

Potentiometric selective determination of hydrogen sulfide by an electropolymerized membrane electrode based on binaphthyl-20-crown-6

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(Received 23rd August 1993; revised manuscript received 11th October 1993)

Abstract

A novel potentiometric selective determination method for hydrogen sulfide (HS^-) by an electropolymerized membrane electrode based on a neutral anion carrier, binaphthyl-20-crown-6, has been developed. The potentiometric response is highly dependent on the pH of the solution and the nature of the buffer medium. The response of the polybinaphthyl-20-crown-6 electrode to HS^- has a linear dynamic range between 2×10^{-7} and 2×10^{-5} M with a "super-Nernstian" slope of about 110 mV/decade concentration and a detection limit of 6×10^{-8} M in phosphate buffer (0.1 M, pH 7.5). Other inorganic anions do not interfere with the determination of HS^- and those interfering problems encountered by potentiometric sulfide ion selective electrode have been circumvented. The potentiometric response mechanism towards hydrogen sulfide (HS^-) is discussed and a mechanistic model of the electrode response is given.

Key words: Potentiometry; Hydrogen sulfide; Binaphthyl-20-crown-6; Electropolymerization

1. Introduction

Carriers are used as active membrane components in the design of novel potentiometric selec-

tive electrodes for inorganic anions, namely, various derivatives of vitamin B₁₂ [1,2] and metalloporphyrins [3–9]. Recently, two potentiometric electrodes based on conducting poly(3-methylthiophene) and poly(tetrakis(*p*-aminophenyl)porphyrin polymer films for iodide were reported [10,11]. Also electrodes developed for organic anions, which are based on lipophilic derivatives of macrocyclic polyamines and calixarene compounds, have been reported [12–14]. Our previous efforts to utilize electropolymerized bi-

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naphthyl-20-crown-6 as the membrane component in the design of a novel molecule selective electrode have yielded a sensor that exhibited unique and analytically useful selectivity responses for molecules containing 1,2-dihydroxybenzene moieties, such as catecholamines [15,16]. In the present study, we have found that an electrode coated with an electropolymerized binaphthyl-20-crown-6 membrane has an excellent capability of potentiometric selective response to HS^- ion, and it can serve as a promising method to determine hydrogen sulfide gas or sulfide ion in environmental monitoring. The detection technique described in this work is based on potentiometry, a simpler approach than those reported earlier [17].

2. Experimental

2.1. Reagents

The lipophilic macrocyclic crown ether, binaphthyl-20-crown-6 was synthesized in our lab and verified by IR and ^1H NMR [16]. The tetrabutylammonium tetrafluoroborate (TBATFB) was purchased from Aldrich and used as is. The acetonitrile was dried by double distillation over calcium hydride. The phosphate buffer stock solution (pH 7.5, 0.5 M) was prepared with potassium dihydrogenphosphate and the pH was adjusted by addition of KOH or H_2SO_4 . The series of standard solutions of sodium sulfide were prepared daily before use.

All chemicals used in the present study were of reagent grade. Deionized water of 17.8 $\text{M}\Omega$ electrical resistance was used throughout.

2.2. Fabrication of the electrode

The details of the electrode preparation have been described in a previous paper [15]. Briefly, a stationary platinum disk electrode with a 1.6 mm diameter (MF-2012, Bioanalytical Systems) was used as a basic substrate matrix. The polymerization of binaphthyl-20-crown-6 on the platinum electrode was carried out in a three electrode single compartment cell containing 20 mM of

binaphthyl-20-crown-6 and 200 mM TBATFB dissolved in freshly distilled acetonitrile. The above mentioned stationary platinum electrode was used as the working electrode, a platinum wire coil as the auxiliary electrode and an Ag/AgCl reference electrode. Electrochemical polymerization was performed with a PAR 175 potentiostat/galvanostat (EG & G Princeton Applied Research) with an applied potential of +3.2 V vs. Ag/AgCl electrode for 5 min. The polymerized electrode was then rinsed with acetone, air dried, and immersed in a three electrode single compartment cell containing a monomer free acetonitrile solution of TBATFB for about 25 min at an applied potential of 0.5 V vs. the Ag/AgCl electrode. This polymerized electrode was then rinsed with water and dried in air about 20 min before use.

