Lanthanide Recognition: an Asymetric Lanthanum(III) Microsensor Based on a New Schiff's Base

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(1-[9{2-[2-2-hydroxy-1-naphtyl)-3-(2-{[(E)-1-(2-hydroxy-1 naphtyl) methylidine) amino} ethyl)-1-imidazolidyl}imino)methyl]-2-naphthol) (HNMN) was found to have a good selectivity and sensitivity towards La(III) ions, in respect with other lanthanide ions, and common transition, alkali and alkaline earth metl ions. HNMN was used as a neutral ion carrier in fabrication of a La(III) microelectrode. The best performance was obtained with a membrane contain 20% poly(vinyl chloride) (PVC), 73% *o*-nitrophenyloctylether (NPOE) as plasticizer, 3% potassium tetrakis(p-chlorophenyl)borate (KTpClPB) as an anionic additive, and 4% HNMN as ionophore. The proposed La(III) microsensor exhibits a nice Nernstian response of 19.5 ± 0.3 mV/decade of lanthanum activity, a wide linear range 4.0×10^{-4}-1.0×10^{-9} M and a detection limit of 4.5×10^{-10} M. It can be used in the pH range of 3.5-8.5.

1. INTRODUCTION

Lanthanum oxide is used in the preparation of glass fibers for optical purposes, in gasoline-cracking catalysts, polishing compounds, carbon arcs, making of the optical glasses, and in the iron and steel industries to remove sulfur, carbon, and other electronegative elements from iron and steel [1]. Lanthanum chloride manifests as anti-tumor [2]. Genotoxicity of lanthanum(III) in human peripheral blood lymphocytes has also been reported [3]. Thus, because of the increasing industrial use of lanthanum compounds as well as their enhanced discharge and its useful and harmful biological activity, monitoring of trace amount of lanthanum has been of a recent increasing concern. There are some main methods for trace amount monitoring of lanthanum ion in solution include X-ray fluorescence pectrometry, ICP-AES, spectrophotometry, isotope dilution mass spectrometry, neutron

activation analysis. These methods are either time consuming, involving multiple sample manipulations, or too expensive for most analytical laboratories [4-8].

Potentiometric electrodes, offer several advantages such as fast and ease of preparations and procedures, simple instrumentations, relatively fast responses, very low detection limit, wide dynamic ranges, reasonable selectivity and low costs. This has led to increasing the number of available sensors and micrsensors over the last few years [9-13].

Although the neutral carrier-type ISEs have been successfully used for monitoring of different metal ions including the alkali, alkaline-earth, transition, and some other heavy metal ions, there are only a limited number of reports on the development of microsensors for lanthanide metal ions based on different ionophors [14-16]. In this work we report a highly selective and sensitive La(III) microsensor based on (1-[9{2-[2-2-hydroxy-1-naphtyl)-3-(2-{[(E)-1-(2-hydroxy-1-naphtyl)methylidine)amino}ethyl)-1-imidazolidyl}imino)methyl]-2-naphthol) (HNMN) for fast monitoring of nanomolar concentration of La(III) ions.

2. EXPERIMENTAL PART

2.1. Reagents

Potassium tetrakis(4-chlorophenyl) borate (KTpClPB), PVC of high relative molecular weight, o-nitrophenyloctyl ether (NPOE), dibutyl phthalate (DBP), tetrahydrofuran (THF), chloride and nitrate salts of cations were of the highest purity available (from Merck and Aldrich), and were used without further purification. All aqueous solutions were prepared with deionized distilled water. The pH of all solutions, were adjusted with dilute nitric acid and sodium hydroxide. The ionophore HNMN (Fig. 1) was synthesized as described elsewhere [17].
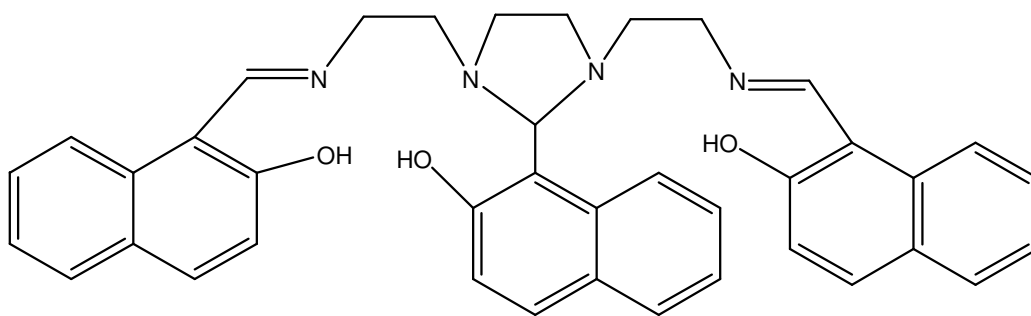

