Membranes of 5,10,15,20-Tetrakis(4-Methoxyphenyl) Porphyrinatocobalt (TMOPP-Co) (I) as MoO $_4^{2-}$ - Selective Sensors

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Abstract: Polyvinyl chloride (PVC) membrane electrodes based on porphyrin 5,10,15,20-tetrakis(4methoxyphenyl)porphyrinatocobalt (TMOPP-Co) (I) incorporating sodium tetra phenyl borate (NaTPB) as anion excluder and dibutyl phthalate (DBP), dioctyl phthalate (DOP), dibutyl butyl phosphonate (DBBP), tri-n-butyl phosphate (TBP), and 1-chloronaphthalene (CN) as plasticizing solvent mediators were prepared and tested for selective detection of molybdate ions. The membrane having anion excluder, NaTPB and DBP as plasticizer (membrane no. 2) proved to be best in terms of working concentration range $5.0 \times 10^{-5} – 1.0 \times 10^{-1}$ M with a near – Nernstian slope of 32.0±1.0 mV/decade of activity over the pH range 5.4- 10.5. The response time of this sensor is 18s with a lifetime of about 4 months. The sensor can be used in non-aqueous medium with no significant change in the value of slope or working concentration range for the estimation of MoO_4^{2-} in solutions having up to 25% (v/v) non-aqueous fraction.

Keywords: Poly(vinyl)chloride (PVC), Near-Nernstian slope, Molybdate selective electrode, Membrane electrode

Introduction

Molybdenum is frequently used in alloys, electrical, electronic, missiles, aircraft and high temperature furnace parts, die- casting ores, thermocouples, nuclear energy application, equipment for glass melting furnaces and corrosion resistive equipment owing to its high melting point, high strength at elevated temperature, high thermal conductivity and good resistance to corrosion. It is also used as

catalyst in many petrochemical and organic reactions. Molybdenum is one of the biologically active transition element. It is intimately involved in the functioning of enzymes and in many other biological processes. Though molybdenum is an essential trace element required by both plants and animals [1], however it is harmful to both at higher concentrations (>5µg/g). Thus the determination of molybdenum at trace levels is of special interest [2]. In solutions, molybdate generally occurs in the form of MoO_4^{2-} at about pH 5 and above.

Ion- selective electrodes are increasingly used in the fields of environmental, industrial, agricultural and medicinal analysis. Not many electrodes have been reported for the determination of molybdenum. Polystyrene based membranes of zirconium molybdate gel have been reported by Malik et al. [3] for its determination. But the electrode exhibited a non-Nernstian response and suffered serious interference from vanadate, halides, thiocyanate and nitrate. Srivastava et al. [4] used zirconium oxide as the membrane phase embedded in polystyrene matrix for the determination of molybdate ions. Some liquid membrane electrodes based on trioctyl ammonium aspartate [5] and Mo-N-Phenylbenzohydroxamic acid chelate [6] have also been reported. Lee and Chen [7] used insoluble lead salts for the above purpose. These electrodes showed narrow working concentration ranges and interference from various anions. It was, therefore, felt worthwhile to develop a new sensor for molybdate ions.

Porphyrins are a class of naturally occurring macrocyclic compounds, which play an important role in the metabolism of living organisms. The porphyrin molecule consists of four pyrrolic units linked by four methine bridges. Almost all metals form complexes with porphyrin molecules. The chelation of metal ion by porphyrin involves the incorporation of the metal ion into the center of the tetrapyrrole nucleus with the simultaneous displacement of 2 protons from the secondary nitrogen atoms. An unusual feature of porphyrin chelate is that the metal ion is bonded to four-nitrogen atom, 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 attracting and donating tendency to all four coordinating atoms, that makes metalloporphyrins so sensitive to the influence of substituents. Preliminary studies showed that 5,10,15,20 tetrakis(4methoxyphenyl)porphyrinatocobalt (TMOPP-Co) (**I**) tend to show affinity for molybdate ions. Thus, 5,10,15,20-tetrakis(4methoxyphenyl)porphyrinatocobalt (TMOPP-Co) has been studied as an electroactive phase in PVC matrix for the fabrication of MoO_4^{2-} selective electrode and the results are presented in this paper. The present electrode shows good selectivity over other cations and is superior to the existing electrodes in many aspects.

