International Journal of Chemistry and Applications.
ISSN 0974-3111 Volume 3, Number 1 (2011), pp. 77-84

http://www.irphouse.com

Fabrication of a Novel Polymeric Membrane for Determination of Monohydrogen Phosphate Ion Based on Phthalocyanine Complex and Applications

Gyanendra Singh, Shiv Prakash Singh and Sanjay Singh

Department of Chemistry of M.M.H. College, Ghaziabad, U.P., India
E-mail: shiv_singh05@yahoo.co.in

Abstract

An extremely selective poly (vinyl chloride) (PVC) membrane electrode based on Zn-Phthalocyanine Schiff base as carrier for monohydrogen phosphate -selective electrode is reported in our study. The membrane sensor exhibits Nernstian response with 29.6 ± 1.0.mV/ decade of activity concentration range of $5.0 \times 10^{-8} – 1.0 \times 10^{-}$ mol/L of HPO42-, performs satisfactorily over wide pH range of 3.5-9.5 with a fast response time of 10 s. The detection limit of the proposed sensor is 1.0×10^{-7} mol/L. It was used as an indicator electrode in the potentiometric titration of monohydrogen phosphate with Ba2+ for the direct determination of HPO42- in granular and liquid fertilizer samples as well waste water samples.

Keywords: Zn-Phthalocyanine Schiff base complex, monohydrogen phosphate-selective electrode, potentiometric titration.

Introduction

Potentiometric sensors are attractive devices for continuous water quality monitoring, either as in situ probes or as chemical analysis systems. The development of a good sensitive sensor for monohydrogen phosphate ion has long been a subject of concern to analytical chemists and lot of efforts has been made in this direction in the last four decades.

Phosphate is a concern of research these days. Recent studies show that leaching of PO_4^{2-} as small as 10 μg/L from agricultural land can contribute to eutrophication [1]. Recently, a number of hydrogen phosphate membrane sensors based on different ion carriers such as dialkyl and diaryltin derivatives, Uranyl salophen, vanadyl salen, vanadyl salophen, bis-thiourea and modified calixarene have been reported [2-10].

Oftenly a liquid membrane allows only the selective permeation of certain ionic species through itself, due to of the incorporation of special ingredients, called “ionophore” or in other words “ion carrier”. A consequence of this selective permeation is a potential difference formation at the two membrane surfaces, measured by the two reference electrodes at both sides of the membrane. Despite the fact that other ingredients such as ionic additives, membrane solvent, and polymeric support can affect the membrane behavior [13].

In this study a new ion selective sensor selective to HPO42 useing Zn-Phthalocyanine have been reported.

Experimental

Reagents and Materials

All reagents were of the highest grade commercially available and used as received. Double distilled water was used for the preparation of solution of metal salts of different combination by diluting stock standard solutions (0.1 M). High molecular weight poly(vinyl chloride), tetrahydrofuran (THF) and dibutyl phthalate (DBP) were purchased from Aldrich. The sodium or potassium salts of the anions, NH_4VO_3, $(NH_4)_6Mo_7O_{24}.4H_2O$, KH_2PO_4 used (all from Merck or Aldrich) were of the highest purity available, and used without any further purification except for vacuum drying over P_2O_5.

Synthesis of ionophore

Zn-Phthalocyanine was synthesized and purified by a new general method, as described in literature [12].

Membrane preparation

Membrane electrode was prepared according to the method reported by Craggs et al (Craggs et al. 1974). Varying amounts of the ionophore and PVC were dissolved in minimum amount of THF. The solvent mediators DBP, DOP, DMS, DBBP and NaTPB were also added in different proportions to get membranes of different compositions. The solution thus obtained, after complete dissolution of various components, was poured into a glass ring placed on a smooth and clean surface and allowed to evaporate at room temperature. After 48 h, non-transparent membrane was obtained with a thickness of 0.3 mm, then cut to size and attached to a glass tube with the help of PVC. The membranes was equilibrated with respective 0.01 M HPO42-solution for 2-3 days and the potential across the membrane was measured by setting up the following cell assembly.

Internal reference Calomel electrode	Internal reference solution (0.01 M HPO42-	Cadmium Selective Membrane	Test solution of HPO42-ion	External reference Calomel electrode

All potential measurements were made by using digital pH metal potentiometer (Elico LI-10, India) in conjunction with saturate calomel electrodes (SCE) as reference electrodes.

Result and Discussion

Preliminary experiments revealed that the plasticized PVC-based membrane electrodes containing the ionophore generate stable potential responses in solutions containing HPO_4^{2-}, after conditioning for about 24 h in 1.0×10^{-2} M HPO42- solution. Therefore, the performance of the electrodes for HPO42- ion was studied in detail. Complexation can actually be defined as a simple interaction between a donor (ligand) and an acceptor (substrate). The characteristics of a ligand and the substrates are important in molecular recognition, because the selective bonding between the ligand and the substrate originates from the information is stored in the ligand and is read out by the substrate. This characteristic information helps define the stability, selectivity, reactivity and transport of the complexes.

