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Square wave voltammetry sensing of ibuprofen on glassy carbon electrode

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Abstract : A glassy carbon was shown to enable the determination of ibuprofen using square wave voltammetry in aqueous alcoholic buffer of p H 1.0. The effect of pH was studied at different medium such as pH 1.0 to pH 13.0. The voltammetric detection of ibuprofen was carried out from −0.5 V to 1.8 V *versus* Ag/AgCl using glassy carbon electrode (GCE) as transducers. The oxidation peak around 1.6 V obtained for ibuprofen while employing electrode showed maximum current response. This peak was chosen for stripping analysis on GCE. The electroanalytical parameters of the biosensors are highly dependent on their configuration and on the dimensions of the carbon electrode. The best limit of detection obtained for ibuprofen was 200 ppb and the linear range from 300 to 800 ppb on GCE configuration. The ibuprofen was after adsorbed on electrode surface was characterized by atomic force microscopy. The adsorbed compound shows fine fiber like structure and good roughness values. The biosensors were successfully applied for the detection of ibuprofen in several drug formulations.
Keywords: ibuprofen, CyclicVoltammetry, Glassy Carbon Electrodes, AFM and Square Wave Voltammetry.

Introduction

Ibuprofen (IBP) is the third most popular drug in the world, non-prescription, non-steroidal drug used as an anti-inflammatory analgesic and antipyretic in the human treatment of fever, migraine, muscle aches, rheumatoid arthritis, tooth aches, and osteoarthritis[1,2]. This compound is a component of various pharmaceuticals, belonging to the most commonly used over-the-counter drugs. Average content of IBP in pharmaceuticals is 200-400 mg. IBP shows a strong analgesic and antipyretic action[3, 4]. The most recent epidemiological studies have indicated that chronic intake of ibuprofen is associated with lower risk of Alzheimer's disease (AD). This beneficial effect is attributed to the reduction of the inflammation response in brain in the AD and hence delays the cognitive decline[5, 6].

Last years, determinations and studies of IBP by electroanalytical methods have drawn attention due to their precision and simplicity[7-9]. Moreover, electroanalytical methods, especially voltammetry, are characterized also by high sensitivity, selectivity, low detection limit and reproducibility of the results, what is very important in identification and quantification of various components in pharmaceuticals[10,11]. Certain similarity in electrochemical and biological reactions which take place at the electrode and in the human body, makes electroanalytical methods very attractive and important tool in investigation of pharmaceuticals effect on

processes in human body[12, 13]. Electroanalytical measurements are helpful in determination of physicochemical parameters for studied compounds (*e.g.*, redox potential, the number of transferred electrons, rate constants of electrode reactions, *etc.*)[14-20]. As it is well known, the effectiveness of the electrochemical methods is strongly depend on the choice of the electrode material.

This work is aimed at developing a simple and sensitive electroanalytical method for the determination of ibuprofen on glassy carbon electrodes. The electrodes, pretreated at a fixed potential, were used to carry out the voltammetric investigations of the oxidation of ibuprofen in aqueous solution.

Experimental

Apparatus and Reagents

CH Instruments Electrochemical Workstation (model CH 650C) all electrochemical measurements were performed using a single-compartment cell with three (Glassy carbon working electrode, Ag/AgCl reference electrode and Platinum counter electrode) electrodes, at room temperature was employed mainly for carrying out electroanalytical studies. A 200 ppm stock solution was made up in aqueous ethanol. For studies in aqueous media, Britton Robinson Buffers, 0.1 mol.dm^{-3} KOH, KCl and 0.1 mol dm^{-3} H_2SO_4 in 50% aqueous alcohol were used as the medium for the analysis. Ibuprofen was purchased from Merck AR grade. Surface analysis done by Nanosurf Easy scan 2 AFM under the following conditions: scan direction – up, Time/Line – 206 ms, Tip voltage -1.0V, Vibration frequency – 169.969 KHz, Measurement environment – air and Operating mode – Dynamic force.

Procedure

Purging and blanketing of nitrogen were done for analyte solution placed in the electrochemical cell of 15-ml capacity for 15 minutes under stirred conditions. Then various voltammograms were recorded. To get reproducible results, great care was taken in the electrode pretreatment. The glassy carbon electrode was pretreated in two ways: Mechanical polishing over a velvet micro-cloth with an alumina suspension and electrochemical treatment by applying a potential of 1.5 V for 2 seconds. The electrochemical pretreatment was done in the same supporting electrolyte solution in which the measurements were carried out.

