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A new Zn(II)-selective potentiometric sensor based on 4-*tert*-butylcalix[4]arene in PVC matrix

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Abstract

Poly(vinyl chloride) (PVC) based membranes containing 4-*tert*-butylcalix[4]arene (I) as an electroactive material alongwith anion excluder sodiumtetraphenylborate (NaTPB) and plasticizer tri-butylphosphate (TBP) have been developed to fabricate a new zinc-selective sensor. Out of various compositions, the best performance was exhibited by the membrane having I, NaTPB, TBP and PVC in the ratio 8:5:100:200 (w/w). The sensor works well in the concentration range 9.8×10^{-6} to 1.0×10^{-1} mol dm^{-3} with a near-Nernstian slope of 28.0 ± 1.0 mV/decade of activity. The detection limit is down to 5.0×10^{-7} mol dm^{-3}. The working pH range of this sensor is 2.5–4.3 and it works well in partially non-aqueous medium up to 15% (v/v) (methanol, ethanol and acetone). It exhibits a fast response time of 30 s and could be used for more than four months without any considerable change in response characteristics. It has excellent selectivity for Zn(II) over other mono-, bi- and trivalent cations which have been reported to cause interference in the working of other sensors. It has been successfully used as an indicator electrode in the potentiometric titration of Zn(II) against EDTA and also to estimate zinc ions in industrial waste waters.

Keywords: Ion-selective electrodes; Sensors; Zinc sensors; Waste water

1. Introduction

Ion selective electrodes have continued to be an important development in the field of analytical chemistry since the end of 1960s. As such they have been the subject of widespread interest for analytical chemists as they provide accurate, rapid and low cost method of analysis. Also analysis by these electrodes is nondestructive, adaptable to small sample volumes and on-line monitoring is also possible. Due to these merits, extensive efforts have been made to develop sensors for alkali and alkaline earth metals, nitrates, halides etc. and sensors for a large number of analytes have been reported so far. However, success with respect to heavy metals, which are toxic beyond certain concentration level, is not up to the commercial standards.

Determination of zinc assumes importance as it is widely used in electroplating; fine chemicals, pharmaceutical and paint industries. Also some biomedical and a number of process wash streams contain less activity of this metal ion. Besides, zinc is also present in high protein foods. Human body contains about 2 g zinc and its large doses can cause fever, chills, pulmonary manifestation and gastroenteritis. It can also cause vomiting, nausea, anaemia, renal failure and internal organ damage. Therefore, a selective sensor for zinc monitoring is required. The efforts made so far to develop a good zinc-selective sensor have not been very successful. Most of the sensors reported for zinc(II) ions have poor sensitivity, selectivity, long response time and short life time [1–15]. A large number of ionophores have been developed and found widespread applications in potentiometric sensors for the determination of respective ions in actual samples. The macrocyclic compounds are being employed as the carriers in metal selective extraction, phase transfer catalysis and membrane transport as they bind the metal ions selectively [16–22,31–34]. 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.

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Table 1
Composition and characteristics of PVC based membranes having 4-*tert*-butylcalix[4]arene as electroactive material

Sensor number	(I)	NaTPB	DBP	DOP	DBBP	TEP	1-CN	TBP	PVC	Working concentration range (mol dm^{-3})	Slope (±1.0 mV/ decade of activity)	Response time (s)
1	8.0	5	–	–	–	–	–	–	200	7.9×10^{-4} to 1.0×10^{-1}	28.2	70
2	8.0	5	100	–	–	–	–	–	200	7.1×10^{-4} to 1.0×10^{-1}	25.0	11
3	8.0	5	–	100	–	–	–	–	200	6.3×10^{-4} to 1.0×10^{-1}	24.6	14
4	8.0	5	–	–	100	–	–	–	200	4.0×10^{-4} to 1.0×10^{-1}	26.0	14
5	8.0	5	–	–	–	100	–	–	200	4.3×10^{-4} to 1.0×10^{-1}	34.2	32
6	8.0	5	–	–	–	–	100	–	200	1.0×10^{-4} to 1.0×10^{-1}	33.1	17
7	8.0	5						100	200	9.8×10^{-6} to 1.0×10^{-1}	28.0	30

Calixarenes are cyclic oligomers of phenol-formaldehyde condensates. The phenolic group of the macrocyclic molecule can also be converted into derivatives containing a wide range of functional groups. These compounds have demonstrated unique ionophoric properties towards many guest molecules [23]. 4-*tert*-butylcalix[4]arene has earlier been tried to develop a Pb(II) ions selective sensor [24] where Zn had shown considerable interference and thus, it is expected that this material may be a good ionophore for zinc(II) ions determination. The results on the PVC based membranes of this ionophore as zinc selective electrodes are presented in this paper.

