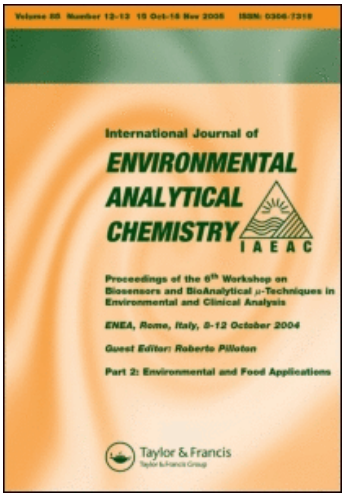

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Calcium(II)-selective potentiometric sensor based on p-isopropylcalix6arene in PVC matrix

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Calcium(II)-selective potentiometric sensor based on *p*-isopropylcalix[6]arene in PVC matrix

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A new PVC-based membrane using *p*-isopropylcalix[6]arene (**I**) as an ionophore has been developed as a calcium-ion-selective sensor. Among various membranes prepared with and without plasticizer, the best performance was shown by a membrane with a composition (mg) I : NaTPB : PVC (2 : 2 : 120). This sensor exhibits a good potentiometric response to Ca^{2+} ion over a wide concentration range (3.9×10^{-6} to 1×10^{-1} M) with a near Nernstian slope (30 mV per decade of activity) and response time of 15 s. The sensor can be used for a period of 3 months without any drift in potential. The selectivity coefficient values are in the order of 1.0×10^{-3} for mono-, bi-, and trivalent cations, which indicates a good selectivity for Ca^{2+} ion. The useful pH range for the electrode was found to be 2.5–6.0, and it works well in mixtures with non-aqueous content up to 25% (v/v). The sensor can also be used successfully as an indicator electrode in the potentiometric titration of Ca^{2+} against EDTA.

Keywords: Potentiometry; Calixarenes; Calcium; Polyvinyl chloride; Ion-selective sensor

1. Introduction

Calcium is one of the most important elements for the growth and maintenance of human body. It is present in milk, meat, vegetables, etc., and it is accumulated in animals in the form of calcium phosphate in bones and teeth. In view of its importance, it is important to determine its concentration in biological and environmental samples [1–3]. A number of sophisticated techniques, such as atomic absorption spectrometry (AAS) [4], electrochemical impedance spectroscopy (EIS) [5], and differential scanning calorimetry (DSC) [6], are currently in use for detecting metal ions. These methods generally require sample pretreatment and infrastructure backup, and are not very convenient for the routine analysis of a large number of environmental samples.

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Ion-selective sensors are potential tools that can overcome these limitations. A number of Ca^{2+}-selective sensors have been developed using *bis*-di [4-(1,1,3,3-tetramethylbutyl) phenyl] phosphoric acid [2,7], *bis* (dialkylphosphate) [8], ETH 129 [9–11], ETH 1001 [9, 11–15], *N*-ethyl-*N*-(2-trimethyl ammonium methyl)-*N*′-heptyl-*N*′-methylsuccinamide [16], dibenzo-18-crown-6 [17], 2-[(2-hydroxyphenyl) imino]-1,2-diphenylethanone [18], tetronasin antibiotic [19], calix[4]arene tetraphosphine oxide[20], nitrated(octaphenyl)-phosphate [21], di (2-ethylhexyl)phosphate [22], poly(methylmethacrylate)/poly(decyl-methacrylate) copolymer [23] and *p*-isopropyl calix[n]arene (n-4, 6, 8) [24] as electroactive materials. Many of these sensors do not show a high selectivity and wide working concentration range, and have a slow response time. Therefore, efforts are still needed to develop a good selective sensor for calcium.

Calixarenes are synthetic macrocycles derived from the condensation of phenols and formaldehydes which, depending on the number of aromatic units in the cyclic array and on the functionalization at the phenolic oxygen atoms (lower or narrow rim), have a hydrophobic cavity capable of encapsulating a variety of ionic and neutral guest species. The introduction of suitable donor groups at the lower rim of calixarenes produces a range of phenolate type metallic compounds, as well as coordination complexes. In addition to the lower rim, calixarenes have reactive *para* positions on the aromatic nuclei (upper or wide rim), which can be used for anchoring binding groups, catalytic centres or other functional units. Their unique three-dimensional structures with almost unlimited derivatization abilities and a tunable shape of the molecules make calixarenes as ideal candidates for building blocks and/or molecular scaffolds in the designing of new and more sophisticated molecules [25, 26]. These can bind metal ions by means of ionic interactions (phenolate-type), coordination, n and π arene interactions. In view of this fact, a variety of calixarene-based ion-selective sensors have been developed for a number of cations [27, 28]. Calixarenes have shown a high affinity for alkali and alkaline earth metal ions as compared with transition metal ions [29]. In this article, efforts have been made to develop a calcium(II)-selective sensor by incorporating *p*-isopropylcalix[6]arene as the sensing ionophore in a PVC membrane. The results showed that the sensor is highly selective and sensitive for calcium ion.

