



Potentiometric determination of Diclofenac using an ion-selective electrode prepared from polypyrrole films



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ABSTRACT

The present work reports preparation and characterization of a new potentiometric sensor for determination of Diclofenac (DCF) based on doped polypyrrole films. The response mechanism for the proposed sensor is based on incorporation of DCF anion into polypyrrole film during polymer electrochemical synthesis in order to form a membrane with selective potentiometric response for the dopant ion. It was observed that the sensor performance is dependent of the measurement parameters used in the synthesis process realized under galvanostatic conditions. So, using the best set of experimental conditions (electric current density of 0.045 mA cm^{-2} and electric charge of 35 mC) the sensor exhibited a linear dynamic response in the concentration range from 3.1×10^{-4} to $1.1 \times 10^{-2} \text{ mol L}^{-1}$ of DCF with a slope 48.2 mV dec^{-1} and a limit of detection of $1.9 \times 10^{-4} \text{ mol L}^{-1}$. The method was successfully applied in the determination of DCF in pharmaceutical commercial samples with good correlation with result provided by official method. The effect of interference species on potentiometric response and morphologic characterization using microscopy of atomic force (AFM) has been also realized.

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1. Introduction

Diclofenac (DCF) is a non-steroidal anti-inflammatory drug (NSAID) with analgesic, anti-inflammatory and antipyretic properties. It is an analgesic that has a fast onset and long action duration. Compared to other NSAIDs, Diclofenac is well tolerated and rarely produces gastrointestinal ulcerations or other serious side-effects. Thus, the use of DCF in treatment of acute and chronic painful and inflammatory conditions is very common and it is present in several commercial pharmaceutical products [1].

There are several analytical methodologies reported for DCF determination in pharmaceutical preparations, such as chromatography [1,2], capillary electrophoresis [3], differential scanning calorimetry (DSC) [4], gravimetric [5], and spectrophotometric [6,7]. The official method for DCF determination by the Brazilian Pharmacopoeia [8] is based on High Performance/Pressure Liquid Chromatography (HPLC). In general, these techniques demand long time-consuming or expensive and sophisticated instruments. Alternatively, electroanalytical methods could offer methodologies with adequate analytical performance for determination of several analytes and sometimes applied without any pretreatment of the sample [9,10]. In addition, electrochemical devices are cheap, easy

construction, provide a rapid response and could be used in field analysis.

Potentiometric methods using ion selective electrodes (ISE) are an interesting alternative to determination of drugs, since provides simple procedures and low-cost electrodes, besides good selectivity and sensitivity [10]. In this way, some potentiometric devices for DCF determination have been reported which are based on plastic membrane containing an ionophore (e.g. ion pair complex as an ion-exchanger) immobilized on transducer surface [11–15]. Kormosh et al. [11–13], developed different Diclofenac-sensitive electrodes by incorporation of ion pair complex formed between DCF and butyl rhodamine B and DCF with Safranin T dye into graphite matrix. The electrodes exhibited a linear response over the concentration range of 5.0×10^{-5} – $5.0 \times 10^{-2} \text{ mol L}^{-1}$ at pH 6–12, a detection limit approximately $10^{-5} \text{ mol L}^{-1}$ with a Nernstian slope between 47 – 61 mV dec^{-1} and showed good sensitivity for DCF in presence of several substances. Using a similar approach, Maleki et al. [15] prepared an ion pair complex between DCF with silver which showed a Nernstian response ($58.9 \pm 0.2 \text{ mV dec}^{-1}$) and a linear range from 5.2×10^{-5} to $1.1 \times 10^{-2} \text{ mol L}^{-1}$ at $25 \pm 1 \text{ }^\circ\text{C}$. The results of DCF assay with the proposed sensor were in good agreement with the official HPLC method.

Nowadays, one of the most successful potentiometric sensors in routine use, mainly in clinical analysis and quality control is based on conducting polymeric membranes containing ionophores

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incorporated directly into the polymeric matrix [15]. There are several conductive polymers [16] which could be used for membrane preparation applied for ISE construction. Among them, polypyrrole films have received great attention in last years [17–19]. Its mechanism of response is based on incorporation of dopant anions that occurs during the polymerization process. The intercalation phenomenon has been well studied for several inorganic ions [20–23] and more recently a selective potentiometric response has been found using organic anions such as saccharinate [24], benzoate [25] among others. Bindewald et al. [18] described the development of a sensitive and selective disposable solid-state potentiometric sensor for dipyrone determination. The dipyrone anion was incorporated in the PPy matrix during electrochemical polymerization realized under galvanostatic conditions at a graphite pencil electrode. The sensor response for dipyrone was linear in the concentration range from 1.0×10^{-4} to 4.0×10^{-2} mol L⁻¹ with a slope of 29 mV dec⁻¹ without interference of inorganic and organic species. The method was successfully applied in the determination of dipyrone in spiked human urine and pharmaceutical commercial samples. The main goal of the present work was to develop, for the first time, a potentiometric sensor for selective determination of Diclofenac based on a doped polypyrrole film.

