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Application of carbon-paste electrode modified with iron phthalocyanine for voltammetric determination of epinephrine in the presence of ascorbic acid and uric acid

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ABSTRACT

A carbon-paste electrode (CPE) modified with iron(II) phthalocyanine was used for the sensitive voltammetric determination of epinephrine (EN). The electrochemical response characteristics of the modified electrode toward EN, ascorbic acid (AA) and uric acid (UA) were investigated by cyclic and differential pulse voltammetry (CV and DPV). The results show an efficient catalytic activity of the electrode for the electro-oxidation of EN, which leads to improvement of reversibility of the electrode response and lowering its overpotential by more than 100 mV. The effect of pH and potential sweep rate on the mechanism of the electrode process was investigated. The modified electrode exhibits an efficient electron mediating behavior together with well-separated oxidation peaks for EN, AA and UA. Under the optimum pH of 4.0 in 0.1 M acetate buffer solution, the DPV anodic peak current showed a linear relation versus EN concentration in the range of 1–300 μM, with a correlation coefficient of 0.998 and a detection limit of 0.5 μM. High sensitivity and selectivity, sub-micromolar detection limit, high reproducibility, together with ease of preparation and regeneration of the electrode surface by simple polishing, make the electrode very suitable for the determination of EN in pharmaceutical and clinical preparations.

1. Introduction

Epinephrine (EN) is one of the most important neurotransmitters in mammalian central nervous systems, which exists in the nervous tissue and body fluids as large organic cations. This compound controls the nervous system in its performance for a series of biological reactions and nervous chemical processes [1]. Many diseases are related to changes of the EN concentration in living systems. It also serves as a chemical mediator for converting the nerve pulse to different organs. Medically, EN has been used as a common emergency healthcare medicine [2].

Quantitative determination of catecholamines, such as EN, is a significant field in developing nerve physiology, diagnosis and controlling medicine [3]. Several methods have been developed to determine EN in pharmaceutical and clinical samples. Determination of EN in the presence of ascorbic acid (AA) and uric acid (UA), because of their coexistence in human fluids, is attractive to biological and analytical researchers. Individual determinations of these compounds have been reported in many references; however, simultaneous determination of them has always been considered as a serious challenge in these studies. The electrochemical detection of EN on the surface of bare (unmodified) electrodes has some fundamental problems, mainly, high overpotential and sluggishness of the kinetics of the electrode process, which result in weak electrochemical responses. Moreover, the voltammetric response of the electrode to EN is commonly very close to those of AA and UA, and their signals usually overlap. As a result, the accuracy of the determinations is remarkably low in mixture samples. Recently, an enormous amount of research has been devoted to the development of new modified electrodes for monitoring EN [4–6]. Gold electrode modified with self-assembled monolayer (SAM) of triazole has been developed for simultaneous determination of EN and AA by adsorptive stripping voltammetry [7].

Application of various nanomaterials for the modification of the electrode surfaces and improvement of their electrochemical characteristics to EN has been the subject of interest in recent years. A mixed self-assembled monolayer of dithioeritritol and dodecanethiol from their solution in ethanol containing colloidal gold were formed onto the gold electrode [8]. The so prepared modified electrode was used for the voltammetric detection of EN. In another report, gold nanoparticles self-assembled with cysteamine

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were used for the modification of glassy carbon electrode [9]. The CV investigations showed an irreversible behavior for EN with a ΔE_p of 414 mV in phosphate buffer solution of pH 7.0.

A pretreated glassy carbon electrode (GCE) by electrochemical activation has been proposed for simultaneous determination of EN and UA by DPV [10]. In this method, the presence of a fivefold AA concentration had a serious interference in the voltammetric determination. Application of organic dyes (such as thionine) for modification of the electrode surfaces has been proposed for the simultaneous voltammetric determination of AA in the presence of dopamine (DA) [11] and UA [12].

Application of functionalized carbon nanotubes for modification of the electrode surfaces and voltammetric detection of EN is another area in the developing of the biosensors for the detection of biologically important compounds [13,14].

Application of transition metal complexes, as the electron mediators for lowering the overpotential of the electrode processes and improvement of the sensitivity of the voltammetric responses, is considered as an alternative for the electrochemical determinations of biologically important compounds [15–18]. Cobalt(II) hexacyanoferrate film on the surface of GCE has been used for the electrocatalytic oxidation of EN [19]. Metallophthalocyanines, in particular, provide an attractive option because of their versatility, high catalytic activity, and low cost of raw materials [20]. Iron(II) phthalocyanine and its complexes are of special interest because of their high catalytic activities in various chemical and electrochemical reactions. Application of these complexes as modifier in preparation of the chemically modified electrodes has shown numerous advantages, e.g., lowering the overvoltage, enhanced sensitivity and low detection limits [21–23]. In some reports, for example for amitrole [22] and ascorbic acid [17], axial coordination of the oxidizing analyte to the central iron ion in the structure of phthalocyanine complex provides a catalytic fashion for the electron transfer process. Electrocatalysis of epinephrine at gold electrode pre-modified with the self-assembled monolayer of cysteamine and subsequently integrated with novel metallo-octacarboxyphthalocyanine (MOCPc, M: Fe, Co and Mn) complexes (Au–Cys–MOCPc) was investigated. The electrodes showed sensitive response to the presence of epinephrine [23]. Self-assembled films of single-walled carbon nanotubes (SWCNT) integrated to cobalt(II) tetraaminophthalocyanine has been applied for the electrocatalytic detection of EN [24]. A carbon-paste electrode modified with multi-walled carbon nanotubes (MWCNT)/Nafion and cobalt(II) nitrosalophen has been reported for simultaneous determination of AA in the presence of UA [25].

