

Comparative Study of Holmium (III) Selective Sensors Based on Thiacalixarene and Calixarene Derivatives as an Ionophore

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The two chelates based on calix[4]arene and thiacalix[4]arene have been synthesized and used as neutral ionophores for preparing PVC based membrane sensor selective to Ho^{3+} ion. The addition of potassium tetrakis(4-chlorophenyl)borate (KTpCIPB) and various plasticizers, viz., NDPE, *o*-NPOE, DOP, TEP and DOS have been found to improve significantly the performance of the sensors. The best performance was obtained with the sensor no. 6 having membrane of L_2 with composition (w/w) ionophore (2%): KTpCIPB (4%): PVC (37%): NDPE (57%). This sensor exhibits Nernstian response with slope 21.10 ± 0.3 mV/decade of activity in the concentration range $3.0 \times 10^{-8} - 1.0 \times 10^{-2}$ M Ho^{3+} ion, with a detection limit of 1.0×10^{-8} M. The proposed sensor performs satisfactorily over a wide pH range of 2.8-10, with a fast response time (5 s). The sensor was also found to work successfully in partially non-aqueous media up to 25% (v/v) content of methanol, ethanol and acetonitrile, and can be used for a period of 4 months without any significant drift in potential. The electrode was also used for the determination of Ho^{3+} ions in synthetic mixtures of different ions and the determination of the arsenate ion in different water samples.

Key Words : Ion-selective electrode, Holmium, Calixarene, Ionophore, Sensors

Introduction

Holmium is a bright, soft, silvery-white, rare earth metal which is both ductile and malleable. It is slowly attacked by oxygen and water and dissolves in acids. It is stable in dry air at room temperature.¹ In moist air or at high temperatures, it gets oxidized into oxides. Like all other rare earths, holmium is not naturally found as free element. In small quantity it is found in minerals such as monazite and bastnasite.^{2,3} Holmium is used as a yellow and red glass colouriser. Holmium has one of the highest known magnetic moment. It has been used to create the strongest artificially generated magnetic fields when placed within high-strength magnets as a magnetic pole piece or magnetic flux concentrator. All holmium compounds should be regarded as highly toxic, although initial information suggests that the danger is limited.⁴ Due to these applications, holmium ion must be determined very accurately at trace levels. The Ho^{3+} ion has been determined directly or indirectly by various conventional and instrumental methods such as spectrometry, inductively coupled plasma-atomic emission spectrometry (ICP-AES), electrochemistry, ICP-MS, neutron activation analysis (NAA), spectrophotometry and X-ray fluorescence spectrometry,⁵⁻¹¹ but all these methods are time consuming, require large infrastructure back up and relatively expensive. The potentiometric sensors based on ion-selective electrode are the best analytical method for such determination because they offer advantages such as selectivity, sensitivity, low detection limit, simplicity and low cost.¹²⁻²⁴ A literature survey revealed that few sensors²⁴⁻³¹ have been reported to determine Ho^{3+} concentration, but they have low detection

limit, narrow concentration range and interference from other ions. Thus, a quick, convenient, fast method is required to determine Ho^{3+} in large number of environmental samples. Calixarenes generally have high melting points, high chemical and thermal stability, low solubility and low toxicity. Their structure can comparatively be readily modified and can provide a direction to molecules with well defined cavities, which offer simultaneous polar (lower rim) and non polar (upper rim) features. These properties make them attractive material for exploring their use as molecular receptors for separation and sensing applications.^{32,33} The introduction of quinoline moieties into the upper rim of calixarene form receptors with improved binding ability towards cations by ion-dipole interactions. Thus two new calixarene derivatives 5,11,17,23-tetra-*tert*-butyl-25,27-bis-[(8-methoxyquinoline)]-26,28-dihydroxycalix[4]arene (L_1)

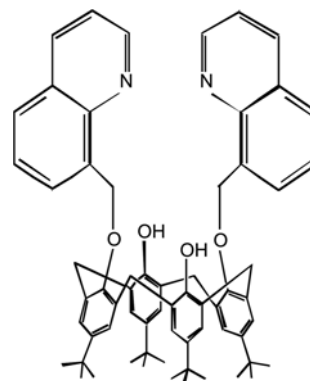


Figure 1. 5,11,17,23-Tetra-*tert*-butyl-25,27-bis-[(8'-methoxyquinoline)]-26,28-dihydroxycalix[4]arene (L_1).

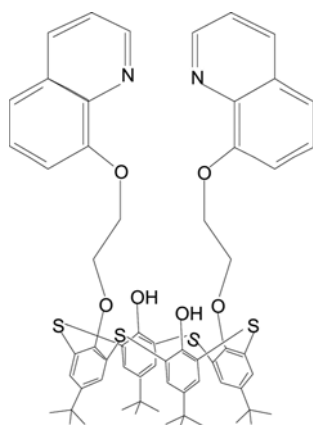


Figure 2. 5,11,17,23-Tetra-*tert*-butyl-25,27-bis-[2'-(8''-oxyquinoline)ethoxy]-26,28-dihydroxy-2,8,14,20-tetrathiacalix[4]arene (L_2).

(Fig. 1) and 5,11,17,23-tetra-*tert*-butyl-25,27-bis-[2-(8-oxyquinoline)ethoxy]-26,28-dihydroxy-2,8,14,20-tetrathiacalix[4]arene (L_2) (Fig. 2) have been synthesized and evaluated for potentiometric study of holmium (III) ion.

