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Novel monohydrogenphosphate ion-selective polymeric membrane sensor based on phenyl urea substituted calix[4]arene

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ABSTRACT

A highly selective and sensitive PVC membrane, containing phenylurea substituted calix[4]arene was found to be a suitable ionophore for monohydrogen phosphate (HPO_4^{2-}) ions that exhibited a Nernstian response (with a slope of -29.4 ± 0.3 mV decade^{-1}). The working concentration range of the electrode was 6.0×10^{-8}–1.0×10^{-1} mol L^{-1} with a detection limit of 2.0×10^{-8} mol L^{-1}. The response time of the sensor in the whole concentration range is very short (<8 s), with a considerable lifetime of at least 15 weeks. The sensor possesses the advantages of short response time, low detection limit and a high selectivity towards a large number of inorganic anions. The developed sensor was used as an indicator electrode in potentiometric titration of monohydrogen phosphate ion with barium chloride. The proposed sensor was successfully applied for the direct determination of monohydrogen phosphate in real life samples.

1. Introduction

Supramolecular chemistry of anions has been a field of growing interest during the last few years and there has been a large number of appealing reviews on the chemistry of anion recognition as well as on the development of host receptors for anions [1–3]. The interest in ion-selective electrodes has grown over recent years as they are easy-to-use devices that allow rapid and accurate analytical determination of chemical species at relatively low concentrations, with a reasonable selectivity and low cost. The rapid determination of minute quantities of ionic species by simple methods is of special attention in analytical chemistry. Ion selective electrodes based on solvent polymeric membrane incorporating ion carriers have shown to be very useful tools for the analysis of many cations and anions.

A great number of ionophores have been developed and found extensive applications in potentiometric sensors for the determination of respective ions in real samples. The macrocyclic compounds, which are excellent ionophores, are being employed as the carriers in metal selective extraction, phase transfer catalysis and membrane transport as they bind the metal ions selectively [4–7]. Macrocyclic compounds are cyclic, organic molecules containing N, S, O, etc. capable of forming electron rich interior cavities and possess the ability to complex with metal ions of compatible dimensions. Complexation studies between macrocyclic ligands and metals provide valuable information for construction and design of sensors. Calixarenes are fascinating objects for the study of host guest interactions with pronounced binding affinities to various metals. The ease of chemical modification is one of the main attractive features of calixarenes as it enables alterations in the ion-complexing selectivity by simply switching from one ligating functional group to another. The uses of calixarenes as the basis for ion-recognition in cation sensor systems is well established [8–12]. A few calixarene derivatives for anion binding have been reported [13–16].

The significance of monitoring phosphate concentration levels spans all areas of science and technology. A system that can continuously and selectively detect phosphates levels in aqueous solutions will find numerous applications in fields, such as environmental monitoring, biomedical research, clinical chemistry and pharmacology because phosphorus is an essential mineral for the human body and all other living organisms [17–21]. Measurement of phosphate levels in environmental water samples is usually achieved using laboratory-based automated flow apparatus. A number of investigations, into the development of several phosphate-selective electrodes, have been reported in the literature [22–25]. Organotin complexes have been flourishing in the past as phosphate-selective ionophores in PVC-based ISEs [26–28], along with thiourea compounds [29,30], uranyl salophene derivatives [31,32], molybdenum-based compound [24], cyclic polyamine compounds [33,34], modified calix[6]arene derivative [35] and also an organoborane complex [36]. Still many problems like interference of other anions, lower detection limit, lifetime and longer response time have been encountered.

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Calixarene derivatives, whose lower rim has been modified with anion-complexing functional groups, such as esters and amides, make excellent ionophores for use in ion-selective electrodes. We have explored the sensing properties of the macrocyclic compounds, and have recently reported the mercury selective [37], thiocyanate selective [38], dihydrogen phosphate selective [39], glucose selective [40] and neodymium selective [41] membrane electrodes. These findings motivated us to synthesize phenylurea substituted calix[4]arene, which may allow selective and efficient ion sensing of anions.

Herein, we report extremely selective and responsive monohydrogenphosphate membrane electrode by phenylurea modified calix[4]arene as an exceptional ion carrier for quick and precise determination of monohydrogenphosphate in real sample.

