A Highly Selective Potentiometric Sensor of Molybdate Based on a μ -Oxo-bridged Manganeseporphyrin Dimer

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A novel high-selective potentiometric sensor for molybdate was prepared with a PVC membrane combining μ -oxo-bis[5,10,15,20-tetra(*p*-methylphenyl)porphinatomanganese(III)] [[Mn(*p*-Me)TPP]₂O] as an electroactive material and 2-nitrophenyl octyl ether (*o*-NPOE) as a plasticizer in the percentage ratio of 3:65:32, [Mn(*p*-Me)TPP]₂O:*o*-NPOE:PVC (w:w). The sensor exhibited a linear response with a Nernstian slope of 30.5 mV per decade within a concentration range of 2.1×10^{-6} to 1.0×10^{-1} M MoO₄²⁻, with a working pH range from 5.0 to 12.5, and a fast response time of less than 15 s. The electrode showed improved selectivity toward molybdate with respect to common coexisting anions compared to monometalloporphyrin counterparts. Several electroactive materials and solvent mediators were compared and the experimental conditions were optimized. The sensor is preliminary applied to the assay of MoO₄²⁻ in corrosion inhibitor samples with satisfactory results.

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Introduction

Owing to its high melting point, high strength at elevated temperatures, good corrosion resistance and high thermal conductivity, molybdenum is widely used in a variety of industrial processes, *e.g.* as an important constituent of metal alloys; pigments for printing inks, paints, and ceramics; solid lubricants; missile and space vehicle parts; reactor vessels; catalyst; cermets; and special batteries. Molybdenum is also an essential trace element for both plants and animals, including humans, and is the only metal of the second transition series, which is of major biological significance. In animals, it is an indispensable cofactor for several enzymes, such as xanthine oxidase and sulfite oxidase.^{1,2} In plants, although present in low levels, molybdenum is an essential micronutrient, and is involved in biochemical processes related to the fixing of the N₂ of atmosphere by bacteria.² Nevertheless, it is harmful to both plants and animals at high concentrations. It appears to be toxic when its concentration in plants is larger than 5 μ g/g.³ Hence, the need for molybdenum ion determination in clinical, biological, environmental and different industrial samples has led to a number of methods for measuring this analyte. Several analytical techniques, such as inductively coupled plasma-atomic emission spectrometry (ICP-AES),⁴ inductively coupled plasma-mass spectrometry (ICP-MS),⁵ atomic absorption spectrometry,^{6,7} spectrophotometry,^{8,9} voltammetry¹⁰ and flow-injection analysis (FIA),¹¹ have been used for molybdenum assay in various samples. Most of these techniques, such as ICP-MS and FIA, necessitate the use of sophisticated and relatively costly apparatus and require complicated pretreatment procedures, not suitable for on-line or field monitoring.

Due to the advantages of being simple, rapid, reliable, low-cost and non-destructive characteristics, ion-selective electrodes (ISEs) have found wide spread use for the direct determination of ionic species in complex samples for chemical, clinical, and environmental analyses as well as for process monitoring.¹²⁻¹⁴ In solutions, molybdate generally occurs in the form of MoO₄²⁻ at about pH 5 and above. There have been, however, not many ISEs being reported for the determination of MoO₄²⁻. ISEs for MoO₄²⁻ based on ionophores including zirconium-containing compounds^{15,16} and insoluble lead salts¹⁷ have been reported. However, these electrodes have not turned out to be good systems, because they generally exhibit a narrow working concentration range or moderate selectivity with interference from various anions.

Gupta *et al.* reported two kinds of cobaltporphyrin complexes based ISEs for a molybdate assay with improved response characteristics compared to the aforementioned ISEs.^{18,19} The μ -oxo-bridged metalloporphyrin dimers have been reported to show improved catalytic capability for functionalization of hydrocarbons as well as electro-activity as carriers for ISEs.²⁰⁻²³ Gao *et al.* reported an μ -oxo-bis-tetraphenyl-porphinatomanganese(III) based electrode showing potentiometric response to SCN⁻ with an anti-Hofmeister selectivity pattern as SCN⁻ > ClO₄⁻ > I⁻ > NO₂⁻ > NO₃⁻ > Br⁻ > Cl⁻.²⁴ Inspired by the successful work of Gupta and Gao, in the context of our long-term interests in searching for novel porphyrin derivatives as carriers for sensors,^{22,23,25-28} we have tried to investigate the μ -oxo-bridged metalloporphyrin dimers as carriers to see whether the response characteristics of the electrode could further be improved. This paper describes the use of several metalloporphyrin complexes as electroactive materials for the preparation of molybdate-sensitive electrodes. An electrode based on μ -oxo-bis[5,10,15,20-tetra(*p*-methylphenyl)porphinatomanganese(III)] [[Mn(*p*-Me)TPP]₂O] shows a potentiometric response toward molybdate with a linear concentration range and response time comparable to

