Electrode with Electrochemically Deposited N,N',N'',N'''-Tetramethyltetra-3,4-pyridinoporphyrazino-cobalt(I) for Detection of Sulfide Ion

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Electroreduction of N,N',N'',N'''-tetramethyltetra-3,4-pyridinoporphyrazinocobalt(II) in aqueous buffer phosphate solution leads to the deposition of an insoluble tetrapyridinoporphyrazinocobalt(I) phthalocyanine film on the highly oriented pyrolytic graphite (HOPG) electrode. This modified HOPG electrode has been further coated with Nafion or Tosflex ion-exchange membranes and used in the determination of concentration of sulfide ion and 2-mercaptoethanol by direct potentiometry.

The use of phthalocyanines as catalysts for the oxidation of sulfide and sulfur-containing organic compounds is well-known. Many processes were patented some 20 years ago, for the treatment of effluent aqueous streams and wastewater[1–8] by autoxidation in the presence of air or oxygen. Yet, today, there remains great interest in the development of new catalysts and the mechanistic aspects thereof, with cobalt phthalocyanine derivatives in general[9–20] and cobalt(II) tetrapyridi-

noporphyrazines, (Co[II](tppa)),[21] in particular being of special concern.

The special properties of the tetramethylated metal porphyrazine cation (Figure 1), M(Tmtppa), have also been investigated in photooxidation processes,[22] intercalation into DNA,[23] and electroconductivity.[24] However, the catalytic behavior of the Co[II](Tmtppa) cation toward sulfur compound oxidation processes has not been reported previously.

We have studied the electrocatalytic properties of Co[II]-(Tmtppa) for the oxidation of sulfide ion in order to compare it with the water-soluble metalated tetrasulfonated phthalocyanine, which has also been reported to catalyze the oxidation of sulfide ion by oxygen.[25]

Our interest in this species is predicated on the fact that the Co[II]/Co[I] couple in Co(Tmtppa) is more positive than any other reported CoPc species and therefore has the largest driving force for oxidation of sulfide ion.

The electrochemical reduction of the Co[II](Tmtppa) cation in water results in the deposition on the electrode surface of a phthalocyanine film which is stable in water under an argon or nitrogen atmosphere. The exploitation of the variation in the potential of metalloporphyrins as ionophores in polymer membrane ion-selective electrodes (ISEs) in last few years[26] led us to consider whether a Co(Tmtppa)-modified electrode might be useful for determination of sulfide ion concentration.

However, in order to protect the phthalocyanine deposition from dissolving back in solution, the electrode is further coated with a perfluoro ion-exchange polymer. These have been applied in electrochemical studies[27,28] because of their ion-exchange capability, good electrical conductivity in contact with electrolytes, and ease of application.

Two common methods for the determination of sulfide ion concentration involve ion chromatography with electrochemical detection[29] or the potentiometric method with a sulfide-based ion-selective electrode.[30–41] Recently, Maekawa et al.[42]

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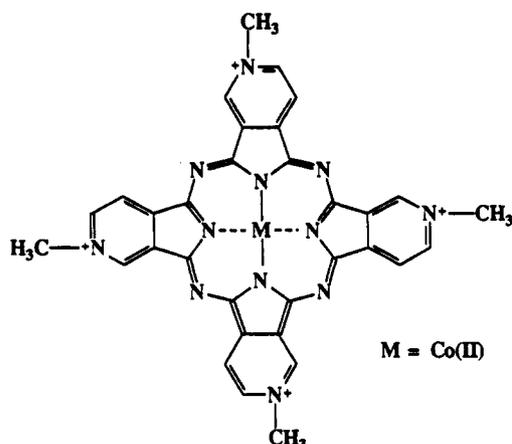
Figure 1. Structure of N,N',N'',N'''-tetramethyltetra-3,4-pyridino-porphyrazinocobaltate(II).

M = Co(II)

have also reported the sensing behavior of a CuO-loaded element for H₂S detection.

Sulfide ISEs obtained by incorporating silver sulfide into a pressed disk membrane,[30] also known commercially as the Orion electrode, have been investigated very intensively. [31-41] The selectivity and sensitivity of this kind of electrode are based on the small value of the solubility constant for silver sulfide and the small degree of dissociation of silver sulfide in different sulfide concentrations. The direct determination of sulfide ion (as distinct from back titration) involves determination of S^{2-}, rather than HS^- and is therefore limited to high pH, usually 12, where S^{2-} dominates.

