

A dynamic electrochemical sensor for europium(III)

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A new calixarene derivative, i.e., *p*-*tert*-butylcalix[4]arene has been used as an excellent ionophore in the construction of a novel PVC based Eu(III)-selective electrode. A master membrane with percentage composition of PVC:DBP:L: NaTPB:: 32:55:4:9 gives the best results. The membrane electrode exhibits a nernstian response with the slope of 19.7 ± 1.0 mV/decade over a wide concentration range of 9.1×10^{-8} – 1.0×10^{-1} M and with detection limit of 8.8×10^{-8} M. The effects of membrane composition and pH as well as the influence of the anionic additive on the electrode performance have been investigated. The potential response of the resulting sensor is not influenced in the pH range 3.0–9.0. Moreover, the membrane electrode has a good reproducibility (RSD 3%), very fast response time (5 s) and ability to detect Eu(III) among other rare earth metal and common cations. The membrane sensor works satisfactorily up to 40% non-aqueous medium and can be used over a period of 6 months. The sensor has been successfully applied for the determination of Eu(III) in analytical and biological samples (urine and serum) and also acts as an electrode indicator.

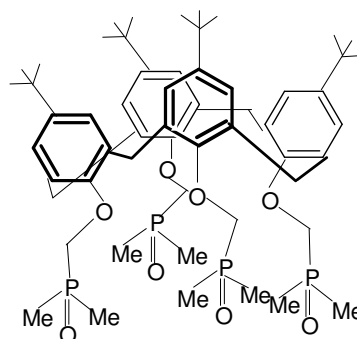
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The last few years have seen growing interest in inorganic and bioorganic chemistry of rare earths because of their wide industrial applications. Their determination is necessary due to toxicity and other adverse effects¹. There are several applications reported for lanthanides, especially europium, which has been used to dope some types of glass to make lasers. Europium complexes are also used for differentiating between genuine and counterfeit currency notes². Europium phosphors are used in television tubes to give a bright red colour and as an activator for yttrium-based phosphors. For powerful street lighting a small amount of europium is added to mercury vapour lamps to give a more natural light. A salt of europium is used for newer phosphorescent powder and paints. However, europium in dust form is a fire and explosion hazard. Around 400 tons of europium are produced worldwide each year^{2,3}.

Voltammetry, mass spectroscopy and Rutherford back-scattering techniques, higher order derivative spectrometry, ICP-MS, NAA (neutron activation analysis) and spectrofluorometric methods have been used for the analysis of europium⁴⁻⁷. These methods are either time consuming, involving multiple sample manipulations or too expensive for most analytical laboratories. But the potentiometric polymeric electrodes, offer several advantages such as fast and ease of preparations and procedures, simple

instrumentations, relatively fast responses, very low detection limit, wide dynamic ranges, reasonable selectivity and low costs. This has led to an increase in the number of available electrodes and microelectrodes over the last few years⁸. However, there are only a few reports available on the europium-selective electrodes in the literature i.e., calix[4]arenetetraphosphineoxide⁹, N,N-diethyl-N-(4-hydroxy-6-methylpyridin-2-yl)guanidine¹⁰, S-N hexadentates Schiff base¹¹, 4-(2-hydroxybenzylideneamino)-6-methyl-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2*H*)-one¹² and 4*E*-4-(2-(CE)-(2-aminoethylimino)methyl)phenyl¹³.

In the proposed work, we have used *p*-*tert*-butylcalix[4]arene derivative (L) as a suitable lipophilic neutral ionophore for the construction of a



p-*tert*-Butylcalix[4]arene derivative
(L)

PVC based membrane electrode for selective determination of europium ion. The proposed electrode has also been utilized in analytical and biological samples. The results are correlated well with the results from inductive coupled plasma, mass spectrophotometry. For determining the concentration of europium, the proposed method is the best method in terms of low detection limit as well as interference due to foreign ions. Also, it is cost effective and an easy method in comparison to other reported methods.