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Fig. 1 Structures of monometalporphyrins and metalloporphyrin dimer.

monometalporphyrin counterparts and better selectivity over other anions. The [Mn(*p*-Me)TPP]₂O based electrode shows a selectivity sequence for anions as follows: MoO₄²⁻ > SCN⁻ > ClO₄⁻ > NO₃⁻ > Cl⁻ > I⁻ > Br⁻ > NO₂⁻, which is obviously different from that of μ -oxo-bis-tetraphenyl-porphinato-manganese(III).²⁴ The electrode has been applied to the determination of molybdate in corrosion inhibitor samples with satisfactory results.

Experimental

Reagents

Doubly distilled water was used throughout all experiments. High molecular weight poly(vinyl chloride) (PVC), dibutyl phthalate (DBP), dioctyl sebacate (DOS) were purchased from Shanghai Chemical Reagent Corporation (Shanghai, China) and used as received. *o*-Nitrophenyl octyl ether (*o*-NPOE) was synthesized according to a reported method.²⁹ Before being used, dichloromethane and benzaldehyde were subjected to simple distillation from K₂CO₃. Pyrrole was distilled at atmospheric pressure from CaH₂. Tetrahydrofuran (THF) was freshly distilled from sodium chips under argon with benzophenone/ketyl as an indicator. Except when specified, other chemicals were of analytical reagent grade, and used without further purification. Tetraphenylporphine (TPPH₂) was synthesized by Adler's method,³⁰ chloro[5,10,15,20-tetra(*p*-methylphenyl)porphinato]manganese(III) [MnT(*p*-Me)PPCl], chloro[5,10,15,20-tetra(*p*-methylphenyl)porphinato]iron(III) [FeT(*p*-Me)PPCl], and chloro[5,10,15,20-tetra(*p*-methylphenyl)porphinato]copper [CuT(*p*-Me)PP] were prepared according to documented procedures³¹ and checked by elementary analysis, UV-Vis spectroscopy and IR spectra. The synthesis of [Mn(*p*-Me)TPP]₂O was reported elsewhere.²¹ The structures of metalloporphyrins are shown in Fig. 1.

Apparatus

The PVC membrane electrodes were prepared according to the procedure of Thomas *et al.*³² The optimized membrane composition consists of 3% active materials, 65% solvent mediator and 32% PVC. The electrodes were conditioned in an aqueous solution of 0.1 M Na₂MoO₄ for 12 h. Potentiometric and pH measurements were carried out on a Model PHS-3E digital ion analyzer (Jiangshu Instruments). The cell assemblies were of the following type:

Hg-HgCl₂, KCl (satd.) | sample solution | membrane | 0.01 M KCl | Ag-AgCl.

Table 1 Response characteristics of electrodes based on different active materials

Electrode No.	Active material	Working concentration range/M	Slope/mV decade ⁻¹
1	FeT(<i>p</i> -Me)PPCl	1 × 10 ⁻³ – 1.0 × 10 ⁻¹	24.0
2	MnT(<i>p</i> -Me)PPCl	4.7 × 10 ⁻⁵ – 1.0 × 10 ⁻¹	27.0
3	CuT(<i>p</i> -Me)PP	Sluggish response	—
4	[Mn(<i>p</i> -Me)TPP] ₂ O	2.1 × 10 ⁻⁶ – 1.0 × 10 ⁻¹	30.5

A standard solution of MoO₄²⁻ was obtained by serial dilution of 0.1 M Na₂MoO₄ solution and buffered with 0.01 M of NaOAc-HOAc (pH 6.0). The performance of each electrode was investigated by measuring its potential in a series of standard solutions of MoO₄²⁻, and potential readings were recorded after they became stable (within ±1.0 mV). ¹H NMR spectra were recorded with a Varian AM 400 MHz spectrometer. UV-visible absorption spectra were recorded on a Varian Cary 50 Bio UV-VIS spectrophotometer. IR spectra were recorded on a Perkin-Elmer Model 783 IR spectrophotometer. A Perkin-Elmer 2400 elementary analyzer was used for elementary analysis.

