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Adsorption effect of a cationic surfactant at carbon paste electrode as a sensitive sensor for study and detection of folic acid



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ABSTRACT

The present study is the first report on the effect of cetyltrimethylammonium bromide (CTAB) on the electrochemical behavior of folic acid (FA) at the surface of carbon paste electrode (CPE) in real samples. The studies were performed by cyclic voltammetry (CV), chronocoulometry and differential pulse voltammetry (DPV). CTAB, with a hydrophobic C–H chain, could adsorb at the CPE surface by hydrophobic interaction and then changed the electrode/solution interface, and eventually affects the electrochemical response of FA, confirming from the remarkable oxidation peak current enhancement. For investigation of the electrode properties, CV technique was used at the various scan rates. Electrochemical parameters including diffusion coefficient (D), electron transfer coefficient (α) and ionic exchanging current density (j_0) were determined for the FA at the surface of the electrode. Under optimized conditions, the proposed method showed acceptable analytical performances for FA in terms of linearity (over the concentration range from 0.01 to 1.5 and 1.5 to 10.0 μM), detection limit (2.89 nM), repeatability (1.37%) and stability (13% reduction in peak current after 60 days). After studying on the effect of probable interferences it was found that the method was free of the interferences. Finally, the proposed method was successfully applied for the determination of FA in real samples.

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1. Introduction

Surfactants, containing hydrophilic and hydrophobic groups, can change the properties of the electrode/solution interface and subsequently influence the electrochemical processes of other substances [1]. Adsorption of a surfactant on the electrode surface might significantly facilitate the electron transfer, greatly enhance the peak current, change the redox potentials and alter the stability of electrogenerated intermediates or electrochemical products [2,3].

Folic acid (FA) (Fig. 1) is a B-group vitamin which has a major role in biological functions of cell metabolism like DNA replication, repair and methylation, synthesis of nucleotides, vitamins, amino acids, etc. An inadequate intake of folates in human beings is associated with an increased risk of colorectal cancer [4] and a risk factor for neural tube defects [5]. Many studies suggest that diminished folate status is associated with enhanced carcinogenesis as FA with vitamin B₁₂ participates in the nucleotide synthesis, cell division, and gene expression [6]. FA is produced by some plants (green leaves and cereals) and microorganisms, e.g. certain bacteria and yeast. It can also be found at higher concentrations in liver, yeast, and bone marrow in human and animals [7].

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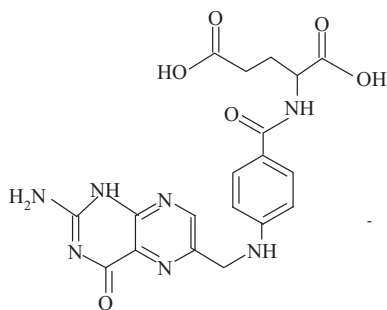


Fig. 1. The chemical structure of FA.

Various techniques have been reported for the detection of FA, such as high-performance liquid chromatography (HPLC) [8–10], spectrophotometry [11–13], fluorimetric method [14], flow injection chemiluminescence [15], mass sensitive sensors such as quartz crystal microbalance [16] and electrochemistry [17–20]. Also different bio-sensing approaches have been applied for large biomolecules [21]. Among these methods, electroanalytical techniques using modified electrodes commonly have some advantages over chromatographic and spectroscopy techniques, such as lower consumption of chemicals, saving in analysis times and lower cost of instrumentation [22]. Cetyltrimethylammonium bromide (CTAB) has been employed for surface modification of electrodes. For instance the influence of CTAB on the electrochemical properties of thiopurines [23], estrogens [24,25], and vanadium [26] has been reported.

The present work reports designing an electrochemical sensor for FA based on adsorption of CTAB at a carbon paste electrode (CPE). The experimental results showed that the oxidation peak current of FA was found to increase to a greater extent at the CPE in the presence of CTAB. After optimization of all experimental parameters, the electroanalytical technique developed under pH 8.0 that has important role in physiological metabolism of the drug. This technique has the advantages such as simplicity, high sensitivity, excellent repeatability, good stability and selectivity and low cost. Also the proposed method was successfully applied for the determination of FA in pharmaceutical formulations and urine samples.

2. Experimental

2.1. Apparatus

Electrochemical measurements were performed with an Autolab potentiostat/galvanostat model PGSTAT 12 (Metrohm, Utrecht, Netherlands) and a system was run on personal computer (Pentium IV) using GPES 4.9 software. A CPE was used as working electrode. A platinum wire (Metrohm, Switzerland) was employed as counter electrode and an Ag/AgCl (3.0 M KCl) (Metrohm, Switzerland) was served as reference electrode and all potentials in the research refer to it. A Metrohm 827 pH meter was used for pH measurements.

2.2. Materials

Pure FA was purchased from DAE JUNG. Other reagents were obtained from Merck and were of analytical grade. These chemicals were used without further purification. All solutions were prepared in deionized water and the experiments were carried out at room temperature. Standard solutions of FA were prepared daily by dissolving of the appropriate amount of the vitamin in deionized water. Phosphate buffers (0.1 M, pH 3.0–9.0), were used as supporting electrolyte for electrochemical studies and determination of FA. For the determination of FA in drug tablets, the drug tablets were dissolved in basic solution. Since some of its components were insoluble in basic solution, the filtration was used. The resulting solution was then diluted into a container.

2.3. Preparation of CPE

The CPE was prepared by mixing 0.5000 g of graphite powder (Merck) and 0.0692 g of paraffin oil (Merck) using a mortar and pestle until homogenous paste was obtained. This paste was then packed into the end of a polypropylene pipe (approximately 2.0 mm i.d. and 8.6 cm length). Electrical contact to the paste was established by inserting a copper wire down the pipe and into the back of the mixture. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing it on a paper.

3. Results and discussion

3.1. Effect of CTAB on voltammetric behavior of FA at CPE

The electrochemical behavior of FA in phosphate buffer solution (pH = 8.0) was investigated using cyclic voltammetry (CV). Fig. 2 shows the cyclic voltammograms a solution containing 10.0 μM FA at the surface of CPE in the absence and presence of CTAB. It can be observed that in the absence of CTAB, FA shows a low oxidation peak (curve a) with peak current about 0.67 μA . But, the

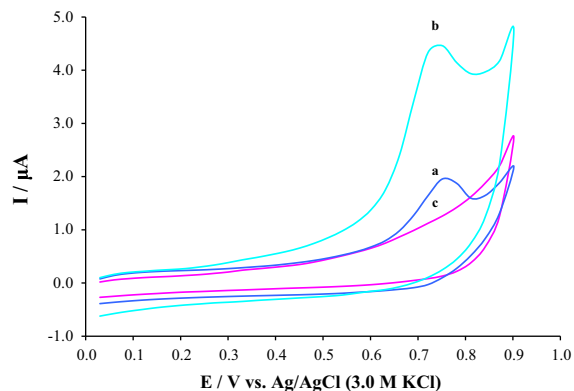


Fig. 2. Cyclic voltammograms of a CPE in 0.1 M phosphate buffer (pH = 8.0) for 10.0 μM FA (a) in the absence of CTAB, (b) in the presence of 50.0 μM CTAB and (c) as (b) in the absence of FA. Scan rate = 0.5 V s^{-1} .

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