

Voltammetric and Potentiometric Behavior of 2-Pyridinethiol, 2-Mercaptoethanol and Sulfide at Iron(II) Phthalocyanine Modified Carbon-Paste Electrode

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ABSTRACT: A carbon-paste electrode modified with iron(II) phthalocyanine (FePc) was used as a sensitive potentiometric sensor for determination of 2-pyridinethiol (2PT), 2-mercaptoethanol (2ME) and sulfide ion in aqueous solutions. The modified electrode acts as an electrocatalyst for oxidation of these compounds, and lowers the overpotential for oxidation reactions by more than 400 mV, compared to the unmodified electrode. The process was dependent on the pH of the supporting electrolyte. The fast rate of electron transfer results in a near-Nernstian behavior of the modified electrode, and makes it a suitable potentiometric sensor for measurement of these compounds. Calibration studies were performed using potentiometry in oxygen or air saturated stirred solutions; linear responses were obtained over the range of about 1×10^{-6} to 5×10^{-3} M (correlation coefficients, r , of ~ 0.999 , $n=8$). The modified electrode exhibited a fast response time (< 20 s), good stability, and had an extended lifetime; the standard deviation of slopes, during a period of two months, was 1.7-2.4% ($n=10$). Appropriate electrochemical and analytical data are presented.

KEY WORDS: Iron phthalocyanine, Modified electrodes, Potentiometry, Electrocatalysis, 2-pyridinethiol, 2-Mercaptoethanol, Sulfide

INTRODUCTION

The development of chemically modified electrodes (CMEs) continues to be an area of great interest [1-5]. One of the most important properties of CMEs, which has been the subject of considerable study, is their ability to catalyze the oxidation or reduction of solute species that exhibit high overvoltages at unmodified surfaces. The major effect of the modifier is to lower the potential

required for electrolysis of the catalyzed redox systems. Therefore, the modified electrodes find direct applications in a variety of analytical situations such as amperometry [6-11], voltammetry [12-14], and potentiometry [1,15].

It has been known for a number of years that some of the transition metal complexes act as redox mediators and

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can catalyze the oxidation of biological and organic compounds. Promising advances towards improved selectivity of carbon-based electrochemical sensors have been achieved through judicious surface modification of electrodes with these complexes [16,17]. Metallophthalocyanines have been shown to act as effective electrocatalysts towards a wide range of redox systems. Electrodes modified with these compounds have shown great promise for electrocatalytic determination of many organic and biologically important compounds [18-25].

Sulfhydryl compounds are known to undergo electrochemical processes at solid electrodes, but their oxidation occurs at relatively high potentials [26,27]. Several types of CMEs have been designed and characterized for electrocatalysis of sulfhydryl compounds, like cysteine and its derivatives [23,28], glutathione [11,29], sulfide ion [15], 2-mercaptoethanol [28-30], and other sulfhydryl compounds [26,31]. Oxidation of thiols by air, without any catalyst present is relatively slow [15,26]. However, in the presence of metallophthalocyanines, due to faster reaction rates, these processes become technologically important in deodorizing of aqueous streams and in wastewater treatment [5,32,33].

In a previous report, *Lever et al.* [21] have studied the electrocatalytic activity of perchlorinated iron phthalocyanine, adsorbed on a graphite electrode, for oxygen reduction. Phthalocyanines that are good catalysts for O_2 reduction are also good catalysts for oxidation of thiols, with cobalt and iron phthalocyanines showing the highest activity [28]. In this regard, *Zagal's* group [5] used perchlorinated iron phthalocyanine, adsorbed on pyrolytic graphite disk, for amperometric determination of 2-mercaptoethanol. The present work is concerned with the development of a potentiometric method for measurement of 2-pyridinethiol, 2-mercaptoethanol and sulfide ion at a carbon-paste electrode modified with FePc. Preliminary investigation for the catalytic activity of the FePc-modified electrode towards the sulfhydryl compounds and sulfide were performed using cyclic voltammetry.