2. Experimental

2.1. Reagents

All reagents were of analytical reagent grade and used without further purification. 4-*tert*-butylcalix[4]arene (I) from Aldrich (USA), sodiumtetraphenylborate (NaTPB) from BDH (England), dibutylphthalate (DBP) and dioctylphthalate (DOP) from Reidel (India), dibutyl(butyl)phosphonate (DBBP) from Mobil USA and 1-chloronapthalene (CN), tris (2-ethylhexyl) phosphate (TEP), tri-*n*-butylphosphate (TBP) from BDH (England) and high molecular weight poly(vinylchloride) (PVC) from Fluka (Switzerland) were used as obtained. Metal salt solutions of their respective nitrates were prepared in doubly distilled water and standardized by appropriate methods [24]. Solutions of different concentrations were prepared by diluting 0.1 mol dm^{-3} stock solution.

2.2. Equipment

A Perkin-Elmer model 3100 atomic absorption spectrophotometer (AAS) with a graphite furnace and a model 8440 inductively coupled plasma atomic emission spectrometer (ICP-AES) (Labtam, Australia) were used. The potential measurements were carried out on a PH 5652 digital pH/millivoltmeter (ECIL, Hyderabad, India) and CVM30 Century microvoltmeter (Century Instruments, Chandigarh, India). pH measurements were made with a digital pH meter (ECIL, India, Model PH 5652 A).

2.3. Preparation of membranes

Varying amounts of the electroactive material (I) and anion excluder NaTPB were dissolved with an appropriate amount of PVC in 10 ml of THF. In some compositions plasticizers, i.e. DBP, DOP, DBBP, TEP, TBP or CN were also added to get different combinations. This solution was shaken vigorously with a glass rod. When the solution gets viscous it was poured in acrylic rings resting on a smooth glass plate. The solution was allowed to evaporate for 24 h at room temperature. Colourless membranes of about 0.5 mm thickness were obtain which were then cut to size and were glued to one end of a pyrex glass tube with Araldite (Ciba Giegy, India). The ratio of membrane ingredients, time of contact and concentration of equilibrating solution were optimized so that the membrane could develop reproducible, noiseless and stable potentials. Membrane to membrane reproducibility was assured by carefully following the optimum conditions of fabrication. Compositions of the best-performed membranes are listed in Table 1 alongwith other characteristics.

2.4. Potential measurements

The prepared membranes were equilibrated for 3–4 days in 1.0 M zinc nitrate solution. All potential studies were carried out at 25 ± 0.1 °C temperature by using the following cell assembly set up.

Internal Reference Electrode (SCE)	0.1 M Zn^{2+} Internal solution	Membrane	Test solution	External Reference Electrode (SCE)

Saturated calomel electrodes (SCE) were used as reference electrodes and the cell potentials were measured by varying the concentration of test solutions in the range 1.0×10^{-6} to 1.0×10^{-1} mol dm^{-3} by serial dilution. The concentration of standard solutions was checked by atomic absorption spectrometer also. Each solution was stirred and potential was recorded when it became stable and then plotted against logarithm function of Zn(II) ion activity. All pH adjustments were made with dil HCl and hexamine. The response time of membrane sensors, i.e. the time required by sensor to produce stable and constant potentials, was arrived by measuring the potentials at different time for every membrane.