Experimental

Reagents and Equipments. The chemicals *viz.*, 8-hydroxyquinoline, *p-tert*-butylcalix[4]arene and *p-tert* butyltetrathiacalix[4]arene were purchased from Fluka (Ronkonkoma, NY), and used as received. 2-Nitrodiphenyl ether (NDPE), *o*-nitrophenyloctylether (*o*-NPOE), dioctylphthalate (DOP), tris(2-ethylhexyl)phosphate (TEP), dioctylsebacate (DOS), oleic acid (OA) and KBF_4 were obtained from SD-Fine Chem. Limited (Mumbai, India). NaTPB and KTpCIPB were obtained from High media Laboratories (Mumbai, India). All metal nitrates were also bought from Sisco research Lab. (Mumbai, India) and the stock solution of metal nitrates were obtained by dissolving weighed amounts of corresponding salt in double distilled water. Double distilled water was used throughout the investigation. All potentiometric measurements were made at 25 ± 1 °C with a digital potentiometer ECIL, Hyderabad, India (Model pH 5662) using Ho^{3+} selective membrane sensor in conjunction with an ECIL, Hyderabad, India double junction $Ag/AgCl$ reference electrode (Model 90-02) containing 10% (w/w) potassium nitrate solution in the outer compartment. All pH measurements were made on a digital pH meter (model pH 5662, ECIL, Hyderabad, India).

Synthesis of Ionophores. The ionophore 5,11,17,23-tetra-*tert*-butyl-25,27-bis-[(8-methoxyquinoline)]-26,28-dihydroxycalix[4]arene (L_1) was prepared as follows:

To a suspension of *p-tert*-butylcalix[4]arene (2.26 mmol) and anhydrous potassium carbonate (42 mmol) in dry acetone (120 mL) 8-(chloromethyl)quinoline (42.0 mmol) was added. The mixture was refluxed for five days in vacuum, then it was filtered and the ligand was obtained as a white crystalline solid, which were washed with 5 mL of cooled absolute ethanol and then recrystallized from acetone-/chloroform. The analytical and physical data of the

ligand are given below.

Empirical formula: $C_{64}H_{70}N_2O_4$, yield: 71%.

Analysis: 1H -NMR ($CDCl_3$) δ 7.62 (s, 2H, ArH), 7.58 (s, 2H, ArH), 7.52 (s, 2H, ArH), 7.45 (d, 2H, $J = 8.5$ Hz, ArH), 7.42 (s, 4H, ArH), 7.21 (s, 2H, OH), 6.85 (s, 4H, ArH), 6.62 (d, $J = 2.8$ Hz, 2H, ArHH), 6.38 (d, 2H, $J = 2.6$ Hz, ArH), 5.16 (d, 4H, $J = 12.6$ Hz, OCH_2Ar), 4.14 (d, 4H, $J = 13.1$ Hz, $ArCH_2Ar$), 3.38 (d, 4H, $J = 12.9$ Hz, $ArCH_2Ar$), 1.32 (s, 18H, Bu^t), 0.97 (s, 18H, Bu^t).

^{13}C -NMR (CD_3CN) δ (42 C aromatic) 171.83, 171.71, 171.12, 170.86, 170.22, 170.14, 170.00, 169.46, 169.18, 169.12, 169.10, 168.65; 168.42, 168.12, 167.64, 165.16, 163.64, 163.76, 162.46, 162.16, 162.12, 160.44, 160.23, 159.85, 158.72, 158.57, 138.32, 137.38, 133.22, 132.76, 132.52, 131.42, 118.67, 117.63, 110.32, 109.72, 109.68, 109.62, 109.54, 109.42, 109.32, 109.25; (22 C aliphatic); 33.68, 32.56, 32.44, 32.26, 32.13, 32.00, 31.76, 31.68, 31.63, 30.58, 30.57, 30.42, 30.38, 30.34, 30.36, 30.29, 30.28, 30.26.

The ionophore 5,11,17,23-tetra-*tert*-butyl-25,27-bis-[2-(8-oxyquinoline)ethoxy]-26,28-dihydroxy-2,8,14,20-tetrathiacalix[4]arene (L_2) was prepared as follows:

To a suspension of *p-tert*-butyltetrathiacalix[4]arene (2.23 mmol) and anhydrous potassium carbonate (40 mmol) in dry acetone (100 mL) 2-chloro-8-ethoxyquinoline (44.21 mmol) was added. The mixture was refluxed for six days, then it was filtered and ligand was obtained as a white solid. The analytical and physical data of the ligand are given below.

Empirical formula: $C_{62}H_{66}N_2O_6S_4$, yield: 68%.

Analysis: 1H -NMR ($CDCl_3$) δ 7.82 (s, 2H, ArH), 7.76 (s, 2H, ArH), 7.75 (s, 2H, ArH), 7.43 (d, 2H, $J = 8.4$ Hz, ArH), (s, 4H, ArH), 7.13 (s, 2H, OH), 6.89 (s, 4H, ArH), 6.85 (d, 2H, $J = 2.5$ Hz, ArHH), 6.82 (d, 2H, $J = 2.4$ Hz, ArH), 5.13 (d, 4H, $J = 13.1$ Hz, OCH_2Ar), 4.91 (d, 4H, $J = 12.8$ Hz, OCH_2Ar), 1.31 (s, 18H, Bu^t), 1.28 (s, 18H, Bu^t).

^{13}C NMR (CD_3CN) δ (42 C aromatic); 172.64, 172.23, 172.12, 171.86, 171.22, 171.16, 170.72, 170.32, 169.78, 169.24, 169.13, 168.95, 168.42, 168.23, 167.52, 165.46, 163.72, 163.46, 162.72, 162.42, 162.38, 160.84, 160.23, 159.95; 159.12, 158.57, 138.12, 137.46, 133.82, 132.46, 132.12, 131.62, 118.38, 117.84, 110.23, 109.92, 119.72, 119.62, 118.38, 117.84, 110.23, 109.95; (20 C aliphatic); 33.73, 32.68, 32.23, 32.12, 31.63, 31.68, 31.23, 30.72, 30.63, 30.61, 30.57, 30.52, 30.50, 30.49, 30.48, 30.46.

Fabrication of Electrodes. The membranes have been fabricated as suggested by Craggs *et al.*³⁴ The PVC-based membranes have been prepared by dissolving appropriate amounts of ionophores (L_1 and L_2), different anionic additives KTpCIPB, NaTPB, KBF_4 , OA, plasticizers NDPE, *o*-NPOE, DOP, TEP, DOS and PVC powder in 15 mL THF. The components were added in terms of weight percentages. The homogenous mixture was obtained after complete dissolution of all membrane components, which was concentrated by evaporating THF and it was poured into a flat Petri dish with inner diameter of 30 mm. The viscosity of the solution and solvent evaporation was carefully controlled to obtain a membrane with reproducible characteristics and

uniform thickness (0.20 mm) otherwise the membrane electrodes have shown significant variation in response characteristics.

