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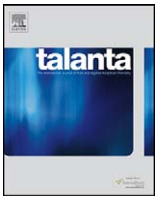

An all-solid-state monohydrogen phosphate sensor based on a macrocyclic ionophore

Pankaj Kumar [1], Dong Min Kim, Myong Ho Hyun, Yoon-Bo Shim *

Department of Chemistry and Institute of BioPhysio Sensor Technology (IBST), Pusan National University, Jangjun-Dong, Busan, 609-735, South Korea

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ABSTRACT

An all-solid-state electrode, containing a synthesized chiral A_2B_2 macrocyclic compound namely (4R,5R,15R,16R)-4,5,15,16-tetraphenyl-3,6,14,17-tetraazatricyclo [13.3.1.18,12] tetracosa-1(23),8,10,12(24)19,21-hexaene-2,7,13,18-tetrone as an ionophore in polyvinyl chloride (PVC)/polyurethane (PU) membrane matrix, has been developed for the selective quantification of monohydrogen phosphate ions. The best performing membrane contained PVC, PU, ionophore, and nitrophenyl octyl ether as a plasticizer in the ratio 32.2:2.6:65.1 (w/w, %). It exhibited a near-Nernstian slope of 31.0 ± 1.0 mV/decade of activity for HPO_4^{2-} ions in the concentration range of 1.0×10^{-6} to 1.0×10^{-2} M at pH 7.4. The detection limit of the electrode was 8.4×10^{-7} M and the life time was six weeks. The electrode displayed excellent selectivity for monohydrogen phosphate over other anions and the selectivity sequence was determined as $HPO_4^{2-} > SO_4^{2-} > Ac^- > NO_3^- > ClO_4^- > Cl^- > I^-$. The selective electrode for the monohydrogen phosphate ions was evaluated with a standard reference material (SRM 1548) and the titration of the sample solution.

1. Introduction

The monitoring of phosphate concentration levels finds its applications in wide areas of science. It includes analytical chemistry, clinical chemistry, pharmacology, and environmental chemistry. Phosphorous exists in living organisms mostly in the form of phosphate ions. For example, phospholipids such as lecithin and cephalin are the major components of cell membranes [1]. Adenosine triphosphate (ATP) is responsible for all energy production and storage processes within the body [2]. DNA and RNA also are the long chains of phosphorous containing molecules. Phosphorous is essential in chemical processes involved in the utilization of carbohydrates and fats [3]. It liberates their energy at the rate, demanded by the body. In combination with calcium, it feeds the nerves and also aids the growth of hair, helps counteract fatigue, regular functioning of heart, and for normal kidney functioning. It helps in regulating the acid alkaline balance of the blood which is vital for the maintenance of health. Its deficiency can cause excessive weight loss, retarded growth, poor mineralization of bones and teeth, and reduced activity of nerves and brain function [4]. Thus, it is essential to monitor the concentration of phosphate in various areas.

There are many techniques available for the determination of phosphate ions. Most common are spectroscopic methods which involve the formation of molybdenum blue [5]. This system is complicated and remains unsuitable for the application to automated sensing and feed back control. Another technique, the automated flow analysis [6] is expensive in labor, and equipment, and produces toxic laboratory waste. Besides, these methods need large infrastructure back up, and are time consuming. Therefore, a reliable, robust, low cost, and quick analytical technique is highly desirable, and such requirements are greatly met with ion sensors. Numerous phosphate selective potentiometric electrodes have been reported in the literature. A variety of active materials have been used to develop these electrodes [7–10]. The earliest reported bivalent phosphate electrode was based on the ion exchange membrane containing amine chloride [11]. Tin (IV) complexes were among the early compounds to be investigated as ionophores in the polymer membrane based electrodes. The derivatives of dibenzyltindichloride [12] and multidentate-tin (IV) carrier [13] have also been used for the development of dibasic phosphate ion-selective electrodes. Binuclear organotin compounds were also explored later [14]. These electrodes exhibited high sensitivity towards HPO_4^{2-} ions but poor selectivity and short life time due to the hydrolysis of the ion-carrier in the membrane phase. Uranyl salophanes were also successfully used as ionophores in the PVC matrix membrane electrodes [15–17]. These electrodes suffered with short life time. Cyclic polyamines like 3-decyl-1,5,8-triazacyclodecane-2,4-dione [18,19] have been used as a carrier in polymeric membranes to obtain highly sensitive and selective electrodes for

