Journal of Molecular Liquids 177 (2013) 32–39

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Sodium do-decyl benzene sulfate modified carbon paste electrode as an electrochemical sensor for the simultaneous analysis of dopamine, ascorbic acid and uric acid: A voltammetric study

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ARTICLE INFO

Article history:
Received 2 February 2012
Received in revised form 27 September 2012
Accepted 1 October 2012
Available online 24 October 2012

Keywords:
Dopamine
Simultaneous
Cyclic voltammetry
Surfactant modified electrode

ABSTRACT

Sodium do-decyl benzene sulfate modified carbon paste electrode (DDBSMCPE) was first employed for the simultaneous determination of dopamine (DA), uric acid (UA), and ascorbic acid (AA). The modified CPE displayed excellent electrochemical catalytic activities. The oxidation over potentials of DA, UA and AA decreases significantly and their oxidation peak currents increases dramatically at DDBSMCPE. Differential pulse voltammetry (DPV) was used for the simultaneous determination of UA, DA and AA in their ternary mixture. The peak separation between UA-DA and DA-AA is 152 mV and 221 mV, respectively, and the detection limit was 0.01 μM for DA. The proposed method improved sensitivity for the determination of DA by more than one order of magnitude. The present method was applied to the determination of DA in real sample by using standard addition method and the obtained results were satisfactory with a good recovery of 98%.

1. Introduction

A large number of molecular processes in chemically, physically and biologically related systems occur at solid–liquid, liquid–liquid and liquid–gas interfaces, which modify the dynamic behaviour of molecules relative to their bulk properties [1]. The structural and dynamic properties of adsorbed surfactant molecular films are therefore of both fundamental and applied interest [2]. Surfactant molecules exhibit an amphiphilic or amphipathic behaviour and they bear an ionic (zwitterionic, anionic, or cationic) or non-ionic polar head group and a hydrophobic portion. The self-assembled aggregates of amphiphilic surfactant molecules formed on solid surfaces are important as models for biological membranes [3]. In fact, the adsorption of surfactants on solid surfaces allows the simulation of membrane-like structures which can be used in diverse biological/industrial processes such as protein immobilization, charge and mass transfer, membrane solubilization and disruption, etc [4–6].

Parkinson's disease is one of the most dreadful neurodegenerative disorders of the central nervous system, as its complete cure is not possible even today. Tremor, rigidity, bradykinesia and postural instability are some of its common diagnostic features. This disease occurs when dopaminergic neurons malfunction, or are destructed, which is accompanied by a sharp decline in dopamine level [7–9]. DA is a catecholamine neurotransmitter which is generated in various parts of central and peripheral nervous system and has an agonist action on β adrenoceptors. DA has positive chronotropic and ionotropic effects on myocardium which stimulates cardiac contractility and enhances heart beat rate. Electrochemical detection of DA is a preferred method because DA is electrochemically active. In addition, electrochemical methods offer advantages such as simplicity, speed, and sensitivity.

A major problem in the electrochemical detection of DA is the coexistence of other biologically important compounds including ascorbic acid (AA) and uric acid (UA) at a higher concentration [10]. Ascorbic acid is a vital component in human diet. It is known to take part in some biological reactions and is present in mammalian brain [11]. Recent clinical studies have demonstrated that the content of ascorbic acid in biological fluids can be used to assess the amount of oxidation stress in human metabolism [12,13] and excessive oxidative stress lead to cancer, diabetes mellitus and hepatic diseases.

