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Construction of a New Lutetium (III) PVC-Membrane Electrochemical Sensor Based on 4'-carboxybenzo-18-crown-6

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A new PVC membrane potentiometric sensor for determination of Lu(III) ions was prepared by using 4'-carboxybenzo-18-crown-6 (4'C18C6) as a suitable sensing material. The sensor exhibits a linear dynamic range between 1.0×10^{-6} and 1.0×10^{-2} mol L^{-1}, with a near Nernstian slope of 19.8±0.4 mV per decade and a detection limit of 6.5×10^{-7} mol L^{-1}. The sensor response is independent of the pH of the solution in the pH range of 2.8–8.7. The sensor possesses the advantages of short conditioning time, fast response time (~5 s), and especially, very good selectivity towards transition and heavy metal, and some mono, di and trivalent cations. The proposed sensor was effectively used as an indicator electrode in the potentiometric titration of Lu^{3+} ions with EDTA and the determination of Lu^{3+} in mixtures of two and three different ions.

Keywords: PVC membrane, Sensor, Ion-selective electrode, Potentiometry

1. INTRODUCTION

During the last decade, there has been a renewed resurgence in developing potentiometric membrane electrodes as devices for rapid, accurate, low cost and non destructive analysis of different samples with small volume samples. The rare-earth industry is growing and the average increase over the past years has been 5-15%. The rare earths are considered only slightly toxic according to the Hodge-Sterner classification system and thus can be handled safely with ordinary care [1]. When rare-earth vapors or dust are inhaled, they are somewhat more toxic but tend to remain in the lungs and are only slowly absorb into the body [2].

Lutetium is a very rare element commonly used as a fluorescent and magnetic material, the uses of which are growing, due to its applicability in the production of catalysts used in oil and gas technologies and glass polish. The element is hence dumped in the environment, mainly from petrolproducing industries [3]. Many techniques have been developed in order to determine the value of Lu(III) in real samples such as: spectrophotometry, inductively couple plasma mass spectrometry (ICP-MS), inductively couple plasma atomic emission spectrometry (ICP-AES), mass spectrometry (MS), Isotope dilution mass spectrometry, X-ray fluorescence spectrometry. But almost all of them are expensive and time consuming. Ion selective electrodes (ISEs) are among the most popular electrochemical devices that usually show fast and selective responses in addition to their low cost and ease of preparation and use. There have been some reports on lutetium sensors based on different ionophores [4, 5].

Recently, several greatly highly selective and sensitive polyvinyl chloride PVC-membrane ion-selective electrodes were reported for various metal ions [6–30]. In this paper, we wish to introduce a new Lu^{3+} ion-selective polyvinyl chloride membrane sensor based on 4'-carboxybenzo-18-crown-6 (4'C18C6) (Fig. 1) as a new neutral ionophore for determination of Lu^{3+} ions.

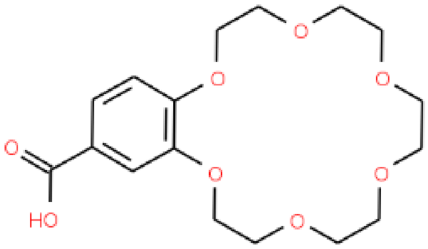

Figure 1. Chemical structure of 4'-carboxybenzo-18-crown-6

2. EXPERIMENTAL

2.1. Reagents

The Merck Chemical and the Aldrich Co. were the suppliers for the nitrate and chloride salts of all cations and the reagent grades of 4'-carboxybenzo-18-crown-6, dibutyl phthalate (DBP), benzyl acetate (BA), acetophenon (AP), oleic acid (OA), nitrobenzene (NB), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) and high relative molecular weight PVC. All reagents were used without any modification. During the experiments, doubly distilled deionized water was used.

2.2. EMF measurements

The cell electromotive force (emf) was measured with the membrane sensor using the following cell assembly:

Ag–AgCl| 1.0×10^{-3} mol L^{-1} $LuCl_3$ | PVC membrane: test solution| $Hg–Hg_2Cl_2$, KCl (satd).

