

Samarium Microsensor: An Asymmetric Potentiometric Membrane Sensor

Mohammad Reza Ganjali*, Zahra Memari, Farnoush Faridbod, Parviz Norouzi

Center of Excellence in Electrochemistry, Faculty of Chemistry, University of Tehran, Tehran, Iran

*E-mail: ganjali@khayam.ut.ac.ir

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The first asymmetric potentiometric Sm(III) micro-sensor is reported here. 2-((2-thioxothiazolidin-4-one)methyl)phenol (TMP) was found to have a very selective behavior towards Sm(III) ions, in comparison to other lanthanide ions, inner transition and representative metal ions. TMP was used as a sensing material in the construction of a Sm(III) microelectrode. The proposed micro-sensor exhibits a Nernstian slope of 18.27 ± 0.3 mV per decade over a wide concentration range of 1.0×10^{-9} - 1.0×10^{-4} M, and a detection limit of 8.0×10^{-10} M of Sm(III) ions. The potentiometric response of the sensor is independent of the solution pH in the range of 3.0-8.0. It has advantages of low detection limit and fast response time (20-25 s).

Keywords: Sm(III); 2-((2-thioxothiazolidin-4-one)methyl)phenol (TMP); Micro-sensor; Potentiometric PVC membrane

1. INTRODUCTION

Potentiometric membrane sensors, according to their construction, are categorized into two important groups [1] symmetrical ion-selective electrodes, and [2] asymmetrical ion-selective electrodes.

Symmetrical ion-selective electrodes are classical electrodes in which the ion-selective membrane is placed between two solutions. In an asymmetrical ion selective electrode, one side of the membrane is in contact with a solid phase while the other is exposed to the measured solution.

Similar to the rest of the chemical sensors, a potentiometric micro-sensor comprises two basic parts; a transducer and an ion-sensitive receptor layer.

The measurement of the electrochemical potential in the ion-selective membrane is conducted with the membrane incorporation into a transduction element. A transducer can be in the form of either a coated wire electrode (CWE) or a device based on an ion-sensitive field effect transistor (ISFET).

In the conventional ion-selective electrodes, the ion-selective membrane is placed between the sample solution and the internal reference solution. This constant composition results in a stable potential at both the inner boundary of the membrane, and the interface of the internal Ag/AgCl electrode [2,3]. This makes the sensors very stable and hence, most of the commercially available potentiometric ion-selective devices are based on the conventional ion-selective electrodes. However, the presence of an internal reference solution causes a disadvantage: the relatively big electrode dimensions. In CWEs, the internal electrode can be either a noble metal wire (platinum, silver, and gold), or even a graphite rod which is directly coated with the ion-selective membrane. Furthermore, the absence of an internal electrolyte leads to a thermodynamically ill-defined electrode membrane interface [1].

In addition, the miniaturization of the working electrode for the *in vivo* or *in vitro* determination of the analyte, or for using the flow injection system has recently become an interesting field of research. Asymmetric sensors exhibit several other attractive possibilities including; exploration of macroscopic domains, detection in micro flow system, time-resolved probing of processes in the single cells and analyses of very small sample volume [1].

Sm(III) is a member of the lanthanide series, originally known as rare earth metals. The interest in lanthanide ions arise because they can be used as probes to study the interactions between Ca^{2+} and biologically important molecules. The lanthanides have similar ionic radii to calcium, but possess a higher charge density, which causes a high affinity for the Ca^{2+} sites on biological molecules and pharmaceuticals [4-7]. This research reports the first asymmetric potentiometric membrane micro-sensor for Sm(III) ion based on 2-((2-thioxothiazolidin-4-one)methyl)phenol (TMP). The proposed micro-sensor is very selective to the Sm(III) ion concentrations in a wide linear range.

2. EXPERIMENTAL PART

2.1. Apparatus

The glass cell, where the Sm(III) ion-selective electrode was placed, consisted of an R684 model Analion Ag/AgCl double junction reference electrode as a reference electrode. The both indicator and reference electrodes were connected to a Corning ion analyzer with a 250 pH/mV meter with ± 0.1 mV precision .

For the conductivity measurements, a Metrohm 660 conductivity meter and a black platinum dip-type conductivity cell (with a 0.83 cm^{-1} cell constant) were used.