The influence of membrane composition

It is well known that the sensitivity, linear dynamic range, and selectivity of the ISEs depend not only on the nature of the carrier used, but also significantly on the membrane composition and the properties of the additives employed [14]. Thus, the influence of the membrane composition, amount of plasticizer, lipophilic additives and ionophore on the potential response of the membrane was investigated. Several membranes were prepared with different compositions. The best response was observed with the membrane composed of the following ingredients as Zn-Phthalocyanine:PVC:DBP:NaTPB: 40:300:470:5 and calibration curve for this composition showed (Figure 1).

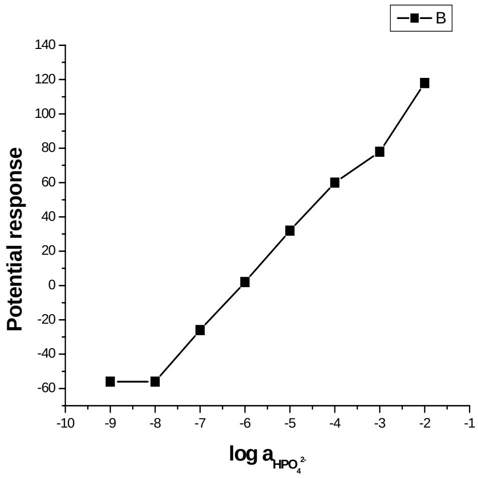

Fig.1: Calibration curve for HPO_4^{2-} cation using Zn-Phthalocyanine Schiff based as an ionophore

Response time and life time

It is notable that the experimental conditions, like the stirring or flow rate, the ionic concentration and composition of the test solution, the concentration and composition of the solution to which the electrode was exposed before performing the experiment measurement, any previous usages or preconditioning of the electrode, and the testing temperature, are effective on the experimental response time of a sensor. In this work, 10 s response time was obtained for the proposed electrode when contacting different HPO42- solutions from 1.0 × 10^{-8} to 1.0 × 10^{-1} mol/L. The average lifetime for most of the reported ion selective sensors is in the range of 4-10 weeks. After this time the slope of the sensor will decrease, and the detection limit will increase (Figure 2)

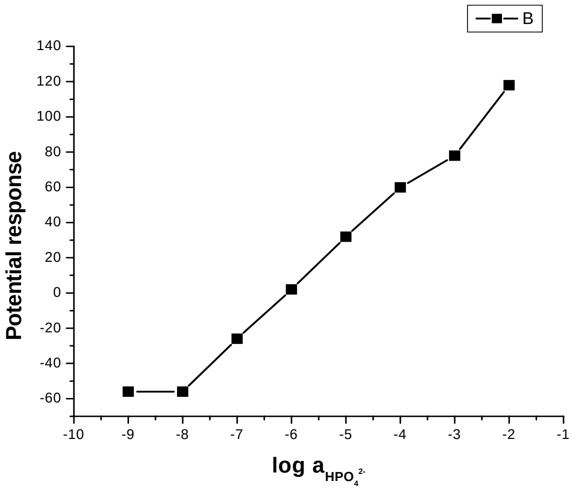

Fig.2: Response time curve for HPO_4^{2-}-selective ion-selective electrode.

Effect of pH

The effect of the pH of the test solution on the potential response of the membrane electrode was tested in the pH range 2.0–12.0 at three HPO42- -concentrations (1.0 × 10^{-2} and 1.0 × 10^{-3}). The pH was adjusted with HCl and NaOH as required. The results in Fig. showed that the potentials remain constant within a pH range of 3.5-9.5 for 1.0 × 10^{-2} M and 1.0 × 10^{-3} M. The variation of the potential at pH ≤ 4.0 could be related to protonation of ionophore in the membrane phase which results in a loss of its ability to interact with HPO42- ions and/or simultaneous response to HPO42- and chloride ions.

At pH > 9.5, in 1.0 × 10^{-3} M of HPO42-, the potential drop may be because of interference of hydroxide ion. In these pH values, the potential did not drop in 1.0 × 10^{-2} M of HPO42- because the selectivity of membrane for HPO42- versus OH^- is high (Figure 3).