The membrane of 0.5 mm diameter were removed carefully from the glass plate and glued to the one end of the "Pyrex" glass tube with araldite. A saturated silver electrode was inserted in the tube for electrical contact and another saturated silver electrode was used as an external reference electrode. To ensure the background potential being produced due to binding material, the membranes with PVC as the only ingredient were prepared. Experiments show that the potentials were not generated without the electroactive material in the membrane.

Conditioning of Membrane and Potential Measurements.

The membranes were conditioned for 20 hrs in 0.01 M $\text{Ho}(\text{NO}_3)_3$ solution. The potentials have been measured by changing the concentration of $\text{Ho}(\text{NO}_3)_3$ in the test solution in the range of 1.0×10^{-10} to 1.0×10^{-2} M by using a buffer solution Tris-HCl (pH 4.3) with a digital potentiometer ECIL, Hyderabad, India (Model pH 5662). The activities of metal ions were calculated using modified form of the Debye-Huckel equation.

The emf measurements were carried out with the cell assembly given below:

Internal reference Silver electrode	Internal reference solution (0.01 M Ho^{3+})	Ho^{3+} ion Selective Membrane	Test Solution	External Reference Silver electrode
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Optimization of Membrane Composition. The selectivity and sensitivity of membrane sensor is highly depending on the addition of other membrane components.³⁵ Therefore different membranes (Table 1) with different composition have been prepared and their response characteristics were evaluated according to IUPAC recommendations.³⁶ It is clear from Table 1 that the best results are obtained by membranes with composition: Ionophore (L_1 or L_2): KTpCIPB: Plasticizer: PVC of 2: 4: 57: 37 (w/w, %).

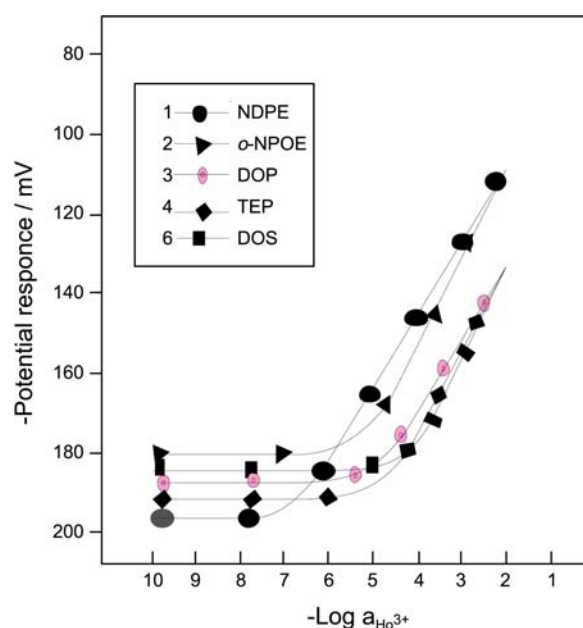


Figure 3. Calibration plot of the Ho^{3+} ion-selective electrode with ionophore L_1 .

Calibration Curves. The optimum response of sensors based on L_1 and L_2 were evaluated and presented in Figure 3 and Figure 4. The Table 1 and Figures 3 and 4 indicates that the sensor no. 6 based on L_2 exhibited a linear working concentration range from 3.0×10^{-8} to 1.0×10^{-2} M. Furthermore, it was observed that the slope of calibration curve was 21.10 ± 0.3 mV decade⁻¹ of activity of the Ho^{3+} ion. The electrode no.1 based on L_1 exhibits Nernstian slope of 19.04 ± 0.3 mV decade⁻¹ of activity in the concentration range 2.0×10^{-7} - 1.0×10^{-2} M. Both the membrane sensors (no. 1 and 6) show best compatible result with NDPE as plasticizer. The membrane (no. 12) without ionophore exhibits a Nernstian slope of 10.70 ± 0.3 mV decade⁻¹ of activity in the concentration range 1.0×10^{-4} - 1.0×10^{-2} M.

Result and Discussion

Table 1. Composition of the different membranes of Ho^{3+} selective electrode

Sensor No.	Membrane Composition (% w/w)				Linear working range (M) ^a	Slope (mV/dec. of activity) ^a	Response Time (sec)
	PVC	Additive	Plasticizer	Ionophore			
1	37	4, KTpCIPB	57, NDPE	2, (L_1)	2×10^{-7} - 1×10^{-2}	19.04 ± 0.3	12
2	37	4, KTpCIPB	57, o-NPOE	2, (L_1)	6×10^{-6} - 1×10^{-2}	20.80 ± 0.3	16
3	37	4, KTpCIPB	57, DOP	2, (L_1)	5×10^{-5} - 1×10^{-2}	14.28 ± 0.3	20
4	36	4, KTpCIPB	58 TEP	2, (L_1)	3×10^{-5} - 1×10^{-2}	14.46 ± 0.3	18
5	37	4, KTpCIPB	57, DOS	2, (L_1)	2×10^{-5} - 1×10^{-2}	14.40 ± 0.3	16
6	37	4, KTpCIPB	57, NDPE	2, (L_2)	3×10^{-8} - 1×10^{-2}	21.10 ± 0.3	05
7	37	4, KTpCIPB	57, o-NPOE	2, (L_2)	1×10^{-7} - 1×10^{-2}	20.30 ± 0.3	10
8	37	4, KTpCIPB	57, DOP	2, (L_2)	3×10^{-6} - 1×10^{-2}	19.40 ± 0.3	16
9	37	4, KTpCIPB	57, TEP	2, (L_2)	1×10^{-6} - 1×10^{-2}	20.60 ± 0.3	18
10	36	4, KTpCIPB	58, DOS	2, (L_2)	1×10^{-6} - 1×10^{-2}	18.30 ± 0.3	20
11	47	9, KTpCIPB	0.0	29, (L_2)	2×10^{-4} - 1×10^{-2}	14.60 ± 0.3	40
12	43	8, KTpCIPB	57, NDPE	0.0	1×10^{-4} - 1×10^{-2}	10.70 ± 0.3	52

