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RESEARCH ARTICLE

Thiacalix[4]arene Derivative as Potential Carrier for Cadmium Sensing using PVC Membrane Electrode

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Abstract: The main aim of this work is to improve the lower detection limit of cadmium selective polymeric membrane. The sensor was fabricated by using thiacalixarene derivative 5,11,17,23-tetra-*tert*-butyl-25,27-bis-[(3′-methoxy phenyl)methoxy]-26,28-dihydroxy-2,8,14,20-tetrathiacalix [4]arene as ionophore. The membrane with composition of ionophore: PVC: DMP: NaTPB of 3.5% : 33% : 1.0% : 62.5% (w/v) has a standard detection limit of 1.0×10^{-8} M and lowest possible detection limit of 6.2×10^{-9} M. The electrode exhibits Nernstian response with slope 35.3±1 mV $decade^{-1}$ of activity in linear concentration range of 4.2×10^{-8} to 1.0×10^{-1} M for Cd^{2+} ion, performs satisfactorily over wide pH range (1.5–7.0), with a fast response time (5s). The selectivity coefficients determined by using fixed interference method (FIM) indicate high selectivity for Cd^{2+} as compared to other tested cations. The practicable utility of electrode has been demonstrated in the titration of Cd^{2+} with standard EDTA solution. The proposed electrode was successfully used for the determination of Cd^{2+} in different biological and environmental samples.

Keywords: Thiacalix[4]arene, Cadmium, ion-selective electrode, PVC, lower detection limit.

Introduction

The knowledge of elemental distribution in biological and environmental samples is a subject of great importance because some of the ions are essential for our biological process while some other are harmful to variety of living organisms including human beings. The industrialization of the world is important for the batter life prospective of our society because the industries associated with the synthesis and manufacturing of several goods which we need in our daily life[1,2]. At the same time industrialization has increase the concentration of some harmful contaminants in our environment which affect our health, food, water, *etc*., day by day. Thus the determination of such types of harmful contaminants now becomes a challenging work for scientist and researchers. Cadmium is used for many industrial and agricultural purposes like metal plating, cadmium-nickel batteries, mining, pigments, stabilizers, alloys and phosphate fertilizers, where it comes into the environment. It is an environmental hazard and one of the most toxic substances which may cause many types of dieases[3,4]. The determination of metal ions especially the toxic ones like cadmium is a subject of great importance and increasingly demanded by the society.

In past years, analytical chemists have shown their interest to develop the selective devices based on neutral ionic carrier for the determination of cations[5-15]. Ion-selective electrode (ISE) is one of them. A conventional ion selective electrode has an ionophore which binds the target metal ion in solution. The selective complexation of metal ion and ligand in solution by ion- selective electrode become a good candidature for the determination of ions because they have several advantages such high sensitivity, selectivity, fast response time, wide concentration range, simple operating system *etc*., over other conventional methods. Several reports based on cadmium selective electrodes are available in the literature, but all these reports have either one or more limitations such as high detection limit, high response time, and narrow concentration range, low sensitivity, serious interference of other ions. The best cadmium selective sensor available in the literature[16] has a detection limit of $9.8x10^{-7}$ with response time of 12 second. Still the improvement in the concentration range, response time and lower detection limit is possible.

In present study we have tested a new ionic carrier based on thiacalix[4]arene for the selective determination of cadmium in biological and environmental samples. The proposed electrode work satisfactorily in the concentration range of has detection limit of $1.0x10^{-8}$ M for Cd^{2+} in a concentration range of $1.8x10^{-8}$ - $1.0x10^{-1}$ and response time of 5 s.

Experimental

All reagent were used as purchase from different places *i.e*. thiacalix[4]arene and 3-methoxy benzyl bromide were purchased from Aldrich. High molecular weight poly(vinyl chloride) (PVC), dimethyl phthalate (DMP), diisobutyl phthalate (DBP), dioctyl phthalate (DOP), tris (ethyhexyl) phosphate (TEP), bis-(2-ethylhexyl sebacate) (BEHS), sodium tetraphenyl borate and (NaTPB), tetrahydrofuran (THF) were purchased from Merck. All metal nitrates were purchased from Merck. Deionized water was used to prepare required solutions.

