Sub-Micro Molar Monitoring of La^{3+} by a Novel Lanthanum PVC-Based Membrane Sensor Based on 3-Hydroxy-*N'*-(pyridin-2-ylmethylene)-2-naphthohydrazide

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A La (III) ion-selective membrane sensor has been fabricated from poly vinyl chloride (PVC) matrix membrane, containing 3-hydroxy-*N'*-(pyridin-2-ylmethylene)-2-naphthohydrazide (HPMN) as a neutral carrier, potassium tetrakis (*p*-chlorophenyl) borate (KTpClPB) as an anionic excluder and ortho-nitrophenyloctyl ether (NPOE) as a plasticizing solvent mediator. The effects of membrane composition and pH as well as the influence of the anionic additive on the response properties were investigated. The sensor with 30% PVC, 62% solvent mediator, 6% ionophore and 2% anionic additive, shows the best potentiometric response characteristics. It displays a Nernstian behavior (19.2 mV per decade) across the range of 1.0×10^{-2}-1.0×10^{-7} M. The detection limit of the electrode is 7.0×10^{-8} M (~10 ng/mL) and the response time is 15 s from 1.0×10^{-2} up to 1.0×10^{-4} M and 30 s in the range of 1.0×10^{-5}-1.0×10^{-7} M. The sensor can be used in the pH values of 3.0-9.0 for about seven weeks. The membrane sensor was used as an indicator electrode in the potentiometric titration of lanthanum ions with EDTA. It was successfully applied to the lanthanum determination in some mouth wash preparations.

Key Words : Lanthanum ion-selective electrode, PVC membrane, 3-Hydroxy-*N'*-(pyridin-2-ylmethylene)-2-naphthohydrazide

Introduction

Lanthanum ions accelerate the hydrolysis of phosphate ester binding by 13 orders of magnitude. This also suggests that the phosphate diester in DNA may 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. Lanthanum chloride manifests as antitumor. Genotoxicity of lanthanum (III) in human peripheral blood lymphocytes has also been reported. Lanthanum chloride caused changes in lipid peroxidation, the redox system and ATPase activities in plasma membranes of rice seeding roots.[1-3]

The available methods for the low-level determination of rare-earth ions in solution include spectrophotometry,[4] ICP-MS and ICP-AES.[5,6] Isotope dilution mass spectrometry,[7] neutron activation analysis[8] and X-ray fluorescence spectrometry[9] are also used.

Potentiometric sensors can offer an inexpensive and convenient analysis method of rare-earth ions in solution, provided that acceptable sensitivity and selectivity are achieved.

Despite the successful progress in the design of highly selective ionophores for various metal ions, there are a number of reports on the development of selective ionophores for lanthanum and other lanthanide ions with relatively good selectivity and sensitivity. Considering the tested ionophores in previous works with different selectivity and sensitivity, there were one, two and in some cases all types of hetero-atoms (nitrogen, oxygen or sulfur). Numerous ionophores have been used in the construction of lanthanum sensors such as (2-mercaptoanil) diacetyl,[10] aza-crown,[11] dicyclohexano-18-crown-6,[12] 1,3,5-trithiacyclohexane,[13] bis(thiophenal)phenylen-1,3-diamine,[14] 1-phenyl-3-methyl-4-octadecanoyl-5-pyrazolone,[15] 5,14-N,N'-hydroxyphenyl-4,15-dioxo-1,5,14,18-tetraaza hexacosane,[16] gliclazide,[17] 1-phenyl-3-methyl-4-acyl-5-pyrazolones.[18] Because of the charge density, the lanthanum ion size and also the concept of soft-hard acid-base, it was decided to design an ionophore that contained suitable intermediate or hard donor atoms. This ionophore had to demonstrate a proper size semi-cavity and it should be able to form wrap-around complexes with lanthanum ions. These requirements, as it is obvious, took place under the optimum free energy regime. With regard to the above mentioned criteria, a conductance complexation test was performed primarily. The results revealed the HPMN tendency to selectively complex with La^{3+}. This can be justified by the intermediate nature of the lanthanum ion, caused by its free d-orbital, which makes it suitable to complex with HPMN that contains intermediate and hard donor atoms.[10-26]

It is important to state that some of the previous researches present one of the following disadvantages; a) high detection limits, b) narrow dynamic range, c) low selectivity. Therefore, the objective of this study is the introduction of a greatly selective and sensitive La^{3+} ion-selective membrane electrode, incorporated with HPMN in a PVC based membrane sensor.

