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An improved method for simultaneous square-wave voltammetric determination of amlodipine and enalapril at multi-walled carbon nanotubes paste electrode based on effect of cationic surfactant

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ABSTRACT

A reproducible and sensitive analytical procedure has been developed for the simultaneous determination of amlodipine (AML) and enalapril (ENP) by square-wave voltammetry using a multi-walled carbon nanotubes paste electrode in the presence of cationic surfactant cetyltrimethylammonium bromide (CTAB). The experimental parameters, such as concentration and type of cationic surfactant, pH of Britton–Robinson (BR) buffer, and amount of carbon nanotubes in the paste were optimized. The anodic peak potentials of AML and ENP at multi-walled carbon nanotubes paste (MWCNTsP) electrode were found to be 0.790 and 1.21 V [vs. Ag/AgCl (3.0 mol L^{-1} KCl)], respectively by square-wave voltammetry, whereas at a GCE was 0.753 V for AML and no peak potential was observed for ENP. In addition, the surfactant has been found to influence the electrochemical determination by the way enhanced of better repeatability of analytical signals for AML and it was possible the simultaneous direct determination of AML and ENP on the MWCNTsP electrode, without pre-concentration of the antihypertensives into the working electrode before each determination. Under optimized conditions in Britton–Robinson buffer (pH 6.0) containing 10 μmol L^{-1} CTAB, linear calibration curves were obtained in the range of 0.58–5.9 μmol L^{-1} for AML and 2.0–57 μmol L^{-1} for ENP, which shows adequate for the quantification in real samples. The limit of detection was 0.049 and 0.81 μmol L^{-1}, respectively, for AML and ENP. The proposed method was used to estimate the amounts of individual and simultaneous antihypertensives in pharmaceutical formulations. Statistical comparison between the results obtained by this method and those obtained by the chromatography method was carried out and no significant difference was observed.

1. Introduction

Amlodipine besylate (AML) and enalapril maleate (ENP) are two antihypertensive drugs found conjugated in several pharmaceutical formulations. Amlodipine besylate (AML) is a calcium channel blocker [1,2] and enalapril maleate (ENP) is a prodrug (an ethyl ester) that after the action of circulating and hepatic esterases is hydrolyzed to an active compound, enalaprilat [1,3]. Many patients have achieved adequate blood pressure control with the use of antihypertensive. The combination AML–ENP is among the preferred antihypertensive combined drugs for the treatment of high blood pressure, heart failure and artery disease in hypertensive patients [1]. Therefore, the development of simple, sensitive and accurate analytical method for simultaneous determination of both compounds in pharmaceuticals is of paramount importance, especially for quality control purpose.

Some of the analytical techniques that have been used for AML and ENP determination in pharmaceutical formulations and biological fluids include high performance liquid chromatography (HPLC) [3–7], colorimetry [8], spectrophotometry [9–14], and potentiometry [15]. The use of HPLC is preferred over other methods because of the possibility of simultaneous determination of AML and ENP, without interferences. However, these techniques may suffer from some disadvantages, such as high maintenance and acquisition cost, time-consuming analysis, and requirement for sample pretreatment, and in some cases low selectivity and sensitivity.

Compared with other methods, voltammetric methods have low-cost instrumentation, high sensitivity, good stability, and

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simplicity in preparation of sample. Square-wave voltammetry constitute a highly convenient alternative technique for the determination of a wide range of analytes [16–21].

Carbon-based materials such as glassy carbon or carbon nanotubes or mercury electrode are widely used as electrode in voltammetric analysis of AML [22–27]. However, stripping methods have been the most used procedure for the determination of AML [20–24]. Kazemipour et al. [22] determined AML in some commercial products using a carbon paste electrode by means of anodic stripping voltammetry. The analytical curve was linear in the AML concentration range 1.0–100 nmol L^{-1}, with a detection limit of 0.20 nmol L^{-1} at pH 11.0. Stoiljković et al. [23] employed a gold electrode modified with oxidized multi-walled carbon nanotubes to determination of AML in tablets using an anodic square-wave stripping voltammetry. This electrode showed a linear response to AML in the concentration range 14–21 μmol L^{-1} in phosphate buffer solution (pH 11.0). Gazy [24] used a glassy carbon electrode (GCE) to adsorptive square-wave anodic stripping voltammetric determination of AML in Britton–Robinson (BR) buffer solution (pH 11.0). This method presented a linear analytical curve in the range 0.04–2.0 μmol L^{-1}, with a detection limit of 0.014 μmol L^{-1}. The procedure was applied in tablets and biological samples. Omar et al. [25] used a Hanging Mercury Dropping Electrode (HMDE) to square-wave adsorptive cathodic stripping voltammetric determination of AML in pharmaceutical and biological samples. The analytical curve was linear in the AML concentration range 0.45–65000 nmol L^{-1}, with detection limit of 0.36 mol L^{-1} using phosphate buffer solution (pH 7.0).