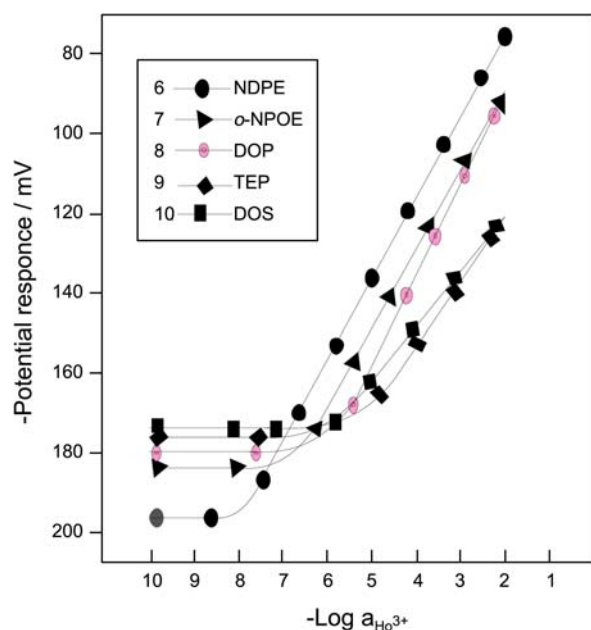


Figure 4. Calibration plot of the Ho^{3+} ion-selective electrode with ionophore L_2 .

Determination of Formation Constant. In this work the complexation between metal cations and the ionophore were measured in terms of formation constant (K_f) using molar conductance ratio³⁷ (Eqs. 1 and 2) in acetonitrile solution at 25 ± 1 °C.

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

where

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

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 ionophore 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,³⁸ and the results are summarized in Table 2. It is clear from Table 2 that the values of formation constant are greater for Ho^{3+} ion than other metal cations. Hence, the ionophores L_1 and L_2 exhibit significant cation-binding characteristics with Ho^{3+} ion.

Effect of Internal Solution. The internal solution may affect the electrode response when the membrane internal diffusion potential is appreciable. The influence of the concentration of internal solution on the potential response of the Ho^{3+} ion-selective electrode based on ionophores L_1 and L_2 was studied and the results corroborate that the variation of the concentration of the internal solution do not cause any significant difference in the potential response of the electrode, except a change in the intercept of the resulting Nernstian plots. It was found that the best results have

Table 2. Formation constants of Ligands (L_1 and L_2) and metals

Metal ions	Formation constants (log K_f)	
	(L_1)	(L_2)
Ho^{3+}	3.8	5.8
K^+	2.2	4.2
Mg^{2+}	3.2	4.2
Ca^{2+}	2.8	3.6
Co^{2+}	2.4	3.2
Pb^{2+}	3.0	3.0
Fe^{3+}	2.9	2.9
La^{3+}	2.0	2.7
Ce^{3+}	2.8	2.6
Pr^{3+}	2.5	2.5
Nd^{3+}	2.6	2.3
Sm^{3+}	2.5	2.2
Eu^{3+}	2.8	2.0
Gd^{3+}	2.7	2.8
Tb^{3+}	2.9	2.9
Dy^{3+}	2.1	2.8
Er^{3+}	2.5	2.5
Tm^{3+}	2.3	2.6
Yb^{3+}	2.2	2.6
Lu^{3+}	2.2	2.5
Hg^{2+}	2.4	2.8
Ni^{2+}	2.5	2.9
Cd^{2+}	2.7	2.4
Al^{3+}	2.9	2.3
Li^+	2.3	2.5
Na^+	2.1	2.2

been obtained with internal solution of activity 1.0×10^{-2} M. Thus 1.0×10^{-2} M concentration of reference solution was quite appropriate for smooth functioning of the electrode assembly.

Effect of Addition of Plasticizer and Detection Limit.

The nature of plasticizer has been found to improve the fluidity, sensitivity and stability of membrane electrode 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 membrane³⁹ Hence, several membranes of various composition and different plasticizers NDPE, *o*-NPOE, DOP, TEP and DOS in PVC matrix were prepared. The best results obtained are shown in the Figures 3 and 4. It is clear from Table 1 and Figures 3 and 4 that the best results are obtained with the sensor prepared by using NDPE as plasticizer. It is noteworthy that the lipophilicity of plasticizer influences both dielectric constant of the polymeric membranes and the mobility of the ionophore and its metal complex.⁴⁰ The effect of plasticizers on the detection limit of membrane sensors was also studied and the results are summarized in Table 3. The observed results clearly indicate that the detection limit of sensors decreases as the dielectric constant of plasticizers decreases. This indicates that NDPE plasticized the membrane, dissolves the ion association complexes and adjusted both permittivity and ion exchanger sites mobility to give highest possible selectivity and sensitivity.

Table 3. Effect of dielectric constant of plasticizer on detection limit of sensors based of L_1 and L_2

Plasticizer	Dielectric constant	Detection limit (L_1)	Detection limit (L_2)
NDPE	50.0	2.0×10^{-7}	1.0×10^{-8}
<i>o</i> -NPOE	23.6	3.0×10^{-6}	3.0×10^{-7}
DOP	5.1	3.0×10^{-5}	1.0×10^{-6}
TEP	4.8	1.7×10^{-5}	2.0×10^{-6}
DOS	3.9	1.0×10^{-5}	4.5×10^{-6}

Effect of Addition of Anionic Additives. The addition of lipophilic anionic additives in cation-selective membrane increases the selectivity and sensitivity of membrane electrodes. To determine the effect of various anionic additives on the working parameters of the electrode, a series of membranes was studied by using lipophilic additives like KTpCIPB, NaTPB, KBF₄ and OA (Table 4). Incorporating KTpCIPB in the membrane composition in the proportion of 4% relative to ionophores (L_1 and L_2) showed best performance characteristics. This is due to the fact that KTpCIPB acts as a charge compensating counter ion in the membrane and thus facilitates the process of ion charge transduction.