A Corning ion analyser 250 pH/mV meter was used for the potential measurements at 25.0 °C. Activities were calculated according to the Debye–Huckel procedure [31].

2.3. Electrode preparation

The general procedure to prepare the PVC membrane was to mix thoroughly, 30 mg of PVC, 2 mg of 4'C18C6, 5 mg of OA and 63 mg of DBP. Then the mixture was dissolved in 3 mL of dry freshly distilled THF. The resulting clear mixture 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, in order to achieve a transparent membrane formation of about 0.3 mm in thickness [32-46]. In the end, the tube was removed from the solution, kept at room temperature for 24 h and filled with an internal filling solution (1.0×10^{-3} mol L^{-1} $LuCl_3$). The electrode was conditioned for 24 h by soaking in a 1.0×10^{-3} mol L^{-1} $LuCl_3$ solution. As an internal reference electrode, a silver/silver chloride coated wire was used.

3. RESULTS AND DISCISSION

3.1. The respone of the 4'C18C6 sensor to the Lu^{3+} ions

In the initial tests, 4'C18C6 was used as a new neutral ionophore to prepare plasticized polymeric membrane for a variety of alkali, alkaline earth, transition and heavy metal ions and their potential responses were measured, used. Among different cation stested, the sensor was found to demonstrate very sensitive responses to Lu^{3+} which could be regarded as a promising result that could be exploited for the design and construction of a suitable sensor for Lu^{3+}. This is due to the selective behavior of the PVC membrane system against Lu(III) in comparison with other metal ions.

3.2. The effect of membrane composition

Sensitivity and selectivity of any given membrane sensor are significantly related to the composition of the ion selective membrane (the properties of the plasticizer, the nature and amount of the ionophore, the plasticizer/PVC ratio and the nature additives used) [47–52]. To investigate these effects, the nature and amount of the plasticizer and the additive on the potential response of the proposed Lu^{3+} sensor were investigated, and the results are summarized in Table 2. In this study, a plasticizer/PVC ratio of about 2.2 was found to be the most suitable. It is reported that the selectivity and working concentration range of membrane sensors are affected by the nature and amount of the plasticizer used. This is due to the influence of the plasticizer on the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of ligands [52–63]. Among the four different solvent mediators tested, DBP acts superior with respect to BA, AP and NB. Moreover, as it can be seen from Table 2, the optimum amount of ionophore (4'C18C6) is 2% (No. 17).

Lipophilic anions in the composition of cationic-selective membrane sensors not only diminishes the ohmic resistance and enhances the potential behavior and selectivity, but also in poor extraction capacities, increases the sensitivity of the membrane electrodes [63–70]. As can be seen from Table 2, the slope of the sensor in the absence of NaTPB and OA is lower than the expected

Nernstian value (membrane No. 16), while, addition of 0% NaTPB and 5% OA will increase the sensitivity of the electrode response considerably, so that the membrane electrode demonstrates a near Nernstian behavior (membrane No. 17). As can be seen from Table 2, addition of more than 5% of OA (10% and 15%) to the membrane causes a decreasing in slope from 19.8 to 11.0 mVdecade^{-1}. However, the membrane sensor with composition of 30% PVC; 63% DBP; 5% OA, and 2% 4'C18C6 exhibits the best performance.

Table 1. Optimization of the membrane ingredients.

