

Square wave voltammetric determination of diclofenac in liquid phase using a novel ionic liquid multiwall carbon nanotubes paste electrode



Maryam Goodarzian^a, Mohammad A. Khalilzade^{b,*}, Fatemeh Karimi^c, Vinod Kumar Gupta^{d,*}, Mohsen Keyvanfard^c, Hassan Bagheri^e, Masoud Fouladgar^f

^a Department of Chemistry, Qaemshahr Branch, Islamic Azad University, Qaem Shahr, Iran

^b Department of Chemistry, Mazandaran Science and Research Branch, Islamic Azad University, Mazandaran, Iran

^c Department of Chemistry, Majlesi Branch, Islamic Azad University, Isfahan, Iran

^d Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247667, India

^e Department of Chemistry, Takestan Branch, Islamic Azad University, Takestan, Iran

^f Department of Biochemistry, Falavarjan Branch, Islamic Azad University, Falavarjan, Iran

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ABSTRACT

The direct electrochemistry of diclofenac (DCF) at a surface of modified carbon paste electrode (CPE) was described. The electrode was modified with multiwall carbon nanotubes (MWCNTs) and 1-butyl-3-methylimidazolium hexafluoro phosphate as a binder. The oxidation peak potential of the DCF at a surface of the ionic liquid carbon nanotubes paste electrode (IL/CNTPE) appeared at 750 mV that was about 70 mV lower than the oxidation peak potential at the surface of the traditional carbon paste electrode under similar condition. Under the optimized conditions at pH 7.0, the peak current was linear to DCF concentrations over the concentration range of 0.3–750 $\mu\text{mol L}^{-1}$, using square wave voltammetry (SWV). The detection limit was 0.09 $\mu\text{mol L}^{-1}$. The proposed method was successfully applied to the determination of DCF in both pharmaceutical and patient urine samples.

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1. Introduction

Nonsteroidal anti-inflammatory drugs (NSAID) such as DCF are usually used for the treatment of acute or chronic conditions where pain and inflammation are present. It can also help to relieve symptoms of arthritis, such as inflammation, swelling, stiffness, and joint pain [1]. DCF has been found to increase the blood pressure in patients with Shy–Drager syndrome and diabetes mellitus. On the other hand, DCF may cause life-threatening heart or circulation problems such as heart attack and stroke, especially if patient uses it long term. It may also cause serious effects on the stomach or intestines, including bleeding or perforation [2]. Therefore, it is very important for fast and sensitive analysis of DCF in pharmaceutical and biological samples. To date, many means have been employed for the determination of DCF sodium, such as gas chromatography–mass spectrometry [3,4], liquid chromatography [5–7], liquid chromatography–tandem mass spectrometry [8], spectrophotometry [9–11], colorimetry [12,13], spectrofluorimetry

[14], and voltammetry [15,16] in biological fluids. In comparison to other methods, electrochemical methods have attracted more attention in recent years for environmental, pharmaceutical and biological compounds analysis due to their fast response, sensitivity, accuracy, lower cost, high dynamic range and simplicity [17–36]. Moreover, the limited number of electrode materials only makes a restricted number of analytes suitable for electrochemical detection with high sensitivity and selectivity [37–40]. Therefore, efforts have been made to modify the electrode surfaces for the purpose of lowering the overpotential, improving the mass transfer velocity for effective enrichment of the desired substance and/or restraining the effect of interferences [41–46].

Ionic liquids have received great interests recently because of their unusual properties as liquids [47–49]. Because ionic liquids are composed of only ions, they show very high ionic conductivity, nonvolatility, and nonflammability. The nonflammable liquids with high ionic conductivity are practical materials for use in electrochemistry [50–57].

Nanomaterials and especially carbon nanotubes (CNTs) have become the topic of intense researches in the last decades because of their unique properties and the promising applications in any aspect of nanoscience and nanotechnology [58–60]. Because of their unique one-dimensional nanostructures, CNTs display fascinating electronic

* Corresponding authors. Tel.: +98 911 113 0400, +91 1332285801.

E-mail addresses: khalilzadeh73@gmail.com (M.A. Khalilzade), vinodfcy@gmail.com (V. Kumar Gupta).

and optical properties that are distinct from other carbonaceous materials and nanoparticles of other types. CNTs are widely used in electronic and optoelectronic, biomedical, pharmaceutical, energy, catalytic, analytical, and material fields [61–63].

Drug analysis and drug delivery play important roles in drug quality control, and have a great impact on public health [64–70]. Therefore, a simple, sensitive and accurate method for the determination of active ingredient is very important in pharmaceutical and clinical investigations.

To the best of our knowledge, a few numbers of studies have been reported on the voltammetric determination of DCF using modified ionic liquid carbon nanotube paste electrodes [71–73], which is the focus of the present study. Compared with the previous reports for the determination of DCF using ionic liquid/carbon nanotube paste electrodes; this modified electrode has the best dynamic range, limit of detection and sensitivity for DCF analysis. The proposed method is selective and sensitive enough for the determination of DCF in real samples such as injection solution, tablet and patient urine samples with good reproducibility.

