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Azo calix[4]arene based neodymium(III)-selective PVC membrane sensor

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ABSTRACT

We found that the PVC membrane, containing azo calix[4]arene is a suitable ionophore, exhibited a Nernstian response for neodymium (Nd^{3+}) ions (with slope of 19.8 ± 0.2 mV decade^{-1} for the triply charged ion) over a wide linear range of 4.0×10^{-8} to 1.0×10^{-1} mol L^{-1} with a detection limit 1.0×10^{-8} mol L^{-1}, a relatively fast response time, in the whole concentration range (<10 s), and a considerable life time at least for four months in the pH range of 4.0–8.0. Furthermore, the electrode revealed high selectivity with respect to all the common alkali, alkaline earth, transition and heavy metal ions, including the members of the lanthanide family other than Nd^{3+}. Concerning its applications, it was effectively employed for the determination of neodymium ions in industrial waste water as well as in lake water.

1. Introduction

The flourishing field of supramolecular chemistry was launched by the discovery of an important class of macrocyclic compounds called calixarene. Calixarenes have received considerable attention in the past decade in host-guest or supramolecular chemistry [1,2]. Calixarenes offer an ideal platform due to the easy modification at their upper and lower rim [3,4]. A recent study on the synthesis of calixarene derivatives gives admirable progress in the fabrication of ion selective electrode [5], liquid crystal derivatives [6,7], electro chemical sensor for cation as well as anion [8,9] and fluorescent devices [10]. The cavity of calixarene has been mostly studied for encapsulation abilities towards alkali and alkaline earth metals [11]. Azo reagents have the benefit of elevated sensitivity and excellent selectivity towards the metal ions [12]. Different azo group has been anchored to the upper rim of calixarene through diazotization [13,14].

Nowadays, determination of rare-earth compounds is considered necessary because of the increasing interest in bioinorganic and inorganic chemistry, increased industrial use, and also due to their enhanced discharge, toxic properties, and other adverse effects. Neodymium is the second most abundant rare earth element. Naturally it is found in minerals such as monazite and bastnasite. The amount of neodymium present in human system is quite small. Although the metal has no biological role, it can affect the parts of the system. Neodymium is generally used for coloring glass in the manufacture of welder goggles as well as for the green color removal caused by iron contaminants from glass. It is also used in the formation of permanent magnets that is used in microphones, professional loudspeakers, headphones and computer hard disks. Neodymium dust and salts are irritating to eyes and are considered as a threat to the liver when it accumulates in the human body. Moreover, neodymium acts as an anticoagulant, especially when given intravenously [15].

Numerous analytical methods have been developed for its determination in different sample matrices such as spectrophotometry, atomic absorption spectroscopy (AAS) [16], inductively coupled plasma atomic emission spectroscopy (ICPAES) [17], gravimetric determination [18] and isotopic dilution mass spectroscopy [19,20]. These methods are having some limitations such as time consuming, requirements of expertise, wide space, high cost and lower detection limit, while potentiometric sensors are very efficient and cost effective technique used for clinical, environmental and chemical analysis. Ion selective electrodes for neodymium have shown great promise to achieve the desired result. Although several ion selective electrodes for neodymium have been developed recently [21–26], many problems like interference of other metal ions and longer response time have been encountered. We have explored the sensing properties of the macrocyclic compounds, and have recently reported the mercury selective [27], thiocyanate selective [28], dihydrogen phosphate selective [29] and glucose selective [30] membrane electrodes. These findings motivated us to synthesize an azodye derived from calix[4]arene, which may allow selective and efficient ion sensing of the rare earth metals.

The aim of this work is the development and comparative study of a neodymium(III) PVC membrane electrodes based on azo calix[4]arene. Herein we report the synthesis and application of a

