

Full Paper

Construction of La(III) Selective PVC Electrode by Using Compound Diaza-trioxo-Dibenzocyclotridecane (DATODBCTD)

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Abstract- In this article a new PVC based La(III) ion selective electrode based on 1, 12-diaza-5,8,13-trioxo-3(4), 9(10)-dibenzocyclotridecane(DATODBCTD) ionophore is described. This sensor has a wide linear range of concentration (3.4×10^{-7} - 1.0×10^{-2}) and a low detection limit of 8.0×10^{-7} mol L⁻¹ of La(NO₃)₃. It has a Nernstian response with slope of 19.4 ± 0.4 mV decade⁻¹ and it is applicable in the pH range of 3.5-8.0 without any divergence in potential. The PVC electrode has a short response time of approximately 20 s and is stable at least for 2.1 days. The electrode shows a good selectivity for La³⁺ ion toward a wide variety of metal ions. The proposed sensor was successfully applied for the determination of La³⁺ ion in different real and environmental samples and as indicator electrode for potentiometric titration of La(III) ion with EDTA.

Keywords – La(III) Electrode, Macrocyclic Ionophore

1. INTRODUCTION

Lanthanides were widely distributed in low concentrations throughout the earth's crust. Because their increasing interest in bioinorganic [1] and coordination chemistry the

determination of these species has been an increasing concern. Lanthanum oxides were extensively used in making of optical glasses [2], gasoline-cracking catalysts, polishing compounds and carbon arcs. In the iron and steel industries lanthanum used to remove sulfur, carbon and other electronegative elements. Lanthanum nitrate enhanced the respiratory rate and promote the germination of natural rice seed [3]. LaCl_3 was used as anti-tumor agent [4]. The main available methods for low-level determination of lanthanum and other lanthanide elements in solution include spectrophotometry [5], induced couple plasma mass spectrometry [6], X-ray fluorescence [7], isotope dilution mass spectrometry [8], neutron activation analysis [9] and ICP-AES [10].

However, these methods are either time consuming, involving sample manipulations or too expensive for most analytical laboratories. Hence, the development of new ion-selective electrodes for La(III) is still a challenging task [11–21]. A variety of acyclic and macrocyclic ligands used as ionophore in the preparation of new ion selective electrodes for lanthanum ions were reported [11-21]. In this paper we report the use of 1, 12-diaza-5, 8, 13-trioxo-3(4), 9(10)-dibenzocyclotridecane (DATODBCTD) as a suitable neutral ionophore for the preparation of a PVC-based polymeric membrane electrode for determination of La(III) ion.

2. EXPERIMENTAL

2.1. Reagents and Apparatus

All the reagents were used of analytical grade. High molecular weight PVC, tetrahydrofuran (THF), 1, 2-dibromoethane, thiourea and salicyldehyde were procured from Aldrich; Plasticizers viz., dibutylphthalate (DBP), Acetophenone (AP) and additives oleic acid (OA) are obtained from Fluka. Metal salts, and all other analytical grade solvents were used received from Merck & Aldrich. In addition, all standard solutions and buffers were prepared using double distilled deionized water. Potential were measured with digital potentiometer EQ-602 Equiptronics (accuracy, 0.001 V, India). The pH measurements were carried out on digital pH meter (Lab India pH Conmeter, India). Auto ranging Conductivity meter/TDS meter TCM-15 (Toshniwal Instruments Mfg. Pvt. Ltd Ajmer).

All the electromotive force (EMF) measurements were carried out with the following cell assembly.

| | | | | |
|--|---|----------|------------------|---------------------------------------|
| External reference electrode (SCE) | Internal solution 0.01 M $\text{La}(\text{NO}_3)_3$ | Membrane | Test solution | Internal reference Electrode (SCE) |
|--|---|----------|------------------|---------------------------------------|

2.2. Synthesis of 1,12-diaza-5,8,13-trioxo-3(4),9(10)-dibenzocyclotridecane Ionophore (DATOBDTD)

Scheme for the synthesis of ionophore is given in Fig. 1. In 10 mL ethanolic solution of salicylaldehyde 5.32 mL (1.0 M) was added in two necks round bottom flask. The solution was warmed up to 40 °C followed by addition of 1, 2-dibromoethane 2.15 mL (0.5 M) with constant mechanical stirring. The reaction mixture was heated for 4 hrs at 65°C. After cooling the mixture for 30 min at 35 °C, 25 ml ethanolic solution of urea (0.5 M, 1.5 g) was added with continuous stirring. Then the mixture was heated again for 10 hrs. On cooling the mixture over night in a refrigerator, a white precipitate was formed. It was filtered washed with ethanol and dried in vacuum over P₄O₁₀. Yield: 72%; Melting point 281 °C.