Results and Discussion

Selection of active materials for electrodes

Several electrodes were prepared using different porphyrins, including MnT(*p*-Me)PPCl, FeT(*p*-Me)PPCl, CuT(*p*-Me)PP and [Mn(*p*-Me)TPP]₂O, with *o*-NPOE as a solvent mediator to study the effect of active materials. The response characteristics of these electrodes are given in Table 1.

From Table 1 one can see that the electrode based on MnT(*p*-Me)PPCl shows better response characteristics than that of FeT(*p*-Me)PPCl in terms of the working concentration range and the slope, while the electrode based on CuT(*p*-Me)PP shows sluggish non-regular responses. The role of the central metal in the electrode response mechanism is obvious. The order Mn-Fe-Cu is just opposite to the Irving-Williams order. In fact, the ligand field stabilization energy for Mn(III) is less than that for Fe(III) or Cu(II). One would expect that the Mn complex is least stable compared to that of Fe and Cu complexes. It is assumed that the potentiometric response of metalloporphyrin derivatives toward MoO₄²⁻ is associated with the coordination with the analyte anions along the axial positions of the central metal, and that Mn matches MoO₄²⁻ best. According to Simon *et al.*,³³ the stability of the complex between the neutral carrier and the analyte ion should be an intermediate one, not necessarily the highest one. An electrode based on monometalporphyrin [MnT(*p*-Me)PPCl] shows slightly worse response characteristics than those of the μ -oxo-bridged metalloporphyrin dimer [[Mn(*p*-Me)TPP]₂O] in terms of the working concentration range and the slope. Monometalporphyrin has only one central metal, while the metalloporphyrin dimer has 2 central metals in a molecule, which might coordinate with two MoO₄²⁻ (Fig. 1). Moreover, the lipophilicity of monometalporphyrin is worse than that of μ -oxo-bridged metalloporphyrin dimer.

To study the influence of membrane compositions, several electrodes with different compositions were prepared using [Mn(*p*-Me)TPP]₂O as the active component. Their response characteristics are listed in Table 2.

As can be seen, the intermediate content of [Mn(*p*-

Table 2 Response characteristics of electrodes utilizing various active materials

Electrode No.	Content of active material, %	Working concentration range/M	Slope/mV decade ⁻¹
5	1	$4.8 \times 10^{-4} - 1.0 \times 10^{-1}$	25.5
4	3	$2.1 \times 10^{-6} - 1.0 \times 10^{-1}$	30.5
6	5	$9.1 \times 10^{-5} - 1.0 \times 10^{-2}$	27.0

Table 3 Response characteristics of electrodes utilizing various solvent mediators

Electrode No.	Plasticizer	Working concentration range/M	Slope/mV decade ⁻¹
4	<i>o</i> -NPOE	$2.1 \times 10^{-6} - 1.0 \times 10^{-1}$	30.5
7	DBP	$7.1 \times 10^{-5} - 1.0 \times 10^{-1}$	24.0
8	DOS	$1.0 \times 10^{-4} - 1.0 \times 10^{-1}$	28.0

[Mn(*p*-Me)TPP]₂O:solvent mediator:PVC = 3:65:32.

Me)TPP]₂O (3%) affords the best response for MoO₄²⁻. With its content less than 1%, the response becomes worse. The response also becomes worse when the content is larger than 5%, which results in the presence of some unsolved [Mn(*p*-Me)TPP]₂O. Our experimental results also show that the intermediate content of solvent mediator affords the best response for MoO₄²⁻. The low content of the solvent mediator causes a long response time of the electrode, while overloading of the solvent mediator (larger than 70%) might lead to a worse stability of the membrane. The experimental results show that the membrane composition consisting of 3% [Mn(*p*-Me)TPP]₂O, 65% *o*-NPOE and 32% PVC (w/w) could provide the best response for MoO₄²⁻.

Effect of solvent mediators

Electrodes with different solvent mediators, *i.e.* DBP, DOS and *o*-NPOE, were prepared using [Mn(*p*-Me)TPP]₂O as an active membrane component. The response characteristics of these electrodes are given in Table 3.

From Table 3 one can see that the electrode with *o*-NPOE as the solvent mediator shows an obvious better response performance for MoO₄²⁻ compared to other solvent mediators with a wide working concentration range and a large response slope. This might be caused by the better dielectric characteristics of *o*-NPOE compared to other solvents, which is favorable for the potentiometric response performance. Moreover, during the course of the experiment, we found that *o*-NPOE is favored with the greater solubility of [Mn(*p*-Me)TPP]₂O in it compared to other solvents.