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* Corresponding author. Tel.: +82 51 510 2244; fax: +82 51 514 2430.
E-mail address: ybshim@pusan.ac.kr (Y.-B. Shim).

[1] Present address: Department of Chemistry, Maharishi Markandeshwar University, Ambala, Haryana, India.

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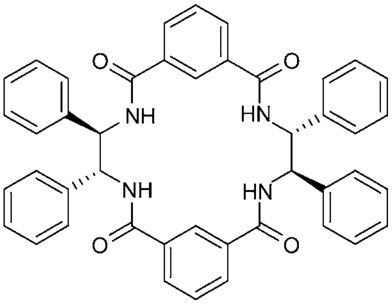

Fig. 1. Chemical structure of the chiral A_2B_2 ionophore.

HPO_4^{2-} ions. A ferrocene bearing macrocyclic amide compound-based sensor has shown a narrow linear working concentration range of 1.0×10^{-2} to 1.0×10^{-5} M [20]. Besides these, various types of electroactive compounds such as heterocyclic macrocycle; 3-allyl-1,5,8-triazacyclodecane-2,4-dione [21], macrocycles [22], zwitterionic bis(guanidinium) ionophore bearing an anionic complex organoborane compound [23], bis-thiourea [24], urea or thiourea-functionalized calix[4]arenes [25], and macrocyclic dithioxamide receptor [26] based electrodes have been developed for the selective quantification of HPO_4^{2-} ions.

Most of these potentiometric ion-selective electrodes are based on the polymeric membranes that use an inner reference solution. The presence of liquid inside the electrode imposes a number of limitations for their applications. It includes the need to work in vertical position, loss of internal reference solution due to evaporation, and leakage of inner solution, and maintenance requirements. Also, for robustness and miniaturization, it is desirable to eliminate the liquid phase of inner reference solution from the conventional electrochemical cells to enhance their practical suitability for medicinal, biological sciences and technology, and in vivo experiments [27–29]. All-solid-state ion-selective polymeric membrane electrodes as well as ISEs containing hydrogels as the inner layers are of special interest because they are free from the above limitations. To our knowledge, there is only one all-solid-state monohydrogen phosphate selective electrode, reported till date [17]. This electrode exhibits a narrow linear range between $1.0 \times 10^{-4.5}$ and 1.0×10^{-1} M, and very short life time which constraint its suitability for real applications. Therefore, an all solid electrode phosphate selective electrode is the need of the day.

In the present work, we report for the first time a better performing all-solid-state ISE (ASISE) for monohydrogen phosphate ions, exhibiting a wide linear range with a long life span. Macrocyclic minireceptor (I) was synthesized starting from isophthaloyl chloride and a chiral diphenylethyldiamine [30]. The electrode has been fabricated by using a newly synthesized macrocyclic ionophore (Fig. 1). The selectivity coefficients of the electrode were measured for a number of common anions such as acetate, chloride, nitrate, sulfate, chlorate, and iodide. The experimental response curve was obtained by using a 0.05 M phosphate solution with varying pH and compared with the predicted response curve. The optimized ASISE was successfully used as an indicator electrode in the potentiometric titration of phosphate ions against the standard barium chloride solution as well as to determine the concentration of phosphate ions in the standard reference material (SRM 1548).