Experimental Section

Reagents. The Merck and the Aldrich Chemical Co. were the providers for the 3-hydroxy-naphthalene-2-carboxylic acid hydrazide, pyridine-2-carboxaldehyde, acetic acid, ethanol, chloride and the nitrate salts of all cations. Furthermore, the Aldrich Co. supplied the following reagents; reagent-grades of dibutyl phthalate (DBP), nitrobenzene (NB), *o*-nitrophenyloctyl ether (NPOE), acetophenone (AP), relatively high molecular weight poly vinyl chloride (PVC), potassium tetrakis (*p*-chlorophenyl) borate (KTpClPB) and tetrahydrofurane (THF). These were of the highest available purity and were P_2O_5-vacuum dried.

All reagents were used without any modification. During the experiments, double distilled deionized water was used.

Ionophore Synthesis. For the preparation of the 3-hydroxy-*N'*-(pyridin-2-ylmethylene)-2-naphthohydrazide (HPMN, Figure 1), a mixture of 3-hydroxy-naphthalene-2-carboxylic acid hydrazide (0.01 mol, 2.02 g), pyridine-2-carboxaldehyde (0.01 mol, 1.07 g) and catalytic amount of acetic acid was refluxed in absolute ethanol (50 mL) for 1 h. Then, the reaction mixture was evaporated to 20 mL and cooled to room temperature. The colorless crystals of the product were filtered, washed with ethanol and dried under reduced pressure, mp 226-228 °C, 2.6 g, and yield 90%.

IR (KBr) (υ_{max}/cm^{-1}): 3256 and 3050 (OH and NH), 1684 (C=O), 1593, 1531, 1464, 1404, 1331, 1196, 1144, 1009, 918, 741, 609.

MS, *m/z* (%): 291 (M^+, 5). Anal. Calcd for $C_{17}H_{13}N_3O_2$ (291.31): C, 70.09; H, 4.50; N, 14.42. Found: C, 70.2; H, 4.6; N, 14.5%.

^{1}H NMR (90 MHz, acetone-d_6 solution): δ 7.20-7.51 (4H, m, 4 CH), 7.62-8.15 (4H, m, 4 CH), 8.23-8.87 (3H, m, 3 CH), 11.24 and 12.12 (2H, 2 br., OH and NH).

^{13}C NMR: δ 112.45, 126.32, 126.47, 126.87, and 127.51 (5 CH), 128.63 (C), 129.14, 129.29, and 130.02, (3 CH), 133.68 and 134.25 (2 C), 136.54 and 150.09 (2 CH), 151.36 and 152.47 (2 C), 153.09 (HC=N), 170.21 (C=O).

Electrode Preparation. The PVC membrane was made by blending completely 30 mg of powdered PVC, 62 mg of NPOE and 2 mg of the KTpClPB additive in 2 ml of THF. Afterwards, 6 mg from the HPMN ionophore were added to this mixture. The solution was mixed well and transferred into a 2 cm glass dish in diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A pyrex tube (3-5 mm o.d.) was dipped into the mixture for about 10 s, so that a transparent membrane of about 0.3 mm in thickness was formed. Finally, the tube was removed from the mixture, kept at room temperature for about 10 h. and filled with an internal filling solution (1.0×10^{-3} M $LaCl_3$). The electrode was conditioned for 24 h by soaking in a 1.0×10^{-3} M $LaCl_3$ solution. A Silver/Silver chloride coated wire was used as an internal reference electrode.[27-36]

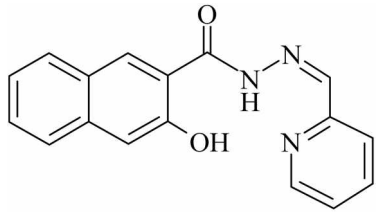

Figure 1. The HPMN ionophore structure.