2.3. Potential measurement

Potential measurements were made with an Orion Model 601A ionalyzer using a Calomel electrode (Mf-2055, BAS) as the reference electrode. The electrochemical cell used can be represented by: $\text{Hg}|\text{Hg}_2\text{Cl}_2, \text{KCl}(\text{sat.})|\text{phosphate buffer}(0.1 \text{ M})|\text{polymer film}|\text{Pt}$. The electrode potential was measured in 25 ml of a 0.1 M phosphate buffer solution (pH 7.5) with stirring at 22°C and recorded with a chart recorder. The polymerized electrodes were preconditioned in stirred water until a steady potential was obtained before use. A stepwise addition method was used for the HS^- calibration.

3. Results and discussion

3.1. The pH dependence of the polycrown ether electrode response to sulfide

Fig. 1 shows the pH dependence of the observed potential of the polycrown electrode in 0.1 M potassium phosphate buffer in the presence of 10^{-6} M sodium sulfide. Stable response potentials were obtained in the pH range 6–9. Fig. 2 shows a series of calibration curves of the electrode in solutions of different pH values. As

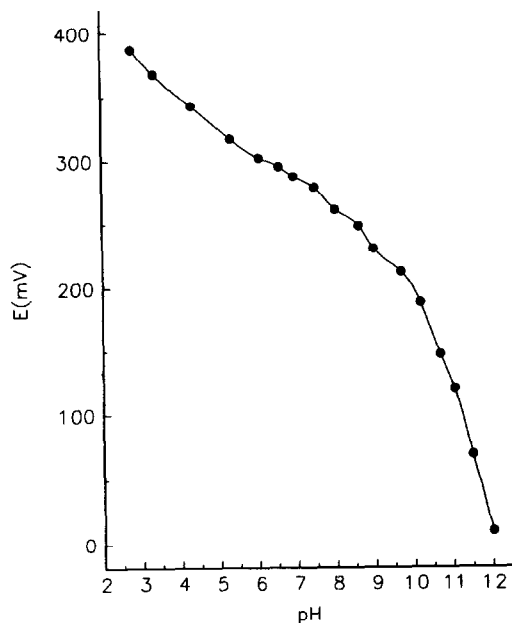


Fig. 1. pH dependence profile of the polybinaphthyl-20-crown-6 electrode (phosphate buffer: 0.1 M).

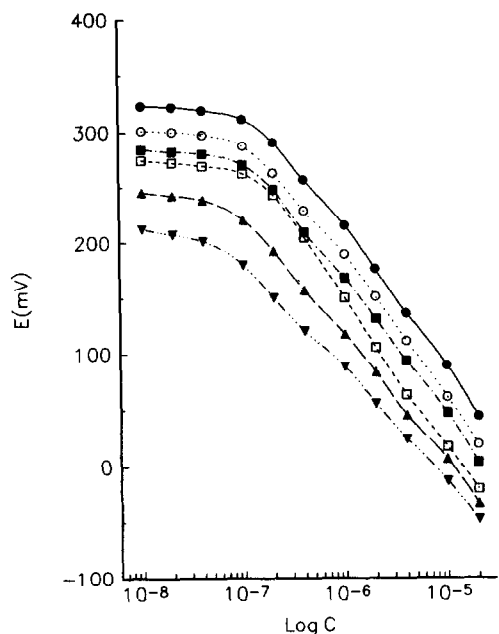


Fig. 2. Effects of pH on the calibration characteristics of the polybinaphthyl-20-crown-6 electrode (phosphate buffer: 0.1 M). ● = pH 6.5, ▲ = pH 8.5, ○ = pH 7.0, ▼ = pH 9.5, ■ = pH 7.5, □ = pH 8.0.

indicated in Fig. 2, the potential responses to the same concentration of sulfide decrease as the pH increases. The response time of the electrode and its recovery after usage improved with pH increases of the buffer. The electrode responded to OH^- at $\text{pH} > 9.5$ with a negative shift in potential reading (Fig. 1). Moreover, the calibration curve characteristics of the electrode showed poor linearity (Fig. 2). If the pH of the solution was lower than 7.0, the detection limit of electrode response was found to decrease. The “best” calibration curve of the electrode was obtained at pH 7.5. As discussed previously, such a high pH dependence suggested that the HS^- ion is the species interacting with the crown ether of the polybinaphthyl-20-crown-6, probably through a hydrogen bond [15].