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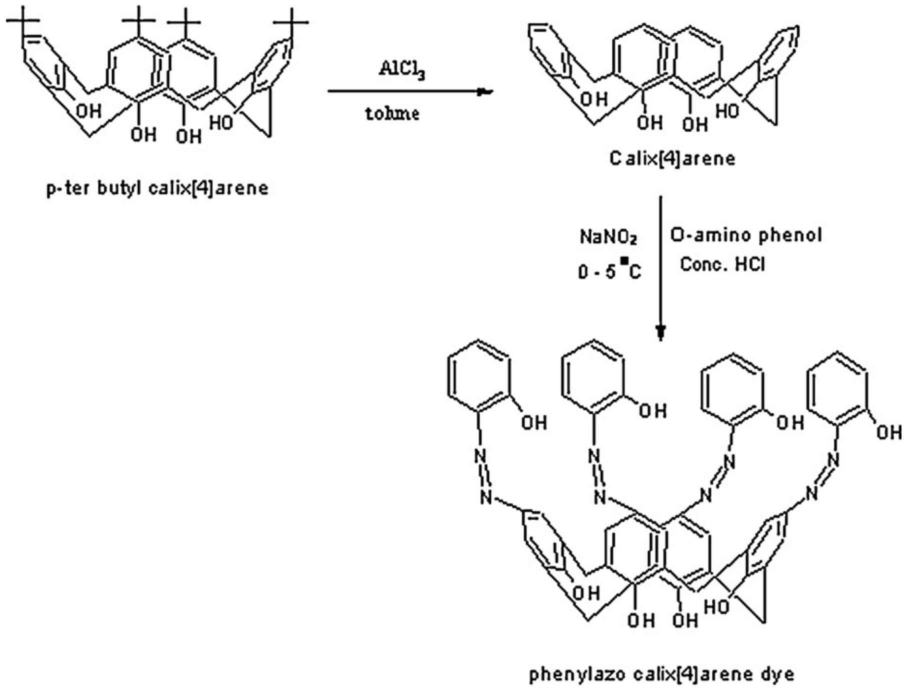

Scheme 1. Synthesis of azo calix[4]arene.

novel Nd^{3+} ion selective sensor with high selectivity and sensitivity, wide linear concentration range and long lifetime.

2. Experimental

2.1. Reagents and materials

All the reagents and chemicals used were of analytical grade. 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. Sodium tetraphenyl borate (NaTPB) and dioctylphthalate (DOP) were purchased from Merck. Polyvinyl chloride (PVC) was obtained from MCC, India and neodymium(III) chloride (Sigma-Aldrich) was used without further purification.

2.2. Synthesis of the ionophore

2.2.1. Synthesis of azo calix[4]arene

The synthesis of p-terbutyl calix[4]arene [31] and calix[4]arene [32] were as described by previously reported methods. After that diazotization was carried out by novel microwave assisted synthesis which has been described below. The synthesis of the novel azo calix[4]arene is shown in Scheme 1.

2.2.2. Synthesis of p-(2-hydroxy phenylazo) calix[4]arene by Micro wave method

A mixture of 2-hydroxy aniline (2.3 g, 21.1 mmol), sodium nitrite (1.30 g, 18.8 mmol) and 3 ml of conc.HCl in 10 ml of H_2O was placed in microwave synthesizer (CEM Discover System) for 30 s. A solution of 2-hydroxyphenyl diazonium chloride was immediately coupled with calix[4]arene (2.0 g, 4.71 mol) dissolved in a mixture 13 ml of DMF:MeOH (8:5 v/v) in presence of about 0.2 g of sodium acetate trihydrate for 2.0 min to get an orange-red suspension. This was filtered and washed with water:MeOH (9:1 v/v) to afford the dark orange solids. Yield, 1.78 g (89%), mp dec. > 230 °C. Anal. Calc. $C_{52}H_{40}N_8O_8$: C, 68.95; H, 4.42; N, 12.37%. Found: C, 68.65; H, 4.28; N, 12.86%. FT-IR (KBr) υ: 3265 cm^{-1} (–OH), 2950 cm^{-1}, 1489 cm^{-1} (–N=N–). ^{1}H NMR ($CDCl_3$) δ 9.95 (s, 8H, Ar–OH), 8.11 (s, 8H, Ar–H), 2.89 (s, 8H, $-CH_2$ (bridge)), 7.48 (s, 16H, Ar–H). ^{13}C NMR ($CDCl_3$) δ 161,154, 150, 145, 141, 128, 125, 120, 117 and 113 (Ar–C), 17.18, 13.0 ($-CH_2-$). FAB MS (*m*/*z*) 905 (M+1).