Response characteristics of the electrode

Figure 2 shows the response curve of an electrode with an optimum membrane composition [[Mn(*p*-Me)TPP]₂O:*o*-NPOE:PVC = 3:65:32]. The linear response range covers from 2.1×10^{-6} to 0.1 M MoO₄²⁻ in a NaOAc-HOAc (pH 6.0) buffered solution and a Nernstian slope of 30.5 mV per decade of activity. The response time (*t*_{90%}) for MoO₄²⁻ concentration $\geq 1.0 \times 10^{-4}$ M is as fast as 10 s; with a concentration lower than 1.0×10^{-4} M, it is less than 15 s. It seems that the response involves a rapid reversible anion exchange process at the solution/membrane interface. The standard deviations of the electrode potential and slope over a period of 12 h for 20

Fig. 2 Response characteristics towards MoO₄²⁻ of a [Mn(*p*-Me)TPP]₂O based electrode.

Fig. 3 Effect of the pH on the electrode's response at: (Δ) 1.0×10^{-3} M MoO₄²⁻; (○) 1.0×10^{-2} M MoO₄²⁻.

measurements in 1.0×10^{-3} M MoO₄²⁻ are found, respectively, to be 2.3 mV and 0.7 mV. The electrode was dipped alternatively into stirred solutions of 1.0×10^{-3} M and 1.0×10^{-4} M MoO₄²⁻ over 4 h for repeated 10 measurements, which show standard deviations of potential readings in these two solutions as 1.3 mV and 2.2 mV, respectively. There is no noticeable hysteresis of the potentiometric response, which also indicates the reversibility of the interfacial processes. The electrodes are stored in a 0.1 M MoO₄²⁻ solution when not in use. The electrodes work well, and no detectable change in the value of slope, working concentration range or response time is found after they have been used for several weeks, which implies that the μ -oxo-bridged metalloporphyrin dimer is stable in a membrane contacting with water.

Effect of the pH and solvent

The effect of the pH of a test solution on the [Mn(*p*-Me)TPP]₂O based electrode potential response was studied at two MoO₄²⁻ concentrations (1.0×10^{-2} M, 1.0×10^{-3} M), where the pH was adjusted from 4.0 to 13.5 with HCl or NaOH solutions. The results shown in Fig. 3 indicate that, in the region of higher pH value (> 12.5, strong basic condition), the potential value of the electrode decreased with increasing pH value. This phenomenon might be caused by the coordination of water molecules as axial ligands to the central metal of porphyrin complexes. The loss of a proton from the water molecule under a strong basic condition can yield a hydroxide-coordinated central metal showing a pH response. A similar result was reported by Meyerhoff *et al.*³⁴ In the region of lower pH value (pH < 4), the increase in the potential value of an electrode with

Fig. 4 Response characteristics of the electrode to MoO_4^{2-} in the presence of different concentrations of Cl^- ions: (O) No Cl^- ; (◇) 5.0×10^{-3} M Cl^- ; (□) 1.0×10^{-2} M Cl^- ; (Δ) 1.0×10^{-1} M Cl^- .

Fig. 5 Response characteristics of the electrode to MoO_4^{2-} in the presence of different concentrations of NO_3^- ions: (O) No NO_3^- ; (◇) 5.0×10^{-3} M NO_3^- ; (□) 1.0×10^{-2} M NO_3^- ; (Δ) 1.0×10^{-1} M NO_3^- .

a decreasing pH value is attributed to decreasing hydroxide concentration. Moreover, under an acidic condition, a change of the form of MoO_4^{2-} to other non-anion forms might decrease the actual concentration of the MoO_4^{2-} anion in the sample solution, which also results in an increase of the potential value. From Fig. 3 one can see that, in the range of pH values from 5.0 to 12.5, the change in the pH does not have an obvious effect on the determination of MoO_4^{2-} with the proposed electrode. It is advantageous to use the proposed electrode for a MoO_4^{2-} assay, since no precise pH control is required for routine analysis. In subsequent experiments, a pH 6.0 NaOAc-HOAc buffer solution was selected for further studies.

To study the applicability of the proposed electrode in partially non-aqueous media, the performance of the sensors was studied in methanol-water and ethanol-water mixtures with different contents of alcohol following the literature method. Similar to Gupta and coworkers reported results,^{18,19} the electrode does not show any appreciable change in working concentration range and slope or drift in potentials with the alcohol content in mixtures of less than 25% (v/v), and shows an erratic potentiometric response behavior with a non-aqueous content larger than 25% (v/v).