There is a very extensive and rapidly growing literature on ISEs, but these are frequently based upon rather similar science.[43] There is yet a need for new classes of ISE.

In this work, we report the behavior of a graphite electrode covered by Co(Tmtppa) as a sulfide, specifically HS^-, and an organic thiol-selective electrode.[44] Although minute quantities of elemental sulfur must exist in equilibrium at the electrode surface, no problems of fouling by sulfur are noted. The use of an ISE which is not based upon silver sulfide is shown to offer certain advantages.

EXPERIMENTAL SECTION

Materials. All chemicals were reagent grade and used as received. Water was purified by double distillation with

KMnO₄, followed by passage through a Barnstead organic removal cartridge and two Barnstead mixed-resin Ultrapure cartridges. Buffer solutions were prepared from 0.1 M solutions of reagent grade H₃PO₄, KH₂PO₄, K₂HPO₄, and KOH and adjusted to the desired pH.

Nafion, a cation-exchange membrane is used as a 5 wt % solution in a mixture of a lower aliphatic alcohol and 10% water (Aldrich). A 0.1 wt % Nafion solution was prepared by diluting the 5 wt % stock solution with 2-propanol or n-butanol.

Tosflex, an anion-exchange membrane, denoted IE-SA48, was obtained from Tosoh Co. Ltd. (Tokyo, Japan). The preparation of the Tosflex membrane in aqueous solution and in a solvent mixture of methanol + 2-propanol + water (1:1:1) was carried out as reported.[45,46] The 0.1 wt % Tosflex solution was prepared by diluting a 0.7 wt % stock solution 7 times with their appropriate solvents. (The 0.7 wt % stock IE-SA48 Tosflex solution was kindly supplied by Dr. J. Weber from J. Heyrovsky Institute.) The film, which was used to protect the phthalocyanine film, was prepared by evaporation of 10 μL of a 0.1 wt % membrane solution on the electrode surface.

Argon gas (Linde) was purified by passage through heated copper fillings. Oxygen gas (Linde) was used as supplied. Buffer solutions were saturated by argon or by oxygen and maintained under 1 atm of the appropriate gas during the experiments.

Highly oriented pyrolytic graphite (HOPG; Union Carbide) was mounted in Teflon to expose a circular area of 0.495 cm² as the working electrode.

Physical Measurements. Cyclic voltammetry was performed using either the Pine Instruments RDE-3 potentiostat and the Pine Instruments PIR rotator or the Wenking Model ST 72 potentiostat coupled with a Mars II programmed voltage generator (J. Heyrovsky's Institute) and an X–Y recorder (EMG 79812, Hungary). The potential was recorded with a Metex M-3630, with a Fluke 75 digital meter, or directly from the Wenking potentiostat.

Before each experiment, the surface of the HOPG electrode was cleaned by removing several layers of the surface using transparent adhesive tape. The usual arrangement of a three-compartment electrochemical cell with an SCE reference and a Pt counter electrode was used for the electrochemical studies. Electronic spectra were recorded with a Cary Model 2400 spectrometer. Electron spin resonance (ESR) spectra were obtained using a Varian E4 spectrometer.

Preparation of Co(Tmtppa)(CH₃SO₄)₄·2H₂O. N,N',N'',N'''-Tetra-3,4-pyridinoporphyrazinocobalt(II) (Co^{II}(Tppa)) was synthesized according to the standard methods for preparation of metalated phthalocyanines.[47] 3,4-Pyridinedicarboxylic acid (1.0 g), urea (4.0 g), and cobalt chloride (1.0 g) were heated under reflux in nitrobenzene (50 mL) for 4 h using ammonium molybdate (0.12 g) as catalyst. The crude product was then washed with water and ethanol and further purified by recrystallization from concentrated HCl (yield 33%). This crude product was used in the preparation of a Co(Tmtppa)

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species without further purification. The water-soluble $Co^{II}(Tmtppa)(CH_3SO_4)_4 \cdot 2H_2O$ species was prepared by methylation of $Co(Tppa)$ with dimethyl sulfate in DMF according to Smith[48] and recrystallized twice from water and acetone (yield 60%). Anal. $Co^{II}(Tmtppa)(CH_3SO_4)_4 \cdot 2H_2O$. Calcd for $C_{36}H_{40}CoN_{12}O_{18}S_4$: C, 38.75; H, 3.60; N, 15.06. Found: C, 38.75; H, 3.47; N, 16.85. (Product is a mixture of isomers where the pyridine N atoms are statistically distributed between the 3 and 4 positions.)