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. All the membranes were tested for the different metal solutions (Table 1). Among all membranes, sensor no. 4 showed good performances in terms of characteristics and reproducibility with following ingredients. Sensor no. 4 was prepared by dissolving 9% ionophore, 28% polyvinyl chloride (PVC), 58% dioctylphthalate (DOP) and 5% sodium tetraphenyl borate (NaTPB) in 10 ml of 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	NaTPB	PVC	DOP	Slope (mV $decade^{-1}$)	Linear range (mol L^{-1})
1	5	5	25	65	17.65	2.4×10^{-5} to 1.0×10^{-2}
2	6	9	22	63	18.22	3.2×10^{-5} to 1.0×10^{-1}
3	6	3	30	61	18.40	1.8×10^{-6} to 1.0×10^{-1}
4	9	5	28	58	19.80	4.0×10^{-8} to 1.0×10^{-1}
5	7	6	32	55	17.50	5.4×10^{-6} to 1.0×10^{-2}
6	7	4	24	65	18.75	3.9×10^{-5} to 1.0×10^{-1}

A final transparent membrane of about ~0.5 mm thickness were 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. Which were then cut to desired size and glued to one end of a Pyrex glass tube with araldite. The tube, containing the membrane, was filled with internal filling solution (1.0×10^{-3} mol L^{-1} $NdCl_3$) in the next step. The resulting membrane electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} mol L^{-1} solution of neodymium chloride. The ratio of different membrane ingredients, concentration of equilibrating solution and the time of contact were optimized to provide membranes, which result in reproducible, noiseless and stable potentials.

2.4. Conditioning of membranes and EMF measurements

The prepared membranes were equilibrated for 2 days in different concentrations of outer (1.0×10^{-1} to 4.0×10^{-4} M) with side by side inner solution of different concentration range (1.0×10^{-1} to 1.0×10^{-3} M) neodymium chloride solution. The potentials were measured by varying the concentration of neodymium(III) in test solution in the range of 4.0×10^{-8} to 1.0×10^{-1} mol L^{-1} M. The standard neodymium(III) solutions were obtained by the gradual dilution of 0.1 M neodymium(III) 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} $NdCl_3$)/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 neodymium(III) were calculated according to the Debye–Huckel procedure, using the following equation [33]:

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

where μ is the ionic strength and z the valency.

3. Results and discussion

In the preliminary investigation, the synthesized novel azo calix[4]arene was used as neutral ion carrier to prepare PVC membrane ion-selective electrodes for a variety of metal ion including alkali, rare earth metals and transition metal ions. Literature survey revealed that all the reported PVC membrane sensors have nitrogen or sulfur or oxygen or any of these two, as donating atoms [34–37]. Literature survey also illustrate that in the field of rare earth metal ions, the ionophores that have been used are mostly crown ethers and calixarenes [38–42].

3.1. Effect of the membrane composition

In order to check the suitability of azo calix[4]arene as an ion carrier for Nd(III) and other metal ions, the ionophore was used to prepare PVC membrane ion-selective electrodes for a wide variety of cations including alkali, alkaline earth and transition metal ions. The potential response for the more sensitive ion-selective electrode based on azo calix[4]arene are depicted in Fig. 1. With the exception of Nd^{3+} ions, all the tested cations showed relatively weak responses in the concentration range 1.0×10^{-2} to 1.0×10^{-6} M, due to their weak interactions with the ionophore whereas the presence of four azo groups as well as hydroxyl groups of the azo calix[4]arene interact strongly with the Nd(III) ion efficiently as well as selectively as compared other ions. As seen, among the different cations tested, Nd^{3+} with the most sensitive potential response seems to be suitably determined with the membrane electrode based on azo calix[4]arene (Fig. 1), since in all other cases the slope of the corresponding potential – pM plots was much lower than the expected Nernstian slopes.

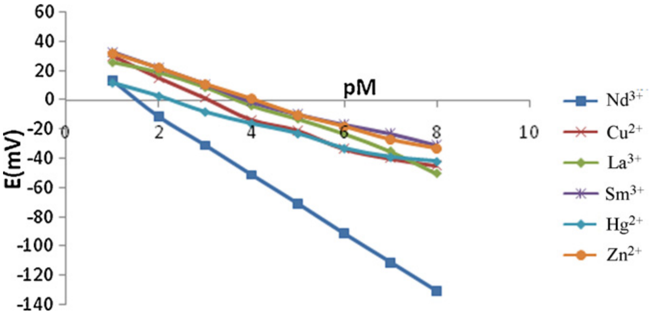

Fig. 1. Potential response of different cations on sensor.