2. Experimental

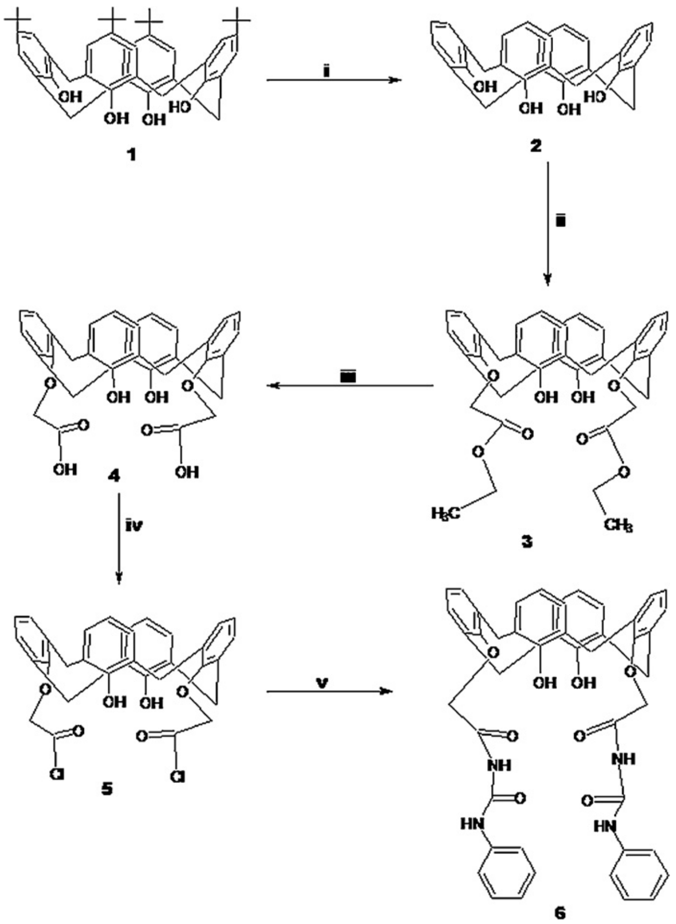
2.1. Reagents and materials

All the reagents and chemicals used were of analytical grade. Sodium tetraphenyl borate (NaTPB) and o-nitrophenyloctylether (O-NPOE) were purchased from Merck. Poly vinyl chloride (PVC) was obtained from MCC, India. Potassium salts of all anions used (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5. Milli-Q water was used for preparing the stock solution of metal salts. Dilutions of the stock solution were also done by Milli-Q water.

2.2. Synthesis of ionophore

2.2.1. Synthesis of phenyl urea substituted calix[4]arene

Scheme 1 illustrates the successive steps of the ionophore synthesis (**1**–**6**). 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrahydroxy calix(4)arene (**1**) and compounds **1**–**5** were synthesized according to the literature methods [42,43]. The synthesis of compounds **6** is illustrated as follows:



Scheme 1. Synthesis of phenyl urea substituted calix[4]arene (i–v). (i) $AlCl_3$, toluene; (ii) dry acetone, ethyl bromoacetate, K_2CO_3; (iii) KOH:EtOH; (iv) $SOCl_2$, dry THF; (v) phenyl urea, dry THF.

2.2.2. Synthesis of 5,11,17,23-tetra-tert-butyl-25,27-bis(phenyl urea)-26,28-dihydroxy calix[4]arene (*6*)

The compound **5** (5,11,17,23-tetra-tert-butyl-25,27-bis(chlorocarbonyl-methoxy)-26,28 dihidroxy calix[4]arene) (1.66 g; 1.89 mmol), obtained in the previous step was dissolved in dry THF (75 mL). The addition of pyridine (2 mL; 12.4 mmol) and the solution of phenyl urea (1.3 g; 9.5 mmol) in THF (15 mL) were made sequentially and added drop wise in a period of 30 min with continuous stirring at room temperature (30 °C). The reaction mixture was then stirred and refluxed for 4 h, after which most of the solvent was distilled off under vacuum. The residue was diluted with water (100 mL) and neutralized by 0.1 M HCl. The solid material was then filtered and washed with 1 N HCl, $NaHCO_3$ and distilled water sequentially. Recrystallization of the residue from ethanol–THF furnished **6**. Yield 1.5 g (81%), m.p. 203–205 °C. Anal. calc. $C_{46}H_{40}N_4O_8$: C: 71.13; H: 5.15; N: 16.49% found: C: 71; H: 5.03; N: 16.26%. FT-IR (KBr) υ: 3390 cm^{-1} (–NH), 1670–1650 cm^{-1} (–NH–CO), 1145 cm^{-1} (–C–O–C). ^1H NMR ($CDCl_3$) δ 9.80 (s, 2H, Ar–OH), 8.50 (s, 4H, –NH), 4.25 (s, 12H, Ar–CH_2–Ar (bridge) and CH_2–O–), 6.70–7.30 (s, 22H, Ar–H). ^{13}C NMR ($CDCl_3$) δ 165,162, 145, 141, 128, 123, 121, 115 and 113 (Ar–C), 23, 17.18, 12.0 (–CH2–). FAB MS (*m*/*z*) 778 (M+2).

2.3. Electrode preparation

The examination was carried out on a number of membranes prepared by varying the concentration of ionophore, plasticizer and different additives and are summarized in Table 1. The route to prepare the best PVC membrane was to mix thoroughly 30 mg of powdered poly vinyl chloride, 60 mg of plasticizer o-nitrophenyloctylether (NPOE), 4 mg of sodium tetraphenyl borate and 6 mg of ionophore. Then the mixture was dissolved in 5 mL of dry THF. The suspension was stirred until all the PVC was dissolved. The resulting solution was carefully cast into a slide glass and left standing for 24 h in a Petri dish to allow THF to evaporate slowly, until an oily concentrated mixture was obtained.

