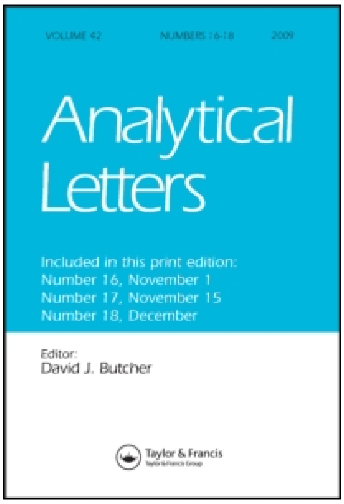

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Electrochemical Reduction and Voltammetric Determination of Metronidazole Benzoate at Modified Carbon Paste Electrode

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VOLTAMMETRY

Electrochemical Reduction and Voltammetric Determination of Metronidazole Benzoate at Modified Carbon Paste Electrode

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Abstract: A metalloporphyrin incorporated carbon paste sensor has been developed for the determination of metronidazole benzoate (MTZB). Zn(II) complex of 5,10,15,20-tetrakis (3-methoxy-4-hydroxy phenyl) porphyrin (TMHPP) was used as the active material. The MTZB gave a well-defined reduction peak at $-0.713\,V$ in $0.1\,mol\,l^{-1}$ phosphate buffer solution of pH around 7. Compared with bare carbon paste electrode (CPE), the TMHPP Zn(II) modified electrode significantly enhanced the reduction peak current of MTZB as well as lowered its reduction potential. Under optimum conditions the reduction peak current was proportional to MTZB concentration over the range $1 \times 10^{-3}\,mol\,l^{-1}$ to $1 \times 10^{-5}\,mol\,l^{-1}$. The detection limit was found to be $4.36 \times 10^{-6}\,mol\,l^{-1}$. This sensor has been successfully applied for the determination of MTZB in pharmaceutical formulations and urine samples.

Keywords: Carbon paste electrode, cyclic voltammetry, electrochemical reduction, metalloporphyrin, metronidazole benzoate

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INTRODUCTION

Metronidazole benzoate, 1-(2-benzyloxy ethyl)-5-nitro methylimidazole, one of the nitroimidazole derivative, is well known for its antimicrobial properties. It is effective against trichomonas, Vincent's organisms, and anaerobic bacteria. Veterinarians also use MTZB to treat bacterial infections as well as giardia in dogs and cats (Edwards 1993). The chemical structure of the drug is shown in Fig. 1.

Several analytical methods have been reported for the determination of MTZB, including spectrophotometry (Parimoo, Prasad, and Vineeth 1996; Nagarajia et al. 2002), titrimetry, thin layer chromatography, gas chromatography (Bhatia and Shanbhag 1984), and high performance liquid chromatography (Turcant et al. 1997). However, the previously mentioned methods do not have sufficient selectivity for MTZB determination. Hence, it is of primary importance to develop an alternative method for MTZB determination with a high degree of selectivity and sensitivity.

Chemically modified carbon paste electrodes (CMCPE) have continued to be of major concern during the past decade and a relatively large amount of electrochemical research has been devoted to the development and applications of different types of CMCPE (Amini et al. 2003; Shahrokhian and Yazdani 2003; Shahrokhian, Souri, and Khajehsharifi 2004; Shahrokhian, Hamzehloei et al. 2004). Modification of carbon paste electrodes with suitable materials facilitates the electrochemical reactions of the redox compounds to proceed without hindrance (Hill 1996; Wring and Hart 1992). This phenomenon generally results in increased selectivity and sensitivity of the determinations (Ortiz et al. 1995; Ruiz, Blazquez, and Pingarron 1995; Xu et al. 1994). It has been known for a number of years that certain transition metal complexes with porphyrins (Dobson and Saini 1997; Griveau and Bedioui 2001) can catalyze the electrooxidation/electroreduction of some chemically and biologically important compounds.

Metalloporphyrins as electrode modifying agents are very attractive because they are rather stable compounds and their properties can be finely tuned by simple modifications of their basic molecular structure. The coordinated metal, the peripheral substituents, and the conformations of the

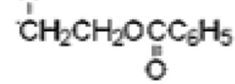

Figure 1. Structure of metronidazole benzoate.

macrocyclic skeleton influence the coordination and the related sensing properties of these compounds. Furthermore, they have also been used extensively as catalysts, semiconductors, anticancer medicine etc. (Collman et al. 1993; Bedioui, Devynck, and Bied-charreton 1995; Ohkita et al. 2002; Li et al. 2005). Various metalloporphyrins have shown potentiometric response to anions with selectivity sequences solely dependent on the centrally bonded metal (Beer, Drew, and Jagessar 1997). Previous studies have shown that porphyrin cobalt(II) displays a selective affinity towards imidazole via strong metal ion-nitrogen ligation (Walker 1973). To the best of our knowledge, no efforts have been made on the application of CPE incorporated with TMHPP Zn(II) for the determination of imidazole analogous species.

