Scientific paper

A Fast Response Membrane Sensor based on Ethyl 1, 2, 3, 4-tetrahydro-6-methyl-4-phenyl-2-thioxopyrimidine-5-carboxylate for Detection of Lanthanum (III) Ions at Wide Concentration Range

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Abstract

A PVC membrane La (III) ion-selective electrode has been constructed using ethyl1,2,3,4-tetrahydro-6-methyl-4-phenyl-2-thioxopyrimidine-5-carboxylate (ETMPTC) as a neutral ionophore. This electrode responds to La (III) ion with a sensitivity of 19.9 ± 0.3 mV/decade over the range 9.3×10^{-8} to 1.0×10^{-1} M at pH 3.0–10.0. The limit of detection was 1.7×10^{-8} M. It has a response time of < 11s and can be used for at least 3 months without any divergence in potentials. The proposed electrode shows fairly good discrimination of La (III) ion from several cations. The effect of organic solvents on electrode response was examined. The results show that this electrode can be used in ethanol media until 20% (v/v) concentration without interference. The isothermal temperature coefficient of this electrode amounted to 0.00013 V/ °C. This sensor not only was used as an indicator electrode in potentiometric titration of lanthanum ion against EDTA but also was used to determination of La^{3+} concentration in the presence of certain interfering ions.

Keywords: La^{3+}-selective electrode; PVC membrane; Potentiometry; Response time

1. Introduction

In the area of membrane-based ISEs, emphasis has been focused on the development of new ionophores and on the composition of the membrane phase, aiming at enhancing the potentiometric responses of the ISEs. Fabrication of a new, ion-specific ISE with high selectivity and sensitivity, wide linear concentration range, long lifetime, good reproducibility and low cost, is always in need.[1] The introduction of new ion-selective membrane electrodes has played a fundamental role in the development of potentiometric measurements. The advantages of ISEs over many other methods are their easy handling, non-destructive analysis and inexpensive sample preparation. Lanthanum ions accelerate the phosphate ester hydrolysis binding by 13 orders of magnitude. This suggests that the phosphate diester in DNA may also suffer such destruction. Thus, lanthanum should be situated among the class of highly toxic metal ions that are potentially effective against micro and higher organisms. On the other hand, Lanthanum chloride manifests as antitumor. Genotoxicity of lanthanum (III) in human peripheral blood lymphocytes has also been reported. Moreover, lanthanum chloride has caused changes in lipid peroxidation, redox system and ATPase activities in plasma membranes of rice seeding roots.[2]

The determination of La (III) ion has been carried out directly or indirectly by a variety of instrumental methods. These methods include flame photometry,[3] atomic absorption spectrometry,[4] inductively coupled plasma-mass spectrometry (ICP-MS),[5] ion chromatography,[6] atomic emission spectrometry,[7] inductively coupled plasma- optical emission spectrometry (ICP-OES),[8] sector field inductively coupled plasma mass spectrometry,[9] electrothermal vaporization inductively coupled plasma mass spectrometry,[10] etc.

However, in comparison with other transition metal cations, very few electrodes have been reported for the estimation of La^{3+} in solution.[2,11–18] All the reported electrodes generally have relatively acceptable performance for monitoring lanthanum but they suffer from some limitations. Ganjali et al. who have reported several La^{3+}-selective electrodes have improved the performance of the sensor by selecting better ionophore that used for construction of the electrodes.[11,14,16,18] Their electrode based on Gliclazide[14] with the limitation on low pH range (4.0–8.0) and relatively low dynamic range (1.0×10^{-6} to 1.0×10^{-1} M) was improved using the 4-methyl-2-hydrazinobenzothiazole to develop a better sensor with a wider pH range (3–10) and dynamic range (1.0×10^{-7} to 1.0×10^{-1} M).[2] Gupta have introduced another sensor for this ion. This sensor has low pH range (4.0–8.0) and approximately low dynamic range (3.16×10^{-5} to 1.00×10^{-1} M).[17] The selective electrode which have been reported by Mittal, suffer from long response time (30s).[13] Therefore, it is obvious that there is still a need for developing better sensor for La^{3+} ion. Electrically neutral lipophilic ligands containing the appropriate number of binding sites of high dipole moment and high polarizability could be employed as ion-active phase for metal ions. The design and synthesis of new macrocyclic ligands for specific analytical applications is a subject of continuous interest.[19,20]

