

La(III) ION SELECTIVE ELECTRODE WITH PTFE MEMBRANE CONTAINING TRIBUTYL PHOSPHATE IONOPHORE

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ABSTRACT

Methods for quantitative determination of lanthanum that have been developed are generally spectroscopic method such as inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and X-ray fluorescence spectrometry, which have relatively high operational costs. The feasibility of potentiometric method using ion selective electrode (ISE) as an alternative method for lanthanum (III) determination needs to be studied because it is simple, easy to use, and has high sensitivity and selectivity. In this study, we developed ion selective electrode using PTFE membrane impregnated with tributyl phosphate (TBP) as ionophore. TBP is commonly used as complexing agent for rare earth ions in supported liquid membrane (SLM) separation process. We found that the compound can be used as ionophore for ISE.

This study aims to make lanthanum ion selective electrode (III) (La-ISE) which has Nernstian response.

The parameters studied in the construction of this electrode were the effects of PTFE membrane immersion ionophore solution, ionic strength adjuster (ISA) and the inner solution composition. The performance parameters studied for the La-ISE were linear range, response time, detection limit, selectivity and life time of the electrode.

Construction of the electrode begins with the preparation of PTFE membrane as the main component. PTFE membrane was impregnated for 12 hours in TBP solution having concentration of 0.25 M or 0.50 M in kerosene. After it was dried, the membrane was attached to the end of electrode tube with adhesive. Then, the electrode was filled with internal solution containing mixture of KCl 10^{-3} M with La (III) 10^{-3} M. The internal reference electrode was Ag/AgCl electrode. Before it was used, the electrode was soaked in a solution of La (III) 10^{-3} M for 12 hours.

The effect of TBP concentration on the electrode performance was studied using two concentrations of TBP: 0.25 M and 0.50 M. The calibration curves obtained using both electrodes has good linearity. Nernst factor obtained from both electrodes are similar, although the Nernst factor obtained with electrode having 0.50 M TBP closer to the theoretical value.

ISA used in the measurement was KNO₃. The effect of ISA on the performance of the electrode was studied using electrodes containing TBP with concentration of 0.25 M or 0.50 M. The concentration of KNO₃ used in this study was 0.01 M and 0.10 M. The Nernst factors obtained with electrodes containing 0.25 M TBP in general higher than those obtained with electrodes containing 0.50 M TBP in the same

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Abstract describes sections of research such as the effects of PTFE membrane immersion ionophore solution, ionic strength adjuster (ISA) and the inner solution composition, that are not explained in the results and discussion sections.

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ISA. Electrode containing 0.50 M TBP resulted in Nernst factor close to theoretical value when measurement was conducted in 0.10 M KNO_3 .

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Keywords: Lanthanum, electrode selective ion, ionophore, tributyl phosphate (TBP)

Introduction

Lanthanum is one of rare earth elements is known as an important element of their nature, especially having a strong magnetic properties. Lanthanum has received much attention electrochemically due to its applications in the hydrogen storage materials of batteries, ion selective electrode, chemical sensor, electrocatalytic hydrogenation, and ion gate effect [1]. Its elements found in nature in the form of minerals such as monazite and xenotime. Monazite and xenotime are minerals that contains lots of rare earth metal element (REE') of the lanthanide group. These mineral also found in Indonesia, but not yet processed and utilized optimally because of the mastery of monazite ore processing technology still needs to be improved and strengthened. REE' these elements, are now widely used for the manufacture of goods innovative high-tech, such as permanent magnets, catalysts, fiber optics, optoelectronics, ceramics pizeoelectric, rechargeable batteries, microwave equipment, etc., so that now the element REE has regarded as one of the 21st century [2,3]. Lanthanides are very important metals in high technology industry because of their unique electronic, optical, and magnetic properties, and therefore their demand has been increasing in recent year. But the element of REE' mostly have physical and have very fundamental chemical properties are similar, which makes it difficult hard splitting into each element. It is also the cause of rare earth metals such as lanthanides become expensive [4].