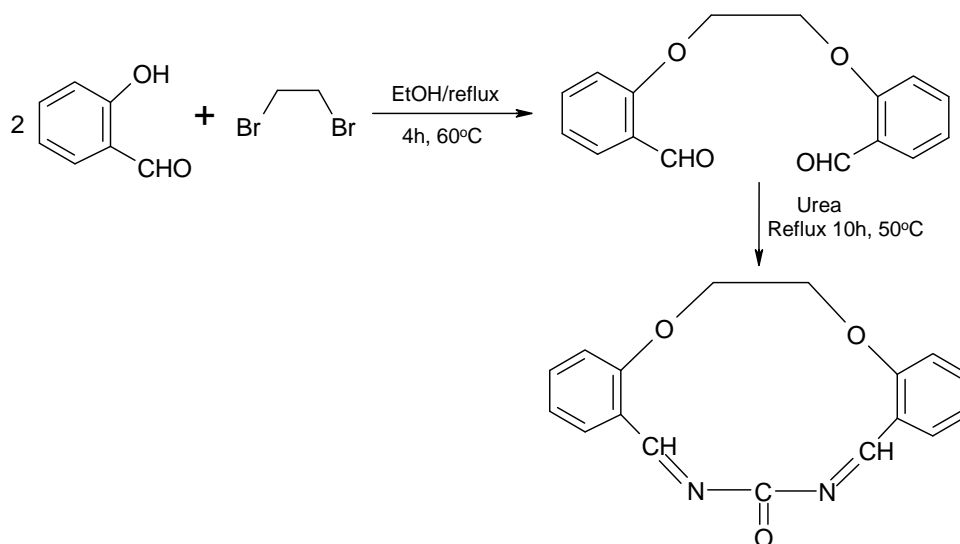


Fig. 1. Scheme for the synthesis of Ionophore

Characterization of the ionophore: Pre-confirmatory test for synthesis ionophore was done primarily through UV and IR spectra. The formation of compound was confirmed by analysis of mass, ¹H NMR spectra and CHN elemental analysis data.

CHN Analysis: Anal. Calcd. For C₁₇H₁₄N₂O₃: C, 69.38; H, 4.76; N, 9.52 Found: C, 69.32; H, 4.73; N, 9.61

IR Characterization: IR (KBr) (ν_{cm⁻¹}): (C=N), 1594, (phenyl) 1492, (-CH₂) 818 cm⁻¹. No peak due carbonyl and amino group suggest the absence of these groups. But presence of >C=O group of urea at 1680 cm⁻¹ and -O-CH₂-1264 cm⁻¹ confirm the purposed structure.

NMR spectra: ^1H NMR (300MHZ, 298K), $\delta=7.99$ (2H, s, HC=N), 3.66 (4H, s, C-O), 6.70 (2H, t, aromatic), 6.95 (2H, d, aromatic), 7.30 (2H, t, aromatic), 7.76 (2H, d, aromatic).

Mass Spectra: The molecular ion peak of compound at 295 according to molecular mass 294 amu and various peaks due to other fragmentations are at 77, 137, 213, 240 and 268.

2.3. Preparation of membrane

The general procedure to prepare the PVC membrane was to mix thoroughly 35 mg of powdered PVC, 7 mg of DATODBCTD and 6 mg of additive OA with 52 mg of AP as solvent mediator. The mixture was then thoroughly dissolved in 5 mL of THF. The resulting mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A polyethylene tube of 5 mm. was dipped into the mixture for about 10 s, So that a yellow color transparent membrane of about 0.3 mm thickness was formed. After removing the tube from the mixture, it was kept at room temperature for about 1 h. The tube was filled with internal filling solution (1.0×10^{-3} M La^{3+}). The electrode was finally conditioned for 24 h by soaking in 1.0×10^{-2} M solution of La(III) nitrate.