Uric acid is the principal final product of purine metabolism in the human body [14]. It has been shown that extreme abnormalities of UA levels are symptoms of several diseases (e.g. gout, hyperuricaemia and Lesch–Nyhan syndrome) [15–17]. Other diseases, such as leukaemia and pneumonia are also associated with enhanced urate levels [16]. In general, electroactive UA can be irreversibly oxidized in aqueous solution and the major product is allantoin [18]. Among many methods for determination of DA, AA and UA in biological samples, electrochemical techniques with modified electrodes have been shown to be powerful tools due to their advantages of being simple, inexpensive and possibility of fast analysis in combination with high sensitivity and selectivity [19]. Thus, different kinds of modified electrodes have been fabricated for detection of DA, AA and UA [19–24]. Even though all these electrodes are having some advantages they have many limitations too. So the real challenge is in developing simple, reliable and efficient sensors with

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http://dx.doi.org/10.1016/j.molliq.2012.10.002

enhanced characteristics for effective sensing of DA, AA and UA simultaneously.

In recent years, surfactant modified electrodes have provoked much more attention in electro analysis because of their novel physical and chemical properties [23,25–27]. In particular, the catalytic properties of some surfactants cause a decrease in the over potential needed for a redox reaction to become kinetically viable, producing voltammetry which appears more reversible than that displayed by the same material in an unmodified electrode form [28]. Moreover, the use of surfactant-modified electrodes presents some other advantages like high effective mass transport catalyzes and controls the local environment [29,30]. Carbon paste electrode (CPE) is one of the convenient conductive matrices to prepare the chemically modified electrodes (CMEs) by the simple mixing of graphite/binder paste and modifier [31,32]. These kinds of electrodes are inexpensive and possess many advantages such as low background current, wide range of used potential, ease of fabrication, and rapid renewal. In this work, a novel biosensor has been fabricated by using a carbon paste electrode (CPE) immobilized with sodium do-decyl benzene sulfate (DDBS) for simultaneous electrochemical determination of AA, DA and UA. As already known, DDBS is an anionic surfactant which contains benzene in its structure and the SDS has a hydroxy group, which could be covalently bound to the edge plane sites of the carbon surface through the oxygen atom.

2. Materials and methods

2.1. Reagents and Chemicals

Dopamine hydrochloride, ascorbic acid, uric acid was purchased from Himedia Company. All chemicals were of analytical grade quality and were used without further purification. 1×10^{-6} M stock solution of DA was prepared by dissolving it in 0.1 M perchloric acid solution. 1×10^{-4} M stock solution of AA was prepared by dissolving it in double distilled water and 1×10^{-4} M stock solution of UA was prepared by dissolving it in 0.1 M NaOH. The supporting electrolyte used was the phosphate buffer solution (PBS). It was prepared by mixing standard stock solutions of 0.1 M disodium-hydrogen phosphate and sodium dihydrogen phosphate by adjusting the pH.

2.2. Apparatus and procedure

Cyclic voltammetry (CV) was performed on Model EA-201 Electroanalyser (EA-201, Chemilink System). All the experiments were carried out in a conventional three electrode electrochemical cell. The electrode system contained a carbon paste working electrode (3.0 mm in diameter), a platinum wire counter electrode and a saturated calomel reference electrode (SCE). The bare carbon paste electrode (BCPE) was prepared by grinding 70% graphite powder (particle size 50 mm and bulk density 20–30 g/100 mL from Loba chemical company) and silicon oil (viscosity 300 cps at 20° from Himedia chemical company) to produce a homogeneous carbon paste electrode. The carbon paste was then packed into the cavity of a homemade carbon paste electrode body and smoothened on a weighing paper. DDBS modified carbon paste electrode (DDBSMCPE) was prepared by immobilizing 25 μL of 0.1 mM DDBS on the surface of the carbon paste electrode for 20 minutes.