2. Experimental

2.1. Apparatus

Electrochemical measurements were carried out using μ Auto-labType III (Eco Chemie) under computer control. Galvanostatic and voltammetric experiments were realized using a conventional electrochemical cell with three electrodes, graphite pencil electrode was used as working electrode, Ag/AgCl (KCl 3.0 mol L⁻¹) as reference electrode and a platinum plate was used as auxiliary electrode. Potentiometric measurements were performed in a two-electrode cell using modified graphite pencil electrode (MGPE) with doped polypyrrole films as indicator electrode and an Ag/AgCl, KCl 3.0 mol L⁻¹ as reference electrode. The potentiometric measurements were performed using GPES software (Eco Chemie) by chronopotentiometry (zero current) and recorded two minutes after DCF addition.

2.2. Reagents and solutions

All solutions were prepared using purified water from Millipore (Milli-Q) system. All chemicals were analytical reagent grade and used without further purification (except pyrrole monomer). Before the polymerization procedure, pyrrole was distilled to insure better reproducibility in the formation of polypyrrole film.

Diclofenac solutions were prepared daily by dissolving of solid standard in 10 mL of hydroalcoholic solution (20%). Potentiometric measurements were performed using an ammonium sulfate solution prepared in hydroalcoholic medium (20%).

2.3. Electrochemical procedures

Modified electrodes were prepared from commercial graphite pencil Faber Castell (soft lead (HB) with 2.0 mm diameter). Pieces of 5.0 cm length were obtained by manual cut, polished and directly connected to the potentiostat by cable without any additional pretreatment. For polymerization steps a total area of 0.659 cm² was immersed in the polymerization solution. The preparation of polypyrrole film was realized using a galvanostatic procedure [26] in a solution containing 1.0 mol L⁻¹ PPy and 0.1 mol L⁻¹ of DCF. Electrochemical parameters: current density and electrical charge were varied from 0.015 and 0.105 mA cm⁻² and from 10 to 50 mC,

respectively. After the polymerization process the MGPE was maintained in a solution containing 0.1 mol L⁻¹ of DCF.

The proposed method was available for DCF determination in commercialized pharmaceutical formulation, using the following procedure: the contents of three tablets were weight and the fine powder dissolved in hydroalcoholic solution (20%). The solution obtained after filtration was transferred quantitatively into a calibrated flask and diluted to a final volume of 100 mL. All others solutions were obtained by direct dilution of this stock solution with the hydroalcoholic solution. The DCF content was determined using standard addition method. For comparison and validation of the proposed sensor, the DCF content in this sample was also analyzed by using an official method (UV-spectrophotometric).

3. Results and discussion

3.1. Morphological and potentiometric characterization

Electropolymerization of doped PPy film was realized by using a galvanostatic procedure. This procedure is based on application of a constant electric current by defined period of time. During this process occurs the oxidation of a pyrrole monomer in order to yield a film at the electrode surface; that structure acquire a positive local charge which is compensated by incorporation of anion from solution yielding the PPy–DCF membrane [26]. The sequence of steps involved during the PPy formation and doping of the polymer chain by DCF could be represented by Scheme 1.

In general, oxidized conducting polymers, like PPy, consist of a polycationic backbone and charge-compensating ions. Depending on the charge and mobility of the incorporated ions, conducting polymers behave as an anion exchanger. The anion-selectivity of PPy seems to be related to the size of the anion incorporated as counter ion in the electropolymerization step [27]. Ozcan et al. [19] prepared a molecularly imprinted polymer (MIP) based on a polypyrrole (PPy) film for selective recognition of paracetamol. The proposed MIP was prepared by cyclic voltammetric deposition of pyrrole monomer in solution in the presence of a supporting electrolyte (LiClO₄) and paracetamol as a template molecule. The molecularly imprinted film exhibited a high selectivity and sensitivity toward paracetamol, showing an effective incorporation of a molecule probe into polymer chain.

In order to verify the effect of the DCF doping in the polymer structure, potentiometric and morphological characterization were performed using different electrodes. The results obtained by potentiometric measurements are shown in Fig. 1.

The morphological characterization of polypyrrole films obtained on ITO surface was realized by AFM using films prepared in KCl solution and DCF solution following the galvanostatic procedure. AFM measurements have shown the morphological aspects of a PPy film prepared in KCl solution (Fig. 2) where largest particles could be found with irregular shapes such as agglomerations. This surface shape presents an uniform aspect and it has been verified over whole surface. Similar results have been reported by Paramo-García et al. [28] analyzing the surface changes of polypyrrole films deposited on vitreous carbon substrates by electrochemical methods in the presence of different doping anions: I⁻, Br⁻, Cl⁻, F⁻, NO₃⁻, ClO₄⁻ and SO₄²⁻. AFM images obtained for PPy film prepared in DCF solution revealed that the agglomerations are less pronounced when compared with films doped with Cl⁻. Besides that, the thickness of PPy films is observed to increase with anion size in halide electrolytes (7.85 nm for Cl⁻ and 12.11 nm for DCF). These results have suggested that DCF has promoted a significative morphological alteration due to their intercalation into the polymeric chain. Tonelli et al. [29] have reported a molecular imprinted polymer for ascorbic acid (AA) determination based on PPy doped

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