In continuation of our work on drug analysis (Girishkumar and Letha 1997; Girishkumar et al. 2005; 2006, 2007, 2008), a novel voltammetric sensor based TMHPP Zn(II) has been developed for the selective determination of MTZB. The prepared MTZB sensor was characterized in terms of selectivity, sensitivity, and reproducibility. A relatively low applied potential and improved selectivity for MTZB detection has been realized. The developed sensor has been successfully applied for the determination of MTZB in commercially available tablets and urine samples.

EXPERIMENTAL

Reagents and Materials

All chemicals used were of analytical grade. Paraffin liquid, 3-methoxy-4-hydroxy benzaldehyde, and propionic acid were purchased from s.d.fine. Chemicals, Ltd, Mumbai, India, and were used as received. Pyrrole and zinc acetate were obtained from Sisco Research Laboratories, Ltd, India. Graphite powder was purchased from Sigma Aldrich. Pure MTZB was obtained as a gift sample. MTZB tablets were purchased from local drug stores. MTZB stock solution was prepared by dissolving in methanol. Pyrrole for synthesis was used after distillation. Double distilled water was used throughout.

Synthesis of 5, 10, 15, 20 TMHPP

The synthesis was performed according to Alder method (Alder, Lonyo, and Finarelli 1967). Freshly distilled pyrrole (1.04 ml, 0.015 mol) and 3-methoxy-4-hydroxy benzaldehyde (2.282 g, 0.015 mol) were added to 30 ml of boiling propionic acid. The mixture was refluxed for 30 min and was allowed to cool for a few minutes. The filter cake was washed thoroughly with methanol. The resulting purple crystals were further purified by column chromatography. The yield was found to be 10%. Elemental analysis of the product gave the following results:

Calcd (%): C, 72.18; H, 4.76; N, 7.01
Found (%): C, 72.08; H, 4.66; N, 6.97
IR (KBr), v (cm^{-1}): 3363 (NH); 3000 (CH); 3539 (OH)
UV-Visible spectrum in CH_2Cl_2, λ (nm): 411, 445, 514, 647
^{1}H NMR (500 MHz, $CDCl_3$) ppm: $\delta = 8.9$ (s, 8H, pyrrollic–β-H), 5.9 (s, 4H, OH), 3.9 (s, 12H, OCH_3), −2.7 (s, 2H, NH), 8.2–7.3 (m, 12H, aromatic)

The structure of TMHPP is shown in Fig. 2.

Synthesis of [5, 10, 15, 20 Tetrakis (3-methoxy-4-hydroxy Phenyl) Porphyrinato] Zn(II)

37 mg of Zn $(OAc)_2 \cdot 2H_2O$ (0.17 mmol) in methanol (10 ml) was added to 50 mg of TMHPP (0.0626 mmol) in chloroform (10 ml) at room temperature. It was then acidified with a drop of glacial acetic acid and refluxed for 12 hrs. TMHPP Zn(II) was obtained as a red powder and it was filtered and washed with water. The yield was found to be 5%. Elemental analysis of the product gave the following results:

Calcd (%): C, 66.86; H, 4.17; N, 6.50
Found (%): C, 66.75; H, 4.07; N, 6.45

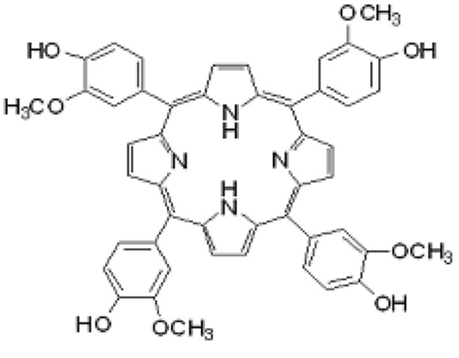

Figure 2. Structure of 5,10,15,20-tetrakis (3-methoxy-4-hydroxy phenyl) porphyrin.

