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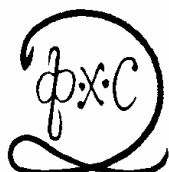
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ELECTROANALYTICAL DETERMINATION OF CHLOROPROMAZINE ON BORON-DOPED DIAMOND ELECTRODE

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ABSTRACT

The electrochemical behavior and determination of chlorpromazine (CPZ) by differential-pulse voltammetry (DPV) at unmodified boron-doped diamond electrode (BDDE) is proposed. Effect of pH on electrochemical oxidation of chlorpromazine in Britton–Robinson (BR) buffer solution was investigated. Cyclic voltammetry results showed four oxidation peaks for CPZ and peaks at 0.6 V and 1.3 V were chosen for CPZ quantification. The electrode reaction is controlled by diffusion as a rate-determining step. Under optimized DPV conditions at pH 4.0, a linear analytical curve was obtained for wide the chlorpromazine concentration range from 1.0×10^{-7} to 4.0×10^{-5} M with a detection limit of 0.3×10^{-7} M.

INTRODUCTION

Chlorpromazine (CPZ) (2-chloro-10-(3-dimethylaminopropyl)phenothiazine) is a member of phenothiazine class of psychotropic drugs with an aliphatic side chain [1]. The most important field of its applications is treatment of schizophrenia and behavioral disorders while CPZ is also active in treatment of cancer, viral and bacterial infections and neurodegenerative illnesses [2]. Bearing in mind the problems that can cause overdose of this drug, it is important to find simple, fast and low cost method which no requires using of several steps, highly evolved instruments and special training.

The aim of this work was to find a new, simple, sensitive and fast analytical procedure for detection of chlorpromazine by differential pulse voltammetry bearing in mind the advantages of BDDE, foremost the sensitivity and wide potential window. This procedure should be primary based on so far not applied determination of chlorpromazine due to quantization of the peak originating from oxidation of nitrogen in phenothiazine side chain.

EXPERIMENTAL

Electrode preparation: BDDE was anodically pretreated as it is previously reported [3].

Electrochemical measurements: Cyclic voltammetric (CV) measurements and differential pulse voltammetry (DPV) measurements were performed using an electrochemical system CH Instruments (USA). The cell (10 mL) consisted of three-electrode system, boron-doped diamond electrode (inner diameter of 3 mm; Windsor Scientific Ltd., Slough, Berkshire, United Kingdom), an Ag/AgCl (saturated KCl) reference electrode and Pt counter electrode. The cyclic and the differential pulse voltammograms of standard chlorpromazine solutions were recorded in the potential range from 0.0 to 1.5 V, using a scan rate from 10 to 300 mV/s (for CV) and 20 mV/s (for DPV), a modulation time of 40 ms, a pulse amplitude of 40 mV and pulse time of 0.2 s. All pH values were measured with pH meter model Jenco Instruments Model No. 6071 (Taiwan). All experiments were obtained at an ambient temperature.

RESULTS AND DISCUSSION

Influence of pH on electrochemical oxidation of chlorpromazine is presented on Figure 1. (a). Cyclic voltammograms of 0.1 mM CPZ in BR buffer solution as supporting electrolyte (pH values from 2 to 10) at BDDE revealed that four oxidation peaks, originated from phenothiazine core and aliphatic chain [4], are highly sensitive to changing of pH. Cyclic voltammograms of 0.1 mM CPZ in BR buffer solution at pH 4 (selected pH for further investigations) on BDDE were recorded at different potential sweep rates and the graph of peak current for all peaks as function of the square root of potential scan rate was shown on Fig. 1 (b). Hence, the mass transport in diffusion layer during oxidation reaction is controlled by diffusion and the adsorption and/or other specific interactions on self-assembled BDDE electrode surface are negligible.