Potentiometric Selectivity of Ho³⁺ Selective Electrodes. The influence of interfering ions on the response behavior is usually described in terms of selectivity coefficients ($\log K_{Ho^{3+}, M^{n+}}^{POT}$). In the present study, the selectivity of membrane sensor was calculated by Fixed Interference Method (FIM) (IUPAC recommendation), and the results were presented in terms of potentiometric selectivity coefficients ($\log K_{Ho^{3+}, M^{n+}}^{POT}$) which has been measured at 1×10^{-3} M concentration of metal ions using modified the Nicolsky equation (Eq. 3).^{41,42}

$$K_{Ho^{3+}, M^{n+}}^{POT} = \frac{a_{Ho^{3+}}}{a_{M^{n+}}^{z_{Ho^{3+}}/z_{M^{n+}}}} \quad (3)$$

Where $a_{Ho^{3+}}$ is the activity of the primary ion and $a_{M^{n+}}$ is the activity of other metal ions $z_{Ho^{3+}}$ and $z_{M^{n+}}$ are their respective charges. The selectivity coefficient pattern (Table 5) clearly indicates that the electrodes are efficiently selective for Ho³⁺ ions. The value of selectivity coefficient equal to 1.0 indicates that the sensor responds equally to primary as well as other metal ions (interfering ions). However, values

Table 5. Selectivity Coefficient values calculated by Fixed Interference Method (FIM)

Interfering Ion	Selectivity Coefficient, [$\log K_{Ho^{3+}, M^{n+}}^{POT}$]	
	Sensor no.1	Sensor no. 6
K ⁺	-3.4	-4.2
Mg ²⁺	-3.3	-3.8
Ca ²⁺	-2.4	-2.9
Co ²⁺	-3.2	-3.6
Pb ²⁺	-2.7	-3.9
Fe ³⁺	-3.1	-4.3
La ³⁺	-2.6	-3.1
Ce ³⁺	-2.8	-3.9
Pr ³⁺	-3.5	-3.7
Nd ³⁺	-3.3	-3.5
Sm ³⁺	-3.1	-3.8
Eu ³⁺	-2.3	-3.9
Gd ³⁺	-3.0	-3.4
Tb ³⁺	-2.7	-3.7
Dy ³⁺	-3.3	-4.1
Er ³⁺	-3.6	-4.2
Tm ³⁺	-3.2	-4.3
Yb ³⁺	-2.7	-3.9
Lu ³⁺	-2.8	-3.6
Hg ²⁺	-2.4	-3.2
Ni ²⁺	-3.0	-3.0
Cd ²⁺	-3.2	-3.1
Al ³⁺	-3.6	-3.4
Li ⁺	-3.3	-4.2
Na ⁺	-3.2	-3.8

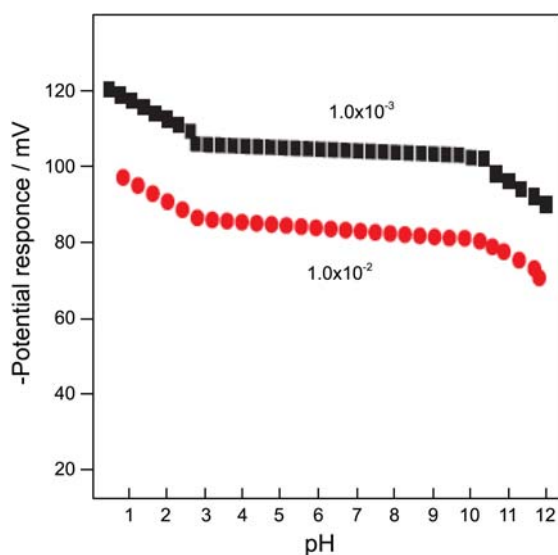
smaller than 1.0 indicate that membrane sensor responds more to primary ion than to other metal ions and in such cases the sensor is said to be selective to primary ion over other metal ions. Further, the smaller is the selectivity coefficient, the higher is the selectivity order. It is clear from Table 5 that the selectivity of electrode no. 6 towards Ho³⁺ is higher over most of the cations as compared to electrode no. 1. The values of selectivity coefficient of the proposed membrane sensor were also compared with the two best electrodes available in the literature, and the results are summarized in Table 6. As electrode no. 6 is better than the other electrodes in terms of wide concentration range, lower

Table 4. Effect of anionic additives on the performance of Ho³⁺ selective electrode

Ionophore (L_1)	Anion Additives 4% (w/w)			
	OA	KBF ₄	NaTPB	KTpCIPB
Concentration range (M)	$1.2 \times 10^{-4} - 1 \times 10^{-2}$	$4.2 \times 10^{-5} - 1 \times 10^{-2}$	$3.6 \times 10^{-6} - 1 \times 10^{-2}$	$7 \times 10^{-8} - 1 \times 10^{-2}$
Detection limit (M)	1.0×10^{-4}	1.5×10^{-5}	1.3×10^{-6}	2×10^{-7}
Slope (± 0.3) mV/dec. of activity	14.82	16.23	17.53	19.04
Ionophore (L_2)				
Concentration range (M)	$3.6 \times 10^{-5} - 1 \times 10^{-2}$	$3.1 \times 10^{-6} - 1 \times 10^{-2}$	$5.4 \times 10^{-7} - 1 \times 10^{-2}$	$3 \times 10^{-8} - 1 \times 10^{-2}$
Detection limit (M)	1.2×10^{-5}	1.4×10^{-6}	2.0×10^{-7}	1×10^{-8}
Slope (± 0.3) mV/dec. of activity	15.75	17.34	19.21	21.1

