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Electrochemical behaviors of adrenaline at acetylene black electrode in the presence of sodium dodecyl sulfate

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Abstract

The electrochemical behaviors of adrenaline at the acetylene black electrode in the presence of sodium dodecyl sulfate (SDS) were investigated by cyclic voltammetry and electrochemical impedance spectroscopy (EIS). The results indicated that the electrochemical responses of adrenaline were apparently improved by SDS, due to the enhanced accumulation of protonated adrenaline via electrostatic interaction with negatively charged SDS at the hydrophobic electrode surface. This was verified by the influences of different kinds of surfactants on the electrochemical signals of adrenaline. The electrochemical parameters of the adrenaline oxidation were explored by chronocoulometry. Under optimal working conditions, the oxidation peak current at 0.57 V was proportional to adrenaline concentration in the range of 5.0×10^{-8} to 7.0×10^{-6} mol/L, with a low detection limit of 1.0×10^{-8} mol/L for 70 s accumulation by differential pulse voltammetry (DPV). This method was applied to determine adrenaline in the hydrochloride injection sample. The results are satisfying compared with that by the standardized method of high performance liquid chromatography (HPLC).

Keywords: Adrenaline; Sodium dodecyl sulfate (SDS); Acetylene black electrode; Electrochemistry

1. Introduction

Adrenaline is a hormone secreted from the adrenal medulla, as an important catecholamine neurotransmitter in the mammalian central nervous system. Adrenaline has important biological functions, such as the effect on the storage and mobilisation of glycogen, fatty acids and the corresponding metabolic pathways, as well as α- and β-receptors. Pharmaceutically, adrenaline can be utilized for the rapid and early detection of neural disorders [1]. Therefore, a study on the detection of adrenaline is of great significance.

So far methods for the analysis of adrenaline mainly include spectrophotometry [2,3], fluorimetry [4], liquid chromatography (LC) [5–8], capillary electrophoresis (CE) [8,9], thermal lens microscopy (TLM) [10], chemi-luminescence (CL) [11] and electrochemical detection with various modified electrodes [12–14]. However, these methods are complicated [5–9] or tedious [10] and need extraction [7] or derivatization [4–6].

In this work a simple, rapid and sensitive electrochemical procedure for determination of adrenaline at the acetylene black electrode in the presence of surfactant SDS was proposed. Surfactants are a kind of amphiphilic ions or molecules with a hydrophilic head on one side and a long hydrophobic tail on the other side. They have been widely used in electrochemistry and electroanalysis chemistry field [15] to change the electrical properties of the electrode solution interface and the electrochemical process through adsorption at interfaces or aggregation into supramolecular structures [16]. Our group has successfully employed surfactants for the analysis of some biomolecules in previous works [17–20]. The results indicated that the electrochemical responses of analyzed objects were remarkably enhanced in the presence of surfactants.

In this paper, the experimental results showed that the anion surfactant SDS had a distinct enhancement effect on the electrochemical responses of adrenaline at the acetylene black electrode. The electrochemical parameters of the adrenaline

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oxidation were investigated by chronocoulometry, in which a fast-rising potential pulse is enforced on the working electrode of an electrochemical cell and the charge is monitored as a function of time. And some experimental conditions for the determination of adrenaline were optimized. The method with high sensitivity and low limit of detection was applied to the determination of adrenaline in the hydrochloride injection sample. The results are satisfying compared with that by the standardized method of HPLC.

2. Experimental

2.1. Reagents and apparatus

Adrenaline (Fluka) stock solution (pH 3.5) of 5.0×10^{-3} mol/L was prepared by dissolving in deoxidized double-distilled water together with several drops of 0.01 mol/L HCl and kept at 4 °C in darkness. The adrenaline standard solutions were diluted to desired concentrations before use with water. Acetylene black was obtained from Shanghai Reagent Corporation, China. SDS (purchased from Shanghai Reagent Corporation, China) was dissolved in double-distilled water to form 1.0×10^{-2} mol/L homogeneous solutions. All chemicals were of analytical grade quality and were used without further purification. The experimental results were obtained at room temperature.

