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Simultaneous determination of epinephrine, ascorbic acid and folic acid using TX-100 modified carbon paste electrode: A cyclic voltammetric study

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ABSTRACT

A sensitive and selective determination method for epinephrine (EN) was developed by immobilization of TX-100 surfactant on the bare carbon paste electrode. Scanning electron microscopy (SEM) and cyclic voltammetry (CV) were employed to characterize the modified surfaces. The catalytic activity of the modified electrode for the oxidation of EN was determined using the cyclic voltammograms recorded at sufficient different scan rates. The effect of the solution pH on the voltammetric response of EN was examined using phosphate buffer solution. This method enabled the determination of EN in the presence of interfering species, including ascorbic acid (AA) and folic acid (FA), in a phosphate buffer solution (pH 7.0). The TX-100/CPE demonstrated a good performance for the determination of EN in the concentration range from 10 μM to 50 μM, with a detection limit of 1×10^{-6} M. The application was conducted for the determination of EN in a human serum sample and the sensor was proven to be rapid, has excellent selectivity and repeatability.

1. Introduction

Epinephrine (EN), ascorbic acid (AA) and folic acid (FA) are compounds of great biomedical interests, playing determining roles in human metabolism. The catecholamines are a group of compound bearing a dihydroxyphenyl moiety [1,2]. Epinephrine [1-(3,4-dihydroxyphenyl)-2-methyloaminoethanol], is a very important catecholamine neurotransmitter in the central nervous system. It exists as an organic cation in the nervous tissue and biological body fluid. Many diseases are ascribed to changes of its concentration [3]. EN has, therefore, been attracted tremendous consideration in biomedically-oriented research. Hence, it is very necessary to develop sensitive, selective, and reliable methods for the direct determination of trace EN due to its physiological function and the diagnosis of some diseases in clinical medicine. Therefore, it is very important to develop sensitive and selective analytical methods for the detection of EN in biological fluids [4]. Various methods, including spectrophotometry [5], fluorimetry [6], liquid chromatography [7], capillary electrophoresis [8], chemiluminescence [9] and electrochemiluminescence [10] have been employed to the determination of EN. Because EN is an electroactive compound, its electrochemical determination has been the focus of research for electroanalytical researchers and neurochemists. Similarly AA is a vital vitamin in the diet of humans and is present in mammalian brain along with several neurotransmitter amines. AA has been used for the prevention and treatment of common cold, mental illness, infertility, cancer and AIDS [11]. Thus, the determination of AA is particularly important in the pharmaceutical and food industry. These techniques include HPLC [12], spectrophotometry [13], liquid chromatography [14], capillary electrophoresis [15], chemiluminescence [16] and electrochemical methods [17–19]. Similarly, folic acid (FA) is an important component of the haematopoietic system and is the coenzyme that controls the generation of ferrohaeme. Lack of FA gives rise to the gigantocytic anemia, associated with leucopoenia, devolution of mentality and psychosis etc. Numerous methods for the measurement of FA are available, including enzyme-linked immunosorbent assays (ELISAs), liquid chromatography/tandem mass spectrometry (LC/MS/MS), capillary electrophoresis (CE), microemulsion electrokinetic chromatography (MEEKC) and high-performance liquid chromatography (HPLC). As FA is an electroactive component, some electrochemical methods have been reported for its determination [20–26]. One of the major problems with the determination of EN comes from the electrochemical interference such as AA because the oxidation of AA occurs at a potential close to that of EN. Therefore, it is essential to develop simple and rapid methods for determination of these biological molecules in routine analysis. EN, AA and FA are electrochemically active compounds co-existing in body fluids and can be determined by electrochemical techniques. However, at the conventional electrode the electrochemical property of EN

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shows that the irreversible nature and requires overpotential. Furthermore, the oxidation potential of AA and FA overlaps with that of EN because AA largely coexists with EN in brain tissue, the content of which is 100–1000 times greater than that of EN. Simultaneous determination of catecholamines neurotransmitters (EN) in the presence of AA and FA is a problem of critical importance in the field of biomedical chemistry and neurochemistry. Moreover the solid electrodes are very often suffered from the fouling effect due to the accumulation of oxidized product on the electrode surface, which results in rather poor selectivity and sensitivity. Electrochemical techniques with modified electrodes have received a great interest for simultaneous determination of neurotransmitters in the presence of AA and FA as they are more selective and less time consuming than those based on other colorimetric or spectrophotometric methods. There are few reports on reporting the determination of EN at modified electrodes [27–30]. Sensing materials and analytes have been analyzed from variety of methods like stoichiometry, density functional theory and spectroscopic methods [31–34]. In recent years, carbon based electro chemical sensors have gained attention to attend to the growing demand for rapid, reliable, and inexpensive sensors [35–40]. Now-a-days voltammetric techniques are getting much attention in the electro analytical field [41–54]. V. K. Gupta et al. reported PVC based sensors for the determination of metal ions by using electrochemical methods (potentiometry and voltammetry) [55–68]. Voltammetric methods were used for the determination of drugs, which is having considerable importance in the pharmaceutical field [69–72].

