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COMPARATIVE ELECTROCHEMICAL ACTIVITY OF THE INSECTICIDE, ENDOSULFAN, AT BARE AND 5,10,15,20-TETRAPHENYLPORPHYRINATO-IRON(III) CHLORIDE-MODIFIED GLASSY CARBON ELECTRODES

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ABSTRACT

Endosulfan, an insecticide used on a variety of vegetables, fruits and several other crops, shows a poor electrochemical activity at bare electrode surfaces. Activity of Endosulfan is significantly enhanced at glassy carbon electrodes coated with a thin film of 5,10,15,20-tetraphenylporphyrinatoiron(III) chloride [Fe(III)TPPCl], as compared to the bare electrode. The highest activity of the modified electrode is observed in sulfuric acid-acetonitrile mixed aqueous/nonaqueous medium.

Keywords: metalloporphyrins, cyclic voltammetry, Endosulfan, electrocatalysis.

Abbreviations: GC - glassy carbon, SCE - saturated calomel electrode, Fe(III)TPPCl - 5,10,15,20-tetraphenylporphyrinatoiron(III) chloride.

1. INTRODUCTION

The discovery of the active role of hemoglobin, an ion-centered porphyrin, to bind oxygen in mammalian systems lead to the study of the electrochemical activity of oxygen in the presence of synthesized metalloporphyrins to mimic the activity of the natural heme environment.[1,2] Such studies were later extended to investigate the catalytic reduction of other molecules, including organohalides, by synthesized metalloporphyrins.[3,4] Most of the early studies on this subject were restricted to nonaqueous solvents due to the lack of solubility of many metalloporphyrins in aqueous medium. This problem has been overcome by employing disk electrodes, on which metalloporphyrin molecules are immobilized, making electrochemical investigation feasible in aqueous medium. For instance, electrocatalytic reduction/oxidation of substances by electrode surfaces modified with various monomeric and polymeric metalloporphyrins have been reported.[5-8] Further, it has been recently reported that thin films of metalloporphyrins can be developed as oxygen and anion selective membranes.[9,10] Nevertheless, reports on voltammetric features of metalloporphyrins with regard to the effect of solvent composition, supporting electrolyte and starting potential are limited.[11]

Application of chemically modified electrodes, prepared by immobilizing foreign substrates on the surfaces of commercial electrodes, has become especially attractive, because of their ability to minimize many problems associated with bare electrodes such as unpredictable surface reactivity, lack of selectivity, complications due to adsorption and sluggish reaction kinetics. Such modified electrodes are now used for electrochemical characterization and detection of both inorganic and organic substances, which may not be possible at bare electrodes.[12,13]

Endosulfan is an organochlorine substance, which is commonly used as an insecticide on tea, potatoes, vegetables, fruits, coffee, cotton and cereals.[14] It is important to characterize this substance due to its neurotoxic behavior. More specifically, adsorption of Endosulfan through human skin may cause nerve stimulation, convolution, reflex excitation, etc. Therefore, this is included in the list of priority pollutants by the Environmental Protection Agency of the United States.[15]

The electrochemical behavior of Endosulfan is complicated due to the fact that its electrochemical reactivity highly depends on the starting potential, medium, type of the electrode, etc.[15] This paper summarizes a logical and a systematic approach to understand the electrochemical features of Endosulfan at bare and Fe(III)TPPCl modified glassy carbon electrodes. Relative catalytic activities of Endosulfan in the presence of Fe(III)TPPCl in many solvent systems are also reported.

2. EXPERIMENTAL

2.1 Materials

The electrode modifying agent, 5,10,15,20-tetraphenylporphyrinatoiron(III) chloride [Fe(III)TPPCl], was purchased from Aldrich Chemical Company, USA. Commercial samples of formulated Endosulfan (35% EC) were purchased from Cepetco, Sri Lanka. Freshly distilled acetonitrile and distilled water were used to adjust the composition of the cell medium. Freshly distilled dichloromethane was used for the preparation of the Fe(III)TPPCl solution, and as a cleaning agent for modified electrodes. Impact of different electrolytes on cyclic voltammetric behavior of Endosulfan was investigated using H_2SO_4 (Avondale Laboratories, England), $NaClO_4$ (Fluka, Germany), LiCl (Vickers, England) and NaCl (FSA Laboratories, England) solutions. Before all electrochemical measurements, the electrolyte solution was saturated with N_2 to maintain an O_2 free environment.