EMF Measurements. All emf measurements were carried out with the following assembly;

Ag-AgCl/internal solution (1.0×10^{-3} M $LaCl_3$)/PVC Membrane/test solution/Ag-AgCl, KCl (satd.)

The potential was monitored by a Corning ion analyzer with a 250 pH/mV meter at 25.0 ± 0.1 °C.

Results and Discussion

At first, the interactions between the ion-carrier (HPMN) and the different cations were tested. To the best of our knowledge, there is no report on the stability of the HPMN complexes with different cations. Thus, the HPMN complexation with several common 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.[37,38] The final molar conductance *vs.* the [HPMN]/[M^{n+}] mole ratio plots (Figure 2) illustrated the 1 : 1 complex formation between the HPMN and all the investigated cations. The complex formation constants, K_f, were evaluated by computer fitting of the molar conductance/mole ratio data with appropriate equations.[37] The respective results are summarized in Table 1. As it is obvious, the stability constant of the La^{3+}-HPMN complex is higher than that of the other tested cations-HPMN complexes. Consequently, HPMN may be used as a suitable selective ionophore in the construction of a La^{3+} ion-selective membrane electrode.

In the next experiments, the employed neutral carrier was HPMN in the PVC-membrane electrodes preparation for many metal ions, including alkali, alkaline earth, transition and heavy metal ions. Their potential responses are depicted in Figure 3. Clearly, while the linear part slopes of the sensor emf responses for all cations are much lower than those

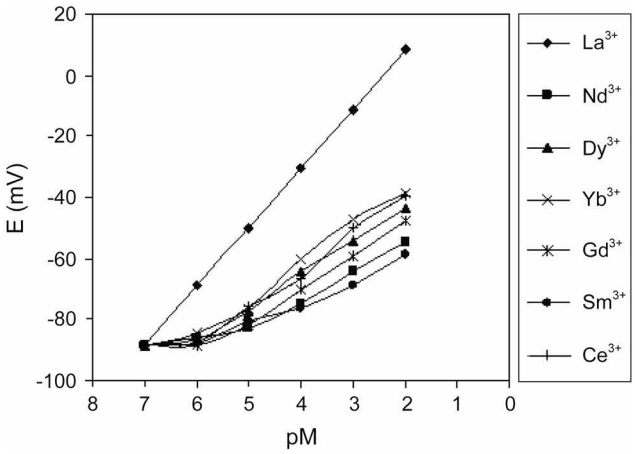

Figure 2. Molar conductance (Ω^{-1}cm^2 mol^{-1}) *vs.* [HPMN]/[Mn^-] curves in acetonitrile solution at 25 °C.

Table 1. Formation constant of La^{3+}-HPMN complexes

Cation	Log K_f
La^{3+}	5.32 ± 0.15
Nd^{3+}	3.12 ± 0.12
Gd^{3+}	2.88 ± 0.10
Dy^{3+}	2.75 ± 0.11
Ce^{3+}	2.66 ± 0.15
Sm^{3+}	3.34 ± 0.11
Yb^{3+}	2.69 ± 0.08
Zn^{2+}	3.02 ± 0.10
Sr^{2+}	2.89 ± 0.12
Cu^{2+}	3.32 ± 0.13
Ca^{2+}	2.72 ± 0.12
Na^{+}	2.56 ± 0.19
Mg^{2+}	2.71 ± 0.09
Cs^{+}	2.57 ± 0.10
Fe^{3+}	2.95 ± 0.17

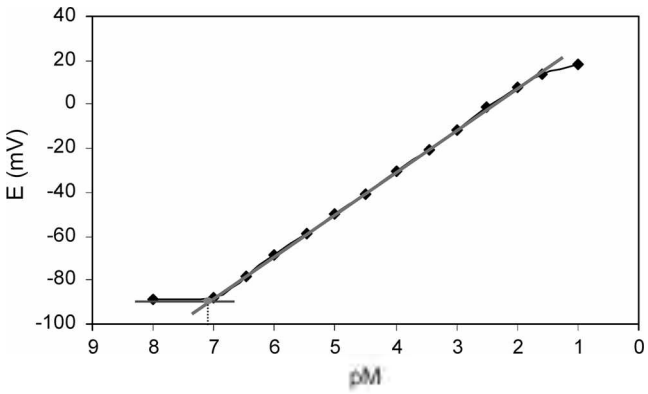

Figure 3. The potential response of various metal ion-selective electrodes based on HPMN.

expected by the Nernst equation, the resulting La^{3+} potential response demonstrates a Nernstian behavior.