2. Experimental

2.1 *Reagents*

All reagents were of analytical grade and used without further purification. *p*-Isopropylcalix[6]arene (**I**) (figure 1) was obtained from Acros Organics (Pittsburgh, PA). High-molecular-weight polyvinyl chloride (PVC) (molecular weight 188,000), Aldrich (Milwaukee, WI); sodium tetraphenylborate (NaTPB), and tri-*n*-butylphosphate (TBP), BDH (Poole, UK); diethylphthalate (DEP), E. Merck, Germany, dioctyl phthalate (DOP) Riedel (New Delhi, India); were used as obtained. Analytical reagent-grade tetrahydrofuran (THF), nitric acid and sodium hydroxide were obtained from Ranbaxy (New Delhi, India). Solutions of metal (nitrates) were prepared in double-distilled water and standardized by the reported methods wherever necessary. Working solutions of different concentrations were prepared by diluting 0.1 M stock solutions.

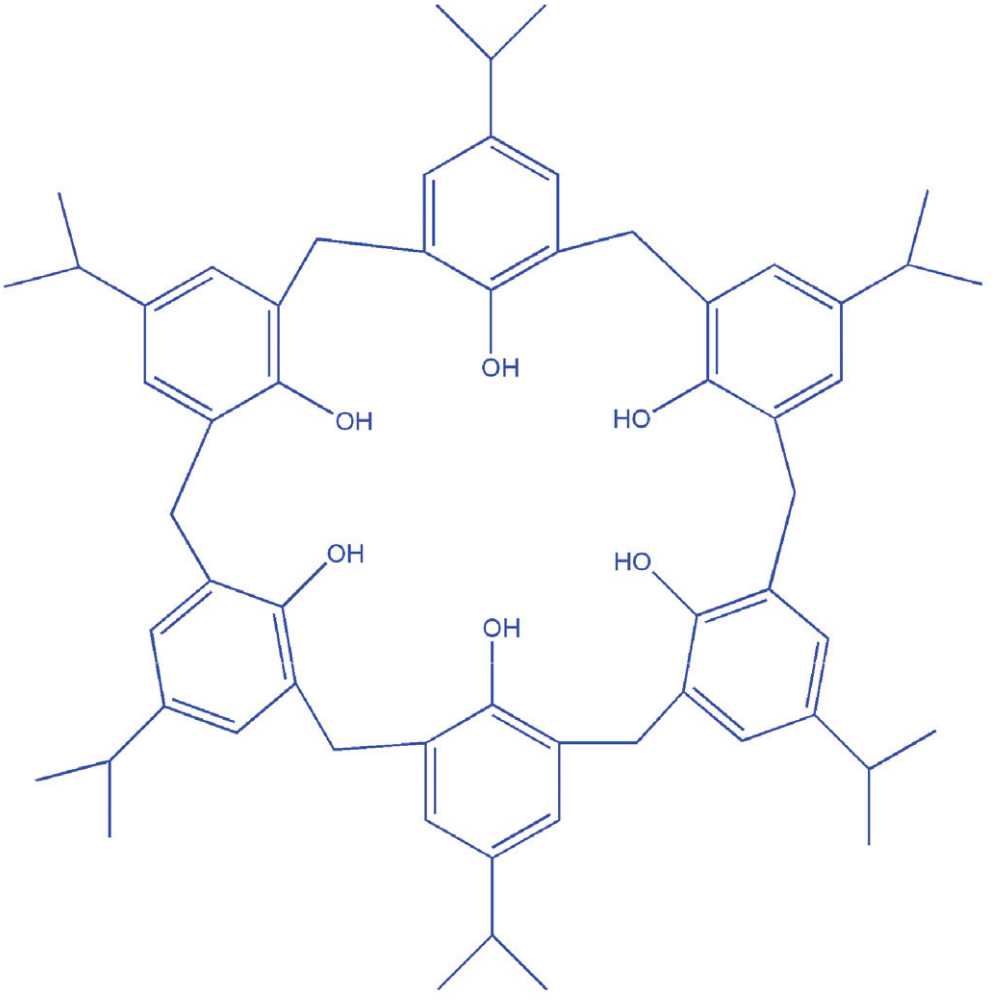

Figure 1. Structure of *p*-isopropylcalix[6]arene.

2.2 *Preparation of membranes*

The PVC-based membranes were prepared by dissolving *p*-isopropylcalix[6]arene (w/w 1%), anion excluder NaTPB (w/w 1%), solvent mediators (TBP, DEP, and DOP) (w/w 66%), and PVC (w/w 33%) in THF (10 mL). After complete dissolution of all the components and thorough mixing, a homogeneous mixture was poured into a polyacrylate ring placed on a smooth glass plate. THF was allowed to evaporate for about 24 h at room temperature. Solvent evaporation was carefully controlled; otherwise, the morphology and thickness of the membranes would show a significant variation, which could affect the sensor response. The transparent membranes (0.5 mm in thickness) were carefully removed from the glass plate. A 5-mm-diameter piece was cut out and glued to one end of a 'Pyrex' glass tube. The membranes thus prepared were equilibrated for 3 days in 0.5 M Ca^{2+} solution.

