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PVC based 5,10,15,20-tetrakis (4-methoxyphenyl) porphyrinatocobalt(II) membrane potentiometric sensor for arsenite

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Abstract

PVC based membranes of 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrinatocobalt(II) (TMOPP-Co) (**I**) as electroactive material with dibutyl butyl phosphonate (DBBP), dioctyl phthalate (DOP), 1-chloronaphthalene (CN), tri-*n*-butyl phosphate (TBP) and tris(2-ethylhexyl) phosphate (TEP) as plasticising solvent mediators have been prepared and tried for arsenite determination. The membrane having a composition 150:5:150 (PVC:**I**:DBBP) exhibited the best results with linear potential response in the concentration range of 7.9×10^{-5} to 1.0×10^{-1} M of AsO_2^- with a slope of 28.8 mV/decade. The useful pH range of the sensor is 6.0–10.5. The membrane worked satisfactorily in non-aqueous medium up to 5% (v/v) non-aqueous content. The selectivity coefficient values for mono- and divalent anions indicate good selectivity for arsenite over a large number of anions.

Keywords: PVC; Arsenite; Potentiometric sensor; Chemical sensors

1. Introduction

Arsenic is widely distributed in the environment, including plant and animal tissues. It forms a variety of inorganic and organic compounds of different toxicity to aquatic organisms. This is due to the varying physico-chemical properties of the arsenicals in different valency states. It appears that the stable, soluble inorganic arsenites and arsenates are readily absorbed by the intestinal tract and muscle tissue. Arsenate is excreted faster than the arsenite, mostly through urine, because of its poor affinity for thiol groups. Thus, arsenate is less toxic than arsenite. Arsenite inhibits thiol-dependent enzymes, retained in the body tissue protein, such as keratin disulfides in hair, nails and skin. Arsenic as sodium arsenite continues to be employed as herbicide, fungicide and wood preservative. Arsenites have longer half-life in mammalian tissues than other arsenicals. Symptoms of chronic intoxication in mammals include decreased motor coordination nervous disorders, respiratory distress and damage to kidneys and respiratory tract [1].

Ion selective electrodes (ISEs) are the chemical sensors of longest history and probably still the largest number of applications as their use is simple and even allows in vivo measurements [2]. Not many electrodes have been reported for the determination of arsenite. An arsenite selective electrode imporous membrane consists of 0.01–50% Ag_3AsO_3 in Ag_2S has been reported by Cheng et al. [3]. It was, therefore, felt worthwhile to develop a better sensor for arsenite ions using a macrocyclic compound.

Porphyrins are a class of naturally occurring macrocyclic compounds which play an important role in the metabolism of living organisms. Almost all metals form complexes with

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porphyrin molecules. An unusual feature of porphyrin chelate is that the metal ion is bonded to four nitrogen atoms, which are themselves linked together in a conjugated system. It is this high degree of mesomerism whereby a substitution anywhere in the porphyrin nucleus can relay its electron donating and attracting tendency to all the four coordinating atoms that makes metalloporphyrins so sensitive to the influence of substituents [4]. In the present studies 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrinatocobalt(II) (TMOPP-Co) (**I**) has been tried as an electroactive phase in PVC matrix for the fabrication of arsenite selective electrodes and the results are presented in this paper.

2. Experimental

2.1. Reagents

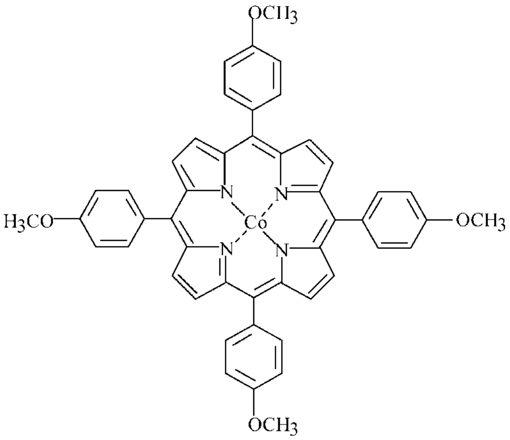
Sodium arsenite was obtained from CDH (India). High molecular weight poly (vinyl chloride) (PVC) was obtained from Fluka (Switzerland) and used as such. All other reagents used were of analytical grade purity (BDH, UK). Aqueous solutions were prepared in doubly distilled water. Dioctyl phthalate (DOP) from Reidal, India, dibutyl butyl phosphonate (DBBP) from Mobil (USA) and 1-chloronaphthalene (CN) and tris(2-ethylhexyl) phosphate (TEP) from Merck (Germany), tri-*n*-butyl phosphate (TBP) from S. D. Fine Chem. (India) were used. Solutions of different concentration were prepared by diluting the stock solution of 0.1 M concentration.