Preparation of the $Co^{II}(Tmtppa)$-Modified Electrode. The electrodeposition of $Co^{II}(Tmtppa)$ was performed by scanning the HOPG electrode in the range of 0 to –0.6 V for 10 min in 10^{-4} M $Co^{II}(Tmtppa)$ solution (0.1 M NaH_2PO_4 buffer solution) under argon-degassed conditions. The electrode was then rinsed with water, dried at room temperature, and covered by a Nafion or Tosflex film to protect the electrodeposited $Co(Tmtppa)$. After being coated with the ion-exchange membrane solution, the electrode was then dried in room temperature for 24 h.

Procedure. Stock solutions of sodium sulfide were prepared by dissolving reagent grade $Na_2S \cdot 9H_2O$ in water. The concentration of the stock Na_2S solution was determined either by a Coulometric method developed in the J. Heyrovsky Institute or by a standard titration method.

The Coulometric method consists of the complete anodic oxidation of iodide ions which are formed upon introducing a sulfide sample into a circulating solution of elementary iodine.

During the standard titration, the concentration of the sulfide is determined by using excess iodine solution as oxidant which is generated by the oxidation of potassium iodide with standard potassium iodate solution. The excess iodine solution is then back-titrated with thiosulfate solution.[49] Potassium iodate is dried in the vacuum oven at 100 °C for 1 h. The sodium thiosulfate solution was standardized with KIO_3 by the iodometry method.

A stock solution of 2-mercaptoethanol (98%, Aldrich) was prepared by diluting 1 mL of 2-mercaptoethanol 100 times with water.

Before the experiment, the electrode was soaked in pH 7 phosphate buffer solution for ~1 h. During the experiment, the stock Na_2S or 2-mercaptoethanol solution was injected into the cell with a microliter syringe and the potential of the $Co(Tmtppa)$-modified electrode vs SCE was measured under magnetic stirring or under rotation of the electrode at room temperature. The time necessary for the steady response and stability of the signal was followed by the time base recorder.

RESULT AND DISCUSSION

(A) Electrochemistry of $Co^{II}(Tmtppa)$. A complete study of the electrochemistry and characterization of the Co^{II}-$(Tmtppa)$-deposited film will be discussed elsewhere,[50] and therefore only a summary of the results is presented here.

A cyclic voltammogram (CV) of $Co^{II}(Tmtppa)$ solution in pH 4 phosphate buffer in the ranges of +0.5 to 0 and 0 to –0.6 V (vs SCE) showed the peak couple I at +0.25 (Figure 2A) and couple II at –0.44 (Figure 2B), respectively.

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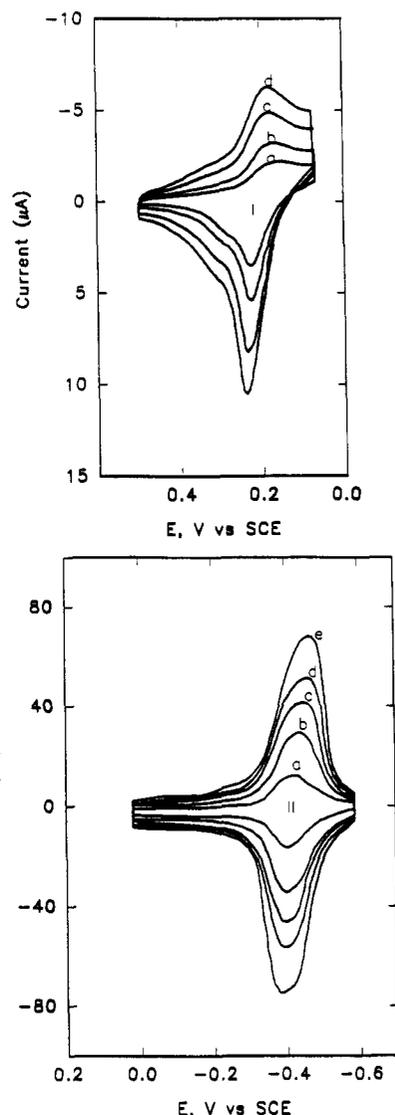
Figure 2. (a) Cyclic voltammogram of Co(Tmtppa), steady state, in 0.1 M phosphate buffer, pH 4; argon-degassed; [Co(Tmtppa)] = 1 × 10^{-4} M. (A, top) Couple I: scan rate (a) 25, (b) 50, (c) 100, and (d) 150 mV/s. (B, bottom) Couple II: scan rate 100 mV/s; cycles (a) 1, (b) 5, (c) 10, (d) 15, and (e) 20.

