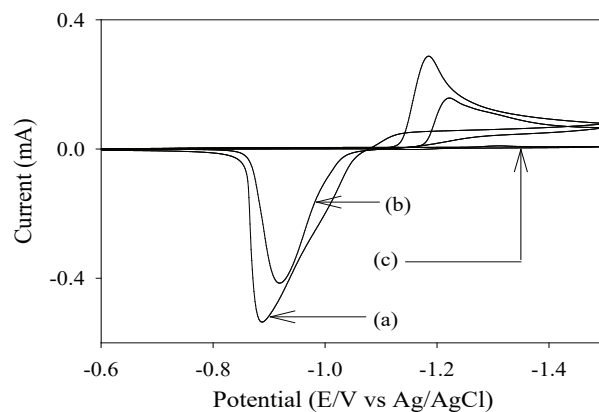


Fig. 17. CV's of (a) free  $\text{Zn}^{2+}$ , (b)  $\text{Zn}^{2+}$  in presence of deprotonated leucine and (c) free deprotonated leucine

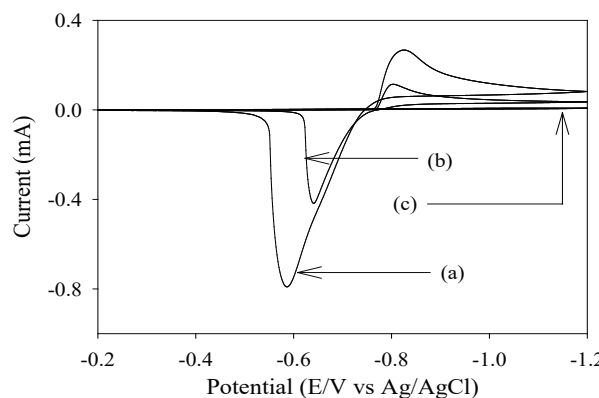


Fig. 18. CV's of (a) free  $\text{Cd}^{2+}$  (b)  $\text{Cd}^{2+}$  in presence of deprotonated isoleucine and (c) free deprotonated isoleucine

The graphical analysis as reported by the current-potential data for the two metals is compared side by side in Fig. 19 to Fig. 24. The results are almost similar to those for the interaction of Copper ion with the ligands leucine and isoleucine. The scan rate variation attested almost a linear elevation of peak currents as the scan rate is varied in square root. The difference in peak potentials is much larger compared to a true reversible response and stepping up the rate to scan the voltammogram is raised. The current function also changes with the change of

scan rate. The current in oxidation process is higher than that of cathodic one. That's why the peak current ratio crosses the unity value. This scrutiny reflects the electrode process to be quasi-reversible where diffusion process competes with chemical reaction<sup>[18-25]</sup>.

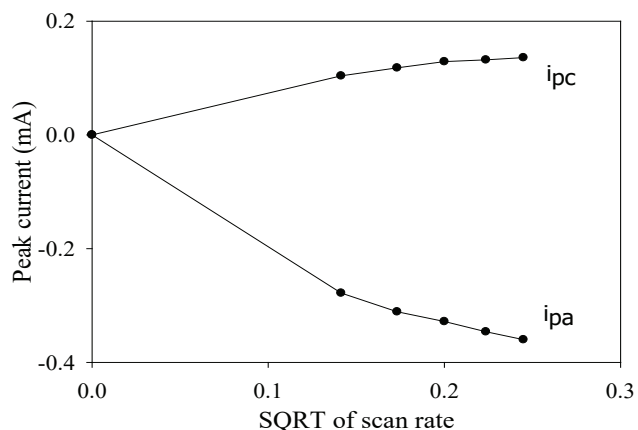


Fig. 19. Change of peak current with SQRT of scan rate for  $\text{Zn}^{2+}$  in presence of deprotonated isoleucine