It is well known that some important features of the PVC-based membranes (such as the nature and the amount of the ionophore, the plasticizer properties, the plasticizer/PVC ratio and, especially, the nature of the used additives) significantly influence the sensitivity and selectivity of the ion-selective electrodes.[38,39] As a result, different types of HPMN membranes were optimized. The associated data are given in Table 2. Solvent polymeric membrane ion-selective electrodes are usually based on a matrix of the solvent mediator/PVC ratio about 2. Polymeric films with such a plasticizer/PVC ratio will result in optimum physical properties and high enough mobility of their constituents. In this study, a plasticizer/PVC ratio of about 2.0 was found to be the most suitable ratio. It is reported that the selectivity and the working concentration range of the membrane sensor are affected by the nature and the amount of the used plasticizer. This is due to the plasticizer influence on the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of ionophore.[40] According to Table 2, NPOE leads to the best sensitivity among five

Table 2. The optimization of the membrane ingredients

Membrane Number	Composition (%)					
	PVC	Plasticizer	Ionophore	NaTPB	Slope	LDR (pM)
1	30	NPOE 68	–	2	3.4	5-2
2	30	NPOE 68	2	–	13.3	5-2
3	30	NPOE 66	4	–	14.6	5-2
4	30	NPOE 64	6	–	16.1	6-2
5	30	NPOE 62	6	2	19.2	7-2
6	30	DBP 62	6	2	11.3	6-2
7	30	BA 62	6	2	17.5	5-2
8	30	AP 62	6	2	18.2	5-1
9	30	NB 62	6	2	18.9	5-1

different plasticizers. This phenomenon can be attributed to the NPOE ability to extract La^{3+} ions with high hydration energy from aqueous solution to the organic membrane phase.

Moreover, the chosen optimum ionophore amount in the PVC membrane was 6 % of the HPMN ionophore (No. 5).

It has been demonstrated that the presence of lipophilic negatively charged additives improves the potentiometric behavior of certain selective electrodes not only by reducing the ohmic resistance and improving the response behavior and selectivity but also, in cases where the extraction ionophore capability is poor, by enhancing the membrane electrode sensitivity.[41-43] The data provided in Table 2 exhibit that in the absence of a proper additive, the sensitivity of the HPMN-PVC membrane is low (No. 4 with a slope of 16.1 mV per decade). However, the presence of 2% KTpClPB as a suitable lipophilic additive will improve the La^{3+} sensor sensitivity considerably (No. 5 with a slope of 19.2 mV $decade^{-1}$).

The optimum equilibration time for the membrane electrode in the presence of 1.0×10^{-3} M $LaCl_3$ was 24 h, after which the electrode would display stable potentials in contact with the lanthanum solutions. Moreover, it was found that the electrode presented a linear response to the

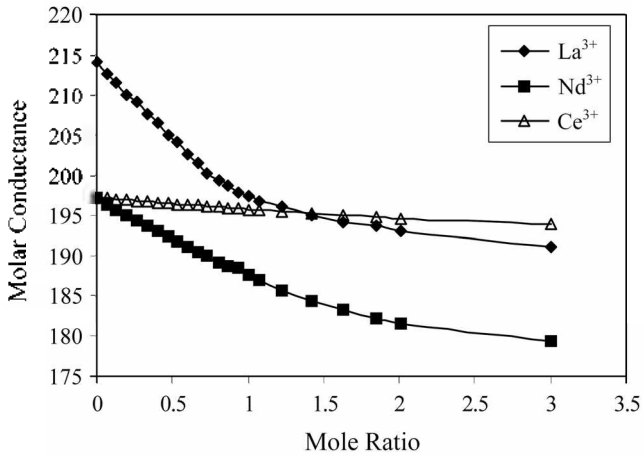

Figure 4. The calibration curve of the La^{3+} membrane sensor based on HPMN.