3. RESULT AND DISCUSSION

3.1. Study of complex formation constant (K_f)

The interactions between the ion-carrier (DATODBCTD) and the different cations were tested. To the best of our knowledge, there is no report on the stability of the (DATODBCTD) complexes with different cations. Thus, DATODBCTD complexation with several cations was conductometrically investigated in an acetonitrile solution, at 25 ± 0.05 °C, in order to obtain a clue about the stability and selectivity of the resulting complexes. The complex formation constant, K_f were evaluated by computer fitting of the molar conductance mole ratio data with appropriate equations 1 and 2. The respective results are summarized in Table 1. As it is obvious, the stability constant of the La^{3+} (DATODBCTD) complex is higher than that of the other tested cations.

Table 1. Formation Constant of metal ions – ligand (DATODBCTD)

| Cation | log K _f |
|------------------|--------------------|
| La ³⁺ | 5.23±0.15 |
| Pb ²⁺ | 1.18±0.14 |
| Sr ²⁺ | 2.79±0.18 |
| Li ⁺ | 1.93±0.12 |
| Ce ³⁺ | 2.66±0.11 |
| Cu ²⁺ | 1.54±0.12 |
| Ni ²⁺ | 1.29±0.18 |
| Hg ²⁺ | 1.14±0.10 |
| Co ²⁺ | 1.35±0.12 |
| Na ⁺ | 1.87±0.19 |
| K ⁺ | 1.43±0.06 |
| Sm ³⁺ | 3.37±0.10 |
| Zn ²⁺ | 1.92±0.17 |
| Cd ²⁺ | 1.67±0.19 |

Consequently, (DATODBCTD) may be used as a suitable selective ionophore in the construction of a La³⁺ ion-selective membrane electrode.



$$K_f = \frac{[ML^+]}{[M^+][L]} \times \frac{f(M^+)f(L)}{f(ML^+)} \quad (2)$$

Where [ML⁺], [M⁺], [L] and f represent the equilibrium molar concentration of complexes, free cation, free ligand, and the activity coefficient of the species indicated, respectively. Under the dilute condition we used, the activity coefficient of the unchanged ligand, f(L) can be reasonably assumed as unity [22]. The use of Deby-Huckel limiting law of 1:1 electrolytes [23] lead to the conclusion that f(M⁺) ~ f(ML⁺), so the activity coefficient in equation (2) is canceled out. Thus the complex formation constant in term of the molar conductance can be expressed as [24-25].

$$K_f = \frac{[ML^+]}{[M^+][L]} = \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})[L]} \quad (3)$$

$$[L] = C_L - \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_M - \Lambda_{ML})} \quad (4)$$

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 (DATODBCTD) 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 [26]. The logarithm of the formation constants ($\log K_f$) of the resulting 1:1 complexes for mono and divalent cations were about two or less than 2, and for trivalent cations (other lanthanides except La(III)) were in the range of 2.41-3.44. However, for La(III) the logarithm of the formation constants was 5.23. Thus (DATODBCTD) is a suitable ion-carrier for the fabrication of a La(III) ion-selective membrane sensor.

3.2. Effect of membrane composition

Potential responses of various ion selective electrodes based on (DATODBCTD) as an ionophore in the PVC membranes were evaluated for different ions separately and are shown in Fig. 2. Except for the La^{3+} ion, in all other cases the slope is much lower than the expected Nernstian slope. The La^{3+} ions concentration can suitably determined by this ISE with high sensitivity. It is well documented that the linear range, sensitivity and selectivity obtained for a given ionophore incorporated PVC-membrane electrode depend significantly on the membrane composition and nature of plasticizers and additives used [27-28].

Thus, the influences of membrane composition, nature and amount of plasticizer and additive on the potential response of the La(III) selective electrode was investigated, and the results are summarized in Table 2. It has been reported that polymeric films with such a PVC/plasticizer ratio (0.5) usually possess optimum physical properties and ensure high enough mobility's of their constituents [29-30].