Figure 1. The chemical structure of the used ionophore (HNMN)

2.2. Electrode preparation

To prepare the PVC membrane, we used dipping method [14-16], after thoroughly mixing 20 mg of powdered PVC, 73 mg of NPOE, 3 mg of additive KTpClPB, and 4 mg of HDB and 3 ml of

THF, the resulting mixture was transferred into a glass dish with a 2 cm in diameter. The solvent was slowly evaporated until a relative oily concentrated was obtained. The gold electrode was prepared by sealing gold micro-wire (Goodfellow Metals Ltd., UK) into a soft glass capillary. The capillary was then cut perpendicular to its length to expose the gold wire. Electrical contact was made using silver epoxy (Johnson Matthey Ltd., UK). Before each experiment the electrode surface was polished for 1 min, using extra fine carborundum paper and then for 10 min with 0.3 μm alumina, sonicated in distilled water and dried in air. The polished gold electrode was dipped into the membrane solution mentioned above and the solvent was evaporated. A membrane was formed on the gold surface and the electrode was allowed to set overnight. The electrode was finally conditioned for 48 h by soaking in a 1.0×10^{-3} M of $LaCl_3$. The surface of conditioned and unconditioned of the La(III) microsensors is shown in Fig.2.

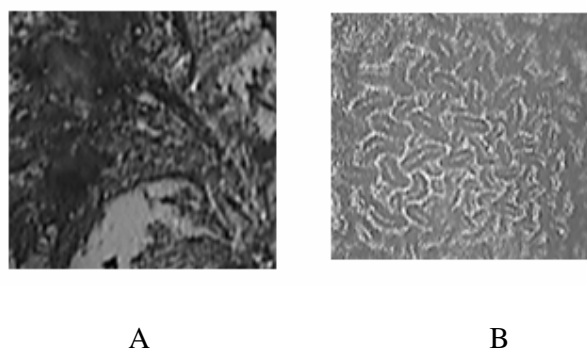A   B

Figure 2. Surface of the microelectrode before (A) and after conditioning (B) with La(III) solution

2.3. Apparatus

Potentials were measured with a Corning ion analyzer Model 250-pH/mV meter. The pH of the sample solutions was monitored simultaneously with a conventional glass pH electrode.

2.4. EMF-Measurement

All emf measurements were carried out with the following assembly:

Hg_2Cl_2, KC1 (satd.) | sample solution | PVC membrane | gold surface
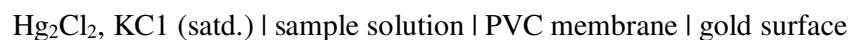
3. RESULTS AND DISCUSSION

Recently, a number of neutral ion carriers, containing nitrogen, oxygen or sulfur donor atoms, have been used in construction of selective and sensitive lanthanide metal ions [18-30]. Due to the existence of nitrogen and oxygen donor atoms in the semi cavity of HNMN, its interaction with

lanthanide ions using spectroscopic method was studied and the results showed that HNMN has special interaction with La(III) ions in comparison with other lanthanide ions and may be acts as a suitable ion carrier in fabrication of La(III) microsensor.

