Potentiometric Selectivity Of Polymer-Membrane Electrodes Based On Lanthanum With Tributyl phosphate (TBP) as Ionophore

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Abstract: The Quantitative analysis of rare earth elements which are considered as the standard method that has a high accuracy, and detection limits achieved by the order of ppm is inductively coupled plasma atomic emission spectroscopy (ICP-AES). But these tools are expensive and valuable analysis of the high cost of implementation. In this study had made and characterized selective electrode for the determination of rare earth ions is potentiometric method. Membrane manufacturing techniques studied is based on impregnation (liquid impregnated membrane) in PTFE 0.45 pore size. As ionophore to be used is tributyl phosphate (TBP). There is no report previously that TBP used as ionophore in polymeric membrane based on lanthanum. Some parameters that affect the performance of membrane electrode such as membrane composition, membrane thickness, and types of membrane materials studied in this research. Manufacturing of Ion Selective Electrodes (ISE) Lanthanum (La) by means of impregnation La membrane in TBP in kerosene solution has been done and showed performance for ISE-La. FTIR spectrum results for PTFE 0.5 pore size which impregnated in TBP and PTFE blank showed difference of spectra in the top 1257 cm⁻¹, 1031 cm⁻¹ and 794.7 cm⁻¹ for P=O stretching and stretching POC from group -OP=O. The result showed shift wave number for P =O stretching of the cluster (-OP=O) in PTFE-TBP mixture that is at the peak of 1230 cm⁻¹ indicated that no interaction bond between hydroxyl group of molecules with molecular clusters fosforil of TBP or R=O. The membrane had stable responses in pH range between 3 and 8. Good responses were obtained using 10⁻³ M La(III) internal solution, which produced relatively high potential. ISE-La showed relatively good performances. The electrode had a response time of 29±4.5 second and could be use for 50 days. The linear range was between 10⁻⁶ M and 10⁻⁴and shown Nernstian slope 19.34 mV/decade activity.

Keywords – Lanthanum, ESI-La, TBP, PTFE, Ionophore

I. INTRODUCTION

Rare earth elements is known as an important element of their nature, especially having a strong magnetic properties. Rare earth elements found in nature in the form of minerals such as monazite and xenotime. Both 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 and xenotime ore processing technology still needs to be improved and strengthened. REE are now widely used for the manufacture of goods innovative high-tech, such as permanent magnets, catalysts, fiber optics, optoelectronics, ceramics pizoelectric, rechargeable batteries, microwave equipment, etc., so that now the element REE has regard.

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Potentiometric Selectivity Of Polymer-Membrane Electrodes Based On Lanthanum and TBP as criteria, simple in execution and relatively inexpensive. One method that has the potential of the electrode is the potentiometric method with membrane. 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 [5]. 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 ionophores required. Therefore, it is feasible the development of methods to make sensors for lanthanide ions with high selectivity using the appropriate ionophores. 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. The extraction solvent has managed quite well for the extraction of REE\textsuperscript{3+} with supported liquid membrane (SLM) using organophosphate compounds such as TBP, TOPO, and EHEHP D\textsubscript{2}EHP. Hence, in this paper the compound will be studied or used as ionophores 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 of lanthanides have been performed and shown to occur transport from the aqueous phase to organic phase by using TBP. In addition, this compound have not been used as ionophore in potentiometric systems. 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\textsuperscript{3+} using TBP as ionophore.

II. MATERIAL AND METHOD

Tributyl phosphate (TBP) was obtained from Sigma Aldrich. High molecular weight poly(vinyl chloride), potassium tetrakis (4-chlorophenyl) borate (KTCPB), o-nitro phenyl octyl ether (NPOE), PTFE (Advantec, Japan) with pore size 0.45 µm pore and 0.2 µm pore. All other reagents used were of analytical grade and the solutions were prepared in doubly distilled water.