Repeated scanning over couple I shows a stable current response within the potential range from +0.5 to 0 V. The cathodic component of couple I had a shape typical for solution voltammetry with $i_p \propto \nu^{1/2}$ (square root scan rate). However, for the current of the sharp anodic peak, $i_p \propto \nu$. Thus electrochemical reduction is controlled by diffusion of the oxidized form while electrochemical oxidation occurs at the electrode surface.

On the other hand, repeated scanning in the potential range from 0 to –0.6 V resulted in an increase of the peak current of couple II with the number of cycles, indicating the formation of a conductive phthalocyanine film by electrodeposition on the electrode surface. A purple film was observed on the electrode surface after removing the electrode from the Co^{II}-$(Tmtppa)$ solution.

The electrode covered by the phthalocyanine film, described as the $Co(Tmtppa)$/HOPG-modified electrode, was then transferred to clean phosphate buffer. Cyclic voltammetry in the potential range 0 to –0.6 V showed a curve identical to the last scan in $Co^{II}(Tmtppa)$ solution.

The linear dependence of the peak current on the scan rate and the peak-to-peak separation of less than 10 mV independent of the scan rate correspond to a fast surface redox reaction. However, this is valid only for a thin layer of the film (see Figure 2B for the change of peak-to-peak separation with increase of the thickness of the film). With increasing thickness of the deposited film, the peak-to-peak separation increases due to iR drop and possibly also due to a decreasing rate of charge transfer in the deposited layer.

The surface film is stable over potentials which range from about 100 mV negative of couple I, –0.1 V, to the reduction limit of the solvent, –1.0 V. However, scanning positively of the potential of oxidation peak I caused loss of current in both couples I and II. Couples I and II have been assigned as the Co(II)/Co(I) metal and phthalocyanine ligand redox couples, respectively.

While the potential of couple I is independent of pH, the potential of couple II is pH dependent. This behavior will be discussed in detail elsewhere.[50]

The reduced forms of the Co(Tmtppa) isomers are insoluble in water and scarcely soluble in common organic solvents.[24,48] Therefore, it is not surprising that the electrochemical reduction of an aqueous solution of Co[II](Tmtppa) results in the deposition of its reduced form on the electrode surface. An ESR study showed that the electrode-deposited material is ESR silent. Our data are consistent with Smith[48] and Kasuga's[24] reports that the first reduction of Co(Tmtppa) corresponds to the reaction scheme

$$[Co^{II}(Tmtppa)]^{4+} + e^- \rightarrow [Co^I(Tmtppa)]^{3+} \qquad (1)$$
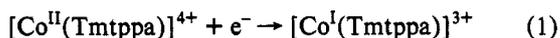
The potential of the electrochemical deposition in this case (couple I), however, is more positive than the Co(II)/Co(I) redox couple compared with other water-soluble cobalt phthalocyanines.[51,52] This is due to the electron-withdrawing ability of the four methylated aza groups, which stabilize the Co(I) oxidation state. The first reduction potential of [Zn[II]-(Tmtppa)] in aqueous solution was reported to be –0.22 V (vs SCE).[53] This is ~500 mV more positive than the first reduction potential of its tetrasulfonated derivative (–0.75 V vs SCE).[53]

(B) Electrodeposition. The electrodeposition of Co[II]-(Tmtppa) occurs when the electrode is polarized negative of the potential of redox couple I. The optimum potential range for electrodeposition was determined by measuring the charge corresponding to the anodic peak of couple II after polarizing the electrode at different potentials negative of couple I for constant time. The independent rate of electrodeposition in the potential range +0.1 to –0.8 V (Figure 3) indicated that the rate of electrodeposition is limited by a diffusion-controlled process. The decrease of the deposition rate on the positive and the negative sides of the potential range was apparently caused by the electrochemical oxidation of the deposit and evolution of hydrogen, respectively, which caused the deposit to fall off.