The sensitivity, selectivity and linearity of ion-selective sensors not only depend on the nature of the ionophore used but also significantly on the membrane composition, the properties of the plasticizers and additives used [43–45]. Moreover cation-slective potentiometric sensors based on neutral carrier in a liquid membrane in most cases require the addition of a lipophilic anionic additive to introduce permselectivity [46,47], without such additives many electrodes do not respond properly. Hence, the effect of the presence of a lipophilic anion salt such as NaTPB into the membrane composition prepared with high molecular weight PVC was tested. 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. 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 effects of the membrane composition and the nature and the amount of the plasticizer on the potential response of the Nd^{3+} sensors were investigated and the results are summarized in Table 1. Among the different composition studied, the membrane in absence of ionophore displayed insignificant selectivity towards cation, whereas in the presence of ionophore the membrane showed remarkable selectivity for Nd^{3+}. The membrane optimized with ingredients 9% ionophore, 5% NaTPB, 28% PVC, 58% dioctylphthalate gave the best response. All the membrane sensors were measured in the range 1.0×10^{-1} to 1.0×10^{-8} M. The electrode showed linear response in the range from 4.0×10^{-8} to 1.0×10^{-1} M with Nernstian slope close to 19.80 mV decade^{-1} as shown in Fig. 1.

3.2. Effect of pH

The pH dependence of the potential response of the proposed membrane sensor at 1.0×10^{-3} and 1.0×10^{-4} M in the pH range of 2–10 was tested and the results are shown in Fig. 2. The results indicated that the optimum pH was 4–8. One of the reason for the change in potentials at higher pH (>8.0) may be hydrolysis of the neodymium(III) ion, while at the lower pH, H^+ ion are likely to interfere in the charge transport of membrane.

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,

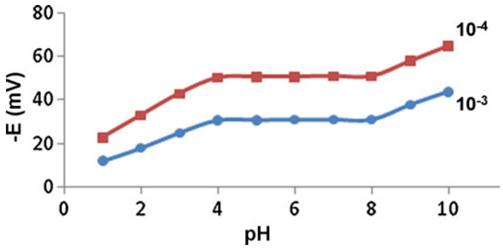

Fig. 2. Effect of pH on the potential response of the Nd^{3+} ion selective electrode.

ethanol–water and acetonitrile–water mixture. The results obtained are compiled in Table 2 and indicate that up to 40% of non-aqueous content, no significant change in the slope and working concentration range of the sensor was observed. At more than 40% non-aqueous medium the working range was significantly reduced, and thus the sensors can only be utilized in mixtures containing up to 40% non-aqueous content.

3.4. Response time of the electrode

Dynamic response time is a factor of considerable value for any sensor in the field of analytical applications. The average time that was required for the Nd^{3+} sensor to reach a potential within ±1 mV of the final equilibrium value was measured. In this study, the practical response time has been recorded by changing the different neodymium ion concentrations (1.0×10^{-6} to1.0×10^{-2} 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 8–10 s. The actual potential versus time curve is shown in Fig. 3 and it can be seen that the electrode reached the equilibrium response in a very short time of about 10 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 (30 s).

3.5. Life time of the ion selective electrode

The experimental result shows that the lifetime of Nd(III) membrane sensor is 120 days. 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 120 days, a gradual decrease in the slope and detection limit was observed.

Table 2
Performance of Nd^{3+} selective electrode in partially non aqueous medium.

Non aqueous content % (v/v)	Working concentration range (M)	Slope (mV decade^{-1})
0	4.0×10^{-8} to 1.0×10^{-1}	19.80 ± 0.3
Ethanol		
10	4.0×10^{-8} to 1.0×10^{-1}	19.80 ± 0.2
20	4.0×10^{-8} to 1.0×10^{-1}	19.80 ± 0.2
30	3.2×10^{-8} to 1.0×10^{-1}	19.40 ± 0.3
40	2.6×10^{-8} to 1.0×10^{-1}	19.32 ± 0.3
50	1.9×10^{-7} to 1.0×10^{-1}	17.50 ± 0.2
Methanol		
10	4.0×10^{-8} to 1.0×10^{-1}	19.80 ± 0.3
20	4.0×10^{-8} to 1.0×10^{-1}	19.80 ± 0.3
30	3.7×10^{-8} to 1.0×10^{-1}	19.56 ± 0.3
40	2.9×10^{-8} to 1.0×10^{-1}	19.20 ± 0.2
50	$2.4 \times 10^{-7}$to 1.0×10^{-1}	18.45 ± 0.3
Acetonitrile		
10	4.0×10^{-8} to 1.0×10^{-1}	19.80 ± 0.2
20	4.0×10^{-8} to 1.0×10^{-1}	19.80 ± 0.2
30	3.1×10^{-8} to 1.0×10^{-1}	19.35 ± 0.3
40	1.9×10^{-8} to 1.0×10^{-1}	19.20 ± 0.4
50	3.5×10^{-7} to 1.0×10^{-1}	16.9 ± 0.3

