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Development of a potentiometric sensor for europium(III) based on *N*, *N*, *N′*, *N′*-tetraoctyldiglycolamide (TODGA) as the ionophore

Bholanath Mahanty[a], A.K. Satpati[b,*], P.K. Mohapatra[a,*]

[a] Radiochemistry Division, Bhabha Atomic Research Centre, Mumbai – 401502, India
[b] Analytical chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai – 400085, India

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ABSTRACT

A polymer inclusion membrane (PIM) with *N,N,N′,N′*-tetraoctyl diglycolamide (TODGA) as the ionophore and polyvinyl chloride (PVC) as the base polymers was synthesized and evaluated for potentiometric membrane sensing of Eu^{3+} ions. Effects of membrane composition, inner filling solution and pH on the electrode performance were investigated and it was found that the membrane with a composition of 30.3% TODGA, 9.1% NaTPB and 60.6% PVC showed a wide linear dynamic range (1.5×10^{-6} M to 1.2×10^{-2} M) with a slope of 17.3 ± 0.1 mV per decade with 1.2×10^{-6} M as the limit of detection for Eu^{3+}. Interference from mono-, di-, tri-, tetra- and hexa-valent ions was investigated by matched potential method. The sensor was also tested as an indicator electrode in the titration of Eu^{3+} with standard EDTA solution. The response time of the proposed sensor was found to be < 10 s. The life time of the sensor electrode was found to be one month under optimized storage conditions. The potentiometric sensor as developed was employed in the determination of Eu^{3+} in the synthetic mixture of uranyl nitrate and europium nitrate, after the removal of major matrix using 30% TBP-*n*-dodecane. The analytical results, compared with those obtained from inductively coupled plasma - atomic emission spectroscopy (ICP-AES), showed good agreement between the two methods.

1. Introduction

Europium is one of the most important elements in the lanthanide series that has a wide range of applications including industrial, nuclear, as well as in house hold appliances. Europium in the form of phosphor is used in colour televisions to produce bright red colour. In street light, europium in small amounts is used in combination with mercury vapour lamp to emit more natural type of light [1]. Europium doped lanthanum fluoride single crystal is used as a sensing agent in fluoride ion selective electrodes [2]. In nuclear industries europium is an important element in controlling excess reactivity for thermal reactors [3]. Europium is also one of the major fission products in lanthanide series of elements [4]. It is also considered as a critical impurity in nuclear fuel due to very high thermal neutron absorption cross section [5]. In view of these, determination of europium in trace level is of paramount importance. Different methods which are employed for the low level determination of europium are spectrophotometry [6], inductively couple plasma optical emission spectrometry (ICP-OES) [7], inductively couple plasma mass spectrometry (ICP-MS) [8,9], isotope dilution mass spectrometry (IDMS) [10], X-ray fluorescence spectrometry (XRF) [11], fast Fourier transform continuous cyclic voltammetry (FFT-CCV) [12] and potentiometric methods [13–16]. Most of these methods involve expensive instruments as well as time consuming and rigorous sample preparation protocols. Electrochemical method of ion sensing possesses many advantages compared to other methods like easy instrumentation and operation, reproducibility, fast response and low cost, etc. [17–19]. Potentiometric sensors based on polymer inclusion membranes (PIMs) [20–23] have been utilized for the determination of important metal ions which would help in their recovery. PIM membranes generally contain four components, viz., ionophore, polymer, plasticizer and ionic sites. The ionophore binds the metal ion of interest, the polymer provides mechanical strength to the membrane, the plasticizer provides flexibility and dissolves the ionophore, whereas the lipophilic additives decrease the membrane resistance and suppresses the uptake of the counter ion [24,25].