EXPERIMENTAL

Materials

Iron(II) phthalocyanine, 2-pyridinethiol, 2-mercaptoethanol and spectroscopic grade mineral oil (Nujol) were obtained from Aldrich, and used as received. Graphite powder, sodium sulfide and all other chemicals

(all from Merck) were of highest purity available and used without any further purification. Doubly distilled, deionized water was used for preparing all of the solutions and throughout the experiments.

Stock solution of sodium sulfide was prepared by dissolving reagent grade $Na_2S \cdot 9H_2O$ in water. The concentration of Na_2S was determined by titration with mercury(II) solution following a method reported in the literature [34]. Solutions of 2PT and 2ME were freshly prepared in supporting electrolyte solutions. The supporting electrolyte solutions were 0.05 M buffers of phosphate (pH 6-8), acetate (pH 5) and borax (pH 9,10), and were prepared from 0.1 M solutions of reagent grade phosphoric acid, potassium dihydrogen phosphate, potassium hydrogen phosphate, sodium acetate, acetic acid, sodium tetraborate and potassium hydroxide, using a pH meter. These were subsequently diluted to provide 0.05 M working solutions. Voltammetric experiments were carried out in 0.05 M buffer solutions, deoxygenated by pure nitrogen. Solutions for potentiometric determination of the thiol compounds were equilibrated with air or oxygen at 25 ± 1 °C.

Apparatus

Cyclic voltammetry was performed with a Bank Potentiostan model POS88 system, which was connected to a Pentium 133 computer via a DAS 1602 interface board. A conventional three-electrode cell was used with a carbon-paste working electrode (with or without FePc), a saturated Ag/AgCl reference electrode and a Pt-wire as the counter electrode.

Potentiometric measurements were carried out with the following cell assembly: FePc-modified electrode | test solution, O_2 or air sat'd || Ag-AgCl-KCl (sat'd). The cell consists of a FePc-modified carbon-paste as the indicator electrode, a saturated Ag/AgCl reference electrode and a magnetic stirrer. The measuring cell was thermostated at 25 ± 1 °C using a Haake model FK2 circulation water bath. A digital pH/mV meter (Corning model 125) was used for measuring the pH and potentials. The meter was connected to a Philips model PM-8277 X-Y recorder for plotting potential-time data.

Modified electrode preparation

The general procedure for preparation of the modified

carbon-paste electrode was to mix graphite powder with FePc (5% w/w) and mineral oil (Nujol). After thorough hand mixing in a mortar and pestle, a portion of the composite mixture was packed into the end of a Pyrex glass tubing (ca. 3 mm id.). Electrical contact was made by forcing a copper wire down the glass tube and into the back of the mixture. Unmodified electrodes were prepared in the same way without addition of FePc. The working surface of the electrode was polished using a polishing cloth. The electrodes were then rinsed with ethanol and distilled water, respectively.

RESULTS AND DISCUSSION

Previous studies have shown that the electrodes modified with phthalocyanines containing transition metal ions exhibit substantial electrocatalytic activities for oxidation of the sulfhydryl compounds [5]. Among the transition metal ions, cobalt [26,35-37] and iron [6,21] show the highest electrocatalytic activity while lowering the overpotential required for the electrochemical oxidation of sulfhydryl compounds. Most of the reported modified electrodes have been used for the development of amperometric sensors and the application of such electrodes, as potentiometric sensors, are sparse. The application of a less demanding potentiometric method yielding a continuous potential response to sulfhydryl compounds and sulfide ion appears to be advantageous, especially when monitoring over a long period of time and measurement over a wide concentration range is required [1]. The potentiometric method with an electrode modified with a suitable mediator represents a convenient way to measure the equilibrium potential in slow and irreversible systems [38,39]. Therefore, we were prompted to use FePc as an electron mediator for potentiometric measurement of sulfhydryl compounds and sulfide ion.

Voltammetric studies

Preliminary experiments to investigate the catalytic activity of the FePc-modified electrodes towards the sulfhydryl compounds and sulfide were performed using cyclic voltammetry. Cyclic voltammograms were recorded using unmodified and modified carbon-paste electrodes in nitrogen-saturated solutions.