2. Experimental

2.1. Synthesis of ionophore

Isophthalic acid (0.4 g, 2.4 mM) in 10 ml of $SOCl_2$ was refluxed for 6 h. The excess $SOCl_2$ was removed under reduced pressure and the residue was directly used in the next step without any further purification. The obtained residue was mixed with commercially available, chiral 1,2-(R,R)-diphenylethylenediamine (0.5 g, 2.36 mM), dissolved in 400 ml of THF, and the mixture was stirred at room temperature. After 5 min diisopropylethylamine (0.8 ml, 4.7 mM) was added to the mixture. Isophthaloyl chloride (0.48 g, 2.4 mM), diluted in 200 ml of THF, was slowly added to the mixture at 0 °C and stirred at room temperature for 24 h. The reaction mixture was washed with 0.1 M HCl followed by brine solution. The organic layer was then dried over anhydrous sodium sulfate, concentrated under reduced pressure and purified on silica gel chromatography (ethylacetate:hexane; 1:1) to give the chiral A_2B_2 product with a 36% yield. ^1H NMR (200 MHz, DMSO) δ 5.49–5.52 (d, 4H), 7.15–7.33 (dd, 20H), 7.51 (t, 2H), 7.75 (d, 4H), 8.38 (s, 2H), 9.22 (d, 4H).

2.2. Reagents and instrumentation

Bis(1-butylpentyl)adipate (BBPA), and tridodecylmethyl ammonium chloride (TDMACl) were purchased from Fluka (Switzerland), 2-nitrophenyl octyl ether (NPOE) from Aldrich (USA), and bis(2-ethylhexyl)adipate (DOA) from Wako (Japan). High molecular weight poly vinyl chloride (PVC), and HEPES buffer were purchased from Sigma (USA) and polyurethane (PU) was purchased from Thermedics (USA). SRM 1548, Total Diet, was obtained from US Department of Commerce, National Institute of Standards and Technology, Gaithersburg. The solvent tetrahydrofuran (THF) was purchased from Kanto Chemical Co. (Japan). Perchlorate, nitrate, chloride, iodide, acetate, and sulfate solutions were prepared from sodium or potassium salts. Aqueous solutions were prepared with deionized water (18 MΩ cm). Muffle furnace from Young Ji Med. Lab. Co., South Korea, and pH meter, model 520A from Orion, were used during the experiments. Potential studies were carried out with a 15 channel pH/Ion meter KST101 (Kosentech. Co., Korea).

2.3. Electrode preparation

Two types of polymer matrix namely PVC and PU were used for the preparation of the electrode membranes and the obtained electroanalytical data were compared to select the better membrane composition. A number of electrodes were prepared with different membrane compositions to ensure the development of the best performing electrode. Varying amounts of the ionophore, 25 mg of PVC/PU, and 50 mg of solvent mediator NPOE, were mixed in 1 ml of THF. The solution was shaken vigorously for about 8 h in a shaker to get a homogeneous solution. The polymer membrane was prepared by dropping 10 μL of the membrane solution cocktail on a thoroughly cleaned and polished carbon electrode and evaporating the solvent 24 h in a closed cabinet at room temperature. The electrode was finally conditioned for one day by soaking it in a 1.0×10^{-2} M K_2HPO_4 solution (pH 7.4).

2.4. EMF measurements

The electrochemical cell used for the potential measurement was composed as follows: Ag/AgCl (sat'd KCl)//sample solution//solid membrane on a carbon rod. Despite the utmost care taken during the preparation of membranes, the thickness and the internal resistance of the resulting membranes varied in each case. Since the standard potentials between electrodes were different, the normalization of the potentials was necessary to allow comparisons of the electrode responses. The potential for each test electrode in a blank solution was set to 0 mV. Standard monohydrogen phosphate solutions were prepared by serial dilution of a 0.1 M K_2HPO_4 solution and then titrated with KOH to pH 7.4. The pH of the solutions under investigation was continuously monitored and maintained throughout. The phosphate activity was

