

PVC-Based Cerium Phosphate Membrane Exhibiting Selectivity for Molybdate Anions

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ABSTRACT: A PVC-based membrane containing cerium phosphate was developed. Unlike the cerium phosphate itself that acts as a cation exchanger, the membrane exhibited anion-exchange properties. Therefore, the utility of this compound as a sensory element for detection of molybdate ions was pursued. The response of molybdate selective electrode based on this membrane was perfectly linear in the concentration range 1.98×10^{-5} to 10^{-1} M. Characteristics of this electrode such as electric resistance, stability and membrane preconditioning process, and regeneration of its sensitivity are reported.

KEY WORDS: Cerium phosphate, Molybdate anions, Ion-selective electrode, Membrane electrode, PVC-based membrane, Ion-exchange membrane

INTRODUCTION

Inorganic ion-exchangers besides their being used in separatory purposes, have been utilized as membrane electrodes [1-3]. Among inorganic exchangers, cerium phosphate mostly has been used as a cation exchanger [4-7]. However, it exhibits anion-exchange properties, too [8]. Previous synthesis of cerium phosphate in the form of fibers or fine powders was unsuitable for cation exchange purposes [4-7]. But, in a different synthesis method the anion exchanging capacity of cerium phosphate was improved [8]. The

cerium phosphate exchanger synthesized by addition of salt to the reaction mixture of cerium ammonium nitrate and orthophosphoric acid have produced materials of acceptable exchange capacities. Its subsequent treatment by hydrochloric acid lowers the sodium ion concentration, reflecting an anion exchange selectivity effect [8].

There have been several attempts to construct electrodes selective to molybdate ions [3, 9-11]. A polystyrene-based zirconium oxide membrane [3] as

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well as a zirconium molybdate membrane [9] showing selectivity to molybdate have been reported. In the present work we have developed a PVC-based membrane containing cerium phosphate and examined the utility of this product as a sensory element for detection of molybdate ions. The characteristics of the constructed molybdate electrode are reported.

EXPERIMENTAL

Reagents

All reagents used were of analytical grade and purchased from E. Merck, Darmstadt., Germany. "Araldite D", an epoxy resin, was from Ciba Geigy, Switzerland. The cerium phosphate exchanger was prepared and characterized by the method reported by Dyer and Jasem [8]. A pH-potentiometer (Consort, model P614) having a resolution of ± 0.1 mV was used for potential measurements.

Preparation of membrane

Homogeneous membranes containing cerium phosphate ion exchanger was not mechanically stable but, heterogeneous membranes obtained by binding the cerium phosphate with Araldite D or polyvinyl chloride (PVC) were found to be quite satisfactory.

The powdered cerium phosphate ion exchanger was further ground in a mortar then mixed with a solution of PVC in tetrahydrofuran (THF). To reduce the hardness of membrane a given amount of dioctylphthalate (DOP) was added as plastisizer to the mixture. The mixture was then cast in a coined shaped die and left to dry slowly at room temperature. When the membrane was dried and relatively hardened a disc, 14 mm in diameter, was cut out. To find out the optimum condition, the ratios of cerium phosphate ion exchanger, PVC and DOP were changed and selectivity of product membranes to molybdate ions and also stability of obtained potentials were examined.

A large number of membranes (thickness between 0.25 and 0.30 mm) with different compositions were prepared and examined. Membranes with the composition of 91 parts of ion exchanger, 3 parts of PVC and 6 parts of DOP showed the best electrochemical performance together with a good conductance and stability. The membranes with such a composition were chosen for further studies.

Membrane preconditioning

To achieve maximum ion exchange properties, the membranes thus obtained were preconditioned in 0.1 M sodium molybdate solution for 7-8 days. During this period the solution was daily renewed. This process is necessary to bring the electrode response to an optimum sensitivity. After preconditioning, the membrane was washed with deionized water to remove the excess sodium molybdate ions from the surface of membrane. The optimum period for this process was determined based on preliminary experiments (data not shown). It was observed that membranes equilibrated at shorter times did not give stable potentials.