In the present study, modification of carbon-paste electrode with iron(II) phthalocyanine is described. The prepared modified electrode was very efficient for the electrocatalytic oxidation of EN, AA and UA, in lowering their corresponding overpotentials and enhancing their voltammetric responses. The electrochemical investigations of mixture solutions of these three compounds showed three well-defined and well-separated sharp peaks. As such, the electrode can be considered as an efficient voltammetric sensor for simultaneous determinations in pharmaceutical and clinical samples, where these compounds may exist. The prepared voltammetric sensor demonstrated high selectivity, wide linear range, low detection limit (sub-micromolar for EN), long-time stability and very good response reproducibility together with ease of preparation and surface regeneration.

2. Experimental

2.1. Chemicals and reagents

EN, AA and UA were purchased from Merck. Graphite powder (1 μm), spectroscopic grade mineral oil (Nujol) and iron(II) phthalocyanine were received from Aldrich. All other chemicals were of analytical reagent grade from Merck.

Voltammetric experiments were carried out in buffered solutions of EN. A 0.1 M acetate solution was used to prepare the buffer solutions of pH 4 and 5. Phosphate buffers, 0.1 M, were used for pH 3, 6 and 7. All aqueous solutions were prepared with doubly distilled deionized water. All voltammetric investigations were performed in deoxygenated media by purging the solutions with pure argon (99.999% from Roham Gas Company, Tehran, Iran). Argon gas was passed over the solutions during all the measurements.

Adrenaline (EN) ampoules were purchased from local pharmacy. An ampoule was dissolved in 100 mL of pH 4.0 acetate buffer solution and used for the determinations by DPV method.

2.2. Preparation of carbon-paste electrodes

The carbon-paste electrode was prepared by mixing fine graphite powder with Nujol (~75:25, w/w) in a mortar and pestle. A portion of the composite mixture was packed into the end of a polyamide tube (ca. 2.5 mm i.d.). Electrical contact was made by forcing a copper pin down into the tube and into the back of the composite. To prepare the modified composite electrodes, 500 mg of the paste composite containing 3% (w/w) of iron(II) phthalocyanine (FePc) was mixed in 3 mL of dichloromethane. The mixture was stirred on a magnetic stirrer until the solvent evaporated. Then, the modified composite was air dried for 24 h and used in the same way as the unmodified electrode.

2.3. Apparatus

Voltammetric experiments were performed on a Metrohm potentiostat/galvanostat model 797VA. A conventional three-electrode system was used including a carbon-paste working electrode (unmodified or modified), a saturated Ag/AgCl reference electrode and a Pt wire counter electrode. A digital pH/mV/Ion meter (CyberScan model 2500) was used for pH measurements.

3. Results and discussion

3.1. Electrochemical behaviors of the FePc-modified electrode

Preliminary experiments to elucidate the catalytic activity of the Fe(II)Pc-modified electrode for EN, AA and UA were performed using CV and DPV. The voltammograms were recorded using unmodified and modified carbon-paste electrodes in argon saturated solutions. The CV of 1 mM solutions of these compounds in buffer solutions of pH 4.0 are shown in Fig. 1. As can be seen in Fig. 1A, electrochemical oxidation of EN (0.1 mM) on the surface of unmodified CPE shows a broad and totally irreversible wave with a peak potential of 523 mV. The corresponding anodic peak at the FePc-modified electrode was shifted to 401 mV. Besides lowering of the peak potential and increasing the peak current, the modified electrode enhanced reversibility of the system, which resulted in sharp waves and appearance of the reverse (cathodic) wave at 312 mV. The results obviously represent the catalytic action of FePc; decreasing the overpotential of the electrode process and facilitating the kinetics of the electron transfer on the surface of the modified electrode.

The catalytic role of FePc is also seen in the electro-oxidation of AA (0.1 mM) by lowering its anodic overpotential by more than 60 mV and improving its wave sharpness (Fig. 1B). However, in the case of 0.1 M UA, the modified electrode only caused a twofold increase in its anodic peak current (Fig. 1C), which can be related to the change in microscopic area of the electrode due to the presence of FePc. However, it can be seen that the peak potential for UA on the surfaces of both unmodified and modified electrodes is