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Exploiting micellar environment for simultaneous electrochemical determination of ascorbic acid and dopamine

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Abstract

A simple and reliable method for simultaneous electrochemical determination of ascorbic acid (AA) and dopamine (DA) is presented in this work. It was based on the use of the cationic surfactant cetylpyridinium chloride (CPC) that enables the separation of the oxidation peaks potential of AA and DA. Cyclic voltammetry (CV) as well as pulse differential voltammetry (PDV) were used in order to verify the voltammetric behaviour in micellar media. In the cationic surfactant CPC, a remarkable electrostatic interaction is established with negatively charged AA, as a consequence, the oxidation peak potential shifted toward less positive potential and the peak current increased. On the other hand, the positively charged DA is repelled from the electrode surface and the oxidation peak potential shifts toward more positive potential in comparison to the bare electrode. Therefore, the common overlapped oxidation peaks of AA and DA can be circumventing by using CPC. Parameter that affects the E_{pa} and I_{pa} such as CPC concentration and pH were studied. Under optimised conditions, the method presented a linear response to AA and DA in the concentration range from 5 to 75 μmol L^{-1} and 10 to 100 μmol L^{-1}, respectively. The proposed method was successfully applied to the simultaneous determination of AA and DA in dopamine hydrochloride injection (DHI) samples spiked with AA.

Keywords: Dopamine; Ascorbic acid; Differential pulse voltammetry; Cyclic voltammetry; Cationic surfactant; Micelles

1. Introduction

The selective determination of dopamine (DA) in the presence of ascorbic acid (AA) has received considerable attention [1]. The concentration of DA, AA and others neurotransmitters in biological samples is changed from species to species, in a wide range, from 10^{-7} to 10^{-3} mol L^{-1} [1]. Hence, selectivity and sensitivity are important in the development of any procedure for the determination of DA, as well as of any neurotransmitter [1]. DA is one of the most significant catecholamines and plays a very important role in the functioning of the central nervous system, as well as in the cardiovascular, renal and hormonal systems [1–4]. Similarly, AA (Vitamin C) has been used for the prevention and treatment of common cold, mental illness, infertility and cancer [2]. In mammalian tissue, AA is present along with several neurotransmitters including dopamine [2,3]. Thus, simultaneous determination of DA and AA is a problem of critical importance in field of neurochemistry and biomedical chemistry [2]. Both, DA and AA, are compounds that can be determined for electrochemical methods based on anodic oxidation [1,2]. However, a major problem is, the oxidation potential for both AA and DA occurs almost in the same potential at unmodified electrodes, which result in overlapped voltammetric responses making their discrimination highly difficult [2,5].

Therefore, a number of chemically modified electrodes have been developed to separate the electrochemical response of DA and AA [6–19]. For instance, self-assembled monolayers of ω-mercapto-carboxylic acid and stearic acid deposited on a gold electrode and on a graphite paste electrode [6,7],

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adsorption of pyrocatechol sulfonephthalein [10] and electrochemical polymerization of *N*,*N*-dimethyl aniline [13] on a glassy carbon electrode were used to shift the oxidation potential of ascorbic acid towards a more positive value, thus, separating its anodic peak from the dopamine ones.

Among other strategies reported to overcome this drawback, a convenient way is to cover the electrode surface with a positive or negative charged permselective membrane. These ion exchange membranes of both cationic and anionic nature have been developed to electrostatically accumulate/trap oppositely charged molecules. Among them, Nafion [20], poly(ester sulfonic acid) and poly(4-vinylpyridine) [21] are the most common. However, there is still an expanding demand for the development of a simple, reliable and efficient methodology for the simultaneous determination of AA and DA [1,2,4].

In the electroanalysis of neurotransmitters, carbon electrodes have been widely used in comparison to the metal electrodes due to its biocompatibility with tissue, having low residual current over a wide potential range and minimal propensity to show a deteriorated response as a result of the electrode fouling [13,22–25].