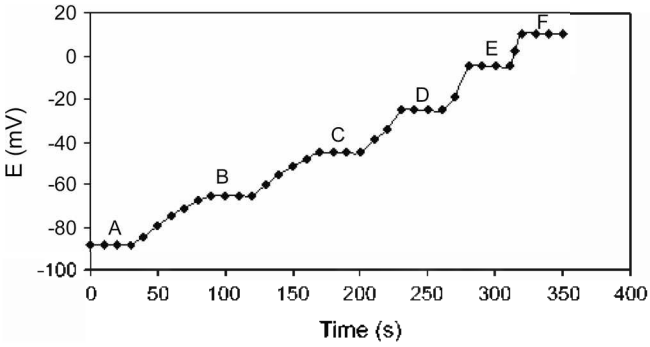

Figure 5. The La^{3+} membrane sensor response time: (A) 1.0×10^{-7} M; (B) 1.0×10^{-6} M; (C) 1.0×10^{-5} M; (D) 1.0×10^{-4} M; (E) 1.0×10^{-3} M; (F) 1.0×10^{-2} M.

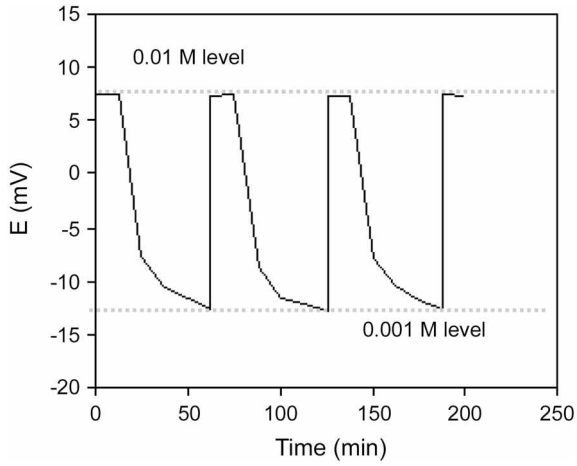

Figure 6. Dynamic response characteristics of the La^{3+} electrode for several high-to-low sample cycles.

La^{3+} ion activity from 1.0×10^{-2} to 1.0×10^{-7} M (Figure 4), the calibration graph slope was 19.2 ± 0.2 mV per decade and the detection limit (as determined from the intersection of the two extrapolated segments of the calibration graph) was 7.0×10^{-8} M.

For analytical applications, dynamic response time is an important factor for any ion-selective electrode. In this study, the practical response time was recorded by changing the La^{3+} concentration in solution across the range of 1.0×10^{-2} - 1.0×10^{-7} M. These resulting data are shown in Figure 5. The electrode response time was 15 s for concentration values of 1.0×10^{-2} - 1.0×10^{-4} M and 30 s for the values from 1.0×10^{-5} up to 1.0×10^{-7} M. Also in Figure 6, the dynamic response characteristics of the La^{3+} electrode for several high-to-low sample cycles are listed.

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 2.0-11.0. The corresponding results are summarized in Figure 7, where it is possible to notice that the potential remains constant for the pH values from 3.0 to 9.0, beyond which the potential changes considerably. The observed drift at higher pH values could be due to the formation of some soluble and insoluble hydroxy complexes of La^{3+} ions in solution such as $La(OH)^{2+}$, $La(OH)_2^+$ and

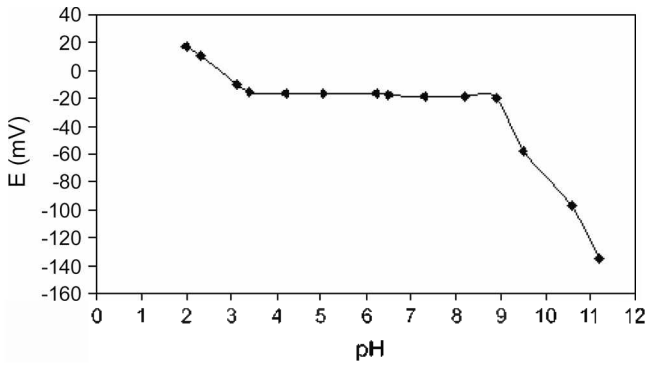

Figure 7. The pH effect of the test solution on the potential response of the HPMN-La^{3+} ion-selective electrode.