Diglycolamide based ligands such as *N*, *N*, *N′*, *N′*-tetraoctyl diglycolamide (TODGA, Fig. 1) have shown their versatility in the extraction of trivalent lanthanides and actinides from acidic feed solutions [26,27]. Extensive study with TODGA containing PIMs for the uptake and transport of actinides (Am^{3+}, Pu^{4+}, Th^{4+}, UO_2^{2+}) from acidic feed solution was reported previously from our group [28]. The results showed that both uptake and transport follow the trend:

* Corresponding authors.
E-mail addresses: asatpati@barc.gov.in (A.K. Satpati), mpatra@barc.gov.in (P.K. Mohapatra).

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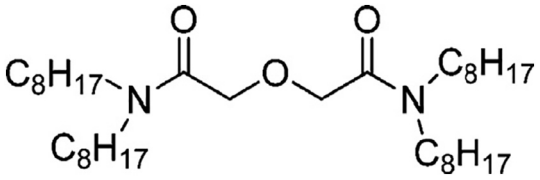

Fig. 1. Structural formula of TODGA molecule.

$Am^{3+} > Pu^{4+} > Th^{4+} > UO_2^{2+}$. The solvent extraction and supported liquid membrane (SLM) studies with Eu^{3+} by us indicated the formation of reverse micelle when TODGA was used as the extractant [4]. Therefore, such reverse micelle system would provide a platform for signaling Eu^{3+}. Legin et al. [29] have studied polymeric sensors based on carbamoylphosphine oxides (CMPO), diphosphine dioxides (DPDO) and TODGA for rare earth (RE) ions at pH 2.0. Their study indicates the sensors show a good promise for the analysis of complex mixture of RE ions by multi-sensor approach. Kirsanov [30] et al. reported a potentiometric multi element sensor array based on ligands with high cross sensitivity for different RE ions with lack of selectivity. The membrane of their study is based on PVC as base polymer, different ligands as ionophore, NPOE as plasticizer and chlorinated cobalt dicarbollide (CCD) as a cation-exchanger. They have used 14 different ligands with 4 different series of model solutions of RE elements, the sensitivity of the sensor based on TODGA as ionophore increases from lanthanum (13 mV/decade) to lutecium (24 mV/decade) and europium has shown the sensitivity of 19 mV/decade in nitric acid solution with pH 1.5 when studied in lean solution. Yu et al. [31] have studied comparative electrochemical response of TODGA and diamide substituted calixarene based sensor in the analysis of RE elements at pH 2.0. Their study indicates TODGA sensors exhibit an increased selectivity with increasing atomic number of the lanthanide and Lu^{3+} is observed to be the most preferable ion. Whereas with the incorporation of diamide groups onto the calixarene scaffold leads to sharp smoothening of selectivity and the sensors do not discriminate between different RE ions which also suggest the latter type of sensor is practically more suitable for the determination of sum of the lanthanides in sample solution using multi-sensor array. These electrodes work in the pH range of 1.5–2.0 where the hydrolysis of Ln^{3+} ion is reported to be negligible. Grandy et al. [32] showed a sub-Nernstian slope (15.1 ± 0.8 mV/decade) for europium ion with a PVC based sensor containing calix[4]arene phosphine oxide; hydrolysis of lanthanide was suggested to be responsible for the lowering of the Nernstian slope. On the other hand, there are many reports on europium [13,15,16,33,34] and other RE ion selective electrodes [35–37] which showed very high sensitivity and selectivity in the working pH > 4. There are examples of actinide potentiometric sensors [38,39] which also indicated the working pH higher than 4.0. The report by Wang et al. [40] indicates that Eu(III) predominantly existed in solution of pH < 6.0. The present work deals with a detailed study on the development of a potentiometric sensor for Eu^{3+} ion based on TODGA as the ionophore in a NPOE plasticized PVC membrane containing sodium tetraphenyl borate (NaTPB) as ionic additives. The effect of variation of composition of the membrane on the development of the potential, different interfering ions, effect of pH of the solution, effect of inner filling solution on the sensor potential was studied in detail. This work has great relevance in detecting minute quantities of Eu in the environment.