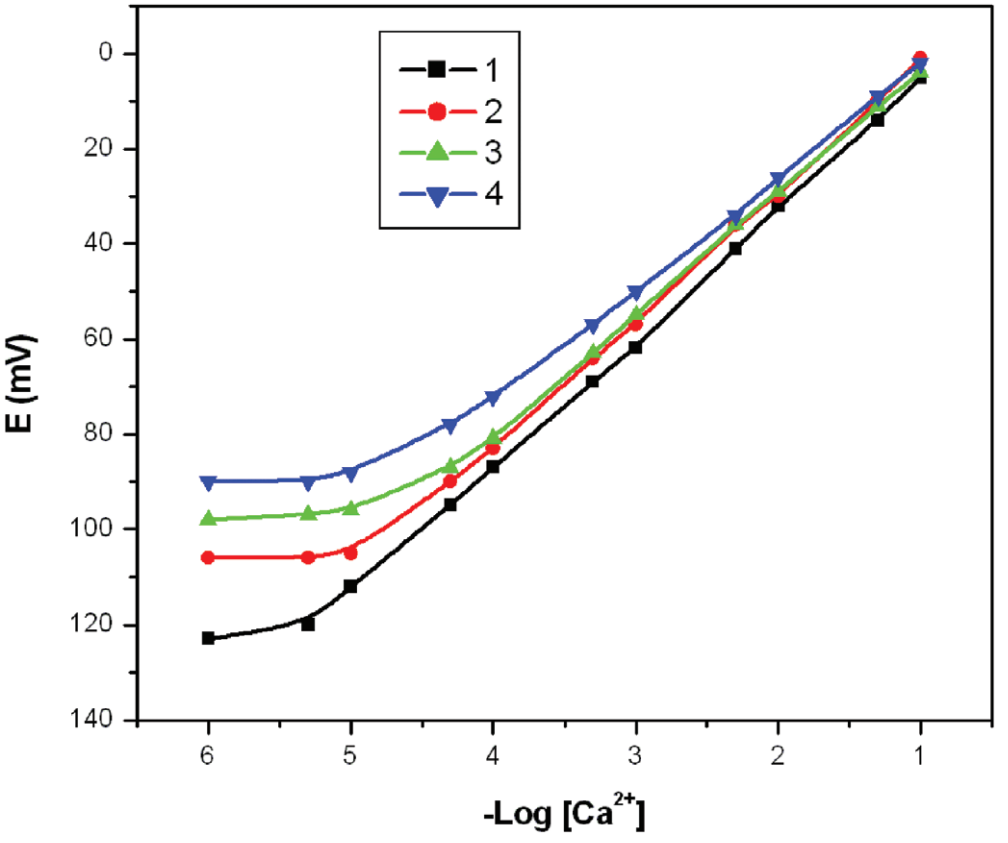

Figure 2. Variation of membrane potential with activity of Ca^{2+} ions of PVC-based membranes of (**I**) without plasticizer (1) and with plasticizers, TBP (2), DEP (3), and DOP (4).

2.3 *Apparatus and potential measurements*

The potential and pH measurements were carried out at 25 ± 0.1°C with a digital potentiometer (Model 5652 A, ECIL, Hyderabad, India) and Century Microvoltmeter (Model CVM 301, Chandigarh, India) by setting up the following cell assembly, employing saturated calomel electrodes (SCE) as reference electrodes: SCE/internal solution (0.1 M, Ca^{2+})/membrane/test solutions/SCE.

The ionic strength of the solution was maintained using 0.1 M NaCl solution.

3. Results and discussion

3.1 *Working concentration range and slope*

The potential of the membranes of (**I**) was investigated as a function of Ca^{2+} concentration in the range of 1.0×10^{-6} to 1.0×10^{-1} M, and the results obtained are shown in figure 2. From this plot, the working concentration ranges and slopes have

Table 1. Composition of PVC membranes of *p*-isopropylcalix[6]arenes (I) and performance characteristics of Ca^{2+}-selective sensors based on them.

Sensor no.	Composition of membranes (mg)						Working concentration range (M)	Slope (mV per decade of conc.)	Response time (s)
	I	PVC	NaTPB	TBP	DEP	DOP			
1	2	120	2				3.9×10^{-6} to 1.0×10^{-1}	30 ± 0.2	15
2	2	120	2	120			1.1×10^{-5} to 1.0×10^{-1}	27 ± 0.4	35
3	2	120	2		120		1.6×10^{-5} to 1.0×10^{-1}	25 ± 0.3	28
4	2	120	2			120	2.0×10^{-5} to 1.0×10^{-1}	26 ± 0.4	32

Table 2. Effect of internal solution on the performance of sensor no. 1.