As with many ionophore based PVC-membrane electrode, the potentiometric response of the proposed La^{3+} ion-selective electrode was found to be dependent on the concentration of ionophore incorporated in the PVC-membranes. The sensitivity of electrode response increase with increasing the ionophore content from 3 to 7% . Further addition of ionophore to 9% will, however, results in diminished response of the electrode, most probably due to some in homogeneities and possible saturation of membrane.

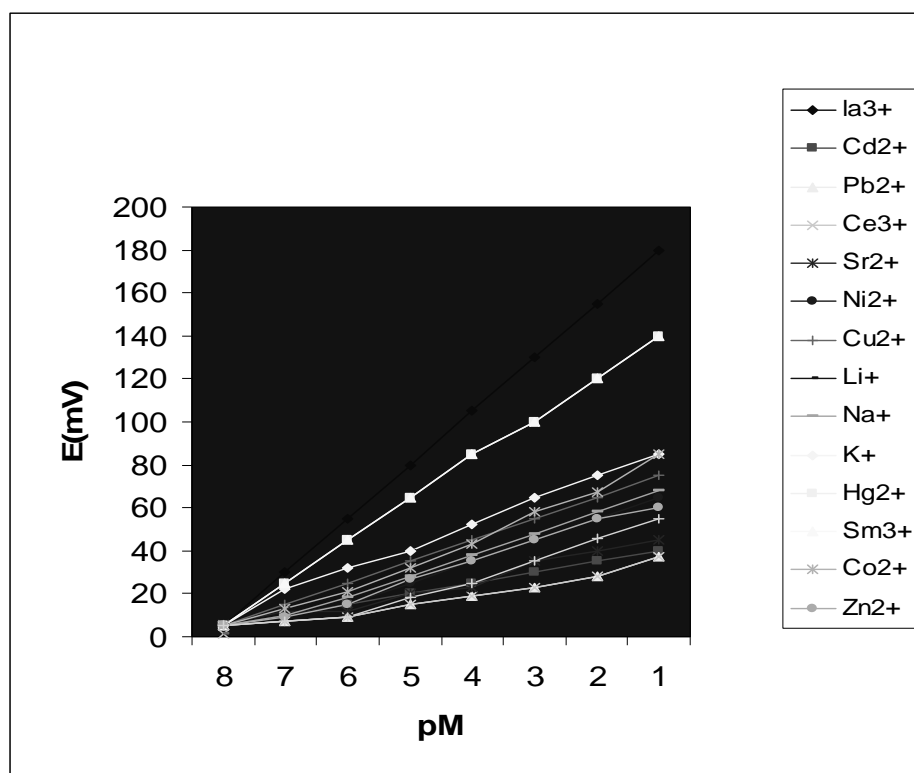


Fig. 2. Potential responses of various ion selective electrodes based on (DATODBCTD)

3.3. Dynamic response time of sensor

It is well known that the dynamic response time of a sensor is one of the most important factor in its evaluation. To measure the dynamic response time of the proposed sensor the concentration of the test solution was successively changed from 1.0×10^{-6} to 1.0×10^{-2} M in a stepwise manner, and the potential versus potential behavior was recorded. The resulting values depicted in Fig.3 shows that the time needed for the sensor to reach ± 1 mV of its equilibrium value for each corresponding concentration is relatively short and about 20 s. For evaluation of the stability and life-time of the La(III) sensor, three electrodes were tested over a period of 7 weeks. During this period, the electrodes were in daily use over extended period of time (1 h per day) and the slopes and detection limits of them were measured. The results are summarized in Table 3. After 5 weeks a slight gradual decrease and increase in the slopes and detection limits, respectively, were observed. This probably arises from the leaching of the membrane components.