Sensor No.	Composition of the membrane (wt, %)				Slope / mVdecade^{-1}	Dynamic Linear range / molL^{-1}
	PVC	Plasticizer	4'C18C6	Additive		
1	30	NB, 66	2	NaTPB,2;OA,0	13.2 ± 0.4	1.0×10^{-5}-1.0×10^{-2}
2	30	AP, 66	2	NaTPB,2;OA0	13.8 ± 0.6	1.0×10^{-5}-1.0×10^{-2}
3	30	BA, 66	2	NaTPB,2;OA,0	14.1 ± 0.4	1.0×10^{-5}-1.0×10^{-2}
4	30	DBP, 66	2	NaTPB,2;OA,0	18.7 ± 0.2	1.0×10^{-6}-1.0×10^{-2}
5	30	DBP, 60	1	NaTPB,9;OA,0	20.1 ± 0.3	1.0×10^{-4}-1.0×10^{-2}
6	30	DBP, 60	2	NaTPB,8;OA,0	27.2 ± 0.2	1.0×10^{-4}-1.0×10^{-2}
7	30	DBP, 60	3	NaTPB,7;OA,0	15.6 ± 0.3	1.0×10^{-5}-1.0×10^{-2}
8	30	DBP, 60	4	NaTPB,6;OA,0	26.3 ± 0.4	1.0×10^{-5}-1.0×10^{-2}
9	30	DBP, 60	5	NaTPB,5;OA,0	16.2 ± 0.2	1.0×10^{-5}-1.0×10^{-2}
10	30	DBP, 60	6	NaTPB,4;OA,0	27.2 ± 0.5	1.0×10^{-4}-1.0×10^{-2}
11	30	DBP, 60	7	NaTPB,3;OA,0	24.5 ± 0.3	1.0×10^{-4}-1.0×10^{-2}
12	30	DBP, 60	8	NaTPB,2;OA,0	22.9 ± 0.2	1.0×10^{-5}-1.0×10^{-2}
13	30	DBP, 60	9	NaTPB,1;OA,0	22.6 ± 0.4	1.0×10^{-5}-1.0×10^{-2}
14	30	DBP, 65	2	NaTPB,3;OA,0	15.5 ± 0.6	1.0×10^{-6}-1.0×10^{-2}
15	30	DBP, 67	2	NaTPB,1;OA,0	27.6 ± 0.2	1.0×10^{-4}-1.0×10^{-2}
16	30	DBP, 68	2	NaTPB,0;OA,0	18.1 ± 0.4	1.0×10^{-5}-1.0×10^{-2}
17	30	DBP, 63	2	NaTPB,0;OA,5	19.8 ± 0.4	1.0×10^{-6}-1.0×10^{-2}
18	30	DBP, 58	2	NaTPB,0;OA,10	11.2 ± 0.6	1.0×10^{-6}-1.0×10^{-2}
19	30	DBP, 53	2	NaTPB,0;OA,15	11.1 ± 0.5	1.0×10^{-6}-1.0×10^{-2}

3.3. Calibration graph

The plot of EMF *vs.* pLu obtained under optimal membrane ingredients for the sensor (Figure 2), indicate that it has a Nernstian behavior over a very wide concentration ranges of Lu^{3+} ion (1.0×10^{-6}-1.0×10^{-2} mol L^{-1}). The slope and linear range of the resulting calibration graph was 19.8 ± 0.4 mVdecade^{-1} and 1.0×10^{-6}-1.0×10^{-2} mol L^{-1}, respectively. The limit of detection, defined as the concentration of Lu ion obtained when the linear regions of the calibration graph extrapolated to the base line potential, is 6.5×10^{-7} mol L^{-1}.

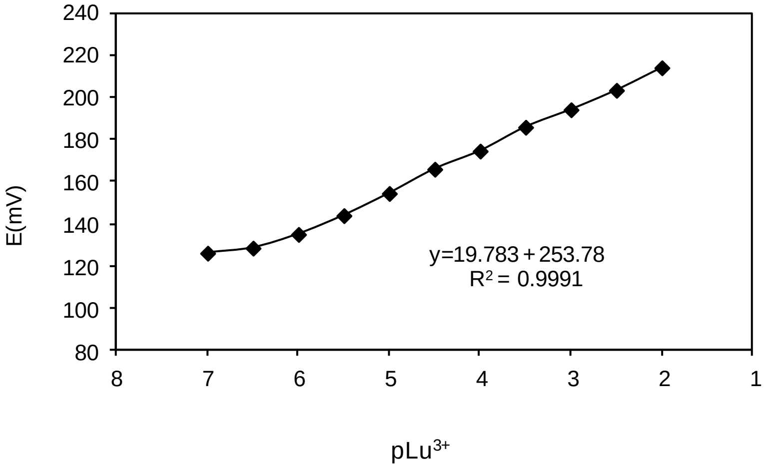

Figure 2. Calibration curve of the 4'C18C6-based lutetium electrode.