Potential measurements

The electrode assembly used in this work is shown in Fig. 1. It was constructed from the ion exchange membrane cemented at the end of a glass tube. The internal solution contains 0.1 M sodium molybdate and a silver wire coated with silver chloride was used as an internal reference electrode. The molybdate selective electrode thus obtained together with a saturated calomel electrode, as external reference, was connected to a pH-potentiometer. All measurements were carried out at $25 \pm 0.1^\circ\text{C}$. The response potentials were read when a steady state was reached.

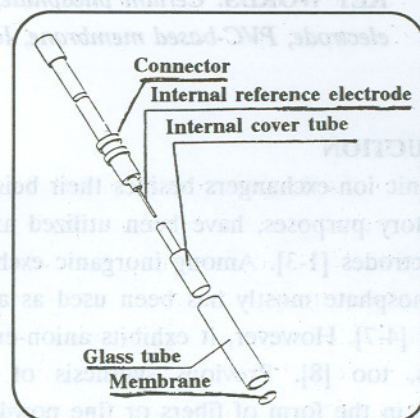


Fig. 1: Components of molybdate membrane electrode

RESULTS AND DISCUSSION

Cerium phosphate is well known to possess cation exchange properties [8]. However, a small uptake of anions such as chloride and fluoride ions has also been reported [8]. The membrane obtained by the procedure mentioned above, showed significant anion

Table 1: Dynamic range of electrode response for five selected membranes

No	Membrane composition weight %			Dynamic range of concentration (M)	Slope (mV/ activity decade)
	PVC	ion exchanger	DOP		
1	40 ^a	60	0	$1.78 \times 10^{-3} - 0.1$	28.2
2	19	45	36	$1 \times 10^{-3} - 0.1$	28.3
3	23	61.5	15.5	$1 \times 10^{-4} - 0.1$	30.7
4	23	72	5	$3.16 \times 10^{-5} - 0.1$	30.8
5	21	76	4	$3.16 \times 10^{-5} - 0.1$	30.8

a: PVC, has been replaced by epoxy resin

exchange characteristics. Therefore, the constructed electrodes were used for potentiometric measurement of molybdate anions. About 25 membranes (thickness between 0.25 and 0.30 mm) with different compositions were prepared and examined. Table 1 shows the electrode linear responses (mV) for five selected membranes with different compositions. From this data it is revealed that the membranes with the above mentioned weight ratio, showed the widest dynamic range. The potentials observed with such a cerium phosphate membrane are shown in Fig. 2. This composition was chosen as the optimized membrane and used for further study.

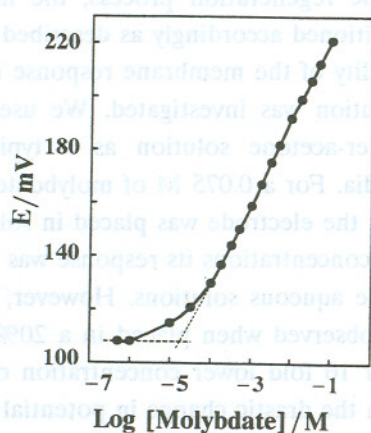


Fig. 2: Potential changes versus logarithm of molybdate ion concentration the points are the mean values of five experiments. (For details see text)

In order to determine selectivity of the membrane electrode for molybdate ions over other anions, the potential changes in the presence of various interfering ions were measured. Selectivity coefficient (K_{ij}) is

defined as ability of an ion-selective electrode to distinguish between different ions in the same solution [12]. For a non-interfering pair, K_{ij} is zero. When K_{ij} is unity, the electrode responds equally to either of the species, i.e; the interferent or the desired ion. We used the fixed interference method [12] to check the electrode selectivity. The values of selectivity coefficients for a number of interfering ions were determined and compared with the selectivity coefficient reported by others [3,9]. From the data depicted in Table 2, it is apparent that the electrode selectivity towards molybdate ions over several other anions is satisfactory. The univalent interferents that show very low K_{AB}^{pot} values, would not interfere even when present at the same concentration as that of molybdate ions. There were some interference by multivalent anions since their selectivity

Table 2: Values of selectivity coefficients for a number of interfering ions comparing with those reported by others