Table 2. Effect of membrane composition

| Membrane No. | Linear range | Composition of membrane (wt %) | | | | Slope (mV/decade) |
|--------------|---|--------------------------------|-------------|-----|--------------|-------------------|
| | | I | Plasticizer | PVC | Additive(OA) | |
| 1 | 2.9×10^{-3} - 1.0×10^{-1} | -- | 60(AP) | 35 | 5 | 2.4 ± 0.8 |
| 2 | 3.5×10^{-4} - 1.0×10^{-1} | 3 | 57(AP) | 35 | 5 | 7.5 ± 0.2 |
| 3 | 2.7×10^{-5} - 1.0×10^{-1} | 5 | 55(AP) | 35 | 5 | 14.3 ± 0.5 |
| 4 | 3.4×10^{-7} - 1.0×10^{-2} | 7 | 52(AP) | 35 | 6 | 19.4 ± 0.4 |
| 5 | 6.8×10^{-4} - 1.0×10^{-1} | 9 | 51(AP) | 35 | 5 | 16.3 ± 0.7 |
| 6 | 6.8×10^{-4} - 1.0×10^{-1} | 8 | 52(AP) | 35 | 5 | 15.7 ± 0.4 |
| 7 | 7.9×10^{-4} - 1.0×10^{-1} | 7 | 51(AP) | 35 | 7 | 12.3 ± 0.6 |
| 8 | 3.3×10^{-4} - 1.0×10^{-1} | 6 | 53(DBP) | 35 | 6 | 8.9 ± 0.4 |

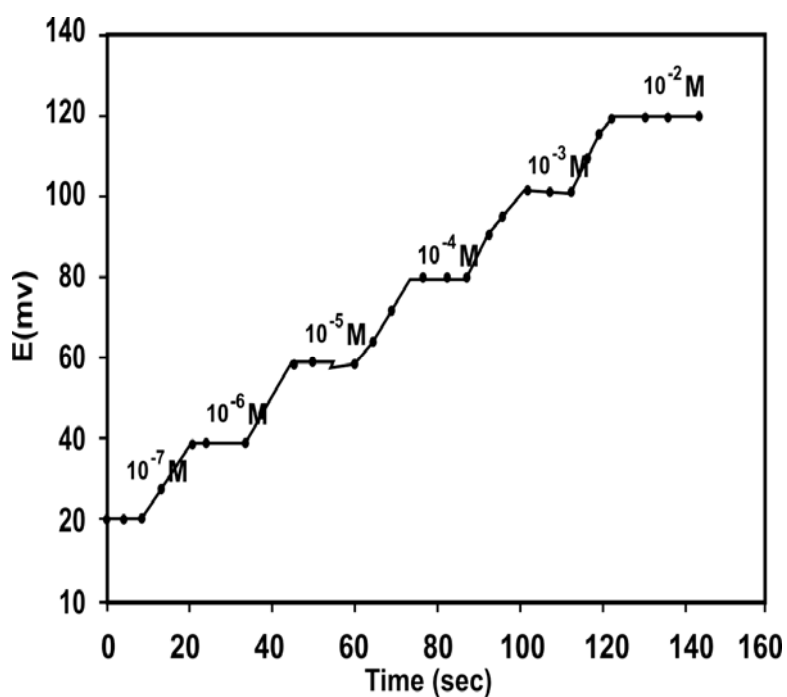


Fig. 3. Dynamic response of membrane electrode for step change in concentration of La^{3+} ion (A) 1.0×10^{-7} M; (B) 1.0×10^{-6} M; (C) 1.0×10^{-5} M; (D) 1.0×10^{-4} M (E) 1.0×10^{-3} M; (F) 1.0×10^{-2} M

Table.3. The life-time of the La³⁺ membrane sensor

| Week | Slope (mV/decade) | Detection limit (mol L ⁻¹) |
|---------|-------------------|--|
| First | 19.4±0.4 | 8.0×10 ⁻⁷ |
| Second | 19.4±0.4 | 8.0×10 ⁻⁷ |
| Third | 19.0±0.3 | 7.0×10 ⁻⁷ |
| Fourth | 18.9±0.5 | 6.0×10 ⁻⁷ |
| Fifth | 18.4±0.3 | 6.0×10 ⁻⁷ |
| Sixth | 17.1±0.6 | 2.0×10 ⁻⁶ |
| Seventh | 15.3±0.4 | 4.0×10 ⁻⁶ |

3.4. Lifetime of sensor

The lifetime of electrodes based on ionophore in solvent polymeric membranes depends on the distribution coefficient of the ionophore and the plasticizer between the aqueous and membrane phases. Hence, the lifetime of electrodes must depend on the components of the solution and the measured specimens with electrodes. The experimental results show that the lifetime of the present electrode was about 21 days. During this time, the detection limit was 6.0×10⁻⁷ mL⁻¹ and the slope of the electrode (19.4 mV/decade) remained almost constant. Subsequently, the electrochemical behavior of the electrode gradually deteriorated. This is attributed to ageing of the polymer (PVC), plasticizers and ionophore (macrocyclic ligand).

