Study of the effect of ionophore carbon chain length on the selectivity of the Nd (III) ion selective electrode

S. Husain1, B Buchari2 and N. Indra2
1Chemistry Department Tadulako University, Palu Indonesia
2Chemistry Department Bandung Institute of Technology, Bandung Indonesia
Email: husainasfah.chem@gmail.com

Abstract. Ion selective electrode method is used for analyzing certain metal ions in a sample with ionophore as the link between two different solutions. The compounds 4-adipoybis (1-phenyl-3-methylpyrazolone-5) (H2AdBP) and 4-sebacoylbis (1-phenyl-3-methylpirazolone-5) (H2SbBP) are the same two types of ionophores but differ in the length of carbon chain. Both ionophores were used in potentiometric analysis of Nd3+ ion and showed that H2AdBP-Nd electrode had a slightly smaller detection limit, namely 1.91 x 10^-5 M with a sensitivity of 15.9 ± 2.2 mV/decade with a response time of 23 seconds, compared to the H2SbBP-Nd electrode with a detection limit of 2.88 x 10^-5 M, sensitivity of 21.9 ± 1.1 mV/decade and response time of 22 seconds. The effect of pH on the electrode performance was studied by varying the pH, concentration of ISA KNO3 and composition of the internal solution. Good electrode performance was obtained at pH 3 and the electrode sensitivity increased to pH 4. The electrode selectivity was carried out using a separate solution method (SPM) for the La3+, Ce3+ and Th4+ ions. The determination results of ESI-Nd electrode showed that ESI-Nd electrode was not selective against La3+ and Ce3+ ions but selective to Th4+ with values $K_{Nd/i}^{pot} < 1$.

1. Introduction
The ion selective electrode (ISE) is a potentiometric analysis method that has high accuracy because it is able to measure concentrations up to ppb units. This ability is supported by several factors, including ionophores as ion carriers from external solutions to internal solutions, membranes that function as boundaries and Ag/AgCl electrodes as electron carriers to potential sensors. Each ionophore has a different character depending on the number of free electron pairs, its molecular structure and also the size of the space or template available.

Neodymium, Nd is a rare earth element that has the potential to be explored because it has great potential in supporting the development of advanced technology such as the development of electric powered vehicles (hybrid). Nd (III) or ISE-Nd ion selective electrodes have been developed using various types of membranes and various types of ionophores.

Pyrazolone derivatives have been developed for use as complex ionophores ligands in this ISE including 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) [1,2], 1-phenyl-3-methyl-4-trifluoroacetylpyrazol-5-one (HPMAP) [3], 1-Phenyl-3-methyl-4-trifluoroacetyl-pyrazolone-5 (HPMTFP) [4], 4-adipoybis (1-phenyl-3-methyl-5-pyrazolone)(H2AdBP) [4], 4-sebakoilbis (1-phenyl-3-methyl-5-pyrazolone)
(H$_2$SbBP) [5,6] and so on. All types of ionophores are derivatives of pyrazolone compounds that are synthesized from phenyl-methyl-pyrazolone (PMP) with various other types of compounds that can provide the ability to bind metal ions in coordination through available free electron pairs [7]. The ability of these pyrazolone derivatives to bind and deliver electrons from metal ions (ionophores) is influenced by the number of available lone pairs, the shape of their structure and the size of the molecule. This is what makes these compounds usable as ligands in the extraction of various metals [8,9].

The shape and size of the ionophores are determined by the type of substituent (reagent) used which will also determine the number of available lone pairs. The HPMBP ionophore compound has an open structure and only has two oxygen atoms which can provide a lone pair of electrons that can bind metal ions [8]. The H$_2$AdBP and H$_2$SbBP compounds each have four oxygen atoms that have a lone pair of electrons but they have different molecular sizes. H$_2$AdBP has four additional carbon chains while H$_2$SbBP has eight additional carbon chains [10].

The difference in the size and molecular structure of the H$_2$AdBP and H$_2$SbBP compounds will affect the mechanism for the formation of ionophore-ion complexes, especially at the distance (between two oxygen atoms and two other oxygen atoms in the molecule) the bonds that occur between ligands (ionophores) and metal (M). Differences in the strength of the ion-to-ion complexes will affect the potential response of the ESI used [11].

2. Material and method

The materials used in this study include Teflon electrode rods, Pt wire, Ag wire, 0.25 micron diameter PTFE membrane, HCl solution, KNO$_3$ solution, Nd$^{3+}$ standard solution, 10$^{-2}$, 10$^{-3}$, 10$^{-4}$, 10$^{-5}$ and 10$^{-6}$ M, PMP powder, adipoyl chloride, sebacoyl chloride, Buchner filter, filter paper, 4-dioxane solvent, Ca(OH)$_2$ powder and chloroform.