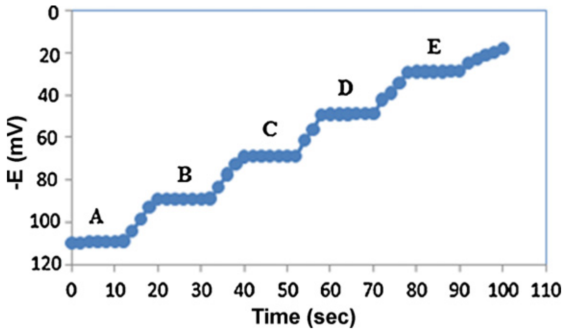

Fig. 3. Dynamic response time of the electrode for step changes in the concentration of the Nd(III) solution: (A) 1.0×10^{-6} M; (B) 1.0×10^{-5} M; (C) 1.0×10^{-4} M; (D) 1.0×10^{-3} M; (E) 1.0×10^{-2} M.

Table 3
Lifetime behavior of Nd^{3+} ion selective electrode.

Days	Slope (mV decade^{-1})	Linear range (M)
15	19.80 ± 0.3	2.0×10^{-8} to 1.0×10^{-1}
30	19.80 ± 0.3	4.0×10^{-8} to 1.0×10^{-1}
45	19.80 ± 0.3	3.6×10^{-8} to 1.0×10^{-1}
60	19.80 ± 0.3	1.0×10^{-8} to 1.0×10^{-1}
75	19.72 ± 0.4	3.7×10^{-8} to 1.0×10^{-1}
100	19.70 ± 0.3	2.8×10^{-8} to 1.0×10^{-1}
120	19.65 ± 0.4	4.5×10^{-8} to 1.0×10^{-1}
135	18.78 ± 0.3	2.5×10^{-7} to 1.0×10^{-1}

3.6. Sensor selectivity

The selectivity behavior is obviously one of the most important characteristics of an ion-selective electrode. This is usually expressed in the term of selectivity coefficient which is evaluated using Match Potential Method (MPM) [48–50]. Different methods of selectivity determination have been found in the literature. But after the narrative work done by Umezawa et al. [51,52]. 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:

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

Table 4
Selectivity coefficients of various interfering ions.

Interfering ions	$K^{MPM}_{Nd^{3+},B}$	Interfering ions	$K^{MPM}_{Nd^{3+},B}$
Hg^{2+}	2.51×10^{-3}	Sm^{3+}	1.25×10^{-3}
Na^{+}	3.16×10^{-3}	Gd^{3+}	2.51×10^{-2}
Dy^{3+}	1.25×10^{-2}	Ni^{2+}	3.98×10^{-3}
Pb^{2+}	1.99×10^{-3}	Co^{2+}	5.01×10^{-3}
La^{3+}	5.01×10^{-2}	Zn^{2+}	3.16×10^{-4}
Ca^{2+}	1.584×10^{-3}	Ce^{3+}	1.58×10^{-3}

Table 5
Comparison of proposed electrode with previous reported electrode.

S.No.	Working concentration range	Slope	pH range	Life time (days)	Response time	Reference
1	1.0×10^{-5} to 1.0×10^{-2}	19.8 ± 0.3	3.5–8.5	42	<15	24
2	1.0×10^{-6} to 1.0×10^{-2}	19.7 ± 0.4	3.7–8.3	60	<10	25
3	5.0×10^{-7} to 1.0×10^{-2}	19.8 ± 0.3	4–8	90	<10	22
4	1.0×10^{-6} to 1.0×10^{-2}	19.7 ± 0.4	3.7–8.3	56	<10	23
5	1.0×10^{-6} to $l \times 10^{-2}$	19.7 ± 0.4	3.7–8.3	42	<10	26
6	1.0×10^{-6} to $l \times 10^{-2}$	19.8 ± 0.3	4–6.5	63	<10	27
Proposed sensor	4.0×10^{-8} to 1.0×10^{-1}	19.8 ± 0.2	4–8	120	<10	

Table 6
Determination of neodymium in spiked water samples using proposed sensor.