Materials and Methods

All the analytical grade reagents were of 99.9 % purity and were used as such. High molecular weight poly(vinyl chloride) (PVC), 1-chloronaphthalene (CN), oleic acid (OA), dibutylbutylphosphonate (DBBP), dioctylphthalate (DOP), dibutylphthalate (DBP), tris(2-ethylhexyl)phosphate (TEP), sodium tetraphenylborate (NaTPB) and tetrahydrofuran (THF) and cyclohexanone were purchased from Merck. All metal nitrates were also bought from Merck. Doubly distilled water was used to prepare the metal nitrate solutions. Stock solutions of metal nitrates of 10^{-1} M concentration were obtained by dissolving weighed amounts of the corresponding salt in doubly distilled water. Solutions of 10^{-2} – 10^{-8} M concentration were obtained by diluting the stock solution. The UV visible spectra were recorded on a computerized double-beam Shimadzu 2550 spectrophotometer, using two matched 10 mm quartz cells. Saturated calomel electrodes (SCE) were used as reference electrodes and a digital potentiometer ECIL, India (model pH 5662) was used for potential measurements at 25 ± 0.1 °C.

The ionophore, *p-tert*-butylcalix[4]arene derivative, was synthesized using well-established synthetic procedures for tetra-substituted calix[4]arene ethers in the cone conformation with phosphorus-containing pendant arms^{14,15}.

Electrode fabrication

Several methods are available for the membrane preparation such as casting method and sol-gel method. In the present study, the membranes were prepared using casting method as reported by Craggs *et al.*¹⁶ Different plasticizers such as DBP, DBBP, TEP, 1-CN, OA, DOP were used individually in same amounts along with the anion excluder NaTPB to get membranes of different compositions. Membranes were prepared by dissolving PVC (32 mg), *p-tert*-butylcalix[4]arene derivative (4 mg),

plasticizer (55 mg) and anion excluder NaTPB (9 mg) in 15 mL of THF. The mixture was shaken vigorously to obtain a homogenous paste and after complete dissolution of all components, it was poured in to the glass cast ring placed on a smooth glass plate and kept for 48 h for solvent evaporation, when a membrane of uniform thickness was obtained. The membrane of 0.5 mm thickness was removed carefully from the glass cast ring and cut to the size of the pyrex glass tube and glued to one end of a glass tube with the help of araldite and M-seal to avoid leakage.

The half-cells were adjoined in the following manner for obtaining the potential measurement:

Internal reference electrode (SCE)	Internal reference solution (0.01 M Eu ³⁺)	Europium selective membrane	Test solution	External reference electrode (SCE)
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Saturated calomel electrodes were used both as internal and external reference electrodes. Two half-cells were combined with the help of a salt bridge. Potential measurements were made from low to high concentration range (9.1×10^{-8} – 1.0×10^{-1} M) to avoid memory effect. Ionic strength of various solutions was maintained with the help of saturated solution of KCl. When the membrane was not in use, it was kept in 0.01 M Eu(NO₃)₃ solution to avoid damage by cracking.

Membrane present in the ion selective electrode frequently contain built-in "fixed" charged sites, or intentionally added, hydrophobically trapped, "mobile" sites (e.g., tetraphenyl borate in plasticized poly(vinyl chloride)). Such membranes with charged sites are named sited membranes. Sited membranes are "permselective" to counterions, i.e., only counterions (Eu³⁺) exchange into the membrane and therefore are mobile to a certain extent in the membrane bulk. A potential arises when a membrane separates two solutions of different activities. Nernstian response occurs when an ion-selective electrode responds according to "local" thermodynamic equilibrium, over a given range of activity (or concentration). For Nernstian response a plot of the potential difference of the ISE cell (ISE with an outer reference electrode) versus the logarithm of the ionic activity of a given species (a_A) is linear with a slope of $2.303 RT/Z_{af}$. Nernstian response implies ideal sensitivity of ion selective electrode¹⁷.

