

Full Paper

Comparative Study of Poly(Vinyl Chloride) Based Polymeric Membrane Sensors for the Determination of Erbium (III)

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Abstract-The three chelates 1,5-bis(*o*-aminobenzoate)-3-thiapentane (**L**₁), 1,5-bis(*o*-methoxybenzoate)-3-thiapentane (**L**₂), 1,5-bis(*o*-chlorobenzoate)-3-thiapentane (**L**₃) have been synthesized and explored as a neutral ionophores for preparing poly(vinyl chloride) based membrane sensors selective to Er³⁺. The addition of sodiumtetrphenylborate and various plasticizers, viz., *o*-NPOE, TBP, DBBP, TEP and DOS has been found to substantially improve the performance of the sensor. The best performance was obtained with the sensor no.6 having membrane of ionophore (**L**₂) with composition PVC: *o*-NPOE: ionophore (**L**₂): NaTPB (%w/w) of 35:56:2:7. This sensor exhibits Nernstian response with slope 22.1±0.3 mV decade⁻¹ of activity in concentration range 3.0×10⁻⁹ to 1.0×10⁻² M Er³⁺, performs satisfactorily over wide pH range (1.5-6.7), with a fast response time (8 s). The sensor was also found to work satisfactorily in partially non-aqueous media up to 20% content of methanol, ethanol or acetone and could be used for a period of 5 months without any change in response characteristics. The Er³⁺ selective sensor was used as an indicator electrode for the titration of 25 ml 1×10⁻³ M EDTA solution and for the determination of Er³⁺ ion in different synthetic samples. The proposed electrode no. 6 was also used for the determination of fluoride ion in two mouth wash sample.

Keywords- Sensor, Potentiometry, Ionophore, Erbium, Selectivity

1. INTRODUCTION

Erbium is a silvery-white solid metal belong to inner transition elements of the periodic table. The pure erbium metal is malleable, soft, stable in air, and does not oxidize as quickly as some other rare-earth metals. It is estimated that the erbium concentration of the earth's crust reaches 24 ppm. Like other rare earths, this element is never found as a free element in nature [1]. It is commonly used as a photographic filter as well as in neutron-absorbing control rods in nuclear technologies. Erbium-doped optical silica-glass fibers are the active element in erbium-doped fiber amplifiers, which are widely used in optical communications. An erbium-nickel alloy Er_3Ni has an unusually high specific heat capacity at liquid-helium temperatures and is used in cryocoolers. It is also used to produce steam for laser enamel ablation in dentistry. The erbium compounds can cause serious problems when inhaled, taken orally, or injected into the blood stream [2, 3]. There are lots of techniques for the determination of erbium metal ion such as atomic absorption spectroscopy (AAS), ICP-MS [4], ICP-AES [5], gravimetric determination [6], isotopic dilution mass spectroscopy [7, 8], absorption spectra of 4f electron transitions [9] available in the literature, but all these methods are time consuming, involving sample manipulations, relatively expensive and required large infrastructure back up. Many reagents have been reported for the determination of lanthanides but they have not been specific and require extractive separation to remove interfering elements. Hence, finding a simple device like an electrode which is able to measure one of these elements selectively is of importance. Selective analytical methodologies which are environmental friendly, cost effective and easily operated have therefore been proposed as alternative to standard methods. Potentiometric sensors based on ion-selective electrodes are especially suited for such determination because they offer advantages such as low cost, simple handling, high selectivity and high sensitivity [10-21]. A literature survey revealed that few ionophores such as 4-(2-Thiazolylazo)resorcinol [22], N,N'-bis(salicylidene)-2-aminobenzylamine[23],N,N'-bis((1H-pyrrol-2-yl)methylene)cyclohexane-1,2-diamine [24], N,N'-bis(quinoline-2-carboxamido)-4,5-dimethylbenzene [25], pyridine-2-carbaldehyde-2-(4-methyl-1,3-benzothiazol-2-yl) hydrazone [26] have been used as membrane carrier for the analysis of Er^{3+} . But these potentiometric sensors suffer from such disadvantage as high detection limits, short linear ranges, high response time and significant interferences from many cations.

The present work, involved the development and comparative study of a Er^{3+} selective PVC membrane sensors based on three newly synthesized 1,5-bis(*o*-aminobenzoate)-3-thiapentane (**L**₁), 1,5-bis(*o*-methoxybenzoate)-3-thiapentane (**L**₂), 1,5-bis(*o*-chlorobenzoate)-3-thiapentane (**L**₃) (Fig. 1) chelates as an ionophore. The values of formation constants show that **L**₂ form stronger complex with Er^{3+} than other two proposed ionophores (**L**₁, and **L**₃) and weaker complex with other metal ions.

2. EXPERIMENTAL SECTION

2.1. Reagents and Equipments

All the analytical grade reagents were used as purchased. Benzoic acid derivatives and 2,2'-dichlorodiethyl thioether were purchased from Aldrich Sigma (Wisconsin, USA). High molecular weight poly(vinyl chloride) (PVC), dibutyl-butylphosphonate (DBBP), dioctylsebacate (DOS), tri-*n*-butylphosphate (TBP), *o*-nitrophenyl octyl ether (*o*-NPOE), tris(2-ethylhexyl)phosphate (TEP), sodium tetraphenylborate (NaTPB), tetrahydrofuran (THF), salicylic aldehyde, ethanol, chloroform, acetone were purchased from Fluka (Ronkonkoma, NY). All metal nitrates were also brought from Aldrich Sigma (Wisconsin, USA), and the stock solution of metal nitrates was obtained by dissolving fixed amounts of corresponding salt in double distilled water. Double distilled water was used throughout the investigation.

All potentiometric measurements were made at $25 \pm 1^\circ\text{C}$ with a digital potentiometer ECIL, India (Model pH 5662) using Er^{3+} selective membrane sensor in conjunction with an ECIL, India double junction Ag/AgCl reference electrode (Model 90-02) containing 10% (w/w) potassium nitrate solution in the outer compartment.