$La(OH)_3$. The observed potential increase at lower pH values than 3.0 indicates that the protonated ionophore possesses a poor response to the La(III) ions and strong response to the H_3O^+ ions in solution.

The potentiometric selectivity coefficients, describing the membrane preference to an interfering ion, were determined by the matched potential method[44] and separated solution methods.[45] According to the MPM method, the specified activity (concentration) of the primary ion (A) is added to a reference solution and, afterwards, the potential is measured. In a separate experiment, interfering ions (B) are successively added to an identical reference solution until the measured potential matches that obtained before the primary ions addition. The matched potential method selectivity coefficient, K_{MPM} is then given by the resulting primary ion to the interfering ion activity (concentration) ratio. The selectivity coefficient, $K_{A,B}^{Pot}$, is determined as:

$$K_{A,B}^{Pot} = a_A/a_B$$

where $\Delta A = a_A' - a_A$, a_A is the initial primary ion activity and a_A' is the activity of A in the presence of the interfering ion, a_B. The employed experimental conditions and the resulting

Table 3. The selectivity coefficients of various interfering cations for the La^{3+} membrane sensor

Cation	$K_{A,B}^{MPM}$
Nd^{3+}	5.78×10^{-4}
Gd^{3+}	1.31×10^{-3}
Dy^{3+}	2.13×10^{-3}
Ce^{3+}	3.41×10^{-3}
Sm^{3+}	3.42×10^{-4}
Yb^{3+}	3.80×10^{-3}
Zn^{2+}	8.96×10^{-4}
Sr^{2+}	6.45×10^{-4}
Cu^{2+}	3.50×10^{-3}
Ca^{2+}	6.77×10^{-4}
Na^+	1.58×10^{-3}
Mg^{2+}	8.33×10^{-4}
Cs^+	4.75×10^{-3}
Fe^{3+}	2.37×10^{-3}

Table 4. Selectivity coefficient comparision of the best La^{3+} sensors with the developed sensor

Ion	Log $K_{A,B}^{MPM}$							
	Ref. 10	Ref. 11	Ref. 12	Ref. 13	Ref. 14	Ref. 17	This work (SSM)	This work (MPM)
Nd^{3+}	–	–	−1.8	–	–	–	−4.24	−4.76
Gd^{3+}	−2.2	–	–	–	−3.3	–	−3.28	−3.11
Dy^{3+}	–	–	−1.8	–	−2.6	–	−3.12	−3.32
Ce^{3+}	−1.3	−2.5	−1.9	−1.4	−1.7	−2.1	−3.87	−3.53
Sm^{3+}	−2.4	–	−1.8	–	−1.2	−1.8	−4.66	−4.53
Yb^{3+}	–	–	–	–	–	–	−3.47	−3.57
Zn^{2+}	−3.4	−1.7	–	−2.4	–	−1.7	−4.35	−4.95
Sr^{2+}	−3.7	−1.8	–	−3.9	–	–	−4.38	−4.80
Cu^{2+}	−3.4	−1.7	−2.5	−2.1	−3.4	−1.7	−3.50	−3.54
Ca^{2+}	–	−1.7	−2.7	−3.8	−3.8	–	−4.65	−4.83
Na^{+}	–	−1.4	–	−3.5	–	–	−3.37	−3.19
Mg^{2+}	–	−1.9	−2.8	−3.8	–	–	−4.74	−4.92
Cs^{+}	–	–	–	–	–	–	−3.87	−3.67
Fe^{3+}	–	–	–	–	–	–	−3.22	−3.37