The purpose of the present work is the development of a La^{3+}-selective electrode based on a poly (vinyl chloride) (PVC) membrane of ethyl 1, 2, 3, 4-tetrahydro-6-methyl-4-phenyl-2-thioxopyrimidine-5-carboxylate (ETMPTC) as an ionophore. The well known procedure [21,22,23] was used for preparation of ETMPTC. To the best of our knowledge this compound has not previously been used in the development of a lanthanum (III) selective electrode or in any other ion-selective electrode.

2. Experimental

2. 1. Reagents

Reagent grade acetophenone (AP), oleic acid (OA), tetrahydrofuran (THF), dibuthyl phthalate (DBP) , high relative molecular weight PVC (all from Merck) , *β*-keto ester, urea or thiourea, $Fe(HSO_4)_3$, absolute EtOH (from Fluka or Aldrich) were used as received. Chloride and nitrate salts of all other cations (all from Merck) were of the highest purity available and used without any further purification. Double distilled deionized water was used throughout.

2. 2. Synthesis of Ionophore (ETMPTC)

ETMPTC was synthesized under solvent-free conditions: A mixture of the substrate (1 mmol), *β*-keto ester (1.2 mmol) urea or thiourea (1.2 mmol) and $Fe(HSO_4)_3$ (1 mmol) was heated in an oil bath (100 °C) for 2h. After completion (monitored by TLC), the reaction was cooled to room temperature and poured onto crushed ice and the solid product separated was filtered and recrystallised from ethanol.

The product has m.p. = 208–210 °C and its structure is shown in Fig. 1. FT-IR (KBr), V (Cm^{-1}): 3440(m), 3240(m), 3105(w), 2990(w), 1725(s), 1700(s), 1640(s), 1450(s), 1415(s), 1310(m), 1285(m), 1220(m), 1085(s), 780–755(s), 700(w), $^1HNMR(CDCl_3)$, δ(ppm): 1.19–1.21(t, 3H), 2.39(s, 3H), 4.09–4.15(m, 2H), 5.44–5.45(d, 1H), 5.57(bs, 1H), 7.29–7.55(m, 5H), 7.55(bs, 1H), $^{13}CNMR(CDCl_3$, 125MHZ): 14.49, 18.89, 56.15, 60.3, 101.81, 126.96, 128.4, 129.62, 144.22, 146.74, 153.97, 166.01.

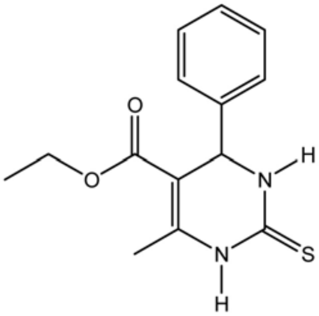

Figure 1. Structure of ethyl 1, 2, 3, 4-tetrahydro-6-methyl-4-phenyl-2-thioxopyrimidine-5-carboxylate used as ionophore.

2. 3. Preparation of Membrane

Membranes containing different PVC/plasticizer ratios were studied and the optimum composition found was 30.0 wt. % of powdered PVC, 60 wt. % of plasticizer (AP), 5 wt. % of additive (OA) and 5 wt. % of the corresponding ionophore (ETMPTC). These were mixed in 1.5 ml of THF. The solvent was evaporated slowly until an oily concentrated mixture was formed. A Pyrex tube (4 mm o.d.) was dipped into the mixture for about 15 s so that a transparent membrane of about 0.4 mm thickness was formed. The tube was then pulled out from the solution and kept at room temperature for about 2 h. The tube was then filled with internal solution 1.0×10^{-3} M La^{3+}. The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-2} M La^{3+} solution. The ratios of various ingredients, concentration of equilibrating solution and time of contact were optimized to provide a membrane that was reproducible, noiseless and stable potential.