Currently, many researchers who give great attention to rare earth metals are widely applied in industry. Therefore, the required development of method for the determination and recovery of rare earth metals. Method has been developed which includes conventional means such as chemical precipitation, reverse osmosis, adsorption, ion exchange and solvent extraction, but many difficulties are found in a variety of methods [5].

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For the purposes of monitoring the treatment process, quality control, and REE' presence in a given material, required analytical methods that have high accuracy and selectivity, low detection limits, and high reproducibility. The method that considered to meet these criteria, among others, spectroscopic techniques such as inductively coupled plasma mass spectrometry (ICPMS), inductively coupled plasma atomic emission spectrometry (ICPAES), and X-ray fluorescence spectrometry. Hence, the available methods for low-level determination of rare-earth ions in solution include spectrophotometry, isotope dilutions mass spectrophotometry, neutron activation analysis, X-ray fluorescence spectrometry, etc [5]. However, many of these spectroscopic methods requires a lot of time involving multiple samples and also expensive for most analytical laboratories [6]. Meanwhile, if using chromatographic methods require a long sample preparation. Therefore, alternative methods are needed that meet the analytical criteria, simple in execution and relatively inexpensive.

One method that has the potential of the electrode is the potentiometric method with membranous. Potentiometric method provides several advantages such as speed and ease of preparation and procedures, simple instrumentation, relatively fast response, very low detection limits, wide measurement range, an acceptable selectivity and low cost. This will make the availability of micro-electrodes and electrodes for the determination of the required REE [7]. The quick determination of minute quantities of ionic species by simple methods has a great importance in analytical chemistry. Potentiometric detection based on ion selective electrodes (ISEs) is the simplest of all and offers unique advantages [8]. Membranous electrode has many types, and in this paper was chosen with reference to the type of tube and the solution in as well as sensor ionophore required. Therefore, it is feasible the

development of methods to make sensors for lanthanide ions with high selectivity using the appropriate ionophore. Electrodes for the potentiometric determination can yield several benefits such as ease and speed of preparation and procedures, simple instrumentation, relatively fast response, wide measurement range and low cost. Therefore, the use of microelectrode and an electrode in the potentiometric analysis REE³⁺ is growing. Potentiometric detectors based on ion selective electrode are specially suited for fast, accurate, reproducible and selective determination of various metal ions. Such potentiometric detectors offer advantages such as selectivity, sensitivity, good precision, simplicity and so on. These methods allow direct on-line monitoring of concentration of selected species without a pretreatment [9].

Carrier-based ion selective electrodes (ISEs) are used extensively for the direct selective detection of ionic species. For this type of electrode, the formation constant of the ion-ionophore complex within the membrane phase is very important parameter that dictates the practical selectivity of the sensor. In the area of membrane based ISEs, emphasis has been focused on the development of new ionophore and on the composition of the membrane phase, aiming at enhancing the potentiometric responses of the ISEs. Fabrication of a new, ion specific ISE with high selectivity and sensitivity, wide linear concentration range, long lifetime, good reproducibility and low cost, is always in need [5,6].

In this paper the compound organophosphates especially TBP will be studied or used as ionophore in membranes in selective electrodes ion. The principle of formation of the measured potential in both surface and transport based on this principle the same as that occurs in the extraction, while the TBP solvent extraction lanthanides have been performed and shown to occur transport from the aqueous phase to organic phase by using TBP. In addition, TBP has not been used as ionophore in potentiometric systems. Hence, to study the character of the membrane on the electrode as a potentiometric sensor, needed characterization, membrane potential, response time, sensitivity, selectivity towards the primary ion and ion bullies are less than 10^{-3} , age (lifetime) is relatively long and has a design size can be miniaturized.

The main objective of this work is to introduce a selective and sensitive electrode for lanthanum, for the potentiometric monitoring of trace amount of La^{3+} , by using TBP as ionophore. In spite of ion selective electrode based on ionophore ligand are well established for many widespread activity in the field of ion selective electrodes during the last two decades, however there is no report previously in the literature TBP as ionophore and its applications for measurement ion La^{3+} .