Sample	Added ($\mu g\,L^{-1}$)	Found by proposed sensor ($\mu g\,L^{-1}$)	Found by AAS ($\mu g\,L^{-1}$)	Recovery (%)
Vatva G.I.D.C. waste water	20.00	20.35	19.86	99.8
Industrial waste water	50.00	51.80	50.55	101.5
Kankaria lake water	100.00	101.05	99.42	100.2

A specified activity of the primary ions (*A*: 1.0×10^{-3} M of Nd^{3+} ions) is added to a reference solution (1.0×10^{-6} M of Nd^{3+} ions) and the potential is measured. In a separated experiment, interfering ions (B: 1.0×10^{-5} to 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 resulting selectivity coefficients of the proposed Nd^{3+} membrane sensor, for all the tested trivalent ions as well as mono and divalent ions are summarized in Table 4. This seems to indicate negligible interferences in the performance of the electrode assembly. Among the cations, La^{3+} was the major interfering ion in the determination of Nd^{3+} cations. Thus, for the other lower selectivity coefficient values, it was considered that the function of the Nd^{3+} selective membrane sensor would not be greatly disturbed. The surprisingly high selectivity of the membrane electrode for the neodymium ions over the other used cations, most probably arises from the strong tendency of the carrier molecules for the neodymium ions. Thus, the proposed sensor was found to be better than the previous one not only in the terms of detection limit and dynamic range but also in terms of selectivity coefficients (Table 5).

3.7. Analytical method

The proposed sensor was used as an indicator electrode in the titration of 25.0 ml neodymium solution (1.0×10^{-3} mol L^{-1}) with a standard EDTA solution (1.0×10^{-1} mol L^{-1}) at a pH of 5.0 and the resulted titration curve is shown in Fig. 4 that has a very sharp end point. As can be seen, the amount of Nd^{3+} ions in solution can be determined with the electrode accurately ($1.0 \pm 0.2 \times 10^{-3}$ mol L^{-1}).

The present membrane sensor was successfully used in the potentiometric determination of neodymium 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 20, 50 and 100 $\mu g\,L^{-1}$ neodymium and analysis was done after filtered through 0.45 μm filter and adjusting pH to 5.0. The data presented in Table 6, shows that the results obtained by sensor are comparable with atomic absorption spectrometer and recovery is 99.8–101.5.

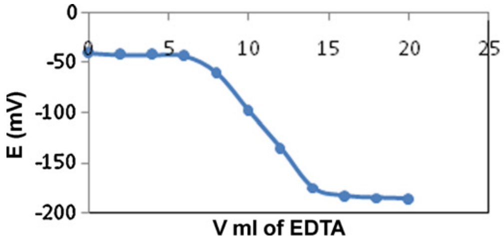

Fig. 4. Potentiometric titration curve of 25.0 ml Nd^{3+} (1.0×10^{-3} mol L^{-1}) with 10^{-1} mol L^{-1} EDTA using the membrane no. 4 as an indicator electrode in pH 5.

Table 7
Determination of Nd^{3+} ion in the binary mixtures.

Nd^{3+} (mol L^{-1})	Added cation (mol L^{-1})	Recovery (%)
4.0×10^{-6}	La^{3+} (2.0×10^{-3})	99.3 ± 0.4
4.0×10^{-6}	Sm^{3+} (1.5×10^{-3})	98.9 ± 0.2
4.0×10^{-6}	Pb^{2+} (1.5×10^{-3})	100.3 ± 0.2
4.0×10^{-6}	Dy^{3+} (2.0×10^{-3})	101.2 ± 0.3
4.0×10^{-6}	Co^{2+} (2.0×10^{-3})	100.8 ± 0.4
4.0×10^{-6}	Gd^{3+} (1.8×10^{-3})	99.7 ± 0.3

Moreover, Table 7 contains the recovery of Nd^{3+} ions in the binary mixtures standard addition method was used of Nd^{3+} ions and different foreign cations. From the results given in Tables 6 and 7, it is obvious that the recovery is quantitative at various neodymium concentrations.