IR (KBr), ν (cm^{-1}): 3363 (NH); 3000 (CH); 3539 (OH); 455 (M-N)
UV-Visible spectrum in DMSO, λ (nm): 411, 530

Apparatus

All electrochemical measurements were carried out with BAS Epsilon Electrochemical analyzer (Bioanalytical system, USA) interfaced to a PC. A conventional three electrode system, including TMHPP Zn(II) modified carbon paste working electrode, a platinum wire counter electrode, and Ag/AgCl reference electrode were employed. The UV-Visible spectrum was recorded using Spectro UV-Visible Double Beam UVD-3500 instrument. FT-IR spectra of the powdered samples were recorded on JASCO 4100 FT IR spectrometer using KBr discs. ^1H NMR spectra were recorded using JEOL GSX 400 NB FT NMR spectrometer. Elemental analyses were performed with VarioEL III CHNS analyzer. A Metrohm 781 pH meter was used for pH measurements.

Preparation of Metalloporphyrin Modified Carbon Paste Electrode

The bare carbon paste electrode was prepared by thoroughly mixing analytical grade graphite and paraffin liquid (plasticizer) in a 70:30 (w/w %) ratio. The metalloporphyrin modified CPE was prepared by mixing different percentages of graphite powder, paraffin liquid, and TMHPP Zn(II). This mixture was mixed in a mortar for at least 10 min to become homogeneous. This paste was packed into one end of a Teflon holder in which electrical contact was made with a copper rod that runs through the center of the electrode body. The electrode surface was polished using a butter paper to produce reproducible working surface. Electrochemical behavior of MTZB at these different electrodes was studied using cyclic voltammetric technique. Best results were obtained at 70:22:8 (w/w %) ratio of graphite powder, paraffin liquid, and TMHPP Zn(II). This optimized electrode composition was then used for the voltammetric determination of MTZB.

Analytical Procedure

A stock solution of MTZB ($5 \times 10^{-3}\,mol\,l^{-1}$) was prepared in methanol. Standard solutions of analyte ($1 \times 10^{-3}\,mol\,l^{-1} - 1 \times 10^{-5}\,mol\,l^{-1}$) were prepared by serial dilution of stock solution using phosphate buffer solution. The analyte solution was taken in the electrochemical cell and then deaerated with N_2 for 10 min. Cyclic voltammograms were recorded from 0 to −1.0 V at a scan rate of 100 mV/s.

RESULTS AND DISCUSSION

The electrochemical behavior of MTZB at TMHPP Zn(II) modified CPE was investigated by cyclic voltammetry (CV), differential pulse voltammetry (DPV) and linear sweep voltammetry (LSV). The reduction of MTZB is a complex process in which nitro group can receive up to six electrons until complete reduction to amino group (Dumanovic and Ciric 1973) and is shown in Fig. 3. Under anaerobic conditions or low oxygen pressure, the reduction of MTZB occurs in a similar way to the reduction of nitrobenzene (Zuman and Fijalek 1990). In the present case, one reduction peak is obtained and this is attributed to the four electron reduction of nitro group in MTZB to the corresponding hydroxylamine according to the currently accepted mechanism for the electroreduction of aromatic and heteroaromatic compounds containing nitrogroup (Zuman and Fijaiek 1990; Jammal et al. 1992).

The cyclic voltammograms of 1×10^{-3} mol l^{-1} MTZB at TMHPP Zn(II) modified CPE and at bare CPE are shown in Fig. 4. At bare CPE, MTZB yields a reduction peak at −0.830 V. Under the same conditions, a well defined reduction peak appears at −0.713 V for MTZB at TMHPP Zn(II) modified CPE resulting shift in reduction potential by 117 mV. Compared with bare CPE, there was also an enhancement of reduction peak current for MTZB from 0.0100 mA to 0.0305 mA at TMHPP Zn(II) modified CPE. The decrease of potential and remarkable peak current enhancement undoubtedly proved the electrocatalytic activity of TMHPP Zn(II) modified CPE towards the reduction of MTZB. No oxidation peak is observed for MTZB in the reverse sweep of CV indicating an irreversible electrochemical process.

Effect of pH

The effect of pH on the cathodic peak current of 1×10^{-3} mol l^{-1} MTZB at the TMHPP Zn(II) modified CPE was investigated by CV. The pH

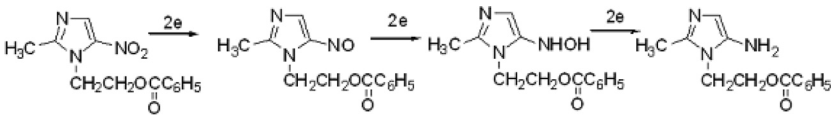

Figure 3. Mechanism of reduction of nitrogroup to amine derivative.

