

## Synthesis and Characterization of 1-phenyl-3-methyl-4-benzoylpyrazolone-5 (HPMBP) and its application as Ionophore in Neodymium (III) Selective Membrane Electrodes

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### Abstract

*It has been successfully synthesized and characterized of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) to be used as ionophore in neodymium(III) selective membrane electrode. This electrode has been used as indicator electrode for determination of Nd(III) potentiometrically. The performance of the electrode has been investigated in  $10^{-6}$  to  $10^{-2}$  M of  $Nd^{3+}$  standard solution at pH 4 and ionic strength adjusted by  $10^{-2}$  M of KCl. Sensitivity and limit detection of the electrode is  $39.91 \pm 1.33$  mV/decade and  $1.02 \times 10^{-4}$  M of  $Nd^{3+}$  respectively. The response time of the electrode is 22 second and its life time is 3 week. The electrode has been tested for determination of  $Nd^{3+}$  concentration in real sample solution of Bangka monasit sand prepared by Centre Research of Mineral and Coal Mine-Bandung. The result has a good agreement with the  $Nd^{3+}$  concentration determined by ICP-OES.*

**Keywords:** ion selective electrode, HPMBP, neodymium.

### 1. Introduction

1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP), can be synthesized by reacting 1-phenyl-3-methyl-5-pyrazolone (PMP) with benzoyl chloride in dioxane as solvent. This condensation reaction may take place with calcium hydroxide,  $Ca(OH)_2$  as catalyst[1]. HPMBP is often used as a ligand, either in solvent extraction or column chromatography to extract and separate lanthanide and actinide metal ions, and some bivalence metal ions such as  $Ba^{2+}$ ,  $Cu^{2+}$ ,  $Pb^{2+}$ ,  $Co^{2+}$  and  $Mg^{2+}$  from water[2]. The extraction of  $Ba^{2+}$  and  $Eu^{2+}$  can be extracted in acidic solution with HPMBP as ligand in chloroform, benzene, and octanol as organic phase[3]. Several experiments which have been performed by liquid-liquid extraction with HPMBP either as single-ligand and as synergistic system with other ligands such as tri-n-octylphosphine oxide (TOPO), tributylphosphat (TBP), the n-oyltrifluoroacetone (HTTA), crown ether (CE), Aliquat-336 (QC) and with n-octylphenyl(N,N-diisobutylcarbamoyl-methyl) phosphine oxide (CMPO)[4]. Table 1 show some investigation of utilization of HPMBP as a single ligand, and as a synergistic system with other ligands for metal extraction purpose. Base on the performance of HPMBP as ligand in the extraction of rare earth element, it is also possible that these compounds are used as ionophore in ion selective membrane electrodes (ISE). The expectation in this investigation is that the membrane electrode will have good selectivity and sensitivity, low detection limits, short response times, and long time of usage. This investigation has been started by synthesizing and characterizing the HPMBP, and studied its potentiometric performance as ionophore for determination of Nd(III).

**Table 1 Utilization of HPMBP as a single ligand, and as a synergistic system with other ligands for metal extraction**

Ion	extractants	solvent	reference
Eu <sup>3+</sup> and Sc <sup>3+</sup>	HPMPBP with TOPO		5 – 10
Pr <sup>3+</sup> , Gd <sup>3+</sup> and Yb <sup>3+</sup>	Synergistic HPMPBP-1-(2-pyridylazo-2-naphthol), HPMPBP- tri-n-octylamine, HPMPBP-TOPO	Synergic of C <sub>6</sub> H <sub>6</sub> , CHCl <sub>3</sub> , CCl <sub>4</sub>	5 – 10
La <sup>3+</sup> , Eu <sup>3+</sup> and Am <sup>3+</sup> ,	Synergistic HPMBP- CMPO, HPMBP-TBP-TOPO, and HPMBP-bis(2ethylhexyl) sulphoxide (B2EMSO), HPMBP-CMPO, HPMBP - B2EMSO		5 – 10
Pr <sup>3+</sup> , Gd <sup>3+</sup> and Yb <sup>3+</sup>	<b>HPMBP-tridodecyl-ammonium(TDAHA), HPMBP-dioctyl-ammonium (DOAHA), and trioctylammonium (TOAHA),</b> HPMBP-Aliquat 336, HPMBP with primary ammonium salts, and HPMBP-Aliquat336-Ion ammonium salts		11-13
Lu <sup>3+</sup> , Th <sup>4+</sup> , Mo <sup>6+</sup> , alkali metals and alkaline earth	HPMBP		14-17
Ce <sup>3+</sup> , La <sup>3+</sup> and Pr <sup>3+</sup>	HPMBP vs HPMBP-TIBPS		18-19
Ce <sup>3+</sup> adsorption	HPMBP incapsulated in alginate		