2.2. Synthesis of ionophore

The ionophore 1,5-bis(*o*-aminobenzoate)-3-thiapentane (**L**₁) was synthesized by stirring 1,5-dichloro-3-thiapentane (1.0 mmol) and *o*-aminobenzoic acid (1.2 mmol) in presence of anhydrous potassium carbonate (42 mmol) and cesium carbonate (15.7 mmol) in dry acetone (120 mL). The mixture was refluxed for 70 min in vacuum. Evaporation of the solution in vacuum gave viscous liquid. The ligand was obtained as white micro crystals. The micro crystals were filtered off, washed with 5 mL of cooled absolute ethanol and then recrystallized from ethanol-/chloroform (2:1 v/v).

The ionophore 1,5-bis(*o*-methoxybenzoate)-3-thiapentane (**L**₂) was synthesized by stirring 1,5-dichloro-3-thiapentane (1.20 mmol) and *o*-methoxybenzoic acid (1.25 mmol) in presence of anhydrous potassium carbonate (40 mmol) and cesium carbonate (12.0 mmol) in dry acetone (100 mL). The mixture was refluxed for 50 min in vacuum. Evaporation of the solution in vacuum gave a crystalline ligand which was filtered off, washed with 5 mL of cooled absolute ethanol and then recrystallized from ethanol-/chloroform (2:1, v/v).

The ionophore 1,5-bis(*o*-chlorobenzoate)-3-thiapentane (**L**₃) was synthesized by stirring 1,5-dichloro-3-thiapentane (1.25 mmol) and *o*-chlorobenzoic acid (1.32 mmol) in presence of anhydrous potassium carbonate (48.5 mmol) and cesium carbonate (15.6 mmol) in dry acetone (120 mL). The mixture was refluxed for 75 min in vacuum. Evaporation of the solution in vacuum gave a crystalline ligand which was filtered off, washed with 5 mL of cooled absolute ethanol and then recrystallized from ethanol-/chloroform (2:1, v/v).

The analytical and physical data of the ligands are given below.

L₁. Molecular formula: C₁₈H₂₀NO₄S, , yield: 70%.

Analysis: **¹H-NMR** (CDCl₃, ppm): δ=7.38 (d, 2H, aromatic), 7.36 (d, 2H, aromatic), 7.24 (m, 2H, aromatic), 7.13 (m, 2H, aromatic), 3.32 (s, 4H, amine), 3.13 (t, 4H, CH₂ aliphatic), 3.00 (t, 4H, CH₂ aliphatic).

¹³C-NMR (CD₃CN, ppm): δ=(12C aromatic); 164.61, 160.16, 159.66, 149.32, 136.45, 134.92, 133.46, 123.25, 121.56, 119.96, 119.02, 109.95; (6C aliphatic); 58.93, 57.6, 38.36, 38.34, 31.82, 31.79.

L₂. Molecular formula: C₂₀H₂₂O₆S, , yield: 75%.

Analysis: **¹H-NMR** (CDCl₃, ppm): δ=7.32 (d, 2H, aromatic), 7.28 (d, 2H, aromatic), 7.14 (m, 2H, aromatic), 6.85 (m, 2H, aromatic), 3.26 (t, 4H, CH₂ aliphatic), 3.17 (t, 4H, CH₂ aliphatic), 3.12 (s, 6H, CH₃)

¹³C-NMR (CD₃CN, ppm): δ=(12C aromatic); 167.43, 166.89, 163.46, 163.32, 160.45, 159.92, 133.46, 133.25, 121.56, 119.96, 110.02, 109.95; (8C aliphatic); 58.85, 58.62, 38.34, 38.31, 31.43, 31.29, 30.56, 30.48.

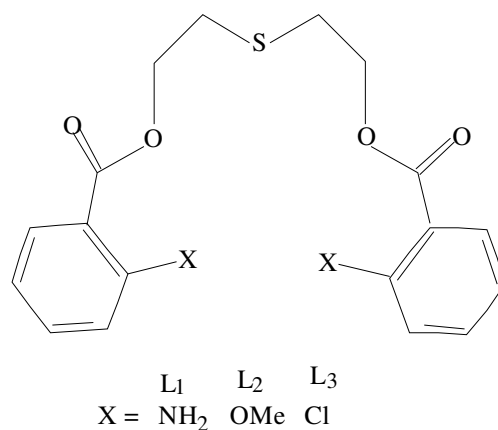


Fig. 1. Structure of ionophores

L₃. Molecular formula: C₁₈H₁₆O₄S, yield: 72 %.

Analysis: **¹H-NMR** (CDCl₃, ppm): δ=7.12 (d, 2H, aromatic), 7.06 (d, 2H, aromatic), 6.83 (m, 2H, aromatic), 6.80 (m, 2H, aromatic), 3.14 (t, 4H, CH₂ aliphatic), 3.08 (t, 4H, CH₂).

¹³C-NMR (CD₃CN, ppm): δ=(12 C aromatic); 167.82, 167.73, 165.36, 165.32, 162.25, 161.89, 132.56, 132.43, 121.42, 121.36, 109.72, 109.52; (6C aliphatic); 58.45, 58.23, 37.84, 37.71, 34.28, 34.12.

2.3. Development of PVC membrane

The membranes have been fabricated as suggested by Craggs et al. [27]. The PVC-based membranes have been fabricated by dissolving a mixture of 35% PVC, 56% plasticizer

(*o*-NPOE, TBP, DBBP, TEP, DOS), 7% NaTPB, and 2% ionophore (**L**₁, **L**₂, and **L**₃) in THF (15 ml). The components were added in terms of weight percentage. The homogenous mixture obtained after complete dissolution of all components, concentrated by evaporation of THF and it has been poured into polyacrylate rings placed on a smooth glass plate. The viscosity of the solution and solvent and was carefully controlled to obtain membrane with reproducible characteristics and uniform thickness otherwise the response of the membrane sensors have shown a significant variation. The membranes of 0.5 mm of thickness and 8 mm diameter were removed from the glass plate and glued to one end of a Pyrex glass tube with the help of araldite and M-seal. The membrane sensor was finally conditioned by soaking in a 0.01 M Er(NO₃)₃ solution for 5 days. A saturated silver electrode was inserted in the tube for electrical contact and another saturated silver electrode was used as an external reference electrode. The ionic strength of various solutions was maintained with the help of saturated solution of KCl. When membrane was not in used, it kept in 0.01 M Er(NO₃)₃ solutions to avoid damage by cracking.

