

Highly Selective Triiodide Polymeric Membrane Electrode Based on Tetra(*p*-chlorophenyl)porphyrinato Manganese (III) Acetate

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A new solvent polymeric membrane sensor based on tetra(*p*-chlorophenyl)porphyrinato manganese (III) acetate is described which demonstrates excellent selectivity toward the triiodide ion. The electrode has a linear dynamic range between 1.0×10^{-2} M and 7.0×10^{-6} M with a Nernstian slope of -59.6 ± 1 mV per decade and a detection limit of 5.0×10^{-6} M. The proposed sensor revealed good selectivities for triiodide over a wide variety of other anions and could be used in a pH range 2-9. The electrode can be used for at least two months without any considerable divergence in potential. It was applied as indicator electrode in potentiometric titration of the triiodide and As(III) ions.

Key Words : Triiodide ion-selective electrode, PVC membrane, Porphyrin-Mn(III), Potentiometry

Introduction

Research on anti-Hofmeister sensing materials for anions is an expeditiously expanding domain in chemical sensors. The useful anion selective electrodes reported in recent years have been mainly based on quaternary ammonium salts,¹⁻³ vitamin B₁₂ derivatives,^{4,6} metal ion complexes,^{7,8} organo-metallic compounds^{9,10} and metalloporphyrin derivatives.¹¹⁻¹⁸ Metalloporphyrins are a class of molecules which, in preliminary studies, have proven useful for such purposes.¹⁹ Indeed, it has been shown previously that anion selectivities of manganese(III)-porphyrin based membranes can be altered by changing the peripheral structure of porphyrin ring surrounding the central metal.¹¹ The anti-Hofmeister selectivity order is believed to originate from the selective axial ligation between the metal ion centers and certain anions. Therefore, the nature of the central metal is expected to play an important role in the realization of the selectivity patterns observed.

Suzuki *et al.*²⁰ have reported the first triiodide PVC membrane electrode based on 5,10,15,20-tetraphenylporphyrinato manganese(III). This electrode, with a super-Nernstian response of -87 mV/decade to I₃⁻ ion, was applied to the indirect determination of some oxidizing agents. We have recently introduced two triiodide PVC membrane sensors based on a charge-transfer complex of I₂ with 2,4,6,8-tetraazabicyclo-[3.3.0]octane²¹ and ketoconazole-triiodide ion pair complex.²²

In this paper tetra(*p*-chlorophenyl)porphyrinato manganese (III) acetate (I) is incorporated into plasticized PVC membranes containing 2-nitrophenyloctyl ether and tetrabutylammonium bromide to prepare electrodes with substantially improved selectivity towards the triiodide ion.

Experimental Section

Reagents. Reagent grade 2-nitrophenyloctyl ether (NPOE),

nitrobenzene (NB), acetophenone (AP), bis(2-ethylhexyl) sebacate (BEHS), dibutyl phthalate (DBP), tetrahydrofuran (THF), and high relative molecular weight PVC were purchased from Aldrich and used as received. Tetraphenylphosphonium chloride (TPPC), tetrabutyl ammonium bromide (TBAB), sodium tetraphenylborate (STPB), iodine and potassium salts of all anions used (all from Merck) were of highest purity available and used without further purification except for vacuum drying. Triply distilled water was used throughout.

Apparatus. All potentiometric and pH measurements were made at 25 ± 1 °C with a digital WTW Multilab 540 Ion Analyzer (Germany). A LKB model 4054 UV-Vis recording spectrophotometer with 10 mm quartz cells was used for absorbance measurements.

Electrode Preparation. The master membrane was fabricated by dissolving 45 mg of powdered PVC, 103.5 mg of plasticizer NPOE, 0.75 mg of (I) and 0.75 mg of TBAB in 5 mL of THF. The resulting mixture was transferred into a glass dish of 2 cm diameter. The THF was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3-5 mm o.d.) was dipped into the mixture for about 10 s so that a membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 2 h. A 1.0×10^{-2} M triiodide ion solution was used as internal reference solution. The electrode was finally conditioned by soaking in 1.0×10^{-2} M triiodide solution for 24 h. A silver/silver chloride electrode was used as an internal reference electrode.