Results and Discussions

Effect of pH

Voltammetric methods are frequently used for the characterisation of compounds which play important role in pharmaceutical industry. IBP electrooxidation and electroreduction at various electrodes is described and reported[21]. According to our best knowledge, electrooxidation of ibuprofen is poorly described in literature. Ibufrofen electrooxidation was investigated at various electrode materials but not at on glassy carbon electrode.

Cycil voltammograms (CV) of 200 ppm of ibuprofen was studied at a sweep rate 100 mV s^{-1} in the pH media (1.0- 13.0) and the results were compared to understand the influence of pH on the voltammetric behaviour of the biological sample of ibuprofen. IBP exhibited single oxidation peak in the CV. The peak potential with higher peak current was chosen for comparison. The peak potential and current (Fig.1) was measured and correlated with pH. As the pH increased, the peak potential decreased showing lesser energy requirement for the oxidation in basic medium. Sharpness of peak was very good in pH 1.0. Peak current decreased in neutral condition and increase was found in base medium (Fig.1). The IBP maximum peak current was noticed at pH 1.0. Hence analytical point of view, pH 1.0 was chosen as the optimum pH.

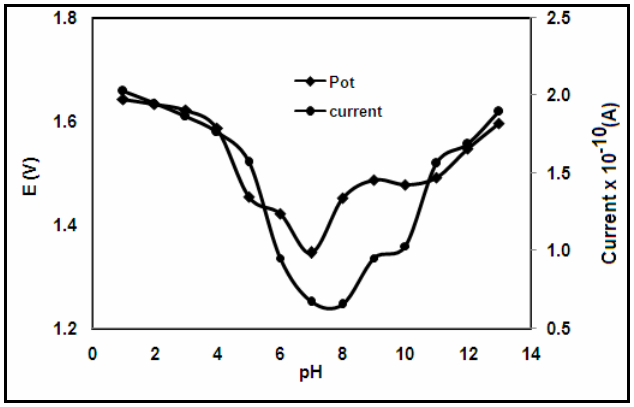

Fig 1. Curve of potential and current vs pH for ibuprofen

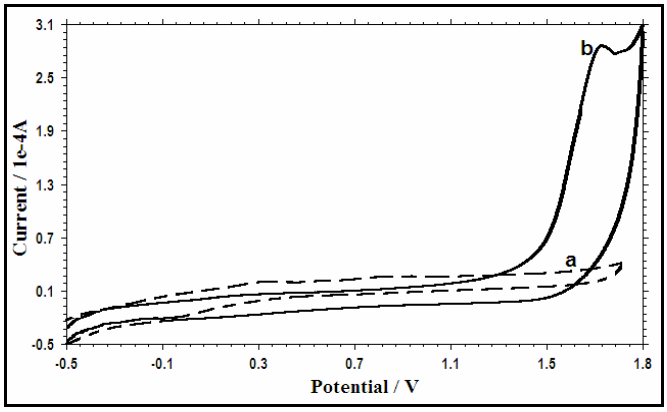

Fig 2. Cyclic voltammetric behavior of (a) Glassy carbon electrode and (b) 200 ppm of ibuprofen on glassy carbon electrode in aqueous alcoholic pH 1.0 at 100 mV/s

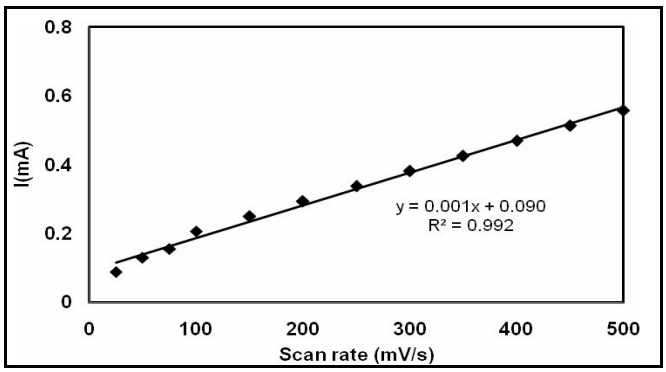

Fig 3. Plot of peak current vs scan rate

Cyclic Voltammetric Studies

Cyclic voltammetric behaviour of IBP was studied in the concentration 200 ppm in aqueous pH 1.0 (Fig.2) at scan rate 100 mVs^{-1}. The compound showed only one well-defined anodic peak. The same number of peak was observed at various sweep rates. Correlation of peak current with sweep rate resulted in a curve line (Fig 3) whereas the plot of ip vs. $\nu^{1/2}$ resulted in straight lines. The plot of log ip vs. log ν correlation equation was also led to a straight line a slope value of 0.3013. All the above facts confirming the diffusion controlled nature of the reaction. As the concentration increased, the peak current also increased and resulted in a straight line. The correlation of peak potential with log ν shows linearity. The transfer coefficient, 'αn' value was calculated from the slope of the straight line. The fractional value of 'αn' and absence of peak in the reverse scan suggest irreversible electron transfer.