3. Results and discussion

The properties of the membranes, namely response time, lifetime, selectivity and chemical stability depend on ratio of

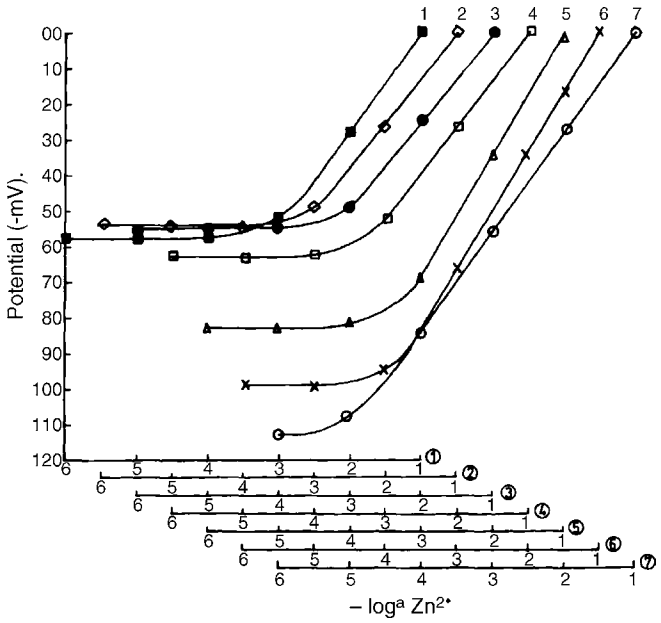

Fig. 1. Variation of potential with activity of Zn^{2+} ions of PVC based membranes of (I) without plasticizer (1), with plasticizers, DBP (2), DOP (3), DBBP (4), TEP (5), 1-CN (6), TBP (7).

electroactive phase and the binder material [8,22–34]. Plasticizers affect the dielectric constant of the membrane phase and hence, the response characteristics. Therefore, several membrane compositions were investigated by varying the amount and nature of plasticizer (Table 1). It is clear that among the six plasticizers used, TBP exhibited the best sensitivity. In presence of lipophilic anions in cation selective membrane electrode, Ohmic resistance diminishes [26] while selectivity and other response characteristics show improvement [27,28]. It is seen in Table 1 that the addition of NaTPB increases the sensitivity of the electrode considerably. Preliminary studies showed that the membrane having composition I and PVC in the ratio 8:200 (w/w) exhibits near-Nernstian behaviour over a concentration range of 8.2×10^{-5} to 1.0×10^{-1} mol dm^{-3}.

3.1. Working concentration range and slope

The membranes without any plasticizer as well as having different plasticizers such as DBP, DBBP, TEP, CN, DOP and TBP were prepared. The potential response of all the membrane sensors as a function of Zn^{2+} activity (Fig. 1) was studied in the concentration range 1.0×10^{-6} to 1.0×10^{-1} M of Zn^{2+}. Membrane no. 1 exhibited a narrow working concentration range of 7.9×10^{-4} to 1.0×10^{-1} mol dm^{-3} with a near-Nernstian slope of 28.2 mV/decade of activity. Further, it attains stable potential in 60 s at higher concentrations and approximately 80 s at lower concentration, i.e. below 1.0×10^{-4} mol dm^{-3}. The effect of addition of plasticizers to the membrane was studied and significant improvement regarding working concentration range, slope and response time was observed. However, the addition of plasticizer DBP did not show any considerable improvement in working concentration range or slope. DOP and DBBP improved the response characteristics of the membrane that now shows a relatively wider concentration range but the slope approached a non-Nernstian value in both the cases. Addition of solvent mediators TEP and CN also improved the working concentration range but slope values of these membranes were also far deviated from Nernstian values. However, the best performance is exhibited by membrane no. 7 incorporating TBP as plasticizer, which works well over a wide working concentration range of 9.8×10^{-6} to 1.0×10^{-1} mol dm^{-3} with a near-Nernstian slope of 28.0 mV/decade of activity (Table 1). The effect of the concentration of internal solution on the potential response of the electrode was studied. The $Zn(NO_3)_2$ concentration was changed from 1.0×10^{-2} to 1.0 mol dm^{-3} and potential versus logarithm of zinc ion activity plot was obtained. No considerable difference was found in the potential response except for a change in intercept of resulting Nernstian plots. A 1.0×10^{-1} mol dm^{-3} concentration of internal solution was found suitable for smooth functioning of the electrode. Many compositions of membrane no. 7 were tried to get optimum composition by varying the amount of electroactive material. It is clear that the best performing membrane has I, NaTPB, TBP and PVC in the ratio 8:5:100:200 (w/w). If the amount of (I) is increased further, there is no considerable improvement in any of the characteristics of the sensor (Table 2). Therefore, sensor D has been chosen for all further studies. Repeated monitoring of potentials (20 measurements) on the same portions of the sample gave a standard deviation of ±0.5 mV. The standard deviation of the slope was ±0.8–1.0 mV that shows good reproducibility. The performance of membranes without ionophores was also investigated and it was seen that they generated no potential.