2. Experimental

2.1. Chemicals

All chemicals used were of analytical reagent grade purchased from Merck (Darmstadt, Germany) unless otherwise stated. Double distilled water was used throughout.

A 1.0×10^{-3} mol L⁻¹ DCF solution was prepared daily by dissolving a 0.032 g diclofenac in water and the solution was diluted to 100 mL with water in a 100-mL volumetric flask. The solution was kept in a refrigerator at 4 °C and in dark. More dilute solutions were prepared by serial dilution with water.

Phosphate buffer (sodium dihydrogen phosphate and disodium hydrogen phosphate plus sodium hydroxide, 0.1 mol L⁻¹) solutions (PBS) with different pH values were used.

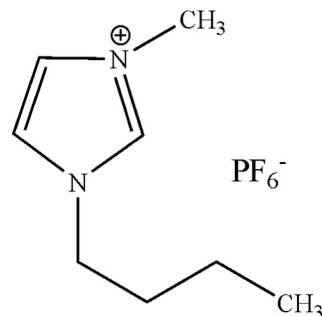
High viscosity paraffin ($d = 0.88$ kg L⁻¹) from Merck was used as the pasting liquid for the preparation of the carbon paste electrodes. Spectrally pure graphite powder (particle size < 50 μm) from Merck and multiwall carbon nanotubes (>90% MWNT basis, $d \times l = (90\text{--}70$ nm) \times (5–9 μm) from Fluka were used as the substrate for the preparation of the electrodes.

2.2. Apparatus

Cyclic voltammetry, chronoamperometry, and square wave voltammetry were performed in an analytical system, Autolab with PGSTAT 302N (Eco Chemie, The Netherlands). The system was run on a PC using GPES software. A conventional three-electrode cell assembly consisting of a platinum wire as an auxiliary electrode and an Ag/AgCl/KCl_{sat} electrode as a reference electrode were used. The working electrode was either an unmodified carbon nanotube paste electrode (CNTPE), or an IL/CNTPE. The prepared electrodes with carbon nanotubes and without carbon nanotubes were characterized by scanning electron microscopy (SEM).

2.3. Preparation of the modified electrode

To eliminate any metal oxide catalysts within the nanotubes, multiwall carbon nanotubes were refluxed in the 2.0 M HNO₃ for 12 h, and then washed with twice-distilled water and dried at room temperature. CNTPE was prepared by hand-mixing of a 0.900 g of graphite powder and 0.100 g multiwall carbon nanotubes plus paraffin at a ratio of 70/30 (w/w) and mixed well for 45 min until a uniformly wetted paste was obtained. The paste was then packed into a glass tube. Electrical contact was made by pushing a copper wire down the glass tube into the back of the mixture. When necessary, a new surface was obtained by



Scheme 1. Structure of 1-butyl-3-methylimidazolium hexafluoro phosphate.

inserting an excess of the paste out of the tube and polishing it on a weighing paper. IL/CNTPE was prepared by mixing of 0.3 g of 1-butyl-3-methylimidazolium hexafluoro phosphate (Scheme 1), 0.70 g of the liquid paraffin, 0.30 g of multiwall carbon nanotubes, and 0.70 g of graphite powder. Then the mixture was mixed well for 45 min until a uniformly wetted paste was obtained. A portion of the paste was filled firmly into one glass tube as described above to prepare IL/CNTPE.

2.4. Preparation of real samples

Urine samples were stored in a refrigerator immediately after the collection (from the Sari Health Centre). Ten milliliters of the sample was centrifuged for 30 min at 2000 rpm. The supernatant was filtered out using a 0.45 μm filter and then diluted 5-times with the PBS (pH 7.0). The solution was transferred into the voltammetric cell to be analyzed without any further pretreatment. The standard addition method was used for the determination of CD in real samples.

Tablet solution was prepared by completely grinding and homogenizing five tablets of glutathione, labeled 25 or 50 mg per tablet (Darou Pakhsh Company, Iran). Then, 10 mg of each tablet powder was accurately weighed and dissolved in 100 mL water by ultrasonication. After mixing completely, the mixture was filtered on an ordinary filter paper, 10 mL of which was subsequently transferred into a 100-mL volumetric flask and diluted to the mark with water. Then, 1.0 mL of the solution plus 4.5 mL of the buffer (pH 7.0) was used for analysis using the standard addition method.

2.5. Recommended procedure

IL/CNTPE was polished with a white and clean paper. To prepare a blank solution, 10.0 mL of the buffer solution (PBS, pH 7.0) was transferred into an electrochemical cell. The initial and final potentials were adjusted to 450 and 850 mV vs. Ag/AgCl, respectively. SWV was recorded with an amplitude potential of 70 mV, and frequency of 12 Hz to give the blank signal and labeled as I_{pb} . Then, different amounts of DCF solution were added to the cell, using a micropipette, and the SWV was recorded again to get the analytical signal (I_{ps}). Calibration curve was constructed by plotting the catalytic peak current vs. the DCF concentration.

3. Results and discussion

3.1. SEM characterization

Fig. 1 shows SEM images for IL/CNTPE and CPE. As can be seen at the surface of CPE (Fig. 1a), the layer of irregularly flakes of graphite powder was present and isolated with each other. After multiwall carbon

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