Experimental

1.1 Equipment

All potentiometric measurement were made at $25 \pm 1^\circ\text{C}$ with Ohmeter instrument pH/mV meter. The glass cell, where the La^{3+} ion selective electrode was placed, and a double junction saturated calomel electrode (SCE) was used as internal reference electrode.

1.2 Chemicals and solutions

Tri butyl phosphate were obtained from Sigma Aldrich. Kerosene from sigma Aldrich, PTFE (Advantec, Japan) with pore size $0,45 \mu\text{m}$ and $0,2 \mu\text{m}$. All other reagents used were of analytical grade and the solutions were prepared in doubly distilled water.

1.3 Membrane and Electrode Preparation

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The method reported by [8,9,10] was adopted for the fabrication of membranes. Membrane prepared in Impregnated Liquid membrane (ILM). Impregnated Liquid membranes used for prepared ESI-La, with Teflon, length 10 cm, and 1,5 diameter. PTFE (Advantec, Japan) with pore size 0,45 μm pore and 0,2 μm pore (impregnated in TBP), immersed for 12 and 24 hours respectively. The saturated calomel electrode and the inner solution (a mixture of 10^{-3} M KCl and 10^{-3} M La^{3+}) was set in the tube and connected to coaxial cable. The electrode was conditioned before potentiometric measurement by immersing it into 10^{-3} M La_2O_3 solution for 12 and 24 hours. A number of membranes of different compositions were prepared and only those which gave reproducible and stable potentials were selected for further studies.

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In this study, the electrode was made and prepared in each different conditions (Membrane thickness, concentration of ionophore TBP, concentration of ionic strength adjuster (ISA), Impregnation time, Influence of pH, Life time, limit detection). The potential response of all the three electrode using PTFE membrane 0,45 μm pore size with TBP in kerosene was investigated by varying the concentration of the test solution from 1.0×10^{-1} - 1.0×10^{-6} [10].

1.4 Potential Measurement

The potential measurements of the solutions, prepared in the concentration range 1.0×10^{-1} - 1.0×10^{-6} M La^{3+} ions, were carried out at 25 ± 1 °C with a Metrohm instrument pH/Ion meter. Saturated calomel electrode were employed as reference electrodes and potential were measured by setting up the following assembly:

Internal Reference electrode (SCE) | internal solutions | Membrane | Test Solutions | External reference electrode

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Result And Discussion

2.1 Working Concentration Range and Slope

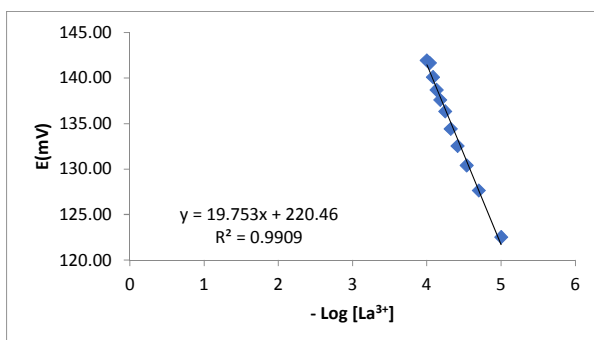


Figure 1. The Calibration curve of the La(III) membrane electrode based on TBP

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2.2 The Effect of pH on the Potential Response