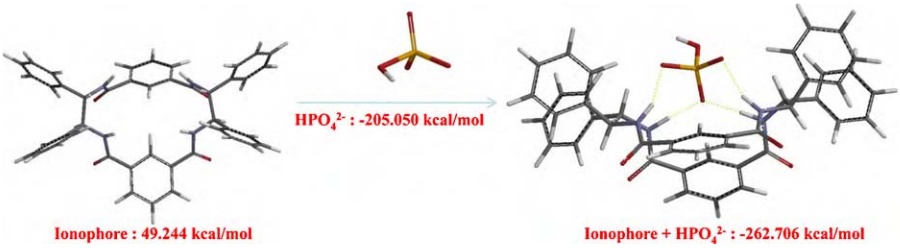

Fig. 2. The energy-minimized structure of the ionophore and monohydrogen phosphate ion.

derived from the Debye-Hückel limiting law. These were calculated using the total phosphate concentration, the pH of standard solution, the equilibrium constant of different phosphate species and the ionic strength. The selectivity coefficients of electrode for the monohydrogen phosphate ion with respect to other anions were determined with the separate solution method using 10^{-2} M concentration of interfering ions. All solutions used for the determination of selectivity coefficient values were adjusted to pH 7.40 ± 0.02. The detection limit for monohydrogen phosphate was determined by the IUPAC recommended method [31].

3. Results and discussion

3.1. Interaction between ionophore and monohydrogen phosphate ions

Ion sensors for hydrophilic ions, e.g. phosphate or sulfate ions are usually based on ion exchangers [32]. In order to prepare a sensor for these ions, the membrane should contain ionophore molecules which must be capable to bind these ions specifically. Neutral anion ionophores containing hydrogen bond forming moieties or immobilized Lewis acidic binding sites can be applied for this purpose. It is especially challenging to achieve the useful selectivity for a strongly hydrophilic anion, particularly in the phosphate species, since their unfavorable standard free enthalpies transfer from samples to ISE membranes have been overcompensated by selective complexation [33]. Fig. 2 shows the energy-minimized structure of polyamide–HPO_4^{2-} complex. The optimum location of captured HPO_4^{2-} ion was the centre of the cavity, which allowed it to form hydrogen bonds with four hydrogen atoms present at the cavity of the polyamide. The formed hydrogen bonds between HPO_4^{2-} and hydrogen atoms of the polyamide have the short P–O···H distances, which are as follows: (a) P–O···H = 1.933 Å, (b) P–O···H = 1.946 Å, (c) P–O···H = 1.979 Å, (d) 1.949 Å. These bond lengths confirm the formation of hydrogen bonds between oxygen atoms of the monohydrogen phosphate ion and the hydrogen atoms at the polyamide cavity. This is further confirmed as the sensor exhibited highly selective behavior towards monohydrogen phosphate ions.

3.2. Characterization of the electrode response

The ionophore based membrane electrode showed a linear potentiometric response towards phosphate ions with an average slope of 31.0 ± 1.3 mV/decade of activity (Fig. 3). The pHs of solutions were adjusted to 7.4 in all the experiments. Although the value of slope itself suggests that the electrode is responding towards divalent monohydrogen phosphate ions with a near-Nernstian slope. However, only the slope is not sufficient for the confirmation because it can also be assumed that the electrode is showing a poor response towards $H_2PO_4^-$ ions with a sub-Nernstian slope. The distribution of phosphate species is pH dependant; therefore, the relative amount of one phosphate species in a solution increases and the other form decreases as the pH of the solution is varied. A method of varying the pH while keeping the total concentration of anion being measured unchanged, was adopted to determine which of the phosphate species is actually being sensed by the electrode [18]. This method was employed by monitoring the response of the electrode in a solution containing 0.5 mM total phosphate ion concentration at varied pH. At the lower pH, the monovalent dihydrogen phosphate form is dominant but as the pH approaches to neutral, the $H_2PO_4^-$ form changes into HPO_4^{2-} and therefore, the divalent monohydrogen form becomes prevalent. The pH of the phosphate solution was varied from 5.0 to 11.0 and the potential changes were measured. Fig. 4 shows the resulting potential responses of the electrode based on the ionophore as a function of pH. It suggests that the electrode is non-responsive when pH of the standard phosphate solution remains near 5.0, i.e. when $H_2PO_4^-$ is dominantly present. As soon as the pH increased above 7.0, electrode shows a steady and stable response. It may be attributed towards the presence of HPO_4^{2-} ions which are formed by the conversion of $H_2PO_4^-$ into the HPO_4^{2-} form. By considering the near-Nernstian slope value of the electrode and its response towards the pH variation, it is concluded that the electrode is responding towards dibasic phosphate ions.