2.1. Synthesis ionophore

H$_2$AdBP and H$_2$SbBP as ionophores were synthesized by mixing PMP with adipoyl chloride and sebacoyl chloride in a synthesis flask using 4-dioxane and Ca(OH)$_2$ as a catalyst. Synthesis was carried out for about 3 hours, the mixture was washed with 2M HCl and filtered until brownish yellow crystals were obtained for H$_2$AdBP and brown crystals for H$_2$SbBP. The results of the synthesis were characterized by FTIR, NMR and MS.

2.2. Electrode prepare

PTFE membranes were immersed in a 1% ionophores solution, the electrodes were immersed in a solution of Nd$^{3+}$ 10$^{-2}$ M for 30 minutes and then dried. The dry membrane was attached to the electrode rod and filled with an inner solution, then the electrode was saturated with a solution of Nd$^{3+}$ 0.2 M.

2.3. Preparation of solutions

The Nd$^{3+}$ 0.1 M solution was prepared by dissolving Nd$_2$O$_3$ in concentrated nitric acid and then diluting it with distilled water. The concentration of the solution varies from 10$^{-2}$M to 10$^{-6}$M with KNO$_3$ solution as an ionic strength adjuster (ISA) made with a concentration of 10$^{-2}$M, the Ag/AgCl electrode is made as a working electrode by inserting into the Teflon electrode rod then filled with internal solution KCl 0.1 M.

2.4. Measurement potential

The Nd$^{3+}$ solution was prepared with a concentration range of 10$^{-2}$ to 10$^{-6}$ M each of 50 mL at pH 5, then the potential was determined using a Metrohm potentiometer and the potential value was recorded in mV units. This potential measurement is done by calculating the electrode response time until a stable potential
number is obtained as the response time. The potential value obtained is directly proportional to the measured concentration of \( \text{Nd}^{3+} \) solution and the electrode response time is independent of the concentration. The electrode potential can be calculated by Nernst equation:

\[
E_{M^{n+}} = E^0 + \frac{2.303 \, RT}{nF} \log a_{M^{n+}}
\]

- \( E_{M^{n+}} \) = potential of electrode (mV)
- \( E^0 \) = standard potential (K)
- \( \frac{2.303 \, RT}{nF} \) = Nernst factor (slope)
- \( a_{M^{n+}} \) = ion activities
- \( n \) = ion charge

3. Results and Discussion

3.1 Synthesis

The results of the synthesis of the two ionophores obtained respectively by \( \text{H}_2\text{AdBP} \) are yellowish brown while \( \text{H}_2\text{SbBP} \) is dark brown. Furthermore, the powder was analyzed with a spectrophotometer (FTIR) showing differences in several wave numbers as listed in Table 1.

| Groups       | \( \tilde{\nu} \) (cm\(^{-1}\)) | \( \tilde{\nu} \) (cm\(^{-1}\)) |
|--------------|----------------------------------|----------------------------------|
| H\(_2\)AdBP  | 3468.01                          | 3458.01                          |
| C-H Ar       | 3074.53                          | 3074.53                          |
| -CH\(_3\)    | 2939.23                          | 2939.52                          |
| -CH\(_2\)-   | 2920.23                          | 2927.94                          |
| C=C          | 1554.63                          | 1631.78                          |
| C=O          | 1625.99                          | 1558.48                          |
| C=N          | 1494.83                          | 1496.78                          |
| C-O          | 1074.35                          | 1292.31                          |

From Table 1 it can be seen that in the two compounds there is a difference in the peak wave number of the -CH\(_2\)- aliphatic group, each of which consists of 4 pieces at 1554.63 cm\(^{-1}\) for \( \text{H}_2\text{AdBP} \) and 8 pieces at 1631.78 cm\(^{-1}\) for \( \text{H}_2\text{SbBP} \) which causes a shift in the peak of C=O group (carbonyl) of 1625.99 cm\(^{-1}\) for \( \text{H}_2\text{AdBP} \) and 1558.48 cm\(^{-1}\) for \( \text{H}_2\text{SbBP} \). The synthesis reactions and the structure of the two ionophores can be seen in Figure 1 and Figure 2 respectively.
Figure 1. H$_2$AdBP synthesis reaction mechanism

Figure 2. H$_2$SbBP synthesis reaction mechanism

Figure 3. The complex formation in membrane a) H$_2$AdBP-Nd and b) H$_2$SbBP-Nd

From the structure of these two compounds, there is only the addition of the -CH$_2$- chain which makes the distance between the oxygen on the left and right sides of the two compounds different which of course will cause a difference in bond strength between the ligands and metal ions. Furthermore, the ionophore is impregnated into the membrane by dissolving into chloroform at a concentration of 1%. The resulting membrane was immersed in a solution of Nd$^{3+}$ 0.1 M to form a ligand-ion complex. The reaction to the formation of ion-ligand complexes can be seen in Figure 3a and 3b, respectively.