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

Internal reference Silver electrode	Internalreference solution (0.01 M Er ³⁺)	Er ³⁺ ion Selective Membrane	Test solution of Er ³⁺ ion	External reference Silver electrode
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3. RESULTS AND DISCUSSION

3.1. Optimization of membrane composition

The selectivity of membrane sensor is highly dependent on the incorporation of additional membrane components. Therefore different membranes with different composition have been prepared and their response characteristics were evaluated according to the IUPAC recommendation [28]. The membrane (no.16) without ionophore exhibits a Nernstian slope of 10.6 ± 0.3 mV dec⁻¹ of activity, over a concentration range of 5×10^{-3} to 1×10^{-2} M of Er³⁺ solution with detection limit 3×10^{-2} M, while the membrane (no.17) based on **L**₂ (without plasticizer) exhibits a Nernstian slope of 14.4 ± 0.3 mV dec⁻¹ of activity, over a concentration range of 3.2×10^{-5} to 1×10^{-2} M of Er³⁺ solution with detection limit 5×10^{-5} M (Table 1).

The influence of the concentration of internal solution on the potential response of the Er³⁺-selective electrode was studied and the results corroborate that the variation of the concentration of the internal solution does not cause any significant difference in the potential response of the electrode, except for an expected change in the intercept of the resulting

Nernstian plots. A 1.0×10^{-2} M concentration of internal solution is quite appropriate for smooth functioning of the electrode assembly.

3.2. The effect of plasticizer and anionic additive

The nature of plasticizer has been found to improve the sensitivity and stability of membrane sensor due to characteristics such as lipophilicity, high molecular weight, low pressure and high capacity to dissolve the substrate and other additives present in the polymeric membrane [29, 30]. The effect of plasticizer on Er^{3+} selective membrane based on different ionophores is shown in Table 1.

Table 1. Optimization of membrane composition of erbium sensors

Sensor No.	Membrane Composition (% , w/w)				Linear working range (M) ^a	Slope (mV/dec. of activity) ^a	Response Time (s)
	PVC	Additive	Plasticizer	Ionophore			
1	35	7, NaTPB	56, <i>o</i> -NPOE	2, (L ₁)	1×10^{-8} - 1×10^{-2}	20.0±0.3	14
2	34	7, NaTPB	56, TBP	2, (L ₁)	3×10^{-8} - 1×10^{-2}	20.8±0.3	16
3	35	7, NaTPB	56, DBBP	2, (L ₁)	5×10^{-8} - 1×10^{-2}	20.4±0.3	20
4	36	7, NaTPB	56, TEP	2, (L ₁)	5×10^{-8} - 1×10^{-2}	20.8±0.3	16
5	35	7, NaTPB	56, DOS	2, (L ₁)	2×10^{-7} - 1×10^{-2}	20.6±0.3	16
6	35	7, NaTPB	56, <i>o</i> -NPOE	2, (L ₂)	3×10^{-9} - 1×10^{-2}	22.1±0.3	08
7	35	7, NaTPB	56, TBP	2, (L ₂)	1×10^{-8} - 1×10^{-2}	20.8±0.3	10
8	35	7, NaTPB	56, DBBP	2, (L ₂)	3×10^{-8} - 1×10^{-2}	19.4±0.3	12
9	35	7, NaTPB	56, TEP	2, (L ₂)	3×10^{-8} - 1×10^{-2}	20.6±0.3	14
10	36	7, NaTPB	56, DOS	2, (L ₂)	5×10^{-7} - 1×10^{-2}	20.8±0.3	16
11	35	7, NaTPB	56, <i>o</i> -NPOE	2, (L ₃)	2×10^{-8} - 1×10^{-2}	18.3±0.3	22
12	35	7, NaTPB	56, TBP	2, (L ₃)	1×10^{-7} - 1×10^{-2}	18.1±0.3	24
13	35	7, NaTPB	56, DBBP	2, (L ₃)	2×10^{-7} - 1×10^{-2}	18.2±0.3	28
14	35	7, NaTPB	56, TEP	2, (L ₃)	5×10^{-7} - 1×10^{-2}	18.3±0.3	26
15	36	7, NaTPB	56, DOS	2, (L ₃)	3×10^{-7} - 1×10^{-2}	16.6±0.3	24
16	35	7, NaTPB	68, <i>o</i> -NPOE	0.0, (L ₂)	5×10^{-3} - 1×10^{-2}	10.6±0.3	46
17	64	20, NaTPB	0.0	16 (L ₂)	3.2×10^{-5} - 1×10^{-2}	14.4±0.3	32

^a Mean value ± standard deviation (three measurements)

This indicates that *o*-NPOE plasticized the membrane, dissolve the ion association complexes and adjust both permittivity and ion exchanger sites mobility to give highest

possible selectivity and sensitivity. The potential responses of all members are shown in Figs. 2, 3 and 4.

The anionic additive sodium tetraphenyl borate (NaTPB) is used to reduce the anionic interference. Incorporating NaTPB in the membrane composition in the proportion of 7% (w/w) relative to the other component, showed best performance characteristics. This is due to the fact that NaTPB acts as charge compensation counter ion in the membrane sensor and thus facilitate the process of ion charge transduction [31]. The values of detection limits for the sensor no. 6 based on ionophore L_2 and different plasticizer follows the order of: *o*-NPOE (1×10^{-9} M), TBP (1×10^{-8} M), DBBP (5×10^{-8}), TEP (8×10^{-8}), DOS (1.0×10^{-7}). These results clearly indicate that the detection limit of the sensors decreases as the dielectric constant of plasticizers decreases.