At the present study, for the first time we have reported fabrication of a TX-100 modified carbon paste electrode and its application to simultaneous investigation of EN, AA and FA by cyclic voltammetric technique. It is shown that the anodic current peaks of AA, EN and FA could be well resolved, and therefore, a sensitive and selective electrochemical sensor for simultaneously determination of these three compounds has been established. The TX100/CPE could have a significant attraction in biological and chemical research. The objective of this experimental set up is to develop an ease of operation, fast and sensitive determination method without complicated preparations of modified electrodes.

2. Materials and methods

2.1. Reagents

Epinephrine hydrochloride, ascorbic acid and folic acid were purchased from Himedia chemicals. All other reagents used in this study were all of analytical grade. A stock solution of 1×10^{-3} M EN was prepared by dissolving in 0.1 N perchloric acid. Phosphate buffer solution (pH-7.0) was prepared by mixing equal volumes of 0.1 M sodium dihydrogen orthophosphate solution and 0.1 M disodium hydrogen orthophosphate solution and adjusting the pH with 0.1 N sodium hydroxide solution or 0.1 N ortho-phosphoric acid solution.

2.2. Apparatus

Cyclic voltammetry (CV) was performed in an analytical system Model CHI-660c potentiostat. A conventional three-electrode cell assembly consisting of an Hg_2/Hg_2Cl_2 reference electrode and a Pt wire counter electrode were used for the electrochemical measurements. The working electrode was either an unmodified carbon paste electrode or TX-100/CPE. All the potentials were reported versus the Hg_2/Hg_2Cl_2 reference electrode. Digital pH meter MK VII from systronics was used to pH adjustment. All the experiments were carried at the room temperature.

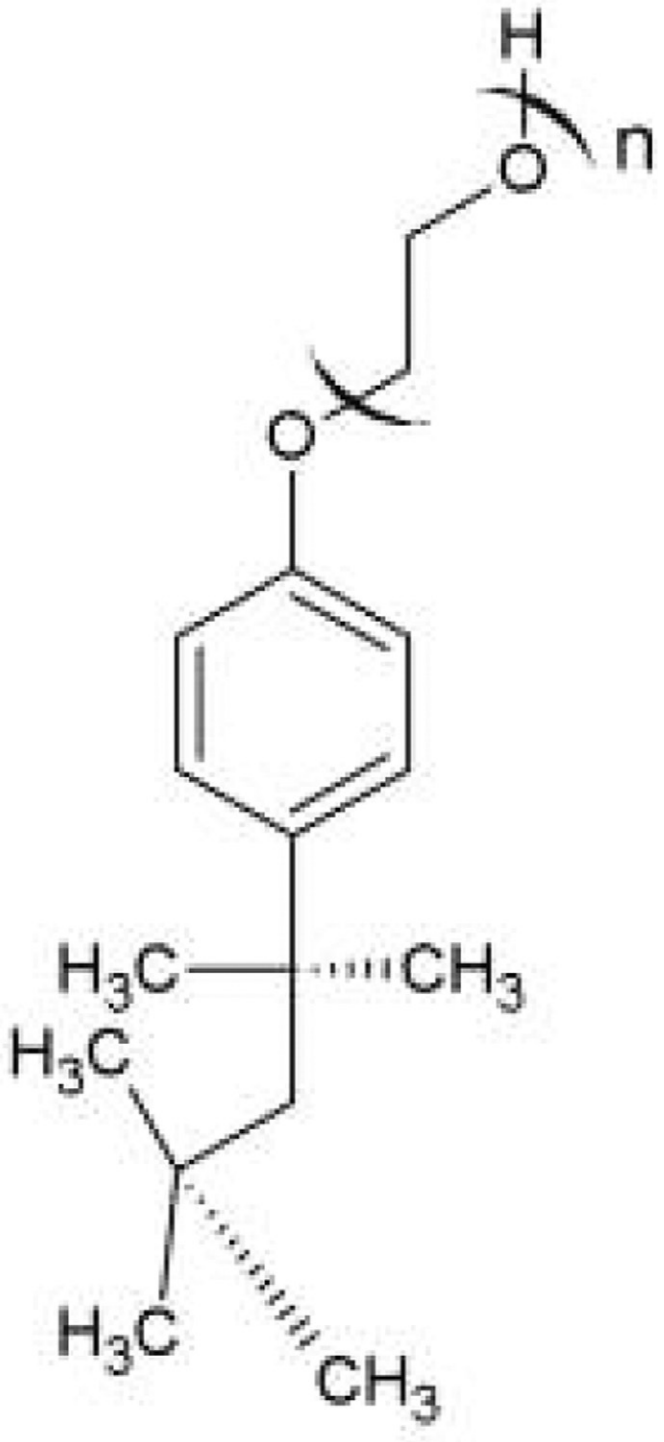
2.3. Preparation of modified electrodes

A ratio of 60:40 of the graphite powder and the silicon oil was mixed thoroughly until the formation of homogenous mixture. Round cylindrical teflon tube pierced with copper wire was packed with carbon paste and then smoothened over the butter paper. The modifier TX-100 solution was immobilized over the surface of the bare carbon paste electrode and left for some time intervals to optimized the TX-100/CPE and later switched into the analyte solution.

3. Results and discussion

3.1. Calibration and electrochemical characterization of TX-100/CPE

TX-100 is a neutral surfactant having long chain hydrophobic and hydrophilic groups is shown in Scheme 1. Different concentration series



Scheme 1. Structure of TX-100.