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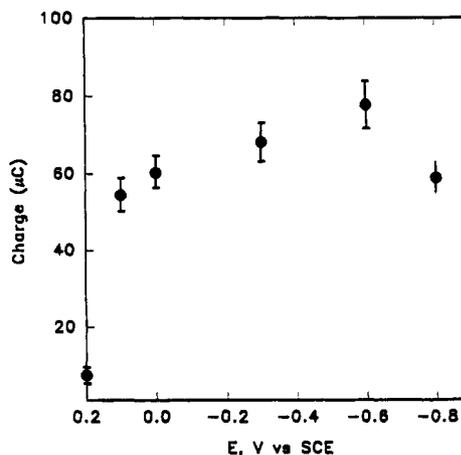
Figure 3. Charge under the cathodic peak of couple II in Figure 2B plotted against the polarization potential. Electrodeposition took place from a solution of [Co(Tmtppa)] in phosphate buffer, pH 4, argon-degassed; polarization time 5 min; [Co(Tmtppa)] = 1 × 10⁻⁴ M. The charge corresponding to the cathodic peak of couple II was determined from the cyclic voltammograms of the Co(Tmtppa) electrode in clean phosphate buffer, pH 4.

When the electrode covered by the electrodeposited film was left in water saturated with air for several hours, some film dissolves to form a green colored solution which showed the same electronic spectrum as the solution of the starting compound, Co[II](Tmtppa). However, the surface film is stable in argon saturated solution, and indeed, even in air, at a carbon electrode, there is some contribution of the [Co[I](Tmtppa)]⁻ form.

In order to protect the phthalocyanine film from dissolving in water in the presence of oxygen, the electrode was covered with a Nafion or Tosflex membrane (see Experimental Section).

(C) Responses of the Co(Tmttpa)-Modified Electrode. (1) Sulfide Ion Determination. A set of six electrodes was protected with perfluoroion-exchange polymeric films. Electrodes A, B, C, and F were covered with the Nafion cation-exchange membrane while electrodes D and E were covered by the Tosflex anion-exchange membrane.

Since the Co[II](Tmttpa) cation was reported to decompose at pH >7.5,[48] all sulfide ion studies were performed in pH 7 phosphate buffer. The potentials of the Co(Tmttpa)-modified electrode vs SCE were measured at different sodium sulfide concentrations while the concentration of oxygen was kept constant at constant ionic strength (see Experimental Section).

All of the electrodes show typical Nernstian behavior during sulfide ion determination. Nernstian plots for sulfide ion determinations with electrodes B and E are shown in Figure 4. The reproducibility of the Nernstian plot was tested by performing four consecutive experiments for each electrode. All the electrodes yielded reproducible values for the slope and intercept within ±5% and ±2.5%, respectively.

The first measurement after storage of the electrodes in the dry showed a slightly higher value for the slope from the other measurements when the electrode was used for further experiments. Also, the slope and intercept for the Nernstian plot deviated slightly for the same electrode, but without pattern, from day to day during the study (see Table 1). However, there is no loss of activity of the electrode following
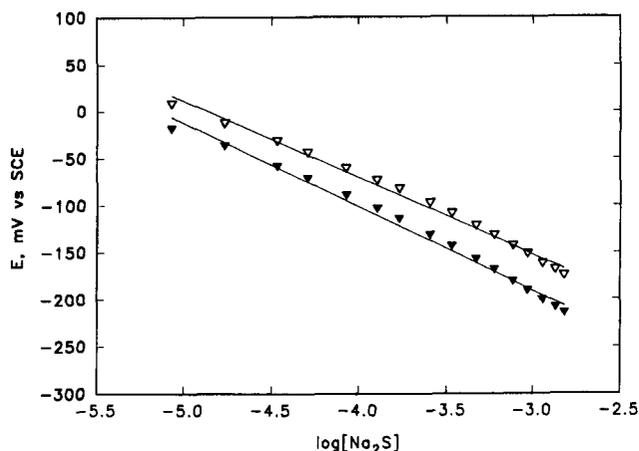
Figure 4. Potential (vs SCE) of the Co(Tmtppa)-modified electrodes B (hollow triangle) and E (solid triangle) plotted against log [Na₂S] in 0.1 M phosphate buffer, pH 7; air-saturated solution.

more than 40 measurements, nor after storage of the electrode in dry air condition for several months.

The different electrodes also show slightly different behavior as noted in Table 1. This is likely because the thickness of the ion-exchange membrane was not controlled from one electrode to another.

The potential of the Co(Tmtppa)-modified electrode is given by the Nernst equation:

$$E = E° + (RT/nF) \ln\{[Co(II)]/[Co(I)]\} \quad (2)$$

where the ratio of [Co(II)] and [Co(I)] is dependent upon the concentration of oxygen and the sulfhydryl ion, HS⁻.