3.3. Optimization of the electrode composition

It is well established that the nature and amount of ionophore as well as the plasticizers, significantly affect the sensitivity, and the selectivity of the ion-selective electrode. The effect of the addition of these membrane ingredients was investigated by preparing a number of electrode membranes having different compositions.

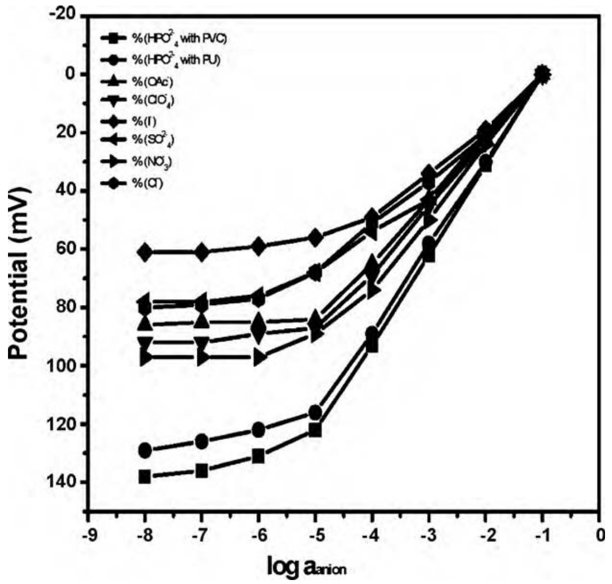

Fig. 3. Potentiometric response of the ionophore containing ISEs towards different anions.

Table 1
Composition of the response characteristics of the electrodes.

Electrode no.	PU	PVC	(I)	Plasticizer	Slope (mV/decade)	Linear range (M)	Response time (s)
1	33.2	–	1.0	NPOE: 65.8	17.0 ± 2.5	1.0×10^{-4} to 1.0×10^{-1}	70
2	33.2	–	2.0	NPOE: 64.8	28.8 ± 1.3	1.0×10^{-5} to 1.0×10^{-1}	50
3	33.2	–	3.0	NPOE: 63.8	23.3 ± 1.7	1.0×10^{-5} to 1.0×10^{-1}	50
4	33.2	–	2.0	DOA: 64.8	27.7 ± 2.1	1.0×10^{-5} to 1.0×10^{-1}	75
5	33.2	–	2.0	BBPA: 64.8	26.0 ± 0.5	1.0×10^{-5} to 1.0×10^{-1}	75
6	–	32.2	2.6	NPOE: 65.1	31.0 ± 1.0	1.0×10^{-6} to 1.0×10^{-2}	5
7	–	33.2	2.0	DOA: 64.8	24.6 ± 1.0	4.8×10^{-6} to 1.0×10^{-3}	20
8	–	33.2	2.0	BBPA: 64.8	33.0 ± 0.5	1.0×10^{-6} to 1.0×10^{-3}	15

All determinations were carried out 3 times.