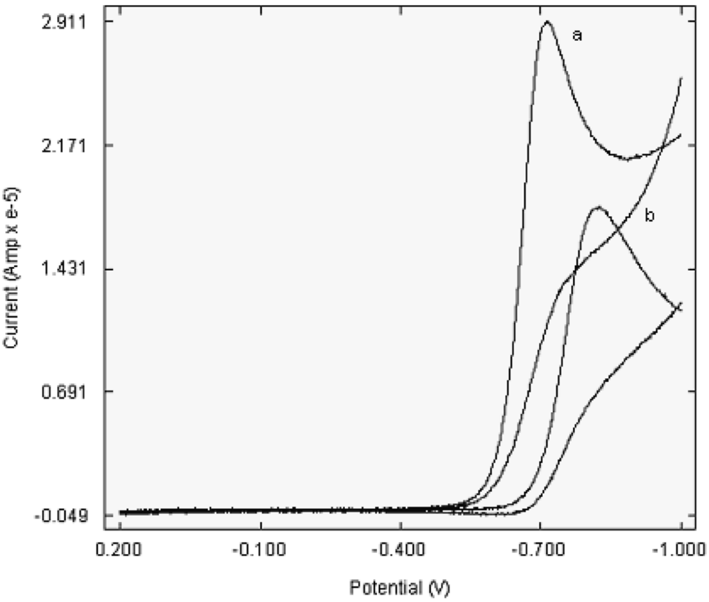

Figure 4. Cyclic voltammogram of MTZB at (a) TMHPP Zn(II) modified CPE (b) Bare CPE.

range was studied from 4–10. A well defined reduction peak and a high peak current was obtained at pH around 7; as a result, further studies were carried out at this pH.

Effect of Scan Rate

The reduction peak current of 1×10^{-3} mol l^{-1} MTZB at different scan rates ranging from 50–250 mV/s was measured by LSV, using the same modified electrode. It was found that cathodic peak current increases with an increase in the scan rate. The results are illustrated in Fig. 5. The reduction peak current varies linearly with square root of scan rate indicating that the reduction of MTZB at the TMHPP Zn(II) modified electrode is diffusion controlled.

Effect of Supporting Electrolyte

The voltammetric behavior of TMHPP Zn(II) modified CPE was studied in 0.1 mol l^{-1} concentrations of different supporting electrolytes such as

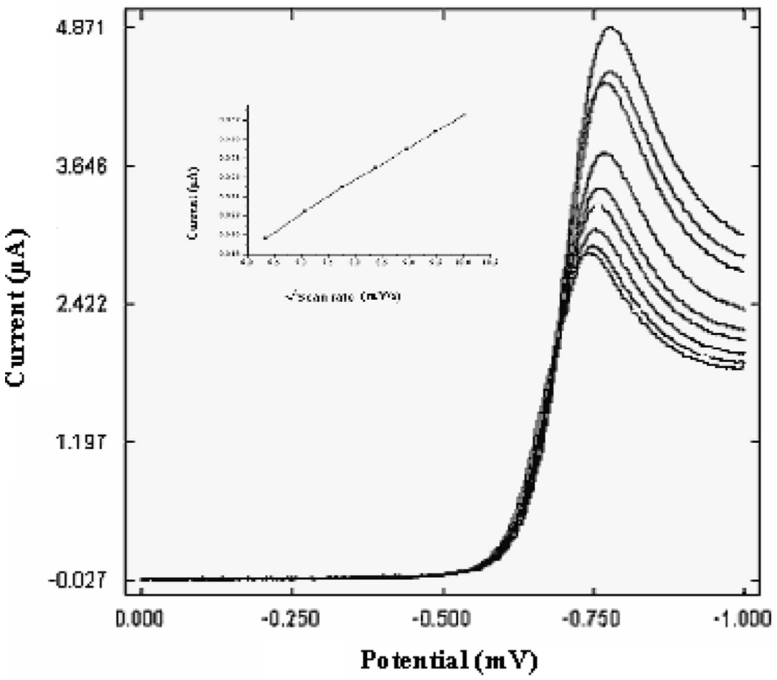

Figure 5. LSV of MTZB at different scan rates in phosphate buffer solution. Inset is the plot of current versus square root of scan rate.

phosphate buffer, acetate buffer, potassium nitrate, potassium chloride, hydrochloric acid, sulfuric acid and tetra-n-butylammonium chloride. The reduction peak obtained was well defined in phosphate buffer solution. Hence, 0.1 mol l^{-1} phosphate buffer solution was taken as the experimental medium.

Calibration Graph

The relationship between cathodic peak current of MTZB and its concentration was investigated by DPV. The results are illustrated in Fig. 6. A linear concentration range was found to occur from 1×10^{-3} mol l^{-1} to 1×10^{-5} mol l^{-1}. The detection limit was found to be 4.36×10^{-6} mol l^{-1}. The reproducibility of the TMHPP Zn(II) modified CPE was examined by repetitive measurement of the reduction peak current of 1×10^{-3} mol l^{-1} MTZB using the same electrode. After several successive measurements, stable electrochemical responses were obtained suggesting that the modified CPE has excellent reproducibility.