Determination of europium in real samples

The bastnasite and monazite ores (0.40 g) were dissolved separately in 25 mL of 55 % HNO₃ and the solutions were heated under a fuming hood until

fumes were observed. Doubly distilled water (5 ml) was added to each solution after it had been cooled to room temperature and the solutions were again heated until fumes were observed. The same treatment was repeated till complete dissolution of the sample and the pH of the resulting solution was buffered at pH 6.0 with sodium hydroxide. Final solution was transferred into a 100 mL volumetric flask and diluted up to the mark with doubly distilled water. Finally, 3 mL of this solution was further diluted to 500 mL in a volumetric flask with doubly distilled water and analysed for Eu^{3+} .

The collected samples were measured and 75 % HNO_3 solution (v/v) was added. The sample was heated overnight at 50 °C with occasionally venting by loosening the caps. The resulting solutions were then diluted with doubly distilled water up to a total dilution of 200 times the original measured sample. These solutions were buffered at pH 6.0 with sodium hydroxide and heated again overnight at 50 °C, cooled and analysed for Eu^{3+} .

Results and Discussion

The calixarene ionophore has relatively low solubility in water due to the existence of hydrophobic alkyl groups in the structure, indicating its lipophilic character which prevents the ionophore from leaching into the solution surrounding the membrane electrode. This is attributed to the presence of four oxygen atoms, which make the ligand a better potential ion carrier for trivalent metal ions in polymeric membrane electrodes. Moreover, it was observed that calixarenes with phosphorus-containing pendant arms (L) are better extractants for lanthanides(III) and actinides(IV) than TOPO (trioctylphosphine oxide) or CMPO ((N,N-diisobutylcarbamoylmethyl)-octylphosphine oxide) used in the nuclear waste management. Ionophore (L) forms hydrated complexes with 1:1 or 1:2 stoichiometry with Ln^{3+} ions ($\text{Ln} = \text{La}, \text{Eu}, \text{Tb}$)¹⁵. Therefore, we were prompted to investigate the behaviour of the ligand with the donating atom as carrier in the fabrication of PVC based membrane for the estimation of various metal ions concentrations in aqueous solution. Figure 1 shows that the ionophore was found to be highly responsive to Eu(III) in comparison to several other metal ions. In order to have a clear picture of the selectivity of calixarene ionophore for various metal ions, its complexes with Eu(III), Nd(III), Hg(II), Sm(III), Er(III), Gd(III),

Dy(III), Ni(II), Zn(II), Zr(IV), Cd(II), Co(II), Ca(II), Pb(II), Al(III), Fe(III), Mg(II), K(I), Na(I) ions were studied by using *ab initio* theoretical calculations. The influence of the nature, size and charge of metal ions on the complexation reaction with the neutral ligand is explained on the basis of the calculation of gap-phase binding energies.

Molecular structures of the uncomplexed calixarene and its complexes with Eu(III) and other metal ions were optimized using the lanl2mb basis set for all atoms at restricted Hartree Fock (RHF) level. No molecular symmetry constraint was applied, and full