3.4. pH effect

The pH dependence of the membrane electrode was evaluated over a pH range of 1.0–11.0 at the test solution (1.0×10^{-3} mol L^{-1}) of lutetium ion concentration and the results are depicted in Figure 3. As can be seen, the potential remains fairly constant in the pH range of 2.8 – 8.7 (the pH of the solutions was adjusted by either HNO_3 or NaOH solutions). Beyond this range, a gradual change in the potential was detected. Above pH 8.7, the Lu^{3+} signal gradually diminishes with further increase in the pH of solution. This is could be due to the formation of insoluble doubly and singly charged $Lu(OH)^{2+}$ and $Lu(OH)_2^+$ species and finally the formation of the totally uncharged and insoluble $Lu(OH)_3$ in the solution. This leads to changes in the potential behavior of the electrode versus pH, which become considerable at pH values over 8.7. At the lower pH values than 2.8, the potentials increase, indicating that the membrane sensor responds to hydrogen ions.

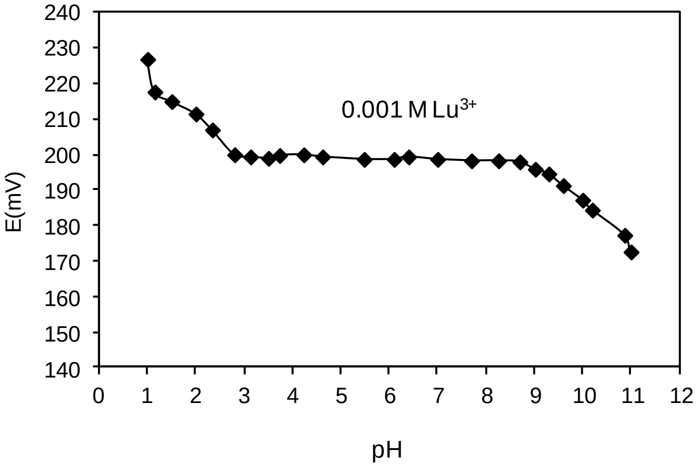

Figure 3. pH effect of the test solution (1.0×10^{-3} $molL^{-1}$ of Lu^{3+}) on the potential response of the Lu^{3+} ion-selective electrode.

3.5. Dynamic response time

Dynamic response time is an important factor for any ion selective electrodes. In this study, the practical response time of the sensor was recorded by changing the solution with different Lu^{3+} concentrations from 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1}. The actual potential versus time trace for the electrode based on 4'C18C6 is shown in Figure 4. As it can be seen, the electrode reaches its equilibrium response in a short time of about 5 s. This is most probably due to the fast exchange kinetics of complexation-decomplexation of Lu^{3+} ion with the ionophore at the test solution membrane interface.