The effect of pH on the potential response of the electrode was studied at different concentration, Standard of 10^{-1} , 10^{-2} , 10^{-3} , 10^{-4} M over the pH range 1-10. A series of solutions of La^{3+} with pH ranging from 1 to 10 were prepared by adding H_2SO_4 and NaOH solutions. Solution potentials were measured by the cell system. pH dependence of the membrane electrode was investigated at 1.0×10^{-3} M La^{3+} concentration in the pH range 1-10 by adjusting the pH solution with H_2SO_4 and NaOH . It was observed that the potential remains constant in the pH range relatively 3-6 and the same was taken as the working pH range of the electrodes. These results indicating the applicability of this electrode in the specific pH range were relatively the same as those reported by other researchers, stating that pH was kept constant at 3-8 [6,7]. On the contrary, relatively noteworthy fluctuations in the potential regarding pH behavior took place below and above the formerly stated pH limit. The fluctuation above the pH value of 6 might be justified by the formation of soluble and insoluble La^{3+} ion hydroxyl complexes in the solution. Hence, the fluctuations below the pH value of 3 were attributed to the partial protonation of the employed ionophore [4]. Considering that deprotonation of the complexes of chelating reagent is one of essential processes for the complex formation. The pH of a sample solutions seem to strongly affect the potentiometric responses. Therefore, influent of protonation and deprotonation complex formation were measured by investigated the pH dependence of the potentiometric responses to the lanthanoid ion.

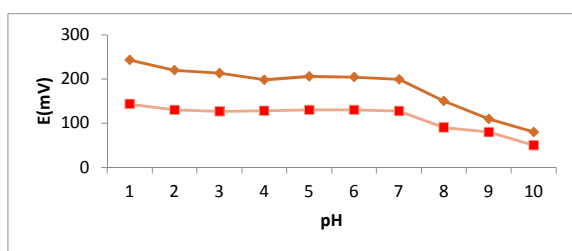


Figure 2. Effect of pH on Potential response of ISE-La(III)

The figure 2 above explained correlation between potentiometric response and pH suggest that the potentiometric responses observed with the membrane to the metal ion are induced by the formation of complexes. A typical potential versus pH curve, increasing solution of pH, potential relatively stable and close to Nernstian slope is 19 mV per decade., was observed from pH ≈ 7 to 2 both 10^{-2} or 10^{-4} concentration. This pH response suggest that TBP impregnated membrane PTFE at the membrane interface successively protonate with increasing the H^+ concentration of the solution.

2.3 The study of sensor properties

The properties of an ion-selective electrode are characterized by parameters like these: measuring range, detection limit, response time.

2.3.1 Measuring range

Range measurements, the linear range of the electrode is defined as part of the calibration curve by linear regression which indicates that the data points do not deviate from linearity by more than 2 mV. Range measurements on an ion selective electrode (ISE) including the linear part of the calibration curve. For some electrodes, this range can be expanded from 1 molar to go down 10^{-6} or even 10^{-7} molar. Under other definitions, measurement range of an ion selective electrode is a range of activity between the highest and lowest limits of detection. But recent studies have shown that the range can be reduced

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to sub-nM detection limit with different methods such as the application of a metal buffer to remove contamination from the aqueous solution, using a cation exchange resin in the internal solution at ISE to keep the main ion activity at a low level constant, uses particles such as silica-gel lipophilic 100 C18 reversed phase into the membrane sensor, using membrane sandwich etc.

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2.3.2 Detection limit

Limits of detection is determined from the graph the relationship between the potential and the concentration of ions La. Based on the graph, it can be determined the limit of detection by the oblique intersection of straight lines and flat. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 9.2×10^{-6} M.

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2.3.3 Response time

Dynamic response time is an important factor for an ion selective electrode [1,6]. In this study, the practical response time was recorded by changing solution with different La(III) concentration from 9.9×10^{-6} - 2.06×10^{-4} M. 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. The response time of the microelectrode was found to be about 20 seconds in the whole concentrations.

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Conclusions

In summary, potentiometric selectivity of polymer-membrane electrodes based on lanthanum is one of method used as quantitative analysis of rare earth elements which are considered as the standard method that has a high accuracy, fast response time, and low detection limits. Hence, electrode was prepared by PTFE impregnated membrane in TBP. The Selectivity of ISE-La showed that electrode didn't respond to alkaline elements and transition element but still respond to lanthanide elements such as Ce^{3+} and Nd^{3+} .

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