2.2 Instrumentation

All electrochemical experiments were conducted in a three-electrode single-compartment cell consisting of a glassy carbon (GC) disk working (BAS, USA), a Pt wire counter and a saturated calomel reference electrode (SCE), and all potentials were measured with respect to SCE. Potential cycles for cyclic voltammetry and appropriate constant potentials for amperometric experiments were applied by means of a CV-1B cyclic voltammograph; and resulting responses were recorded on a BAS X-Y recorder (both from BAS, USA).

2.3 Electrode Preparation

Glassy carbon electrodes were polished with alumina slurry by rubbing it on a polishing pad (BAS, USA) for about thirty seconds followed by rinsing with distilled water. It was sonicated in an ultrasonic bath for 5 minutes and again rinsed with distilled water. The electrode was then allowed to air-dry, and rinsed with distilled dichloromethane. Surface modification of the electrode was accomplished by introducing two drops of the $1x10^{-3}$ mol dm^{-3} coating solution, prepared in distilled dichloromethane, on to the dry electrode surface. After the solvent is evaporated, the modified GC electrode was kept in the electrochemical

cell for several minutes so as to establish the equilibrium with the contact solution before voltammetric and amperometric experiments.

3. RESULTS AND DISCUSSION

Effect of starting (initial) potential and supporting electrolyte on the cyclic voltammetric behavior plays a major role in electrochemistry. Although GC surfaces show clean electrochemistry in chloride electrolytes, as expected, presence of other ionic species may complicate the behavior. On the other hand, acidic medium should be used for the investigation of Endosulfan because it may be hydrolyzed in basic medium. Sulfuric acid-based electrolyte systems were specially selected because a stripping voltammetric study of Endosulfan has already been reported in such solutions.[15]

Thus, a complete understanding of the electrochemistry of sulfuric acid as a supporting electrolyte at bare GC surfaces is a necessity. Further, it is desirable to use mixed water/acetonitrile solvent systems as Endosulfan does not show adequate solubility in the pure aqueous medium.

Although no significant electrochemical features of 0.1 mol dm^{-3} sulfuric acid solution prepared in water/acetonitrile (1:1) solvent system were observed between +0.5 V and -1.0 V, increase in the initial potential up to +1.0 V introduced a minor reduction peak centered at + 0.25 V (Fig. 1a). Further increase in the initial potential resulted in an intense reduction peak at about -0.20 V (Fig. 1b), in addition to the minor reduction peak observed in Fig. 1a. These two peaks are attributed to the reduction of two types of chemical species associated with sulfuric acid that are formed at anodic potentials greater than +1.0 V. Therefore, subsequent experiments with Endosulfan were conducted selecting +1.0 V (or a lower value) as the initial potential to avoid complications due to the supporting electrolyte.

Electrochemical behavior of Endosulfan depends heavily on cell constituents (Table 1). Such changes are typical for organic molecules that show sluggish electrode kinetics. Among the electrolytes used, LiCl offers the most significant reduction peak for Endosulfan at the bare glassy carbon surface (Fig. 2). However, the low peak current-background current ratio observed in $5x10^{-3}$ mol dm^{-3} Endosulfan solution suggests that cyclic voltammetry at the bare electrode would not be a good choice for characterization of Endosulfan. More sensitive steady-state amperometry would also be not suited for this purpose as it would not result in responses with significantly high signal-to-noise ratios. Further, high operational potentials (-0.65 V) at the bare electrode does not lead to precise amperometric results due to increased noise levels. In order to minimize these unfavorable factors, chemically modified electrodes prepared by incorporating Fe(III)TPPCl can be employed.