Serial no.	Internal solution concentration (M)	Working concentration range (M)	Slope (mV per decade of concentration)	Response time (s)
1	1.0×10^{-2}	1.0×10^{-5} to 1.0×10^{-2}	28 ± 0.3	17
2	5.0×10^{-2}	5.6×10^{-6} to 5.0×10^{-2}	30 ± 0.2	17
3	1.0×10^{-1}	3.9×10^{-6} to 1.0×10^{-1}	30 ± 0.2	15

been determined and compiled in table 1. It can be seen from figure 2 that sensor no. 1, which has the membrane of (I) without plasticizer, exhibits a linear response to log $[Ca^{2+}]$ over a working concentration range of 3.2×10^{-6} to 1.0×10^{-1} M with a slope of 30 mV per decade of concentration. Lipophilic NaTPB salt (sodium tetraphenylborate) was added to reduce the anionic interference and to lower the electrical resistance of the membrane. The effect of plasticizer on the performance of the membrane was studied by the addition of appropriate amount of plasticizer to the membranes. It can be seen from table 2 that the addition of different plasticizers to the membrane has deteriorated its performance. The membranes containing TBP, DEP, and DOP plasticizer showed a reduced working concentration range of 1.1×10^{-5} to 1.0×10^{-1}, 1.6×10^{-5}, 1.0×10^{-1}, and 2.0×10^{-5} to 1.0×10^{-1} M with a non-Nernstian slope of 27, 25, and 26 mV per decade of activity, respectively. As such, membrane no. 1 without plasticizer and having a composition of (mg) of I : NaTPB : PVC (2 : 2 : 120), which gave the best performance (widest working concentration range and near Nernstian slope), was used for further studies.

3.2 *Effect of internal solution*

In accord with the generally adopted ion sensor response formalism, the concentration of internal solution may affect the sensor response. Thus, the effect of concentration of the internal solution on the functioning of the membrane sensors was studied. The potentials were measured by varying the internal solution concentration, viz. 1.0×10^{-2}, 5.0×10^{-2}, and 1.0×10^{-1} M Ca^{2+}. It was found that the best results in terms of slope and working concentration range were obtained with an internal solution of concentration 1.0×10^{-1} M (table 2). Thus, the concentration of the internal solution was kept at 1.0×10^{-1} M in all studies.

3.3 *Response and lifetime*

The response time has been measured as the time taken by the sensor to attain a stable potential, and their values are included in table 1. The lowest response time (15 s) was obtained for sensor no. 1, which had a membrane without plasticizer. The plasticized membranes (nos 2–4) showed a higher response time of 35, 28, and 32s, respectively. The membranes were used over a period of 3 months without any significant change in the value of slope or working concentration range. The sensing behaviour of the membrane remained reasonably constant over a period of 3 months, beyond which a drift in potentials was observed because the membrane became mechanically weak and swelled up, leading to leaching of ions from the membrane phase. However, they were stored in 0.5 M Ca^{2+} solutions when not in use.

3.4 *Effect of pH and solvent*

In order to investigate the pH effect on the electrode response, the potential was measured at the fixed concentration of Ca^{2+} solution, i.e. 1.0×10^{-3} M, with different pH values, and the results are shown in figure 3. The pH was adjusted by adding small volumes of dilute nitric acid or sodium hydroxide solutions. It can be seen that a useful pH range for this sensor is 2.5–6.0 because, in this range, the potential remains constant. The change in potential below pH 2.5 and above pH 6.0 is due to H^+ ions cofluxing and hydrolysis of Ca^{2+} ions, respectively. The performance of the sensor

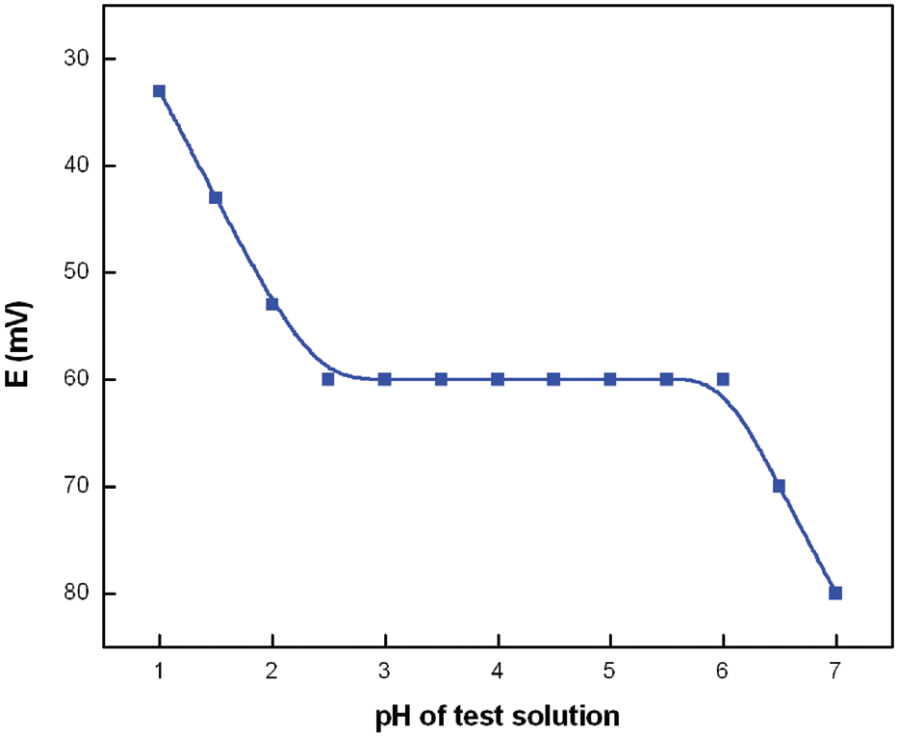

Figure 3. Effect of pH on cell potential; $[Ca^{2+}] = 1.0 \times 10^{-3}$ M.

