

MONITORING OF IRON (III) IONS WITH A Fe^{3+} -PVC MEMBRANE SENSOR BASED ON 4, 4'-DIMETHOXYBENZIL BISTHIOSEMICARBAZONE

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ABSTRACT

A new poly(vinyl chloride) membrane electrode that is highly selective to Fe^{3+} ions was prepared by using 4,4'-Dimethoxybenzil bisthiosemicarbazone (DBTS) as a suitable neutral carrier. Membrane incorporating 4,4'-Dimethoxybenzil bisthiosemicarbazone (DBTS), as ionophore with composition DBTS:NaTPB:NB:PVC in the ratio 2:2:64:32 (w/w) exhibits the best result for potentiometric sensing of Fe^{3+} ions. The electrode exhibited a near-Nernstian response to Fe^{3+} in the concentration range of 1.0×10^{-6} to 1.0×10^{-2} M with a slope of 19.4 ± 0.5 mV per decade. The proposed sensor can be used over a period of 2 months. The lower limit of detection was 3.6×10^{-7} M. This electrode showed high selectivity with respect to alkaline, alkaline earth, and heavy metal ions and could be used over a pH range of 1.8–5.0. It has been successfully used as an indicator electrode in potentiometric titration of Fe^{3+} against EDTA as well as for the determination of Fe^{3+} in water sample solutions (tap and mineral water samples).

Keywords: PVC Membrane; Iron(III); Sensor; Potentiometry; Ion-selective electrode; 4,4'-Dimethoxybenzil bisthiosemicarbazone

INTRODUCTION

The utility of ion-selective electrodes (ISEs) is being increasingly realized by analytical chemists in view of the rapid growth of industry and technology all over the world as they represent a rapid, accurate and low-cost method of analysis. In recent decades, many intensive studies on the design and synthesis of highly selective and sensitive ion carriers as sensory molecules for ion-selective electrodes (ISEs) have been reported.

Iron is one of the most important elements in the biological systems, playing a significant role in the oxygen transport, storage and in the electron transport. It is a fact that, with only a few possible exceptions in the bacterial world, there would be no life without iron.¹ On the one hand, if the iron concentration exceeds the normal level in the body, it may become a potential health hazard. On the other hand, iron deficiency leads to anemia. Excess iron in the body causes liver and kidney damage (hemochromatosis). Some iron compounds are suspected to be carcinogens.²⁻⁸ Despite the urgent need for iron-selective sensors for the potentiometric monitoring of Fe^{3+} ions in chemical, biological, industrial and environmental samples, there are only limited reports on development of iron selective electrodes in the literature.⁹⁻¹³

We and other researchers have recently introduced a number of PVC-membrane ion selective electrodes for various metal ions.¹⁷⁻⁴⁴ In this work, we wish to introduce a highly selective and sensitive Fe^{3+} sensor based on 4, 4'-Dimethoxybenzil bisthiosemicarbazone (DBTS) (Fig. 1) as an excellent ion carrier for the monitoring of Fe^{3+} ions in sample solutions.

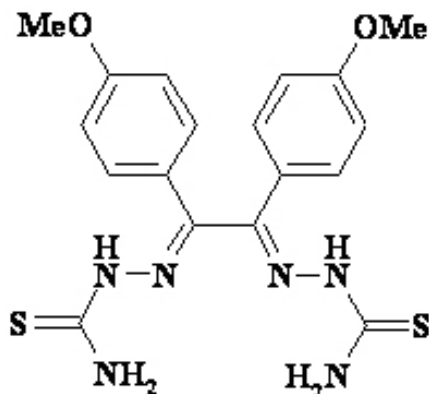


Figure 1. The DBTS structure.

EXPERIMENTAL

Reagents

Reagent grade nitrobenzene (NB), dibutyl phthalate (DBP), benzyl acetate (BA), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) and high relative molecular weight PVC were purchased from Merck and Aldrich, used as received. Ligand 4, 4'-Dimethoxybenzil bisthiosemicarbazone (DBTS) was synthesized and purified as described elsewhere.⁴⁵ As far as the nitrate and chloride salts of all the employed cations are concerned, they were of the highest available purity and were P_2O_5 vacuum dried. During the experiments, triply distilled deionized water was used.