Glassy carbon electrodes modified with Fe(III)TPPCl shows the electrochemistry of Fe(III)/Fe(II) couple between the potential limits of -0.40 V and -0.60 V.[16] When Endosulfan is present, the catalytically active Fe(II) interacts with Endosulfan molecules according to the catalytic ECE mechanism. Consequently, the reduction potential of Endosulfan is shifted towards the zero potential at Fe(III)TPPCl modified glassy carbon surfaces, demonstrating

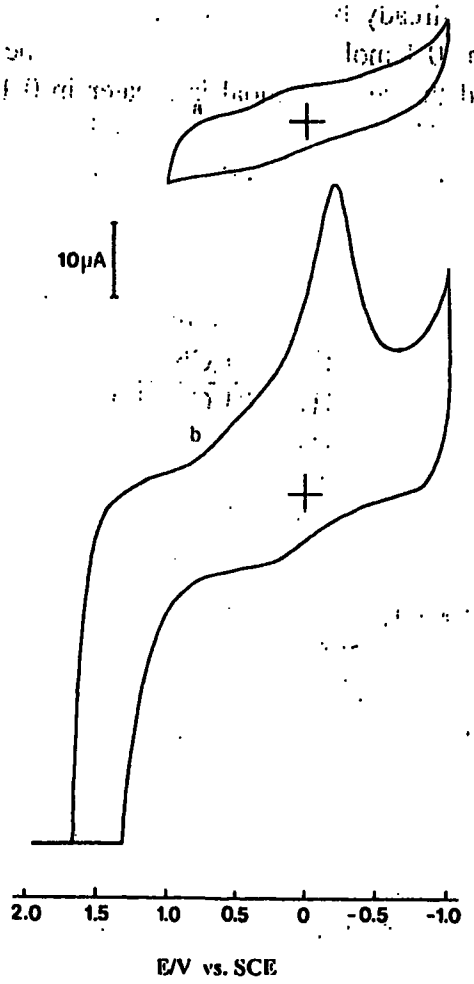

Fig 1 : Cyclic voltammogram of bare GC electrode in H_2O/CH_3CN (1:1) under N_2 satd. Supporting electrolyte 0.1 mol dm^{-3} H_2SO_4, scan rate 100 mV s^{-1} (a) +1.0 V to -1.0 V (b) +2.0 V to -1.0 V.

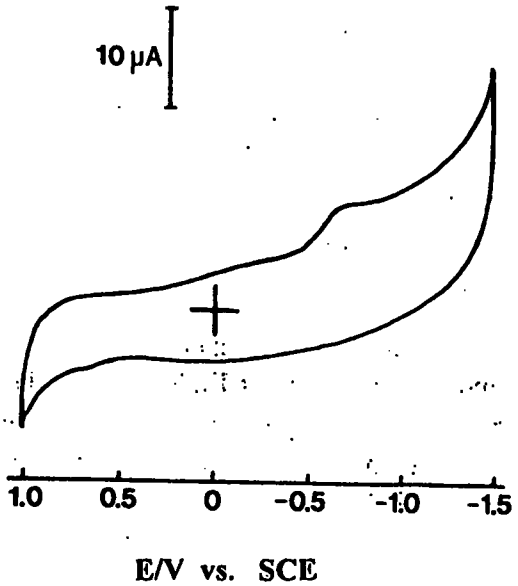

Fig 2 : Cyclic voltammogram of 5×10^{-3} mol dm^{-3} Endosulfan in H_2O/CH_3CN (1:1) at bare GC electrode under N_2 satd. Supporting electrolyte 0.1 mol dm^{-3} LiCl, scan rate 100 mV S^{-1}.

the strong catalytic activity on Endosulfan. Electrocatalytic behavior of metalloporphyrins toward organic substances has already been reported by several researchers.[17] Although the catalytic current is higher in the 0.1 mol dm^{-3} LiCl electrolyte, the shift in the reduction peak potential of Endosulfan toward the zero potential is greater in 0.1 mol dm^{-3} H_2SO_4. Hence, sulfuric acid was selected to study the voltammetric behavior of Endosulfan at the modified electrode in contrast to LiCl, selected for bare electrochemical studies.