2. 4. Potential Measurement

Potentials were measured with a Corning ion analyzer pH/mV meter relative to a double junction saturated calomel electrode (SCE) with the chamber filled with an ammonium nitrate solution at constant temperature (25 ± 0.1 °C). A silver / silver chloride electrode containing a 3 M solution of KCl was used as the internal reference electrode. The electrode cell assembly of the following type was used:

Ag–AgCl | KCl (3 M) | internal solution, 1.0 × 10^{-3} M La^{3+} | PVC membrane | test solution | $Hg–Hg_2Cl_2$, KCl (saturated).

3. Results and Discussion

3. 1. Effect of Membrane Composition on the Electrode Response

The potential responses of various ion-selective electrodes are shown in Fig. 2. Except for the La^{3+} ion-selective electrode, in all other cases the slope of the corresponding potential–pM plots is much lower than the expected Nernstian slopes. It is well known that the sensitivity and selectivity obtained for a given ionophore depends significantly on the membrane composition and the nature of solvent mediator and additive used.[24–29] The composition of membranes with different plasticizers, performing best is given along with their characteristics in Table 1. It is seen that the membrane with AP plasticizer performs best as it exhibits the widest working concentration range and near-Nernstian slope. The effect of ionophore (ETMPTC) amount on the functioning of membrane was also investigated. It was found that the membrane having a composition as PVC: AP: OA: ETMPTC as 30:60:5:5 wt. % exhibits the best results. The sensitivity of electrode response increases with increasing ionophore content from 1 to 5%. Further addition of ionophore to 8% will, however, result in diminished response of the electrode, most probably due to some inhomogeneities and possible saturation of the membrane. It is obvious from Table 1 that between two different plasticizers used, AP gives better response. It should be noted that the nature of plasticizer influences both the dielectric constant of the membrane and the mobility of ionophore and its interaction with La^{3+}.[30]

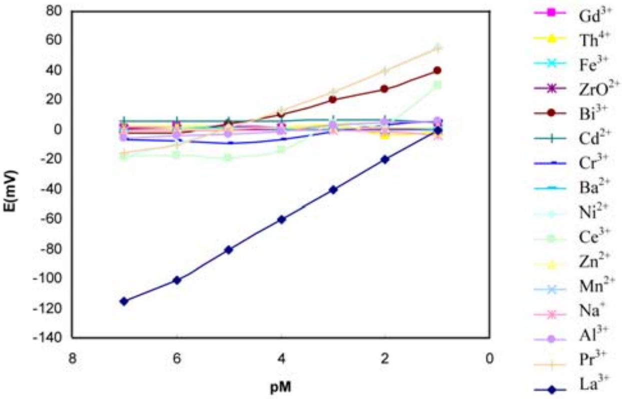

Figure 2. Potential response of various ion-selective membranes based on ETMPTC.

3. 2. Influence of Internal Reference Solution

The working of membrane electrode in relation to variation of reference solutions was investigated. It was found that, the variation of the concentration of the internal solution from 10^{-1} to 10^{-4} mol l^{-1} of La^{3+} solution did not cause any significant difference in potential response except for an expected change in the intercept of the resulting plots. Therefore a solution of 10^{-3} mol l^{-1} La^{3+} would be used as a suitable internal solution, it had a good slope 19.9 ± 0.3 mVdecade^{-1}.

3. 3. Effect of pH

The effect of pH on the response of the electrode was studied over the pH range from 1 to 13 at different concentrations (10^{-2} to 10^{-3} mol l^{-1}) of La (III) solution. The pH of solutions was adjusted with either HCl or NaOH solutions. Potential remains constant at pH range from 3 to 10 (Fig. 3). Below pH 3, the change in the potential is due to co fluxing of hydrogen ions and above

Table 1. Composition and optimization of membrane ingredients.

No.	Ionophore (mg)	PVC (mg)	Plasticizer (mg)	Additive (mg)	Slope (mV/decade)	r
1	5	30	DBS(60)	$KT_pClPB(5)$	38.1	0.9903
2	5	30	AP(60)	$KT_pClPB(5)$	35.1	0.9608
3	3	30	AP(62)	$KT_pClPB(5)$	32.8	0.9646
4	3	30	DBS(62)	$KT_pClPB(5)$	29.5	0.9892
5	3	30	AP(62)	OA(5)	22.0	0.9732
6	5	30	AP(60)	OA(5)	19.9	0.9980
7	5	30	AP(65)	–	11.3	0.9978
8	–	30	AP(65)	OA(5)	5.6	0.8916

pH 10, the variation of potential may be due to formation of some hydroxyl complex of the La (III) ions in solution.