Interfering ion	Selectivity coefficient K_{AB}^{pot}		
1×10^{-3}	Ref. 3	Ref. 9	Present work
VO_3^-	—	1.2	0.099
Cl^-	14	0.9	0.17
NO_3^-	12.5	0.8	0.17
CH_3COO^-	—	—	0.14
ClO_4^-	15.5	—	0.216
SCN^-	15.5	—	0.22
WO_4^{2-}	0.22	0.022	0.53
$S_2O_3^{2-}$	—	0.018	0.59
CrO_4^{2-}	—	0.014	0.75
$C_2O_4^{2-}$	0.13	—	0.595

coefficient are ranged from 0.5 to 0.8.

Potential changes observed with the electrode when interposed between sodium molybdate solutions (10^{-7} - 10^{-1} M concentration) are shown in Fig. 2. Potential changes depicted in Fig. 2 revealed that the potential versus logarithm of molybdate anion concentration, is perfectly linear in the concentration range 3.16×10^{-5} to 10^{-1} M ($R = 0.9985$). The slope of plot (29 with a standard deviation of ± 0.56) is very close to that of *Nernst* equation. The membrane electrode under investigation can thus be used for selective determination of molybdate ions within the linear range mentioned above.

According to the IUPAC recommendations for ion selective electrodes [12] in practice, the detection limit, may be taken as the concentration corresponding to the point of intersection of the two extrapolated lines as shown in Fig. 2. Thus, the lowest concentration of molybdate ion to which this electrode is applicable, is about 1.98×10^{-5} M. This ability makes the electrode particularly useful in the continuous analyses.

To determine the electrode response time, the IUPAC recommendations were followed [12]. The experimental response time was 30 s. when the solution in contact with the electrode was in the range from 0.001 M to 0.01 M. The electrode shows a response time of 100 s. when the molybdate solution was changed from 0.01 M to 0.1 M.

The pH dependence of the membrane electrode was also investigated. Fig. 3 shows the potential vs. pH plots of 0.1 and 0.01 and 0.001 M concentration of molybdate ions at room temperature. It is clear that

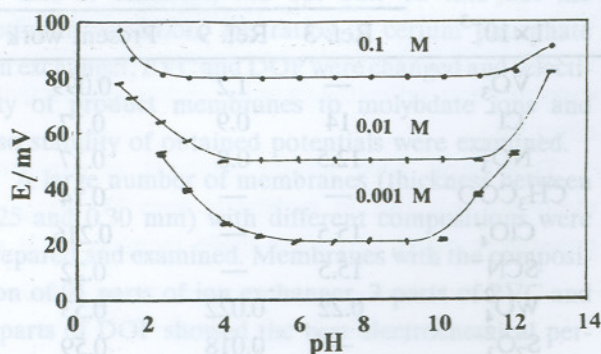


Fig. 3: pH dependence of membrane electrode response at three different concentrations of sodium molybdate solution

in the pH range of 6 to 10, the electrode response is quite independent of the pH. In the pH range lower than 6 a deviation in potential was observed (data not shown) probably due to formation of para-, tri- and/or tetramolybdate ions [13].

For determination of membrane electric resistance, the membrane was installed between two reference electrodes in a 0.1 M sodium molybdate solution. The resistance was measured when the reference electrodes were connected to a digital multimeter. The resistance difference of the solution with and without membrane was designated as the membrane resistance. The membrane with the thickness of 0.25 mm and the mentioned composition showed an electric resistance of 29.5 K Ohms.

Stability of the membrane was also considered. The results (data not shown) indicated that the response of membrane after preconditioning was quite stable. The constructed electrode showed a reproducible response for at least six months. In the case when the membrane lose its sensitivity, we were able to regenerate their sensitivity. For this purpose, first the internal reference solution of the electrode was exchanged with deionized water and for a period of 72 h. the deionized water was renewed daily. Following the regeneration process, the membrane was preconditioned accordingly as described earlier.