The catalytic function of the FePc-modified electrode is demonstrated in Fig. 1 by cyclic voltammograms of 1.0×10^{-3} M solutions of 2PT, 2ME and sulfide ion, obtained at the surface of the chemically modified carbon-paste electrodes in the potential range of -0.2 to 0.8 V vs. Ag/AgCl reference electrode. Under the same experimental conditions, the direct oxidation of these compounds at an unmodified carbon-paste electrode showed relatively weak anodic waves with a peak potential at about $+0.6$ V for 2PT and not well defined peaks for 2ME and sulfide (Fig. 1, waves A). However, the FePc-modified electrode exhibited only a single irreversible anodic wave for each compound in the potential range examined, with peak potential at 0.20 , 0.3 and 0.24 V for 2PT, 2ME and sulfide, respectively (Fig. 1, waves B). The modified electrode did not show a measurable anodic wave in supporting electrolyte in the absence of thiols. The catalytic currents were proportional to the thiol concentration, and no cathodic currents were observed on the reverse scan. Such irreversible anodic waves have also been observed for other sulfhydryl compounds such as cysteine and glutathione at the surface of cobalt phthalocyanine modified carbon-paste electrodes [6]. The modified electrode incorporates a Fe(II)Pc doping level of 5% by weight. CMEs containing higher modifier concentrations were not found to yield significantly higher current levels and thus were not investigated further.

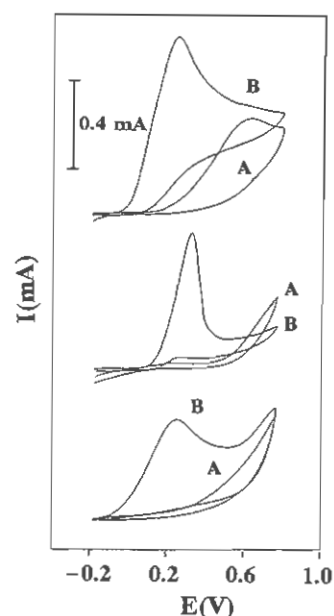


Fig. 1: Typical cyclic voltammograms for oxidation of 1×10^{-3} M 2PT (upper curves), 2ME (middle curves) and sulfide (lower curves) at the (A) unmodified electrode and (B) modified carbon-paste electrode. Scan rate, 200 mV s^{-1} .

Oxidation of these thiol compounds at the modified electrode gives rise to typical electrocatalytic responses with anodic peak currents that are greatly enhanced over those observed for the unmodified electrode. The maximum current for the oxidation of 2PT, 2ME and sulfide at the modified electrodes occurred at potentials much more negative than those obtained in the absence of the modifier. This behavior, which was observed at several concentrations and different potential scan rates, clearly demonstrates that the FePc mediator functions electrocatalytically towards these compounds.

In order to determine whether the current due to the oxidation of these compounds were diffusion controlled, plots of i_p vs. square root of the scan rate, $v^{1/2}$, were constructed for the oxidation of 2PT, 2ME and sulfide. The linear dependence of i_p vs. $v^{1/2}$ for 2PT and 2ME (Fig. 2) indicates that the oxidation of these compounds at the modified electrode surface is indeed diffusion-controlled. However, in the case of sulfide the anodic peak current varies linearly with the potential scan rate, v (Fig. 3), indicating that it corresponds to a reaction occurring on an adsorbed species [40]. This peak can then be assigned to the oxidation of an adduct formed between sulfide and Fe center. This adduct or adsorbed species reacts at a lower overpotential compared to the one at the unmodified electrode [5]. Cyclic voltammograms for the oxidation of 2ME show an anodic dip in current as the potential was cycled back in the cathodic direction. Halbert and Baldwin [6] have observed such a behavior for the phthalocyanine oxidation of sulfhydryl and several other organic compounds. A possible explanation for the adsorption-like cyclic voltammogram behavior is that one of the steps in the oxidation process consists of the slow or irreversible chelation of the thiol group to the phthalocyanine metal center [6]. Some evidence for the involvement of such a complexation steps in the electrocatalytic processes have been demonstrated in the previous electrochemical and spectroscopic investigations [5,41,42].