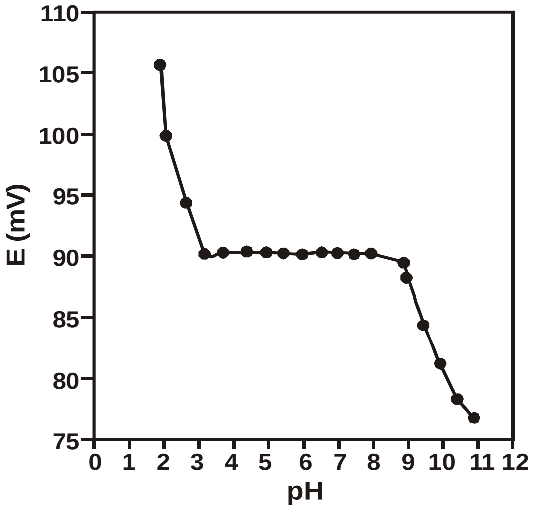

Fig.3: Effect of pH on potentiometric response of the proposed HPO_4^{2-} ion selective electrodes.

Effect of non-aqueous solution on the electrode response (Calibration curve and response time)

The performances of the sensors were also investigated in partially non-aqueous medium using 30% (v/v) non-aqueous content. In these mixtures, the working concentration range and slope remain almost the same. However, above the 30% non-aqueous contents, the slope decreased appreciably, which indicates that the sensor has become less sensitive to HPO42- ions in non-aqueous media. In addition to this, the response times of the membrane electrodes have also been investigated in non-aqueous systems and it was found that the response time was steady for a few hours, and after that the potential deviated drastically (table 1) (table 2).

Table-1

Solvent	Composition (v/v) %	Slope (mV/decade concentration change)
		HPO_4^{2-}-electrode
Water	----	29.45
Ethanol	5	29.45
Ethanol	10	29.45
Ethanol	15	29.40
Ethanol	20	29.45
Ethanol	30	29.45
Acetone	5	29.45
Acetone	10	29.45
Acetone	15	29.40
Acetone	20	29.45
Acetone	30	29.40

Table-2

S.No.	Time (Sec)	Potential(-mV) 10% Ethanol	Potential(-mV) 30% Ethanol	Potential(-mV) 10% Acetone	Potential(-mV) 30% Acetone
		HPO_4^{2-}- electrode	HPO_4^{2-} electrode	HPO_4^{2-} electrode	HPO_4^{2-} electrode
1	0	02	08	09	09
2	5	09	09	10	11
3	10	17	010	12	14
4	15	23	010	14	15
5	20	24	11	19	18
6	25	27	11	22	20
7	30	28	12	22	20
8	35	28	14	22	20
9	40	28	15	22	20
10	45	28	15	22	20
11	50	28	15	22	20
12	55	28	15	22	20
13	60	28	15	22	20

Selectivity

The selectivity of the membrane electrode proposed was analyzed by investigating the presence of various interfering foreign cations using the Matched Potential Method (MPM) (Gadzekpo and Christain, 1984).

According to the MPM, the selectivity coefficient is defined as the activity (concentration) ratio of the primary ion and the interfering ion, which gives the same potential change in a reference solution (Tohda et al., 2001) [15]. Thus the measured change in potential varies with the primary ion activity, and so the interfering ion would be added to an identical reference solution until the same potential change is obtained. The concentration of anion used as the primary ion in this study was 5.0×10^{-5} M (table 3).

Table-3

Interfering ions	$K^{Pot}_{HPO4^{2-},B}$	Interfering ions	$K^{Pot}_{HPO4^{2-},B}$
F^-	-2.1×10^{-4}	Salicylate	-2.5×10^{-4}
Cl^-	-6.6×10^{-4}	CO_3^{2-}	-1.1×10^{-4}
NO^{3-}	-2.4×10^{-4}	CrO_4^{2-}	-5.7×10^{-4}
SCN^-	-6.2×10^{-4}	SO_3^{2-}	-5.6×10^{-4}
ClO_3^-	-1.7×10^{-3}	SO_4^{2-}	-5.0×10^{-4}
CN^-	-3.5×10^{-3}	Citrate	-5.7×10^{-4}

HCO_3^-	-3.4 x 10^{-4}	NO^{2-}	-4.7 x 10^{-4}
BrO_3^-	-3.0 x 10^{-3}	Br^-	-3.9 x 10^{-4}
I^-	-3.2 x 10^{-3}	CH_3COO^-	-5.0 x 10^{-4}
OH^-	-3.2 x 10^{-3}	HSO_3^-	-6.0 x 10^{-4}
ClO_4^-	-6.5 x 10^{-3}	H_2PO^{4-}	-2.0 x 10^{-4}

Potentiometric titration

The HPO42--selective membrane electrode is introduced not only to be used for direct determination of HPO42- ions, but also to be useful as an indicator electrode in titration of HPO42- with Br^{2+} solution. The results of the titration of 50.0 mL of 1.0 × 10^{-3} M solution of HPO42- ion with a 1.0 × 10^{-2} M Br^{2+}solution are shown (figure 4).