The method reported by Suyanta [6] and Jain A.J et. al., [7] was adopted for the fabrication of membranes. Membrane prepared in two method, Impregnated Liquid membrane (ILM). Impregnated Liquid membranes used for prepared ESI-La, with Teflon, length 10 cm, 1.5 diameter. PTFE (Advantec, Japan) with pore size 0.45 µm pore and 0.2 µm pore (impregnated in TBP), for 12 and 24 hours respectively. The electrode was prepared by gluing the electrode tube to the membrane. The inner reference electrode Ag/AgCl and the inner solution (a mixture of 10\textsuperscript{-3} M KCl and 10\textsuperscript{-3} M La\textsuperscript{3+}) was set in the tube and connected to coaxial cable.

III. POTENTIAL MEASUREMENT

The potential measurements of the solutions, prepared in the concentration range 1.0×10\textsuperscript{-1} - 1.0×10\textsuperscript{-6} M La\textsuperscript{3+} ion, were carried out at 25±1 °C with a Keithly 6 ½ instrument pH/Ion meter. Leak less Ag/AgCl electrode (EDAQ) were employed as reference electrodes and potential were measured by setting up the following assembly:

Internal Reference electrode/internal solutions/ Membrane/ Test Solutions/External reference electrode

IV. RESULT AND DISCUSSION

WORKING CONCENTRATION RANGE AND SLOPE

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\textsuperscript{-1} - 1.0×10\textsuperscript{-6}.

![Figure 1](image1.png)

**FIGURE 1.** Curve calibration for Electrode 3
The electrodes was made three electrodes, electrode 1, 2, and electrode 3. Hence, each electrode was impregnated in TBP which is various concentration. The electrodes 1 and electrodes 2 exhibit linear potential in the concentration range 2.5×10^{-1}-1.0×10^{-6} and 2×10^{-1}-1.0×10^{-6} with near-Nernstian slope 15.44 and 18.66 mV per decade activity, respectively. Meanwhile, the result showed that electrode 3 which is impregnated in TBP not only exhibit more linear potential response in the concentration range 1.5×10^{-1}-1.0×10^{-6} but also with more a ideal-Nernstian slope of 19.34 mV per decade activity. It is important to mention that the addition of plasticizers did not improve the performance of the membranes. This observation may be ascribed to the fact that TBP themselves act as plasticizers and have been used earlier for this purpose [7].

The spectrum results showed in Figure 2 below (circle) for PTFE 0.2 pore size which impregnated in TBP and PTFE blank showed difference of spectra in the top 1257 cm^{-1}, 1031 cm^{-1} and 794.7 cm^{-1} for P=O stretching and stretching POC from group -OP=O. The result showed shift wave number for P=O stretching of the cluster (-OP=O) in PTFE-TBP mixture that is at the peak of 1230 cm^{-1} indicates that no interaction bond between hydroxyl group of molecules with molecular clusters fosforil of TBP or R_3P = O.

**Figure 2.** Spectrums FTIR for PTFE membrane impregnated in TBP

**Effect of pH on the Potential Response**

A series of solutions of La^{3+} with pH ranging from 1 to 10 were prepared by adding H_2SO_4 and NaOH solutions was showed in Figure 3 below. 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 4-9 and the same was taken as the working pH range of the electrodes. These results were relatively the same as those reported by other researchers, stating that pH was kept constant at 3-8 [6] and 3-9 [5].

**Figure 3.** Effect of pH on the potential response
From the table 1 it is seen the potential response of all the three electrodes using membranes of PTFE and TBP of different composition was investigated by varying the concentration of the test solution from 105×10⁻¹ to 1.0×10⁻⁶. The results obtained are given in Table 2 for the response time each electrode. It is seen that the electrodes no. 1 and 2 having membranes of exhibit linear potential response in the concentration range but slope are closely to Nernstian-law. Hence, the electrode 3 showed ideal to Nernstian-law. Moreover, the table 2 shown response time of electrode 1, 2, and 3 respectively. It is seen that electrode 3 has the faster response comparing with electrode 1 and 2.

V. CONCLUSION

Among the three PTFE impregnated membrane, the ones having good performance with regard to the working electrodes and shown Nernstian slope 19.34 mV per decade activity. This electrode based on lanthanum with TBP as ionophore can give fast response and used as a sensor for analytical application for Lanthanum from monazite and xenotime ore.

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