Only the best performing membrane compositions, and the results obtained for them are presented in Table 1. In the case of PU matrix, the membranes containing 2.0 wt% of the ionophore (electrode no. 2) showed the near-Nernstian slope (28.8 ± 1.3 mV/decade) within the concentration range of 1.0×10^{-5} to 1.0×10^{-1} M. This is not similar to the ISE containing 1.0 wt% of ionophore (electrode no. 1) and 3.0 wt% of ionophore (electrode no. 3) which showed a sub-Nernstian slope in the concentration range of 1.0×10^{-4} to 1.0×10^{-1} M. This was obviously due to the decreased number of active sites at <2.0 wt%, and some inhomogenities in the membrane at >2.0 wt%. Among three plasticizers having different polarities, the most polar one, NPOE, was the most effective in comparison with DOA (electrode no. 4) and BBPA (electrode no. 5). This indicates the effect of plasticizer on the dielectric constant of the membrane as well as on the mobility of the ionophore and its complex. For PVC matrix membranes, a similar pattern was observed. The membranes prepared with DOA, and BBPA plasticizers (electrode nos. 7, and 8) exhibited the narrow working concentration range of 4.8×10^{-6} to 1.0×10^{-3}, and 1.0×10^{-6} to 1.0×10^{-3} M respectively. The electrode no. 6, having a membrane composition of 2.6:32.2:65.1 (ionophore:PVC:NPOE) wt%, shown the widest working concentration range of 1.0×10^{-6} to 1.0×10^{-2} M with a sub-Nernstian slope of 28.0 ± 1.0 mV/decade of activity. This may be due to the high polarity of NPOE, which facilitates the complex formation between ionophores and the anion. It is important to emphasize that the addition of lipophilic cation additive, tetradodecyl ammonium chloride showed little effect on the response characteristics of the proposed electrode. The slope of the potential response curve for the TDMACl containing electrode was improved to Nernstian value. The electrode with the composition ionophore/PVC/TDMACl/NPOE exhibited a slope of 31.0 ± 1.0 mV/decade of activity.

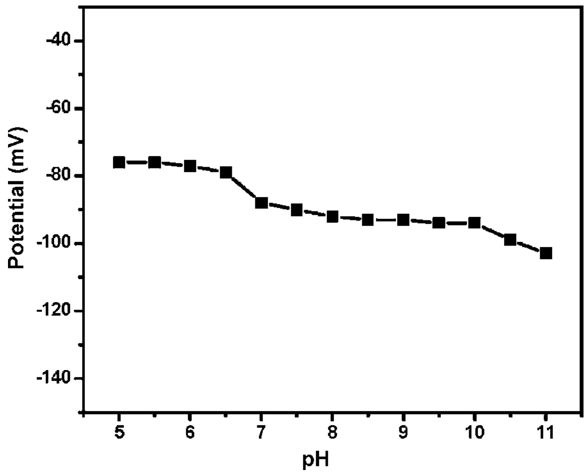

Fig. 4. A response curve for HPO4^{2-} solutions containing 0.05 M total phosphate concentration at different pHs.

3.4. Response time and stability

Response times of the electrodes were determined by measuring the time required to achieve a steady potential when the concentration of $HPO_4{}^{2-}$ increased from 1.0×10^{-5} to 1.0×10^{-4} M. All the electrodes containing PU as a matrix exhibited comparatively higher response time than the PVC based electrodes. It seems that PVC is more compatible with plasticizers and forms a homogeneous solution when mixed together. On the other hand, PU based membranes were found to be mechanically more stable and long lasting but their response times were longer than that of PVC based membranes. Electrode no. 6 using PVC exhibited the quickest response with the response time of 5 s (Table 1). The response behavior of the membrane electrodes remained unchanged when the potentials were recorded either from higher to lower concentration or vice versa.