Emf Measurements. All emf measurements were carried out with the following cell assembly:

Ag/AgCl, KCl (3 M) | internal solution KI₃ (1.0×10^{-2} M) | PVC membrane | test solution | Ag/AgCl, KCl (3 M)

Activities were calculated according to the Debye-Hückel procedure.²³

Results and Discussion

The wide use of ISEs in routine chemical analysis has been accompanied by a search for ionophores that can chemically recognize specific ions and offer either new or improved selectivities for different ions. For the development of a truly anion-selective electrode, a strong interaction between the ionophore and anions is required in order to complex the anions in a selective fashion. Metalloporphyrins, as ionophores for anions, show such specific metal-ligand interactions and also it is well established that the central metal and the bulkiness of the side chains that surround the porphyrin ring control the selectivity of the ISEs.²⁴

In this work, we were interested in investigating the possibility of the use of tetra(p-chlorophenyl)porphyrinato manganese(III) acetate, recently synthesized in our research laboratories, as an ionophore in PVC-based membranes for I_3^- ion. Thus, in preliminary experiments the mentioned ionophore was used to prepare PVC membrane ion-selective electrodes for a wide variety of anions. The potential responses of various anion-selective electrodes based on (I) are shown in Figure 1. The first point which should be noted in Figure 1 is that the initial potentials of the electrodes for various anions differ significantly. This is most probably due to the fact that each electrode was conditioned separately in a 1.0×10^{-2} M of the corresponding anion.

As it is obvious from Figure 1, with the exception of I_3^- ion, all anions tested show negligible responses in the concentration range 4.0×10^{-6} - 1.0×10^{-2} M, due to their very weak interactions with membrane. Noteworthy, among these anions, I^- shows a higher potential responses at lower concentrations. This is most probably due to the specific interaction between I^- and manganese porphyrins.²⁵ However, the triiodide ion results in a Nernstian potential response at a wide concentration range.

The influence of porphyrin structure¹¹ as well as the axial ligation of Co(III)-tetraphenylporphyrin complex²⁴ on the potentiometric response and anion selectivity of the metalloporphyrin-based polymeric membranes have been reported in the literature. It has been shown that not only the presence of various anions as axial ligand but also the substitution of different groups on the porphyrin structure can strongly influence the selectivity pattern of the resulting membrane sensors for anionic species.^{11,24} In the case of the ionophore used in this study, the presence of p-chloro substitution on the phenyl groups of porphyrin as well as the axial ligation of acetate ion seem to induce the selective behavior of the resulting membrane sensor towards I_3^- ion.

It is well understood that the sensitivity, linearity and selectivity obtained for a given ionophore depend significantly on the membrane composition and nature and amount of additive used.^{16,21,22,26-28} Thus, the influence of the amount of ionophore, and amount and nature of the plasticizers and lipophilic anionic additives on the potential response of the I_3^- sensor was investigated, and the results are summarized in Table 1. As it is seen, in most cases, the electrodes show a super-Nernstian response to triiodide ion, a behavior which

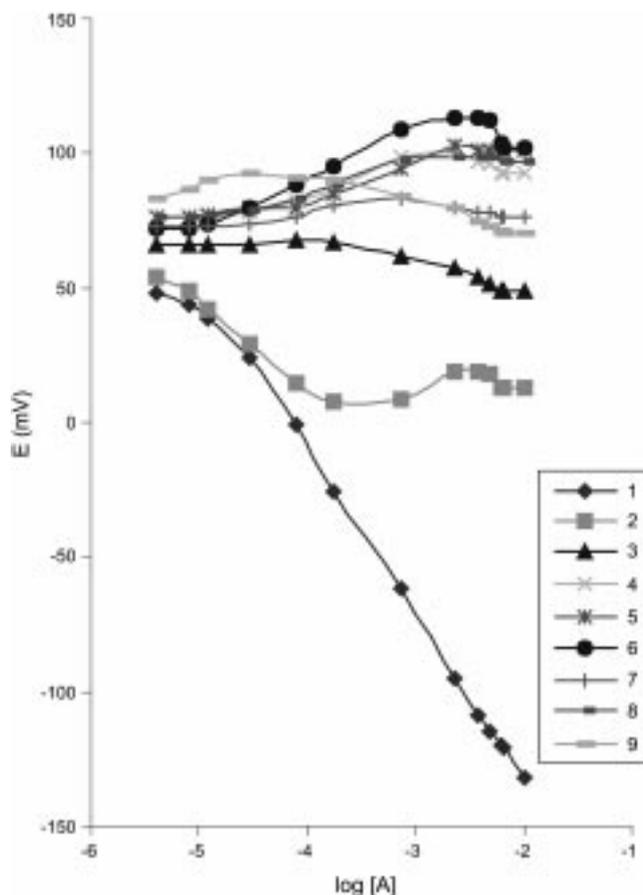


Figure 1. Potential response of various anion-selective membranes based on (I).

has already been reported for ionophore-based selective electrodes for such lipophilic anions as I_3^- ²⁰ and SCN^- ions.²⁵ This is most probably due to the high tendency of the anionic species to diffuse into the lipophilic membrane.

