

## Polarographic study of mixed coordinated system: Cu(II)-glycine-isoleucine

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The mixed-ligand ternary system Cu(II)-glycinate ion ( $\text{glyc}^-$ )-isoleucinate ion ( $\text{isoleuc}^-$ ) has been studied polarographically at  $25 \pm 0.1^\circ\text{C}$  and at ionic strength = 1.0 M, adjusted with sodium perchlorate. The formation of the mixed complex  $[\text{Cu}(\text{glyc}^-)(\text{isoleuc}^-)]$  has been verified, with stability constant  $\beta_{11} = 4.4 \times 10^{15}$ .

Mixed complexes of Cu(II) with amino acids serve as models for biological systems, such as complexation of metals with enzymes and proteins. Mildvan and Cohn<sup>1</sup> while studying metal-pyruvate-kinase system made important contributions to understanding the mode of interaction between an enzyme-bound metal and the substrate i.e. the formation of enzyme-metal-substrate bridge structure. Presently, we have undertaken a polarographic study of the mixed system Cu(II)-glycinate ion-isoleucinate ion.

### Experimental

Metrohm E506/E505 polarographic equipped with thermostated cell ( $25 \pm 0.1^\circ\text{C}$ ), Metrohm EA 285 platinum electrode, Ingold 303 NS saturated calomel reference electrode and DME ( $m = 1.62 \text{ mg s}^{-1}$ ,  $\tau = 3 \text{ s}$ ) were used. Ionic strength was adjusted to 1.0 M by the addition of sodium perchlorate.

Radiometer PHM84 digital pH meter with Radiometer G-202-B glass electrode and an Ingold 303 NS saturated calomel electrode (sat. NaCl bridge) were also used.

All the reagents used were of AR grade. Cupric perchlorate was prepared from cupric oxide and perchloric acid (both Merck, pro analysi) and its concentration in the cell was always  $1 \times 10^{-5} \text{ M}$ . Mercury, chemically treated, was triply distilled under reduced pressure before use.

### Results and discussion

The polarograms were recorded under the following conditions:

- (a) pH = 8.47; [isoleucine]<sub>T</sub> = 0.020 M;  
[glycine]<sub>T</sub> =  $1.99-9.40 \times 10^{-2} \text{ M}$   
(b) pH = 8.60; [isoleucine]<sub>T</sub> = 0.015 M;  
[glycine]<sub>T</sub> =  $1.99-6.92 \times 10^{-2} \text{ M}$

Constant pH was maintained by the addition of NaOH or HClO<sub>4</sub>. Suitable volume corrections were made for every solution.

The ionization constants for glycine ( $pK_{a1} = 2.36$  and  $pK_{a2} = 9.56$ ) and isoleucine ( $pK_{a1} = 2.51$  and  $pK_{a2} = 9.55$ ) were taken from literature.

Polarographic reduction, in the presence of ligands, follows a two-electron and reversible process, as indicated by the plots of  $\log[(i_d - i)/i]$  versus  $-E$  from which the reversible half-wave potentials,  $E_{1/2}^r$  were determined.

The stability constants determined polarographically by Schaap and McMasters' method<sup>4</sup>, for the simple binary systems Cu(II)-glycinate ion and Cu(II)-L-isoleucinate ion are  $\beta_{01} = 1.8 \times 10^8$ ,  $\beta_{02} = 1.7 \times 10^{15}$ , and  $\beta_{01} = 2.2 \times 10^8$ ,  $\beta_{02} = 1.8 \times 10^{15}$ , respectively, and were obtained under the same experimental conditions.

Following Schaap and McMasters' method<sup>4</sup>, the formation of the mixed complex  $[\text{Cu}(\text{glyc}^-)(\text{isoleuc}^-)]$  has been established and its stability constant,  $\beta_{11}$ , works out to be  $4.4 \times 10^{15}$ , which is in good agreement with the value found theoretically from Watters' equation<sup>5</sup>,  $\beta_{11} = 2 (1.7 \times 10^{15})^{1/2} \times (1.8 \times 10^{15})^{1/2} = 3.5 \times 10^{15}$ .

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