All emf measurements were carried out with the following assembly:



In all measurements, the ionic strength of the solutions was maintained by using 10^{-4} M of NaCl [8].

2.2. Reagents and materials

Reagent grade dibutyl phthalate (DBP), nitrobenzene (NB), benzyl acetate (BA), high relative molecular weight poly vinyl chloride (PVC), sodium tetraphenyl borate (NaTPB) and tetrahydrofuran (THF) were purchased from Merck and used as received. Nitrate salts of the cations used (from Merck and Aldrich) were all of the highest purity available and used without any further purification. Distilled deionized water was used throughout.

2.3. Synthesis of the ionophore

2-((2-thioxothiazolidin-4-one)methyl)phenol TMP (Fig. 1) was synthesized as follow:

A mixture of salicylaldehyde (0.02 mol), N-aminorhodanine (0.02 mol) and catalytic amount of acetic acid was refluxed in absolute ethanol (20 ml) for 1h. The reaction mixture was then cooled to the room temperature and the yellow microcrystal product were filtered washed with ethanol, and dried under the reduced pressure. This imines is mixed with silica and the powder is then treated with a solution of $Zn(BH_4)_2$ in the diethyl ether for 6h. Then the reaction mixture was cooled to room temperature and the residue was purified by column chromatography using 1:2 n-hexane and ethyl acetate as eluent. The solvent was removed and the solid residue was re-crystallized from 1:1 n-hexane ethyl acetate to afford product.

1H NMR: δ 4.05 (2H, s, CH_2), 4.75 (2H, s, CH_2), 5.35 (1H, br, NH), 6.25 (1H, br, OH) 6.40 (1H, d, $J=7.2$ Hz, CH), 6.65-6.75 (2H, m, 2CH), 6.89 (1H, t, $J=7.5$ Hz, CH)

^{13}C NMR: δ 37.25 (CH_2), 45.33 (CH_2), 115.35,120.20 (2CH), 124.45 (C), 126.75, 129.09 (2CH), 160.61 (C-O), 171.40 (C=O), 175.33 (C=S)

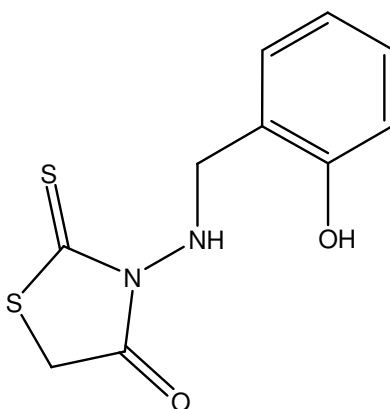


Figure 1. Chemical structure of 2-((2-thioxothiazolidin-4-one)methyl)phenol (TMP)

2.4. Electrode preparation

The general procedure to prepare the PVC membrane was to varying amounts of the ionophore along with appropriate amount of PVC, plasticizer and additive were dissolved in tetrahydrofuran (THF) and the solution was mixed well. 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. The gold electrode was prepared by sealing gold micro-wire (Good fellow 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 SmCl_3 [9-12].

3. RESULTS AND DISCUSSION

Lanthanide has 15 members, which are rather similar. However, the ionic radii, the charge density and the hydration energy of the lanthanide ions are not similar. These different radii of the lanthanum ions (from Ce^{3+} to Lu^{3+} their radii vary from 1.02 to 0.80 \AA , respectively) causes their different properties, such as charge densities and size as well as hydration energy (from Ce^{3+} to Lu^{3+} their hydration energy ranges from 3370 to 3760 kJ/mol). Thus, the only way to design an ion-selective electrode for the lanthanide ions is using ionophores having semi-cavity, heteroatoms (N, O and S as donor atoms), and high flexibility. Such an ionophore can easily form a template with reference to the size of the cation. Furthermore, these kinds of ionophores are able to form a stronger complex with one of the lanthanide cations than the other ones with the optimum free energies. Regarding that some neutral ion carriers, containing nitrogen, sulfur or both nitrogen and sulfur donor atoms, have been reported, to be used in construction of selective and sensitive transition and heavy metal ion membrane sensors [13-23] and considering the existence of donating hetero-atoms such as N, O, and S in TMP structure, it was expected to act as a suitable neutral ionophore in the PVC membranes. In this work, conductance study had been carried out to understand the fundamental interaction between metal ions and neutral molecules and their relationship to molecular recognition better.