Thus, HNMN was used as sensing material in the construction of a number of membrane microsensors for lanthanide ions (La^{3+}, Pr^{3+}, Sm^{3+}, Dy^{3+}, Er^{3+}, Ho^{3+}, Tm^{3+}, Nd^{3+}, Gd^{3+}, Ce^{3+}, Yb^{3+}, Eu^{3+}, and Lu^{3+}) and some common transition, alkali and alkaline earth metal ions. The results shown among the lanthanide and common metal ions, La(III) ion with the Nernstian response, can be suitably determined with the membrane microsensor based on HNMN.

It is well understood the sensitivity and selectivity of a potentiometric microsensor is significantly related to the composition of the membrane, the nature of the solvent mediators and additives used [31-33]. In this study the effects of the nature and amount of the plasticizer, the amount of PVC, and the additive on the potential response of the proposed La(III) microsensor were investigated, and the results are given in Table 1. These data show that between two plasticizers used, DBP and *o*-NPOE. *o*-NPOE with higher polarity than DBP, increases the extraction of the polar La(III) ion from aqueous solution to the organic membrane phase .

Table 1. PVC membrane composition

Membrane	PVC (%wt.)	Plasticizer (%wt.)	Ionophore (%wt.)	Additive (%wt.)	Slop (mV/decade)
1	20	DBP, 77	3	-	10.1±0.4
2	20	DBP, 76	4	-	10.8±0.3
3	20	DBP, 75	5	-	10.6±0.2
4	20	NPOE, 76	4	-	12.7±0.2
5	20	NPOE, 75	4	1	17.4±0.5
6	20	NPOE, 74	4	2	18.9±0.3
7	20	NPOE, 73	4	3	19.5±0.2
8	20	NPOE, 72	4	4	19.4±0.2
9	20	NPOE, 77	-	3	2.3±0.1

The data in Table 1 shows the optimum amount of the ion carrier is 4% (No. 2), while the slope of the resulting emf vs. log La(III) activity plot is about two-thirds of the expected Nernstian value (membranes No. 2). However, addition of 3% KTpClPB (membrane No. 7) will increase the sensitivity of the microsensor response to a great extent. The fact that the presence of lipophilic anions in the composition of cationic-selective membrane microelectrodes, 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, has long been known [34-36].

The potential response of the microelectrode was evaluated using the optimum composition of all ingredients, while lacking the ionophore, and it was found that under these conditions the response of the microelectrodes falls to very low values of 2.5 mV/decade, indicating that the sensitivity of the microsensor is major due to the complexing behavior of HNMN.

The optimum equilibration time for the microsensor, after which it generates stable potentials when placed in contact with La(III) solutions, is found to be 60 h.
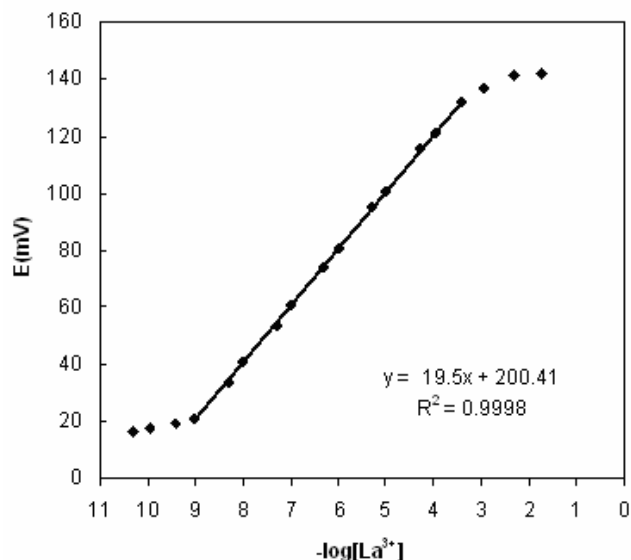