Table 1
Composition (%) of membranes and response characteristics of the electrode.

No.	Ionophore	PVC	O-NPOE	NaTPB	Slope (mV decade^{-1})	Linear range (mol L^{-1})
1	5	25	65	5	-31.1 ± 0.3	2.4×10^{-5}–1.0×10^{-2}
2	6	28	60	6	-21.9 ± 0.4	3.2×10^{-5}–1.0×10^{-1}
3	7	30	55	8	-24.0 ± 0.3	1.8×10^{-6}–1.0×10^{-1}
4	5	32	58	5	-32.8 ± 0.2	4.0×10^{-6}–1.0×10^{-2}
5	6	30	60	4	-29.4 ± 0.3	6.0×10^{-8}–1.0×10^{-1}
6	7	25	65	3	-27.3 ± 0.4	3.9×10^{-5}–1.0×10^{-1}

A final transparent membrane of about ~0.5 mm thickness was obtained. In order to avoid drastic variation in the thickness and morphology of the membrane, the viscosity of the solution and solvent evaporation was carefully controlled. The membrane was then cut to desired size and glued to one end of a Pyrex glass tube with araldite. The assembly was filled with an internal solution (1.0×10^{-3} M K_2HPO_4). The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} M K_2HPO_4 solution. Membranes that gave reproducible results as well as fast response time were selected for further studies. A silver/silver chloride electrode was used as an internal reference electrode.

2.4. Conditioning of membranes and EMF measurements

The prepared membranes were equilibrated for 2 days in different concentrations of outer solution (1.0×10^{-1}–4.0×10^{-4} M) with side by side inner solution of different concentration range (1.0×10^{-1}–1.0×10^{-3} M) of K_2HPO_4 solution. The potentials were measured by varying the concentration of monohydrogenphosphate in test solution in the range of 1.0×10^{-6}–1.0×10^{-1} mol L^{-1}. The standard monohydrogenphosphate solutions were obtained by the gradual dilution of 0.1 M monohydrogenphosphate stock solution. The best results were obtained when the concentration of inner electrolyte was 10^{-3} M.

All the EMF measurements were carried out with the following assembly:

Ag/AgCl/internal solution (1.0×10^{-3} mol L^{-1} K_2HPO_4)/PVC membrane/sample solution/Hg/Hg_2Cl_2, KCl (satd.). A Meterlab Model PHM 95 pH/ION Meter was used for potential measurements at 25 ± 1 °C.

The activities of monohydrogenphosphate were calculated according to the Debye–Huckel procedure, using the following equation [44]:

$$\log \gamma = -0.511 z^2 \left[\frac{\mu^{1/2}}{1 + 1.5\mu^{1/2}} - 0.2\mu \right]$$

where μ is the ionic strength and z the valency.

3. Results and discussion

Literature revealed that in the present Hofmeister selectivity patterns monohydrogenphosphate stands towards the end of the series, which has necessitated the development of monohydrogenphosphate selective polymeric membranes that exhibit non-Hofmeister selectivity patterns. Among several possible approaches to invert the Hofmeister behavior, the most common is the use of ionnophores suitable to form strong complexes with hydrophilic anions. Among these ionophores relevant examples relaying in metal-anion and hydrogen bonding or electrostatic interactions have been reported [35,45–50]. In the preliminary experiments, the ionophore was used as a potential ion carrier in the construction of ion-selective sensors for some common anions. The potential responses of these electrodes are shown in Fig. 1, the membrane sensor displayed outstanding selectivity for $HPO_4{}^{2-}$ ions over other anions. Such anti-Hofmeister selectivity is believed to be the result of a specific interaction between the ionophore and $HPO_4{}^{2-}$ ions. On the contrary, to check the interaction of the positive ion with the ionophore, membrane has been tested with phosphoric acid and two different phosphate salts like diammonium hydrogenphosphate and disodium hydrogenphosphate but no significant changes were found in the slope as well as in the linear range. Hence we can conclude that positive ions like $NH_4{}^{+}$ or Na^{+} were not responding to the electrode in analysis; the electrode senses only $HPO_4{}^{2-}$ ions.

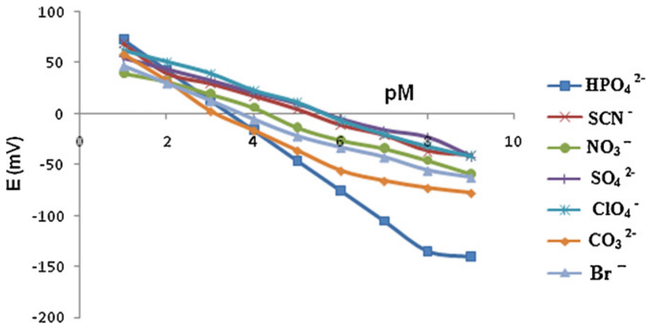


Fig. 1. Potential response of different anions on sensor.