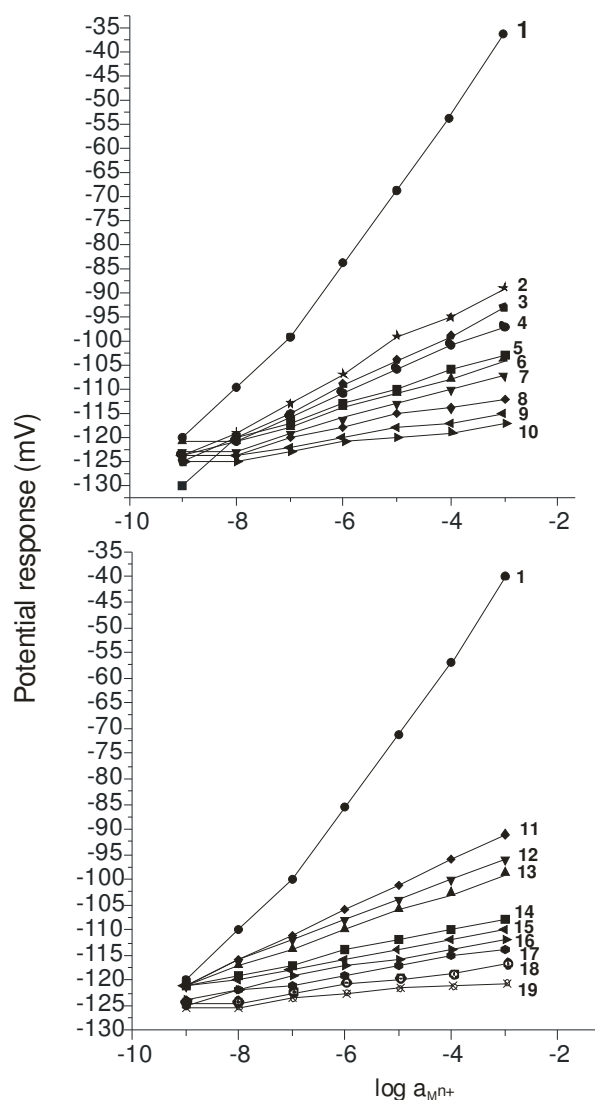


Fig. 1 — Potentiometric calibration response of a PVC-based sensor using *p*-*tert*-butyl-calix[4]arene derivative as an ionophore towards various metal ions. [1, Eu^{3+} ; 2, Zr^{4+} ; 3, Al^{3+} ; 4, Fe^{3+} ; 5, Nd^{3+} ; 6, Sm^{3+} ; 7, Er^{3+} ; 8, Gd^{3+} ; 9, Dy^{3+} ; 10, Ho^{3+} ; 11, Hg^{2+} ; 12, Mg^{2+} ; 13, Pb^{2+} ; 14, Cd^{2+} ; 15, Na^+ ; 16, K^+ ; 17, Ca^{2+} ; 18, Ni^{2+} ; 19, Zn^{2+}].

optimization of all bond lengths, angles and torsion angles was carried out using the Gaussian 98 program. The binding energy (ΔE) was calculated with the enlarged basis sets using the equation, $\Delta E = E_{\text{complex}} - (E_{\text{ligand}} + E_{\text{cation}})$, where E_{complex} , E_{ligand} and E_{cation} are the total energies of the complex, uncomplexed calixarene and the metal ion, respectively.

Optimization of the uncomplexed calixarene ionophore was also carried out with the semi-empirical PM3 method using gHyperchem software (ver. 6.01). No adequate parameterization of the metal ions was available in PM3, so semi-empirical calculations could not be carried out on the complexes. The theoretical data were obtained for the stability of the *p*-tert-butylcalix[4]arene derivative complexes with Nd(III), Hg(II), Sm(III), Er(III), Gd(III), Dy(III), Ni(II), Zn(II), Zr(IV), Cd(II), Co(II), Ca(II), Pb(II), Al(III), Fe(III), Mg(II), K(I), Na(I) and Eu(III) ions. Table 1 shows that the cation binding energies with calixarene ionophore has a pronounced dependence on the nature of metal ions used. In fact, the stability of the resulting complexes is in the decreasing order as follows:

Eu(III) > Nd(III) > Hg(II) > Sm(III) > Er(III) > Gd(III) > Dy(III) > Ni(II) > Zn(II) > Zr(IV) > Cd(II) > Co(II) > Ca(II) > Pb(II) > Al(III) > Fe(III) > Mg(II) > K(I) > Na(I).

Table 1 — Binding energy of complexes of different metal ions with calixarene ionophore

Metal ion	Total energy (Hartee)		Binding energy ΔE (kcal/mol)
	Metal ion	Ion complex	
Na ⁺	-10.1454	-897.2373	-98.6
K ⁺	-12.7942	-898.3479	-213.1
Mg ²⁺	-13.8925	-899.8082	-264.3
Ca ²⁺	-35.6124	-904.5722	-411.7
Pb ²⁺	-31.2811	-903.8695	-371.2
Al ³⁺	-28.6554	-902.1905	-358.5
Co ²⁺	-42.1541	-905.9664	-426.8
Fe ³⁺	-27.8346	-901.9819	-346.4
Ni ²⁺	-62.6321	-929.8981	-479.5
Zn ²⁺	-52.7348	-918.6879	-472.9
Zr ⁴⁺	-50.8723	-907.4599	-469.8
Cd ²⁺	-45.7232	-906.8739	-425.4
Hg ²⁺	-81.5246	-969.8395	-549.7
Nd ³⁺	-83.4229	-979.9369	-557.5
Sm ³⁺	-80.2892	-965.7824	-528.3
Gd ³⁺	-69.2859	-948.9988	-498.2
Dy ³⁺	-68.3929	-937.9596	-487.6
Er ³⁺	-79.1082	-959.9269	516.4
Eu ³⁺	-85.6952	-988.5889	-599.8