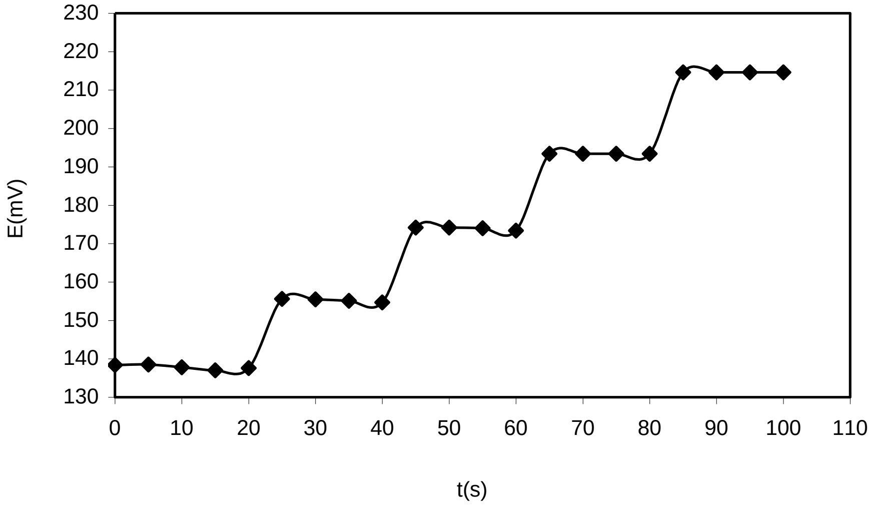

Figure 4. Dynamic response time of the lutetium electrode for step changes in the Lu^{3+} concentration: A) 1.0×10^{-6} $molL^{-1}$, B) 1.0×10^{-5} $molL^{-1}$, C) 1.0×10^{-4} $molL^{-1}$, D) 1.0×10^{-3} $molL^{-1}$, E) 1.0×10^{-2} $molL^{-1}$.

3.6. The selectivity of the Lu^{3+} sensor based on 4'C18C6

The influence of the interfering ions on the response behavior of any ion-selective sensor is usually described in terms of selectivity coefficients, K_{sel}. In this work, the selectivity coefficients were determined with the aid of the matched potential method (MPM) [71-80]. According to this method, primary ion (A) of a specified activity is added to a reference solution, and the potential is measured. In a separate experiment, interfering ions (B) are successively added to an identical reference (containing primary ion) solution until the measured potential matches to that obtained only with the primary ions. The matched potential method selectivity coefficient, K^{MPM}, is then given by the resulting primary ion to interfering ion activity (concentration) ratio, $K^{MPM}=\Delta a_A/a_B$. The result of selectivity coefficient values are given in Table 2. As it is immediately obvious, for all diverse ions used, the selectivity coefficients of the electrode are in the order of 1.0×10^{-3} or smaller, indicating they would not significantly disturb the functioning of the lutetium(III) selective membrane sensor and the proposed Lu^{3+} sensor is highly selective with respect to most of cations. The surprisingly high selectivity of the membrane electrode for lutetium ions over other cations used, most probably arises from the strong tendency of the carrier molecules for lutetium ions.

Table 2. Selectivity coefficients of the developed Lu^{3+} electrode.

Interfering ions (B)	This work
Method	MPM
Er^{3+}	8.3×10^{-4}
Tb^{3+}	5.5×10^{-4}
La^{3+}	5.0×10^{-4}
Nd^{3+}	5.3×10^{-4}
Pr^{3+}	7.2×10^{-4}
Ho^{3+}	6.0×10^{-4}
Gd^{3+}	8.5×10^{-4}
Tm^{3+}	5.8×10^{-4}
Eu^{3+}	1.0×10^{-3}
Sm^{3+}	5.8×10^{-4}
Cr^{3+}	7.5×10^{-4}
Al^{3+}	8.3×10^{-4}
Na^{+}	1.0×10^{-3}
K^{+}	5.0×10^{-4}
Ca^{2+}	4.2×10^{-4}
Ba^{2+}	4.8×10^{-4}
Ni^{2+}	4.5×10^{-4}
Sr^{2+}	7.7×10^{-4}
Hg^{2+}	8.3×10^{-4}
Pb^{2+}	7.4×10^{-4}
Response time (s)	~5
Linearity range (mol L^{-1})	1.0×10^{-6}-1.0×10^{-2}
Limit of detection (mol L^{-1})	6.5×10^{-7}

Table 3. Comparison of selectivity coefficients, detection limit, linearity range, response time and pH range of the proposed Lu^{3+} sensor and the formerly reported Lu^{3+} sensor.