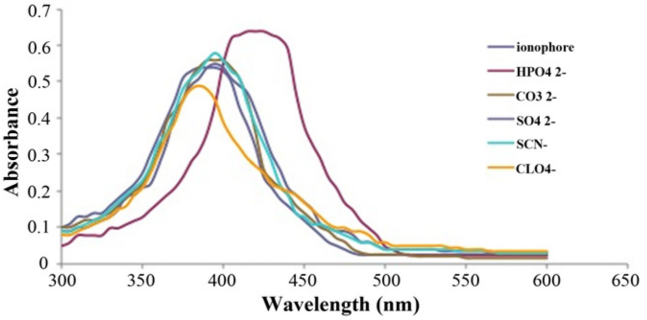


Fig. 2. UV–vis spectra of ionophore.

3.1. UV–vis study

In the preliminary experiments, the phenylurea substituted calixarenes was tested for its selectivity towards different anions with UV/vis spectral analysis, as illustrated in Fig. 2. It was likely to distinguish the interactions between the ionophore and MHP. A bathochromic shift of 32 nm in the spectra gave the evidence of interaction between the ionophore with the analyte anion ($HPO_4{}^{2-}$). At the same time, the effects of other anions such as chloride, bromide, sulfate, perclorate on the spectrum of the carrier were investigated and no detectable changes in the UV/vis spectra were noted. These results revealed that the ionophore has especial tendency to the MHP ions compared to other common anions.

3.2. Effect of the membrane composition

It is 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 [51–53]. Moreover, the effect of the presence of a lipophilic anion salt such as NaTPB into the membrane composition prepared with high molecular weight PVC was also tested.

Recently, Umezawa et al. demonstrated that anionic sites (including the sodium tetraphenylborate, NaTPB, employed in the present study) within the membrane phase can play an important role in modulating receptor protonation and thus their interaction with targeted anionic analytes. As such, they serve not only to enhance receptor protonation, they also help suppress unfavorable charge–charge repulsions between the resulting protonated receptor molecules and protons present at the interface. An excess of added anionic sites (*i.e.*, sodium tetraphenylborate) could compete with the protonated receptor and actually reverse the potentiometric response of a membrane such that it displays a cationic response rather than the expected anionic response. By decreasing the concentration of anionic sites in the membrane phase, the anionic potentiometric response resulting from the

Table 2
Performance of MHP selective electrode in partially non aqueous medium.

Non aqueous content % (v/v)	Working concentration range (M)	Slope (mV decade^{-1})
0	6.0×10^{-8}–1.0×10^{-1}	−29.40 ± 0.4
Ethanol		
10	6.0×10^{-8}–1.0×10^{-1}	−29.40 ± 0.3
20	6.0×10^{-8}–1.0×10^{-1}	−29.25 ± 0.4
25	4.2×10^{-8}–1.0×10^{-1}	−28.45 ± 0.3
30	2.5×10^{-7}–1.0×10^{-2}	−25.81 ± 0.2
Methanol		
10	6.0×10^{-8}–1.0×10^{-1}	−29.40 ± 0.4
20	6.0×10^{-8}–1.0×10^{-1}	−29.15 ± 0.2
25	5.0×10^{-8}–1.0×10^{-1}	−27.89 ± 0.3
30	1.5×10^{-7}–1.0×10^{-1}	−26.60 ± 0.3
Acetone		
10	6.0×10^{-8}–1.0×10^{-1}	−29.30 ± 0.4
20	6.0×10^{-8}–1.0×10^{-1}	−29.10 ± 0.2
25	4.5×10^{-8}–1.0×10^{-1}	−28.25 ± 0.4
30	1.0×10^{-7}–1.0×10^{-2}	−25.20 ± 0.3

receptor protonation is expected to become stronger. In contrast to what is seen with anionic sites, the presence of cationic sites was expected to enhance the discrimination between anionic interferents in accord with the number of receptor–analyte hydrogen bonds that could be stabilized.

The nature of plasticizer has been found to improve the sensitivity and stability of sensors due to characteristics such as lipophilicity, high molecular weight, low vapor pressure and high capacity to dissolve the substrate and other additives present in the polymeric membrane. PVC membranes are the ideal material due to their low electrical resistance and easiness of construction. In addition, with the membrane supported by a tough material, they are solid and not breakable. It is well known that selectivity and working concentration range of the membrane sensors are affected by the nature and the amount of the plasticizer used. This is due to the influence of the plasticizer on the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of ligands. Thus, the influence of the membrane composition, nature, and amount of plasticizer, and lipophilic additives on the potential response of the membrane was investigated. Several membranes were prepared with different compositions. The optimized membrane compositions are summarized in Table 1. The best response was observed with the membrane composed of the following ingredients: 30% PVC, 60% NPOE, 6% ionophore, 4% NaTPB resulted in a Nernstian behavior of the membrane electrode over a very wide concentration range.