Square Wave Stripping Voltammetry

Square wave stripping voltammetric experiments were carried out to ascertain the best conditions for the adsorption process. Many preconcentration-stripping experiments were performed for accumulation potentials (E_{acc}) varying from –0.5 to 1.8 V and at an accumulation time (t_{acc}) of 5 seconds, to evaluate the electrostatic attraction/repulsion between electrode surface and the pesticide substrate. Maximum peak current was found at 1.6 V accumulation potential. This might be due to the electrostatic interaction between the positive nature of electrode at this potential and the electron rich substrate. The accumulation times 20 s led to the maximum peak current. The maximum current signal condition was due to maximum electrode surface coverage under these conditions. AFM was employed to study the surface morphology of the ibuprofen accumulated on the electrode presented in figure 4. Two diminution image of ibuprofen adsorbed surface exhibit bunches of fine fiber like structure. Three-dimensional AFM images of topography (height) give information on structure including roughness, defects, amorphous and crystalline phases, and nucleation and growth modes. Topographic imaging is usually performed in tapping mode. The inhibitors were demonstrated good smooth surface and the roughness parameters of Sa, Sq, Sy, Sp, Sv and Sm values are presented.

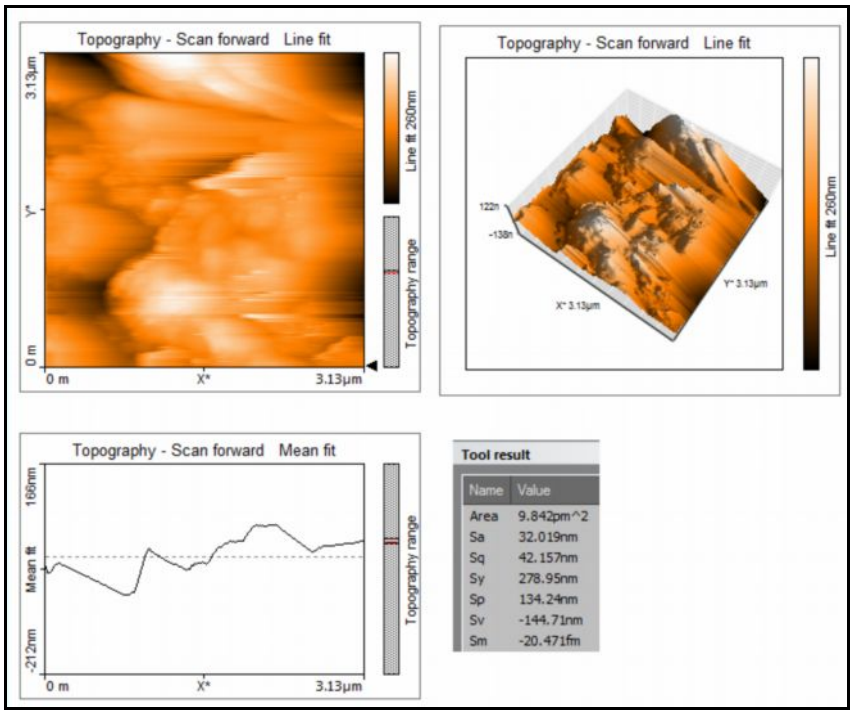

Fig 4. AFM photographs of Ibuprofen accumulated on electrode surface 2D, 3D, size distribution graph and surface roughness data

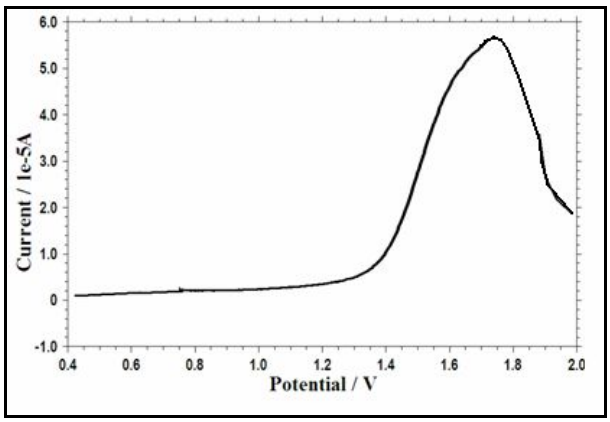

Fig 5. Square wave stripping voltammetric behavior of 500 ppb ibuprofen on GCE under optimum condition