4. Conclusion

A simple construction procedure was used to develop novel azo calix[4]arene based ion selective electrode for the detection of Nd^{3+} ions at low concentration. The electrode responded to Nd^{3+} ion in a Nernstian fashion. The electrode characteristics such as pH range, lower detection limit, response time and specially selectivity were comparable to the previously reported neodymium ion-selective electrodes. The electrode can be successfully applied to the determination of neodymium ion in different water samples containing the different foreign ions and also binary mixtures of neodymium and different cations.

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References

[1] C.D. Gutsche, J.F. Stoddart, (Ed.), Calixarenes Monograph in Supramolecular Chemistry, The Royal Society of Chemistry, Cambridge, 1989.
[2] J. Vicens, V. Bohmer (Eds.), Calixarenes, A versatile Class of Macrocyclic Compounds, Kluwer Academic Publishers, Dordrecht, 1991.
[3] J.D. van Loon, A. Arduini, W. Verboom, R. Ungaro, G.J. van Hummel, S. Harkema, D.N. Reinhoudt, Tetrahedron Lett. 30 (20) (1989) 2681–2684.
[4] P. Jose, S.K. Menon, Bioinorg. Chem. Appl. (2007).

[5] S.T. Ganjali, R. Zadmard, M. Zeyaei, K. Rahnama, F. Faridbod, M.R. Ganjali, Synthesis of a New Calix[4]Arene and Its Application in Construction of a Highly Selective Silver Ion-Selective Membrane Electrode, Hindawi Publishing Corporation, 2009. (Research Article).
[6] K. Yonetake, T. Nakayama, M. Ueda, J. Mater. Chem. 11 (2001) 761–767.
[7] Y. Liu, H. Wang, L.H. Wang, Z. Li, H.Y. Zhang, Q. Zhang, Tetrahedron 59 (40) (2003) 7967–7972.
[8] B. Tomapatanaget, T. Tuntulani, O. Chailapakul, Org. Lett. 5 (9) (2003) 1539–1542.
[9] J.H. Bok, H.J. Kim, J.W. Lee, S.K. Kim, J.K. Choi, J. Vicens, Tetrahedron Lett. 47 (8) (2006) 1237–1240.
[10] A.I. Costa, L.F.V. Ferreira, J.V. Prata, J. Polym. Sci. B: Polym. Phys 46 (19) (2008) 6477–6488.
[11] M.M. Paula, A.R. José, A.P.S. Manuel, J.L.C. Pereira, J. Phys. Org. Chem. 12 (9) (1999) 695–702.
[12] T.L. Kao, C.C. Wang, Y.T. Pan, Y.J. Shiao, J.Y. Yen, C.M. Shu, G.H. Lee, S.M. Peng, W.S. Chung, J. Org. Chem. (2005) 2912–2920, 15;70(8).
[13] F. Karc, I. Sener, H. Deligoz, Dyes Pigments 59 (2003) 53–61.
[14] I. Sener, F. Karc, E. Kılıc, H. Deligoz, Dyes Pigments 62 (2004) 141–148.
[15] Available online: http://en.wikipedia.org/wiki/Neodymium.
[16] N. Wang, Z. Si, W. Jiang, Spectrochim. Acta A: Mol. Biomol. Spectrosc. 53 (6) (1997) 829–834.
[17] Y.M. Liu, Spectrosc. Spect. Anal. 24 (2004) 1257.
[18] B.L. An, B. Li, G.R. Zhang, Rare Met. Mater. Eng. 28 (1999) 333.
[19] J.S. Benco, H.A. Nienaber, W.G. McGimpsey, J. Anal. Chem. 75 (2003) 152–156.
[20] M. D'Orazio, S. Tonarini, Anal. Chim. Acta 351 (1997) 325–335.
[21] S. Chandra, D.R. Singh, Mater. Sci. Eng. A 502 (2009) 107–110.
[22] V.K. Gupta, R.N. Goyal, R.A. Sharma, Anal. Chim. Acta 647 (2009) 66–71.