The life span of membrane electrodes was studied by monitoring the change in the electrode slope and the linear response range according to time. The electrode did not show significant changes either in the slope or in the working concentration range for over two months which is much better than PVC based electrodes. The longest life time of PVC based electrode was recorded for electrode no. 6 as six weeks which is much lower than any of the PU based electrodes. The electrodes were stored in a 10^{-2} M $HPO_4{}^{2-}$ solution (pH 7.4) between experiments. The standard deviation of potentials for 10 measurements at a fixed concentration of 1.0×10^{-4} M was found to be ±1.0 mV. After careful examination of all the response characteristics of PU as well as PVC based electrodes, only PVC based electrodes were found suitable for further studies. Out of all the prepared electrodes, the electrode no. 6 remained the best performing electrode as it exhibited the widest working concentration range, lowest response time, and the stable potential response. Therefore, the same was chosen for further studies.

3.5. Selectivity

When analyzing real samples with ISEs, the response of the electrode to the primary ion can be affected by the presence of other ions of the similar charge. The influence of interfering ions on the response behavior of ISEs is usually described in terms of log values of selectivity coefficients; $K^{ij}{}_{Pot}$. The selectivity coefficients were obtained by the separate solution method [31] using 10^{-2} M concentration of the expected interfering anions (Fig. 5). Electrode no. 6 displays the better selectivity when compared with electrode nos. 7, and 8. The observed selectivity coefficients for OAc^- −3.15, $NO_3{}^-$ −3.31, $ClO_4{}^-$ −3.78, Cl^- −3.80, I^- −4.30, and $SO_4{}^{2-}$ −2.51 are significantly lower, which indicate the high selectivity of the electrode for monohydrogen phosphate ions over these anions. The selectivity sequence for this electrode was observed as $HPO_4{}^{2-} > SO_4{}^{2-} > OAc^- > NO_3{}^- > ClO_4{}^- > Cl^- > I^-$, which is not consistent with the Hofmeister series. This anti-Hofmeister selectivity response pattern clearly reveals the mechanism of recognition of $HPO_4{}^{2-}$ which takes place via hydrogen bonds of the ionophore

Table 2

Comparison of potentiometric selectivity coefficients, obtained for electrode no. 6, with the existing monohydrogen phosphate selective electrodes.

Interfering ion, j.	Present work	Ref. [23]	Ref. [14]	Ref. [12]	Ref. [20]	Ref. [15]	Ref. [21]	Ref. [26]
OAC$^-$	−3.15	−1.4	−3.2	−2.3	−1.66	NM[a]	NM	−1.5
Cl$^-$	−3.8	−0.5	−3.0	−2.5	−2.92	−1.8	−1.0	−2.0
NO$_3$$^-$	−3.31	+4.1	−2.4	−1.7	−2.19	−1.3	−0.3	−2.3
I$^-$	−4.3	+8.8	−0.04	−0.6	−1.26	NM	−0.2	−2.4
ClO$_4$$^-$	−3.78	+13	NM	NM	NM	NM	NM	−2.3
SO$_4$$^{2-}$	−2.5	−1.8	−4.3	NM	−1.45	−2.3	NM	−1.8

[a] Not mentioned.

(Fig. 1). The selectivity coefficients obtained for the proposed electrode are compared with earlier reported phosphate ion-selective electrodes (Table 2). It shows that the proposed phosphate ion-selective electrode displays comparable [13,19] and even better selectivity than some of the previously reported phosphate ion-selective electrodes [11,14,20,22,25,26].

3.6. Analytical applications

Standard reference material, SRM 1548, a complex mixture of different foods which represents the daily intake, was selected for the real sample analysis. 1.0 g of homogenized sample was weighed into acid cleaned and thoroughly washed and completely dried quartz tube and placed into a muffle furnace. The temperature was raised slowly to 480 °C and sample was kept overnight [34]. The obtained ash was treated with 1 ml concentrated nitric acid and then dried completely on a heating block. It was placed again into the muffle furnace at 480 °C overnight. The sample ash was diluted to a final volume of 25 ml by adding deionized water. pH of the obtained solution was adjusted to 7.4 and the potential response was recorded. The results exhibited that the phosphorous concentration present in the test sample was 3000 mg/kg which is in the close agreement with the standard value, i.e. 3240 mg/kg (Certificate of Analysis, Standard Reference Material 1548, National Institute of Standards and Technology, 1991). The test sample analysis results were recorded on different days by using the same electrode, and same test sample. The standard deviation for 10 measurements was determined as 2.4 ± 0.1 which suggests that the results obtained by using the prepared electrode are satisfactorily reproducible and reliable.