Values of αn_a (where α is the transfer coefficient and n_a is the number of electrons involved in the rate-determining step) were calculated for the irreversible oxidation of thio compounds according to the equation $\alpha n_a = 0.048 / (E_p - E_{p/2})$ [8], where $E_{p/2}$ is the potential corresponding to $i_{p/2}$. The values of αn_a at the modified electrodes were ~ 0.5 for all of the compounds and

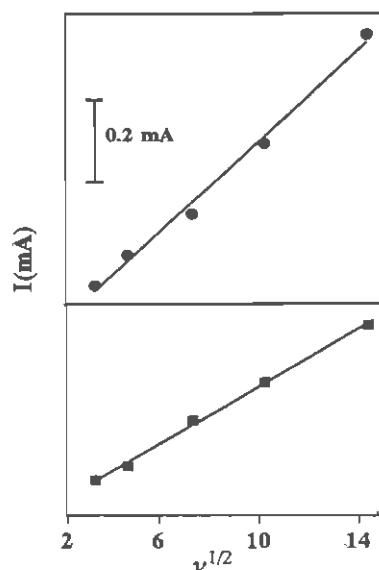


Fig. 2: Dependence of peak current on the square root of the scan rate for 1×10^{-3} M 2PT (●) and 2ME (■) at the FePc-modified electrode.

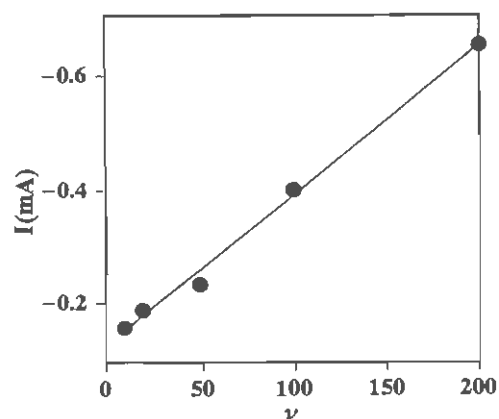


Fig. 3: Dependence of peak current on the scan rate for 1×10^{-3} M sulfide at the FePc-modified electrode.

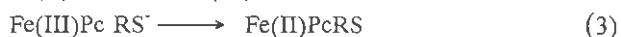
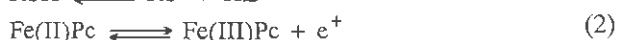
estimated to be much lower at the unmodified electrodes. These values clearly show that not only is the overpotential for the sulfhydryl and sulfide oxidation reduced at the modified electrode, but also the rate of the electron transfer process is greatly enhanced. This is confirmed by the relatively larger i_p values recorded during cyclic voltammetry at the modified electrode.

In order to ascertain the nature of the electrode reaction producing the anodic peak, a graph of the current function, $i_p/Cv^{1/2}$, versus $v^{1/2}$ was drawn; the slightly negative slope for all of the systems is typical of a catalytic process for the oxidation of these compounds at the surface of the modified electrode [27,34]. The anodic

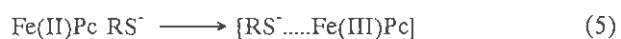
peak is considered to result from the electrocatalytic oxidation of 2PT, 2ME or sulfide. The results indeed suggest an EC mechanism (electron transfer process followed by a chemical reaction), and a one-electron transfer in the rate-determining step for the electrocatalytic oxidation of all the systems (assuming that the electron transfer coefficient, α , is 0.5 for these irreversible systems).

The graph of the anodic peak potential vs. pH showed that the peak shifts to more negative potentials with increasing pH. Such a behavior suggests that the dissociation of a proton from the SH group occurs at or before the rate-determining step [5].

In the light of our results and previous works on other sulfhydryl compounds [5,15,29,41], the catalytic effect of FePc modified carbon-paste electrode towards 2PT can be explained by a two-step electrocatalytic process, initiated by the electrochemical oxidation of the Fe(II)Pc to Fe(III)Pc and completed by the chemical oxidation of 2PT in a redox reaction, which also serves to regenerate the Fe(II) form of the phthalocyanine.