3.2. Response and lifetime

The membranes without plasticizer required 60 s at higher concentrations (above 1.0×10^{-4} mol dm^{-3}) and about 80 s at

Table 2
Response characteristics of the PVC based membranes having different amounts of 4-*tert*-butylcalix[4]arene as electroactive material

Sensor number	I	NaTPB	TBP	PVC	Working concentration range (mol dm^{-3})	Slope (±1.0 mV/ decade of activity)	Response time (s)
A	5.0	5	100	200	9.0×10^{-4} to 1.0×10^{-1}	28.0	~120
B	6.0	5	100	200	1.4×10^{-4} to 1.0×10^{-1}	28.0	~95
C	7.0	5	100	200	4.0×10^{-5} to 1.0×10^{-1}	28.0	45
D	8.0	5	100	200	9.8×10^{-6} to 1.0×10^{-1}	28.0	30
E	8.5	5	100	200	9.8×10^{-6} to 1.0×10^{-1}	28.0	30
F	9.0	5	100	200	9.8×10^{-6} to 1.0×10^{-1}	28.0	30
G	10.0	5	100	200	9.8×10^{-6} to 1.0×10^{-1}	28.0	30

lower concentrations to produce a potential within ±1 mV of the final equilibrium value (Table 1). The addition of plasticizers reduced the response time significantly. The best result was exhibited by electrode no. 2 (11 s) over the whole working concentration range. The potentials remained constant for more than 4 min after which a very slow divergence was recorded. Electrode no. 4, 5 and 6 also performed satisfactorily as the response time for these electrodes were recorded as 14, 32 and 17 s, respectively. The electrode could be used over a period of four months without observing any significant drift in working concentration range, slope and response time. After this period a slight change was observed in response time and slope, which could be corrected by re-equilibrating the electrode with 1.0 mol dm^{-3} Zn^{2+} solution for 2–3 days. With this treatment the assembly could be used over a period of one more month and then it was replaced by a fresh membrane. During usage, the electrodes were stored in 0.1 mol dm^{-3} Zn^{2+} solution to avoid cracking of membranes due to drying.

3.3. pH and non-aqueous effect

The pH dependence of the electrode potential for 1.0×10^{-3} and 1.0×10^{-2} mol dm^{-3} Zn^{2+} was tested over the pH range 1.0–8.0 (adjusted with HNO_3 or Hexamine). It can be seen (Fig. 2) that the potentials are independent of pH in the range 2.5–4.3 and the same can be taken as the working pH range of the electrode. Above and below these pH values, the sharp change in potential may be due to the hydrolysis of Zn^{2+} and H^+ co-transport respectively. The utility of the membrane sensor was also investigated in partially non-aqueous medium using methanol–water, ethanol–water and acetone–water mixtures. The electrode works satisfactorily in the mixtures having up to 15% (v/v) non-aqueous content without showing any considerable change in working concentration range or slope. However, above 15% non-aqueous content the potentials show drift with time (Table 3).

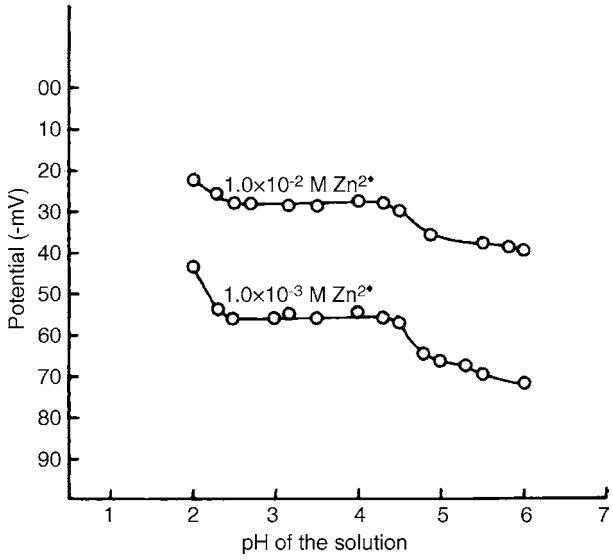

Fig. 2. Effect of pH on potential of sensor 7 at (a) 1.0×10^{-2} and (b) 1.0×10^{-3} mol dm^{-3} Zn^{2+}.