3.2. Effects of buffer media on electrode response

Fig. 3 shows the effects of different buffer media at the same pH and concentration on the response behaviour of the electrode. This polybinaphthyl-20-crown-6 electrode had the best response performance in the phosphate buffer and the worst in the triethanolamine buffer. The order of preferable buffer media is: phosphate > $\text{NH}_3\text{-NH}_4\text{Ac}$ > Tris > DIPSO > triethanolamine. Both the detection limit and response slope of the electrode were found to decrease gradually in that order.

3.3. Performance of the polycrown ether electrode

A typical calibration curve of the electrode is shown in Fig. 4. The electrode has a linear response over the range of 2×10^{-7} – 2×10^{-5} M with a super Nernstian response slope of about 110 mV/decade and a detection limit of 6×10^{-8} M.

The typical dynamic response time of the electrode (t_{95}) was about 2 min under stirred conditions as the concentration of sulfide was increased from 2×10^{-7} to 2×10^{-6} M. The steady state potential response after addition of sulfide standard solution remained constant for about 2–5 min, then increased in the positive direction and reached a final steady potential value. The

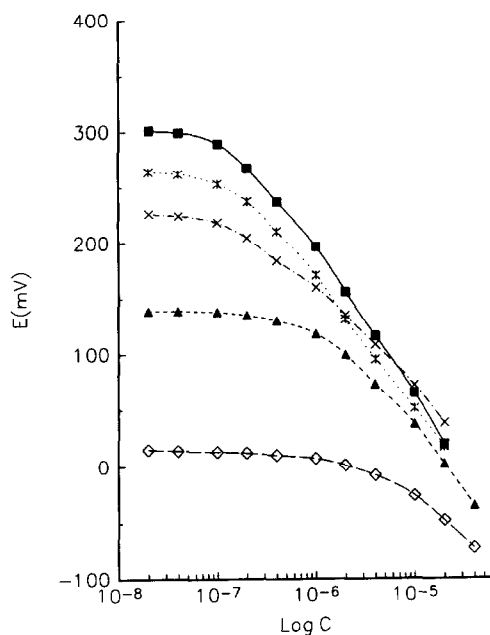


Fig. 3. Effects of different buffer media on the responses of the electrode to HS^{2-} . Buffers: 0.1 M pH 7.5, ■ = phosphate, ▲ = DIPSO, * = $\text{NH}_3\text{-NH}_4\text{Ac}$, ◇ = triethanolamine, × = Tris.

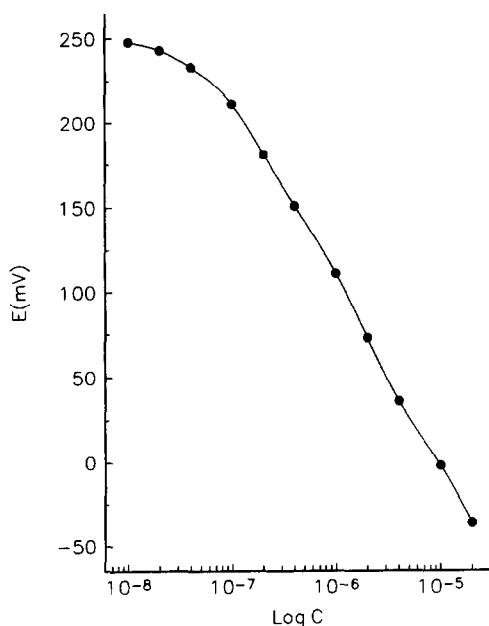


Fig. 4. A typical calibration curve of polybinaphthyl-20-crown-6 electrode for HS^{2-} (phosphate buffer: 0.1 M, pH 7.5).

first steady state responses were used in all experiments in the present study.

The selectivity coefficients of the polycrown ether electrode were determined by the matched potential method [18,19]. The conventional cations did not interfere with the determination of sulfide. The anion selectivity coefficients of the electrode are shown in Table 1.