2.2. Apparatus

The potential measurements were carried out at 25 ± 0.1 °C on digital pH meter/millivoltmeter (Toshniwal Inst. Mfg. Pvt. Ltd. Ajmer, India). pH measurements were made on a digital pH meter (LabIndia pH Conmeter, India).

2.3. Synthesis of 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrinatocobalt(II) (TMOPP-Co) (I)

5,10,15,20-tetrakis(4-methoxyphenyl)porphyrinatocobalt (II) (TMOPP-Co) (**I**) was synthesized by the method of Dorough et al. [5] by boiling a mixture of 50 mL of 2.5×10^{-4} M 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin (TMOPP) and 1.25 g of cobalt acetate in 50 mL glacial acetic acid for about 5 min. The solution was then transferred to separating funnel with benzene. Water was then added to the separating funnel and the resulting benzene layer was washed several times with water to completely remove the reaction solvents and inorganic salts. The benzene layer was then dried over anhydrous sodium sulphate and after that it was evaporated to yield the final product which was dried in a vacuum desiccator.



5,10,15,20-tetrakis(4-methoxyphenyl)porphyrinatocobalt (II)

I

2.4. Membrane preparation

The PVC based membranes of ionophore **I** were prepared by the method of Craggs et al. [6]. Varying amounts of the ion active phase 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrinatocobalt(II) (TMOPP-Co) and an appropriate amount of PVC were dissolved in a minimum amount of THF. The solvent mediators DOP, DBBP, TBP, TEP and CN were also added to improve the response of the membranes. The solutions thus obtained, after complete dissolution of various components, were poured into acrylic rings placed on a smooth glass and allowed to evaporate at room temperature. After 24 h, transparent membranes were obtained which were then cut to size and attached to a Pyrex tube with the help of Araldite. The ratio of various membrane ingredients, time of contact and the concentration of equilibrating solution were optimised first so that the membranes develop reproducible, stable, and noiseless potentials. Membrane to membrane and batch to batch reproducibility was assured by carefully following the optimum conditions of fabrication.

2.5. Potential measurements

Proper equilibration of membranes is essential to have a sensor showing good response characteristics. All the membranes were equilibrated in different concentrations of metal solutions for which the sensor is desired. The time of contact in each case was also varied. Potentials were measured by direct potentiometry at 25 ± 0.1 °C with the help of ceramic junction calomel electrodes and the cell set up was the same as reported earlier [7]. 1.0×10^{-1} M sodium arsenite was taken as inner reference solution and saturated calomel electrodes (SCE) were used as reference electrode. All pH adjustments were made with appropriate acid or base.

Table 1
Composition and response characteristics of PVC based TMOPP-Co (**I**) membranes selective to AsO_2^-

Sensor/ membrane no.	Composition of the membrane (w/w)							Working concentration range (M)	Slope (±1.0 mV/decade of activity)	Response time (s)
	(**I**)	DBBP	TEP	TBP	CN	DOP	PVC			
1	5						150	7.0×10^{-4} to 1.0×10^{-1}	27.27	60
2	5	150					150	7.9×10^{-5} to 1.0×10^{-1}	28.8	60
3	5		150				150	6.3×10^{-4} to 1.0×10^{-1}	32.5	75
4	5			150			150	6.3×10^{-4} to 1.0×10^{-1}	30.9	60
5	5				150		150	3.5×10^{-4} to 1.0×10^{-1}	30.0	50
6	5					150	150	3.1×10^{-4} to 1.0×10^{-1}	26.6	50

3. Results and discussion

3.1. Membrane characteristics

Investigation revealed that proper equilibration of the membranes was achieved when these were dipped in a solution of 1.0 M AsO_2^- for 7–10 days. The different membranes needed different equilibration time. Of the various membranes prepared, one having **I** and PVC in the ratio 5:150 (w/w) gave satisfactory results.

3.2. Effect of plasticizer

The effect of addition of plasticizers, viz., dioctyl phthalate (DOP), dibutyl butyl phosphonate (DBBP), tri-*n*-butyl phosphate (TBP), tris(2-ethylhexyl) phosphate (TEP) and 1-chloronaphthalene (CN) was also studied for optimizing the composition of the membranes for obtaining best response characteristics and the same are listed in Table 1.