3.4. Potentiometric selectivity

The selectivity behaviour is one of the most important characteristics of a sensor, which determines its response for primary ion in presence of foreign ions. This parameter is measured in terms of potentiometric selectivity coefficient ($K^{Pot}_{Zn^{2+},B}$). In order to determine the selectivity coefficient of the proposed zinc selective electrode, matched potential method (MPM) [29] as well as a modified fixed interference method (FIM) was used [30]. In the MPM, the primary ion activity was increased from 5.0×10^{-5} to 8.0×10^{-5} mol dm^{-3} and activity of interfering ions was experimentally determined. However, in the FIM, concentration of interfering ion was kept at 1.0×10^{-2} M. Selectivity parameter data for various ions are presented in Table 4. Selectivity coefficient values are quite low for polyvalent cations

Table 3
Performance of electrode no. 7 in partially non-aqueous media

Solvent composition (% (v/v))	Slope (±1.0 mV/decade of activity)	Working concentration range (mol dm^{-3})
0	28.0	9.8×10^{-6} to 1.0×10^{-1}
Methanol		
5	28.0	9.8×10^{-6} to 1.0×10^{-1}
10	28.0	9.8×10^{-6} to 1.0×10^{-1}
15	27.5	2.5×10^{-5} to 1.0×10^{-1}
20	24.0	4.8×10^{-4} to 1.0×10^{-1}
Ethanol		
5	28.0	9.8×10^{-6} to 1.0×10^{-1}
10	27.8	9.8×10^{-6} to 1.0×10^{-1}
15	27.4	3.4×10^{-5} to 1.0×10^{-1}
20	24.2	3.9×10^{-4} to 1.0×10^{-1}
Acetone		
5	28.0	9.8×10^{-6} to 1.0×10^{-1}
10	28.0	9.8×10^{-6} to 1.0×10^{-1}
15	27.6	2.7×10^{-5} to 1.0×10^{-1}
20	24.5	4.0×10^{-4} to 1.0×10^{-1}

Table 4
Selectivity coefficient $K^{Pot}_{Zn^{2+},B}$ values of interfering ions for 4-*tert*-butylcalix[4]arene as obtained by modified fixed interference method and also by matched potential method (interfering ion concentration 1.0×10^{-2} mol dm^{-3})

Interfering ion	Selectivity coefficient values	
	Fixed interference method	Matched potential method
K^+	3.2×10^{-2}	0.12
NH_4^+	2.8×10^{-2}	0.11
Na^+	3.1×10^{-2}	0.28
Tl^+	2.0×10^{-2}	0.17
Ag^+	8.1×10^{-1}	0.77
Cs^+	2.0×10^{-2}	0.16
Ca^{2+}	1.9×10^{-2}	0.15
Cu^{2+}	3.8×10^{-2}	0.34
Sr^{2+}	2.2×10^{-2}	0.20
Ba^{2+}	2.2×10^{-2}	0.18
Mg^{2+}	3.5×10^{-2}	0.40
Cd^{2+}	1.0×10^{-1}	0.11
Co^{2+}	3.9×10^{-2}	0.40
Pb^{2+}	8.0×10^{-1}	0.78
Hg^{2+}	1.0×10^{-2}	0.14
Fe^{3+}	1.3×10^{-3}	0.14
Cr^{3+}	1.1×10^{-2}	0.15
Al^{3+}	1.1×10^{-2}	0.10
Ce^{3+}	1.4×10^{-2}	0.10