Synthesis of ionophore

The ionophore 5,11,17,23-tetra-*tert*-butyl-25,27-bis-[(3′-methoxy phenyl)methoxy]-26,28-dihydroxy-2,8,14,20-tetrathiacalix[4]arene (Figure 1) was prepared by the reported methods[17].

To a suspension of *p*-*tert*-butyltetrathiacalix[4]arene (1.20 mmol in 10 mL THF) 3-methoxy-benzyl bromide (1.25 mmol in 10 mL THF) was added and refluxed for two days. The ligand was obtained as pale yellow crystals.

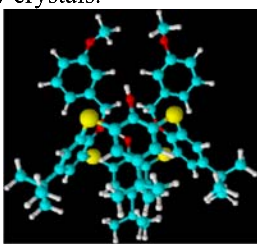

Figure 1. 5,11,17,23-Tetra-*tert*-butyl-25,27-bis-[(3′-methoxy phenyl)methoxy]-26, 28-dihydroxy-2,8,14,20-tetrathiacalix[4]arene

Development of membrane and potential measurements

The membrane of thiacalix[4]arene derivative was fabricated by adding the components in the ratio of ionophore: PVC: DBP: NaTPB: 3.5%:33%: 62.5%:1% (w/w) in 15 mL of THF. The resulting solution was stirred for 4 h well poured in a glass ring. The THF was allowed to evaporate at room temperature for 24 hours in order to obtain the uniform membrane. A membrane sheet about 0.5 mm of thickness and 5 mm diameter was cut away from inner edge and glued it to one end of a glass tube with the help of araldite to avoid leakage. Saturated calomel electrodes (SCE) were used as reference electrodes, a digital potentiometer ECIL, India (Model pH 5662) was used for potential measurements at 25±1 ^{0}C. The potential measurements were made by the following cell assembly.

Internal reference electrode	Internal reference solution (0.01 M Cd^{2+})	Cd^{2+} ion-Selective Membrane	Test solution	External reference electrode (0.01 M KCl)

Results and Discussion

The selectivity of membrane sensor depends on the selective interaction between ionophore and target ion, as well as on other additional membrane components. The proposed ionophore has sufficient number of electron donor atoms which can form stable complex with certain metal ions. The binding ability of proposed thiacalix[4]arene based ligand was investigated in terms of complex formation constant (K_f), which was calculated by using Deby-Huckel limiting law of 1:1 electrolytes (Eq no. 1)[18].

$$K_f = \frac{[ML^+]}{[M^+][L]} \times \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})[L]} \quad (1)$$

where

$$[L] = C_L - \frac{C_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_M - \Lambda_{ML})} \quad (2)$$

Here, Λ_M is the molar conductance of the cation before addition of ligand, Λ_{ML} the molar conductance of the complex, Λ_{obs} the molar conductance of the solution during titration, C_L the analytical concentration of the diureidocalix[4]arene added and C_M the analytical concentration of the cation. The complex formation constants, K_f and the molar conductance of complex, Λ_{obs}, were obtained by using a nonlinear least squares program KINFIT[19]. The values of formation constant in terms of log K_f are presented in Table 1.

Table 1. Formation constant of metal ions-ligand (diureidocalix[4]arene)

Cation	Log K_f
Cd^{2+}	4.36 ± 0.1516
Ca^{2+}	3.13 ± 0.1496
Hg^{2+}	3.85 ± 0.1502
Zn^{2+}	2.96 ± 0.1500
Cu^{2+}	3.31 ± 0.1499
Mg^{2+}	3.82 ± 0.1510
Co^{2+}	2.16 ± 0.1513
Ni^{2+}	2.27 ± 0.1515
Pb^{2+}	2.46 ± 0.1490
Mn^{2+}	2.32 ± 0.1526
Fe^{3+}	2.73 ± 0.1491
Na^+	2.16 ± 0.1508
K^+	2.12 ± 0.1517
Li^+	2.28 ± 0.1521

This table clearly indicates that the proposed ionophore forms satble complex with Cd^{2+} ion as compared to other divalent and mono-valent ions. Thus the proposed ionophore can be used to construct cadmium selective membrane sensor. The high molecular weight (~ 936) and insolubility of ionophore prevent the leaching of ionophore from membrane, and hence indicates the ability of ionophore to be used as potential ion carrier.