[23] H. Behmadi, H.A. Zamani, M.R. Ganjali, P. Norouzi, Electrochim. Acta 53 (2007) 1870–1876.
[24] P. Norouzi, M.R. Ganjali, A. Ahmadalinezhad, M. Adib, J. Braz. Chem. Soc. 17 (2006) 1309–1315.
[25] M.R. Ganjali, A. Ahmadalinezhad, P. Norouzi, M. Adib, J. Appl. Electrochem. 36 (2006) 931–936.
[26] M. Shamsipur, M. Hosseini, K. Alizadeh, M.F. Mousavi, A. Garau, V. Lippolis, A. Yari, Anal. Chem. 77 (2005) 276–283.
[27] B. Patel, A. Kumar, S.K. Menon, J. Inclusion Phenom. Macrocyclic Chem. 64 (2009) 101–108.
[28] B. Patel, A. Kumar, S.K. Menon, J. Inclusion Phenom. Macrocyclic Chem. 64 (2009) 239–247.
[29] A. Kumar, S.K. Menon, Supramol. Chem. 22 (2010) 46–56.
[30] A. Kumar, B. Patel, G. Patel, S.K. Menon, Fullerenes Nanotubes Carbon Nanostruct. 18 (2010) 186–197.
[31] C.D. Gutsche, B. Dhawan, K. Hyun, R. Muthukrishnan, J. Am. Chem. Soc. 103 (1981) 3782–3792.
[32] C.D. Gutsche, M. Iqbal, D. Stewart, J. Org. Chem. 51 (1986) 742–745.
[33] S. Kamata, A. Bhale, Y. Fukunage, A. Murata, Anal. Chem. 60 (1988) 2464.
[34] M.R. Ganjali, M. Qomi, A. Daftari, P. Norouzi, M.S. Niasari, M. Rabbani, Sens. Actuators B 98 (2004) 92–96.
[35] M.R. Ganjali, F. Faridbod, P. Norouzi, M. Adib, Sens. Actuators B 120 (2006) 119–124.
[36] M.R. Ganjali, P. Norouzi, A. Daftari, F. Faridbod, M.S. Niasari, Sens. Actuators B 120 (2007) 673–678.
[37] A. Soleymanpour, N.A. Rad, K. Niknam, Sens. Actuators B 114 (2006) 740–746.
[38] M.Yu. Alyapyshev, V.A. Babain, V.I. Boyko, I.I. Eliseev, D.O. Kirsanov, O.V. Klimchuk, A.V. Legin, E.S. Mikhailina, R.V. Rodik, I.V. Smirnov, J. Inclusion Phenom. Macrocyclic Chem. 67 (2010) 117–126.
[39] D.S. Guo, Z.P. Liua, J.P. Ma, R.Q. Huang, Tetrahedron Lett. 48 (2007) 1221–1224.
[40] Ernesto Brunet, Olga Juanes, R. Ubis, C. Juan, Curr. Chem. Biol. 1 (2007) 11–39.
[41] M.R. Ganjali, P. Norouzi, F. Faridbod, M. Rezapour, M.R. Pourjavid, J. Iran. Chem. Soc. 4 (2007) 1–29.
[42] S. Amarchand, S.K. Menon, Y.K. Agrawal, Electroanalysis 12 (2000) 522–526.
[43] U. Oesch, W. Simon, Anal. Chem. 52 (1980) 692–700.
[44] D. Ammann, E. Pretsch, W. Simon, E. Lindner, A. Bezegh, E. Pungor, Anal. Chim. Acta 171 (1985) 119–129.
[45] T. Rosatzin, E. Bakker, W. Simon, K. Suzuki, Anal. Chim. Acta 280 (1993) 197–208.
[46] U. Schaller, E. Bakker, U.E. Spichiger, E. Pretch, Anal. Chem. 66 (1999) 391–398.
[47] P. Buhlmann, E. Pretch, E. Bakker, Chem. Rev. 97 (1997) 3083–3132.
[48] H.A. Zamani, M.R. Ganjali, M.J. Pooyamanesh, J. Braz. Chem. Soc. 17 (2006) 149–155.
[49] H.A. Zamania, G. Rajabzadeh, M.R. Ganjali, Sens. Actuators B 119 (2006) 41–46.
[50] H.A. Zamani, M.R. Ganjali, P. Norouzi, S. Meghdadi, J. Appl. Electrochem. 37 (2007) 853–859.
[51] Y. Umezawa (Ed.), Handbook of Ion-Selective Electrodes: Selectivity Coefficients, CRC Press, Boca Raton, FL, 1990.
[52] Y. Umezawa, K. Umezawa, H. Sato, Pure Appl. Chem. 67 (1995) 508–518.