The anions SCN^- , I^- , $\text{S}_2\text{O}_3^{2-}$ and Br^- exhibit some interference, but this electrode has excellent potentiometric selectivity toward other anions, F^- , Cl^- , HCO_3^- , Ac^- , NO_3^- , NO_2^- , ClO_4^- , $\text{B}_4\text{O}_7^{2-}$ and SO_4^{2-} . Compared to the conventional sulfide ion selective membrane electrodes, which used to exhibit serious interferences from the anions I^- and SCN^- , this polybinaphthyl-20-crown-6 electrode has circumvented those problems.

3.4. Possible response mechanism of the polybinaphthyl-20-crown-6 electrode towards hydrogen sulfide

As indicated above, the polybinaphthyl-20-crown-6 electrode has an optimal buffer condition of pH 7.5. Hydrogen sulfide has an acid dissociation constants of $\text{p}K_1 = 7.04$ and $\text{p}K_2 = 11.96$. The dominant form in the solution of pH 7.5 would be HS^- . Therefore, this electrode actually responds to anion HS^- . Fig. 1 has shown that the response of the polybinaphthyl-20-crown-6 electrode to HS^- is highly pH dependent just like its response to catecholamine molecules [15]. As discussed in our previous study, [15], the response mechanism of this electrode to the molecules containing 3,4-dihydroxylbenzene moieties was suggested to be relative to the formation of hydrogen bonds and mononegative charged anions between polycrown ether and guest molecules on the electrode surface. A similar hydrogen bond model is suggested in the present case.

In the case of conventional ion selective electrodes, monovalent ions ($n = 1$) have a Nernstian response slope of 59 mV/decade, and 29 mV/decade for divalent ions ($n = 2$). It corresponds to net charge effects on the surface of the electrode membrane which are one and two respectively. In other words, ion exchange or diffusion between

the membrane phase and the solution phase leads to an unbalanced charge distribution. If one monovalent ion is adsorbed in or out the membrane, it makes the membrane obtain or lose one charge. Thus, the electrode should have a Nernstian slope of 59 mV/decade. If one divalent ion is adsorbed in or out of the membrane, this results in the gain or loss of two charges and the electrode will have an approximate Nernstian slope of 29 mV/decade.

In the present case, the super Nernstian response to HS^- with a slope of 110 mV/decade suggests that the net charge effect on the electrode membrane surface should be one half of a charge, e.g., $n = 0.5$ in the Nernstian equation. Such a half charge effect can be explained as follows. If one ion diffuses into the ion or molecule selective membrane and occupies one ion exchange site (or one receptor molecule), the net charge effect on the membrane surface should be the same charge value. If two ion exchange sites combine with one ion and share one charge, the net charge effect on the membrane surface will be half of the ion charge. Then, we can propose that one HS^- diffuses into the polymer membrane and complexes with two crown ether rings, resulting in half of the net charge effect and a “double” Nernstian response slope.

Recently, Kliza and Meyerhoff [10] summarized four possible potentiometric anion response mechanisms of polyporphyrin derivatives electrodes: (1) ion-exchange process with the anion-doped polymer backbone, (2) ion-exchange resulting from entrapped quaternary ammonium ion supporting electrolyte, (3) redox response at the

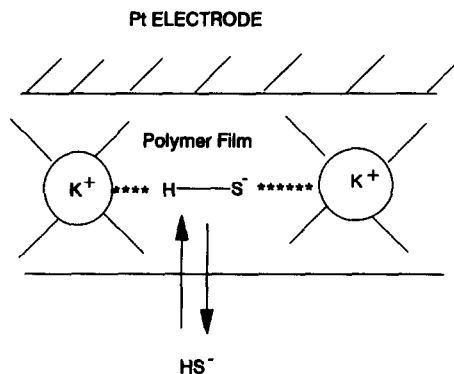


Fig. 5. A possible response mechanism model for HS^- response.

underlying electrode surface, and (4) redox response due to redox reaction within the conducting polymer. They suggested that the overall potentiometric anions response of the polyporphyrin electrode may result from a combination of each of four mechanisms. The second mechanism is not applicable here as a cationic species can not be present. If the third and/or fourth mechanisms are the dominant pathway, then some redox species may interfere with the potentiometric measurement of the electrode. In the present study, the polybinaphthyl-20-crown-6 electrode exhibits a very poor response towards many anions. Thus, the first mechanism is more likely to be the response mechanism (Fig. 5). EDA studies had previously shown that K^+ is incorporated in the crown as expected [15]. Thus, as HS^- diffuses into the polymer film, the hydrogen terminal of the HS^- forms the hydrogen bond with the oxygen of the crown ether and the sulfur terminal complexes with K^+ of another crown by ion pair, resulting in a double Nernstian response.