3. Results and discussion

3.1. Electrochemical response of potassium Ferro cyanide on DDBSMCPE

Fig. 1 demonstrates the cyclic voltammograms of $K_4Fe(CN)_6$ (1 mM) at BCPE and DDBSMCPE at sweep rate of 50 mV/s. The $K_4Fe(CN)_6$ showed poor sensitivity and reproducibility at BCPE (dashed line) compared to DDBSMCPE. The cyclic voltammogram of $K_4Fe(CN)_6$, in 1 M KCl as supporting electrolyte at sweep rate of 50 mV/s showed its anodic (Epa) and cathodic peak potentials (Epc) at 240 mV and 208 mV

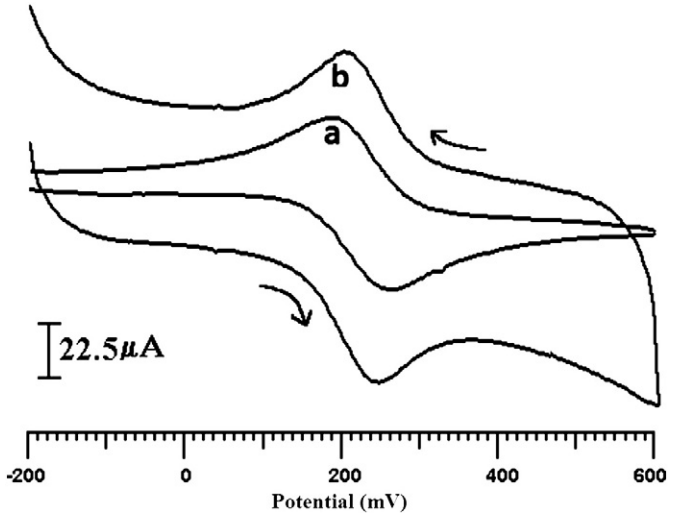

Fig. 1. Cyclic voltammogram 1 mM potassium ferrocyanide in 1 M KCl at BCPE (a) and DDBSMCPE (b) with a scan rate of 50 mV/s.

respectively. The peak potential difference (ΔEp) was found to be 32 mV. However, in the same condition DDBSMCPE exhibited good sensitivity for $K_4Fe(CN)_6$ and both anodic and cathodic peak current signals got enhanced when compared to the BCPE. The Epa and Epc were located at 257 mV and 196 mV. The ΔEp was found to be 61 mV. The enhancement of peak current shows electro catalytic activity of DDBSMCPE.

3.2. The effect of concentration and immobilization time of DDBS on voltammetric response of $K_4Fe(CN)_6$

To improve the performance of the biosensor, various factors influencing the response of the sensor such as the concentration of surfactant and the immobilization time were investigated. It can be seen that the biosensor prepared with 25 μL of 0.1 mM DDBS surfactant solution has a maximum current response. The reason may be that DDBS surfactant molecule diffuses into the carbon paste electrode along with the $K_4Fe(CN)_6$, which results in the increase in current signal. If the concentration of DDBS is low, the rate of diffusion is low and the response of the biosensor is also low. However, if the concentration of DDBS is 0.1 mM it can show maximum current response at 25 μL DDBS. Therefore 25 μL of 0.1 mM DDBS was selected as the suitable amount for further studies. However, a higher concentration of mediator produced a larger background current. Thus, 25 μL DDBS was chosen in the subsequent experiments.

25 μL DDBS was immobilized on the surface of carbon paste electrode and the immobilization time was varied from 5 to 30 minutes. Fig. 2 shows the current response of the modified electrode increased gradually with increase in immobilization time, reaching a maximal value at 20 minutes and then decreases with further increase of immobilization time. Therefore a time gap of 20 minutes was chosen for the diffusion of the DDBS molecule into the porous carbon paste electrode. Such a behavior is typical of a mediator-based sensor [33,34]. Therefore, 20 minutes was selected as the immobilization time for the further analysis.

3.3. Surface morphology of DDBSMCPE

Fig. 3 explains the surface morphology of bare carbon paste electrode (A) and DDBSMCPE (B) using scanning electron microscopy. The surface of bare carbon paste electrode was irregularly shaped micrometer sized flakes of graphite. However, the DDBS film coated carbon paste electrode has typical uniform arrangement of DDBS molecules on the surface of carbon paste electrode. This confirms that the carbon paste electrode was coated by the modifier film.