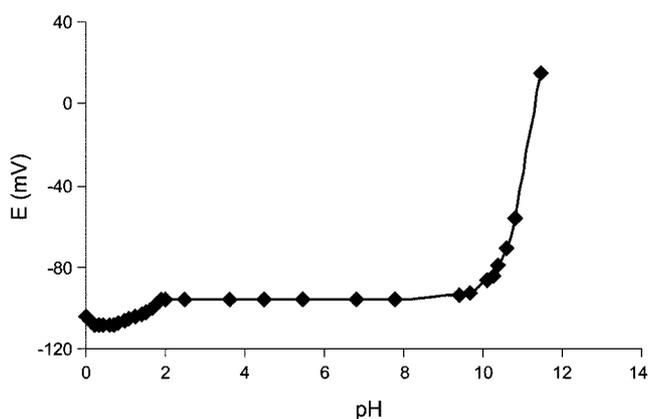
It is seen that, among different membrane compositions tested, membrane No. 13 with 0.5% ionophore (I), 30% PVC, 69% NPOE and 0.5% TBAB offers the widest linear range with a Nernstian slope of -59.6 ± 1 mV per decade. It has been demonstrated that the presence of lipophilic electrically charged additives improves the potentiometric behavior of certain anion selective electrodes including ones prepared with metalloporphyrins.²⁹

The pH dependence of the membrane electrode was tested over the pH range 2-11 at an I_3^- concentration of 1.0×10^{-3} M and the results are shown in Figure 2. As is obvious, the electrode potential is independent of the pH in the range 2-9. Over this range, the potential does not vary more than ± 1.0 mV for 10^{-4} - 10^{-3} M I_3^- solutions. However, in highly alkaline media, the potential increased sharply, most probably due to the disproportionation reaction of I_3^- resulting in the formation of hypoiodate and iodide,³⁰ both of which being insensitive to the membrane electrode. Thus, for further studies, the pH of sample solutions was adjusted to 5.0 using a 1.0×10^{-2} M phosphate buffer.

The I_3^- concentration of the internal solution was changed from 1.0×10^{-4} to 5.0×10^{-2} M, and the resulting emf vs.

Table 1. Optimization of membrane ingredients

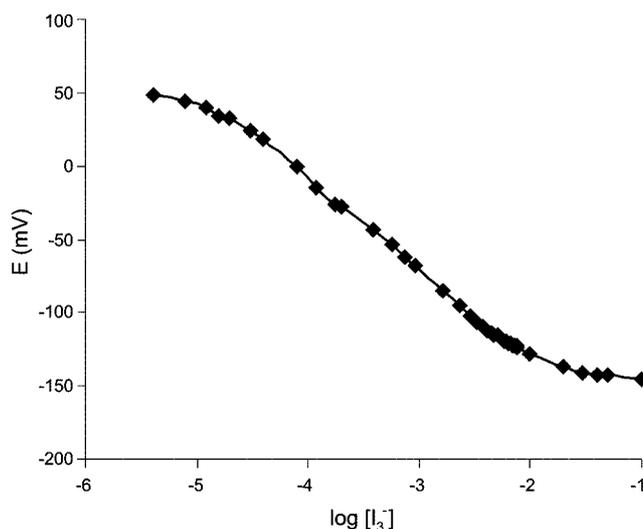
| No. | Composition (%) | | | | Slope mV/decade | Linear range (M) |
|-----|-----------------|-------------|-----------|-----------|--------------------|---|
| | PVC | Plasticizer | Ionophore | Additive | | |
| 1 | 31.0 | 67.9, NPOE | 1.1 | — | -108.7 | $6.0 \times 10^{-5} - 3.7 \times 10^{-3}$ |
| 2 | 29.7 | 69.7, NPOE | 0.5 | — | -69.4 | $1.2 \times 10^{-5} - 3.3 \times 10^{-3}$ |
| 3 | 28.3 | 71.2, NPO | 0.4 | — | -83.3 | $3.9 \times 10^{-5} - 3.7 \times 10^{-3}$ |
| 4 | 30.2 | 68.8, AP | 1.0 | — | — | — |
| 5 | 28.7 | 70.3, NB | 1.0 | — | — | — |
| 6 | 29.6 | 69.4, DBP | 1.0 | — | -76.5 | $1.2 \times 10^{-5} - 1.7 \times 10^{-3}$ |
| 7 | 29.0 | 70, BEHS | 1.0 | — | — | — |
| 8 | 30.0 | 69.5, DBP | 0.5 | — | -59.5 | $1.2 \times 10^{-5} - 9.1 \times 10^{-4}$ |
| 9 | 40.0 | 59.5, NPOE | 0.5 | — | -73.3 | $8.0 \times 10^{-6} - 2.8 \times 10^{-3}$ |
| 10 | 31.0 | 67.5, NPOE | 0.5 | 1.0, NTPB | -74.9 | $1.2 \times 10^{-5} - 5.2 \times 10^{-3}$ |
| 11 | 31.0 | 67.5, NPOE | 0.5 | 1.0, TPPC | -88.8 | $4.0 \times 10^{-5} - 6.0 \times 10^{-3}$ |
| 12 | 31.0 | 68.0, NPOE | 0.5 | 0.5, TPPC | -89.9 | $3.0 \times 10^{-5} - 5.2 \times 10^{-3}$ |
| 13 | 31.0 | 68.0, NPOE | 0.5 | 0.5, TBAB | -59.6 | $7.9 \times 10^{-6} - 1.0 \times 10^{-2}$ |
| 14 | 30.0 | 68.5, NPOE | 0.5 | 1.0, TBAB | -60.2 | $8.0 \times 10^{-6} - 6.7 \times 10^{-3}$ |
| 15 | 30.0 | 66.5, NPOE | 0.5 | 3.0, TBAB | -60.6 | $8.0 \times 10^{-6} - 5.0 \times 10^{-3}$ |