3.1. Complexation study

The complexation of TMP with Sm(III) and some metal ions was investigated conductometrically in an acetonitrile solution at $25.0 \pm 0.1^\circ\text{C}$ [24, 25], in order to obtain a clue about the stability and selectivity of the resulting complex. The complex formation constant, K_f , and the molar conductance of the resulting 1:1 complexes were evaluated by computer fitting the molar conductance–mole ratio data to appropriate equations [2, 26, 27]. The K_f for the complex of TMP and

Sm(III) is 5.63 ± 0.3 . For the other lanthanide ions tested, the K_f was between 3.50-2.20 and for other mono and divalent ions the K_f were less than 2.0.

3.2. Sm(III) asymmetric membrane sensors

The microelectrode 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 microelectrodes, the wire coated and the graphite coated detection limit is about 10^{-8} - 10^{-11} M (based on there is no leaking of the internal solution). Due to the high tendency of the asymmetric microelectrode to the low Sm(III) concentration, the selectivity will be drastically improved [8]. The proposed Sm(III) micro-sensor has detection limit of 8.0×10^{-10} M of Sm(III) ions.

3.3. Membrane composition effect on the potential response of the sensor

Because the degree of sensitivity and selectivity for a certain ionophore is greatly related to the membrane ingredients, the influence of membrane composition on the potential responses of the Sm(III) micro-sensor was inspected [28-31]. In this study, different membrane compositions, as shown in Table 1, were tested. As can be seen, the membrane with the composition of 20% PVC, 5% TMP, 2% NaTPB and 73% DBP (no. 5) was the optimum one in the development of this sensor. This membrane composition was selected after many considerations.

Table 1. The optimization of the membrane ingredients

Membrane No.	Composition (%)				Slope (mV per decade)
	PVC (%wt.)	Plasticizer (%wt.)	TMP (%wt.)	NaTPB (%wt.)	
1	20	DBP, 76	4	-----	11.22 ± 0.3
2	20	DBP, 75	5	-----	15.61 ± 0.3
3	20	DBP, 74	6	-----	14.92 ± 0.4
4	20	DBP, 74	5	1	16.25 ± 0.3
5	20	DBP, 73	5	2	18.27 ± 0.3
6	20	BA, 73	5	2	15.86 ± 0.5
7	20	NB, 73	5	2	16.11 ± 0.4

The high Sm(III) ion extraction into the liquid membrane was a result of the elevated ionophore tendency to form a selective complex with the Sm(III) ions. From Table 1, it was obvious that in the presence of 5% ionophore and with the other components (no. 5), the response of the recommended electrode was the best.

The second factor which helps Sm(III) to extract from an aqueous solution to the membrane as an organic phase is a plasticizer. After the evaluation of three solvent mediators (NB, BA and DBP), BA having the intermediate dielectric constant values, leads to the better extraction of the trivalent samarium ions.

The presence of lipophilic anions in a cation-selective membrane was also considered. Actually, the presence of such anions in a cation-selective membrane, which is based on a neutral carrier, decreases the ohmic resistance and improves the response behavior and selectivity. In addition, when the extraction capability is poor, it increases the membrane electrode sensitivity [28, 31-33].

3.4. pH effect on the electrode response

In an approach to understanding the impact of pH on the electrode response, the potential was measured at two particular concentrations of the Sm(III) solution (1.0×10^{-5} M and 1.0×10^{-6} M) from the pH value of 2.0 up to 12.0 (concentrated NaOH or HCl solutions were employed for the pH adjustment). In agreement with the resulting data, the potential remained constant despite the pH change in the range of 3.0 to 8.0, indicating the applicability of this electrode in the specific pH range.

On the contrary, relatively noteworthy fluctuations in the potential vs. pH behavior took place below and above the formerly stated pH limits. In detail, the fluctuations above the pH value of 8.0 might be justified by the formation of the soluble and insoluble Sm(III) ion hydroxy complexes in the solution, such as $\text{Sm}(\text{OH})^{2+}$, $\text{Sm}(\text{OH})_2^+$ and $\text{Sm}(\text{OH})_3$. On the other hand, the fluctuations below the pH value of 3.0 were attributed to the partial protonation of the employed ionophore [30].