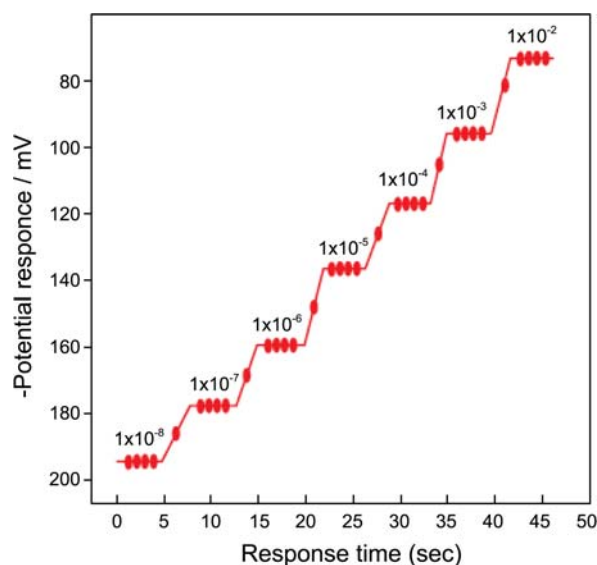
Table 6. Comparison of selectivity Coefficient values of sensor no. 6 with two best electrodes available in literature

Interfering Ion	Selectivity Coefficient, [$\log K_{\text{Ho}^{3+}, \text{M}^{n+}}^{\text{Pot}}$]		
	This work (FIM)	Ref. no. 26 (SSM)	Ref. no. 25 (MPM)
K ⁺	-4.2	-3.7	-3.1
Mg ²⁺	-3.8	-3.5	-3.1
Ca ²⁺	-2.9	-3.1	-3.1
Co ²⁺	-3.6	-3.7	-3.2
Pb ²⁺	-3.9	-3.5	-2.6
Fe ³⁺	-4.3	-3.8	-2.6
La ³⁺	-3.1	-2.0	-
Ce ³⁺	-3.9	-3.7	-
Pr ³⁺	-3.7	-3.3	-3.3
Nd ³⁺	-3.5	-3.1	-
Sm ³⁺	-3.8	-3.4	-
Eu ³⁺	-3.9	-3.5	-
Gd ³⁺	-3.4	-2.7	-2.5
Tb ³⁺	-3.7	-3.4	-3.2
Dy ³⁺	-4.1	-3.0	-
Er ³⁺	-4.2	-3.6	-3.4
Tm ³⁺	-4.3	-3.0	-2.4
Yb ³⁺	-3.9	-2.2	-3.0
Lu ³⁺	-3.6	-2.3	-3.1
Hg ²⁺	-3.2	-	-2.5
Ni ²⁺	-3.0	-	-3.2
Cd ²⁺	-3.2	-	-3.2
Al ³⁺	-3.6	-	-
Li ⁺	-4.2	-	-
Na ⁺	-3.8	-3.8	-3.9

**Figure 5.** Effect of pH on cell potential of sensor no. 6 at 1.0×10^{-2} and 1.0×10^{-3} M Ho^{3+} solutions.

detection limit, high selectivity and Nernstian compliance, therefore further studies were carried out with electrode no. 6 only.

pH and Non-aqueous Effect. The pH effect on the potential response of sensor no.6 was investigated in the range of 1.0-12 for 1.0×10^{-2} and 1.0×10^{-3} M Ho^{3+} solu-

**Figure 6.** Response time behavior of the membrane sensor (no. 6) based on L_2 .

tions (Fig. 6). The pH of the solution was adjusted by adding 0.1 M HNO_3 or hexamine-HCl buffer solution. Figure 5 indicates that the potential is independent of pH in the range of 2.8-10 for sensor no. 6 based on L_2 . Therefore, the pH range 2.8-10 was taken as the working pH range of the electrode assembly. One of the reason for the change in potential at higher pH (> 10) may be due to the hydrolysis of Ho^{3+} ion, while at lower pH, hydrogen ion are likely to interfere in the charge transport of membrane. The performance of the sensor no. 6 was further studied in partial non-aqueous media, *i.e.* methanol-water, ethanol-water and acetonitrile-water mixture. The results obtained are compiled in Table 7 and indicate that up to 25% of non-aqueous content no significant change in the slope and working concentration range of the sensor observed. The increase in non-aqueous content beyond 25% causes a significant interference in slope. This may be due to the dynamic complexation or decomplexation between ionophore and Ho^{3+} ion.

Dynamic Response Time of the Proposed Electrode.

Response time is an important factor for sensor to become sensitive. In the present study, the practical response time has been recorded (for sensor no. 6) by changing solution with different Ho^{3+} ion concentration. In first experiment the measurement sequence was from lower (1.0×10^{-8} M) to the higher (1.0×10^{-2} M) concentration of Ho^{3+} ion. The actual potential *versus* time curve is shown in Figure 6. This figure shows that the proposed sensor reached the constant potential response in a very short time of about 5 s. To evaluate the reversibility of the electrode assembly a similar procedure was repeated in the opposite direction. The measurements have been performed in the sequence of high to low concentration (1.0×10^{-2} - 1.0×10^{-8} M) of sample solutions. The result showed that the time needed to reach the constant potential response was longer (19 s) than that of low to high concentration of sample solutions. Thus the potentiometric

Table 7. Effect of partially non-aqueous medium on the working of Ho³⁺ sensor (No. 6)

Non-aqueous content (%v/v)	Slope (mV/decade) of activity	Working Conc. range (M)	Response time (Sec)
0	21.10 ± 0.3	3.0 × 10 ⁻⁸ -1.0 × 10 ⁻²	05:00
Methanol			
10	21.1 ± 0.3	3.0 × 10 ⁻⁸ -1.0 × 10 ⁻²	05:00
20	21.1 ± 0.3	2.3 × 10 ⁻⁸ -1.0 × 10 ⁻²	05:00
25	21.0 ± 0.3	1.7 × 10 ⁻⁸ -1.0 × 10 ⁻²	05:00
30	17.20 ± 0.3	4.2 × 10 ⁻⁶ -1.0 × 10 ⁻²	10:00
40	16.50 ± 0.3	2.6 × 10 ⁻⁵ -1.0 × 10 ⁻²	13:00
Ethanol			
10	21.1 ± 0.3	3.0 × 10 ⁻⁸ -1.0 × 10 ⁻²	05:00
20	21.1 ± 0.3	2.1 × 10 ⁻⁸ -1.0 × 10 ⁻²	05:00
25	21.0 ± 0.3	1.3 × 10 ⁻⁸ -1.0 × 10 ⁻²	06:00
30	17.3 ± 0.3	1.0 × 10 ⁻⁶ -1.0 × 10 ⁻²	10:00
40	16.30 ± 0.3	1.0 × 10 ⁻⁵ -1.0 × 10 ⁻²	13:00
Acetonitrile			
10	21.1 ± 0.3	3.0 × 10 ⁻⁸ -1.0 × 10 ⁻²	05:00
20	21.05 ± 0.3	2.0 × 10 ⁻⁸ -1.0 × 10 ⁻²	05:00
25	21.03 ± 0.3	1.6 × 10 ⁻⁸ -1.0 × 10 ⁻²	05:00
30	18.50 ± 0.3	3.5 × 10 ⁻⁶ -1.0 × 10 ⁻²	12:00
40	16.80 ± 0.3	1.0 × 10 ⁻⁵ -1.0 × 10 ⁻²	14:00