3.2. Determination of the optimum pH

A series of Nd$^{3+}$ solutions with concentrations of 10$^{-2}$, 10$^{-3}$, 10$^{-4}$, 10$^{-5}$ and 10$^{-6}$ M respectively with a pH 2 with a volume of 50 mL. The potential solution was measured from a concentration of 10$^{-6}$ M to 10$^{-2}$ M by immersing the electrode in it. The potential value of the solution is recorded once it is stable. Furthermore, the same treatment for solutions with pH 1, 2, 3, 4, 5 and 6. The potential measurement results can be seen in Figure 4. below.
From Figure 4 and 5 above, it can be seen that each membrane has a good response at pH=3 with a Nernst value of 15.9 ± 2.2 mV / dec with $R^2 = 0.8952$ for H$_2$AdBP and 21.9 ± 1.1 mV / decade with $R^2 = 0.9158$ for H$_2$SbBP. The results of this calculation provide data that the H$_2$AdBP-Nd membrane is under Nernstian (<19.73 mV/decade), while the H$_2$SbBP membrane is upper Nernstian (> 19.73 mV / decade).

3.3 Response time electrode

After knowing the pH which has the appropriate Nernst value, the potential for the same solution with a certain pH is measured to calculate the electrode response time. The average response time of the electrodes was calculated based on the measurement data obtained respectively 23 seconds for H$_2$AdBP-Nd and 22 seconds for H$_2$SbBP-Nd electrodes. This data shows that electro has a fairly good response time because it is less than 30 seconds.

3.4 Selectivity ($K$)

The selectivity is determined by making a solution with the appropriate pH but the solution used contains different ions, namely Nd$^{3+}$, La$^{3+}$, Ce$^{3+}$ and Th$^{4+}$ solutions. All solutions were made with the same concentration and pH variations. The determination of the selectivity of the Nd electrode against other metal ions is calculated according to the following formula.

$$K_{Nd^{3+}/N^{m+}}^{pot} = \frac{10^{\Delta E/0.057}[Nd^{3+}]}{[N^{m+}]}$$  \hspace{1cm} (2)
The results of measurement and calculation of the electrode potential selectivity coefficient $K_{Nd^{3+}/N^{3+}}^{pot}$, it is found that the two electrodes are not selective to the La$^{3+}$ ion, Ce$^{3+}$ ($K_{Nd^{3+}/N^{3+}}^{pot} = 1$), while the Th$^{4+}$ ion is selective ($K_{Nd^{3+}/N^{3+}}^{pot} < 1$) or 0.58.

4. Conclusion

The results of research regarding the manufacture and use of selective electrodes of Nd (III) ions with two ionophores with different carbon chain lengths, obtained the following conclusions. First, H$_2$AdBP electrode with a shorter –CH$_2$– carbon chain has a lower Nernst value of 19.73 which is 15.9 ± 2.2 mV/decade, while the H$_2$SbBP electrode is 21.9 ± 1.1 mV/decade. Second, electrode selectivity only occurs in different types of Th$^{4+}$ ions (0.58), while the same type of ion is not selective ($K_{Nd^{3+}/N^{3+}}^{pot} = 1$). Overall, pH and concentration of ISA KNO$_3$ highly influence the potential electrode response.

Reference

[1] Sosidi H, Noviandri I and Buchari B 2017 Int. J. of Appl. Science and Tech. 7 47-59
[2] Rusnadi R, Buchari B and Widyaningrum D 2012 International Journal of Engineering Research and Applications (IJERA) 2 496-499
[3] Sosidi H, Noviandri I and Buchari B 2019 J. Scientific net. 811 153-157
[4] Chukwu U J and Godwin J 2013 American Chemical Science Journal 3 479-488
[5] Devadas B, Rajkumar M, Chen S M and Saraswathi R 2012 Int. J. Electrochem. Sci. 7 3339–3349
[6] Qizhou D, Hong S, Yijing X, Jianmeng C 2012 Int. J. Electrochem. Sci. 7 10054-10062
[7] Saraswathyamma B and Kumar K G 2016 International Journal of Advanced Research in Chemical Science (IJARCS) 3 30-37
[8] Singh K. A, Singh J and Jain K A 2010 Electroanalysis 22 2447-2452
[9] Tyagi D S and Singh A 2013 Journal of Analytical Chemistry Research 1 37 - 45
[10] Dhanapala L, Colleen E Krause, Abby L Jones and James F Rusling 2020 Biosensors 10 115
[11] Jeromiyas N, Mani V, Chang P-C, Huang C-H, Salama K N and Huang S-T 2020 Sensors & Actuators: B. Chemical 326 128844