Optimization of membrane components

It is well known fact that the response of membrane electrode is highly dependent on the membrane components[20,21]. Thus the optimization of membrane components is necessary to get the membrane with best potential response and good reproducibility. In present study, several membranes with different compositions and different plasticizers were fabricated and their responses were investigated. After several experiments, it was observed that 3.5% of ionophore in membrane components gives the best performance in terms of concentration range, detection limit and response time. The excess amount of ionophore does not improve the response characters of membrane electrode. The background potential of membrane electrode without ionophore was investigated in absence of ionophore and the results are presented in Table 2 (Electrode no. 1). It was observed that electrode without ionophore works only in the range of 4.3×10^{-2} - 1.0×10^{-1} M, with a response time of 45 s. The potential response of ionophore is shown in Figure 2.

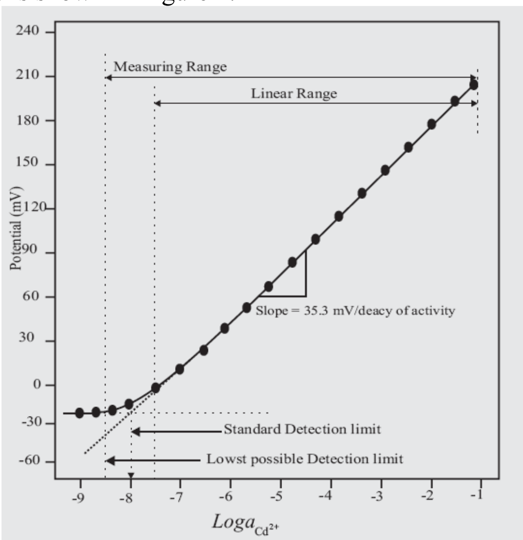

Figure 2. Potential response of cadmium selective ion using thiacalix[4]arene ionophore and DMP as plasticizer

The sensitivity and selectivity of membrane electrode is highly dependent of additional membrane components. In present study, the response of membranes of various compositions and plasticizers were investigated (Table 2). The data presented in Table 2 shows that the plasticizers DBP and DOP have almost the same results if the optimum composition is used. Similarly TEP and BEHS also have the same effect. However DMP gives the best results (electrode no. 2) in terms of linear concentration range, detection limit, response time etc. Thus DMP was chosen as the solvent mediator for further studies. The membrane electrode with 62.5% DMP has a standard detection limit of 1.0×10^{-8} M and lowest possible detection limit of 6.2×10^{-9} M for Cd^{2+} ion. Thus DMP provides the best complexation environment for the interaction of ionophore and target ion and improved the slope of calibration curve, selectivity and sensitivity of membrane electrode. The detection limit of membrane sensor presented in Table 2 is in good agreement with the dielectric constants of solvent mediator.