Potentiometric selectivity

The selectivity behavior is one of the most important characteristics of ion-selective electrodes. The selectivity coefficients, $K_{\text{MoO}_4^{2-},j}^{\text{pot}}$, for a number of anions were determined by

Table 4 Selectivity coefficients, $K_{\text{MoO}_4^{2-},j}^{\text{pot}}$, for various interfering anions using a modified form of the fixed interference method

Interfering ion	$K_{\text{MoO}_4^{2-},j}^{\text{pot}}$ for electrode proposed in this work	$K_{\text{MoO}_4^{2-},j}^{\text{pot}}$ for TPP-Co based electrode ¹⁸	$K_{\text{MoO}_4^{2-},j}^{\text{pot}}$ for TPP-Co based electrode ¹⁹
Cl^-	5.8×10^{-3}	1.9×10^{-1}	1.8×10^{-1}
Br^-	2.1×10^{-3}	7.8×10^{-2}	5.6×10^{-2}
I^-	2.9×10^{-3}	6.5×10^{-2}	3.9×10^{-2}
NO_2^-	1.0×10^{-3}	1.2×10^{-2}	1.7×10^{-2}
NO_3^-	6.9×10^{-3}	1.0×10^{-2}	1.0×10^{-2}
ClO_4^-	9.3×10^{-3}	1.2×10^{-2}	1.9×10^{-2}
IO_4^-	1.6×10^{-2}	2.0×10^{-2}	2.8×10^{-2}
SCN^-	2.9×10^{-1}	2.1×10^{-1}	2.1×10^{-1}
SO_4^{2-}	1.0×10^{-3}	1.0×10^{-2}	1.5×10^{-2}
PO_4^{3-}	1.0×10^{-3}	1.0×10^{-2}	1.3×10^{-2}
VO_3^-	2.5×10^{-3}	6.8×10^{-2}	—
$\text{C}_2\text{O}_4^{2-}$	1.0×10^{-3}	1.0×10^{-2}	1.2×10^{-2}

the modified form of the fixed interference method according to references³⁵ at 1.0×10^{-2} M concentration of the interfering ions. The resulting values of the selectivity coefficient are summarized in Table 4.

The results presented in Table 4 reveal that the electrode based on $[\text{Mn}(p\text{-Me})\text{TPP}]_2\text{O}$ was fairly selective to MoO_4^{2-} over other anions. From Table 4 one can also see that the selectivity of the proposed electrode toward MoO_4^{2-} with respect to, for instance, Cl^- , NO_3^- , and SO_4^{2-} is better than that of the electrode reported in the literature.^{18,19} Excesses of Cl^- and NO_3^- are usually present in MoO_4^{2-} analyte solution samples. To evaluate the actual level of tolerance, some mixed-run studies were carried out at different background concentrations of Cl^- (Fig. 4) and NO_3^- (Fig. 5). From Fig. 4 one can see that Cl^- ions present in concentrations of less than 5.0×10^{-3} M can be tolerated over the whole working concentration range of the proposed electrode, which is obviously improved compared to that of monometalloporphyrin reported in the literature.^{18,19} Similarly, NO_3^- can also be tolerated over the whole working concentration range at concentrations of less than 5.0×10^{-3} M. While the Cl^- or NO_3^- concentration is larger than 5.0×10^{-3} M, the working concentration range tends to narrow. Mixed-run studies at different background concentrations of SCN^- were also carried out; similar to the electrode based on monometalloporphyrin, it causes obvious interference for MoO_4^{2-} when its concentration is larger than 1.0×10^{-4} M.

Preliminary analytical application

To assess the applicability of the proposed MoO_4^{2-} -sensitive electrode to real samples, an attempt was made to determine the content of MoO_4^{2-} in corrosion inhibitor samples. In order to reduce the pH influence in the detection, 9 ml of a buffer solution was added to 1 ml of the samples to keep the pH value at 6.0. The samples were then analyzed using the proposed sensor. Results are given in Table 5.

It can be seen that the content of MoO_4^{2-} , as determined by the electrode, was in good agreement with the actual content in corrosion inhibitor samples with a relative error less than $\pm 3\%$. The $[\text{Mn}(p\text{-Me})\text{TPP}]_2\text{O}$ based electrode seems to be useful for the determination of MoO_4^{2-} in actual samples. An obvious advantage of the method is the rather simple sample preparation procedure for potentiometry with an electrode that requires just a ten-fold dilution of the sample with an appropriate buffer solution.

Table 5 Determination of MoO_4^{2-} in corrosion inhibitor samples using the proposed sensor

Sample	Content of the sample/M	Found by the electrode/M	Relative error, %
1	0.97×10^{-3}	0.95×10^{-3}	-2.06
2	1.05×10^{-4}	1.08×10^{-4}	2.86

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