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Voltammetric Determination of Cysteine at a Carbon Paste Electrode Modified with Cu(II)-Salen Complex

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Abstract

The electrochemical behavior of a modified carbon paste electrode (MCPE) with *N,N′* ethylenbis(salicylideneiminato)copper(II) complex ([Cu(II)-Salen]) was investigated as a new sensor for cystein. The Britton-Robinson buffer with pH 5, 10% modifier in electrode, potential scanning rate of 20 mVs^{-1} and puls height of 50 mV were used as the optimum condition for the determination of cysteine using carbon paste electrode modified with Cu(II)-Salen complex. Under these optimum conditions, the resulting electrode demonstrated linear response with cysteine concentration in the range of 1-10 and 10-80 μM. The effects of potential interfering species were studied and it was found that only thiocyanate ion interfered in cysteine determination and the proposed procedure was free from most other interferences.

Keywords: Modified carbon paste, Cu(II)-Salen,Voltammetric determination, Cysteine

Introduction

Cysteine is known as an active site in the catalytic activity of enzymes known as cysteine protease. It is also found in the structure of vasopressin, an antidiuretic hormone. Cystinuria is a hereditary malfunction in which the transmitter of the brain for cysteine and some other basic amino acids in epithelial cells are damaged and large amounts of these amino acids are excreted in urine [1,2]. Cysteine also has several pharmaceutical applications. It is used in some antibiotics and treatment of skin damages [3] and as a radio-protective agent [4,5]. Therefore, measurement of cysteine in body fluids is very important from the biological and pharmacological stand point.

Chemically modified electrodes (CMEs) have continued to be of major concern during the past decades and a relatively large numbers of electrochemical researches have been devoted to the development and applications of different types of CMEs [6]. Modification of electrodes with suitable biocompatible

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materials enables the electrochemistry of the redox biological compounds to proceed without hindrance [7]. This phenomenon generally results increasing selectivity and sensitivity of the determinations [8].

Transition metal-Salen complexes are functional mimics of metalloproteins in dioxygen binding and oxidation of olefins and aromatic compounds [9]. The Salen complexes are conformationally flexible and adopt a variety of geometries to generate several active sites who allows different oxidation reactions [10].

Carbon paste electrodes, due to the ease of construction, renewability, and compatibility with various types of modifiers, have been widely used as a suitable matrix for preparation of modified electrodes. Further, they show rather low background current compared to solid graphite or noble metal electrodes [10].

In the present study, the preparation, properties and application of a carbon paste electrode modified with the Cu(II)-Salen complex for voltammetric determination of cysteine is reported. The influence of several parameters such as pH, potential window and interferences of several compounds on the electrode voltammetric profile is reported.

2. Experimental

2.1. Materials

All solutions were prepared with distilled water. All chemicals were of analytical grade and used without further purification. The supporting electrolyte used in all the experiments was a 0.1 mol L^{-1} Britton-Robinson buffer solution CySH standard solution (0.01 mol L^{-1}) was prepared by dissolution of an appropriate amount of cysteine in 25 mL of water. Cu(II)-Salen, was synthesized and purified according to a previously reported method [11]. Graphite powder (1-2□μm particle size-Aldrich) and high purity mineral oil (Aldrich) were used in the preparation of the carbon paste.

2.2. Apparatus

All electrochemical experiments were conducted with a computer-controlled potentiostat, the Autolab electrochemical analyzer model PGSTAT30 (Eco Chemie, Utrecht, The Netherlands). Electrochemical measurements were carried out under Argon atmosphere in a conventional one-compartment cell with an Ag/AgCl (3 M KCl) reference electrode, a platinum auxiliary electrode and a carbon paste or modified carbon paste electrode. All redox peak potentials were measured and reported versus the Ag/AgCl, KCl (3 M) reference electrode. A Metrohm 728 pH meter was used to determine the pH of solutions.

2.3. Fabrication of the modified carbon paste electrodes

The modified carbon paste electrode was prepared by mixing 0.10 g of Cu(II)-Salen complex with 0.65 g of graphite powder and subsequently adding 0.25 g of mineral oil. This mixture was homogenized by magnetic stirring in a 10 mL beaker containing 1 mL of dichloromethane. The final paste was obtained by evaporation of the solvent. The modified carbon paste was packed into an electrode body, consisting of a plastic cylindrical tube (o.d. 8 mm, i.d. 6 mm) equipped with a stainless steel rod serving as an external electric contact. Appropriate packing was achieved by pressing the electrode surface against a filter paper.

3. Results and discussion

3.1. Electrochemical properties of the MCPE

Fig. 1. shows differential pulse voltammograms of bare carbon paste electrode in absent (a) and presence (b) of 10 μM cysteine and modified carbon paste electrode with Cu(II)-Salen complex in absent (c) and presence (d) of 10 μM cysteine in a 0.1 M Britton-Robinson buffer (pH 5).