3.3. Working concentration range and Nernstian slope

The result presented in Table 1 and Figs. 2, 3 and 4 indicates that the best sensor (no. 1) based on L_1 exhibits a Nernstian slope of 20.0 ± 0.3 mV dec $^{-1}$ of activity, over a wide concentration range of 1×10^{-8} to 1×10^{-2} M of Er^{3+} solution with detection limit 5×10^{-8} M, the sensor (no. 11) based on L_3 exhibits a Nernstian slope of 18.3 ± 0.3 mV dec $^{-1}$ of activity, over a wide concentration range of 2×10^{-8} to 1×10^{-2} M of Er^{3+} solution with detection limit 5×10^{-7} M, while sensor (no. 6) based on L_2 exhibits a Nernstian slope of 22.1 ± 0.3 mV dec $^{-1}$ of activity, over a wide concentration range of 3×10^{-9} to 1×10^{-2} M of Er^{3+} solution with detection limit 1×10^{-9} M.

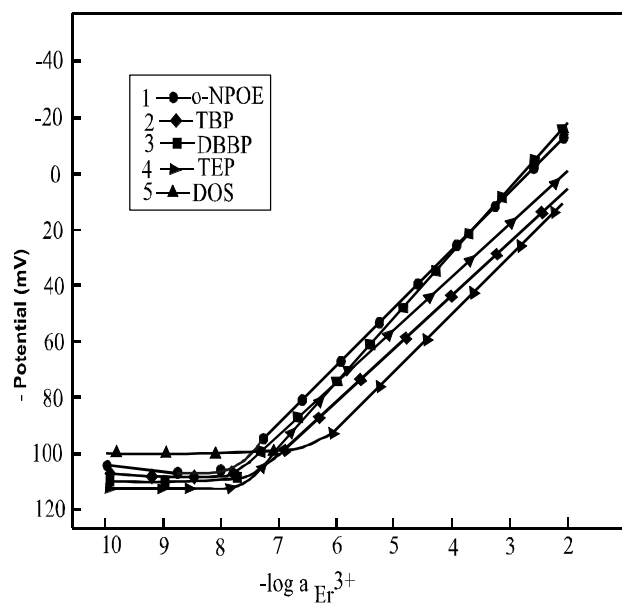


Fig. 2. Potentiometric calibration response of a PVC-based Er^{3+} -selective sensor using (L_1), as an ionophore with different plasticizers

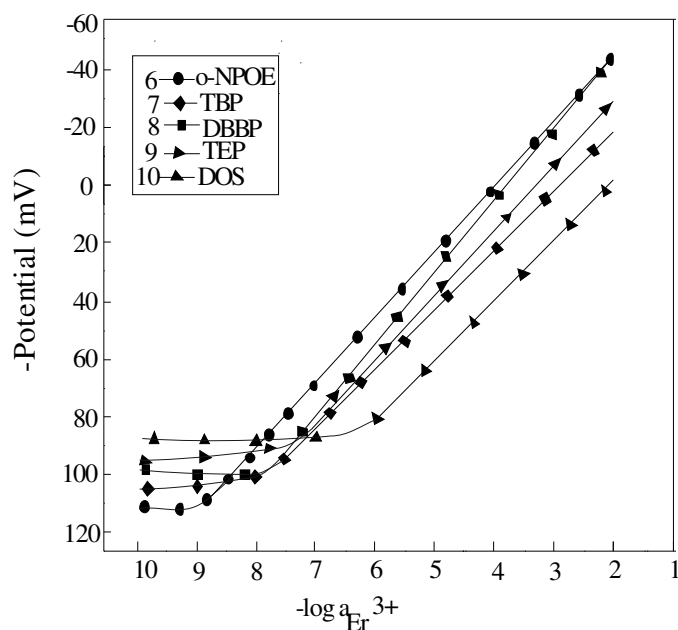


Fig. 3. Potentiometric calibration response of a PVC-based Er^{3+} -selective sensor using (L_2) , as an ionophore with different plasticizers

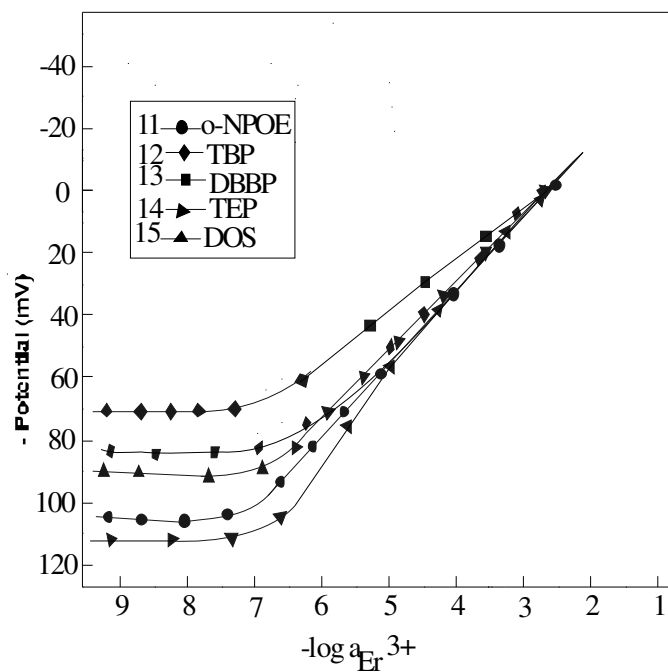


Fig. 4. Potentiometric calibration response of a PVC-based Er^{3+} -selective sensor (L_3) , as an ionophore with different plasticizers

3.4. Determination of formation constant

Formation constant (K_f) of the ion-ionophore complex within the membrane phase is very important parameter that dictates the practical selectivity of the sensor. The formation constant indicates the complexation between metal cations and the ionophore and was measured using molar conductance ratio (equation 1 and 2) in acetonitrile solution at 25 ± 1.0 °C [32].