3.5. Effect of pH

The pH influence of the test solution (1.0×10⁻⁴ M) on the potential response of the membrane sensor was tested in the pH range of 1.0-10.0, the pH of solution was adjusted by addition of dilute HNO₃ or NaOH. It is clear from the Fig. 4 that the potential remains constant for the pH values from 3.5-8.0, beyond which the potential changes considerably. This sharp change in potential at high pH value may be due to hydrolysis of La³⁺ ions while at lower pH value H⁺ start contributing to the charge transport process of the membrane thereby causing interference.

3.6. Effect of non-aqueous media

The performance of electrode in partially non-aqueous media using acetone-water, methanol-water and ethanol-water mixtures have been assed and the results obtained are presented in Table 4. It was observed that in presence of methanol the slope decrease remarkably. The slope is acceptable in the presence of ethanol until about 25% (v/v) in the water and for the higher percentage of ethanol, the slope decreases. This effect is drastic in

acetone –water mixture where the slope is considerably decreased even in 10% (v/v) acetone. Therefore the electrode assembly is suitable in ethanol water mixture up to 25%, there is only a small decrease in slope and working concentration range, hence the electrode can be satisfactorily used in this media for estimation of La^{3+} ions in solutions.

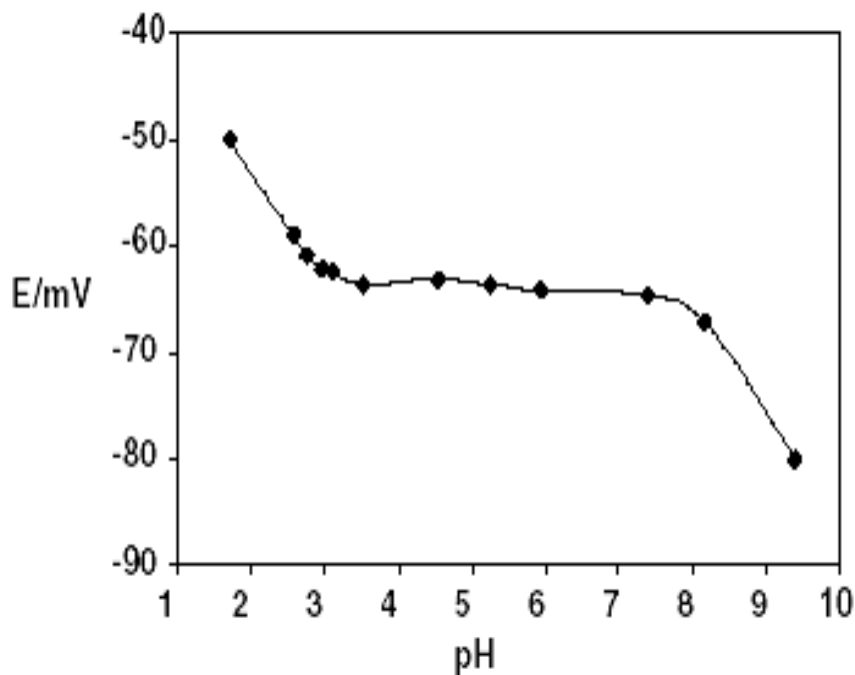


Fig. 4. Plots showing the variation of membrane potentials with pH at $1.0 \times 10^{-3} \text{ mol L}^{-1}$ La(III) solutions

3.7. Selectivity coefficient

The potentiometric selectivity coefficients, which reflected the relative response of the membrane sensor for the primary ion over other ions, present in solution, is perhaps the most important characteristics of an ion-selective electrode. In this work, the potential response of the proposed La(III) ion-selective sensor was investigated by the match potential method (MPM) [31-32]. The selectivity coefficient is determined as :

$$K_{A,B}^{\text{pot}} = \frac{\Delta A}{a_B}$$

Where $\Delta A = 'a_A - a_A$, a_A is the initial primary ion activity and $'a_A$ the activity of A in the presence of interfering ion, a_B . As is seen, in table 5 for all diverse the selectivity coefficients are in the range 4.0×10^{-2} to 1.1×10^{-4} M indicating that they do not disturb the functioning of the La(III) sensor.