Table 1: Voltammetric peak potentials of Endosulfan at bare GC electrode under different conditions.

Electrolyte	Medium	Peak potential, V
0.1 mol dm^{-3} LiCl	H_2O/CH_3CN (1:1)	-0.70
0.1 mol dm^{-3} NaCl	H_2O/CH_3CN (1:1)	-0.59
0.1 mol dm^{-3} H_2SO_4	H_2O/CH_3CN (1:1)	-0.56
0.1 mol dm^{-3} $NaClO_4$	CH_3OH/CH_3CN (1:1)	no peak

Effect of solvent composition on the electrochemical behavior of Endosulfan in H_2SO_4 is interesting. The highest peak current and the best reversible condition of Endosulfan are observed in 0.1 mol dm^{-3} H_2SO_4 prepared in H_2O/CH_3CN (2:1) medium which is in agreement with the results reported earlier (Fig. 3).[15] The increase in the amount of water in the cell medium with respect to the organic solvent favors the reversibility of the system (Fig. 3a and 3b), probably due to the increased rate of electron transfer between the solution and the GC surface through the coating. On the other hand, organic molecules are more soluble in organic media resulting in higher rates of mass transfer. As a result, the highest reversible condition would be observed in mixed solvent systems of moderate H_2O/organic solvent ratio, as reported in Fig. 3b. Similar observations for other organic substances have been reported even at bare electrodes.[11] Hence, this composition is recommended for further investigation.

Cyclic voltammetric experiments performed at different concentrations of Endosulfan at the coated electrode in 0.1 mol dm^{-3} H_2SO_4 prepared in H_2O/CH_3CN (2:1) medium produce calibration curves with a linear dynamic range of 2.5×10^{-4} mol dm^{-3} to 4.0×10^{-3} mol dm^{-3}. Scan rate dependence experiments conducted at a constant Endosulfan concentration suggest that the mode of mass transfer toward the electrode surface is also complicated. At low scan rates, it is due to both adsorption and diffusion, because the slope of the log i_p vs. log v plot, where i_p is the peak current and v is the scan rate, is about 0.9. However, high scan rates lead mainly to diffusion (Fig. 4).

Electrochemical behavior becomes more complicated in CH_3OH/CH_3CN nonaqueous systems prepared in the $NaClO_4$ electrolyte. The polarity of this solvent system is low enough to dissolve the adsorbed metalloporphyrin coating resulting in a pale brown colored solution. Consequently, the observed electrochemistry is a combination of the solution chemistry of Fe(III)TPPCl and the chemistry of Endosulfan at the coated GC electrode. This yields two reversible couples and a single irreversible reduction peak within the potential window of 0.0 V and -1.0 V (Fig. 5). Due to the complex electrochemical behavior, such solvent systems are not recommended to investigate the reactivity Endosulfan.