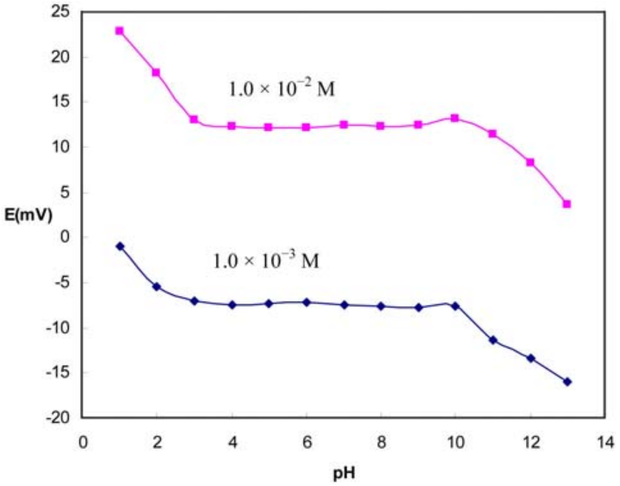

Figure 3. Effect of pH at 1.0×10^{-2} and 1.0×10^{-3} M La^{3+}solutions on the potential response of membrane no. 6.

3. 4. Response Time, Lifetime and Reversibility

The response time of the electrodes, tested by measuring the time required to achieve a steady potential (within ± 1 mV), was less than 11 s and was sustained for about 10 min over the linear range of the concentration. The detection system was very stable, and after a period of 3 months, calibration sensitivity decreased about 1.1 mV without any considerable change in its linear range. The reproducibility of the slope of calibration graphs was within ± 0.3 mV per decade over a period of 3 months (*n* = 6).

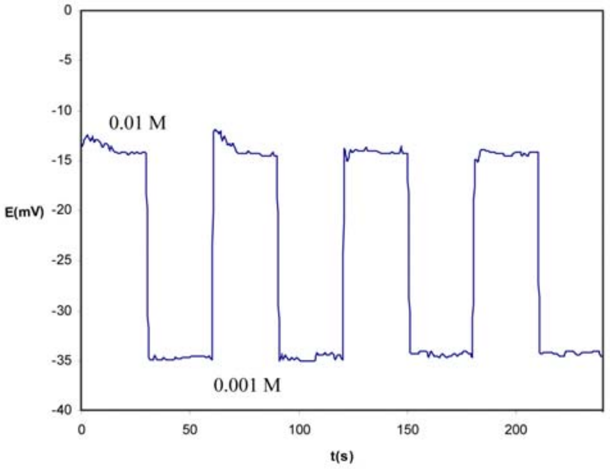

Figure 4. Dynamic response characteristics of the La^{3+}-electrode for several high-to-low sample cycles.

Reversibility is an important factor for an ion selective electrode. Fig. 4 shows that the potentiometric response of the electrode is reversible, although the times needed to reach equilibrium values were longer than that of low-to-high sample concentrations.[31] The detection limit, taken at the point of intersection of the extrapolated linear segment of the calibration curve, was 1.7×10^{-8} M.

3. 5. Selectivity

The influence of interfering ions on the response behavior of ion-selective membrane electrode is usually described in terms of selectivity coefficient ($K_{La,j}$). The potentiometric selectivity coefficients $K_{La,j}$ of lanthanum electrode were evaluated by matched potential method.[32]

The resulting values of the selectivity coefficients are summarized in Table 2. It is evident from the selectivity coefficients data, that the sensor exhibits a high performance for La (III) ion compared with alkali, alkaline earth, transition and heavy metal ions. Comparison of the main analytical features of some the previously described La (III) ion selective electrodes [2,11–18] with the proposed La (III) electrode revealed that; the present electrode exhibited a better selectivity.

Table 2. Selectivity coefficients ($K_{La,j}$) of various ions with La(III)-selective electrode, determined by MPM.