Table 4. Performance of La³⁺ selective electrode in partially non-aqueous media

| Non-aqueous content (%v/v) | Slope (mV/decade) | Detection limit (mol L ⁻¹) |
|----------------------------|-------------------|---|
| Methanol | | |
| 15 | 11.5 | 1.0×10 ⁻¹ - 1.4×10 ⁻⁶ |
| 25 | 10.1 | 1.0×10 ⁻¹ - 1.3×10 ⁻⁶ |
| 35 | 13.8 | 1.0×10 ⁻¹ - 2.9×10 ⁻⁵ |
| Ethanol | | |
| 15 | 16.5 | 1.0×10 ⁻¹ - 3.7×10 ⁻⁶ |
| 25 | 19.4 | 1.0×10 ⁻¹ - 1.3×10 ⁻⁷ |
| 35 | 14.8 | 1.0×10 ⁻¹ - 1.0×10 ⁻⁶ |
| Acetone | | |
| 15 | 9.4 | 1.0×10 ⁻¹ - 3.1×10 ⁻⁶ |
| 25 | 16.6 | 1.0×10 ⁻¹ - 7.5×10 ⁻⁵ |
| 35 | 11.2 | 1.0×10 ⁻¹ - 1.8×10 ⁻⁵ |

Table.5. Selectivity coefficient of various interfering cations for La³⁺ selective membrane sensor

| Cation | log K _{A,B MPM} |
|------------------|--------------------------|
| Pb ²⁺ | -3.78 |
| Sr ²⁺ | -3.75 |
| Ce ³⁺ | -4.00 |
| Cu ²⁺ | -3.87 |
| Ni ²⁺ | -4.98 |
| Hg ²⁺ | -3.81 |
| Co ²⁺ | -4.58 |
| Na ⁺ | -3.75 |
| K ⁺ | -4.98 |
| Sm ³⁺ | -4.61 |
| Zn ²⁺ | -4.98 |
| Cd ²⁺ | -5.23 |

4. APPLICATIONS

4.1. Potentiometric titration

The analytical application of the sensor was tested and so it was used as an indicator electrode to determine the end point in the potentiometric titration of La^{3+} with EDTA. 25.0 mL 1.1×10^{-4} M solution of La^{3+} was titrated with 1.1×10^{-2} M of EDTA, and the resulting titration curve is shown in Fig. 5 The sigmoid shape curve sharp end point corresponds to sufficient selectivity of this sensor towards La^{3+} ions.

4.2. Analysis of water samples

The proposed sensor has been used as an indicator electrode was directly applied determination of La(III) ions in tap water and river water samples. Different spiked samples were prepared by adding aliquots of La^{3+} solution into river water and tap water and the amount of spiked La^{3+} in samples was directly determined by proposed electrode and another instrumentation technique AAS. It is shown in Table 6 there is close agreement between the results obtained.