Table 2. Optimization of membrane composition of Cd^{2+} selective electrodes

Electrode No.	Membrane composition %				Linear working range, M	Slope mV/dec. of activity	Response Time sec	Standard detection limit
	PVC	Additive	Plasticizer	Ionophore				
1	32	4, NaTPB	64, DMP	0	4.3x10^{-2}- 1x10^{-1}	18.8±1.0	45	-
2	33	1, NaTPB	63, DMP	3.0	4.2x10^{-8}- 1x10^{-1}	35.3±1.0	5	1.0x10^{-8}
2	33	1, NaTPB	62.5, DBP	3.5	2.6x10^{-7}- 1x10^{-1}	30.2±1.0	11	1.2x10^{-6}
3	33	1, NaTPB	62.5, TOP	3.5	8.6x10^{-7}- 1x10^{-1}	29.8±1.0	11	2.4x10^{-6}
4	33	1, NaTPB	62.5, TEP	3.5	4.6x10^{-6}- 1x10^{-1}	28.8±1.0	14	3.2x10^{-5}
5	33	1, NaTPB	62.5, BEHS	3.5	4.5x10^{-6}- 1x10^{-1}	27.6±1.0	16	3.8x10^{-5}
6	33	3, NaTPB	60, DMP	4.0	4.6x10^{-8}- 1x10^{-1}	35.2±1.0	5	1.1x10^{-8}
7	32	3, NaTPB	60.5, DMP	4.5	4.5x10^{-8}- 1x10^{-1}	35.3±1.0	5	1.1x10^{-8}
8	30	3, NaTPB	61, DMP	6	4.4x10^{-8}- 1x10^{-1}	35.4±1.0	5	1.2x10^{-8}

The presence of lipophilic anions in the composition of cationic-selective membrane microelectrodes, not only diminishes the ohmic resistance and enhances the potential behavior and selectivity, but also in poor extraction capacities, increases the sensitivity of the membrane electrodes, has long been known[22]. After various experiments it was observed that the presence of 1% NaTPB as membrane component significantly increases the sensitivity of membrane electrode.

The critical response characteristics of the Cd^{2+} selective membrane electrode were assessed according to IUPAC recommendations[23]. The potential response of the membrane at varying concentration of cadmium ions (Figure 2) indicates a linear range from 4.2x10^{-8} - 1.0x10^{-1} M. The slopes of the calibration curves were 35.3±1 mV/decade of Cd^{2+} activity. The standard deviation of 5 replicate potential measurements for the proposed electrode is ±1.0. The potential drift within 5 minutes after each measurement is ±0.3 mV.

The response time of electrode no. 2 was investigated for 1.0x10^{-2} M solution of Cd^{2+} ion. It was observed that the electrode produces a stable potential in a very short time of ~6 second (Figure 3). The sensing behavior of the membranes did not change when the potentials were recorded from lower to higher concentrations or vice versa. However the response time to get a stable potential from higher concentration to lower concentration is more. The life time of membrane electrode was investigated in terms of slope of calibration curve, detection limit and response time. It was observed that the membrane no. 2 based on thiacalixarene ionophore can be used for a period of one year, without observing any change in response time, slope and detection limit. The difference in potential could be corrected by re-equilibrating the membrane with 0.5 M Cd^{2+} solution for 2-3 days. When not in use the sensor was kept stored in 0.01 M Cd^{2+} ion solution.

The presence of hydrogen ion can change the potential response of membrane electrode, thus the effect of pH on potential response of membrane electrode was studied in the range of 0 to 9.0 at 0.01 and 0.001 M $Cd(NO_3)_2$ solution. The pH of solution was adjusted by addition of standard 0.01 M HNO_3 solution and hexamine–HCl buffer solution. It was observed the potential of membrane sensor remains constant in a pH range of 1.5 to 7.0, thus the proposed electrode can be successfully used within this pH range. In basic medium Cd^{2+} can form stable hydroxyl complex that is why a sharp change in potential was observed at pH > 7.0, while at lower pH (< 1.5) hydrogen ion decreases the binding ability of ionophore due to its protonation and interfere in the charge transfer process (Figure 4)