Experimental

Reagents

Sodium molybdate and Cobalt acetate were obtained from S.D. Fine Chem. (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. Anion excluder, sodium tetraphenyl borate (NaTPB) from BDH (England), dibutyl
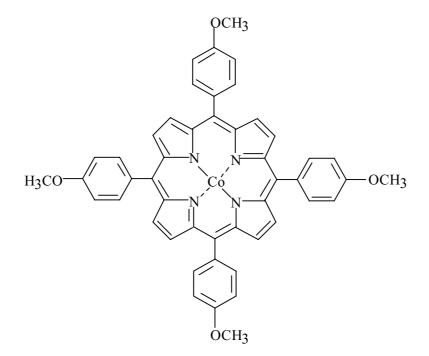
phthalate (DBP) and dioctyl phthalate (DOP) from Reidal, India, dibutyl butylphosphonate (DBBP) from Mobil (USA) and chloro naphthalene (CN) and tri (n-butyl) phosphate (TBP) from Merck (Germany) were used. Solutions of different concentration were prepared by diluting the stock solution of 0.1 M concentration.

Apparatus

The potential measurements were carried out at 25 ± 0.1 ^{o}C on a PH 5652 digital pH meter/millivoltmeter (ECIL, Hyderabad, India) and CVM 301 Century microvoltmeter (Century Instruments, Chandigarh, India). Saturated calomel electrodes were used as reference electrodes. pH measurements were made on a digital pH meter (model PH 5652, ECIL, Hyderabad, India; Glass electrodes as pH electrode and calomel as reference electrode).

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

5,10,15,20-tetrakis(4-methoxyphenyl)porphyrinatocobalt (TMOPP-Co) was synthesized by the method of Dorough *et al.* [8] 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 separator funnel with benzene. Water was then added to the separator 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 (I)

Membrane preparation

The method reported by Craggs *et al.* was adopted for the preparation of membrane [9]. Varying amounts of the ion active phase (5,10,15,20-tetrakis(4-methoxyphenyl)porphyrinatocobalt (TMOPP-Co) and an appropriate amount of PVC were dissolved in a minimum amount of THF. The anion excluder, NaTPB and solvent mediators; DBP, DOP, DBBP, TBP, and CN were also added to get membranes of different compositions. 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 48 hours, 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 optimized 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 condition of fabrication.

Potential Measurements

The membranes were equilibrated for 5 days in 1.0 M solution. Potentials were measured by direct potentiometry at 25 ± 0.1 ^{o}C with the help of ceramic junction calomel electrodes by setting a following cell as reported earlier [10].

Internal reference electrode (SCE)	Internal solution 0.1 mol l^{-1}	Membrane	Test Solution	External reference electrode (SCE)

1.0×10^{-1} M sodium molybdate was taken as inner reference solution and saturated calomel electrodes (SCE) were used as reference electrodes. All pH adjustments were made with appropriate acid or base.

Results and Discussion

Membrane Characteristics

The composition of the PVC based membranes incorporating TMOPP-Co (**I**) was optimized by varying the ratio of metalloporphyrin and PVC so as to obtain membranes showing best performance with regard to working concentration range, slope and response time. Investigation revealed that the membranes incorporating **I** and PVC in the ratio 12:100 (**I**: PVC) exhibited best performance. The membranes were equilibrated in sodium molybdate solutions of different concentrations for different periods of time. Results showed that perfect equilibration was achieved when the membranes were dipped in 1.0 M MoO_4^{2-} solution for 5 days. Various plasticizers, *viz*. dibutyl phthalate (DBP), dibutyl butylphosphonate (DBBP), dioctyl phthalate (DOP), tri-n-butyl phosphate (TBP) and chloronaphthalene (CN) were tried in varying amounts for improving the performance of the

membranes. The compositions of the best performing membranes along with the response characteristics are listed in Table 1.