Table 8. The lifetime of Ho³⁺ membrane sensor (no. 6) based on L₂

S. No.	Week	Slope (mV/decade)	Detection Limit (mol/L)
1	First	21.1 ± 0.3	1.0 × 10 ⁻⁸
2	Third	21.1 ± 0.3	1.0 × 10 ⁻⁸
3	Sixth	21.06 ± 0.3	1.0 × 10 ⁻⁸
4	Ninth	21.05 ± 0.3	1.1 × 10 ⁻⁸
5	Twelfth	21.04 ± 0.3	1.2 × 10 ⁻⁸
6	Sixteenth	21.03 ± 0.3	1.2 × 10 ⁻⁸
7	Seventeenth	17.08 ± 0.3	5.6 × 10 ⁻⁸
8	Twenty first	14.57 ± 0.3	1.3 × 10 ⁻⁷

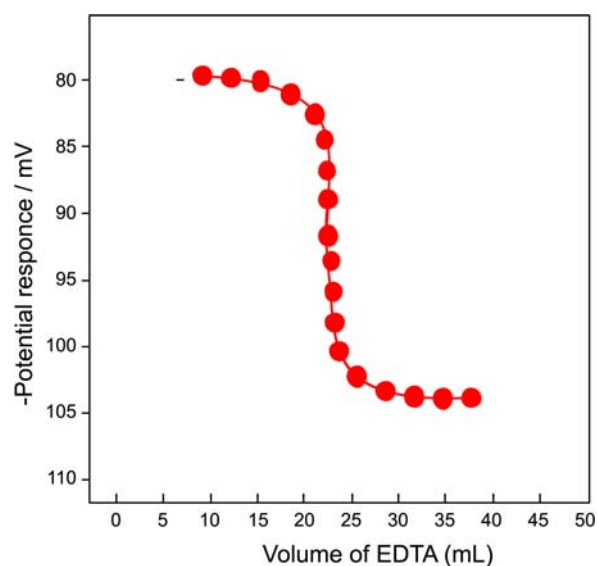
response of the proposed sensor (no. 6) is sufficiently reversible.

Life Time of Proposed Sensor. The high lipophilicity of ionophore and plasticizer ensure stable potential and longer

life time for the membrane.⁴³ Among all the membranes prepared, the life time of membrane sensor (no. 1) based on L₁ was found to be 1 month, and for sensor (no. 6) based on L₂ was 4 months (Table 8). During these days the response characteristics of electrode remains almost constant. However, a slight gradual decrease in the slope was observed after this period which may be due to slight leaching of the plasticized PVC membrane components. The best values were obtained for NDPE based sensors probably because of their greater polarity. It was noticed that during this period, the membranes were used for at least two hours per day and it was observed that the potentials were within the standard deviation (± 0.3 mV). However, it is important to emphasize that the membranes were stored in a 0.01 M Ho³⁺ ion solution when not in use.

Comparison Study

The response characteristics of the proposed PVC based membrane electrode (no. 6) are compared with those of the best Ho³⁺ ion-selective electrodes reported earlier (Table 9). It is apparent that the proposed electrode is superior in terms

**Figure 7.** Potentiometric titration plots of 1.0 × 10⁻² M Ho³⁺ solution (25 mL) with 1.0 × 10⁻² M EDTA solution.**Table 9.** Comparative analysis of proposed electrode (no. 6) with the reported electrodes

Interference of tested cations	Working Conc. range (M)	Slope (mV/decade of activity)	pH range	Response time (sec)	Detection limit (M)	Ref.
None	3 × 10 ⁻⁸ - 1 × 10 ⁻²	21.10 ± 0.3	2.8-10	5	1.0 × 10 ⁻⁸	This work
None	1.0 × 10 ⁻⁶ - 1.0 × 10 ⁻² M	20.40 ± 0.3	2.4-7.4	5	4.2 × 10 ⁻⁷	25
La ³⁺	1.0 × 10 ⁻⁶ - 1.0 × 10 ⁻² M	19.97 ± 0.3	4.5-9.0	10	6.3 × 10 ⁻⁷	26
Na ⁺ , Dy ³⁺ , Er ³⁺ , Pb ²⁺ , Nd ³⁺	1.0 × 10 ⁻⁵ - 1.0 × 10 ⁻² M	19.60 ± 0.2		5	8.0 × 10 ⁻⁶	27
None	1.0 × 10 ⁻⁶ - 1.0 × 10 ⁻² M	19.50 ± 0.3	3.2-9.8	5	4.6 × 10 ⁻⁷	28
Na ⁺ , Dy ³⁺ , Lu ³⁺ , Pb ²⁺ , La ³⁺ , K ⁺ , Ca ²⁺ , Cu ²⁺	1.0 × 10 ⁻⁵ - 1.0 × 10 ⁻² M	19.70 ± 0.2		15	7.0 × 10 ⁻⁶	29
Cu ²⁺ , Pb ²⁺ , Nd ³⁺	2.0 × 10 ⁻⁵ - 1.0 × 10 ⁻² M	19.5 ± 0.3		5	5.0 × 10 ⁻⁵	30
Pb ²⁺ , Tb ³⁺	1.0 × 10 ⁻⁶ - 1.0 × 10 ⁻² M	19.70 ± 0.3		15	8.5 × 10 ⁻⁷	31