3.5. Study of micro-sensor properties

The properties of an ion-selective electrode are characterized by parameters like these: (1) Measuring range, (2) Detection limit, (3) Response time, (4) Selectivity, (5) Lifetime

3.5.1. Measuring range

The measuring range of an ion-selective electrode includes the linear part of the calibration graph as shown in Fig. 2. Measurements can be performed in this lower range, but it must be noted that more closely spaced calibration points are required for more precise determinations. According to another definition, the measuring range of an ion-selective electrode is defined as the activity range between the upper and lower detection limits. The applicable measuring range of the proposed sensor is between 1×10^{-9} and 1×10^{-4} M.

3.5.2. Detection limit

By extrapolating the linear parts of the ion-selective calibration curve, the detection limit of an ion-selective electrode can be calculated. In this work the detection limit of the proposed membrane

sensor was 8.0×10^{-10} M which was calculated by extrapolating the two segments of the calibration curve (Fig. 2).

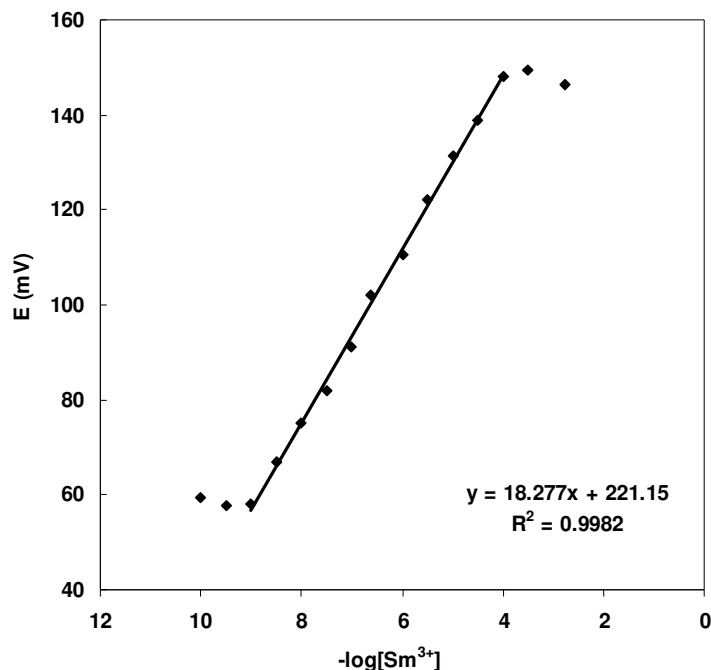


Figure 2. Calibration curve of the Sm(III) sensor of membrane.

3.5.3. Response time

The response time of an electrode is evaluated by measuring the average time required to achieve a potential within ± 0.1 mV of the final steady-state potential, upon successive immersion of a series of interested ions, each having a ten-fold difference in concentration. It is notable that the experimental conditions-like the stirring or flow rate, the ionic concentration and composition of the test solution, the concentration and composition of the solution to which the electrode was exposed before experiment measurement was performed, any previous usages or preconditioning of the electrode, and the testing temperature--have an effort on the experimental response time of a sensor [1].

In this work, about 20 s response time was obtained for the proposed electrode when contacting different Sm(III) solutions from 1.0×10^{-4} to 1.0×10^{-6} M, and about 25 s in low concentration solutions, which is due to the effect of analyte concentration on the response time of ion selective electrode.

3.5.4. Selectivity

Selectivity, which describes an ion-selective electrode's specificity toward the target ion in the presence of interfering ions, is the most important characteristic of these devices. The

potentiometric selectivity coefficients of the Sm(III) sensor were evaluated by the matched potential method (MPM) and separated solution method (SSM) [34,35].

The resulting values of the selectivity coefficients are given in Table 2. As can be seen from Table 2, for the all mono and bivalent metal ions and trivalent lanthanide ions tested, the selectivity coefficients are about 10^{-3} , which seems to indicate negligible interferences in the performance of the electrode assembly.