The stability of the membrane response in a non-aqueous solution was investigated. We used a mixture of water-acetone solution as a typical non-aqueous media. For a 0.075 M of molybdate concentration when the electrode was placed in solutions of low acetone concentrations its response was the same as that of the aqueous solutions. However, a drastic change was observed when placed in a 20% acetone solution. For 10 fold lower concentration of molybdate solution the drastic change in potential began at about 17% acetone solution. It seems that strong and also effective interaction between membrane and ions in solution, would not be obtained in this nonaqueous solutions.

In conclusion we have been able to introduce a heterogeneous PVC-based membrane that exhibits selectivity towards molybdate anions. Due to its longterm stability in a wide range of pHs and in low concentration of aqueous organic solutions, it seems

to be applicable as a molybdate ion-selective electrode. Comparing to the previously reported electrodes [3,7] this electrode showed a Nernstian response to molybdate anions in a wider dynamic range, and exhibited a lower selectivity coefficient over other univalent interferents ions.

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REFERENCES

- [1] Malik, W. U., Srivastava, S. K. and Kumar, S., *J. Electroanal. Chem.*, **72**, 111(1976).
- [2] Srivastava, S. K., Singh, R. P. and Agarwal, S., *J. Chem. Techn. Biotech.*, **27**, 680(1977).
- [3] Srivastava, S. K., Sharma, A. K. and Jain, C. K., *Talanta*, **30**(4), 285(1983).
- [4] Cleardfield, A., "Inorganic Ion Exchange Materials", CRC Press, Florida (1981).
- [5] Herman, R. G. and Clearfield, A., *J. Inorg. Nucl. Chem.*, **37**, 1697(1975).
- [6] Alberti, G., Massucci, M. A. and Torracca, E., *J. Chromatography*, **30**, 583(1967).
- [7] Van So, Le. and Szirtes, L., *Radiochem. Radioanal. Letters*, **46**, 95(1981).
- [8] Dyer, A. and Jasem, A. K. J., "Ion Exchange Processes, Advances and Applications", The Royal Society of Chemistry, England (1993).
- [9] Malik, W. U., Srivastava, S. K. and Bansal, Amla, *Anal. Chem.*, **54**, 1399(1982).
- [10] Kraus, K. A. and Philips, H. O., *J. Am. Chem. Soc.*, **78**, 249(1956).
- [11] Singh, N. J. and Tandon, S. N., *Talanta*, **24**, 459(1977).
- [12] Guilbault, G. G., Recommendations for Publishing Manuscripts on Ion-Selective Electrodes, "Ion-Selective Electrode Rev.", Vol. 1, pp. 139-143, Pergamon Press Ltd., Printed in Great Britain (1979).
- [13] Kirk-Othmer, "Encyclopedia of Chemical Technology", Vol. 15, Third Edition, John Wiley and Sons (1978).

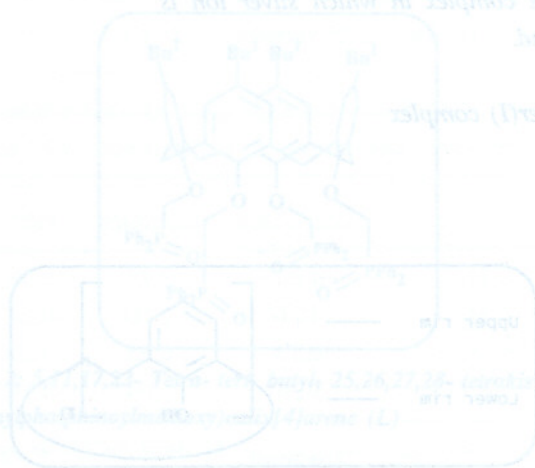


Fig. 1: Calix[4]arene ($n=4$) and its complex with cerium ion (Ce^{3+})

EXPERIMENTAL

Reagents and physical measurements
Calix[4]arene (n=4) and its complex with cerium ion (Ce^{3+}) were prepared by the method described in the literature [12]. The complex was prepared by the reaction of calix[4]arene with cerium ion in the presence of phosphate groups. The complex was characterized by its molecular weight (MW) and its ^{13}C -NMR spectrum. The ^{13}C -NMR spectrum was recorded by Bruker WP-300 SY instrument. The 1H -NMR data (Fig. 3)