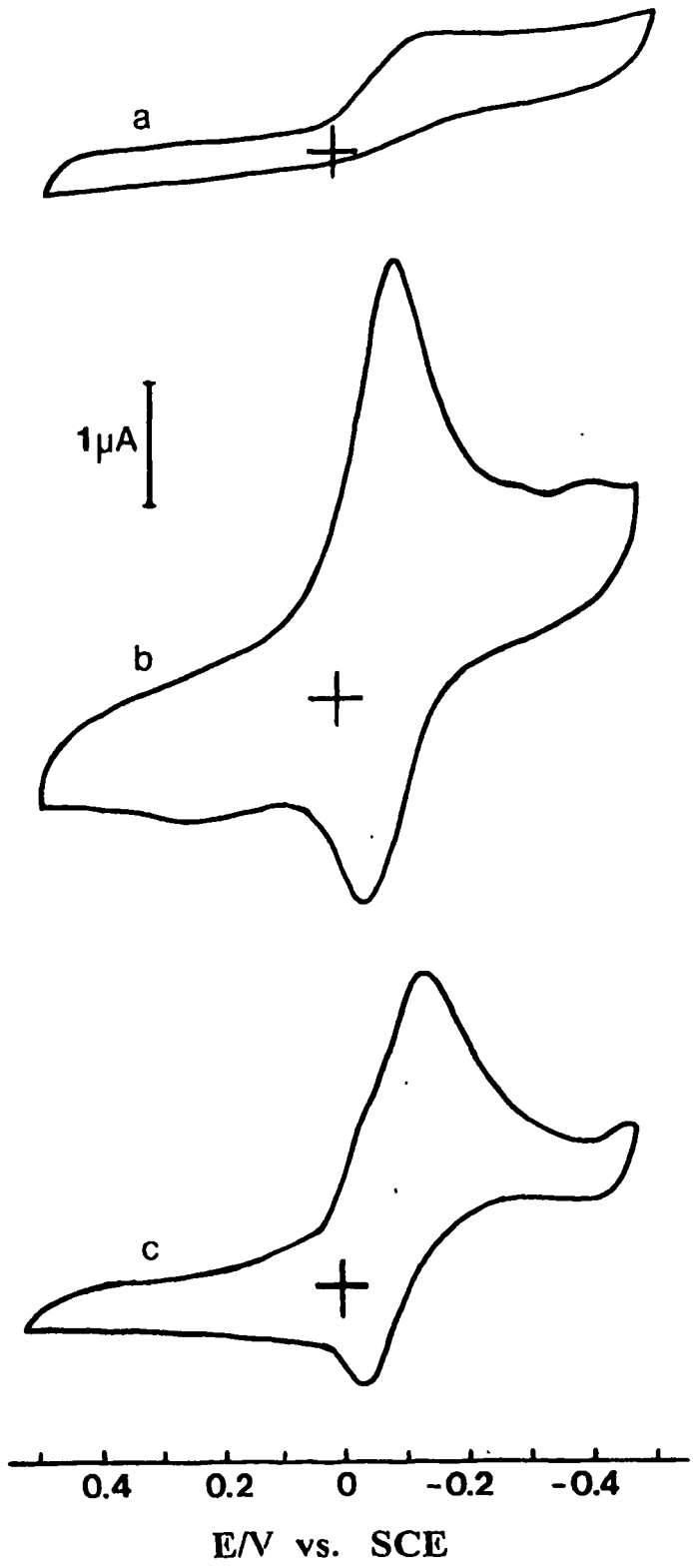

Fig 3 : Cyclic voltammograms of 5×10^{-3} mol dm^{-3} Endosulfan at Fe(III)TPPCl coated GC electrode in 0.1 mol dm^{-3} H_2SO_4 under N_2 satd. with different solvent compositions of H_2O and CH_3CN (a) 1:1 (b) 2:1 (c) 3:1. Scan rate 10 mV s^{-1}.