In pH buffer, the percentage of hydrogen sulfide, bisulfide, and sulfide in the solution can be calculated from[31]

$$[HS_2]\% = 100[H^+]^2/\{[H^+]^2 + K_1[H^+] + K_1K_2\} \quad (3)$$

$$[HS^{2-}]\% = 100K_1[H^+]/\{[H^+]^2 + K_1[H^+] + K_1K_2\} \quad (4)$$

$$[S^{2-}]\% = 100K_1K_2/\{[H^+]^2 + K_1[H^+] + K_1K_2\} \quad (5)$$

where K_1 and K_2 are the thermodynamic ionization of H_2S and HS⁻, respectively ($K_1 = 9.1 \times 10^{-3}$ and $K_2 = 1.1 \times 10^{-12}$ at an ionic strength of 0.1 N).[31] At pH 7, $H^+/K_1 \gg K_1K_2 \approx [H^+]^2$ and

$$[HS^-]\% \approx 100\% \quad (6)$$

Therefore, we can consider that HS⁻ and O_2 are the main reactive species in solution. The possible relevant chemical reactions for the surface-bound Co^{II}(Tmtppa) species are[25]

$$2Co^{2+} + HS^- \xrightarrow{k_1} H^+ + S + 2Co^+ \quad (7)$$

$$2Co^+ + O_2 \xrightarrow{k_{-1}} O_2^{2-} + 2Co^{2+} \quad (8)$$
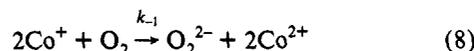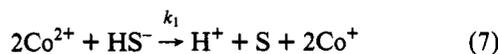
At constant O_2 concentration, a plot of E vs [Na₂S] (at pH 7, [HS⁻] = [Na₂S]) yields a straight line with the slope found experimentally to be close to, but generally above, −59 mV/ [HS⁻], at 25 °C; i.e. the potential follows the expected equation (in V)

$$E = E° - 0.059 \log [HS^-] \quad (9)$$

Certain electrodes show considerably higher slopes than required for Nernstian behavior (−59 mV/log [HS⁻]). The

reaction is possibly complicated by sulfur deposition and transport of ions through the protective membranes and requires further study. We note in Figure 6 the shift in potential upon replacing air by pure oxygen (at 1 atm) is close to the 41-mV shift (in the value of 0.059 log [O₂] with [O₂] = 1.1 × 10⁻³ M, [O₂,air] = ¹/₅[O₂]) expected for a reaction which is first order in oxygen.

(2) Effect of the Membrane. The response times for electrodes B and E plotted against the amount of sulfide ion added is shown in Figure 5. At lower sulfide ion concentration, e.g., 8.5 × 10⁻⁶ M, the electrode covered with Tosflex, electrode E, reaches an equilibrium reading within about 150 s. However, for the electrode covered with Nafion membrane, electrode B, the time required to reach equilibrium is ∼450 s. However, at concentrations above 1 × 10⁻³ M, both electrodes reach equilibrium within ∼30 s.

The relatively slow response for the Co(Tmtppa)-modified electrode covered with the Nafion membrane relative to the electrode covered with the Tosflex is probably due to the slow diffusion of sulfide ion through the cation ion-exchange channels across the Nafion membrane.

(D) 2-Mercaptoethanol Determination. All the electrodes show a typical Nernstian response for the determination of 2-mercaptoethanol, as would be anticipated on the basis of earlier studies.[11-20] Figure 7 shows the Nernstian plots for electrodes C and D during the 2-mercaptoethanol determination. The slope and intercept for the Nernstian plot for individual electrodes are shown in Table 1. The reproducibility of the Nernstian plot was tested by performing three consecutive experiments for each electrode. All the electrodes yielded reproducible values for the slope and intercept within ±5.5% and ±2.5%, respectively (generally not including the "first measurement of the day").