Table 10. Recovery of Ho³⁺ ion in mixtures of different ions

S. No	Composition of solution	Recovery (%)	
		Proposed sensor	AAS
1	0.00010 M Ho(NO ₃) ₃ + 0.001 M NaNO ₃ + 0.0001 M Mg(NO ₃) ₂	102.7	102.6
2	0.00010 M Ho(NO ₃) ₃ + 0.001 M Mg(NO ₃) ₂ + 0.0001 M Ca(NO ₃) ₂	102.6	102.8
3	0.00010 M Ho(NO ₃) ₃ + 0.001 M Co(NO ₃) ₂ + 0.0001 M Pb(NO ₃) ₂	100.0	100.1
4	0.00010 M Ho(NO ₃) ₃ + 0.001 M Pb(NO ₃) ₂ + 0.0001 M Fe(NO ₃) ₃	102.3	102.1
5	0.00010 M Ho(NO ₃) ₃ + 0.001 M La(NO ₃) ₃ + 0.0001 M Fe(NO ₃) ₃	101.4	101.1
6	0.00010 M Ho(NO ₃) ₃ + 0.001 M La(NO ₃) ₃ + 0.0001 M Ce(NO ₃) ₃	101.2	101.2
7	0.00010 M Ho(NO ₃) ₃ + 0.001 M Pr(NO ₃) ₃ + 0.0001 M Ce(NO ₃) ₃	102.7	102.5
8	0.00010 M Ho(NO ₃) ₃ + 0.001 M Pr(NO ₃) ₃ + 0.0001 M Nd(NO ₃) ₃	104.1	104.2
9	0.00010 M Ho(NO ₃) ₃ + 0.001 M Sm(NO ₃) ₃ + 0.0001 M Pr(NO ₃) ₃	102.2	102.3
10	0.00010 M Ho(NO ₃) ₃ + 0.001 M Eu(NO ₃) ₃ + 0.0001 M Gd(NO ₃) ₃	101.4	101.5
11	0.00010 M Ho(NO ₃) ₃ + 0.001 M Gd(NO ₃) ₃ + 0.0001 M Tb(NO ₃) ₃	102.1	102.2
12	0.00010 M Ho(NO ₃) ₃ + 0.001 M Tb(NO ₃) ₃ + 0.0001 M Dy(NO ₃) ₃	101.2	101.2
13	0.00010 M Ho(NO ₃) ₃ + 0.001 M Tb(NO ₃) ₃ + 0.0001 M Er(NO ₃) ₃	101.3	101.4
14	0.00010 M Ho(NO ₃) ₃ + 0.001 M Lu(NO ₃) ₃ + 0.0001 M Er(NO ₃) ₃	102.7	102.8
15	0.00010 M Ho(NO ₃) ₃ + 0.001 M Nd(NO ₃) ₃ + 0.0001 M Gd(NO ₃) ₃	102.5	102.6
16	0.00010 M Ho(NO ₃) ₃ + 0.001 M Hg(NO ₃) ₂ + 0.0001 M Cd(NO ₃) ₂	102.3	102.4
17	0.00010 M Ho(NO ₃) ₃ + 0.001 M Cd(NO ₃) ₂ + 0.0001 M Ni(NO ₃) ₂	102.4	102.5
18	0.00010 M Ho(NO ₃) ₃ + 0.001 M Al(NO ₃) ₃ + 0.0001 M Pr(NO ₃) ₃	103.6	103.6

Table 11. Determination of arsenate ion in different water samples

Sample	Proposed Sensor (ppm)	AAS (ppm)	ICP (ppm)
Tape Water	0.020	0.021	0.020
Hindon river	0.046	0.045	0.046
Industrial waste water (Ghaziabad)	0.053	0.054	0.053

of response characteristics such as working concentration range, pH range, life time and low detection limit as compared to the existing electrodes.

Analytical Applications

Potentiometric Titration. The practical utility of the proposed membrane electrode was investigated by using it as an indicator electrode for the titration of 25 mL of 1.0 × 10² M Ho³⁺ with a 1.0 × 10² M EDTA solution, and the curve obtained is shown in Figure 7. The curve is of standard sigmoid type indicates the sufficient selectivity of the proposed electrode for Ho³⁺ ion and sharp inflection point at the titrant volume corresponding to the 1:1 stoichiometry of Ho³⁺-EDTA complex.

Recovery Test of Ho³⁺ Ion in Mixtures of Different Ions. In addition, the proposed membrane sensor was successfully applied for the potentiometric determination of Ho³⁺ ion in some synthetic samples containing different metal ions. The obtained values are quite comparable to those obtained with AAS, thereby illustrating the utility of the sensor for determining the Ho³⁺ in real samples (Table 10). The proposed holmium selective electrode was also used for the determination of arsenate ion in different water samples and the values were compared with those obtained by AAS and ICP (Table 11).

Conclusion

The present study involves the synthesis and characterization of new calixarene and thiacalixarene derivatives (L₁ and L₂) and their use in PVC based membrane sensors for the determination of various metal ions. The investigation of PVC based membranes of L₁ and L₂ shows that they act as Ho³⁺ selective sensor. However of the two chelates, the sensor no. 6 based on L₂ shows maximum selectivity, widest concentration range (3 × 10⁻⁸ - 1 × 10⁻²), minimum detection limit (1.0 × 10⁻⁸), and minimum response time (5 s) with a slope of 21.10 ± 0.3 mV/dec. of activity between pH range 2.8-10.0. The proposed membrane sensor no. 6 is inert towards non-aqueous media (up to 25%) and can be used for the period of 4 months without any change in response characteristics. The proposed membrane electrode (no. 6) was successfully applied as an indicator electrode for the titration of Ho³⁺ ion (1.0 × 10⁻² M) with a standard EDTA solution (1.0 × 10⁻² M).

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