$K_{La,j}$	Interfering ion	$K_{La,j}$	Interfering ion
Na^+	4.0×10^{-6}	Fe^{3+}	2.6×10^{-4}
Al^{3+}	2.3×10^{-4}	Yb^{3+}	3.9×10^{-5}
Cr^{3+}	2.8×10^{-2}	Th^{4+}	5.3×10^{-5}
Tb^{3+}	8.5×10^{-3}	ZrO^{2+a}	8.9×10^{-4}
Nd^{3+}	7.0×10^{-4}	Gd^{3+}	1.6×10^{-5}
Zn^{2+}	1.2×10^{-6}	Pr^{3+}	2.3×10^{-2}
Cd^{2+}	3.5×10^{-5}	Sm^{3+}	3.6×10^{-3}
Mn^{2+}	2.5×10^{-6}	Pb^{2+}	1.4×10^{-4}
Cu^{2+}	4.1×10^{-6}	Hg^+	3.0×10^{-4}
Bi^{3+}	6.2×10^{-3}	Ba^{2+}	1.2×10^{-6}
Sn^{2+}	1.0×10^{-5}	Ni^{2+}	6.7×10^{-6}

[a] Various hydroxide species exist simultaneously

3. 6. Effect of Non-aqueous Media

Because of important role of organic solvents on the proposed membrane response, the functioning of the electrode was investigated in partially non-aqueous media using acetone–water, methanol–water and ethanol–water mixtures and the results obtained are presented in Table 3. It is observed that in the presence of methanol and acetone, the slope decreases remarkably. The slope is acceptable in the presence of ethanol until about 20% (v/v) in the water and for the higher percentage of ethanol, the slope decreases. Therefore, the electrode is not suitable for using in acetone–water and methanol-water mixtures. However, in ethanol–water mixture (up to 20%), there is only a small decrease in slope and working concentration

Table 3. Performance of the membrane sensors in partially non-aqueous media.

Non aqueous content % (v/v)	Slope (mV/decade)	DLR (M)
Methanol		
5	11.17	1.0×10^{-1} to 1.0×10^{-4}
10	11.30	1.0×10^{-1} to 1.0×10^{-4}
15	10.95	1.0×10^{-1} to 1.0×10^{-4}
20	10.21	1.0×10^{-1} to 5.0×10^{-4}
Ethanol		
5	19.94	1.0×10^{-1} to 5.0×10^{-8}
10	19.36	1.0×10^{-1} to 1.0×10^{-8}
15	19.02	1.0×10^{-1} to 1.0×10^{-7}
20	19.18	1.0×10^{-1} to 5.0×10^{-7}
25	15.34	
Acetone		
5	10.60	1.0×10^{-1} to 1.0×10^{-5}
10	11.70	1.0×10^{-1} to 1.0×10^{-5}
15	10.20	1.0×10^{-1} to 1.0×10^{-5}
20	11.75	1.0×10^{-1} to 5.0×10^{-4}

range and hence the electrode can be satisfactorily used in this media with above-mentioned percentages.

3. 7. Effect of Temperature

Trend of changes of electrode performance with temperature, at test solution temperatures 10, 20, 30, 40, 50 and 60 °C for the La (III) -electrode was studied. The electrode exhibits good Nernstian behavior in the temperature range (10–50 °C). At higher temperatures, the slope of electrode did not show a good Nernstian behavior. This behavior may be due to the disturbances occurring in phase boundary equilibrium at the gel layer-test solution interface produced by the thermal agitation of the solution. The standard cell potentials (E^0_{cell}), were determined at different temperatures from the respective calibration plots as the intercepts of these plots at *p* La (III) = 0, and were used to determine the isothermal temperature coefficient (dE^0/dt) of the cell with the aid of the following equation:[33,34]

$$E^0_{\mathrm{cell}} = E^0_{\mathrm{cell\ (25\ °C)}} \pm (dE^0/dt)_{\mathrm{cell}}\,(t-25) \qquad (1)$$

Plot of E^0_{cell} *versus* (t – 25) produced a straight line. The slope of this line was taken as the isothermal temperature coefficient of the cell. It amounts to 0.00057 V/ °C. The standard potentials of the reference electrode (Hg/Hg_2Cl_2; KCl (saturated)) were calculated using the following equation:

$$E^0_{\mathrm{Hg/Hg2Cl2}} = 0.241 - 0.00066(t-25) \qquad (2)$$

The values of the standard potentials of La (III) – electrodes were calculated at the different temperatures from the following relation:

$$E^0_{\mathrm{cell}} + E^0_{\mathrm{reference}} = E^0_{\mathrm{electrode}} \qquad (3)$$

Plot of E^0 electrode *versus* (t – 25) gave a straight line. The slope of the line was taken as the isothermal temperature coefficient of the La (III) electrode. It amounts to 0.00013 V/°C. The small values of $(dE^0/dt)_{\mathrm{cell}}$ and $(dE^0/dt)_{\mathrm{electrode}}$ reveal the high thermal stability of the electrode within the investigated temperature range.