However, the response time to reach equilibrium for both Tosflex and Nafion electrodes at concentrations of mercaptoethanol below 5.7 × 10⁻⁵ M can exceed 30 min. At concentrations of about 5 × 10⁻⁶ and 2 × 10⁻³ M, all the electrodes reach equilibrium within 200 and 50 s, respectively. Figure 8 shows a plot of the response time for electrodes C and D in the concentration range from 5.7 × 10⁻⁵ to 2.0 × 10⁻³ M. Similar to the sulfide determination, the electrode
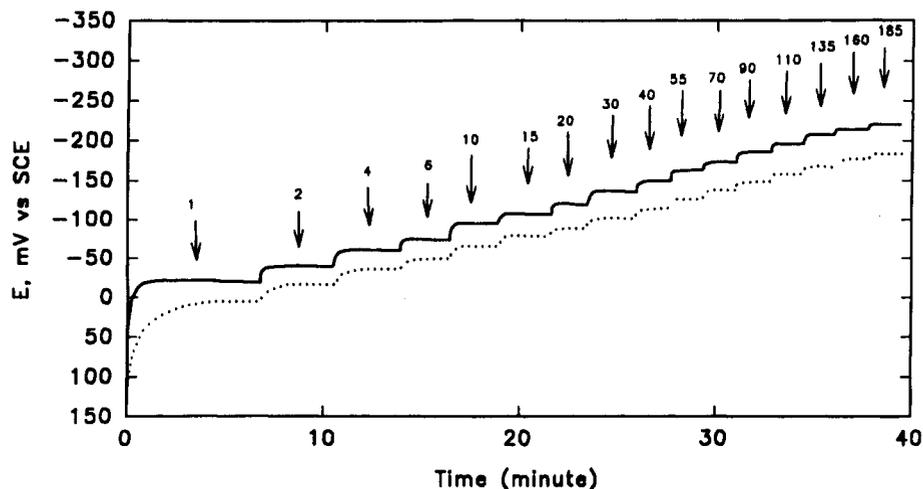
Figure 5. Potential (vs SCE) response vs time of the Co(Tmtppa)-modified electrodes B (dotted line) and E (solid line) vs SCE in 0.1 M phosphate buffer during a sulfide determination, pH 7; air-saturated solution; [Na$_2$S] = 2.12 × 10^{-1} M. The number in the diagram indicated the amount (μL) of Na$_2$S stock solution added to 25 mL of pH 7 buffer solution.
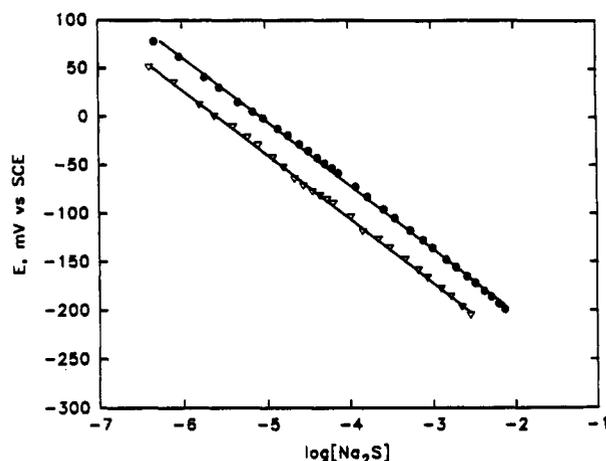
Figure 6. Potential (vs SCE) of Co(Tmtppa) electrode, I, plotted against log [Na$_2$S] in 0.1 M phosphate buffer, pH 7; oxygen-saturated solution (solid circle); air-saturated solution (hollow triangle).
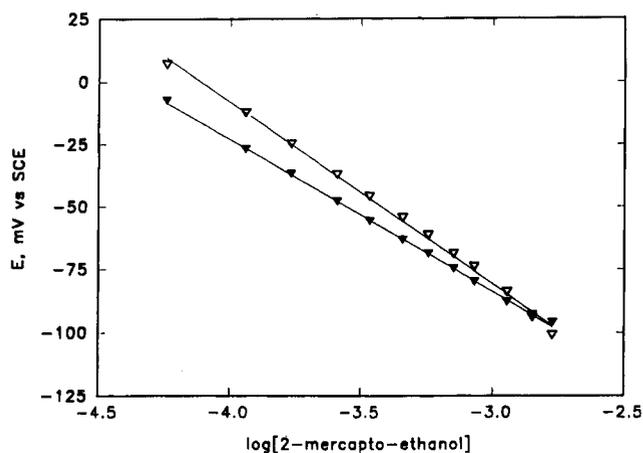
Figure 7. Potential (vs SCE) of the Co(Tmtppa)-modified electrodes C (solid triangle) and D (hollow triangle) plotted against log [2-mercaptoethanol] in 0.1 M phosphate buffer, pH 7; air-saturated solution.