Parameters	Ref. 4	Ref. 5	This work
Detection limit (mol L^{-1})	8.0×10^{-7}	7.2×10^{-7}	6.5×10^{-7}
Linear range (mol L^{-1})	1.0×10^{-6}-1.0×10^{-2}	1.0×10^{-6}-1.0×10^{-2}	1.0×10^{-6}-1.0×10^{-2}
Response time (s)	<10	<10	~5
Interfering ion (B) K_{sel} More than 5.0×10^{-3}	Nd, Gd, Dy	Nd, Ho, Tm, Dy	-
pH range	4.5-8.0	2.7-10.6	2.8-8.7

Table 3 compares the selectivity coefficients, pH range, response time, detection limit, and dynamic linearity range of the proposed sensor with the best previously reported Lu(III) sensors [4, 5]. As seen, the proposed sensor not only, in term of selectivity, but also, in terms of detection limit and response time is superior than the reported Lu(III) sensors.

3.7. Analytical application

3.7.1. Titration with EDTA

The optimized lutetium(III) electrode was found to work well under the laboratory conditions. The lutetium(III) PVC-membrane sensor was used as an indicator electrode in the titration of a 1.0 × 10^{-4} mol L^{-1} lutetium ion solution with a standard 1.0 × 10^{-2} mol L^{-1} EDTA. The respective titration curve is shown in Figure 5. Obviously, the amount of Lu^{3+} ions in solution can be determined with the electrode.

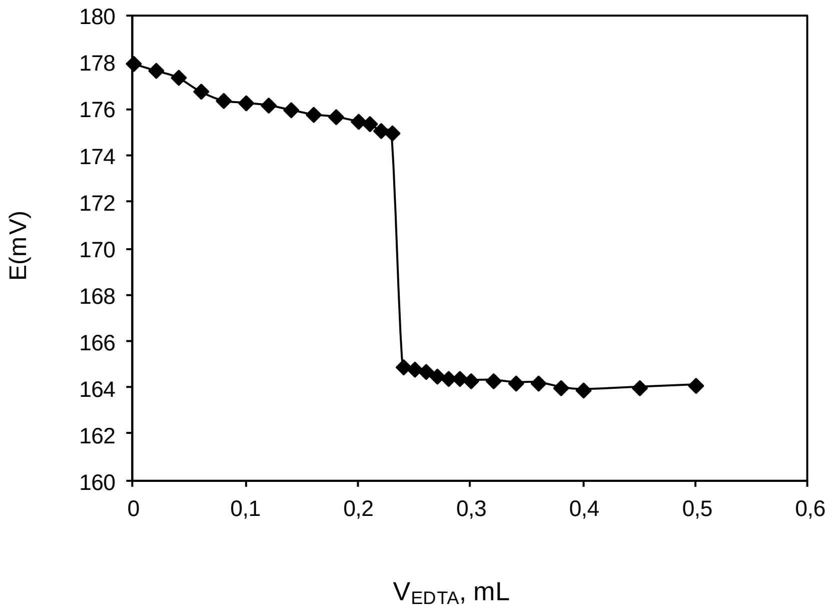

Figure 5. Potential titration curve of 25.0 mL from a 1.0 × 10^{-4} molL^{-1} Lu^{3+} solution with 1.0×10^{-2} molL^{-1} of EDTA.

3.7.2. The Lu^{3+} ion determination in mixture of different ions

The proposed Lu^{3+} electrode was also applied for the monitoring of the Lu^{3+} ions concentration in various mixtures of two and three different ions. These results are listed in Table 4, demonstrating that the recoveries of the Lu(III) ions in all mixtures are acceptable and in the range of 96.0-104.0%.

Table 4. Determination of Lu^{3+} ions in mixtures of different ions.