Table 2. The selectivity coefficients of various interfering cations for membrane

Ion	Log K_{MPM}	Log K_{SSM}
Na ⁺	-3.9	-3.8
K ⁺	-3.5	-3.7
Mg ²⁺	-3.4	-3.4
Ca ²⁺	-3.3	-3.2
Co ²⁺	-3.6	-3.5
Pb ²⁺	-3.5	-3.7
Fe ³⁺	-3.7	-3.8
La ³⁺	-3.6	-3.7
Ce ³⁺	-3.2	-3.1
Pr ³⁺	-3.5	-3.5
Nd ³⁺	-3.7	-3.8
Ho ³⁺	-3.8	-3.9
Eu ³⁺	-3.4	-3.5
Gd ³⁺	-3.2	-3.1
Tb ³⁺	-3.3	-3.4
Dy ³⁺	-4.1	-4.3
Er ³⁺	-3.8	-3.6
Tm ³⁺	-3.7	-3.5
Yb ³⁺	-3.3	-3.4
Lu ³⁺	-3.4	-3.4

3.5.5. Lifetime

The average lifetime for most of the reported ion-selective sensors is in the range of 4–10 weeks. After this time the slope of the sensor will decrease, and the detection limit will increase. The

sensors were tested for 10 weeks, during which time the electrodes were used extensively (one hour per day). Fig. 3 shows the changes in the slope and detection limits of a sensor with time. The proposed sensors can be used for six weeks. First, there is a slight gradual decrease in the slopes (from 18.27 to 15.0 mV per decade) and, second, an increase in the detection limit (from 8.0×10^{-10} M to 1.0×10^{-8} M). It is well established that the loss of plasticizer, carrier, or ionic site from the polymeric film due to leaching into the sample is a primary reason for the limited lifetimes of the sensors.

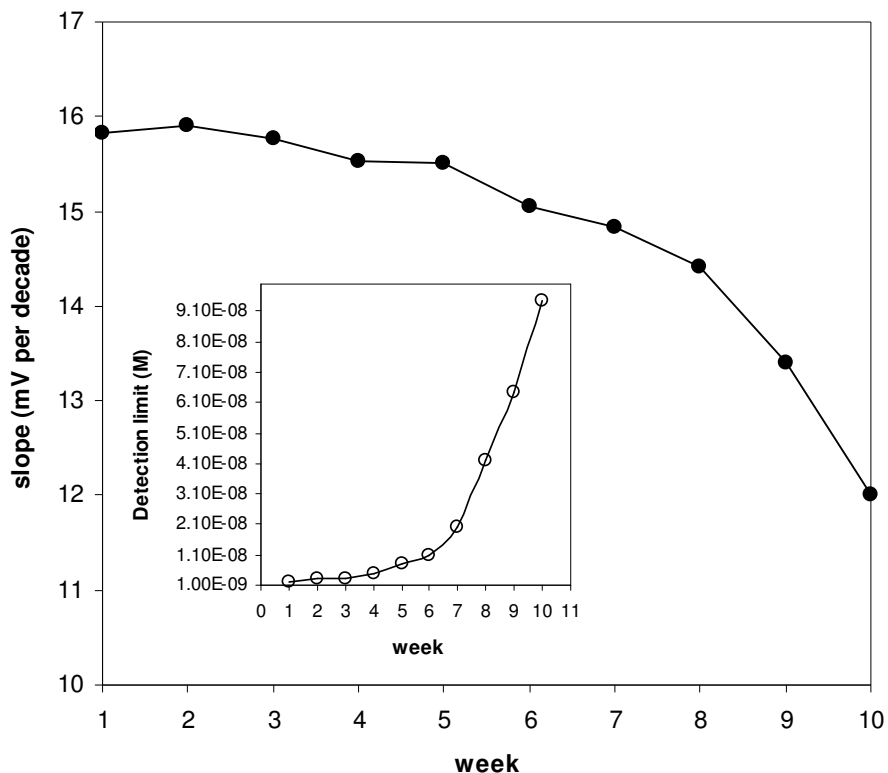


Figure 3. The lifetime of the Sm(III) membrane sensor (membrane no. 5)

4. CONCLUSIONS

The results obtained from the above mentioned study revealed that a potentiometric PVC-based membrane microelectrode based on TMP functions as an excellent Sm(III) selective membrane microelectrode 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 microelectrode make it a superior device both compared to other methods used for the determinations of this ion in vivo or in vitro or for in flow injection system in future applications.

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