3.3. *Effect of non-aqueous solvent*

The performance of the proposed membrane sensor was further assessed in partial non-aqueous media, *i.e.*, methanol–water, ethanol–water and acetone–water mixture. The results obtained are compiled in Table 2 and indicate that up to 25% of non-aqueous content, no significant change in the slope and working concentration range of the sensor is observed. At more than 30% non-aqueous medium the working range is significantly reduced, thus the sensor can only be utilized in mixtures containing up to 30% non-aqueous content.

3.4. *ISE response to phosphate*

In aqueous solution phosphates exist in various forms ($H_3PO_4 \leftrightarrow H_2PO_4^- \leftrightarrow HPO_4^{2-} \leftrightarrow PO_4^{3-}$), the prevalence of which depends on the medium, which can be distinguished by varying the pH of the solution. $H_2PO_4^-$ prevails in acidic conditions and HPO_4^{2-} is more predominant under basic conditions; at a neutral pH both forms are present. Therefore, under neutral conditions the slope of the ISE response curve can be used to indicate whether the electrode is responding to the mono or dihydrogen phosphate anion [26,35].

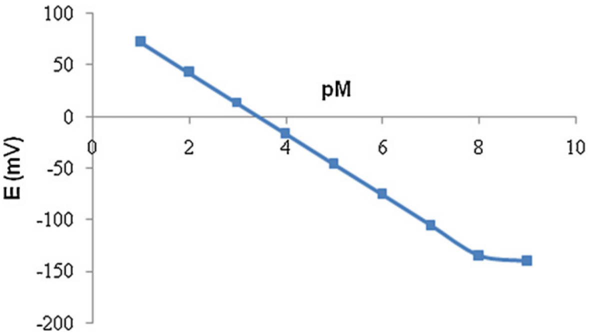


Fig. 3. Calibration curve of MHP ion-selective membrane electrode.

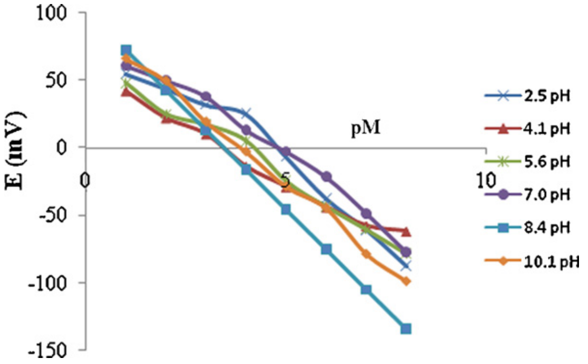


Fig. 4. Effect of pH on the potential response of the MHP ion selective electrode.

The potentiometric response of the prepared ion selective electrode was investigated against the MHP ion concentration. For this purpose, appropriate aliquots of a stock solution of MHP were introduced to the cell, and the corresponding potentials were determined. The potential readings were plotted against −log of the MHP concentration. Over the concentration range 1.0×10^{-9}–1.0×10^{-1} M of MHP in the calibration solution, the electrode potential response was linear with the concentration of MHP (Fig. 3). The calibration curve slope was −29.4 ± 0.3 mV decade^{-1} and the detection limit, calculated as recommended by the IUPAC, was 2.0×10^{-8} M [18]. The influence of the concentration of the internal solution on the potential response of the monohydrogenphosphate electrode was studied in the range 1.0×10^{-1}–1.0×10^{-4} M of HPO_4^{2-}. The results showed that the concentration of the internal solution does not cause any significant difference in the potential response of the electrodes, except for an expected change in the intercept of the resulting Nernstian plots. A 1.0×10^{-3} M concentration of the internal solution is quite suitable for smooth functioning of the electrode system.

A slope of −29.4 ± 0.3 mV decade^{-1} obtained from the calibration curve (Fig. 3) proposed that calixarene ISE respond to the monohydrogen phosphate (HPO_4^{2-}) species with a Nernstian slope value. To investigate which phosphate species the ISE membrane was responding, we adopted the procedure proposed by Carey and Riggan [16], a procedure mainly focused on the effect of pH on the function of the electrode in phosphate solutions. In order to do this, the solution pH was varied while maintaining the total phosphate concentration constant, at 4×10^{-3} M. As can be seen from the pH study (Fig. 4), the sensor at pH 8.4 (monohydrogenphosphate) shows a Nernstian response. At other values lower than