Electrochemical measurements were performed on a CHI 660 electrochemical analyzer (Chenhua Co., Shanghai, China) in a three-electrode system containing an acetylene black working electrode (2.7 mm in diameter), a Pt wire counter electrode and a saturated calomel reference electrode (SCE). The acetylene black electrode was prepared as follows [21]: 100 mg acetylene black and 150 μL paraffin oil were mixed in a small mortar to form a homogeneous acetylene black mixture. The mixture was pressed by hand into the end cavity of a home-made polytetrafluoroethylene (PTFE) cylindrical electrode body and the electrode surface was polished manually on a piece of weighing paper. The electrochemical impedance spectroscopy (EIS) was carried out with the EG&G Model 273 electrochemical workstation and EG&G Model 5210 lock-in amplifier (Princeton Applied Research, PAR, USA) powered by Echem Software. The frequency range was from 100 MHz to 100 kHz. The dc potential was the average potential of the oxidation and the reduction peaks and the amplitude was 5 mV. Prior to the measurements, the working electrode was held at rest for 10 s to ensure equilibrium unless stated otherwise. HPLC system consisted of a LC-10AD model pump (Shimadzu, Japan), SPD-10AV UV–vis detector, Kromasil ODS analytical column (5 μm, 4.6 mm × 250 mm), N2000 chromatographic workstation (Zhida, China) and 20 μL injection loop. The chromatographic conditions at the Chinese Pharmacopoeia (ChP, 2000 version) included the C18 column and the mobile phase was prepared with 0.14% sodium heptanesulfonate solution and methanol (65:35, v/v) adjusted pH to 3.1 by phosphoric acid and delivered at a constant flow-rate of 0.6 mL/min.

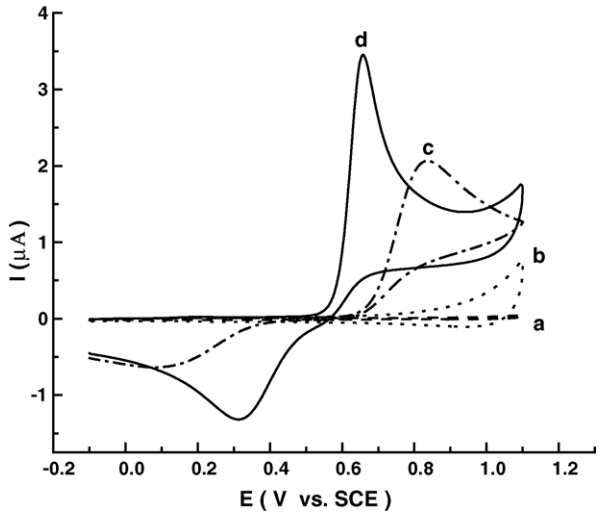

Fig. 1. Cyclic voltammorgrams in 0.5 mol/L sulfuric acid at an acetylene black electrode: (a) in the absence of adrenaline and SDS; (b) in the presence of SDS; (c) in the presence of adrenaline; (d) in the presence of adrenaline and SDS. Scan rate: 100 mv/s; accumulation time: 70 s; adrenaline: 1.0×10^{-4} mol/L; SDS: 1.0×10^{-4} mol/L.

2.2. Analytical procedure

The electrochemical experiments were carried out in a conventional electrochemical cell, containing 5 mL volume of 0.5 mol/L sulfuric acid as the supporting electrolyte and a certain concentration of adrenaline and SDS. After accumulating at open circuit for 70 s with stirring the solution and keeping quiescent for 10 s, the voltammograms were recorded with the potential swept from −0.1 to 1.1 V and a scan rate of 100 mv/s.

3. Results and discussion

3.1. The cyclic voltammetric behaviors of adrenaline

Fig. 1 illustrates the cyclic voltammetric responses of adrenaline at the acetylene black electrode. It can be seen that no apparent cyclic voltammetric signals appear in the blank buffer solution (curve a). In the absence of SDS adrenaline exhibits a weak anodic peak at 0.83 V and a broad cathodic peak at 0.10 V in the reverse scan (curve c). After the addition of 1.0×10^{-4} mol/L SDS, the anodic and cathodic currents of adrenaline are both markedly enhanced. The anodic peak potential shifts negatively to 0.65 V and the cathodic peak potential shifts positively to 0.31 V (curve d). And no peak is observed in the solution only containing SDS (curve b). It suggests that the redox process of adrenaline is facilitated by the added anionic surfactant SDS.

As is well known, adrenaline contains two phenolic substituents, which may be oxidized [22]. The electrochemical reaction of adrenaline can be written as Scheme 1. The redox peaks of adrenaline correspond to the oxophenic acid/*o*-quinone couple.

It is known that the anion surfactant SDS can be adsorbed on the acetylene electrode surface via hydrophobic interaction with the paraffin oil and then forms a negatively charged hydrophilic