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The effects of point of substitution on the formation of manganese phthalocyanine-based molecular materials: Surface characterization and electrocatalysis

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ABSTRACT

Molecular films of manganese phthalocyanine (MnPc) complexes, tetra-substituted with 2-diethylaminoethanethio at the peripheral (Mn(OAc)-β-TDEAETPc, **1**) and non-peripheral (Mn(OAc)-α-TDEAETPc, **2**) positions were formed on glassy carbon electrodes by electropolymerization and electrodeposition respectively. Atomic force microscopy images confirmed the presence of the films and revealed significant morphological differences. The films exhibited an electrocatalytic activity towards the oxidation of the insecticide, bendiocarb. Hydrodynamic technique, using rotating disc electrode voltammetry, was used to investigate the kinetics of electro-oxidation of the insecticide. Morphological differences of the films significantly influenced kinetic parameters. Values of Tafel slopes, obtained from Tafel plots, suggested that catalysis of bendiocarb occurred via outer sphere mechanism.

1. Introduction

The use of metallophthalocyanine (MPc) complexes, containing electroactive metals, as electrochemical sensors is facilitated by the formation of thin insoluble films of these macrocycles. Thin films of MPc complexes can be fabricated by electrochemical polymerization, electrodeposition and self-assembly techniques, among others. Electrochemical polymerization is aided by the presence of polymerizable substituent (containing nitrogen and sulphur) [1], while self-assembly technique is promoted by sulphur containing substituents. [2–4].

Phthalocyanine and porphyrazine complexes of electroactive metals, such as Co and Fe, have been employed for the detection of various analytes [5–8]. MnPc complexes are rarely used for electrocatalysis, despite having electrocatalytic properties comparable with that of their Co and Fe analogues, hence the motivation for the use of MnPc complexes in this study. We have recently reported on the electropolymerization of MnPc complex, octa-substituted at the peripheral position with 2-diethylaminoethanethio [9]. In this work, we report on the formation of molecular materials (films) using peripherally (β) and non-peripherally (α) tetra-substituted MnPc complexes, Fig. 1, with the aim of determining the effect of point of substitution (α versus β) on mode of film formation. Tertiary amine nature of the nitrogen atom of the substituent (Fig. 1) should allow the formation of polymers by electrochemical method. Surface characteristics of the films were studied using cyclic voltammetry and atomic force microscopy (AFM). Electrocatalytic property of the films towards the electro-oxidation of bendiocarb, and kinetics of electro-oxidation of this insecticide were also investigated.

Bendiocarb is an N-methyl carbamate insecticide (Scheme 1), which is highly toxic if ingested or absorbed through the skin [10]. Therefore, electrocatalytic oxidation and detection of bendiocarb are environmentally significant. Differential pulse voltammetric method, using carbon paste electrode modified with octadecane, has been reported for the detection of bendiocarb [11]. The use of MPc complexes for electrocatalytic oxidation of this pesticide is reported in this work. Bendiocarb is electrochemically inactive but can be converted to the electroactive phenolic analogue by hydrolysis. In the present study, alkaline hydrolysis was used to form the phenolic derivative (2, 3-isopropylidendioxyphenoxide) (Scheme 1).

2. Experimental

2.1. Materials

Bendiocarb and tetrabutylammonium tetrafluoroborate ($TBABF_4$) were obtained from Sigma-Aldrich. Dimethylformamide (DMF) and methanol were distilled before use. Stock solution of bendiocarb (4.8×10^{-3} M) was prepared in freshly distilled methanol, because of its limited solubility in water. All solutions were prepared with ultrapure water of resistivity 18.2 MΩ cm obtained from a Milli-Q Water system. Electrochemical experiments were carried out in argon-saturated aqueous solutions containing small amounts of methanol from the stock solution of bendiocarb. The synthesis of

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