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

Where

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

Here, Λ_M is the molar conductance of the cation before addition of ligand, Λ_{ML} the molar conductance of the complex, Λ_{obs} the molar conductance of the solution during titration, C_L the analytical concentration of the 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 [33], and the results are summarized in Table 2.

Table 2. Formation constant of metal ions-ligand (L_1 , L_2 and L_3)

Metal ions	Formation Constants (log K_f)		
	(L_1)	(L_2)	(L_3)
Er ³⁺	5.8	7.2	3.8
Tb ³⁺	4.2	4.8	3.4
Dy ³⁺	3.2	4.2	2.6
La ³⁺	2.8	4.6	1.7
Eu ³⁺	2.4	3.2	1.8
Sm ³⁺	3.0	3.0	2.4
Gd ³⁺	2.9	2.9	1.8
Yb ³⁺	2.0	2.7	1.5
Cu ²⁺	1.8	2.6	1.3
Mn ²⁺	2.5	2.5	1.6
Co ²⁺	2.6	2.3	1.9
Pr ³⁺	2.5	2.2	1.4
Ni ²⁺	2.8	2.0	1.8
Pb ²⁺	1.7	1.8	1.6
Hg ²⁺	1.9	1.9	1.2
Zn ²⁺	2.1	1.8	1.5
Ag ⁺	2.5	1.5	1.4
Fe ³⁺	1.3	1.6	1.2
Al ³⁺	1.2	1.6	1.2
Na ⁺	1.2	1.5	1.1

3.5. Response time and life time of proposed electrode

The average time required for the electrode to produce the static potential known as static response time, which is an important factor for a sensor to become sensitive. In this study, the static response time has been recorded (for sensors no.1, 6 and 11) by changing the concentration of Er^{3+} from 1.0×10^{-6} M to 1.0×10^{-2} M. It was observed that the electrodes reached the equilibrium response in a time of about 15 s, 8 s and 22 s respectively (Fig. 5).

To evaluate the reversibility of the electrode (no.6) the static response time was recorded with different concentration of Er^{3+} ion. In first experimental setup the measurement sequence was higher (1×10^{-2}) to lower (1×10^{-9}) concentration of Er^{3+} ion (Fig. 6). In another experimental setup the similar procedure was repeated in the opposite direction for the same concentration range. The result showed that the potential *vis* time curve for the sensor assembly remains same and illustrated the sufficient reversibility of proposed sensor (No. 6).

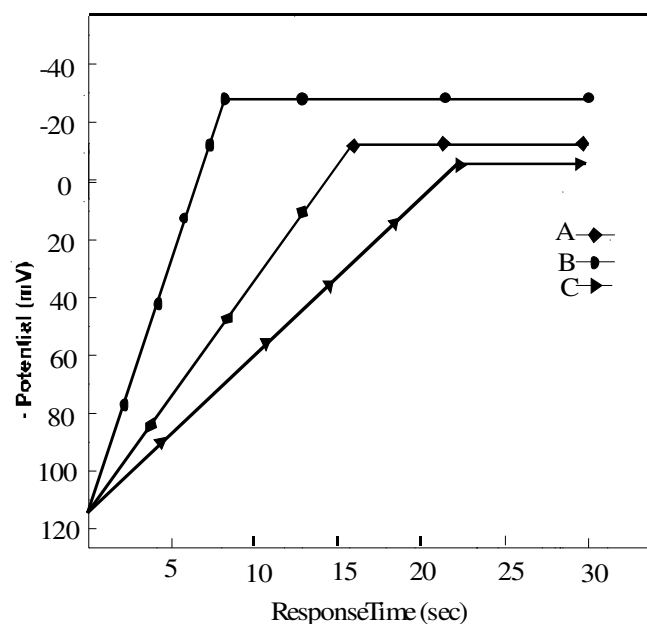


Fig. 5. Response time curve of Er^{3+} -selective electrodes. (A) based on L_1 , (B) based on L_2 , and (C) based on L_3 for 1.0×10^{-2} M solution of Er^{3+}

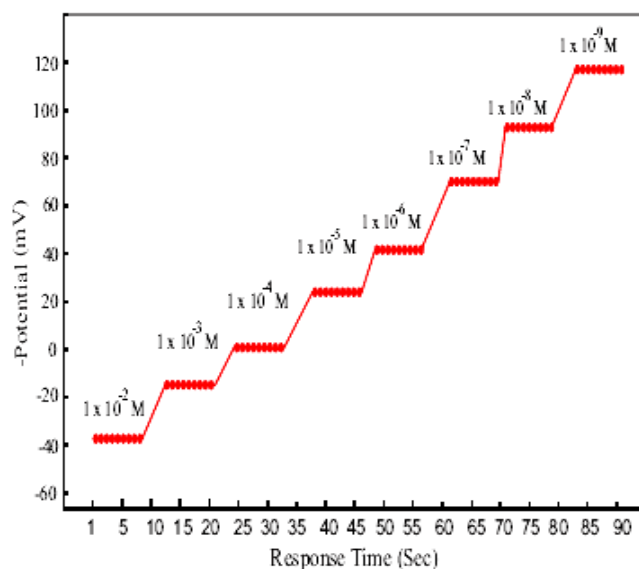


Fig. 6. Response time behavior of membrane sensor (no. 6) based on L_2

The experimental result showed that the lifetime of membrane sensor no. 6 is 5 months. During these days, the membrane sensors were in daily use over an extended period of time (at least one hour per day). After five months, gradual changes in the slopes and detection limit have been observed. This is due to the leaking of membrane ingredients from membrane to the solution. The similar procedure was repeated to evaluate the life time of sensor no. 1 (4 months) and sensor no. 11 (2 months).

3.6. pH and non-aqueous effect

The effect of pH on the potential response of sensor (no.6) was investigated in the pH range 1.0–9.5 for 1×10^{-2} and 1×10^{-3} M Er^{3+} solutions (Fig. 7). The pH of the tested solution was adjusted by the addition of nitric acid or sodium hydroxide. Fig. 7 indicates that the potential is independent within the pH range of 1.5–6.7 for sensor no. 6 based on ionophore L_2 . Therefore, the pH range 1.5–6.7 was taken as the working pH range for the sensor assembly (no.6). The sharp change in potential at higher pH values may be due to the formation of some hydroxyl complexes of the charge transport process by the membrane thereby causing interference.