Emf measurements

The electromotive force (emf) measurements with the polymeric membrane electrodes were carried out with the following cell assembly:

Ag–AgCl|3M KCl|internal solution, 1.0×10^{-3} M $Fe(NO_3)_3$ |PVC membrane|test solution|Hg–Hg₂Cl₂, KCl (saturated)

A Corning ion analyzer 250 pH/mV meter was used for the potential measurements at 25.0 ± 0.1 °C. The activities were calculated according to the Debye–Hückel procedure.⁴⁶

Electrode preparation

The Fe^{3+} -PVC membranes were prepared according to a general procedure. The required ingredients for the membrane construction (32 mg PVC, 64 mg NB, 2 mg NaTPB and 2 mg DBTS) were mixed and dissolved in 3 mL of dry THF. The resulting mixture was transferred into a glass dish (2 cm in diameter) and the solvent was evaporated slowly until an oily concentrated mixture could be obtained. A Pyrex tube (3 - 5 mm in top) was dipped into the oily mixture for about 5 s, so that a transparent film of about 0.3 mm thickness was formed. After the tube removal from this mixture, the tube was kept at room temperature for about 24 h and it was filled with the internal filling solution (1.0×10^{-3} M of $Fe(NO_3)_3$). In the end, the electrode was conditioned by soaking in a 1.0×10^{-2} M ferric nitrate solution for 24 h.⁴⁷⁻⁵⁸ A silver/silver chloride wire was used as an internal reference electrode.

RESULTS AND DISCUSSION

The membrane composition influence

The ionophore DBTS was used as a neutral carrier to prepare PVC ion-selective membrane electrodes for a number of metal ions, including alkali, alkaline earth, transition, and heavy metal ions. Among these ions, except for the Fe^{3+} ion, for all other ions, the slope of the corresponding potential pM plots is much lower than the expected Nernstian slopes of 59, 29.5 and 20 mV per decade for the uni, di and trivalent cations, respectively. This likely due to the high selectivity of the ionophore for Fe^{3+} ion over other metal ions as well as the rapid exchange kinetics of the resulting Fe^{3+} – Fe^{3+} complex.

It is well known that the membrane composition and especially in some cases, the nature of plasticizer have many significant influence in the sensitivity and selectivity obtained for a given ionophore.⁵⁹⁻⁶¹ The performance characteristics of several membranes having ingredients of different proportions are listed in Table 1. It is seen that the membrane number 5 with the PVC:NB:DBTS:NaTPB ratio of 32:64:2:2 exhibits a Nernstian slope over a very wide concentration range of the Fe^{3+} ions.

Table 1. Optimization of the membrane ingredients

Sens. No.	Composition (wt. %)					Concentration range (M)
	PVC	Plasticizer	NaTPB	DBTS	Slope (mV/decade)	
1	32	NB,67	0	1	10.4 ± 0.5	1.0×10^{-5} - 1.0×10^{-2}
2	32	NB,66	1	1	12.6 ± 0.3	1.0×10^{-6} - 1.0×10^{-2}
3	32	NB,65	2	1	16.3 ± 0.4	1.0×10^{-6} - 1.0×10^{-2}
4	32	NB,64	3	1	15.2 ± 0.2	1.0×10^{-6} - 1.0×10^{-2}
5	32	NB,64	2	2	19.4 ± 0.5	1.0×10^{-6} - 1.0×10^{-2}
6	32	NB,63	2	3	18.5 ± 0.6	1.0×10^{-6} - 1.0×10^{-2}
7	32	BA,64	2	2	17.4 ± 0.5	1.0×10^{-6} - 1.0×10^{-2}
8	32	DBP,64	2	2	16.8 ± 0.3	1.0×10^{-6} - 1.0×10^{-2}

It is interesting to note that the presence of lipophilic and immobilized ionic additives⁶²⁻⁶⁵ could influence membrane resistance and, in some cases, the selectivity pattern of the ion-selective PVC membrane, resulting in a good working performance. As can be seen from Table 1 in the absence of a proper additive, the sensitivity of the PVC membrane is quite low (no. 1 with slope of 10.4 mV per decade). However, the presence of additives will improve the sensitivity of the Fe^{3+} sensor considerably (no. 5 with slope of 19.4 mV per decade).

Working concentration range and slope

The potential response of the best membrane as a function of the Fe^{3+} activity is depicted in Figure 2. It is seen that membrane (No. 5) exhibits a wide working concentration range (from 1.0×10^{-6} to 1.0×10^{-2} M) with a detection limit, as determined from the intersection of the two extrapolated segments of the calibration graph, of 3.6×10^{-7} M Fe^{3+} and a Nernstian slope of 19.4 ± 0.5 mV/decade of activity. The developed electrode was stable and it could be used for at least 2 months without observing any change in its response characteristics.