The chemical process (Eq. 3) for the oxidation of 2ME and sulfide can be represented as following:



The product of sulfide oxidation, according to the relevant literature [15, 38], is expected to be polysulfide ion. Adduct formation between 2PT and phthalocyanine seems to be inhibited by the steric effects of the bulky side-ring of the thiol substitution. Further work is necessary to understand the nature of the adducts or intermediates formed between FePc and the thio compounds.

Potentiometric response of the modified electrodes

The direct oxidation of sulfhydryl compounds by oxygen without any catalyst present is relatively slow [15,26]. Potentiometric measurement methods based on a redox mediator represents a convenient way to measure the equilibrium potential of such slow and irreversible reactions. The FePc-modified electrode can be used as a

mediator for indirect oxidation of 2ME, 2PT and sulfide by oxygen. The Fe(III)Pc is reduced by these compounds, forming Fe(II)Pc (Eqs. 3 or 6), which can be reoxidized back in the second step through a chemical reaction with oxygen according to Eq. (7).



In fact the FePc mediator provides a reversible redox couple, Fe(III)Pc / Fe(II)Pc, for measuring the equilibrium potential of the thiol-oxygen system. The ability of metallophthalocyanines to catalyze the analyte oxidation and oxygen reduction, and their application as potentiometric sensors for determination of several compounds such as sulfide, thiols and ascorbic acid have been previously reported (1,5,43-45). As can be seen from Eqs. (3) and (7), the potential of the electrode is determined by the Fe(III)Pc / Fe(II)Pc concentration ratio, which is determined not only by the thiol concentration, but also by the pH and oxygen concentration in solution. In the case that the concentration of oxygen and other parameters, such as pH and temperature are kept constant, the potential of the modified electrode is determined by the concentration of the thiol compounds in solution.

The response time of the modified electrodes, tested by measuring the time required to achieve a steady state potential (within ± 1 mV) upon sequential addition of 100 μL of 0.01 M solution of the thiols to 0.05 M buffer solution, saturated with oxygen at $25 \pm 1^\circ\text{C}$, was within 20 s, depending on the efficiency of stirring during the sample injection. A typical potential versus time curve for the response of the modified electrode to changes in 2ME concentration is shown in Fig. 4. Similar behavior was observed for the solutions saturated with air. The important point about the response time of the electrode is the effect of pH; it was observed that the response time of the electrode becomes faster by increasing pH, which can be related to increasing the concentration of thiolate anion (RS^-) in solution [15].

The calibration plots of potential of the modified electrode vs. logarithm of concentration of thiols, in air or oxygen saturated solutions, were linear over the concentration range of $1 \times 10^{-6} - 5.0 \times 10^{-3}$ M. Response curves for the oxygen saturated 2PT, 2ME and sulfide solutions at pH 7 are shown in Fig. 5. The response characteristics of the electrode, together with the least squares analysis of the data are given in Table 1. The sensitivity expressed

Table 1: Response characteristics of the FePc-modified carbon paste electrode towards 2PT, 2ME and sulfide at different pH values.

| Parameter | 2PT | | | | 2ME | | | Sulfide | | | |
|-----------------------------|-----|--|--------|--------|--------|--------|--------|---------|--------|--------|--------|
| | pH | 7.0 | 8.0 | 9.0 | 10.0 | 5.0 | 6.0 | 7.0 | 5.0 | 6.0 | 7.0 |
| Slope mV/decade | | 58.04 | 62.68 | 68.82 | 70.68 | 49.22 | 52.09 | 54.99 | 60.46 | 65.26 | 69.46 |
| Correlation coefficient (r) | | 0.9991 | 0.9989 | 0.9994 | 0.9993 | 0.9987 | 0.9992 | 0.9991 | 0.9989 | 0.9990 | 0.9993 |
| Limit of linear range | | $5 \times 10^{-3} - 1 \times 10^{-6}$ M in all cases except sulfide at pH 7.0, which was $1 \times 10^{-3} - 1 \times 10^{-6}$ M | | | | | | | | | |
| Limit of detection | | $\sim 1 \times 10^{-6}$ M | | | | | | | | | |
| Slope variation | | $\pm 1.7-2.4\%$ RSD over a period of two months (n=10) | | | | | | | | | |