The performance of proposed membrane sensor no. 6 was further observed in non aqueous medium, *i.e.* methanol-water, ethanol-water and acetone-water mixture. The results obtained are compiled in Table 3 and indicate that up to 20% (v/v) solution of non-aqueous content no significant change in the slope and working concentration range of the proposed sensor no. 6 were observed. But above 20% of non-aqueous content, electrode sensor showed

potential drift with time. This may be due to the dynamic complexation or decomplexation between ionophore and Er^{3+} ion.

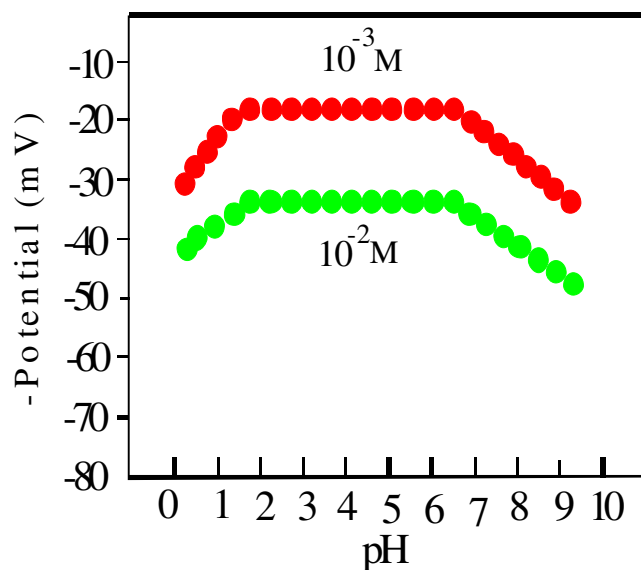


Fig. 7. Effect of pH on cell potential of sensor no. 6 at: (A) $1.0 \times 10^{-2} \text{ M}$, (B) $1.0 \times 10^{-3} \text{ M}$, Er^{3+} solutions

Table 3. Effect of partially non-aqueous medium on the working of Er^{3+} sensor (No.6)

Non-aqueous content %v/v)	Slope (mV/decade) of activity	Working Conc. Range (M)	Response time (s)
0	22.1 ± 0.3	$3.0 \times 10^{-9} - 1.0 \times 10^{-2}$	08:00
Methanol			
10	22.1 ± 0.3	$3.0 \times 10^{-9} - 1.0 \times 10^{-2}$	08:00
20	22.1 ± 0.3	$2.7 \times 10^{-9} - 1.0 \times 10^{-2}$	08:00
25	19.3 ± 0.3	$5.0 \times 10^{-8} - 1.0 \times 10^{-2}$	10:00
30	18.5 ± 0.3	$1.0 \times 10^{-8} - 1.0 \times 10^{-2}$	12:00
40	15.8 ± 0.3	$1.0 \times 10^{-7} - 1.0 \times 10^{-2}$	16:00
Ethanol			
10	22.1 ± 0.3	$2.8 \times 10^{-9} - 1.0 \times 10^{-2}$	08:00
20	22.1 ± 0.3	$2.6 \times 10^{-9} - 1.0 \times 10^{-2}$	08:00
25	19.8 ± 0.3	$5.0 \times 10^{-8} - 1.0 \times 10^{-2}$	10:00
30	17.1 ± 0.3	$1.0 \times 10^{-8} - 1.0 \times 10^{-2}$	12:00
40	14.3 ± 0.3	$1.0 \times 10^{-7} - 1.0 \times 10^{-2}$	15:00
Acetone			
10	15.8 ± 0.3	$2.0 \times 10^{-9} - 1.0 \times 10^{-2}$	08:00
20	22.1 ± 0.3	$2.0 \times 10^{-9} - 1.0 \times 10^{-2}$	08:00
25	18.2 ± 0.3	$5.0 \times 10^{-8} - 1.0 \times 10^{-2}$	12:00
30	16.3 ± 0.3	$1.0 \times 10^{-8} - 1.0 \times 10^{-2}$	18:00
40	14.2 ± 0.3	$3.0 \times 10^{-7} - 1.0 \times 10^{-2}$	14:00

3.7. Potentiometric selectivity of erbium (III) electrode

The potentiometric selectivity of sensor is another important parameter that determines the relative response of membrane sensors for the Er^{3+} over other ions present in the solution. The selectivity studies were carried out for sensor no. 1, 6 and 11, which exhibit the best performance in terms of working concentration range, slope, static response time and life time. Different methods of selective determination have been found in the literature. In the present study, the selectivity of membrane sensor was detected by Fixed Interference Method (FIM), and the results was presented in terms of potentiometric selectivity coefficients $\left(-\log K_{\text{Er}^{3+}, \text{M}^{n+}}^{\text{Pot}}\right)$ which has been measured at 1×10^{-2} M concentration of interfering ions (IUPAC recommendation) using equation (Eq.3) [33-36].

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

Where $a_{\text{Er}^{3+}}$ is the activity of the primary ion and $a_{\text{M}^{n+}}$ is the activity of interfering ion $z_{\text{Er}^{3+}}$ and $z_{\text{M}^{n+}}$ are their respective charges. 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 smaller than 1.0 indicate that membrane sensor is responding more to primary ion than to other metal ions and in such a cases the sensor is said to be selective to primary ion over other metal ions. Further, smaller is the selectivity coefficient, higher is the selectivity order.

It is seen from the Table 4 that the sensor no. 6 is more selective as compare to the sensor no. 6 and sensor no. 11. The selectivity coefficient in Table 4 also indicates that the ions such as Pb^{2+} , Hg^{2+} , Ag^+ , Fe^{3+} , Al^{3+} , Na^+ caused interference in the determination of Er^{3+} by using sensor no. 1 and sensor no. 11. However such type of problem was not observed by using sensor no. 6. It is clear form Table 4 that the sensor no. 6 is highly selective towards Er^{3+} over a variety of cations. Thus the sensor no. 6 can be used for the direct determination of Er^{3+} in different samples.