Table 1
Selectivity coefficients of hydrogen sulfide electrode

Anion	$\log K_{ij}^{\text{pot}}$	Anion	$\log K_{ij}^{\text{pot}}$
F^-	-5.0	SCN^-	-3.1
Cl^-	-4.5	NO_3^-	-4.1
Br^-	-3.7	NO_2^-	-4.1
I^-	-3.5	ClO_4^-	-6.4
HCO_3^-	-4.4	B_4O_7^-	-4.6
Ac^-	-4.0	S_2O_3^-	-3.6
		SO_4^-	-6.0

4. Acknowledgement

This research was supported in part by a grant under the Superfund Basic Research Program from the National Institute of Environmental Health Sciences and the Department of Chemistry of the University of Cincinnati.

5. References

- [1] P. Schulthess, D. Ammann, B. Krautter, C. Caderas, R. Stepanek and W. Simon, *Anal. Chem.*, 57 (1985) 1397.
- [2] P. Schulthess, D. Ammann, W. Simon, C. Caderas, R. Stepanek and B. Krautter, *Helv. Chim. Acta*, 67 (1984) 1027.
- [3] N.A. Chaniotakis, A.M. Chasser, M.E. Meyerhoff and J.T. Groves, *Anal. Chem.*, 60 (1988) 185.
- [4] D. Ammann, H. Huser, B. Krautter, B. Rusterhoz, P. Schulthess, B. Lindemann, E. Halder and W. Simon, *Helv. Chim. Acta*, 69 (1986) 849.
- [5] A. Hodinar and A. Jyo, *Chem. Lett.*, 6 (1988) 993.
- [6] N. Chaniotakis, S. Park and M. Meyerhoff, *Anal. Chem.*, 61 (1989) 566.
- [7] D. Brown, N. Chaniotakis, I. Lee, S. Ma, S. Park and M. Meyerhoff, *Electroanalysis*, 1 (1989) 477.
- [8] S. Park, W. Matuszewski, M. Meyerhoff, Y. Liu and K. Kadish, *Electroanalysis*, 3 (1991) 909.
- [9] S. Dounert, S. Wallace, A. Florido and L. Bachas, *Anal. Chem.*, 63 (1991) 1676.
- [10] D.M. Kliza and M.E. Meyerhoff, *Electroanalysis*, 4 (1992) 841.
- [11] A.E. Karagozler, O.Y. Atama, A. Galal, Z.-L. Xue, H. Zimmer and H.B. Mark, Jr., *Anal. Chim. Acta*, 248 (1991) 163.
- [12] Y. Umezawa, M. Kataoka, W. Takami, E. Kimura, T. Koike and H. Nada, *Anal. Chem.*, 60 (1988) 2392.
- [13] Y. Umezawa, M. Sugawara, M. Kataoka and K. Odashima, 5th Symposium on Ion-Selective Electrodes, Pergamon, Oxford, 1989, pp. 211–234.
- [14] K. Odashima, K. Yagi, K. Tohda and Y. Umezawa, *Anal. Chem.*, 65 (1993) 1074.
- [15] Y.-L. Ma, A. Galal, H. Zimmer, H.B. Mark, Z.-F. Wang and P.L. Bishop, *Anal. Chem.*, in press.
- [16] F. Wang, Y.-L. Ma, X. Hu and Z.-F. Wang, *Anal. Chem.*, (Chin.), in press.
- [17] D.G. Taylor, NIOSH Manual of Analytical Methods, 3rd edn., U.S. Dept. of Health and Human Services, Washington, DC, 1984.
- [18] K. Srinivasan and G.A. Rechnitz, *Anal. Chem.*, 41 (1969) 1203.
- [19] V.P.Y. Gadzekpo and G.D. Christia, *Anal. Chim. Acta*, 164 (1984) 279.