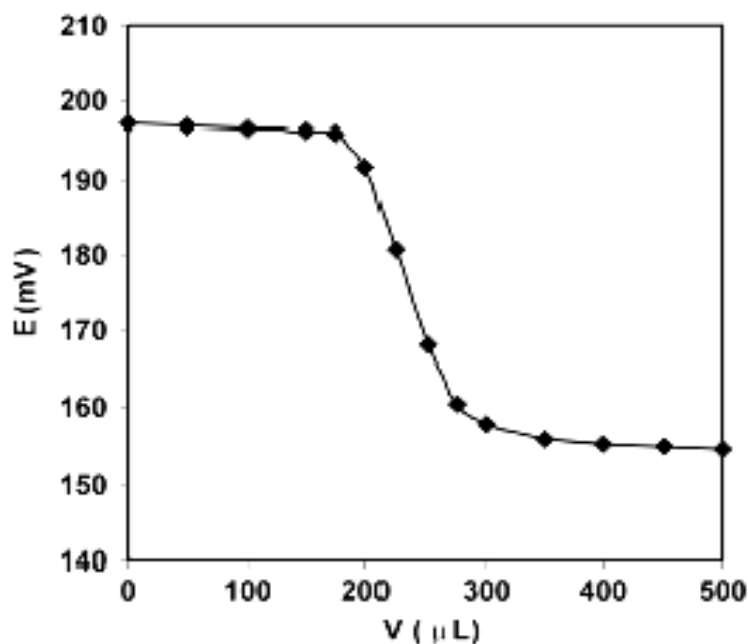


Fig. 5. Potentiometric titration curve of 25.0 mL 1.0×10^{-4} M solution of La^{3+} with 1.0×10^{-2} M of EDTA

Table 6. Determination of lanthanum spiked in tap and river water samples

| S.N. | Sample | Added(mol/L) | Found(mol/L) | Recovery (%) |
|------|-------------|----------------------|----------------------------------|--------------|
| 1 | Tap water | 1.5×10^{-3} | $(1.54 \pm 0.05) \times 10^{-3}$ | 102.0 |
| | | 1.3×10^{-4} | $(1.45 \pm 0.10) \times 10^{-4}$ | 111.5 |
| 2 | River water | 1.0×10^{-3} | $(1.18 \pm 0.04) \times 10^{-3}$ | 118.0 |
| | | 2.0×10^{-4} | $(2.17 \pm 0.12) \times 10^{-4}$ | 108.5 |

4.3. Comparison of the proposed electrode with previously reported electrodes

Proposed electrode compare with previously best reported La^{3+} electrodes in terms of working concentration range, response time and pH range Table 7.

Table 7. Comparison of selectivity coefficient of the proposed sensor with previously reported La^{3+} sensor

| Ion | ref.12 | ref.13 | ref.14 | ref.15 | ref.16 | ref.17 | ref.18 |
|------------------|--------|--------|--------|--------|--------|--------|--------|
| Pb^{2+} | -3.40 | -3.21 | -- | -- | -1.74 | -3.17 | -3.78 |
| Sr^{2+} | -- | -- | -- | -- | -- | -3.43 | -3.75 |
| Na^{+} | -3.68 | -- | -- | -- | -1.96 | -- | -4.00 |
| Ce^{3+} | -3.64 | -- | -- | -- | -- | -2.23 | -3.87 |
| Cu^{2+} | -3.30 | -6.00 | -1.82 | -- | -- | -2.29 | -4.98 |
| Ni^{2+} | -4.96 | -3.51 | -2.30 | -- | -- | -3.37 | -3.81 |
| Hg^{2+} | -3.70 | -2.41 | -1.30 | -2.7 | -- | -3.82 | -4.58 |
| Co^{2+} | -4.29 | -- | -- | -2.5 | -1.89 | -3.54 | -4.74 |
| K^{+} | -3.52 | -6.00 | -- | -- | -1.36 | -- | -4.61 |
| Sm^{3+} | -- | -- | -- | -- | -- | -- | -4.98 |
| Zn^{2+} | -4.00 | -2.85 | -1.70 | -- | -1.68 | -2.15 | -4.33 |
| Cd^{2+} | -4.00 | -6.00 | -1.68 | -2.5 | 1.78 | -2.43 | -5.87 |

5. CONCLUSION

We have prepared PVC-based membrane electrodes selective to La(III) , containing a neutral ionophore 1,12-diaza-5,8,13-trioxo-3(4),9(10)-dibenzocyclotridecane (DATODBCTD). The membrane selective electrodes prepared under optimal PVC-

membrane ingredients, revealed near theoretical sensitivity ($19.4 \text{ mV decade}^{-1}$), very fast response time 6 s, good linear range (3.4×10^{-7} – 1.0×10^{-2} M), long lifetime (at least 35 days) and selectivity over a large number of metal ions. In general the electrochemical properties were comparable to those of the previously recorded for La(III) ion-selective electrodes. The proposed La(III)-membrane electrode was directly applied to the estimation of lanthanum in presence of diverse ion.

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