was also investigated in a partially non-aqueous medium using methanol–water, ethanol–water, and acetone–water mixtures. Thus, the electrode response was determined in 10, 20, 25, and 30% (v/v) methanol–water, ethanol–water, and acetone mixtures, and the results are given in figures 4–6. From these plots, working concentration ranges and slopes were evaluated, and these are compiled in table 3. It can be seen from the table that the electrode worked satisfactorily in a partially non-aqueous medium up to 25% (v/v) non-aqueous content. The membranes were mechanically and chemically stable up to 25% (v/v) non-aqueous content. Above this non-aqueous content, the performance was not satisfactory, as the slope had reduced, and the working concentration range was shortened.

3.5 *Potentiometric selectivity*

Selectivity is the most important characteristic of any sensor, defining the extent to which it may be employed in the determination of particular ion (primary ion) in the presence of other interfering ions. In order to investigate the selectivity of the sensor, its response was examined in the presence of various ions by the IUPAC recommended Matched Potential Method (MPM) [30] as well as by the Fixed Interference Method (FIM) [31]. In the MPM method, the selectivity coefficient K_{AB}^{Pot} is given by equation (1) and is determined by measuring the change in potential upon increasing by a definite amount the primary ion activity from an initial value of a_A to a_A^I, and a_B represents the

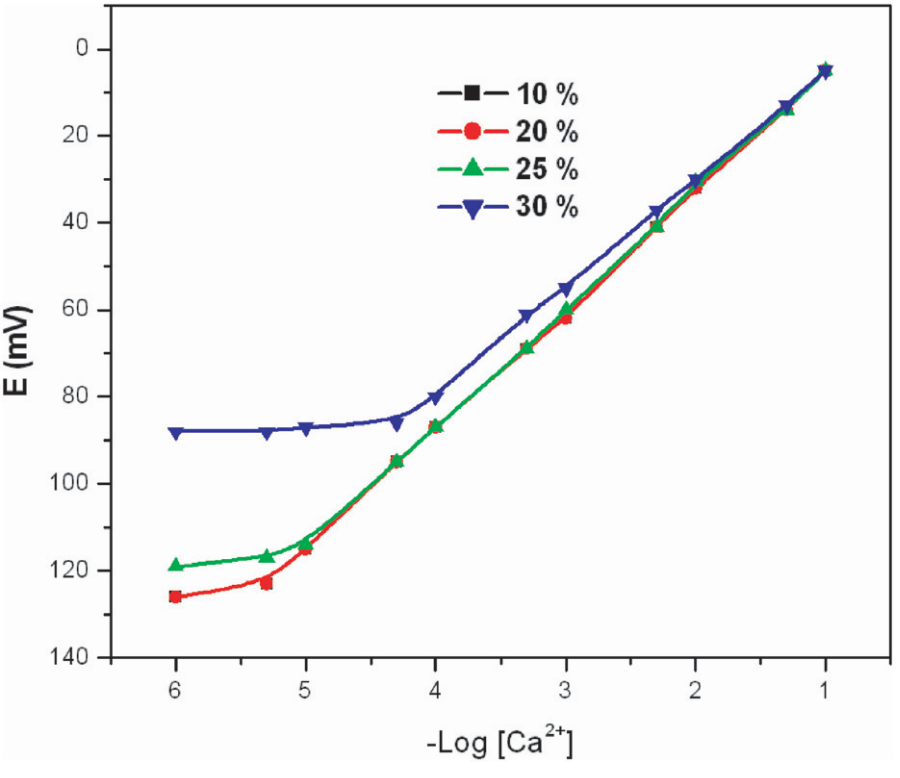

Figure 4. Potential response of the sensor in the presence of 10, 20, 25, and 30% methanol.