2. Experimental

2.1. Reagents

TODGA, procured from Thermax Ltd., India, was used without any further purification. Polyvinyl choride (PVC) (Sigma-Aldrich), 2-nitrophenyl *n*-octyl ether (NPOE) (Fluka), sodium tetraphenyl borate (NaTPB) (Sigma-Aldrich), dichloromethane (Merck), sodium acetate (SD fine chemical, India), acetic acid (SD fine chemical, India) were used as received. Acetate buffer solution (pH = 5.0 ± 0.1) was prepared by mixing required volumes of acetic acid (0.01 M) and sodium acetate (0.01 M) solution. Dilute solutions of nitric acid were prepared using suprapur nitric acid (Merck). Europium oxide was procured from Sigma-Aldrich and the required quantity of the reagent was dissolved in concentrated suprapur nitric acid. Subsequently, it was diluted using Millipore water to prepare a stock solution of 0.1 M. All the other reagents were of analytical reagent grade.

2.2. Membrane preparation

The PIMs were prepared following the method as reported previously [24]. About 2 g of PVC was dissolved in 100 mL of THF while in another container, 1.0% (*w/v*) of NaTPB was prepared in THF. The PVC and NaTPB solutions were taken together in a 25 mL beaker along with NPOE and a solution of TODGA in THF was added into the mélange and homogenized by ultrasonication (for about 5 min). The resultant solution was poured into a flat bottom Petri dish (90 mm diameter) and covered loosely with a watch glass. The Petri dish was kept undisturbed to allow the solvent to evaporate slowly at room temperature. After 48 h, a few drops of Millipore water were swirled on top of the film to help loosen it from the glass surface of the Petri dish. The PIM was carefully peeled off from the Petri dish with the help of a tweezers. The resultant PIM was transparent and smooth looking. The thickness of the PIM was measured using a Mututoya digital micrometer and it was found to be uniform (0.0084 ± 0.0009 cm).

2.3. Sensor preparation

Potentiometric sensor electrode was fabricated using the PIMs of varying composition. A small piece of the PIM was cut and screwed at the base of a glass tube. The sensor, thus fabricated, was filled (3/4th of the volume of the tube) with 0.1 M $Eu(NO_3)$ solution as the inner filling liquid. The electrode was conditioned for overnight by soaking in 0.1 M $Eu(NO_3)_3$ solution. A silver/silver chloride electrode was used as an internal reference electrode. A saturated calomel electrode was used as external reference electrode in conjunction with the sensor electrode to measure the potential. The ionic strength and pH of the solution was maintained constant throughout the experiment by using an acetate buffer solution at pH 5.0 ± 0.1. The EMF generated from the sensor out of the test solution has the following cell assembly:

Ag-AgCl (3 M KCl) / 0.1 M $Eu(NO_3)_3$ / Membrane / Test solution / Hg-Hg_2Cl_2, KCl (sat.)

A digital potentiometer (Radiometer Ion 85 Ion Analyzer) was used for measuring the potential at 25 °C. The pH of the solution was measured using a pH-electrode (Micro pH Analytica, SDFCL, India). Eu^{3+} concentration in the solution was measured by ICP-AES (Ultima 2 CHR, Horiba Jobin Yvon).

2.4. Characterization of PIM

The FTIR spectra were obtained using an ATR-IR platinum Bruker spectrometer. Thermal analysis was carried out using Netzsch thermal analyzer Model number STA 409 PC.

2.5. Potentiometric studies

The potentiometric studies were carried out by taking 20 mL of acetate buffer solution (pH 5.0 ± 0.1) in a 50 mL glass beaker where the sensor electrode and the reference electrode were dipped and connected to the respective terminal of the digital potentiometer. The solution was stirred at a fixed speed of 100 rpm using a precisely controlled magnetic stirrer. The electrode potential response was recorded

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