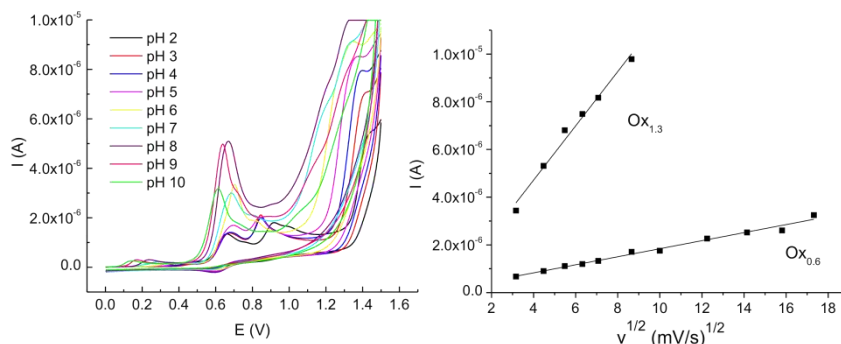


Figure 1. Cyclic voltammetric profiles of 0.1 mM CPZ in different pH BR buffer solutions at BDDE, scan rate of 20 mV/s; b) The peak current as function of $v^{1/2}$ derived from cyclic voltammograms of 0.1 mM CPZ for various scan rates (v) ($10\text{--}300\text{ mV s}^{-1}$) in BR buffer solution at pH 4 on BDDE.

Differential pulse voltammetry (DPV) was selected as a suitable electroanalytical technique for detection of trace amounts of CPZ. By varying one parameter while others were kept fixed, the optimal modulation time of 40 ms and pulse amplitude of 50 ms were chosen taking into account the width and height of the peaks of quantification (0.6 V and 1.3 V). Peak on 0.6 V is usually used for quantization of phenothiazines [5, 6], while peak at 1.3 V is originated from specific CPZ side chain group [4] and it is more selective due to high potential value.

Differential pulse voltammograms of various concentrations of CPZ from 3.0×10^{-7} to 4.5×10^{-5} M recorded on BDDE were showed in Fig.2 (a).

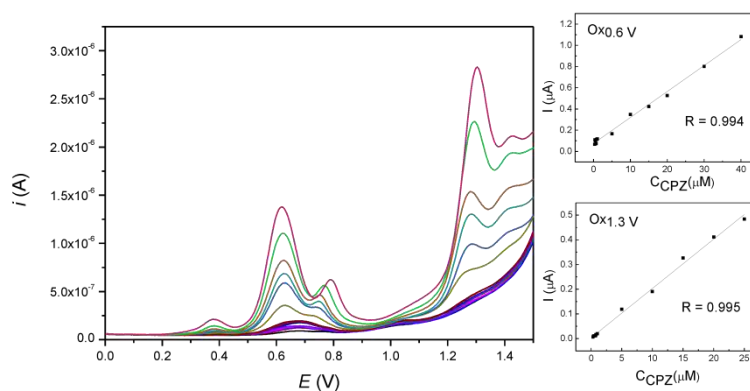


Figure 2. DPV of CPZ added in concentration of 1.0×10^{-7} – 4.5×10^{-5} M, pH = 4 (a); calibration curves for Ox_{0.6} v (b) and Ox_{1.3} v (c)

The calibration curve was constructed by plotting the current density of anodic peaks at 0.6 and 1.3 V vs. the concentration of CPZ. The resulting calibration plots for both oxidation peaks (Fig. 4, b) and c)) are followed by equations:

$$\text{Ox}_{0.6 \text{ V}}: I_p \text{ (A)} = 2.45 \times 10^{-8} \times C_{\text{TFP}} + 7.53 \times 10^{-8}$$

$$\text{Ox}_{1.3 \text{ V}}: I_p \text{ (A)} = 1.99 \times 10^{-8} \times C_{\text{TFP}} + 0.31 \times 10^{-8}$$

Detection limit (LOD) of CPZ determination for oxidation peaks on 0.6 and 1.3 V are $0.6 \times 10^{-7} \text{ M}$ and $0.3 \times 10^{-7} \text{ M}$, respectively. The repeatability of method was evaluated by five replicate DPV measurements at the $15 \times 10^{-6} \text{ M}$ CPZ concentration under the same operating conditions. The relative standard deviation for peak current for $\text{Ox}_{0.6 \text{ V}}$ and $\text{Ox}_{1.3 \text{ V}}$ were 2.72 % and 1.64 %, respectively.

CONCLUSION

The present study is related to the application of unmodified BDDE for determination of prominent phenothiazine derivate, chlorpromazine. The proposed sensor exhibited the advantage of simple preparation, good reproducibility and electrochemical surface stability. As BDDE is, up to date, one of the best solid electrode materials, this investigation provides valuable information about the possibility of a selective determination of CPZ over many interfering compounds from biological samples. The developed procedure has potential for use in analyzing of biological fluids and pharmaceutical formulations.

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