**Figure 2.** Effect of pH of test solution on the potential response of the I_3^- ion-selective electrode.

$-\log [I_3^-]$ plots showed that the variation in the concentration of the internal solution changes linear range and intercept of the resulting plots. Thus, based on the results of these studies, a 1.0×10^{-2} M solution of KI_3 was chosen for further studies.

For analytical applications, the response time of a membrane sensor is an important factor. The average time required for the I_3^- selective membrane electrode to reach a potential within ± 1 mV of final equilibrium value after successive immersion of a series of I_3^- ion solutions, each having a 10 fold difference in concentration was measured. The static response time of the PVC-membrane thus obtained was less than 8 s over the entire linear concentration range. The potentials remained constant for more than 5 min, after which a very slow divergence was observed. The proposed electrode system was very stable and could be used over a period of at least 2 months without any significant change in its response characteristics.

Under optimal conditions, the emf response of the sensor at varying activity of I_3^- indicates a rectilinear range from 1.0

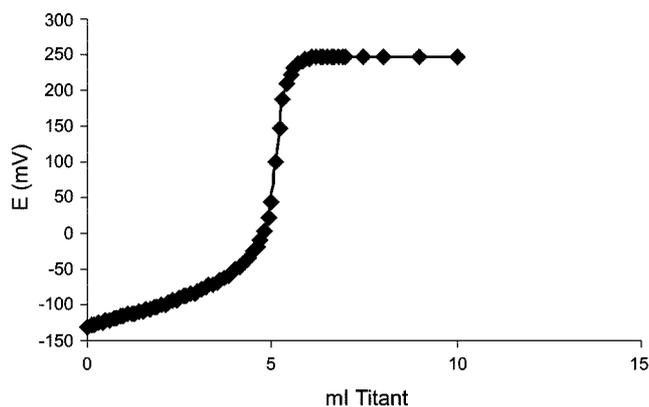
**Figure 3.** Calibration graph for the I_3^- ion-selective electrode.

$\times 10^{-2}$ to 7.5×10^{-6} M (Figure 3). The slopes of calibration curves were -59.6 ± 0.9 mV per decade of I_3^- concentration. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 5.0×10^{-6} M.

The selectivity is clearly one of the most important characteristics of a sensor, as it often determines whether a reliable measurement in the target sample is possible. This is usually expressed in terms of potentiometric selectivity coefficient. In this work, the potential response of the proposed I_3^- ionselective sensor to other anions were investigated by the matched potential method (MPM).³¹⁻³³ This is a recently recommended method by IUPAC³² which gets ride of the limitations of the corresponding methods based on Nicolsky-Eisenman equation for the determination of potentiometric selectivity coefficients (including the fixed interference and the mixed solution methods).³⁴ These limitations include non-Nernstian behavior of interfering ions and inequality of