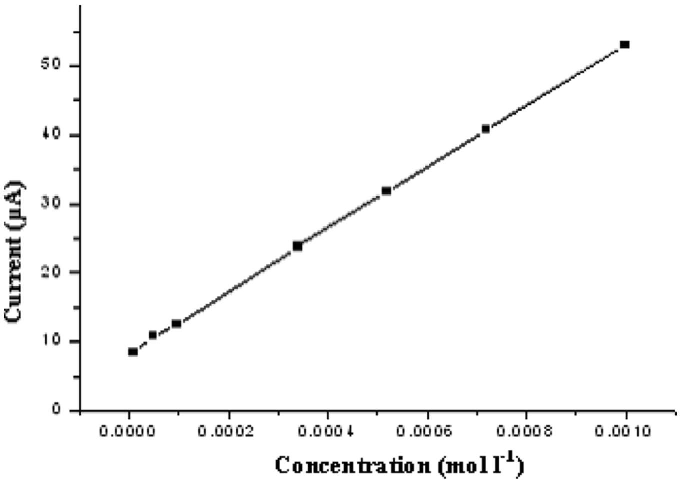

Figure 6. Effect of concentration.

Interference Study

To evaluate the interference of various species in the determination of MTZB, a systematic study was carried out with various interferents in deaerated medium to avoid interference from dissolved oxygen. Cyclic voltammograms were recorded and the results are given in Table 1. A 100 mol l^{-1} excess of glucose, sodium chloride, ascorbic acid, uric acid and norfloxacin have almost no influence on the current response of MTZB (signal change below 0.5%).

APPLICATIONS

Determination of MTZB in Tablet

The TMHPP Zn(II) modified CPE was used for the quantitative determination of MTZB in tablets (Metrogyl and Flagyl). Ten tablets of each

Table 1. Interference study

Interferent	Concentration (M)	Signal change (%)
Glycine	1×10^{-1}	0.25
Sodium chloride	1×10^{-1}	0.26
Norfloxacin	1×10^{-1}	0.12
Ascorbic acid	1×10^{-1}	0.15
Glucose	1×10^{-1}	0.13

Table 2. Determination of MTZB in tablets

Sample	Declared amount (mg/tablet)	Found* (mg/tablet)	S.D*	C.V*
Flagyl (Rhone-Plc, India)	200	199	1.4	0.71
Metrogyl (Unique, India)	400	402	1.6	0.41

*Average of six replicates.

type were accurately weighed and ground to a fine powder. An adequate amount of this powder corresponding to 1×10^{-3} mol l^{-1}, MTZB, was weighed and transferred to a beaker. The powder was dissolved in methanol and filtered through Whatman 41 filter paper to a volumetric flask (50 ml). The beaker was washed several times and the washings were collected in the standard flask and then it was quantitatively diluted. Solutions of different concentrations were prepared by serial dilution of the stock solution with supporting electrolyte. DPV was recorded and the unknown concentrations were determined from the calibration graph. The results are shown in Table 2. The results obtained are in good agreement with the declared MTZB content and showed a high degree of precision. From the aforementioned experimental results, it is very clear that the developed sensor has good practical applicability.

Determination of MTZB in Urine Sample

Urine samples of 5 ml were taken in different 25 ml standard flasks. Different quantities of MTZB (ranging from 0.004 g to 0.009 g) were added to these urine samples and then quantitatively diluted using the supporting electrolyte. DPV were recorded and the unknown concentrations were determined from calibration graph. The results are shown in Table 3. The TMHPP Zn(II) modified sensor gave satisfactory results.

Table 3. Determination of metronidazole benzoate in urine sample

Added (mg)	Found (mg)	Recovery %
6.5	6.4	98.5
7.5	7.4	98.7
8.5	8.3	97.6

CONCLUSION

Voltammetric behavior of MTZB was investigated at TMHPP Zn(II) modified CPE by CV, DPV, and LSV. The reduction of MTZB was found to be an irreversible process. The TMHPP Zn(II) modified CPE showed electrocatalytic action for the reduction of MTZB, characterized by the enhancement of the peak current and the reduction of peak potential. The proposed method is a better method for the analytical determination of MTZB, because it is simple, fast, and it has sufficient precision, accuracy, and sensitivity. The developed sensor has been successfully applied for the voltammetric determination of MTZB in pharmaceutical formulations and urine samples.

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