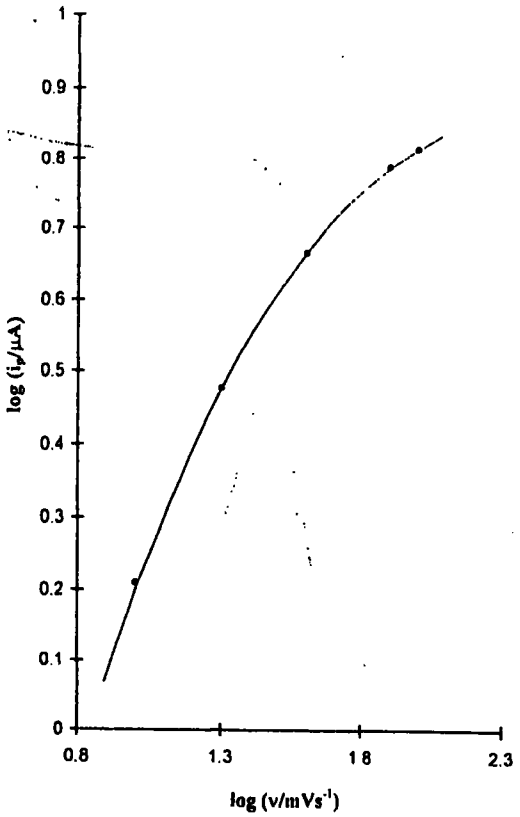

Fig 4 : The graph of log i_p vs. log v for Fe(III)TPPCl coated GC electrode in 5×10^{-3} mol dm^{-3} Endosulfan solution under N_2 satd. where i_p is the peak current and v is the potential scan rate. Supporting electrolyte 0.1 mol dm^{-3} H_2SO_4 in H_2O/CH_3CN (2:1).

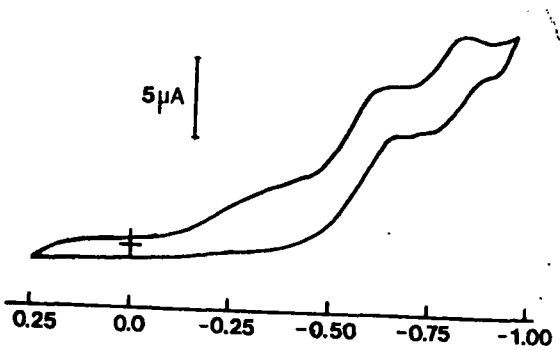

Fig. 5: Cyclic voltammograms of 5×10^{-3} mol dm^{-3} Endosulfan at Fe(III)TPPCl coated GC electrode in CH_3OH/CH_3CN (1:1) under N_2 satd. Supporting electrolyte 0.1 mol dm^{-3} $NaClO_4$, scan rate 20 mV s^{-1}.

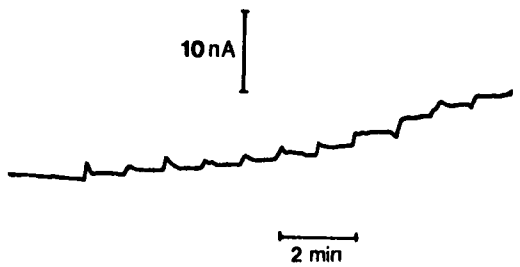

Fig. 6 : Amperometric current-time responses obtained with Fe(III)TPPCl coated GC electrode with increasing concentration of Endosulfan in 40 μmol dm^{-3} steps under N_2 saturation. Applied potential +0.05 V, supporting electrolyte 0.1 mol dm^{-3} H_2SO_4 in H_2O/CH_3CN (2:1).

Under the optimized conditions of 0.1 mol dm^{-3} H_2SO_4 in H_2O/CH_3CN (2:1) solvent system at the Fe(III)TPPCl coated GC electrode, steady-state amperometric experiments were conducted at different potentials in the vicinity of the reduction peak potential. However, reproducible amperograms were not obtained at the peak potential indicating that amperometric characterization of Endosulfan is complicated. This feature is probably due to the strong overlap of the reduction peak potential with that of the oxidation potential as observed in Fig. 3b. In order to solve this problem, a potential more positive than the peak potential, where there is less overlap with the oxidation peak, is selected as a compromise between reproducibility and sensitivity of amperometric responses. Under these conditions, satisfactory amperograms are obtained at micromolar levels (Fig. 6).

4. CONCLUSION

Electrochemical activity of Endosulfan at bare GC electrodes is significantly enhanced by introduction of the Fe(III)TPPCl catalyst. The optimum solvent system of H_2O/CH_3CN (2:1) produces the most attractive cyclic voltammetric features among the other systems. However, the behavior of Endosulfan at the Fe(III)TPPCl modified electrode is complicated, resulting in several modes of mass transfer, significant variations with solvent changes and ill-defined adsorption. Nevertheless, analytical responses of Endosulfan within the micromolar concentration range are demonstrated at the Fe(III)TPPCl modified GC electrode, suggesting that metalloporphyrin-based electrodes have the potential ability for detection of Endosulfan.

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