In addition, the electrode could be successfully used as an indicator electrode to determine the end point in the potentiometric titration of phosphate with a standard barium chloride solution. A 20 ml of 1.0×10^{-4} M phosphate solution was titrated against a 1.0×10^{-2} M barium chloride solution. The phosphate content of the final solution was determined by the sensor using the calibration curve (Fig. 6). A sigmoid curve showed the break end point corresponding to the stoichiometry of barium phosphate, suggesting that the electrode can be used as an indicator electrode for the determination of barium ion concentration.

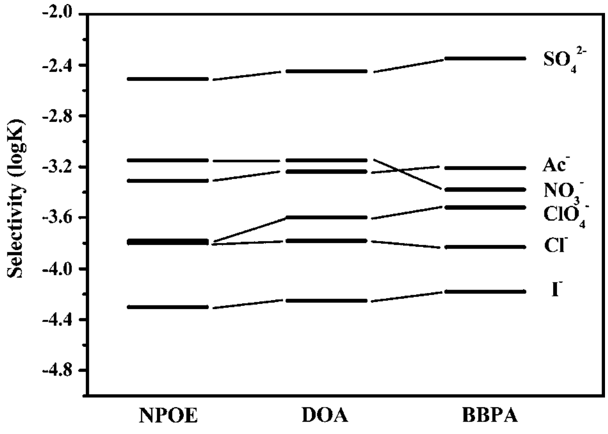

Fig. 5. Selectivity coefficients for HPO$_4^{2-}$ ions determined by the separate solution method at pH 7.4 using 10^{-2} M interfering anions.

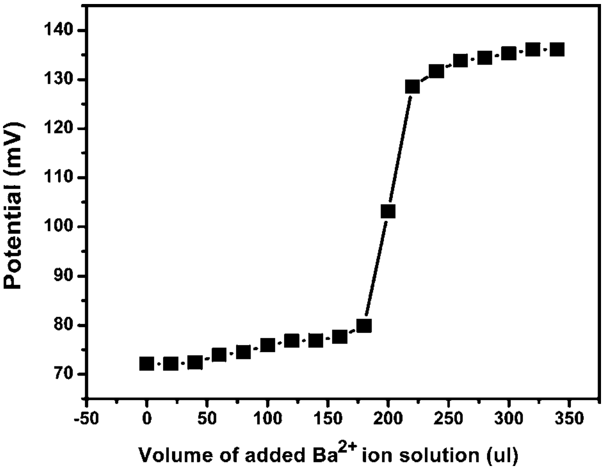

Fig. 6. A potentiometric titration curve obtained for a 20 ml of 1.0×10^{-4} M HPO$_4^{2-}$ solution against the standard 1.0×10^{-2} M Ba^{2+} ion solution.

4. Conclusion

An all-solid-state monohydrogen phosphate ion sensor has been developed by using a newly synthesized macrocyclic polyamide, as an ionophore in polyvinyl chloride (PVC) membrane matrix. It exhibited a near-Nernstian response in a wider linear range. The detection limit of the electrode was 8.4×10^{-7} M. It is free from the interference due to the presence of the common bivalent and monovalent ions and shows highly selective response towards HPO$_4^{2-}$ ions. It could be successfully used as an indicator electrode for the end point determination in the potentiometric titration of phosphate solution against standard barium chloride solution as well as to determine the concentration of phosphate in the standard reference material. Apart from being an advantageous all-solid-state electrode, it exhibited better response time, working concentration range, and life time than many of the existing electrodes.

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