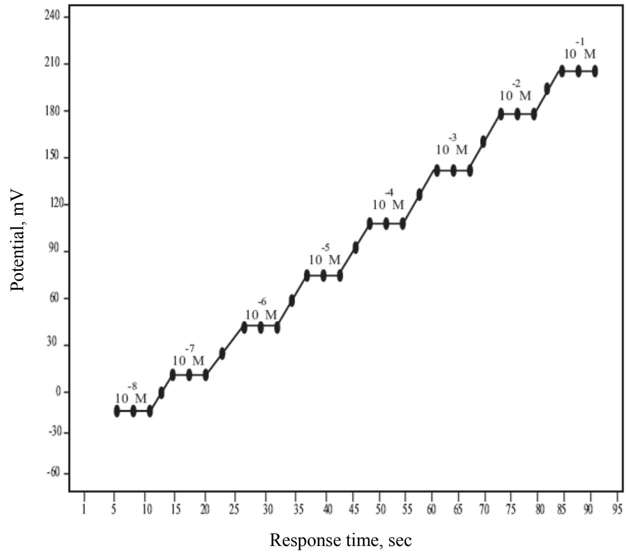

Figure 3. Response time curve for sensor no. 2

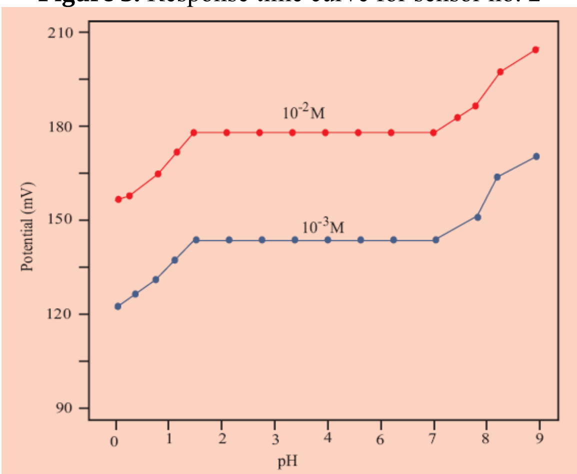

Figure 4. Effect of pH on potential response of electrode no. 2

The selectivity of proposed membrane electrode no. 2 towards Cd^{2+} over other interfering cations was evaluated in terms of potentiometric selectivity coefficients $\left(\log K^{Pot}_{Cd^{2+},M^{n+}}\right)$. In present study the selectivity coefficient was calculated using Fixed Interference Method (FIM) at 0.01 M concentration of interfering ions as recommended by IUPAC using modified Nicolsky equation (Eq. 3)[23].

$$K^{POT}_{Cd^{2+},M^{n+}} = \frac{a_{Cd^{2+}}}{a_{M^{n+}}^{z_{Cd^{2+}}/z_{M^{n+}}}} \quad (3)$$

Where $a_{Cd^{2+}}$ is the activity of the primary ion and $a_{M^{n+}}$ is the activity of interfering ion $z_{Cd^{2+}}$ and $z_{M^{n+}}$ are their respective charges. The result of selectivity coefficients are presented in terms of $\log K^{Pot}_{Cd^{2+},M^{n+}}$ (Table 3). This figure clearly indicates that the proposed membrane sensor is highly selective towards Hg^{2+} ion over different heavy, alkali and alkaline metal ion in solution.

Table 3. Selectivity coefficients for membrane electrode no. 2 (FIM)

Interfering ion	-logK POTCd^{2+}M^{n+} Fixed interference method
Na^+	3.92
Na^+	3.92
Ag^+	3.43
Ca^{2+}	3.54
Cu^{2+}	3.56
Zn^{2+}	3.64
Co^{2+}	3.82
Ni^{2+}	3.67
Pb^{2+}	3.55
Hg^{2+}	3.85
Fe^{3+}	3.53
Li^+	3.53
Mg^{2+}	3.65
K^+	3.46
Al^{3+}	3.56

The selectivity coefficient of proposed membrane electrode no. 2 was also compared with the best electrode available in the literature. The data presented in Table 3 indicates that the electrode no. 2 based on 5, 11, 17, 23-Tetra-*tert*-butyl-25, 27-bis-](3′-methoxy phenyl) methoxy]-26, 28- dihydroxy-2, 8, 14, 20-tetrathiacalix[4]arene has good selective towards Cd^{2+} over tested cations, and its selectivity is better than the previously reported electrodes. Thus the electrode can be used for the direct determination of cadmium in presence of these interfering ions.