indicating no interference. The selectivity coefficient pattern clearly indicates that the electrode is moderately selective to Zn^{2+} over a number of other cations except for Ag^+ and Pb^{2+} as the selectivity coefficient values for these two ions are much higher. Even these ions are likely to cause no interference if present at low concentrations as the selectivity is a concentration dependent property. Some mixed run studies [13,31–34] were carried out to determine the maximum tolerable concentration limit of these interfering ions in the determination of Zn^{2+}. It can be seen from Fig. 3 that Ag^+ at $\leq 5.0 \times 10^{-5}$ mol dm^{-3} cause no significant deviation in the original potential versus logarithm of zinc(II) ion activity plot. Thus it can be concluded that the sensor can tolerate Ag^+ at concentration up to 5.0×10^{-5} mol dm^{-3} over the entire concentration range. For higher concentrations of Ag^+, the sensor can be used to determine Zn^{2+} over a reduced concentration range only. Fig. 3 shows that at 1.0×10^{-4} and 1.0×10^{-3} mol dm^{-3} Ag^+ the electrode assembly can be used to determine Zn^{2+} in the concentration ranges 8.2×10^{-5} to 1.0×10^{-1} and 4.5×10^{-4} to 1.0×10^{-1} mol dm^{-3}, respectively. Similarly Pb^{2+} can be tolerated over the entire concentration range if present at the concentration $\leq 5.0 \times 10^{-5}$ mol dm^{-3} while in the presence of 1.0×10^{-4} and 1.0×10^{-3} mol dm^{-3} Pb^{2+}, the proposed sensor can be used in the reduced concentration ranges 3.2×10^{-4} to 1.0×10^{-1} and 7.0×10^{-3} to 1.0×10^{-1} mol dm^{-3} Zn^{2+}, respectively.

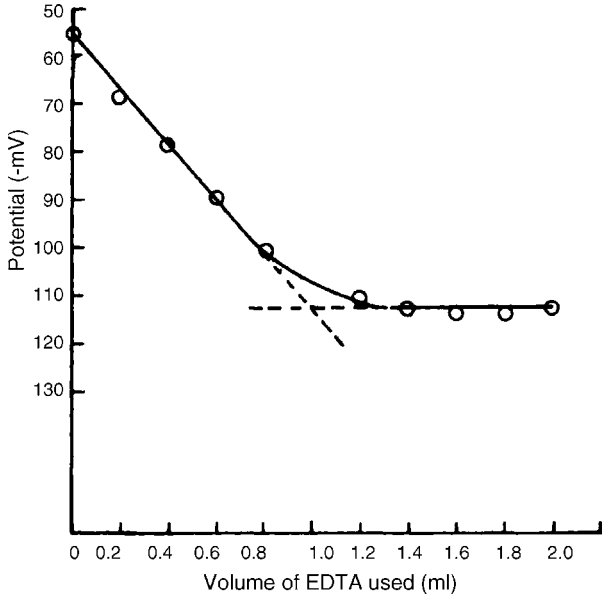

Fig. 4. Potentiometric plot for the titration of Zn^{2+} (1.0×10^{-3} M, 10 ml) against EDTA (1.0×10^{-2} M) using sensor 7 as indicator electrode.

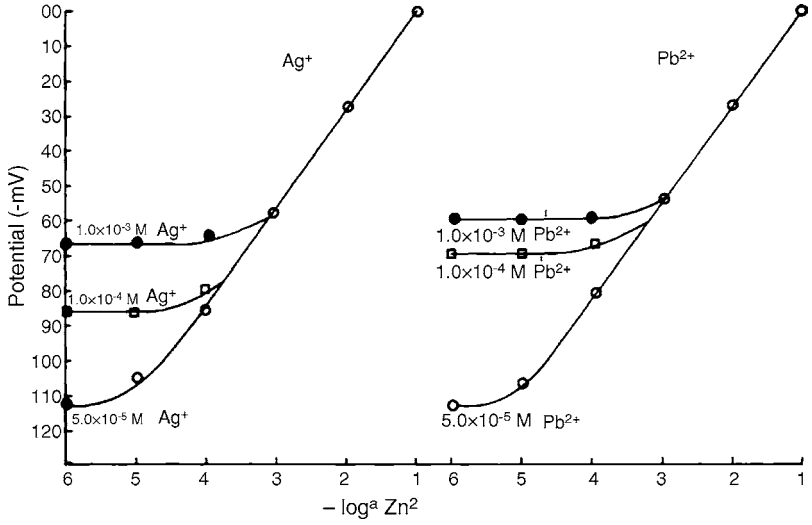

Fig. 3. Variation of potential of sensor 7 with Zn^{2+} activity in presence of different concentrations of (a) Ag^+ and (b) Pb^{2+}.

Table 5
Analytical data for Eveready Battery waste as determined by ICP-AES, AAS and electrode no. 7 after pH adjustments to 3.0 of the wastes

Sensor number	Concentration of Zn(II) as determined by ICP-AES[a] ($mg\,dm^{-3}$)	Concentration of Zn(II) as determined by AAS[a] ($mg\,dm^{-3}$)	Concentration of Zn(II) as determined by sensor no. 7[a] ($\pm 0.2\,mg\,dm^{-3}$)
1	13.30	11.30	11.17
2	10.92	10.88	10.69
3	11.00	10.98	10.92

[a] Average value ($n = 3$).