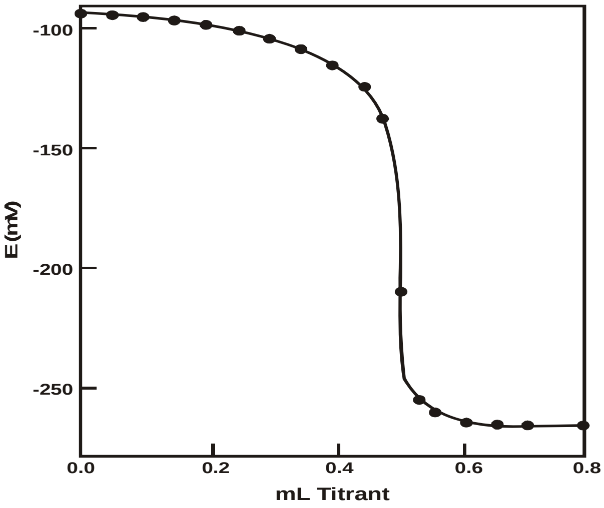

Fig.4 Potentiometric titration curve of 50 ml of 4.9 x 10^{-4} M HPO_4^{2-} solution with 5.0 x 10^{-2} M of Br^{2+} using the proposed membrane electrode as an indicator electrode.

HPO42- detection

The electrode was also successfully applied to the direct determination of HPO42- content of a water sample and in fertilizer smple, the results, together with those obtained by AAS, are summarized in Table 4.

Table-4

Sample	Proposed	ISE AAS
Water sample	(6.3 ± 0.2) 10^{-5} M	(6.2 ± 0.1) 10^{-5} M
Agricultural Fertilizer sample	(5.1 ± 0.3) 10^{-5} M	(5.0 ± 0.1) 10^{-5} M

As observed from Table 4 the results obtained by the proposed HPO42--selective electrode are in satisfactory agreement with those obtained by AAS.

Conclusion

The proposed electrode exhibits a variety of good performance characteristics, including easy preparation and procedures, high selectivity and sensitivity, good stability (6-8 months) and reproducibility, fast response time (10 s) and low cost. The electrode can be applied to the determination of HPO_4^{2-} in actual samples.

References

[1] Foy, R. H.; Withers, P. J. A.; Proceedings of the Fertilizer Society, No. 365, London, 1995.

[2] Glazier, S. A.; Arnold, M. A.; Anal. Chem. 1988, 60, 2540.

[3] Glazier, S. A.; Arnold, M. A.; Anal. Chem. 1991, 63, 754.

[4] Chaniotakis, N. A.; Jurkschat K.; Rühlemann, A.; Anal. Chim. Acta 1993, 282, 345.

[5] Tsagatakis, J. K.; Chaniotakis, N. A.; Jurkschat, K.; Helv. Chim. Acta 1994, 77, 2191.

[6] Liu, D.; Chen, W. C.; Yang, R. H.; Shen, G. L.; Yu, R. Q.; Anal. Chim. Acta 1997, 338, 209.

[7] Liu, J.; Masuda, Y.; Sekido, E.; J. Electroanal. Chem. 1990, 291, 67.

[8] Carey, C. M.; Riggan, W. B.; J. Anal. Chem. 1994, 66, 3587.

[9] Wróblewski, W.; Wojciechowski, K.; Dybko, A.; Brzózka, Z.; Egberink, R. J. M.; Snellink-Ruël, B. H. M.; Reinhoudt, D. N.; Sens. Actuators B 2000, 68, 313.

[10] Wróblewski, W.; Wojciechowski, K.; Dybko, A.; Brzózka, Z.; Egberink, R. J. M.; Snellink-Ruël, B. H. M.; Reinhoudt, D. N.; Anal. Chim. Acta 2001, 432, 79.

[11] E. Pungor, K. Toth, P. G. Klatsmanyi and K. Izutsu, Pure & Appl. Chem., Vol. 55, No. 12, pp. 2029—2065, 1983.

[12] A. Shaabani, J. Chem. Res., 1988,672.

[13] T. Sokalski, A. Ceresa, T. Zwickle, E. Pretsch, J. Am. Chem. Soc. 119 (1997) 11347-11356.

[14] Gadzekpo V P Y and Christain G D (1984), “Determination of Selectivity Coefficients of Ion-Selective Electrodes by a Matched-Potential Method”, Anal. Chim. Acta., Vol. 164, pp. 279-282.

[15] Tohda K, Dragoe M and Umezawa Y (2001), “Determination of Selectivity Coefficients of Ion-selective Electrodes by a Matched-Potential Method”, Anal. Sci.,Vol. 17, pp. 733-743.