Furthermore, in order to obtain more information about the complexation of the ionophore with europium(III) ions, the electronic absorption spectra of the ionophore (L) ($6.0 \times 10^{-5} M$) in the presence of increasing concentration of Eu³⁺ ion in acetonitrile solution at room temperature were studied. As seen, the strong absorption of ionophore at 360 nm decreases with increasing concentration of the metal ion at the expense of a new broad band at > 405 nm. The resulting absorbances of the ionophore (at 360 nm) and its europium complex (at 420 nm) against [Eu³⁺]/[L] mole ratio plots (Fig. 2), reveal a distinct inflection point corresponding to metal-to-ligand molar ratio of about 1, emphasizing the formation of a 1:1 complex in solution. Moreover, the existence of a sharp isosbestic point at 380 nm is in support of the occurrence of simple 1:1 complexation equilibrium in solution.

For evaluation of the conditional formation constants, the mole ratio data obtained at the two wavelengths (Fig. 3) were fitted to a previously reported equation using a non-linear least-squares curve fitting program KINFIT¹⁸. The conditional formation constants of the complex was evaluated as $\log K_f = 9.26 \pm 0.02$ at 340 nm and $\log K_f = 9.75 \pm 0.03$ at 420 nm, which are actually the same within the corresponding experimental errors. It was found that the stability of ligand-complexes with other tested metal ions viz., Nd(III), Hg(II), Sm(III), Er(III), Gd(III), Dy(III), Ni(II), Zn(II), Zr(IV), Cd(II), Co(II) is much less than that with Eu(III) ion.

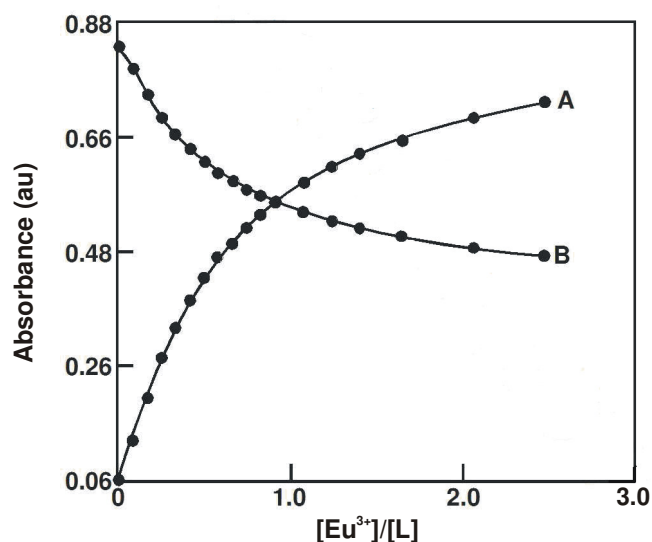


Fig. 2 — Mole ratio plots for the titration of $6.0 \times 10^{-5} M$ of ionophore with $\text{Eu}(\text{NO}_3)_3$ solution in acetonitrile at 420 nm. [A = abs. of the europium complex; B = abs. of the ionophore].