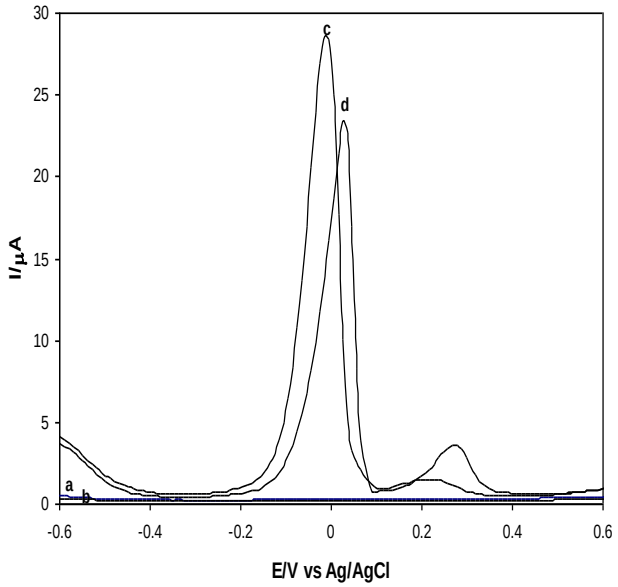

Fig. 1. Differential pulse voltammograms of unmodified carbon paste electrode in absent (a) and presence (b) of 10 μM cysteine and modified carbon paste electrode with Cu(II)-Salen complex in absent (c) and presence (d) of 10 μM cysteine in a 0.1 M Britton-Robinson buffer (pH = 5) at 20 mVs^{-1}.

3.2. Determination of cysteine at the modified electrode

3.2.1. Effect of pH

The pH effect over the voltammetric response of the modified electrode in 0.10 mol L^{-1} Britton-Robinson buffer containing 50 μM of cysteine is represented in Fig. 2.

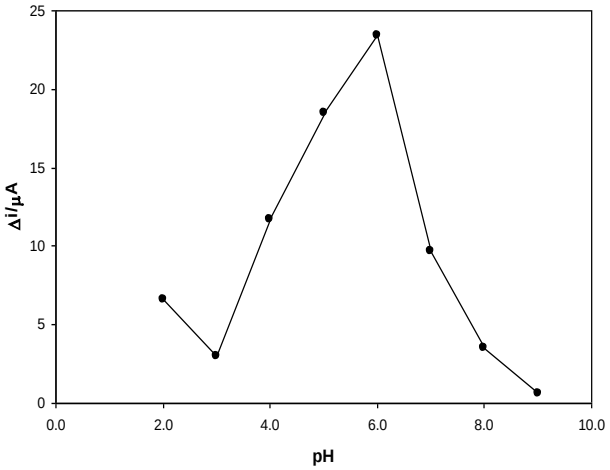

Fig. 2. Influence of the pH on the anodic peak current of the carbon paste electrode modified with Cu(II)-Salen in 0.10 mol L^{-1} Britton-Robinson buffer containing 50 mM cysteine, at scan rate 20 mVs^{-1}. The anodic peak current (ΔI/μA) was obtained by difference of the currents in the absence and presence of cysteine

3.2.2. Calibration curve and repeatability

After optimizing the operating conditions for the modified electrode with Cu(II)-Salen complex, differential pulse voltammetric measurements were carried out in solutions containing different cysteine concentrations in order to obtain an calibration curve. Fig. 3 shows that the anodic peak current was linearly dependent on the cysteine concentration in the range of 1.0-10.0 and 10.0-80.0 μM with a detection limit [12] of 0.95 μM in Britton-Robinson buffer (pH 5.0). The linear regression equations are, respectively:

*I*pa (μA)= 15.985+1.4612 [cystein] ($molL^{-1}$) (r= 0.9928) (1)

*I*pa (μA)= 29.131+0.1570 [cystein] ($molL^{-1}$) (r= 0.9928) (2)

Cystein concentration levels of 5 and 40 μM was selected to examine the repeatability of the voltammetric measurements of the modified electrode in Britton-Robinson buffer (pH 5.0). The relative standard deviation of 5 measurements was 11% and 1.3% respectively,

indicating that the modified electrode presented good stability and repeatability, within a confidence level of 95%.

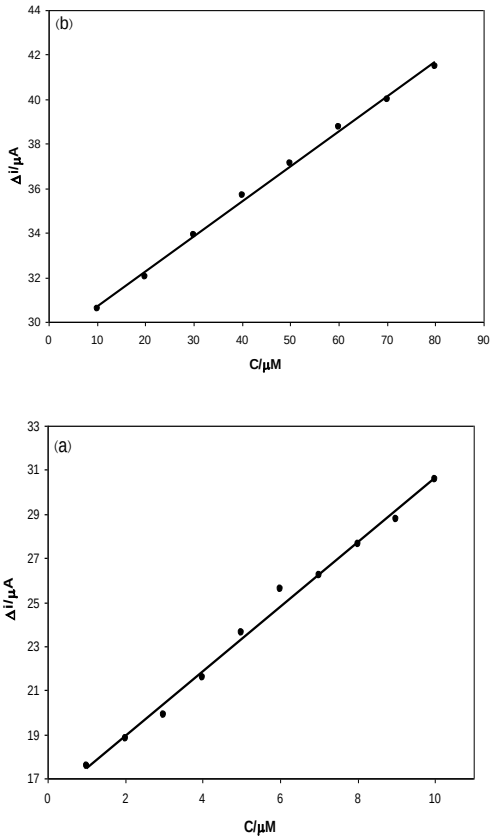

Fig. 3. Calibration curve of cysteine at the concentration range of 1.0-10.0 μM(a) and 10.0-80.0 μM(b) at optimum conditions

3.2.1. Studies of interference

The effects of potential interfering species were studied, and it was found that only thiocyanate ion interfered in cysteine determination and the proposed procedure was free from most of other interferences.

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