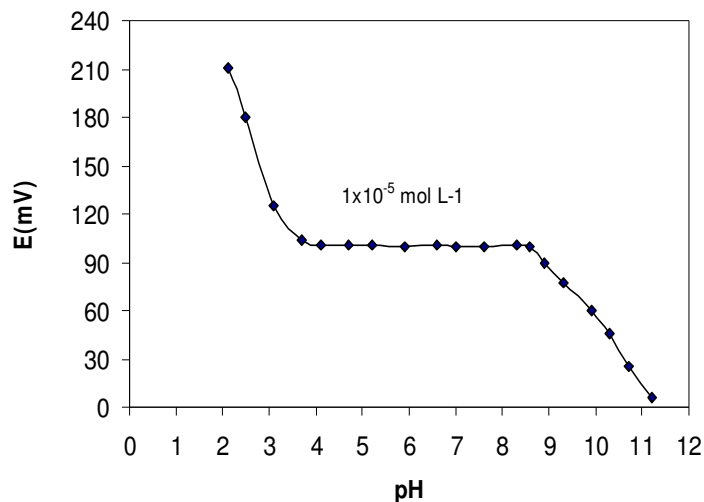**Figure 3.** The calibration curve of the La(III) membrane microsensor based on HNMN

Figure 4. pH effect of the test solution on the potential response of the lanthanum microsensor

The critical response characteristics of the La(III) microsensor were assessed according to IUPAC recommendations [37]. The potential response of the membrane at varying activity of La(III) ions (Fig. 3) indicates a rectilinear range from 4.5×10^{-4}-1.0×10^{-9} M. The slopes of the calibration curves were 19.5 ± 0.3 mV/decade of La(III) activity. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 4.5×10^{-10} M. The standard

deviation of 10 replicate potential measurements for the proposed electrode is ±0.4. The potential drift within 5 minutes after each measurement is ±0.2 mV.

The proposed microsensor is an asymmetrical sensor without any internal reference electrode and internal solution. The main problem of the symmetric ion selective liquid membrane electrodes is the leaking of the internal solution to the outer surface of the membrane, causing changes in the surface potential. Therefore, the detection limit of this kind of electrode is about 10^{-6} M. In the case of asymmetric sensors, the wire coated and the graphite coated detection limit is about 10^{-8}-10^{-11} M (on the grounds that there is no leaking of the internal solution). Due to the high tendency of the asymmetric microsensor to the low La(III) concentration, the selectivity will be drastically improved .

The influence of pH on the response of the La(III) microsensor for a 1.0×10^{-5} M La(III) solution, was evaluated over a pH range of 2.0 to 11.0, and the results (Fig. 4) show that in the pH range of 3.5 to 8.5, the potential does not change with changing pH that indicates the applicability of this microsensor in the mentioned pH range. Beyond these limits, however, relatively drastic drifts in the potential vs. pH behavior were observed. The observed drift at the higher pH values of this range could be due to the formation of insoluble La(OH)$_3$ and other hydroxy complexes of La(III) ion in the solution. In acidic solutions having pH values of less than the minimum of this range, the nitrogen donor atoms of ionophore used could be protonated to some extent, which results in improper functioning of the microsensor to the La(III) ion concentration.

Table 2. Life time of the La(III) microsensor

Week	Slope (mV/decade)	Detection limit (M)
1	19.5±0.2	4.5×10^{-10}
2	19.6±0.4	4.6×10^{-10}
3	19.4±0.3	4.6×10^{-10}
4	19.4±0.4	4.9×10^{-10}
5	19.5±0.3	5.3×10^{-10}
6	19.4±0.6	5.8×10^{-10}
7	19.2±0.3	6.2×10^{-10}
8	19.1±0.4	6.4×10^{-10}
9	18.2±0.3	1.4×10^{-9}
10	17.5±0.3	2.5×10^{-9}

The lifetime of the microsensor, which is a measure of microsensor durability, was also considered in a 10 weeks period. During this period the microsensor was used for at least 2 hours a day, and 5 days a week. After each usage it was washed completely and dried. The results are given in Table 2. As can be seen from Table 2 after nine weeks only a relatively slight changes in the microsensor's slope and detection limit from 19.5±0.2 and 4.5×10^{-10} M to 18.2±0.3 mV/decade and 1.4×10^{-9} M of La(III) activity .