Table 6
Comparison of the proposed electrode no. 7 assembly with the existing solid state electrodes

Sensor number	Working concentration range (M)	Slope (mV/decade of activity)	pH range	Response time (s)	Detection limit (M)	Interference	Reference number
1	2.8×10^{-5} to 1.0×10^{-1}	30.1	2.1–6.9	20	$>2.0 \times 10^{-7}$	–	[10]
2	9.0×10^{-5} to 1.0×10^{-1}	30.0	3.0–7.0	20	$>2.0 \times 10^{-7}$	–	[12]
3	6.2×10^{-6} to 1.0×10^{-1}	29.0	3.8–7.7	–	$>2.0 \times 10^{-7}$	–	[32]
4	1.5×10^{-5} to 1.0×10^{-1}	29.0	2.1–4.0	10	$>2.0 \times 10^{-7}$	Na^+, Ca^{2+}	[13]
5	7.0×10^{-5} to 1.0×10^{-1}	30.1	2.1–6.9	–	$>2.0 \times 10^{-7}$	Na^+	[14]
6	2.9×10^{-7} to 1.0×10^{-1}	29.9	2.0–9.0	10	$>2.0 \times 10^{-7}$	–	[15]
7	9.2×10^{-5} to 1.0×10^{-1}	29.0	4.8–6.2	12	$>2.0 \times 10^{-7}$	Na^+, Ca^{2+}	[33]
8	1.0×10^{-6} to 1.0×10^{-1}	30.0	3.2–7.1	8		Cu^{2+}	[34]
9	9.8×10^{-6} to 1.0×10^{-1}	28.0	2.5–4.3	30	$>5.0 \times 10^{-7}$	Ag^+, Pb^{2+}	Proposed sensor

4. Analytical applications

4.1. Potentiometric titration

The analytical application of the electrode was investigated by using it as an indicator electrode in the potentiometric titration of Zn^{2+} against EDTA. Ten milliliters of 1.0×10^{-3} mol dm^{-3} Zn^{2+} solution was titrated against 1.0×10^{-2} mol dm^{-3} EDTA solution at pH 3.0. The plot given in Fig. 4 does not have a standard sigmoid shape. This may be due to the interference caused by Na^+ ions as di-sodium EDTA salt has been used. However, the sharp break point observed corresponds to the stoichiometry of Zn^{2+}-EDTA complex and therefore Zn^{2+} can be determined potentiometrically by using this electrode.

4.2. Waste analysis

The practical utility of the sensor is tested by applying it for the estimation of Zn^{2+} in an Eveready Battery waste from Eveready Industries Ltd., Lucknow, India. The waste was dissolved in distilled water by adding a few drops of 16N nitric acid. It was then filtered and analyzed by AAS and ICP-AES. It was found that the waste contains various metals at different concentrations besides Zn^{2+}. The concentration of zinc was also determined at pH 3.0 by using the sensor for the sake of comparison (Table 5). It is clear from the data that these are in very good agreement with those obtained by ICP-AES and AAS. Hence the sensor can be successfully employed for the estimation of Zinc in real samples.

5. Conclusion

The studies demonstrated that the membrane sensor incorporating 4-*tert*-butylcalix[4]arene as electroactive material is superior to the existing electrodes (Table 6). The membrane no. 7 having I, NaTPB, TBP and PVC in the ratio 8:5:100:200 (w/w) can be used to determine Zn^{2+} in the concentration range 9.8×10^{-6} to 1.0×10^{-1} mol dm^{-3} with a detection limit down to 5.0×10^{-7} mol dm^{-3}. The functional pH range is 2.5–4.3 and most of the ions, commonly present with Zn^{2+} do not cause any interference with this sensor. It exhibits good reproducibility, fast response time and can be used for more than four months in aqueous as well as partially non-aqueous medium up to 15% (v/v). Further, the sensor has successfully been used as an indicator electrode in the potentiometric titration of Zn^{2+} with EDTA as well as to determine zinc(II) in real waste water samples.