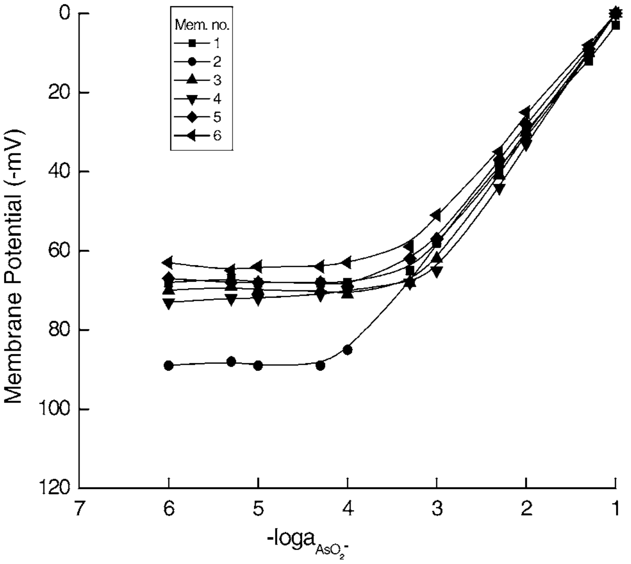


Fig. 1. Variation of membrane potential of PVC based membranes of (**I**) with varying concentrations of AsO_2^- ions (1) without plasticizer (2) with DBBP (3) TEP (4) TBP (5) CN (6) DOP.

3.3. Working concentration range and slope

Potential studies on the membrane sensors were carried out with the varying concentration of arsenite (1.0×10^{-6} to 1.0×10^{-1} M). Table 1 depicts the results of the working concentration range, slope and response time of each membrane. It was observed that membrane which contained only **I** in PVC matrix exhibited a narrow working concentration range of 7.0×10^{-4} to 1.0×10^{-1} M of AsO_2^-. This electrode has a slope of 27.27 mV/decade of concentration and response time of 60 s. As evident from Fig. 1 and Table 1, the electrodes having membranes with plasticizers show response different from electrode 1 having membrane without plasticizer. The working concentration range is increased to 7.9×10^{-5} to 1.0×10^{-1}, 6.3×10^{-4} to 1.0×10^{-1}, 6.3×10^{-4} to 1.0×10^{-1}, 3.5×10^{-4} to 1.0×10^{-1} M and 3.1×10^{-4} to 1.0×10^{-1} M with the addition of DBBP, TBP, TEP, CN and DOP, respectively. The, membrane no. 2 having a composition of 150:5:150 (PVC:**I**:DBBP) with the best working concentration range of 7.9×10^{-5} to 1.0×10^{-1} M was used for further investigation.

3.4. pH and solvent effect

The pH dependence of the electrode potentials was tested over the pH range 2.5–11.5 for 1.0×10^{-3} M AsO_2^-. The pH was adjusted with hydrochloric acid and sodium hydroxide. Fig. 2 depicts that the pH dependence of the potentials is insignificant in the pH range 6.0–10.5 and the same can be taken as the working pH range of the sensor.

The performance of the sensor system was also investigated in partially non-aqueous media using methanol-water and acetone-water mixtures. The membranes do not show any appreciable change in working concentration range or slope in mixtures up to 5% (v/v) non-aqueous contents (Table 2). Above this, developed potential showed an erratic behavior.

3.5. Potentiometric selectivity

The selectivity coefficients $K^{\mathrm{Pot}}_{AsO_2^-,\,B}$ for the proposed electrode were evaluated by modified form of the fixed interference method as suggested by Sa'ez de Viteri et al. [8] and Gadzekpo et al. [9] at 1.0×10^{-2} M concentration of interfering ions. The selectivity coefficient

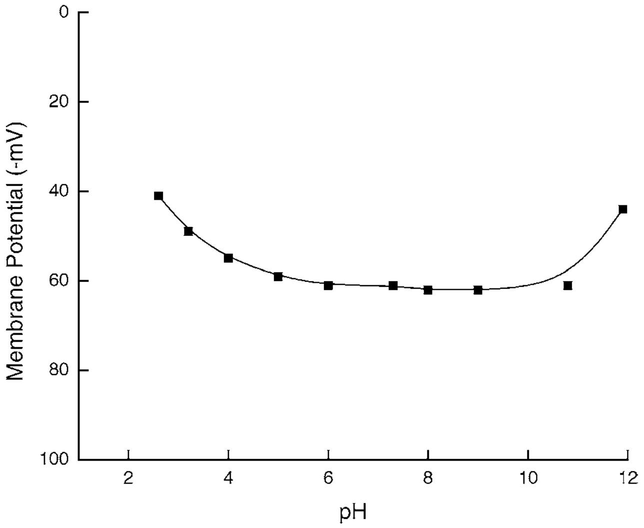


Fig. 2. Effect of pH on potential; $[AsO_2^-] = 1.0 \times 10^{-3}$ M for sensor no. 2.