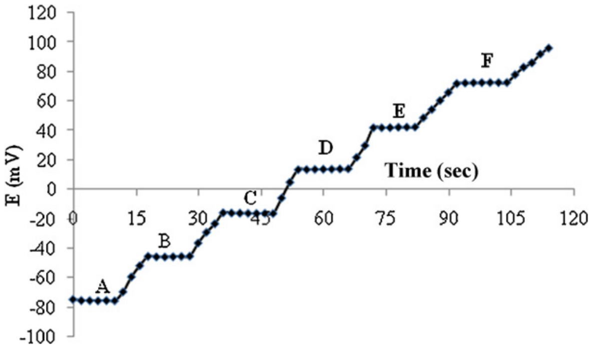


Fig. 5. Dynamic response time of the electrode for step changes in the concentration of the HPO_4^{2-} ion solution: (A) 1.0×10^{-6} M; (B) 1.0×10^{-5} M; (C) 1.0×10^{-4} M; (D) 1.0×10^{-3} M; (E) 1.0×10^{-2} M; (F) 1.0×10^{-1} M.

8.4 pH, the response of the sensor is not linear. Therefore, taking into consideration of both the factors, a Nernstian response slope and the response to pH, it can be concluded that these electrode containing ionophore respond to the dibasic HPO_4^{2-} anions.

3.5. *Response time of the electrode*

The response time is the time required for the sensors to reach 95% steady potentials after successive immersion in a series of solutions, each having a 10-fold difference in concentration. The average time that was required for the HPO_4^{2-} sensor to reach a potential within ±1 mV of the final equilibrium value was measured. In this study, the practical response time was recorded by changing with different monohydrogenphosphate ion concentrations (1.0×10^{-6}–1.0×10^{-1} M). In the first case the measurement sequence was from the lower to higher concentrations. After each measurement, the solution was rapidly changed. Such a change required nearly 8 s. The actual potential versus time curve is shown in Fig. 5 and it can be seen that the electrode reached the equilibrium response in a very short time of about 8 s. To evaluate the reversibility of the electrode, a similar procedure was adopted in the opposite direction. The measurements were performed in the sequence of high-to-low sample concentrations and the results displayed that the potentiometric response of the sensor was reversible, although the time needed to reach the equilibrium values was longer than that for the low-to-high sample concentration procedure (25 s).

3.6. *Life time of the ion selective electrode*

The investigational result shows that the lifetime of MHP membrane sensor is 15 weeks. During this period, the electrode was in daily use over an extended period of the time (1 h per day), there was no deviation in electrode features and the results are given in Table 3. After 15 weeks, a gradual decrease in the slope and detection limit was observed.

Table 3
Lifetime behavior of MHP ion selective electrode.

Week	Slope (mV decade^{-1})	Linear range (M)
1	−29.4 ± 0.3	6.0×10^{-8}–1.0×10^{-1}
2	−29.4 ± 0.2	6.0×10^{-8}–1.0×10^{-1}
5	−29.4 ± 0.3	6.0×10^{-8}–1.0×10^{-1}
7	−29.4 ± 0.4	5.0×10^{-8}–1.0×10^{-1}
9	−29.4 ± 0.2	5.0×10^{-8}–1.0×10^{-1}
11	−29.2 ± 0.4	4.0×10^{-8}–1.0×10^{-1}
13	−29.2 ± 0.4	3.0×10^{-8}–1.0×10^{-1}
15	−29.0 ± 0.2	1.0×10^{-8}–1.0×10^{-1}
17	−27.5 ± 0.3	3.0×10^{-7}–1.0×10^{-2}

Table 4
Selectivity coefficients of various interfering ions.

Interfering ions	log $K^{\mathrm{MPM}}_{\mathrm{HPO_4^{2-}},B}$	Interfering ions	log $K^{\mathrm{MPM}}_{\mathrm{HPO_4^{2-}},B}$
F^-	−3.65	SO_4^{2-}	−2.9
Cl^-	−2.8	$H_2PO_4^-$	−3.5
Br^-	−3.5	CO_3^{2-}	−2.86
I^-	−1.2	Oxalate	−1.5
SCN^-	−4.25	NO_3^-	−4.1
Citrate	−3.1	ClO_4^-	−3.7

3.7. *Sensor selectivity*

The selectivity behavior is apparently one of the most vital characteristics of an ion-selective electrode, which is usually expressed in the term of selectivity coefficient, which is evaluated using match potential method (MPM) recommended by IUPAC [54–56]. Different methods of selectivity determination have been found in the literature, after the narrative work done by Umezawa et al. [57,58]. In the present study, the selectivity coefficients have been evaluated using modified form of fixed interference method at 1.0×10^{-2} M concentration of interfering ions as per IUPAC recommendation. In this method, the electromotive force (EMF) values were measured for solutions of constant activity of the interfering ion, a_B and varying activity of the primary ion, a_A in a cell comprising of an ion-selective electrode and a reference electrode. The EMF values obtained were plotted versus the logarithm of the activity of the primary ion. The intersection of the extrapolated linear portions of the plot indicates the value of a_A that is to be used to calculate the potential from the following equation:

$$K^{\mathrm{pot}}_{A,B} = \frac{\Delta a_A}{a_B} = \frac{a'_A - a_A}{a_B}$$

A specified activity of the primary ions (A: 1.0×10^{-3} M of HPO_4^{2-} ions) is added to a reference solution (1.0×10^{-6} M of HPO_4^{2-} ions) and the potential is measured. In a separate experiment, interfering ions (B: 1.0×10^{-5}–1.0×10^{-1} M) are successively added to an identical reference solution, until the measured potential matches the one obtained before the primary ion addition. The consequential selectivity coefficient values are summarized in Table 4. The data given in this table present the selectivity coefficients of the proposed MHP membrane sensor for all the tested anions. This seems to indicate negligible interferences in the performance of the electrode assembly. As can be seen from Table 4, among the anions, iodide and oxalate were the major interfering ions in the determination of HPO_4^{2-} ions. For the other lower selectivity coefficient values, it was considered that the function of the MHP selective membrane sensor would not be greatly disturbed.

3.8. *Ion–ionophore binding mode*

Calixarenes can be chemically modified by substitution of the phenolic hydrogens with various functionalities known for their affinity to anions of interest. Anion recognition is associated with the shape of anion, and anion requires a receptor with specific size and shape. Calixarene based anion receptors are important when considering their binding interactions with anions. With regard to the binding mode of the HPO_4^{2-} anion to these calixarene molecule, the target anions coordinate to the urea moiety of the calixarene molecule through hydrogen-bonding interactions to the protons of these groups, and perhaps favour anions with a tetrahedral or spherical geometry to some extent. HPO_4^{2-} is tetrahedral in shape and therefore is likely to bind with calixarene through hydrogen bonding (Fig. 6). This was supported by the findings of Lhotak et al. [59] and Evans et al. [60]. In the case of ferrocene functionalised calix[4]arene molecule [59] and ureido-thiacalix[4]arene

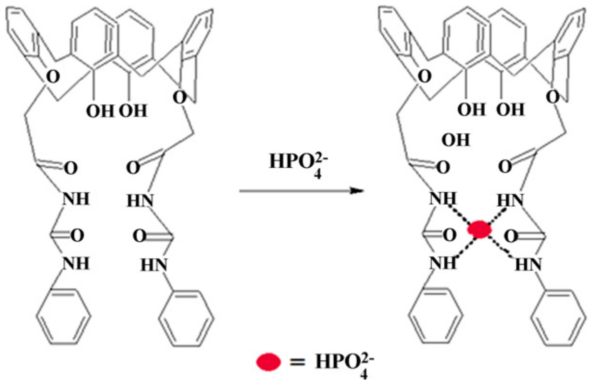


Fig. 6. Ion–ionophore binding mode.

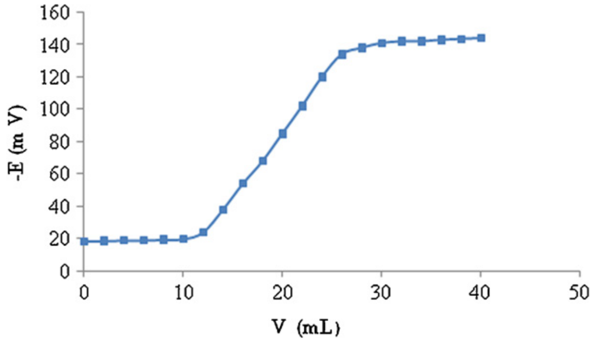


Fig. 7. Potentiometric titration curve of 25.0 mL $HPO_4{}^{2-}$ (1.0×10^{-3} mol L^{-1}) with 10^{-2} mol L^{-1} Ba^{2+} using the membrane as an indicator electrode in pH 9.

[60] functionality, the molecule binds to phosphate through hydrogen bonding. The same was observed during our investigation on the interaction of dihydrogen phosphate with crown ether based fullerobis–pyrrolidine [39].

3.9. Analytical application

The monohydrogenphosphate sensor was found to work well under laboratory conditions. It was used as an indicator electrode in the successful titration of a 25 mL phosphate ion solution (1.0×10^{-4} M) with the Ba^{2+} ion (1.0×10^{-2} M), at pH 9.0, and the results is shown in Fig. 7, the sharp break point corresponds to the stoichiometry of the MHP–Ba precipitate ($BaHPO_4$). So, the amount of barium ion can be determined with the sensor within acceptable accuracy.

To evaluate the practical applicability of the sensor in real samples, an attempt was made to determine MHP in the three phosphate fertilizer samples, like mixed nitrogen phosphate potassium fertilizer (NPK), triple super phosphate (TSP), and single super phosphate (SSP), and the results are given in Table 5. An amount of 0.1 g of each fertilizer was taken and dissolved in water in a 100 mL volumetric flask, and 10.0 mL of 0.01 M EDTA (pH of 10.0) was added and diluted to the mark with Milli-Q water. Before the analysis was carried out all the samples have been filtered through 0.45 μm filter. The phosphate content of the final solution was determined by the proposed sensor using the calibration curve method. The results obtained by the MHP sensor and colorimetric method are given in Table 5. As can be seen, there is a satisfactory agreement between both methods.