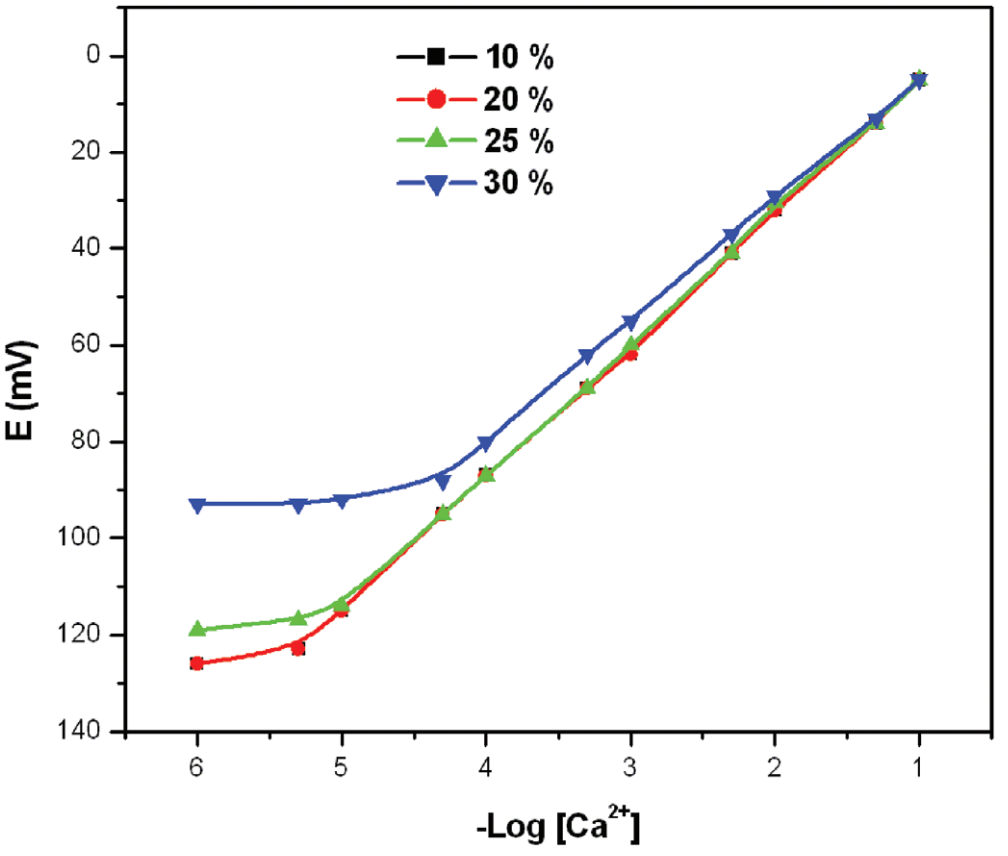

Figure 5. Potential response of the sensor in the presence of 10, 20, 25, and 30% ethanol.

activity of the interfering ion added to same reference solution of activity a_A, which brings about the same potential change:

$$K_{A,B}^{Pot} = \frac{a'_A - a_A}{a_B} = \frac{\Delta a_A}{a_B}. \quad (1)$$

In the present study, the primary ion activity was increased from 1.0×10^{-5} to 3.0×10^{-5} M, and the activity of the interfering ions was experimentally determined. In FIM, the concentration of the interfering ion was kept at 1.0×10^{-2} M, whereas that of the primary ion was varied from 1.0×10^{-6} to 1.0×10^{-1} M, and potential measurements were made. Before taking any potential measurements, the membranes were equilibrated in 0.5 M Ca^{2+} solution for 3 days. The selectivity coefficients thus determined by MPM and FIM are summarized in the form of logarithmic values in table 4. A selectivity coefficient value of 1.0 indicates that the membrane responds equally to primary as well as interfering ions. A value smaller than 1.0 indicates that it responds more to primary ions than to interfering ions, and in such a case, the sensor is said to be selective to primary ions over interfering ions. Furthermore, the smaller the selectivity coefficient value, the higher the selectivity order. It can be seen from the table that selectivity coefficients are in the order of 10^{-3} or lower for almost all