Table 3. Selectivity coefficients of various interfering ions for La(III) microsensor

Interfering ion	Selectivity coefficients
Li^+	1.7×10^{-6}
Na^+	1.8×10^{-6}
K^+	2.1×10^{-6}
Mg^{2+}	5.3×10^{-6}
Ca^{2+}	5.5×10^{-6}
Cu^{2+}	2.9×10^{-5}
Co^{2+}	1.7×10^{-5}
Cd^{2+}	2.3×10^{-5}
Pb^{2+}	2.1×10^{-5}
Ni^{2+}	2.0×10^{-5}
Cr^{3+}	3.8×10^{-5}
Fe^{3+}	7.4×10^{-5}
Tb^{3+}	3.8×10^{-5}
Ce^{3+}	1.95×10^{-5}
Sm^{3+}	1.9×10^{-5}
Gd^{3+}	3.9×10^{-5}
Eu^{3+}	2.3×10^{-5}
Dy^{3+}	4.1×10^{-5}
Lu^{3+}	2.0×10^{-5}
Yb^{3+}	2.2×10^{-5}
Pr^{3+}	2.2×10^{-5}
Nd^{3+}	2.1×10^{-5}
Er^{3+}	2.3×10^{-5}
Ho^{3+}	2.5×10^{-5}
Tm^{3+}	2.0×10^{-5}

Selectivity is one of the most important factors for any sensors. In this work, matched potential method (MPM) [38] was used for determination of selectivity coefficients of the proposed La(III) microsensor. According to MPM method, the specified activity (concentration) of the primary ion (A, 1.0×10^{-7} M of Lanthanum ion) is added to a reference solution (1.0×10^{-9} M) and, afterwards, the potential is measured. In a separation experiment, the interfering ions (B, 1.0×10^{-7}-1.0×10^{-3} M) are added to an identical reference solution until the measured potential matches that obtained before by adding the primary ions. 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;

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

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 resulting selectivity coefficients are given in Table 3. As seen, the proposed La(III) microsensor is highly selective with respect to the most of cations. In the case of lanthanide ions

(thulium, europium, neodymium, presidium, holmium, cerium, samarium, dysprosium, erbium, ytterbium, lutetium gadolinium) the selectivity coefficients are in the order of 1.7×10^{-5} or smaller, which seems to indicate that the La(III) ions can be determined in the presence of other lanthanide ions. The selectivity coefficients for common metal ions used are also smaller than 7.4×10^{-5}, and they can not disturb the functioning of the La(III) microsensor. Such remarkable selectivity of the LaIII) microsensor over other metal ions reflects the high affinity of the HNMN toward La(III) ions .

The dynamic response time of the microelectrode, being another very important parameter in the evaluation of a microelectrode, was studied by varying the concentration of a solution from 1.0×10^{-9} M to 1.0×10^{-4} M and recording the times needed for the microelectrode to reach ± 1 mV of its equilibrium potential. The response time of the microelectrode was found to be about 8 seconds in the whole concentrations. This is highly likely due to the fast complexation-decomplexation exchange kinetics of La(III) ion with the HNMN at the test solution-membrane interface. To evaluate the microsensor reversibility, a similar procedure in the opposite direction was adopted. The measurements were performed in the sequence of high-to-low sample concentrations. The results showed that the potentiometric response of the sensor is reversible, although the time needed to reach the equilibrium values was longer than that for the low-to-high sample concentration procedure.

4. CONCLUSIONS

The results obtained from the above mentioned study revealed that a potentiometric PVC-based membrane microsensor based on HNMN functions as a excellent La(III) selective membrane microsensor and can be used for the determination of this ion in the presence of considerable concentrations of common interfering ions. Applicable pH range, lower detection limit, and potentiometric selectivity coefficients of the proposed microsensor make it a very good device used for the determinations of La(III) ion.

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