The proposed membrane sensor was also applied for the fast and direct potentiometric determination of phosphate ion concentration in three different kinds of detergents. 0.1 g of each detergent powder was dissolved in distilled water in a 100 mL volumetric flask, and 10.0 mL of 0.1 M EDTA (pH of 10.0) was added to the flask and the resulted solution was diluted to the mark with distilled water. Before the analysis was carried out all the samples were

Table 5
Determination of MHP in various fertilizer samples using proposed sensor.

Sample no.	Sample name	ISE (%)	Colorimetric (%)
1		10.42 ± 0.15	10.18 ± 0.06
2	NPK	10.15 ± 0.22	10.04 ± 0.15
3		10.85 ± 0.18	10.80 ± 0.10
1		42.20 ± 0.35	42.10 ± 0.15
2	TSP	43.00 ± 0.20	42.45 ± 0.30
3		42.70 ± 0.17	42.52 ± 0.35
1		18.50 ± 0.40	18.30 ± 0.35
2	SSP	18.72 ± 0.65	18.50 ± 0.09
3		18.35 ± 0.30	18.10 ± 0.20

Table 6
Determination of MHP in various detergent samples using proposed sensor.

Detergent sample	ISE (%)	Colorimetry (%)
A	19.50 ± 0.40	19.35 ± 0.08
B	12.95 ± 0.25	12.45 ± 0.20
C	15. 21 ± 0.30	15.80 ± 0.40

Table 7
Determination of MHP in spiked water samples using proposed sensor.

Sample	Added (μg L^{-1})	Found by proposed sensor (μg L^{-1})	Found by colorimetric (μg L^{-1})
Tape water	20.00	20.35	19.86
Kankaria lake water	75.00	74.80	74.75
Industrial waste water	50.00	51.15	50.92
Vatva G.I.D.C. waste water	120.00	121.36	121.43

Table 8
Comparison of proposed electrode with previous reported electrode.

Sr. no.	Name of Sensor	Working concentration range	Detection limit	Slope	Life time (Days)	Response time	Reference
1	–	5.0×10^{-5}–1.0×10^{-1}	1.0×10^{-5}	−28.0	N.R[a]	N.R[a]	[22]
2	Vanadyl salophen (VNSP)	1.0×10^{-6}–1.0×10^{-1}	5.0×10^{-7}	−30.1 ± 0.6	98	<20	[23]
3	Molybdenum bis(2-hydroxyanil) acetylacetonate complex (MAA)	1.0×10^{-7}–1.0×10^{-1}	6.0×10^{-8}	−29.5 ± 0.3	70	<8	[24]
4	Vanadyl salen complex (VS)	5.0×10^{-6}–1×10^{-1}	3.0×10^{-6}	−28.8	56	<25	[25]
Proposed sensor	Phenyl urea substituted calix[4]arene	6.0×10^{-8}–1.0×10^{-1}	2.0×10^{-8}	−29.4 ± 0.3	105	<8	

[a] N.R: not reported.

filtered through 0.45 μm filter. The monohydrogen phosphate concentration of the final solutions, were determined by the proposed sensor, using the calibration method. The results that obtained by the sensor and spectrophotometric methods are given in Table 6. As seen, there is a satisfactory agreement between both methods.

The present membrane sensor was successfully used in the potentiometric determination of MHP in spiked water samples. The water samples which have been collected from the different areas of Ahmedabad city like vatva G.I.D.C., Naroda industrial estate and Kankaria Lake were prepared by the addition of 120, 50 and 75 μg L^{-1} MHP in a 100 mL volumetric flask. To this solution 10.0 mL of 0.1 M EDTA (pH of 10.0) was added to the flask and diluted to the mark with distilled water. Before the analysis was carried out all the samples were filtered through 0.45 μm filter. The concentration of each sample was measured by the monohydrogenphosphate sensor, using the calibration method. The results obtained by the direct potentiometry and spectrophotometry are depicted in Table 7. As can be seen, there is a good correlation between the both methods. Thus, the proposed sensor is better than previously reported MHP selective membrane sensor (Table 8), not only in the terms of detection limit and dynamic range but also in terms of selectivity coefficients.

4. Conclusion

In summary, a simple construction procedure was used to develop ion selective electrodes for the detection of monohydrogenphosphate (MHP) ions at low concentration. The electrode responded to monohydrogenphosphate ion in a Nernstian fashion. The electrode characteristics such as pH range, lower detection limit, response time and selectivity were comparable to the previously reported monohydrogenphosphate ion-selective electrodes. The electrode can be successfully applied as the indicator electrode to determine the end point in the potentiometric titration of Ba^{2+} ions and also for the estimation of MHP ions in real environmental (industrial waste, tap and lake water) samples.

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