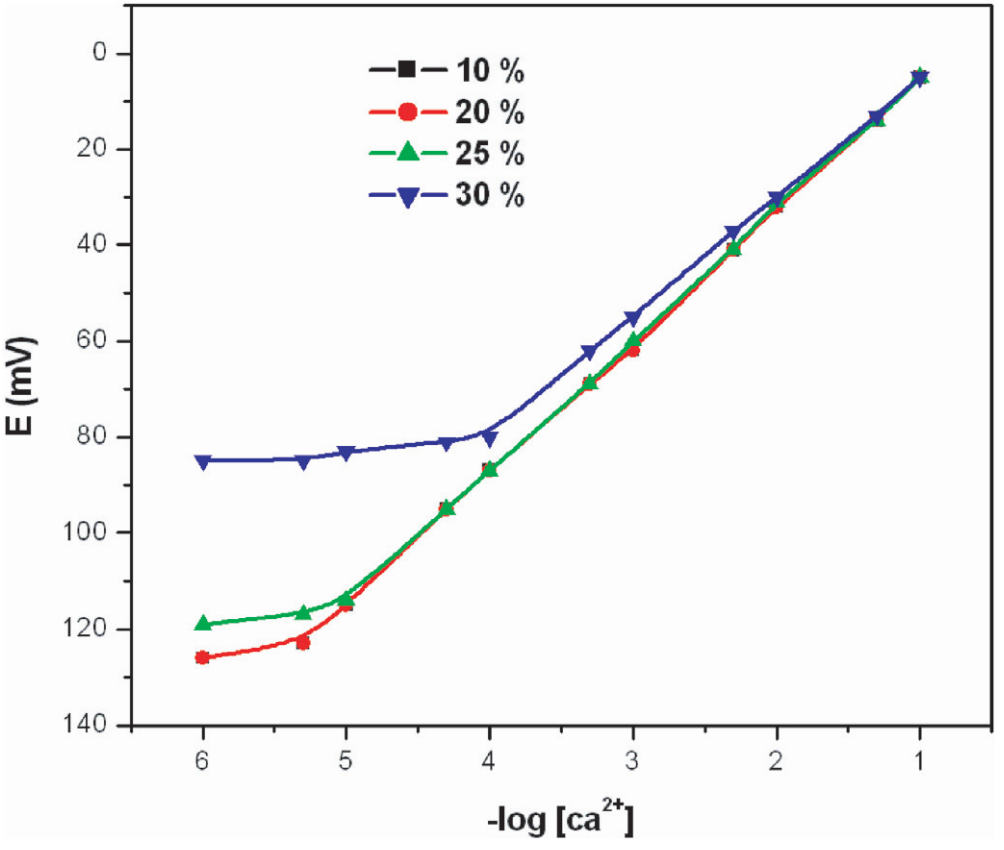

Figure 6. Potential response of the sensor in the presence of 10, 20, 25, and 30% acetone.

Table 3. Performance of Ca^{2+}-selective sensor no. 1 in non-aqueous media.

Non-aqueous content (% v/v)	Slope ± 0.2, mV per decade of activity	Working concentration range (M)
0	30.0	3.9×10^{-6} to 1.0×10^{-1}
Methanol		
10	30.0	3.9×10^{-6} to 1.0×10^{-1}
20	30.0	3.9×10^{-6} to 1.0×10^{-1}
25	29.5	4.0×10^{-6} to 1.0×10^{-1}
30	25.0	5.0×10^{-5} to 1.0×10^{-1}
Ethanol		
10	30.0	3.9×10^{-6} to 1.0×10^{-1}
20	30.0	3.9×10^{-6} to 1.0×10^{-1}
25	29.6	4.1×10^{-6} to 1.0×10^{-1}
30	26.0	4.8×10^{-5} to 1.0×10^{-1}
Acetone		
10	30.0	3.9×10^{-6} to 1.0×10^{-1}
20	30.0	3.9×10^{-6} to 1.0×10^{-1}
25	29.0	4.1×10^{-6} to 1.0×10^{-1}
30	25.0	5.2×10^{-5} to 1.0×10^{-1}

Table 4. Selectivity coefficients of sensor no. 1 as determined by the Fixed Interference Method (FIM) and Matched Potential Method (MPM).

	Selectivity coefficient ($\log k^{pot}_{ca,B}$)	
Interfering ion (B)	FIM	MPM
Li^{+}	−2.65	−2.92
Na^{+}	−2.30	−2.69
K^{+}	−2.50	−2.85
Rb^{+}	−2.72	−3.06
Cs^{+}	−2.60	−2.82
Mg^{2+}	−2.15	−2.30
Sr^{2+}	−2.25	−2.58
NH^{4+}	−2.44	−2.79
Cu^{2+}	−2.05	−2.22
Co^{2+}	−2.30	−2.49
Zn^{2+}	−2.20	−2.33
Cd^{2+}	−2.25	−2.45
Ni^{2+}	−2.20	−2.37
Pb^{2+}	−2.25	−2.46
Mn^{2+}	−1.25	−1.52
Hg^{2+}	−1.55	−2.00
Ag+	−1.92	−2.03
Cr^{3+}	−1.58	−2.01
Fe^{3+}	−1.92	−2.02
Al^{3+}	−2.52	−2.88