Table 1. Response characteristics of MoO_4^{2-} - selective sensors based on TMOPP-Co (I).

Sensor / Membrane No.	Composition of the membrane (w/w)							Working Concentration range (M)	Slope (±1.0mV/ decade of activity)	Response time (s)
	(I)	PVC	DBP	DOP	TBP	CN	DBBP			
1	12	100	-	-	-	-	-	8.9×10^{-4}-1.0×10^{-2}	38.0	60
2	12	100	60	-	-	-	-	5.0×10^{-5}-1.0×10^{-1}	32.0	18
3	12	100	-	55	-	-	-	7.0×10^{-4}-1.0×10^{-1}	36.5	30
4	12	100	-	-	54	-	-	5.0×10^{-4}-1.0×10^{-1}	35.0	25
5	12	100	-	-	-	48	-	3.2×10^{-4}-1.0×10^{-1}	34.0	25
6	12	100	-	-	-	-	70	8.9×10^{-5}-1.0×10^{-1}	33.5	20

Working Concentration Range and Slope

The potential response of all the membranes for MoO_4^{2-} was studied at 1.0×10^{-1} M concentration of internal solution and by varying the concentration of the test solution from 1.0×10^{-6}-1.0×10^{-1} M. The potentials observed are plotted against the activity of MoO_4^{2-} in Fig. 1. The non-plasticized membrane (membrane no. 1) exhibited a narrow working concentration range of 8.9×10^{-4}-1.0×10^{-2} M with a slope 38.0 mV/decade of activity. The addition of plasticizers to the membrane improved the performance, as working concentration range became wider and the slope approaches near-Nernstian value. Table 1 shows that the best results are exhibited by the membrane incorporating DBP as solvent mediator (membrane no.2). It worked well over a concentration range of 5.0×10^{-5}-1.0×10^{-1} M with a near-Nernstian slope of 32.0 ± 1.0 mV/decade of activity.

Further, to obtain optimum concentration of the ingredients in this membrane, different amounts of (**I**) were tried by keeping the amounts of other ingredients constant (Table 2). It is clear from Table 2 that the composition 12:100:60 (**I**: PVC: DBP) (w/w) is best. If the amount of (**I**) was further increased, there was no considerable improvement in any of the characteristics of the sensor. Therefore sensor no. C has been chosen for all further studies.

Responses and Lifetime

The response time i.e., the time taken by a membrane to attain stable potentials was determined for all the membranes. Membrane no. 1 (Table 1) (without plasticizer) showed a response time of 1 min while those incorporating the solvent mediators DBP, DOP, TBP, CN and DBBP (membrane no. 2-6, respectively) exhibited comparatively faster response times of 18, 30, 25, 25 and 20s, respectively. Table 1 clearly indicates that the membrane no. 2 shows best performance with regard to working concentration range, slope and response time and thus was chosen for all further studies. The electrode worked well over a period of four months and no appreciable change in the value of slope, working

concentration range and response time was observed. When the membranes were not in use, they were stored in 0.1 M MoO_4^{2-} solution and re-equilibrated with 1.0 M MoO_4^{2-} solution whenever any drift in potentials was recorded. The reproducibility of the potential data was checked by making twenty measurements on a same portion of solution (1.0×10^{-2} M). The standard deviation observed was ± 0.5 mV. The standard deviation for slope was found to be $\pm$ 1.0 mV, which shows good reproducibility.
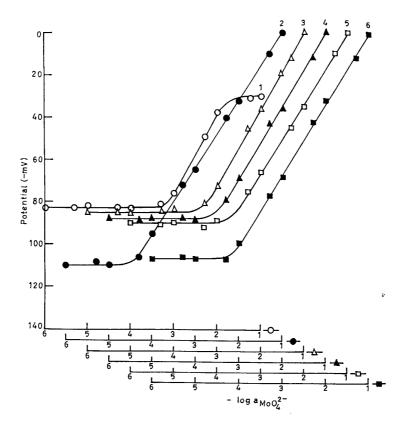

Figure 1. Variation of membrane potential of PVC based membranes of (**I**) with varying concentrations of MoO_4^{2-} ions (1) without plasticizer (2) with DBP (3) with DOP (4) with TBP (5) with CN and (6) with DBBP, respectively.