Figure 8. Potential (vs SCE) response vs time of the Co(Tmtppa)-modified electrodes C (bottom) and D (top) in 0.1 M phosphate buffer during a 2-mercaptoethanol determination, pH 7; air-saturated solution; [2-mercaptoethanol] = 1.43 × 10^{-1} M. The number in the diagram indicated the amount (μL) of 2-mercaptoethanol stock solution added in 25 mL of pH 7 buffer solution.

M) comparable to the sulfide concentration, the modified electrode does not show a significant response to Cl$^-$ and Br$^-$ (Figure 9) but it appears that the other ions interfere quite strongly, although the nature and extent of this interference is not completely certain.

A Co(Tmtppa)-modified electrode catalyzes the decomposition of [S$_2$O$_4$]$^{2-}$ in the presence of oxygen and does respond to CN$^-$, [SO$_3$]$^{2-}$, and I$^-$. In the concentration range 1.0 × 10^{-5}–1.0 × 10^{-3} M [SO$_3$]$^{2-}$ (sulfide free), a linear Nernstian plot yields a straight line of slope 22 ± 1 mV/log [SO$_3^{2-}$]. A nonlinear Nernstian plot was observed for the CN$^-$ ion, probably due to complexation of CN$^-$ ion to the axial sites of the cobalt phthalocyanine center.[54]

Since this electrode responds to a redox reaction, it is likely that the sulfide response is modified in the presence of any reducing anion. Indeed, it may be used as a sensor for ascorbic acid.[55]

covered with the Tosflex membrane has a shorter response time.

(E) Response of the Co(Tmttpa)-Modified Electrode to Other Species. The response to some common anions such as Cl$^-$, Br$^-$, I$^-$, [SO$_3$]$^{2-}$, CN$^-$, and [S$_2$O$_4$]$^{2-}$ has been studied at the Co(Tmtppa)-modified electrode. In a range (up to 10^{-3}

(54) Metz, J.; Hanack, M. *J. Am. Chem. Soc.* **1983**, *105*, 828.
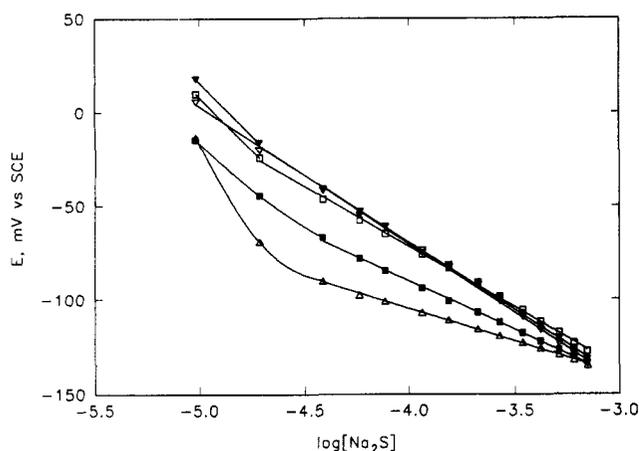
Figure 9. Potential (vs SCE) of the Co(Tmtppa)-modified electrode F plotted against log [Na$_2$S] in the 0.1 M phosphate buffer, pH 7; air-saturated solution; without any interference (hollow downward triangle), 4 × 10^{-3} M Cl$^-$ (filled downward triangle), 4 × 10^{-3} M Br$^-$ (hollow square), 4 × 10^{-3} M I$^-$ (filled square), and 7 × 10^{-4} M [SO$_3$]$^{2-}$ (hollow upward triangle).

SUMMARY

An ion-selective electrode for sulfide ion determination based on the electrocatalytic behavior of Co^{II}(Tmtppa) toward hydrosulfide ion in the presence of oxygen has been reported.

(55) Janda, P.; Weber, J.; Dunsch, L.; Lever, A. B. P., submitted for publication in *Anal. Chem.*

The detection range for the sulfide ion using this Co-(Tmtppa)-modified electrode can vary from 1 × 10^{-6} to 1 × 10^{-2} M. This Co(Tmtppa)-modified electrode also shows a fast response compared to some of the commercial sulfide potentiometric indicators for which a waiting period of several minutes is necessary to reach steady-state potential and special cleaning procedures are recommended prior to measurement.

Further, this electrode will usually be employed at a pH of 7, which will generally offer advantages over the required use of pH $\sim$12 for direct sulfide determination with the silver sulfide based electrodes.

Studies of real systems must be carried out under constant oxygen pressure. While this could prove a problem in some applications, aeration of samples to reach equilibrium with the ambient temperature will usually solve the problem.