3.8. Effect of ionic and nonionic surfactants

The ionic and nonionic surfactants interact with the polymeric membrane which cause increased in the background potential and decreased the binding ability of ionophore. Such effects should result in decrease in detection limits, slopes and lower selectivity for the primary ion. In the present study the performance of electrode (no. 6) was evaluated by contaminating sample solution with different concentration of surfactants and results were compiled in Table 5. It is clear from the Table that the sensor no.6 can tolerate surfactants concentration up to 1.0×10^{-3} M.

Table 4. Selectivity coefficient values sensors nos. 1, 6 and 11 of membranes of L₁, L₂ and L₃ respectively

Interfering Ion	Selectivity Coefficient, $\left[-\log K_{E_r^{3+}, M^{n+}}^{Pot}\right]$		
	Sensor no.1	Sensor no. 6	Sensor no. 11
Tb ³⁺	4.5	4.8	3.6
Dy ³⁺	4.2	4.6	2.9
La ³⁺	3.5	4.2	2.4
Eu ³⁺	3.3	3.6	1.7
Sm ³⁺	2.8	4.3	1.8
Gd ³⁺	2.6	3.2	2.4
Yb ³⁺	2.3	2.9	1.6
Cu ²⁺	2.5	3.7	1.4
Mn ²⁺	2.4	3.6	1.2
Co ²⁺	1.9	2.1	1.3
Pr ³⁺	1.5	2.9	1.2
Ni ²⁺	1.8	2.7	1.4
Pb ²⁺	1.3	3.0	1.2
Hg ²⁺	1.2	2.4	1.1
Zn ²⁺	1.3	3.6	2.4
Ag ⁺	1.6	2.8	1.2
Fe ³⁺	1.4	2.5	1.1
Al ³⁺	1.3	2.6	1.2
Na ⁺	1.6	2.8	1.2

Table 5. Effect of ionic and nonionic surfactants on the performance of sensor no. 6

Concentration of surfactants (M)			Detection limit (M)	Slope (±0.3 mV /decade of activity)
SDS	TBC	Triton X-100		
0.0	0.0	0.0	1.0×10 ⁻⁹	22.1
1.0×10 ⁻³	0.0	0.0	1.2×10 ⁻⁹	21.9
0.0	1.0×10 ⁻³	0.0	1.1×10 ⁻⁹	22.0
0.0	0.0	1.0×10 ⁻³	1.0×10 ⁻⁹	22.1
1.5×10 ⁻²	0.0	0.0	6.7×10 ⁻⁹	21.3
0.0	1.5×10 ⁻²	0.0	6.2×10 ⁻⁹	21.2
0.0	0.0	1.5×10 ⁻²	1.2×10 ⁻⁹	22.0

4. COMPARISON STUDY

The performance characteristics of the proposed electrode and those of some reported electrodes [22-26] were compared (Table 6) and it was found that the proposed electrode has wide concentration range, fast response time (8 s), wide pH range (2.5-10) and long life time (5 months).

Table 6. Comparison of response characteristics of proposed sensor with previously reported sensors selective to Er^{3+}

S. No	Ionophore	Working Conc. range (M)	Slope (mV/decade pH of activity)	pH range	Response time (sec)	Detection limit	Ref.
1	4-(2-Thiazolylazo)resorcinol	1.0×10^{-6} – 1.0×10^{-2}	19.6 ± 0.6	2.8-9.3	<10	6.6×10^{-7}	22
2	N,N'-bis(salicylidene)-2-aminobenzylamine	1.0×10^{-6} – 1.0×10^{-2}	19.5 ± 0.2	2.6-9.5	10	5.0×10^{-7}	23
3	N,N'-bis((1H-pyrrol-2-yl)methylene)cyclohexane-1,2-diamine	1.0×10^{-6} – 1.0×10^{-2}	19.7 ± 0.4	2.7-10.2	<10	5.8×10^{-7}	24
4	N,N'-bis(quinoline-2-carboxamido)-4,5-dimethylbenzene	1.0×10^{-6} – 1.0×10^{-2}	21.3 ± 0.5	3.0-8.5	<10	5.8×10^{-7}	25
5	pyridine-2-carbaldehyde-2-(4-methyl-1,3-benzothiazol-2-yl)hydrazone	1.0×10^{-5} – 1.0×10^{-1}	21.8 ± 0.2	2.5-12	<10	5.0×10^{-6}	26
6	1,5-bis(o-methoxybenzoate)-3-thiapentane	3.0×10^{-9} – 1.0×10^{-2}	22.1 ± 0.3	2.5-10	8	1.0×10^{-9}	This work

5. ANALYTICAL APPLICATION

5.1. Titration with EDTA

The proposed membrane sensor was successfully applied as an indicator electrode for the titration of 30 mL Er^{3+} ion (1.0×10^{-3} M) with a standard EDTA solution (1.0×10^{-3} M). The

resulting titration curve is shown in Fig. 8. It has a sharp inflection point, at the titrant volume corresponding to the 1:1 stoichiometry of Er^{3+} -EDTA complex.