3. 8. Analytical Application

It should be noted that the La (III) selective membrane electrode not only can be used for direct determination of the La (III) ions but also it was found useful as an indicator electrode in titration of La^{3+}ions in aqueous solutions. As an example, a 5.0 ml solution of La^{3+} (1.0×10^{-3} M) was titrated against EDTA solution (1.0×10^{-2} M) at pH 10 using ammonia buffer, and the potentials obtained are plotted in Fig. 5. The titration plot is not conventional sigmoid-type because the sensor, though selective towards La^{3+}, is not specific to it and responds to a small extent to other ions. Thus, the sensor is responding mainly to the La^{3+} concentration and to some extent increase in the Na^+ ion concentration (available from EDTA). The combined potential response leads to the plot achieved with a sharp break, which corresponds to a 1:1 stoichiometry of the La^{3+}-EDTA complex. This type of behavior is characteristic for many ISEs, which are not specific to the primary ion and have been used to determine the concentration of primary ions by potentiometric titration.[19,35] Thus, the present sensor might be used as an indicator electrode for determining La^{3+} by potentiometric titration.

The present La (III) – electrode has been successfully used for the determination of La^{3+} in aqueous solution by using the standard addition method,[36,37] and the results are summarized in Table 4. The recovery and relative stan-

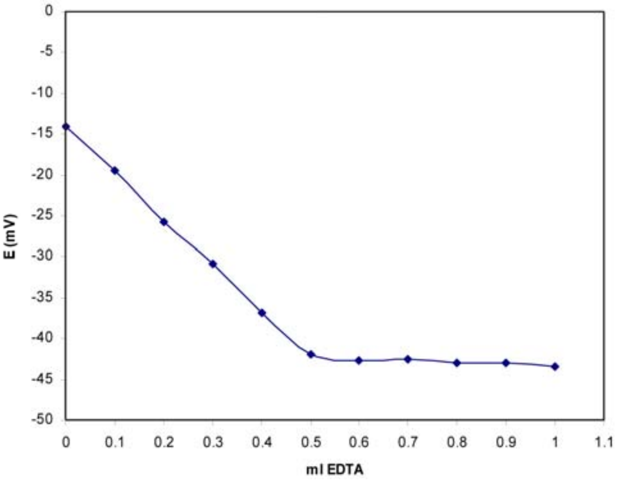

Figure 5. Potentiometric titration plot of 1.0×10^{-3} M La^{3+} solution (5.0 ml) with EDTA (1.0×10^{-2} M).

Table 4. Potentiometric determination of La^{3+} in aqueous solutions in presence of interfering ion(s)[a] by the standard addition method, at 25 °C

Sample	La^{3+} concentration (M)	Recovery (% of nominal value)	R.S.D. (%)
La^{3+}, Na^+	5.0×10^{-3}	98.1	1.0
La^{3+}, Pb^{2+}	5.0×10^{-3}	97.0	0.9
La^{3+}, Pr^{3+}	5.0×10^{-3}	96.4	1.1
La^{3+}, Na^+, Pb^{2+}	5.0×10^{-3}	96.2	1.4
La^{3+}, Na^+, Pr^{3+}	5.0×10^{-3}	95.8	0.8
La^{3+}, Pb^{2+}, Pr^{3+}	5.0×10^{-3}	95.3	1.3
La^{3+}, Na^+, Pb^{2+}, Pr^{3+}	5.0×10^{-3}	95.1	1.5

[a] the concentration of interfering ion(s) in each sample: 1.0×10^{-3} M.