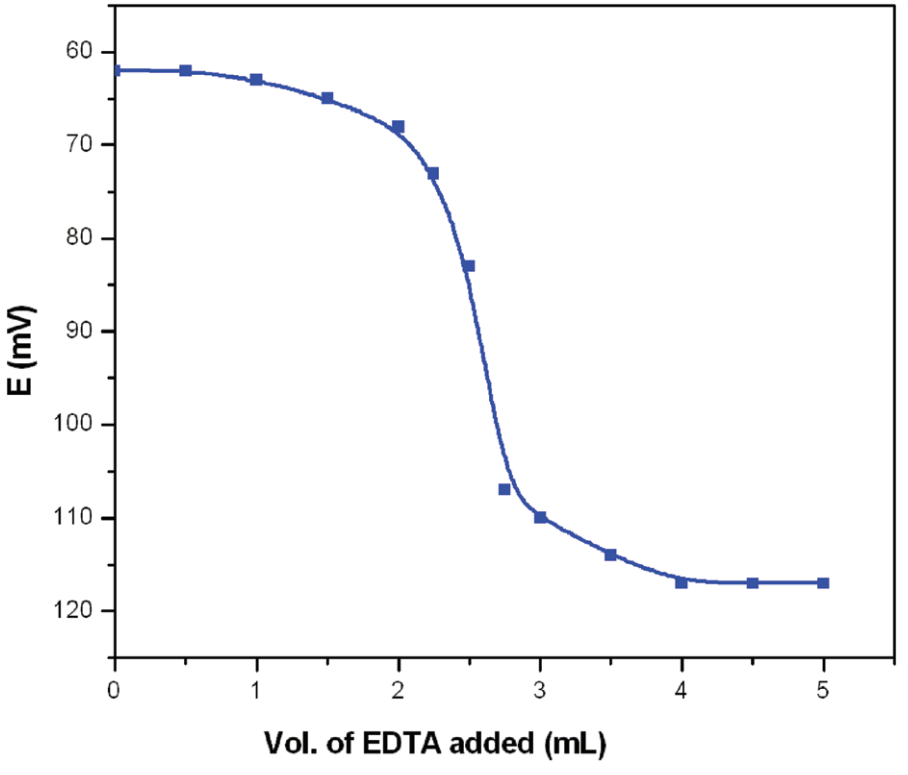

Figure 7. Potentiometric titration curve of 25 mL of Ca^{2+} (1.0×10^{-3} M) with EDTA solution.

Table 5. Comparison of the proposed Ca^{2+} sensor with reported electrodes[a].

Serial no.	Working concentration range (M)	Slope (mV per decade of activity)	pH range	Response time (s)	Life time (months)	Interfering ion	Reference
1	5.0×10^{-6} to 8.0×10^{-2}	26	3.5–10.0	NM	8	Mg^{2+}	[7]
2	1.0×10^{-5} to 1.0×10^{-1}	29	3.0–10.0	NM	12	Ba^{2+}, Mg^{2+}, Ni^{2+}, Fe^{3+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}	[8]
3	2.0×10^{-5} to 3.0×10^{-4}	22.2	NM	NM	NM	Mg^{2+}	[9]
4	1.0×10^{-5} to 1.0×10^{-1}	28	3.0–11.0	< 30	5	K^{+}, Ag^{+}, Cd^{2+}	[17]
5	1.0×10^{-6} to 1.0×10^{-1}	28.5	4–11.5	< 20	2.5	NM	[18]
6	1.0×10^{-4} to 1.0×10^{-1}	26.3	NM	NM	1.5	NM	[20]
7	1.0×10^{-3} to 1.0×10^{-1}	27	4.5–9.7	NM	NM	Mg^{2+}	[22]
8	1.0×10^{-9} to 1.0×10^{-1}	NM	NM	NM	NM	NM	[23]
9	3.9×10^{-6} to 1.0×10^{-1}	30	2.5–6.0	15	3	NM	This sensor

[a]NM: not mentioned.

diverse ions tested. Thus, these ions would not cause any significant interference in the estimation of Ca^{2+} ions by this sensor unless present in large amounts. In view of the good selectivity of the sensor, it can be used for Ca^{2+} determination in the presence of many foreign ions by direct potentiometry.

3.6 *Potentiometric titration*

The utility of sensors has also been used successfully to determine the end-point in the potentiometric titration of Ca^{2+} with EDTA. A 25-mL sample of 1.0×10^{-3} M Ca^{2+} was titrated against 1.0×10^{-2} M EDTA, and the change in potential was noted and plotted in figure 7. The titration plot is of a sigmoidal shape, thus indicating that the sensor is selective to Ca^{2+} ions. The inflexion point of the plot corresponds to the formation of 1 : 1 stoichiometry for the calcium–EDTA complex. Thus, the sensor can be used to determine calcium by potentiometric titration.

4. Conclusion

The application of *p*-isopropylcalix[6]arene in the polymeric membrane phase as an active substance creates a selective sensor for calcium. Among the membranes examined, the membrane with a composition of (mg) of I : NaTPB : PVC (2 : 2 : 120) showed the widest working concentration range of 3.9×10^{-6} to 1.0×10^{-1} M with a near-Nernstian slope of 30.0 mV per decade of concentration. This membrane also showed the lowest response time of 15 s and works satisfactorily in a partially non-aqueous medium. The selectivity studies of the sensor, evaluated with the fixed interference method, showed that the sensor under consideration is selective to Ca^{2+} over a large number of mono-, bi-, and trivalent cations. In view of the good selectivity of the sensor, it is able to work successfully in high-ionic-strength solutions and, therefore, with a variety of real samples. Thus, the sensor can be used for Ca^{2+} determination in the presence of other ions by direct potentiometry. A comparison of the proposed sensor with reported electrodes presented in table 5 clearly indicated an enhancement in the behaviour of the proposed Ca^{2+} sensor in terms of working concentration range, response time, lifetime and pH range. A comparison of the selectivity data presented in table 6 showed that the proposed p-isapropylcalix [6]arene sensor exhibited good selectivity than the reported sensors except the sensors which are based on 2-[(2-hydroxyphenyl)imino]-1,2-diphenylethanone [18] and poly(methylmethacrylate)/poly(decylmethacrylate) copolymer [23] ionophores.

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