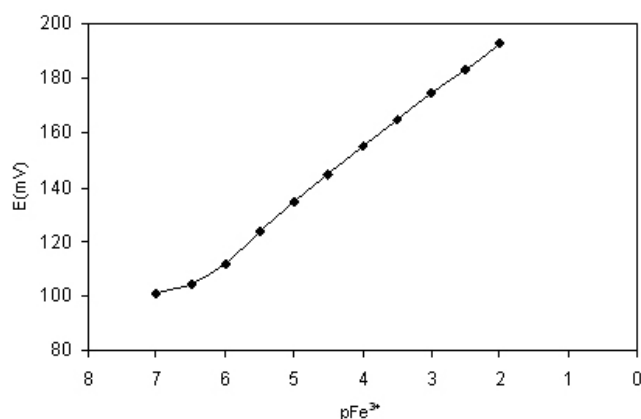


Figure 2. The calibration curve of the iron electrode, based on DBTS.

The reproducibility of the Fe^{2+} electrode was also investigated. The standard deviations of the slope of eight replicate constructed electrodes were ± 0.4 .

The robustness was examined while the parameter values (pH of the solution and the laboratory temperature (were being slightly changed. Fe^{3+} recovery percentages were not showing any significant changes when the critical parameters were modified.

The pH effect

The pH dependence of the membrane sensor was tested over a pH range of 1.0-8.0 in a 1.0×10^{-3} M Fe^{3+} solution. The corresponding resulting data are illustrated in Figure 3. As it can be seen, the potential remains fairly constant in the pH range of 1.8-5.0. Beyond this range, a gradual change in the potential was detected. The observed potential drift at higher pH values could be due to the formation of some Fe^{3+} hydroxyl complexes in the solution. At lower pH values, the potentials increased, indicating that the membrane sensor responded to proton ions, too.

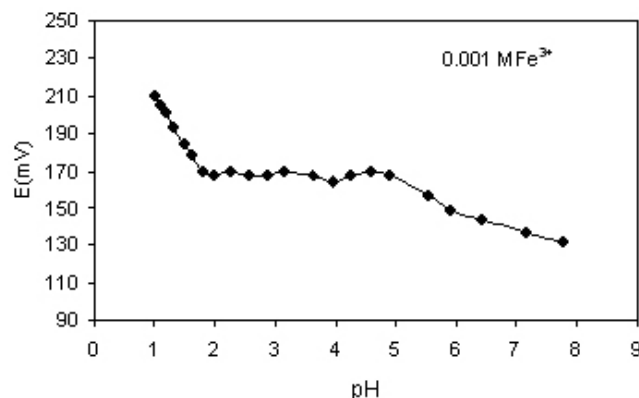


Figure 3. The pH effect of the test solution on the potential response of the iron sensor.

Dynamic response time of the Fe^{3+} sensor

For any ion-selective electrode, the dynamic response time is one of the most important factors. In this study, the practical response time of the sensor was recorded by changing the Fe^{3+} concentration in the solution across the range from 1.0×10^{-6} to 1.0×10^{-2} M. The plot of potential versus time traces is depicted in Figure 4. Obviously, the plasticized membrane electrode reaches its equilibrium responses in a very short time (~ 10 s) over the entire concentration range.

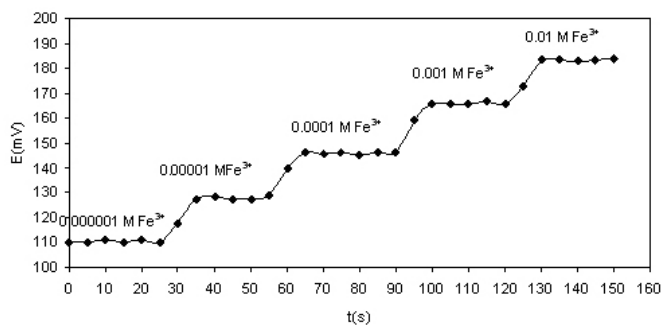


Figure 4. The dynamic response time of the iron electrode for step changes in the Fe³⁺ concentration: A) 1.0×10⁻⁶ M, B) 1.0×10⁻⁵ M, C) 1.0×10⁻⁴ M, D) 1.0×10⁻³ M, E) 1.0×10⁻² M.