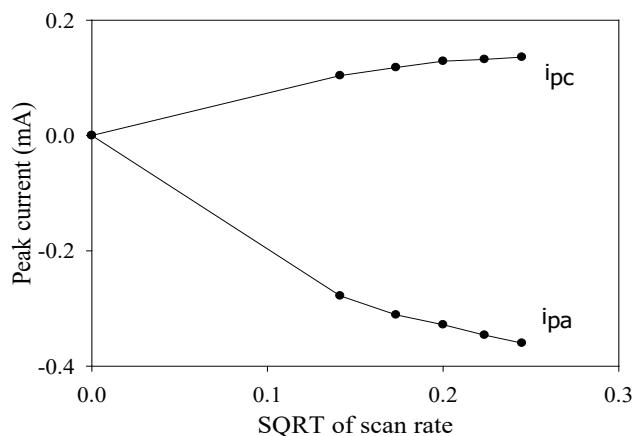


Fig. 20. Change of peak current with SQRT of scan rate for  $\text{Cd}^{2+}$  in presence of deprotonated isoleucine

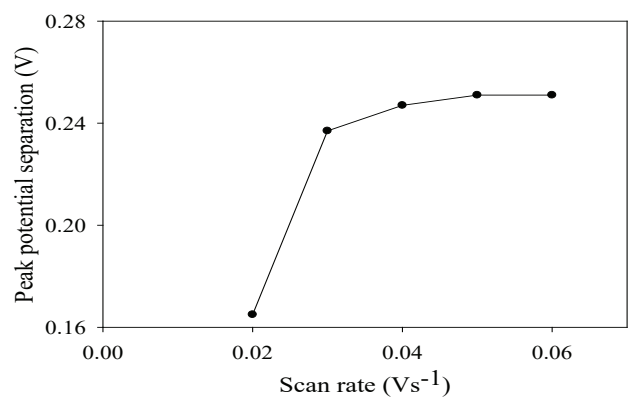


Fig. 21. Variation of peak potential separation with scan rate for  $\text{Zn}^{2+}$  in presence of deprotonated isoleucine

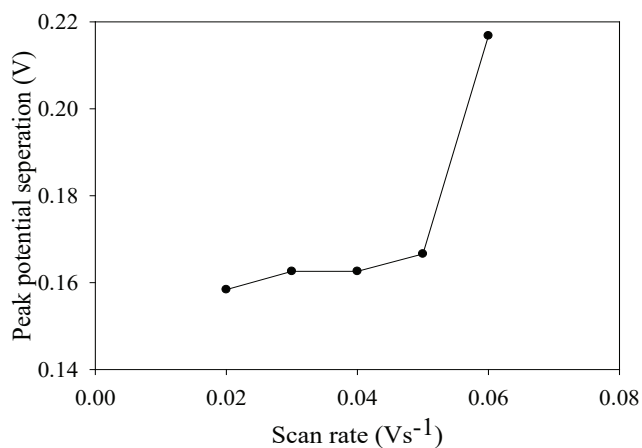


Fig. 22. Change of peak potential separation with scan rate for  $\text{Cd}^{2+}$  in presence of deprotonated isoleucine

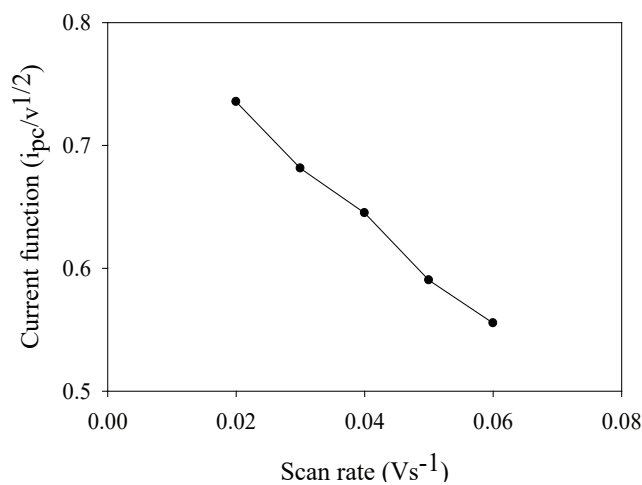


Fig. 23. Change of current function with scan rate for  $\text{Zn}^{2+}$  in presence of deprotonated isoleucine