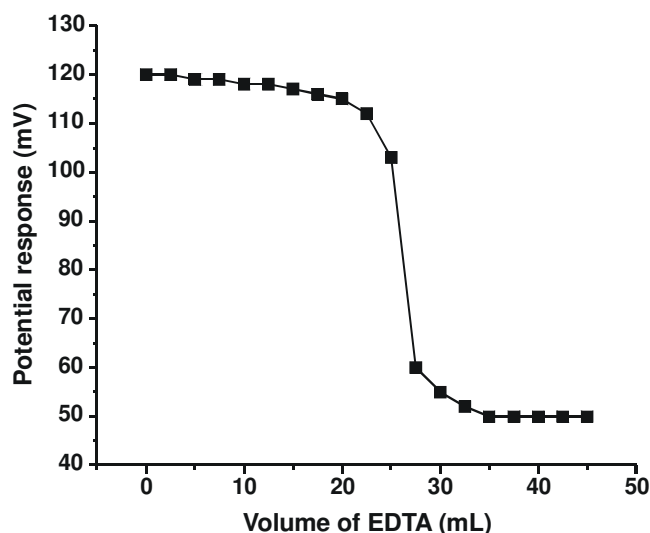


Fig. 3 — Potentiometric titration curve of 50 mL of $10^{-3} M$ Eu^{3+} solution with $1 \times 10^{-2} M$ EDTA using the membrane electrode as an indicator electrode.

Membrane optimization and effect of membrane composition on the electrode response

Out of seven membrane compositions, we got one optimized membrane with plasticizer PVC, DBP, *p*-tert-butyl-bis[4]arene and NaTPB having percentage composition ratio (32:55:4:9). Membrane electrode without plasticizer (membrane electrode no.1) exhibited a narrow working concentration range (6.0×10^{-6} to $1.0 \times 10^{-1} M$) with a slope of 07.00 mV/decade of activity and a response time of 30 s. Since the nature of plasticizer influences the dielectric constant of the membrane phase, the mobility of the ionophore and state of ligand¹⁹, it was expected to play a key role in determining the ion-selective characteristics. Hence, various plasticizers (DBP, DBBP, TEP, CN, OA, and DOP) were added in different amounts to the membranes and ion-selective characteristics were studied. The optimization of permselectivity of the membrane sensor is known to be highly dependent on the incorporation of additional membrane components. Thus, sodium tetraphenyl borate (NaTPB) (anionic excluder) was also added to the membrane components to increase the conductivity and minimize interference from lipophilic anions²⁰. The addition of solvent mediators, DBBP and CN, (electrodes no. 3 and 5) improved the working concentration range to 9.5×10^{-8} - $1.0 \times 10^{-1} M$ and 9.6×10^{-8} - $1.0 \times 10^{-1} M$ and the slopes to 23.0 and 22.0 mV/decade of activity, respectively. The membrane containing DOP as plasticizer (electrode

no. 7) showed a linear potential in the concentration range 8.1×10^{-7} - $1.0 \times 10^{-1} M$ with slope of 11.05 mV/decade of activity. However, the addition of the plasticizers TEP and OA (membranes no. 4 and 6) did not improve the performance of the electrodes. The membrane having DBP as plasticizer exhibited the best results (electrode no. 2). This sensor gave a Nernstian response (slope 19.70 ± 1.0 mV/decade of activity) in the concentration range 9.1×10^{-8} - $1.0 \times 10^{-1} M$ of Eu^{3+} and a response time as fast as 5 s. Therefore, electrode no. 2 with the optimum composition PVC:DBP:L:NaTPB::32:55:4:9) was chosen for all further studies. Repeated monitoring of potentials (20 measurements) on the same portion of the sample with this electrode gave a standard deviation of ± 1.0 mV. The sensing behavior of the membranes did not change when the potentials were recorded from lower to higher concentrations or vice-versa.

Influence of internal reference solution

Calibration curves using different concentrations of the internal solution from 10^{-1} - 10^{-4} mol/L of Eu^{3+} solution show that the concentration of internal solution also affects the potential response of ion selective electrodes. It was observed that 10^{-2} mol/L of Eu^{3+} solution did not cause any significant change in potential response plot (calibration plot). Therefore, a solution of 1×10^{-2} mol/L $\text{Eu}(\text{NO}_3)_3$ would be quite satisfactory as a suitable internal solution for proper functioning of the electrode system.