The Fe³⁺ electrode selectivity

Selectivity is perhaps the single electrode characteristic, which defines the nature of the device and the extent to which it may be employed in the determination of a particular ion in the presence of other interfering ions. For the selectivity assessment of the PVC membrane electrodes, their corresponding potentiometric selectivity coefficients were evaluated by the matched potential method (MPM).⁶⁶⁻⁷¹ According to this method, a specified activity of the primary ion (A) is added to a reference solution and the potential is measured. In a separate experiment, an interfering ion (B) is successively added to an identical reference solution (containing the primary ion), until the measured potential matches the one obtained with the primary ions. The MPM selectivity coefficients were then given by the resulting primary ion activity (concentration) to the interfering ion activity ratio. The resulting selectivity coefficient values are summarized in Table 2. In accordance with this Table, the selectivity coefficients for the monovalent tested cations (Li⁺, Na⁺, K⁺, Ag⁺) and for the divalent tested cations (Fe²⁺, Cu²⁺, Zn²⁺, Ni²⁺, Cd²⁺, Co²⁺, Pb²⁺, Hg²⁺, Sr²⁺, Ba²⁺) are smaller than 3.5×10⁻⁴ and 1.3×10⁻³, respectively. In the case of trivalent cations (Pr³⁺, Eu³⁺, Nb³⁺, Tm³⁺, Sm³⁺, Er³⁺, Lu³⁺, La³⁺, Ce³⁺, Al³⁺, Cr³⁺), the selectivity coefficients are relatively small (2.0×10⁻³-8.3×10⁻⁵). The resultant selectivity coefficients indicate that the disturbance produced by these cations during the function of the sensor is negligible.

Table 2. Selectivity coefficients of the various interfering ions

Interfering ions	Selectivity coefficient (K _{Fe³⁺,B})	Interfering ions	Selectivity coefficient (K _{Fe³⁺,B})
Pr ³⁺	3.8 × 10 ⁻³	Na ⁺	3.4 × 10 ⁻⁵
Eu ³⁺	4.2 × 10 ⁻³	K ⁺	6.2 × 10 ⁻⁵
Nb ³⁺	9.6 × 10 ⁻⁴	Ag ⁺	3.5 × 10 ⁻⁴
Tm ³⁺	7.6 × 10 ⁻⁴	Pb ²⁺	4.7 × 10 ⁻⁵
Sm ³⁺	8.7 × 10 ⁻⁵	Hg ²⁺	3.3 × 10 ⁻⁴
Er ³⁺	2.0 × 10 ⁻³	Ba ²⁺	3.4 × 10 ⁻⁴
Lu ³⁺	8.3 × 10 ⁻⁵	Sr ²⁺	4.8 × 10 ⁻⁴
La ³⁺	6.8 × 10 ⁻⁴	Zn ²⁺	1.3 × 10 ⁻³
Ce ³⁺	8.3 × 10 ⁻⁵	Co ²⁺	2.8 × 10 ⁻⁴
Al ³⁺	4.1 × 10 ⁻⁴	Cd ²⁺	5.7 × 10 ⁻⁴
Cr ³⁺	2.3 × 10 ⁻⁴	Cu ²⁺	5.5 × 10 ⁻⁴
Li ⁺	7.6 × 10 ⁻⁵	Ni ²⁺	4.6 × 10 ⁻⁴
Fe ²⁺	2.5 × 10 ⁻³		

Table 3 lists and compares the selectivity coefficients of the Fe³⁺ sensor with those of the best Fe³⁺ electrodes reported in the literature.⁹⁻¹² From the data given in Table 3, it is directly obvious that the selectivity coefficients of the sensor are superior to those reported by other researchers.

Table 3. Comparison of the selectivity coefficients, linearity range and detection limit of the different Fe(III) electrodes.