Table 5. Comparison of the potentiometric parameters of the proposed La (III)-selective electrode with other La (III)-selective electrodes

Ionophore	Slope (mVdecade^{-1})	Linear range (M)	Limit of detection (M)	Reference
8-amino-*N*-(2-hydroxybenzylidene) naphthyl amine	20.3 ± 0.3	1.0×10^{-7} –1.0×10^{-1}	8.0×10^{-8}	[2]
Rubeanic acid	20.0 ± 0.2	3.2×10^{-8} –1.0×10^{-2}	2.5×10^{-8}	[12]
dicyclohexano-18-crown-6	19.0	1.0×10^{-6} –1.0×10^{-1}	5.0×10^{-7}	[13]
N-[hexahydrocyclopentapyrol-2((1H)yl) amino]carbonyl]-4-methyl benzene sulfonamide (gliclazide)	20.1	1.0×10^{-6} –1.0×10^{-1}	8.0×10^{-7}	[14]
2,2_-dithiodipyridine	20.0 ± 0.1	7.1×10^{-6} –2.2×10^{-2}	3.1×10^{-6}	[15]
N-2,4-dimethylphenyl-*N*_-ethylformamidine (amitraz)	19.8 ± 0.2	1.0×10^{-7} –1.0×10^{-1}	8.0×10^{-8}	[16]
monoaza-12-crown-4	20.5 ± 1.0	3.16×10^{-5} –1.0×10^{-1}	a	[17]
4-methyl-2-hydrazinobenzothiazole	19.8	1.0×10^{-7} –1.0×10^{-1}	2.5×10^{-8}	[11]
bis(thiophenal)phenylen-1,3-diamine	19.6	1.0×10^{-7} –1.0×10^{-1}	2.0×10^{-8}	[18]
ethyl 1,2,3,4-tetrahydro-6-methyl-4-phenyl-2-thioxopyrimidine-5-carboxylate	19.9 ± 0.3	9.3×10^{-8} –1.0×10^{-1}	1.7×10^{-8}	This work

[a] Not reported.

dard deviation values given in Table 4 were calculated from eight determinations. Collective results, given in Table 4, indicate the high accuracy and precision of the present work.

Table 5 lists the slope, linear range, detection limit and interferents for some La (III) –selective electrodes[2,11–18] in comparison with the proposed La (III) –selective electrode. As can be seen from the table, the figure of merits obtained for the proposed electrode are superior to those reported for some other La(III) –selective electrode.

4. Conclusion

On the results discussed in this paper, ethyl 1, 2, 3, 4-tetrahydro-6-methyl-4-phenyl-2-thioxopyrimidine-5-carboxylate can be considered as a suitable neutral ionophore for construction of a PVC-based membrane selective electrode for the direct determination of La (III) ion in solution. The results show that oleic acid is a good lipophilic additive for electrode construction. The proposed electrode responds to La^{3+} in a Nernstian fashion and presents high selectivity and sensitivity to La^{3+}ion, relatively wide dynamic range, low detection limit, long lifetime and fast response time. The proposed electrode reveals excellent selectivity for La^{3+} over a wide variety of alkali, alkaline earth, some transitions, and heavy metal ions. The electrode performs successfully in partially non aqueous medium. The proposed La^{3+} ion-selective electrode was found to work well under laboratory conditions and it was successfully applied to the determination of La^{3+} ions in solution.

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Povzetek

Izdelana je bila La (III) ionoselektivna elektroda na osnovi PVC membrane in etil 1,2,3,4-tetrahidro-6-metil-4-fenil-2-tiooksipirimidin-5-karboksilatom (ETMPTC) kot nevtralnim ionoforom. Elektroda, ki ima ustrezne karakteristike (delovno območje od $9{,}3 \times 10^{-8}$ do $1{,}0 \times 10^{-1}$ M pri pH od 3,0–10,0, meja zaznave $1{,}7 \times 10^{-8}$ M, odzivni čas manjši od 11 s) je obstojna več kot 3 mesece. Kaže tudi zadovoljivo selektivnost glede na druge katione. Lahko jo uporabljamo tudi v etanolnih raztopinah (do 20% (v/v) etanola). Elektroda je bila uporabljana kot indikatorska elektroda pri potenciopmetričnih titracijah lantana z EDTA ter pri določevanju La^{3+} v prisotnosti motečih ionov.