The initial scan potential, (E_{is}), is also an important parameter in controlling the peak characteristics. The initial potential was varied between –0.5 to 1.0 V and an initial scan potential of - 0.5 V was chosen for stripping voltammetric studies of the drug because of maximum current signals. The stripping peak current increased with an increase in square wave amplitude from 25 to 150 mV and decreased above 150 mV. However, amplitude of 100 mV was selected owing to maximum current peak response. The dependence of the peak current on the frequency was studied between 10 and 1000 Hz. This experiment was carried out for a constant value of the step potential 4 mV and the results showed the maximum peak current at 70 Hz. Lower current response was observed for higher frequency values between 80 and 1000 Hz. At higher frequencies, the background current increased sufficiently and hence the peak shape is affected. Broadening of the peak was also seen. When the step potential was varied between 2 and 10 mV, a decrease in peak current was observed above 5 mV. Hence, a frequency of 70 Hz and a step potential of 5 mV were used which provided sufficiently sensitive analytical signal at a reasonable scan rate of 350 mV s^{-1}. The effects of stirring rate (100 to 2000 rpm) and rest period (2 to 30 s) were studied. The optimum values were found to be 300 rpm and 5 seconds respectively. The experimental conditions for maximum signal from square wave stripping voltammetry are given in Table 1. A representative stripping voltammograms of the drug are given in figure 5.

Table 1.Optimum experimental conditions in SWSV

Parameters	Range studied	Optimum value
pH	1.0 to 13.0	1.0
Accumulation potential (V)	-0.5 to 1.8	1.6
Accumulation time (Sec)	5 to 60	20
Initial scan potential (V)	-0.5 to 1.0	-0.5
Square wave amplitude (mV)	25 to 150	50
Frequency (Hz)	20 to 100	70
Scan Increment (SI) mV	2 to 20	4
Stirring rate (rpm)	50 to 250	250
Rest period (Sec)	2 to 10	5

Analytical Characteristics

Square wave stripping voltammograms at different concentrations of IBP was recorded using their maximum signal conditions. The peak current linearly increased with an increase in concentration. The calibration plots of i_p vs. Conc. are presented good linear correlation (Fig 6). The range of determination was from 300 to 800 ppb, the LOD was 200 ppb. The relative standard deviation found for five identical measurements of the stripping current at 400 ppb analyte concentration was 2.5%.

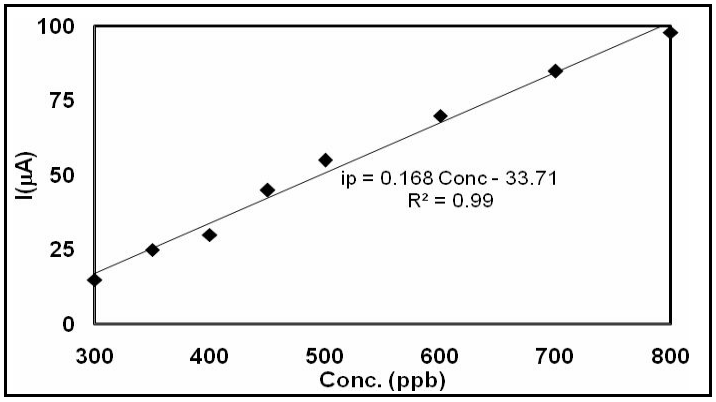

Fig 6. Calibration plot of peak current vs conc.

Proposed method for the determination of drugs in pharmaceutical samples

The pharmaceutical samples analyzed were collected from medical shops. Various tablets having IBP were examined for estimation of content of drugs. Stripping voltammograms of the drugs at pH 1.0 were recorded under optimised conditions. The concentration of the drug in commercial formulations determined by the proposed method was in good agreement with the reported value of the company (Table 2).

Table 2. Amount of IBP presented in tablets determined by SWSV

Brand name	Company name	Tablets (mg)	Experimental value (mg)	% of RSD
Ibuorifen 400	Modern laboratories	400	385	2.7
Brufen	Abbott India Ltd	200	193	2.1
Ibuorifen 200	200Modern laboratories	200	194	1.7
Ibuorifen	Synmedic laboratories	200	191	1.7
Ibugesic	Cipla	200	193	2.6

Conclusion

Electrooxidation of IBP showed irreversible oxidation on glassy carbon electrode in the pH range 1.0 to 13.0. The oxidation of drug was controlled by diffusion. The study on the influence of pH revealed pH 1.0 as the best pH for the development of analytical procedure. Detailed square wave stripping voltammetric studies were carried out at pH 1.0 and optimum accumulation and stripping conditions were arrived at. The concentration was varied under optimum experimental conditions and calibration was made. From the AFM photographs accumulation of drugs was understood. Lower limit of detection are reported. This method can very well be used for the determination of drug in real samples also.

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