	Ref. 9	Ref. 10	Ref. 11	Ref. 12	This work
Linearity rang (M)	1.0 × 10 ⁻⁶ -1.0 × 10 ⁻¹	3.5 × 10 ⁻⁶ -4.0 × 10 ⁻²	6.3 × 10 ⁻⁶ -1.0 × 10 ⁻¹	1.0 × 10 ⁻⁶ -1.0 × 10 ⁻¹	1.0 × 10 ⁻⁶ -1.0 × 10 ⁻²
Detection limit (M)	6.8 × 10 ⁻⁷	2.5 × 10 ⁻⁶	5.0 × 10 ⁻⁶	—	3.6 × 10 ⁻⁷
Selectivity coefficient	Log K _{MPM}	Log K _{SSM}	Log K _{MPM}	Log K _{MMSM}	Log K _{MPM}
Pr ³⁺	—	—	—	—	-2.42
Eu ³⁺	—	—	—	—	-2.38
Nb ³⁺	—	—	—	—	-3.02
Tm ³⁺	—	—	—	—	-3.12
Sm ³⁺	—	—	—	—	-4.06
Er ³⁺	—	—	—	—	-2.70
Lu ³⁺	—	—	—	—	-4.08
La ³⁺	-3.28	—	—	—	-3.17
Ce ³⁺	-3.28	—	—	—	-4.08
Al ³⁺	—	—	-3.00	—	-3.39
Cr ³⁺	-3.09	-3.10	-2.50	-2.29	-3.63
Li ⁺	—	—	-3.50	—	-4.12
Na ⁺	—	—	-3.40	-2.30	-4.47
K ⁺	-3.00	-3.10	-3.70	-2.96	-4.21
Ag ⁺	—	—	—	-1.88	-3.45
Pb ²⁺	-3.11	-3.30	-3.20	-3.00	-4.33
Hg ²⁺	-3.52	—	—	-2.31	-3.48
Ba ²⁺	-3.38	—	—	—	-3.47
Sr ²⁺	-3.30	—	—	—	-3.32
Zn ²⁺	-2.46	-2.50	—	-2.70	-2.87
Co ²⁺	-3.00	-3.20	-2.80	-2.80	-3.55
Cd ²⁺	-3.17	—	-3.20	-2.90	-3.24
Ni ²⁺	-3.02	-2.10	-3.00	-2.20	-3.34
Cu ²⁺	-3.06	-2.30	-2.60	-2.90	-3.26

Analytical applications

Titration with EDTA

The developed electrode was employed for potentiometric titrations. In detail, it was used as an indicator electrode for the titration of a 1.0×10⁻⁴ M Fe³⁺ solution with a 1.0×10⁻² M EDTA solution. The respective titration curve is presented in Figure 5, where it is concluded that the sensor can monitor the amount of iron ions.^{72,73}

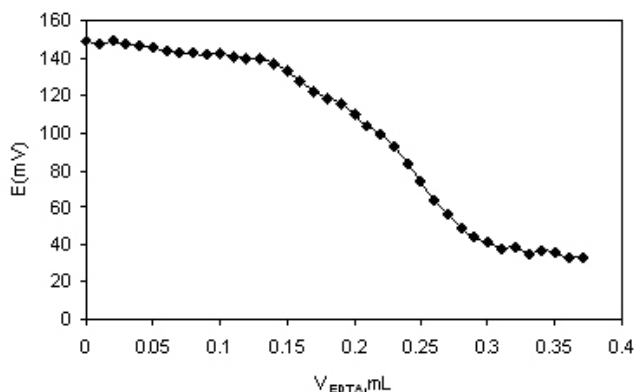


Figure 5. The potentiometric titration curve of 20.0 mL 1.0×10⁻⁴ M Fe³⁺ solution with 1.0×10⁻² M of EDTA.

Fe(III) ions detection in tap and mineral water

The proposed sensor was also applied to the Fe³⁺ detection in tap and bottled drinking mineral water samples. The 5 mL of H₂O₂ solution (1 N) and 5 mL of HNO₃ solution (1 N) were added to 10 mL of sample to oxidize Fe(II) to Fe(III). Then, the resulting solution was diluted with distilled water in a 100 mL volumetric flask. The pH was adjusted to 2.5 by using 0.01 M glycine/HCl buffer to the effective pH range of the sensor. The Fe(III) concentration in the samples was determined directly by using the calibration method.

The results are given in Table 4 and compared with those obtained by atomic absorption spectrophotometry (AAS). It is clear that the resulting data of the fabricated device were in satisfactory agreement with those of AAS.

Table 4. Determination of Fe(III) in water samples

Samples	Proposed Sensor (ppm)*	AAS (ppm)
Tap water1	4.6 ± 0.4	4.4 ± 0.3
Tap water2	4.8 ± 0.3	4.5 ± 0.4
Tap water3	4.7 ± 0.2	4.4 ± 0.2
Mineral water1	1.8 ± 0.2	1.6 ± 0.4
Mineral water 2	1.6 ± 0.4	1.3 ± 0.3
Mineral water 3	1.5 ± 0.3	1.3 ± 0.4

* The results are based on triplicates measurements

CONCLUSION

PVC membrane electrode incorporating 4,4'-Dimethoxybenzil bisthiosemicarbazone (DBTS) showed high selectivity and sensitivity to wards iron ions. The proposed sensors have a good characteristics such as; wide concentration range from 1.0×10⁻⁶ to 1.0×10⁻² M, fast response time of ~10s and good selectivity coefficient with respect to alkaline, alkaline earth, and heavy metal ions and could be used over a pH range of 1.8–5.0. The iron ion-selective electrode can be employed as an indicator electrode in potentiometric titration and the determination of iron ions in water samples.

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