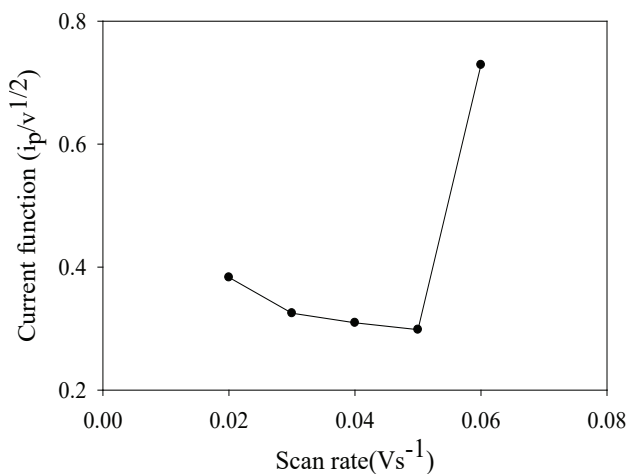
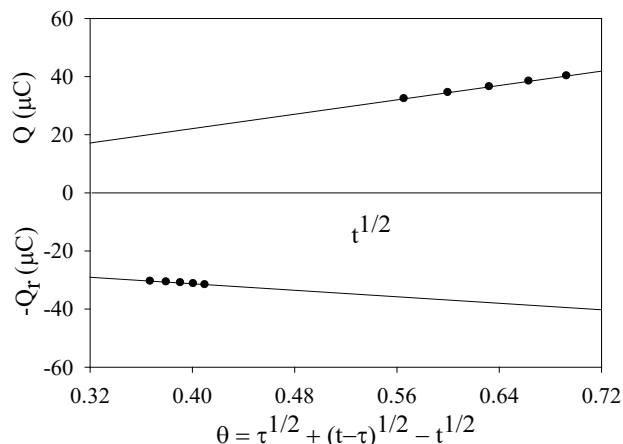


Fig. 24. Change of current function with scan rate for  $\text{Cd}^{2+}$  in presence of deprotonated isoleucine

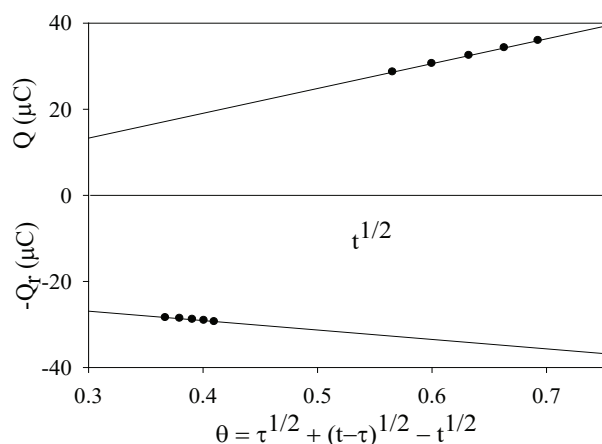
*Chronoamperometric (CA) and chronocoulometric (CC) study of Zn<sup>2+</sup> and Cd<sup>2+</sup> in presence of leu and ile*

Chronoamperometric study of Zn<sup>2+</sup> and Cd<sup>2+</sup> in presence of deprotonated leu and ile in 1:2 mol ratio was done.



**Fig. 25.** Plots of  $Q$  vs  $t^{1/2}$  and  $-Q_r$  vs  $\theta$  for  $Cd^{2+}$  in presence of deprotonated leucine

The corresponding charge responses show that the charges at  $\tau$  are declined when ligand is mixed with the metal ions. This may be due to metal ligand interaction. The Anson plots evinced the adsorption of reactant or products on the electrode (Fig. 25 and Fig. 26) [18-26].



**Fig. 26.** Plots of  $Q$  vs  $t^{1/2}$  and  $-Q_r$  vs  $\theta$  for  $Cd^{2+}$  in presence of deprotonated isoleucine

*Comparison of interaction of the metal ions with leu and ile*

The oxidation-reduction nature of the metal ions in presence of the two ligands was compared. We obtained similar trends in behaviors. The current-potential, current-time and charge-time responses are identical. The metal ions transfer electrons at almost same potential. Unvarying amount of

current was required to reduce or oxidize the species. This means, the metal-leucine and metal-isoleucine interaction is equivalent. The isomeric nature of the two ligand accounts for this equivalency in interaction. The ligands supposed to coordinate with the metals through their amino and carboxylic acid functional groups. The hydrocarbon tail remains latent in coordination and electrochemical change.

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