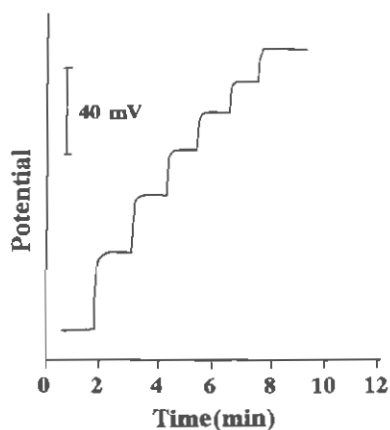


Fig. 4. Potential-time curve for the response of the FePc-modified electrode to successive addition of 100 μ L 0.01 M 2ME to 25 mL of 0.05 M phosphate buffer, pH 5, saturated with oxygen at 25 $^{\circ}$ C.

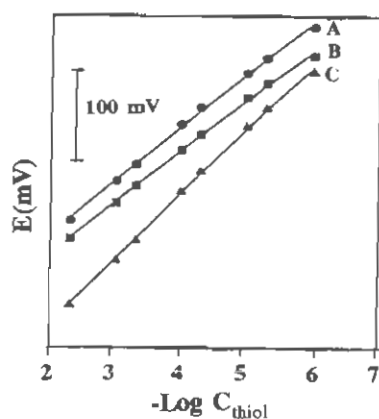


Fig. 5: Calibration plot of potential of FePc-modified electrode versus logarithm of 2PT (A), 2ME (B) and sulfide (C) concentrations, in 0.05 M phosphate buffer pH 7 and oxygen saturated solution at 25 $^{\circ}$ C.

as the slope of the calibration graph, was calculated to be between 50 to 70 mV/decade of thiol concentration, indicating a near-Nernstian behavior.

The reproducibility of the potential response of the electrode was obtained by determining the slope of the calibration graph in a period of one month (n=10). The electrode retained its full activity during this period. The relative standard deviation of slope for different thiols was in the range of 1.7 to 2.4%. The complex, FePc, is very insoluble in aqueous solutions, and it seems to be very stable in carbon-paste matrix, which results in high stability of the electrode response. The theoretical limit of detection was $\sim 1 \times 10^{-6}$ for the thiols studied. Since carbon paste is a reservoir of the modifier, a slight polishing on a soft polishing cloth can easily renew the surface of the electrode.

The response of the modified electrode to several common anions such as chloride, bromide, iodide and sulfate was investigated. The modified electrode response was only slightly changed by the addition of these ions. These common anions do cause a slight deviation in the slope and intercept of the calibration graph while maintaining linearity, but assuming calibration in their presence, would not preclude the use of the electrode to analyze 2PT, 2ME and sulfide. However, these thiol compounds could not be determined in the presence of each other. Other compounds with reducing properties and redox potentials close to these compounds also may interfere if they are present.

CONCLUSION

The FePc-modified carbon-paste electrode has been

successfully applied as a sensitive potentiometric sensor for determination of the thiol compounds. The electrocatalytic system for the determination of these compounds shows relatively long-term operational stability (over a month). The proposed potentiometric method offers advantages of very simple instrumentation and wide linear range of the calibration plot (about 4 decades of concentration). Voltammetric methods require a potentiostatic system and periodic regeneration of the working electrode to obtain reproducible responses [1], and generally offer lower linear range. Potentiometric measurements are carried out at ambient atmosphere, which further contributes to the simplification of the analytical procedure. The above advantages together with the very easy preparation and easy regeneration of the electrode surface by simple polishing make the system useful in constructing simple devices for determination of sulfhydryl compounds, especially as electrochemical detectors in chromatography. Further work is necessary to understand the nature of the possible adducts or intermediates formed between FePc and the thiol compounds.

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