Effect of pH on the electrode response

Sensitivity of the electrode towards pH was checked over the pH range of 1.0-12.0 using the test solution of europium nitrate in three different concentration ranges at 1.0×10^{-3} , 1.0×10^{-4} and $1.0 \times 10^{-5} M$. All the working solutions were prepared in distilled water with 10^{-2} mol L⁻¹ TRIS buffer and the pH was adjusted to the required value by adding NaOH or HCl. Beyond pH range of 3.0-9.0, a gradual change in the potential was detected. The observed potential drift at higher pH value could be due to the formation of some hydroxy complexes of Eu^{3+} in the solution. At the lower pH values the potential increased indicating that the membrane electrode responds to hydrogen ions (H^+). The performance of electrode membrane no. 2 was also checked in partially non-aqueous media using water-ethanol, water-methanol, water-acetone and water-acetonitrile mixtures. It works satisfactorily in non-aqueous

medium having up to 35 % (v/v) content of ethanol, methanol, acetone and acetonitrile (Table 2). The working concentration range and slope remain unchanged for these mixtures but above the 35 % non-aqueous content, the working concentration range and slope were reduced and showed potential drift with time.

Dynamic response time and life time

Dynamic response time for this membrane electrode was determined by measuring the time required to achieve a stable potential. The response time of the membrane electrode is considerably fast (5 s) and potential remained constant for more than 4-5 min. The experimental results show that the Eu^{3+} membrane sensor was stable for nearly 6 months. During this period, the membrane electrodes were used daily use over an extended period of time (one hour per day). After six months, a gradual decrease in the slopes and detection limits were observed²¹.

Potentiometric selectivity

Selectivity coefficient is one of the most important parameter for any membrane electrode. It is relative to the response from the primary ion over other ions present in solution. To investigate the selectivity of the proposed membrane electrode, its potential response was investigated in the presence of various

interfering foreign cations using the matched potential method (MPM), recommended by IUPAC in 1995^{22,23}. The procedure is expected to report analytically the selectivity coefficient relevant for practical applications.

According to the MPM, the selectivity coefficient is defined as the activity (concentration) ratio of the primary ion and the interfering ion, which gives the same potential change in reference solution. Thus, one should measure the change in potential upon changing the primary ion activity. Then, the interfering ion would be added to an identical references solution until the same potential change is obtained. The selectivity coefficient, $K_{A,B}^{\text{MPM}}$ is calculated as $K_{A,B}^{\text{MPM}} = \Delta A / \alpha_B$, where $\Delta A = \alpha'_A - \alpha_A$, α_A is the initial primary ion activity and α'_A the activity of A in the presence of interfering ion α_B . The concentration of Eu^{3+} used as primary ion in this study was $6.0 \times 10^{-7} M$. The resulting selectivity coefficients are summarized in Table 3. As seen, the hardest, soft and borderline metal ions used do not affect the performance of the Eu^{3+} ion selective membrane electrode significantly.

Analytical applications

Europium concentrations were determined in bastnasite and monazite ores and biological sample of urine and serum. The results obtained with the proposed work correlate well with the results obtained by inductive coupled plasma mass spectrophotometry (Table 4).

Table 2 — Effect of partially non-aqueous medium on the working of Eu^{3+} sensor. [PVC:DBP:L: NaTPB (32:55:4:9)]

Non-aq. content (% v/v)	Slope of activity (mV/decade)	Working conc. range (M)	Response time (s)
0	19.70 ± 1.0	$9.1 \times 10^{-8} - 1.0 \times 10^{-1}$	5
Methanol			
5	18.05 ± 1.0	$8.9 \times 10^{-8} - 1.0 \times 10^{-1}$	5
15	18.00 ± 1.0	$8.9 \times 10^{-8} - 1.0 \times 10^{-1}$	6
25	17.40 ± 1.0	$8.2 \times 10^{-8} - 1.0 \times 10^{-1}$	7
35	17.00 ± 1.0	$8.1 \times 10^{-8} - 1.0 \times 10^{-1}$	6
Ethanol			
5	19.05 ± 1.0	$8.8 \times 10^{-8} - 1.0 \times 10^{-1}$	5
15	18.50 ± 1.0	$8.5 \times 10^{-8} - 1.0 \times 10^{-1}$	6
25	18.01 ± 1.0	$8.3 \times 10^{-8} - 1.0 \times 10^{-1}$	6
35	18.00 ± 1.0	$8.1 \times 10^{-8} - 1.0 \times 10^{-1}$	7
Acetone			
5	19.00 ± 1.0	$8.9 \times 10^{-8} - 1.0 \times 10^{-1}$	5
15	19.03 ± 1.0	$8.7 \times 10^{-8} - 1.0 \times 10^{-1}$	6
25	17.99 ± 1.0	$8.1 \times 10^{-8} - 1.0 \times 10^{-1}$	6
35	17.50 ± 1.0	$8.1 \times 10^{-8} - 1.0 \times 10^{-1}$	7
Acetonitrile			
5	19.50 ± 1.0	$9.0 \times 10^{-8} - 1.0 \times 10^{-1}$	5
15	19.10 ± 1.0	$8.9 \times 10^{-8} - 1.0 \times 10^{-1}$	6
25	18.90 ± 1.0	$8.8 \times 10^{-8} - 1.0 \times 10^{-1}$	6
35	18.01 ± 1.0	$8.8 \times 10^{-8} - 1.0 \times 10^{-1}$	6