Table 2
Performance of arsenite sensor (no. 2) in non-aqueous media

Non-aqueous content (%, v/v)	Slope (±1.0 mV/ decade of activity)	Working concentration range (M)
0	28.8	7.9×10^{-5} to 1.0×10^{-1}
Methanol		
5	28.5	7.9×10^{-5} to 1.0×10^{-1}
10	27.2	1.1×10^{-4} to 1.0×10^{-1}
Acetone		
5	28.8	7.9×10^{-5} to 1.0×10^{-1}
10	28.8	8.9×10^{-5} to 1.0×10^{-1}

Table 3
Selectivity coefficient ($K^{\mathrm{Pot}}_{AsO_2^-, B}$) values for AsO_2^- selective sensor as obtained by fixed interference method (interfering ion concentration 1.0×10^{-2} M)

Interfering ion (B)	Selectivity coefficient $K^{\mathrm{Pot}}_{AsO_2^-, B}$ Without superscript
I^-	6.3×10^{-2}
Cl^-	3.4×10^{-2}
NO_2^-	3.5×10^{-2}
NO_3^-	5.0×10^{-2}
IO_3^-	1.99×10^{-1}
SCN^-	5.6×10^{-2}
MoO_4^{2-}	1.0×10^{-1}
SO_4^{2-}	6.3×10^{-2}
$C_2O_4^{2-}$	7.0×10^{-2}

values are listed in Table 3. The selectivity sequence of TMOPP-Co containing membranes employed for different organic and inorganic anions obeys the following order:

$$AsO_2^- > IO_3^- > MoO_4^{2-} > C_2O_4^{2-} > SO_4^{2-}, I^- > SCN^- > NO_3^- > NO_2^- > Cl^-$$

The selectivity sequence significantly differs from the so called Hofmeister selectivity sequence [10] (i.e. selectivity solely based on lipophilicity of anion). The data given in Table 3 indicates that electrode is moderately selective to AsO_2^- ions over a number of anions. However, IO_3^- may cause some interference as the values for this anion is slightly higher but at low concentrations it would also not cause any interference, as selectivity is concentration dependent. To know the extent to which this ion may be tolerated, mixed run studies were carried out (Fig. 3). It can be seen from Fig. 3 that IO_3^- at concentration $\leq 1.0 \times 10^{-4}$ M do not cause any deviation in the original plot obtained in pure AsO_2^- solution which clearly shows that the electrode can tolerate IO_3^- at concentrations $\leq 1.0 \times 10^{-4}$ M over the entire working concentration range. When present at higher concentrations, the electrode can be used over reduced concentration ranges. Fig. 3 shows that in the presence of 1.0×10^{-3} and 1.0×10^{-2} M IO_3^-, the sensor assembly can be used to determine AsO_2^- in the reduced concentration ranges of 1.25×10^{-4} to 1.0×10^{-1} and 1.99×10^{-3} to 1.0×10^{-1} M, respectively.

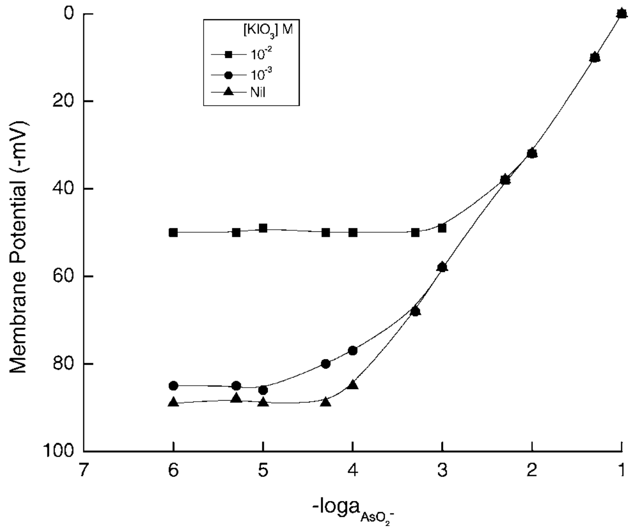


Fig. 3. Variation of cell potential with varying concentrations of AsO_2^- at different concentration levels of IO_3^- for sensor no. 2.

4. Conclusions

The membrane sensor with 5,10,15,20-tetrakis(4-methoxyphenyl) porphyrinatocobalt(II) (TMOPP-Co) (**I**) as electroactive material and DBBP as plasticizer in a PVC matrix in the ratio 5:150:150 (**I**:DBBP:PVC) is suitable for AsO_2^- estimation. It gives a Nernstian slope (28.8 ± 1.0 mV/decade of activity) in the concentration range 7.9×10^{-5} to 1.0×10^{-1} M of AsO_2^- and performs well over the pH range 6.0–10.5. The response time of this sensor is 60 s with a lifetime of about 2 months in aqueous as well as in non-aqueous medium.

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