There are few methods for direct determination of AML, without pre-concentration of analyte in the electrode surface. Altiokka et al. [26] developed a procedure to voltammetric determination of AML using a GCE under rotating conditions by the differential-pulse voltammetry in 0.2 mol L^{-1} KCl, 0.1 mol L^{-1} phosphate buffer, and 10% (v/v) of methanol (pH 5.5). This procedure showed a detection limit of 70 μmol L^{-1} and it was applied in pharmaceutical formulations. Goyal and Bishnoi [27] used a single- and multi-walled carbon nanotubes modified edge plane pyrolytic graphite electrodes (EPPGE) to square-wave voltammetric determination of AML in phosphate buffer solution (pH 7.2). The analytical curves were linear in the range 5.0–1000 nmol L^{-1} with detection limit of 1.0 nmol L^{-1} and 5.0 nmol L^{-1}, respectively, for SWNT/EPPGE and MWNT/EPPGE. A comparison of electrocatalytic activities of SWNT and MWNT modified electrodes indicated that SWNT/EPPGE was more sensitive in comparison to MWNT/EPPGE. The SWNT/EPPGE was employed to determination of AML in tablets and human body fluids.

Very few electrochemical methods have been described for the voltammetric determination of ENP in pharmaceutical and biological samples [28,29] and no studies related to voltammetric determination of ENP on carbon-type electrode were reported. Mercury film electrodes [28] and static mercury dropping electrode (SMDE) [29] were employed for determination of ENP in pharmaceutical formulations and biological samples. Linear calibration curves were obtained in concentration range 4.0–2600 μmol L^{-1} and 53–2700 μmol L^{-1}, respectively. Despite the previously published reports, at the best of our knowledge, there are no attempts at the development of voltammetric methods for simultaneous determination of AML and ENP in pharmaceutical forms or biological fluids.

In this sense, the use carbon paste electrode aiming at development of simple, low cost, reproducible and sensitive electroanalytical procedure seems to be very attractive due to easy renewal and easy modification of surface. It is constructed by a mixture of carbon material and binder in a suitable holder, in which your response is affected by both materials. The carbon material used in composition of paste can be functionalized carbon nanotubes, which facilities the electron transfer and offer an improvement in the analytical sensitivity and selectivity [19,30–34].

The use of surfactants in electroanalytical procedure has also been reported for improving the electrochemical measurements. They are molecules that have hydrophobic and/or hydrophilic structural regions. They can be adsorbed in the surface of electrode and modify the properties of electrode/solution, enhancing stability, selectivity and detection sensitivity, as reported in the literature [35–39]. Cetyltrimethylammonium bromide (CTAB) is a cationic surfactant, the positive charges of CTAB can adsorb in the oxidized carbon nanotubes and influencing the electrochemical response of analyte at electrode surface.

According to aforementioned, this work deals with the use of surfactant CTAB and the functionalized MWCNTsP electrode for simultaneous voltammetric determination of AML and ENP for the first time. This study involves the adsorption of CTAB at the functionalized carbon nanotubes (oxidized by use of acid treatment) from aqueous surfactant solution. Oxidation potentials for both analytes are distinct without the need for prior separation or deposition steps for simultaneous determination. The performance obtained by multi-walled carbon nanotubes paste (MWCNTsP) electrode was also compared with a GCE. The proposed procedure was applied in determination of AML and ENP in single and combined pharmaceutical formulations.

2. Experimental

2.1. Reagents and solutions

Amlodipine besylate, enalapril maleate, and mineral oil (Nujol®) from Sigma-Aldrich, boric acid, acetic acid, orthophosphoric acid, and sodium hydroxide from Merck, ethanol from Synth, cetyltrimethylammonium bromide (CTAB) and cetylpyridinium bromide (CPB) from Acros were used as received without purifications. Solutions were prepared with ultra-purified water supplied by a Milli-Q system (Millipore®) with resistivity greater than 18 MΩ cm.

Multi-walled carbon nanotubes (MWCNTs; of 10–40 nm in diameter and 5–20 μm in length; purit: 93%) was obtained from CNT Co. Ltd., Korea.

Commercial pharmaceutical samples used in this studies were: amlodipine tablets labeled 13.8 mg AML, enalapril tablets labeled 10 mg ENP, and amlodipine:enalapril capsules labeled 3.47:10, 6.9:10, and 6.9:20 mg. AML in dosages 3.47, 6.9, and 13.8 mg are equivalent for 2.5, 5mg, and 10 mg of amlodipine base per capsule, respectively. These samples were purchased from local drugstore in city of Londrina, state of Paraná, in Brazil.

A 10 mmol L^{-1} AML and 10 mmol L^{-1} ENP ethanolic stock solutions were prepared before use. All AML and ENP working solutions were prepared by dilution of these stock solutions with a Britton–Robinson (BR) buffer solution (pH 6.0). This BR buffer solution was used as supporting electrolyte for all experiments. It was prepared by mixing 0.04 mol L^{-1} acetic, orthophosphoric, and boric acid solutions; the final pH was adjusted by adding suitable amounts of a 2.0 mol L^{-1} sodium hydroxide solution.

A 10 mmol L^{-1} CTAB aqueous stock solution was prepared before use. All CTAB working solutions were prepared by dilution of this stock solution with a BR buffer solution (pH 6.0).

2.2. Equipments and electrodes

Voltammetric measurements were carried out using a PalmSens potentiostat/galvanostat controlled with the PalmSens PC