Table 3 — Selectivity coefficient of the membrane by match potential method. [PVC:DBP:L: NaTPB (32:55:4:9)]

Interfering ion (M^{n+})	Selectivity coeff. $K_{Eu^{3+}, M^{n+}}^{\text{Pot}}$
Na^+	5.5×10^{-7}
K^+	5.3×10^{-7}
Ca^{2+}	3.4×10^{-6}
Mg^{2+}	3.0×10^{-6}
Pb^{2+}	2.5×10^{-6}
Al^{3+}	8.0×10^{-6}
Co^{2+}	6.5×10^{-6}
Fe^{3+}	5.1×10^{-6}
Ni^{2+}	6.9×10^{-6}
Zn^{2+}	4.2×10^{-6}
Cd^{2+}	2.8×10^{-6}
Hg^{2+}	4.4×10^{-6}
Nd^{3+}	6.8×10^{-6}
Sm^{3+}	3.5×10^{-6}
Gd^{3+}	2.8×10^{-6}
Dy^{3+}	2.0×10^{-6}
Er^{3+}	2.3×10^{-6}
Lu^{3+}	2.2×10^{-6}

Table 4 — Determination of Eu^{3+} in europium ores and biological samples

Samples	Eu^{3+} ($\mu\text{g/L}$)	
	ICPMS	Proposed method
Monazite ore	120.5 ± 0.50	121.1 ± 0.20
Bastnasite ore	119.5 ± 0.50	119.5 ± 0.60
Urine	00.8 ± 0.50	00.8 ± 0.60
Serum	00.5 ± 0.80	00.5 ± 0.85

The proposed ion selective membrane electrode was successfully applied as an indicator electrode in conjunction with saturated calomel electrode in potentiometric titration of Eu^{3+} solution with EDTA as a suitable titrant. Eu^{3+} solution (50 ml , $1.0 \times 10^{-3} \text{ M}$) was titrated against $1.0 \times 10^{-2} \text{ M}$ EDTA solution. The titration curve was of conventional sigmoid shape, indicating sufficient selectivity of the sensor towards Eu^{3+} ions (Fig. 3). The quantity of Eu^{3+} ions in the test solution may be determined accurately from the titration curve providing a sharp end point.

Conclusions

The present study reveals that the membrane electrode incorporating *p*-tert-butylcalix[4]arene to be an excellent sensing material and far superior to the other existing Eu^{3+} -electrodes. The membrane sensor having percentage composition of PVC:DBP:L:NaTPB ::32:55:4:9 can be used to determine Eu(III) within the concentration range $9.1 \times 10^{-8} - 1.0 \times 10^{-1} \text{ M}$ with the lowest detection limit of $8.8 \times 10^{-8} \text{ M}$. The functional *pH* range of membrane sensor is 3.0-9.0 and most of the ions commonly present in the solution do not cause any interference. The sensor exhibits excellent reproducibility, fast response time (5 s) and can be used for about six months in aqueous as well as in non-aqueous medium. The practical utility of this electrode both in analytical as well as in biological samples, is also demonstrated.

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