Table 2. Response characteristics of PVC based membranes
having different amounts of TMOPP-Co(I) as active material.

Sensor / Membrane No.	Composition of the membrane (w/w)			Working Concentration range (M)	Slope (±1.0mV/ decade of activity)	Response time (s)
	(I)	DBP	PVC			
A	10.0	60	100	1.0×10^{-4}-1.0×10^{-1}	31.5	25
B	11.0	60	100	6.5×10^{-5}-1.0×10^{-1}	32.0	20
C	12.0	60	100	5.0×10^{-5}-1.0×10^{-1}	32.0	18
D	13.0	60	100	5.0×10^{-5}-1.0×10^{-1}	32.0	18
E	14.0	60	100	5.1×10^{-5}-1.0×10^{-1}	32.0	18

pH and Solvent Effect

The working pH range of the sensor was ascertained by recording potentials over a pH range of 4.0 to 12.0 at 1.0×10^{-2} and 1.0×10^{-3} M MoO_4^{2-} solutions. The pH of the solutions was adjusted with HNO_3 and NaOH. It can be seen from Fig. 2 that potentials remain constant in the pH range 5.4-10.5 and the same may be taken as the working pH range of the sensor.
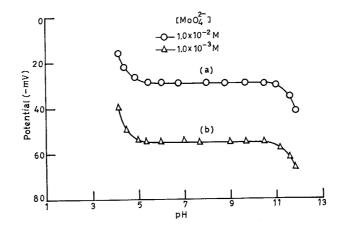

Figure 2. Effect of pH on cell potential; $[MoO_4^{2-}]=1.0 \times 10^{-2}$ M (a) and 1.0×10^{-3} M (b) for sensor no. 2.

The functioning of the membrane sensors was also investigated in partially non-aqueous media using methanol-water and ethanol-water mixtures (Table 3). The membrane worked satisfactorily in partially non-aqueous medium up to a maximum 25% (v/v) content of methanol and ethanol. In these mixtures, the working concentration range and slope remained almost constant. However, above a 25% non-aqueous content, the potential developed showed an erratic behavior.

Potentiometric Selectivity

The selectivity coefficients were determined by the modified form of fixed interference method [11,12] at 1.0×10^{-2} M concentration of the interfering ions. A perusal of $K_{MoO_4^{2-},B}^{Pot}$ values presented in Table 4 indicates that the sensor is moderately selective to MoO_4^{2-} over a number of anions. As the selectivity coefficient values were high for Cl^- and SCN^-, they are expected to cause interference. In order to know the concentration of Cl^- and SCN^- that can be tolerated in the determination of MoO_4^{2-}, some mixed run studies were carried out. It is seen from Fig. 3 that the presence of Cl^- at a concentration of 5.0×10^{-5} M caused negligible divergence in the potential versus MoO_4^{2-} activity plot as obtained in the case of pure MoO_4^{2-} solution for sensor no. 2. Thus, the sensor can tolerate Cl^- at concentration $\leq 5.0 \times 10^{-5}$ M over the entire working concentration range. However, higher concentrations caused divergence from the original plot. It can be seen from Fig. 3 that MoO_4^{2-} can be determined in the ranges of 7.1×10^{-5}-1.0×10^{-1} and 2.0×10^{-4}-1.0×10^{-1} M in the presence of 1.0×10^{-4} and 1.0×10^{-3} M Cl^-, respectively. Similar mixed run studies (Fig. 4) with SCN^- show that $\leq 1.0 \times 10^{-5}$ M of

SCN$^-$ can be tolerated over the whole working concentration range in the determination of MoO$_4^{2-}$. MoO$_4^{2-}$ can be determined in the reduced working concentration ranges of 9.9×10^{-5}-1.0×10^{-1} and 3.2×10^{-4}-1.0×10^{-1} M in the presence of 1.0×10^{-4} and 1.0×10^{-3} M SCN$^-$, respectively.