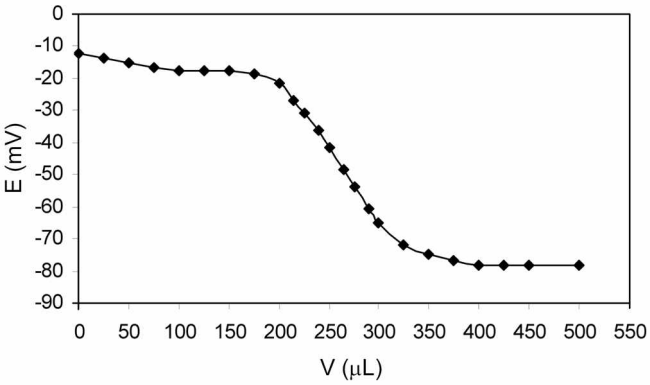

Figure 8. The potentiometric titration curve of 25.0 mL La^{3+} (1.0×10^{-3} M) with 10^{-2} M EDTA using the suggested membrane sensor as an indicator electrode.

values for both methods are provided in Table 3. Evidently, the selectivity coefficients for all diverse ions are in the order of 1.31×10^{-3} or smaller, indicating they would not significantly disturb the function of the La^{3+} ion-selective electrode.

Table 4 compares the selectivity coefficients of the recommended La(III) sensor with those of the best previously reported lanthanum membrane electrodes.

The developed La^{3+}ion-selective electrode was found to work well under laboratory conditions and, in addition, it was successfully applied as an indicator electrode in the La^{3+} (1.0×10^{-4} M) titration with 25 mL of EDTA solution (1.0×10^{-2} M). The resulting titration curve is depicted in Figure 8, where it is clear that the titration end point is sharp and the La^{3+} ions amount in solution can be accurately determined with the electrode, being equal to $(1.0 \pm 0.1) \times 10^{-4}$ M.

Furthermore, the sensor was successfully applied to the F^{-} ion determination in three different pharmaceutical samples. The results in Table 5, deriving from triplicate measurements, demonstrated that there was a satisfactory agreement between the declared fluoride content and the determined values.

Table 5. Results from the Fluoride Determination in Different Mouth Wash Solutions

Sample	Labeled	Found
Sodium fluoride mouth wash solution (Chimia Daru Co., Tehran, Iran)	2.0%	(2.02 ± 0.03)%
Sodium fluoride mouth wash solution (Shahre Daru Co., Tehran, Iran)	0.2%	(0.20 ± 0.02)%
Sodium fluoride tablets (Loghman Pharmaceutical Co., Tehran, Iran)	1.0	(0.99 ± 0.02)%

Table 6. The La^{3+} membrane sensor lifetime

Week	Slope (mV per decade)	Detection Limit
First	19.2 ± 0.8	7.0×10^{-8} M
Second	19.2 ± 0.2	7.0×10^{-8} M
Third	19.0 ± 0.3	7.0×10^{-8} M
Fourth	18.9 ± 0.6	8.0×10^{-8} M
Fifth	18.3 ± 0.5	1.5×10^{-7} M
Sixth	18.1 ± 0.3	3.0×10^{-7} M
Seventh	18.1 ± 0.4	4.0×10^{-7} M
Eighth	17.8 ± 0.2	4.5×10^{-7} M
Ninth	17.4 ± 0.5	4.5×10^{-7} M
Tenth	17.1 ± 0.7	5.0×10^{-7} M

The La(III) membrane sensor lifetime was tested for a period of 70 days. During this period, the electrodes were in daily use over an extended time period (one hour per day). The reported data of Table 6 indicate that after 49 days a slight gradual decrease and increase were observed in the slopes and the detection limit, respectively. These certain changes could be caused by the membrane ingredients leakage from the membrane to the solution. This kind of behavior has already been demonstrated by most of the introduced liquid membrane sensors.

Conclusion

The results obtained from the above-mentioned study reveal that a potentiometric HPMN-PVC-based membrane sensor functions as an excellent La^{3+} selective sensor and it can be used for the determination of this ion in the presence of considerable concentrations of common interfering ions. The benefits of applicable pH range, lower detection limit and potentiometric selectivity coefficients make this sensor a superior device, compared with the other applied methods for the La^{3+} detection.

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