Serial no.	Composition	Observed content (mol L^{-1})
1	0.000010 mol L^{-1} $Lu(NO_3)_3$ + 0.0001 mol L^{-1} $Pr(NO_3)_3$ + 0.0001 mol L^{-1} $Ho(NO_3)_3$	0.0000098
2	0.000010 mol L^{-1} $Lu(NO_3)_3$ + 0.0001 mol L^{-1} $Tb(NO_3)_3$ + 0.0001 mol L^{-1} $Dy(NO_3)_3$	0.0000102
3	0.000010 mol L^{-1} $Lu(NO_3)_3$ + 0.0001 mol L^{-1} $Er(NO_3)_3$ + 0.0001 mol L^{-1} $Sm(NO_3)_3$	0.0000097
4	0.000010 mol L^{-1} $Lu(NO_3)_3$ + 0.0001 mol L^{-1} $Eu(NO_3)_3$ + 0.0001 mol L^{-1} $Tm(NO_3)_3$	0.0000096
5	0.000010 mol L^{-1} $Lu(NO_3)_3$ + 0.0001 mol L^{-1} $Yb(NO_3)_3$ + 0.0001 mol L^{-1} $Nd(NO_3)_3$	0.0000104
6	0.000010 mol L^{-1} $Lu(NO_3)_3$ + 0.0001 mol L^{-1} $La(NO_3)_3$ + 0.0001 mol L^{-1} $Gd(NO_3)_3$	0.0000098
7	0.000010 mol L^{-1} $Lu(NO_3)_3$ + 0.0001 mol L^{-1} $Cr(NO_3)_3$ + 0.0001 mol L^{-1} $Hg(NO_3)_2$	0.0000099
8	0.000010 mol L^{-1} $Lu(NO_3)_3$ + 0.0001 mol L^{-1} $Cd(NO_3)_2$+ 0.0001 mol L^{-1} $Ni(NO_3)_2$	0.0000098
9	0.000010 mol L^{-1} $Lu(NO_3)_3$ + 0.0001 mol L^{-1} $Ca(NO_3)_2$+ 0.0001 mol L^{-1} $Co(NO_3)_2$	0.0000097
10	0.000010 mol L^{-1} $Lu(NO_3)_3$ + 0.0001 mol L^{-1} $NaNO_3$+ 0.0001 mol L^{-1} KNO_3	0.0000102
11	0.000010 mol L^{-1} $Lu(NO_3)_3$ + 0.0001 mol L^{-1} $Tb(NO_3)_3$+ 0.0001 mol L^{-1} $Fe(NO_3)_3$ + 0.0001 mol L^{-1} $NaNO_3$	0.0000096
12	0.000010 mol L^{-1} $Lu(NO_3)_3$ + 0.0001 mol L^{-1} $Gd(NO_3)_3$+ 0.0001 mol L^{-1} $La(NO_3)_3$ + 0.0001 mol L^{-1} $Hg(NO_3)_2$	0.0000104
13	0.000010 mol L^{-1} $Lu(NO_3)_3$ + 0.0001 mol L^{-1} $Ca(NO_3)_2$+ 0.0001 mol L^{-1} $Mg(NO_3)_2$ + 0.0001 mol L^{-1} KNO_3	0.0000097
14	0.000010 mol L^{-1} $Lu(NO_3)_3$ + 0.0001 mol L^{-1} $Al(NO_3)_3$+ 0.0001 mol L^{-1} $Co(NO_3)_2$ + 0.0001 mol L^{-1} $Co(NO_3)_2$	0.0000104
15	0.000010 mol L^{-1} $Lu(NO_3)_3$ + 0.0001 mol L^{-1} $Er(NO_3)_3$+ 0.0001 mol L^{-1} $Tm(NO_3)_3$ + 0.0001 mol L^{-1} $Ni(NO_3)_2$	0.0000103

4. CONCLUSION

This study revealed that a potentiometric PVC-based membrane sensor based on 4'C18C6 functioned as a good Lu^{3+}-selective membrane sensor with a Nernstian behavior (19.8±0.4 mVdecade^{-1}) in a concentration range of 1.0×10^{-6}-1.0×10^{-2} mol L^{-1} Lu^{3+}. The detection limit of the electrode is 6.5×10^{-6} mol L^{-1} and could be used for the determination of this ion in the presence of the considerable concentrations of common interfering ions. The sensor has a fast response time of ~5 s in the entire concentration range. Wide applicable pH range, lower detection limit, and potentiometric selectivity coefficients of the proposed sensor make it as a suitable device for the determination of this ion.

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