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References

[1] L. Gorton, U. Fiedler, Anal. Chim. Acta 90 (1977) 233.
[2] U.F. Linnersund, K.M. Bhatti, Anal. Chim. Acta 111 (1979) 57.
[3] M. Uchida, E. Ikeda, I. Ohba, T. Kashima, Kyoritsu Yakka Daigaku Kenkyu Nempo 23 (1978) 19.
[4] A.G. Rodichev, T.P. Ushangishvili, V.A. Dolidze, V.G. Krunchak, Latv. PSR Zinat. Akad. Vestis. Kim. Ser. 8 (1986) 263.
[5] O.A. Lebedeva, E. Jansons, Latv. PSR Zinat. Akad. Vestis. Kim. Ser. 4 (1987) 483.
[6] A. Viksna, E. Jansons, S. Pastare, A. Klajse, Otkrytiya Izobert 15 (1986) 154.
[7] M.J. Rocheleau, W.C. Purdy, Talanta 37 (1990) 307.
[8] R. Kojima, S. Kamata, Anal. Sci. 10 (1994) 409.
[9] S.K. Srivastava, V.K. Gupta, S. Jain, Anal. Chem. 68 (1996) 1272.
[10] V.K. Gupta, A.K. Jain, L.P. Singh, U. Khurana, Electrochim. Acta 355 (1997) 33.
[11] V.K. Gupta, Sens. Actuat. B 55 (1999) 30.

[12] M. Shamsipur, S. Rouhani, M.R. Ganjali, H. Sharghi, H. Eshghi, Sens. Actuat. B 59 (1999) 30.
[13] V.K. Gupta, A. Kumar, R. Mangla, Sens. Actuat. B 76 (2001) 617.
[14] A.R. Fakhari, M. Shamsipur, Kh. Ghanbari, Anal. Chim. Acta 460 (2002) 177.
[15] M.B. Gholivand, Y. Mosaffari, Talanta 59 (2003) 399.
[16] S. Bouen, J. Dale, P. Groth, J. Krane, J. Chem. Soc. Chem. Commun. 20 (1982) 1172.
[17] R.D. Nobel, J.D. Way, Liquid Membranes: Theory and Applications, American Chemical Society, Washington DC, 1987.
[18] M. Hiroka, Crown Ethers and Analogous Compounds, Elsevier, Amstedam, 1992.
[19] H. Tsukube, Liquid membranes: Chemical Applications, CRC Press, Boca Raton, FL, 1990, p. 51.
[20] H. Tsukube, K. Yamashita, T. Iwachiso, M. Zenki, J. Org. Chem. 56 (1991) 268.
[21] G.W. Gokel, Crown Ethers and Cryptands, The Royal Society of Chemistry, London, 1991.
[22] E. Bakker, P. Buhlmann, E. Pretsch, Chem. Rev. 97 (1997) 3083.
[23] C.D. Gutsche, Calixarenes, The Royal Society of Chemistry, London, 1992.
[24] V.K. Gupta, R. Mangla, S. Agarwal, Electroanalysis 14 (2002) 1127.
[25] A.I. Vogel, A Textbook of Quantitative Chemical Analysis, fifth ed., ELBS Publication, London, England, 1989.
[26] D. Amman, E. Pretsch, W. Simon, E. Lindler, A. Bezegha, E. Pungor, Anal. Chim. Acta 171 (1991) 1380.
[27] M.H. Mashhadizadeh, M. Shamsipur, Anal. Chim. Acta 381 (1999) 111.
[28] M. Shamsipur, M.H. Mashhadizadeh, Talanta 53 (2001) 1065.
[29] V.P.Y. Gadzekpo, G.D. Christian, Anal. Chim. Acta 164 (1984) 279.
[30] F.J. Sa'ez de Viteri, D. Diamond, Analyst 119 (1994) 749.
[31] V.K. Gupta, R. Prasad, P. Kumar, R. Mangla, Anal. Chim. Acta 420 (2000) 19.
[32] A.K. Jain, V.K. Gupta, P. Kumar, R. Mangla, Electroanalysis 13 (2001) 1036.
[33] V.K. Gupta, M. Al Khayat, A.K. Minocha, P. Kumar, Anal. Chim. Acta 532 (2005) 153.
[34] V.K. Gupta, S. Agarwal, A. Jacob, H. Lang, Sens. Actuat. B, in press.