The proposed electrode no. 2 was also used as an indicator electrode in precipitation titration of 0.1 M $Cd(NO_3)_2$ with 0.01 M $NaIO_3$ solution and the titration curve is presented in Figure 5. The titration curve has sharp inflation point which indicates the end point of the titration.

The proposed electrode no. 2 was used to determine the concentration of cadmium ions in industrial wastewater and blood samples. The obtained values are quite comparable to those obtained with AAS thereby illustrating the utility of the sensor for determining the Cd^{2+} in real samples (Table 4). The dogfish sample was prepared by digestion of about 3 g of tissue sample with concentrated HNO_3 solution at room temperature.

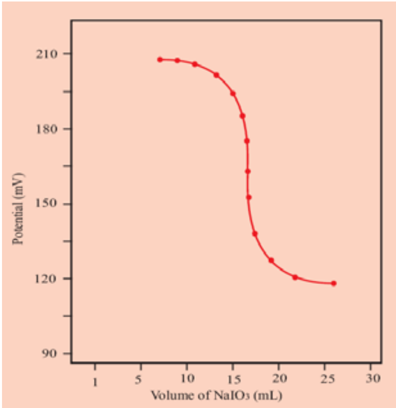

Figure 5. Potentiometric titration curve of Cd^{2+} ion with $NaIO_3$ solution

Table 4. Determination of cadmium in industrial waste water and cigarettes samples[a]

Sample	Cd^{2+}-ISE[a] µg/L	AAS µg/L	ICP µg/L
Blood Sample	1.35	1.36	1.35
Industrial waste	12.65	12.64	2.63
Dogfish Muscle	1.16	1.16	1.15

[a]*Average of three replicate measurements*

The superiority of proposed membrane electrode no. 2 was also compared with previously reported electrodes. The data presented in Table 5 clearly indicates that the proposed electrode no. 2 is superior that previously reported electrode and has batter detection limit, response time and sensitivity.

Table 5. Comparison of the reported electrodes with proposed electrode assembly

Electrode no.	Working Conc. range M	Slope mV/decade pH of activity	pH range	Response time, s	Life time Months	Standard detection limit, M	Ref.
1	$4.2x10^{-8}$ – $1.0x10^{-1}$	35.3±1.0	1.0 - 7.0	6	12	$1.0x10^{-8}$	This work
2	$9.9x10^{-8}$- $1.0x10^{-1}$	30.0±1.0	1.0-7.0	12	10	$9.8x10^{-7}$	16
3	$6.31x1\ 0^{-5}$ – $1.0x1\ 0^{-1}$	26.0±1.0	Low	High	-		24
4	$3.16x1\ 0^{5}$ – $1.0x1\ 0^{-1}$	20.0±1.0	Low	High	-		25
5	$3.9x1\ 0^{-5}$ – $1.0x1\ 0^{-1}$	30.0±1.0	Low	High	-		26
6	$3.16x1\ 0^{-6}$- $1.0x1\ 0^{-1}$	29.8±1.0	2.0-6.0	20	2		27
7	$7.8x10^{-8}$ – $1.0x10^{-2}$	29.4±1.0	Low	High	-	$4.37x10^{-8}$	28
8	$2.1x1\ 0^{-5}$ – $1.0x10^{-1}$	29.0±1.0	1.9-7.0	17	6		29
9	$7.9x10^{-8}$ – $1.0x10^{-1}$	30.0±1.0	2.8	10	2	$5.0x10^{-8}$	30

Conclusion

In this study we have tested thiacalix[4]arene derivation as an ionophore for the construction of Cd^{2+} selective membrane electrode. The use of plasticizers significantly increases the response characters of the membrane electrode. The membrane electrode no. 2 with DMP as plasticizer was found best out of all membranes prepared. The membrane electrode has standard detection limit of 1.0×10^{-8} with slope 35.3 mV/decay of activity. The membrane electrode can be used in a pH range of 1.5-7.0 and has response time of about 5s. The proposed membrane electrode was also used for the determination of Cd^{2+} in different samples.

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