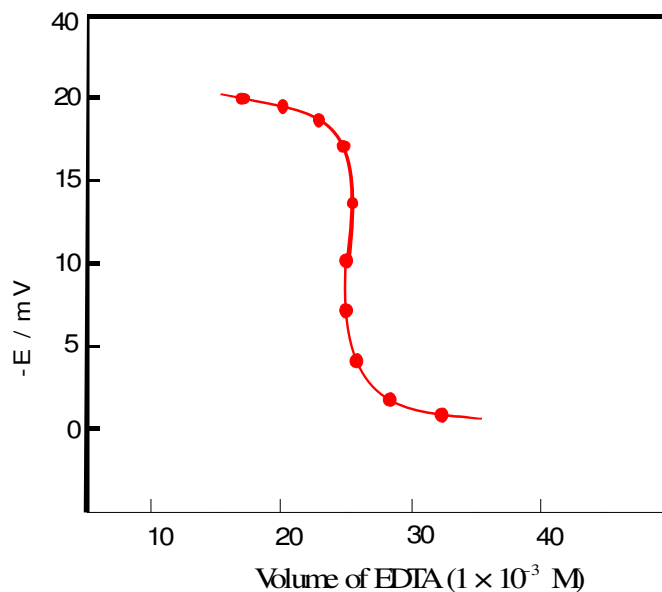


Fig. 8. Potentiometric titration curve of 10^{-3} M Er^{3+} ion solution with 25 ml, 1×10^{-3} M EDTA solution

5.2. Recovery of Er^{3+} in different synthetic samples

In addition, the electrode was successfully applied for the recovery of Er^{3+} ion in some synthetic samples. The obtained values are quite comparable to those obtained with AAS and ICP-MS, thereby illustrating the utility of the sensor for determining the Er^{3+} in real samples (Table 7).

5.3. Determination of fluoride ion

The proposed electrode no. 6 was also used for the determination of fluoride ion in different mouth wash samples. The results are listed in Table 8. Table 8, indicates a satisfactory agreement between the declared fluoride content and the determined values. The data presented in Table 7 and Table 8 clearly indicates the quantitative utility of the proposed sensor.

Table 7. Recovery of Er^{3+} in different samples using sensor no. 6

S. No	Comosition of solution	Recovery (%)	
		Proposed electrode	ICP-MS
1	0.00010 M $\text{Er}(\text{NO}_3)_3$ +0.001 M $\text{Mg}(\text{NO}_3)_2$ +0.00010 M $\text{Ca}(\text{NO}_3)_2$	101.8	102.1
2	0.00010 M $\text{Er}(\text{NO}_3)_3$ +0.001 M $\text{Co}(\text{NO}_3)_2$ +0.00010 M $\text{Ho}(\text{NO}_3)_3$	101.6	101.2
3	0.00010 M $\text{Er}(\text{NO}_3)_3$ +0.001 M $\text{Zn}(\text{NO}_3)_2$ +0.00010 M $\text{Al}(\text{NO}_3)_3$	100.4	101.7
4	0.00010 M $\text{Er}(\text{NO}_3)_3$ +0.001 M $\text{La}(\text{NO}_3)_3$ +0.00010 M $\text{Al}(\text{NO}_3)_3$	100.3	102.2
5	0.00010 M $\text{Er}(\text{NO}_3)_3$ +0.001 M $\text{Al}(\text{NO}_3)_3$ +0.00010 M $\text{Pr}(\text{NO}_3)_3$	101.8	101.3
6	0.00010 M $\text{Er}(\text{NO}_3)_3$ +0.001M $\text{Mg}(\text{NO}_3)_2$ +0.00010 M $\text{Cd}(\text{NO}_3)_2$	101.1	102.5
7	0.00010 M $\text{Er}(\text{NO}_3)_3$ +0.001 M $\text{Cd}(\text{NO}_3)_2$ +0.00010 M NaNO_3	101.6	101.0
8	0.00010 M $\text{Er}(\text{NO}_3)_3$ + 0.001 M $\text{Pr}(\text{NO}_3)_3$ +0.00010 M $\text{Cd}(\text{NO}_3)_2$	102.1	102.2
9	0.00010 M $\text{Er}(\text{NO}_3)_3$ +0.001 M $\text{Ni}(\text{NO}_3)_2$ +0.00010 M $\text{Co}(\text{NO}_3)_2$	102.2	101.4
10	0.00010 M $\text{Er}(\text{NO}_3)_3$ +0.001 M $\text{Cu}(\text{NO}_3)_2$ +0.00010 M $\text{Zn}(\text{NO}_3)_2$	103.1	101.1
11	0.00010 M $\text{Er}(\text{NO}_3)_3$ +0.001 M $\text{Cr}(\text{NO}_3)_3$ +0.00010 M $\text{Dy}(\text{NO}_3)_3$	101.1	101.4
12	0.00010 M $\text{Er}(\text{NO}_3)_3$ +0.001 M $\text{Mg}(\text{NO}_3)_2$ +0.00010 M $\text{Cd}(\text{NO}_3)_2$	102.2	102.3

^a Mean value \pm standard deviation (three measurements)

Table 8. Recovery test for fluoride ion

Sample	Labeled Value (ppm)	Observed value by sensor no. 6 (ppm)
Colgate dry mouth relief (Colgate Oral Pharmaceuticals, India)	210	2118 \pm 5
Sodium fluoride mouth wash solution (Aquafresh, Brentford, U.K.)	1350	1358 \pm 5

6. CONCLUSIONS

This study involved the synthesis and characterization of three chelates 1,5-bis(*o*-aminobenzoate)-3-thiapentane (**L**₁), 1,5-bis(*o*-methoxybenzoate)-3-thiapentane (**L**₂), 1,5-bis(*o*-chlorobenzoate)-3-thiapentane (**L**₃) as neutral carrier for the selective determination of Er^{3+} ion. The investigation of PVC-based membranes of three (**L**₁, **L**₂ and **L**₃) ionophores shows that they act as Er^{3+} selective sensor. However of the three proposed ionophors the sensor no.6 based on **L**₂ shows maximum selectivity, high sensitivity, low detection limit

(1.0×10^{-9} M), fast response time (8s), good Nernstian slope (22.1 mV/decade of activity) and wide concentration range (3.0×10^{-9} - 1.0×10^{-2} M) within the pH range of 1.5-6.7. The proposed membrane sensor was successfully applied as an indicator electrode for the titration of Er^{3+} ion (1.0×10^{-3} M) with a standard EDTA solution (1.0×10^{-3} M). The proposed membrane sensor was also used for determination of Er^{3+} in different syntactic samples as well as for the determination of fluoride ion two mouth wash samples. The proposed sensor no. 6 can also tolerate the ionic and non-ionic surfactants up to 10^{-3} M concentration.

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