ELECTROCHEMICAL STUDIES OF *DL*-LEUCINE, *L*-PROLINE AND *L*-TRYPTOPHAN AND THEIR INTERACTION WITH COPPER AND IRON

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Introduction

In vitro study of the charge transfer reactions coupled with chemical reactions can give important indication of about actual biological processes occurring in human Understanding of such charge-transfer system. mechanism will help to determine the effectiveness of nutrition, metabolism and treatment of various biological disorders. In the previous research, the redox behaviour of various amino acids and biochemically important compounds and their charge transfer reaction and their interaction of metal ions were studied [1,2]. In the present research, the redox behavior and the charge transfer kinetics of *DL*-Leucine, *L*-Proline and *L*-Tryptophan in the presence and absence of copper and iron will be investigated.

Experimental

A computerized electrochemistry system developed by Advanced Analytics, Virginia, USA, (Model-2040) consisting of three electrodes micro-cell with a saturated Ag/AgCl reference, a Pt-wire auxiliary and a pretreated Pt-button working electrode is employed to investigate different amino acids and metal-amino acid systems. Cyclic voltammetry (CV) and chronocoulometry (CC) were employed to investigate these systems.

Results and Discussion

Cyclic voltammogram of DL-Leucine, L-Proline and L-Tryptophan at a Pt-button electrode shows a single step, one electron-transfer, reversible redox reaction (Fig 1a, 2a, 3a). The determination of the number of electrons involved in the electron transfer process for the free amino acids and metal-amino acid complexes is determined by using the Randles-Sevcik equation [3]. A dramatically change in the voltammetric behaviour of the above amino acids is observed in the presence of metals especially copper ion (Fig 1b & 1c, 2b & 2c and 3b & 3c). In the presence of Cu(II) ion, two pair of cathodic and anodic peak is observed. These observations are consistent with the occurrence of a two step mechanism due to the presence of stabilizing ligands in solution towards Cu(I) and Cu(II). This behaviour is different for the Cu-DL-Leucine complex. It shows two anodic and one cathodic peak at slower scan rates (not shown in the figure). The cathodic peak corresponding to the anodic peak for Cu(II) at 328 mV is absent at the slower scan rate. The process for the reduction of [Cu(II)-DL-Leucine] follows the following electrochemical reaction.

[Cu(II)-DL-Leucine] \Im [Cu(0)-DL-Leucine] \Im [Cu(I)-DL-Leucine].

In this case, only [Cu(II)-*DL*-Leucine] is supposed to present in the solution. The other amino acids, *L*-Proline and L-Tryptophan shows two-step reversible reactions in the presence of copper. In these cases, more than one complex for Copper may be present in the solution. The lower value for the calculated k_f (charge transfer rate constant) of [Copper-amino acid] and [Iron-amino acid] complex suggesting that a considerable interaction is occurred between the above amino acids with iron and copper.

References:

1) R.J. Mannan and G.C. Sarker, *J. Bangladesh Acad. Sci*, **21**(1), 35-41 (1997). 2) M. A. Jabbar and others, unpublished works. 3) A.J. Bard, L.R. Faulkner, "Electrochemical methods, Fundamentals and applications", Wiley, New York (1980).



Fig.1. Comparison of the cyclic voltammogram of 5.0mM (a) *DL*-Leucine, (b) Cu-*DL*-Leucine ion and (c) [Fe-*DL*-Leucine] in 0.1M KCl solution at a Pt-button electrode. Scan rates 50 mV/s.



Fig.2. Comparison of the cyclic voltammogram of 5.0mM (a) *L*-Proline, (b) Cu-*L*-Proline and (c) Fe-*L*-Proline in 0.1M KCl solution at a Pt-button electrode. Scan rate 50 mV/s.



Fig.3. Comparison of the cyclic voltammogram of 5.0mM (a) *L*-Tryptophan (b) Cu-L-tryptophan and (c) Fe-*L*-Tryptophan in 0.1M KCl solution at a Pt-button electrode. Scan rate 50 mV/s.

Table Comparative results for the charge transfer rate constants (k_f) of amino acids and metal-amino acids obtained from *CC* kinetic plot.

| System | k _f |
|------------------------|-----------------|
| (Concentration: 5.0mM) | $(cm/s) x 10^4$ |
| DL-Leucine | 26.44 |
| L-Proline | 28.40 |
| L-Tryptophan | 48.68 |
| Cu(II) | 1.65 |
| Cu-DL-Leucine | 15.20 |
| Cu-L-Proline | 5.10 |
| Cu-L-Tryptophan | 11.29 |
| Fe(II) | 6.92 |
| Fe-DL-Leucine | 2.14 |
| Fe-L-Proline | 4.69 |
| Fe-L-Tryptophan | 1.77 |