According to Rusling [26] and Sivagnam and Palaniandavar [27], micellar aggregates (composed by surfactants) may mediate catalytic systems, thus, presenting strong attractive for the development of new methodologies based on the surfactants at the electrode surface. Among these strong attractive, significant change in the redox potential, charge transfer and diffusion coefficients of the electrode processes, stability of electrogenerated intermediates and products derived from electrochemical reactions, as well as in redox events in biological systems can be considered [26–28]. Thus, Szymula and Narkiewicz-Michalek [29] have studied the behaviour of electrochemical oxidation of ascorbic acid in aqueous solution with the surfactants sodium dodecylsulphate (SDS-anionic), sodium-bis(2-ethylhexyl)sulfosuccinate (AOT-anionic), octylphenol ethoxylate (Triton X-100-nonionic) and cetyltrimethylammonium bromide (CTAB-cationic). It was verified that surfactants shift the oxidation peak potential of the ascorbic acid and change the peak current value, mainly due to the surfactant film formed at the electrode/solution interface. Based on this fact, the negative charged ascorbic acid has a tendency to accumulate in the positively charged crown of cationic micelles, which enhances the rate of oxidation and consequently provoke an increase in the peak current. However, the nonionic and anionic surfactants act in an opposite way.

Moreover, surfactants play a very important role in the increase of the solubility of an organic substance, which is either insoluble or sparingly soluble in water [26,27]. Jaiswal et al. [30] reported that the oxidation potential of the Vitamin E (α-tocopherol) was shifted, in cationic surfactant medium, toward more positive value in comparison to the anionic or nonionic surfactants, in mixed solvent systems of surfactant/ethanol/water and surfactant/acetonitrile/water. The simultaneous determination of Vitamin E and ascorbic acid was carried out in the above solvent systems.

Thus, the present work describes a study based on cyclic voltammetry and differential pulse voltammetry techniques, for simultaneous determination of AA and DA in cationic CPC micellar system (cetylpyridinium chloride), using a glassy carbon electrode as a working electrode. Since these compounds exhibit opposite micellar effect their overlapped anodic peaks can be separated in the micellar solution.

2. Experimental

All electrochemical experiments were performed using a potentiostat/galvanostat Autolab® PGSTAT-12 (Eco Chemie B.V., The Netherlands). Experiments were performed in a conventional single-compartment three-electrode cell. A glassy carbon electrode (Metrohm, 2.0 mm in diameter) employed as a working electrode was carefully polished with 0.5 μm alumina slurry on a flat surface, rinsed thoroughly with deionized water, and then sonicated immediately before using in deionized water for 2 min. A platinum wire was employed as an auxiliary electrode. All potentials were recorded in relation to a saturated calomel reference electrode (SCE).

All reagents such as 3,4-dihydroxyphenylamine (dopamine, DA, Sigma–Aldrich), ascorbic acid (AA, Sigma–Aldrich) and cetylpyridinium chloride (CPC, Sigma–Aldrich), were used as received without further purification. Aqueous solutions were prepared with deionized water ($\rho > 18.2\,M\Omega$, Millipore Milli-Q system) and other chemicals used were of analytical grade. All electrochemical experiments were carried out under an atmosphere of high purity nitrogen and at room temperature. For voltammetric experiments, unless otherwise indicated, a 0.1 mol L^{-1} aqueous phosphate buffer ($4.0 \leq pH \leq 8.0$) solution was used as supporting electrolyte. The potential for voltammetric experiments was recorded from −200 to +700 mV.

3. Results and discussion

3.1. Electrochemical oxidation of DA and AA

The cyclic voltammograms recorded with DA at glassy carbon electrode in 0.1 mol L^{-1} phosphate buffer (pH 6.0) in the absence (dashed line) and in the presence of cationic surfactant CPC (solid line) are shown in Fig. 1A. As shown, in the absence of CPC the oxidation of DA takes place at 250 mV and a quasi-reversible cyclic voltammogram is verified. The electron transfer for the oxidation of DA, in the presence of cationic surfactant cetylpyridinium chloride, is rather sluggish presumably due to the electrostatic repulsion of positively charged DA (pK_a 8.92) [1,3,31,32] with the cationic surfactant CPC (Fig. 1A, solid line). Adding CPC to the solution a shift of the anodic peak potential, E_{pa}, toward more positive values and cathodic peak potential, E_{pc},