Table 2. Selectivity coefficients ($\log K_{A,B}^{Pot}$) of various interfering anions

| Anion | $\log K_{A,B}^{Pot}$ | Anion | $\log K_{A,B}^{Pot}$ |
|-----------------------------|----------------------|--------------------|----------------------|
| Br^- | < -6 | SO_4^{2-} | -3.5 |
| Cl_2^- | < -6 | IO_3^- | -2.9 |
| NO_2^- | < -6 | SCN^- | -2.6 |
| NO_3^- | < -6 | ClO_4^- | -1.9 |
| CH_3COO^- | < -6 | I^- | -1.8 |
| $\text{C}_2\text{O}_4^{2-}$ | -4.0 | | |

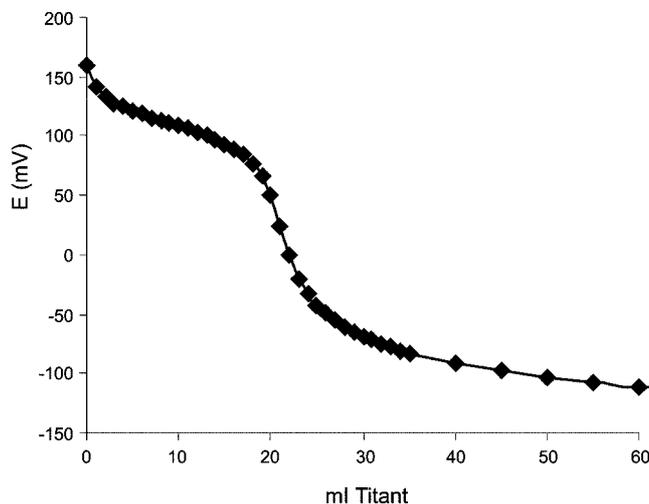
**Figure 4.** Potentiometric titration curve for 50.0 mL of 5.0×10^{-3} M triiodide solution with a 0.10 M solution of sodium thiosulfate, using the proposed sensor as an indicator electrode.

charges of primary and interfering ions.

According to the MPM, the selectivity coefficient is defined as the activity ratio of the primary ion (A) and the interfering ion (B) that gives the same potential change in a reference solution.³¹ Thus, one should measure the change in potential upon changing the primary ion activity. Then the interfering ion would be added to an identical reference solution until the same potential change is obtained. The selectivity coefficient, $K_{A,B}^{Pot}$, is determined as expression $K_{A,B}^{Pot} = \Delta A / a_B$ where $\Delta A = a'_A - a_A$, a_A is the initial primary ion activity and a'_A the activity of A in the presence of interfering ion, a_B . It should be noted that concentration of triiodide ion used as a primary ion in this study was 1×10^{-4} M. The resulting $K_{A,B}^{Pot}$ values thus obtained for the proposed triiodide selective electrode are summarized in Table 2. As seen, most of the diverse anions used cannot significantly disturb the functioning of the I_3^- ion-selective membrane electrode. It is interesting to note that the observed selectivity pattern (*i.e.* $\text{I}_3^- > \text{I}^- > \text{ClO}_4^- > \text{SCN}^- > \text{SO}_4^{2-} > \text{C}_2\text{O}_4^{2-} > \text{Cl}^-, \text{NO}_3^-, \text{CH}_3\text{COO}^-, \text{NO}_2^-, \text{Br}^-$) considerably differs from the so-called Hofmeister selectivity sequence (*i.e.*, selectivity based solely on lipophilicity of anions).³⁵

The practical utility of the proposed triiodide membrane sensor was initially tested by its use as indicator electrode for the titration of 50 mL of 5×10^{-3} M triiodide solution with 0.1 M sodium thiosulfate. The resulting titration curve is shown in Figure 4. As seen, the amount of I_3^- ions in solution can be accurately determined by using the proposed electrode.

The proposed triiodide membrane electrode was also used

**Figure 5.** Potentiometric titration curve for 50.0 mL of 0.04 M As(III) with 0.01 M triiodide solution, using the proposed sensor as an indicator electrode.

as an indicator electrode for the direct potentiometric titration of As(III) with a standardized solution of iodine. A typical potentiometric titration curve obtained from the titration of 50 mL of 0.04 M As(III) (pH = 8.3) with a 0.01 M triiodide standard solution is presented in Figure 5. As seen, the amount of As(III) in solutions can be accurately determined from the resulting titration curve providing a sharp end point.

It is worth mentioning that the proposed membrane electrode may be used for the determination of a number of some important environmental as well as pharmaceutical organic molecules in the field related to chemist, such as clinical analysis and drug analysis, after the oxidation of iodide to triiodide or direct titration with iodine solutions.

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