Table 3. Response of MoO$_4^{2-}$ sensor (no. 2) in partially aqueous medium.

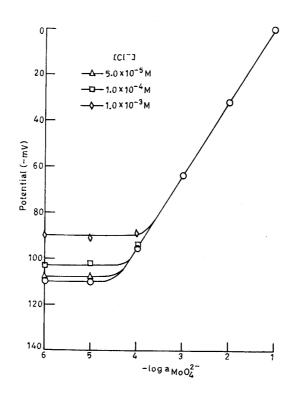| Non-aqueous content (% v/v)	Working concentration range (M)	Slope (± 1.0 mV/decade of activity)
0	5.0×10^{-5}-1.0×10^{-1}	32.0
Methanol		
15	5.0×10^{-5}-1.0×10^{-1}	32.0
20	4.8×10^{-5}-1.0×10^{-1}	31.8
25	4.5×10^{-5}-1.0×10^{-1}	31.5
30	1.2×10^{-4}-1.0×10^{-1}	28.0
Ethanol		
15	5.0×10^{-5}-1.0×10^{-1}	32.0
20	4.9×10^{-5}-1.0×10^{-1}	32.0
25	4.5×10^{-5}-1.0×10^{-1}	31.7
30	2.5×10^{-4}-1.0×10^{-1}	28.3

Figure 3. Variation of cell potential with varying concentrations of MoO$_4^{2-}$ at different concentration levels of Cl$^-$ for (**I**) membrane.

Table 4. Selectivity coefficient values $K^{Pot}_{MoO_4^{2-},B}$ observed for MoO_4^{2-} selective sensor as obtained by using modified form of Fixed Interference Method.

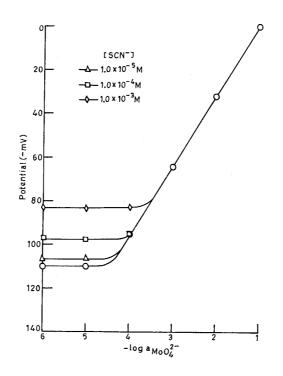| Interfering ion (B)	Selectivity coefficient $K^{Pot}_{MoO_4^{2-},B}$
Cl^-	1.8×10^{-1}
I^-	3.9×10^{-2}
Br^-	5.6×10^{-2}
NO_3^-	1.0×10^{-2}
NO_2^-	1.7×10^{-2}
ClO_4^-	1.9×10^{-2}
IO_4^{3-}	2.8×10^{-2}
SCN^-	2.1×10^{-1}
SO_4^{2-}	1.5×10^{-2}
$C_2O_4^{2-}$	1.2×10^{-2}
PO_4^{3-}	1.3×10^{-2}

Figure 4. Variation of cell potential with varying concentrations of MoO_4^{2-} at different concentration levels of SCN^- for (**I**) membrane.

Conclusion

PVC based membrane sensor of 5,10,15,20 tetrakis (4methoxyphenyl) porphyrinatocobalt (TMOPP-Co) (**I**) with anion excluder, NaTPB and DBP as plasticizer with a composition **I**: PVC: DBP

(12:60:100) proved to be best in terms of working concentration range $5.0 \times 10^{-5} - 1.0 \times 10^{-1}$ M with a near – Nernstian slope of 32.0 ± 1.0 mV/decade of activity over the pH range 5.4- 10.5. The electrode exhibits good reproducibility with a useful lifetime of 4 months and can be used in non-aqueous medium with no significant change in the value of slope or working concentration range for the estimation of MoO_4^{2-}.

Acknowledgements

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Sample Availability: Available from the authors.