The Nd<sup>3+</sup>-ISE prepared is an indicator electrode with internal filling solution type, using a Teflon tube as body of the electrode, and 0.45µm pore size of polytetrafluoroethylene (PTFE) membrane as sensing material. The membrane was prepared by impregnation procedure in ionophore solution. Therefore, potential's response of the electrode is strongly influenced by the ionic strength and pH of the solution, it is necessary to examine the influence of these two factors.

The standard method for REE's analysis in general are AAS, ICP/ICP-MS, and ICP-OES. Meanwhile, the conventional method of REE's analysis is gravimetric[20-21]. However, such methods require sample manipulation, time consuming, substantial cost and expensive equipment. The ion selective electrode (ISE) is one of the simple potentiometric methods used for analyzing Nd<sup>3+</sup>, Pr<sup>3+</sup> and Dy<sup>3+</sup>. Ion selective electrode for determination of La<sup>3+</sup>, Nd<sup>3+</sup>, Pr<sup>3+</sup>, Dy<sup>3+</sup>, and Ce<sup>3+</sup> have been designed using trithiane as ionophore. In the last of 2 decades, potentiometric analysis by ISE is still well developed because this method is cheap, simple to operate, sensitive, selective, and environmentally friendly(22-24).

## 2. Experiments

### Chemicals

All chemicals used were pro-analysis grade such as 1-phenyl-3-methylpyrazolone-5 (PMP) (Fluka), Ca(OH)<sub>2</sub>, (Sigma Aldrich), HCl (Merck), benzoyl chloride (Merck), 1,4-dioxane (Merck), Nd<sub>2</sub>O<sub>3</sub> (Sigma Aldrich), NaOH (Merck), HNO<sub>3</sub> (Merck), Ag wire, and Teflon tube.

### Instrument

The equipment involved in this investigation were, hotplate (Thermolyte), three-neck flask, thermocouple (Mirak), Büchner funnel, melting point apparatus, Fourier transform infrared spectrophotometer (Shimadzu/Prestige), nuclear magnetic resonance spectrophotometer (<sup>1</sup>HNMR) and (<sup>13</sup>CNMR), mass spectrophotometer (MS) and potentiometer/ion meter (Metrohm, type 692).

### 3. Procedure

#### 3.1. Synthesis and characterization of HPMBP

The synthesis was carried out by dissolving 57.4mmol of 1-phenyl-3-methylpyrazolon-5 (PMP) in 50mL of 1,4-dioxane which placed in a three-neck flask. The mixture was heated to 50°C for 20 minutes, and than added 8 grams of Ca(OH)<sub>2</sub>, 10mL of benzoyl chloride dropwise and 50mL of 1,4-dioxane. The mixture temperature was raised slowly until it reached 110-120°C and then was allowed for 3 hours while stirring with a magnetic stirrer. After 3 hours the mixture was allowed to cooldown to room temperature, and added with 100mL of 2M HCl, and was shaken for 10 minutes to obtain a yellowish brown precipitate. The precipitate was filtered with a Buchner funnel and then washed with water until neutral. Other organic impurities are removed with ethanol treatment. The obtained HPMBP crystal was a bright yellow powder. Characterization was performed by determination of its melting point, infrared absorption spectrum (FTIR), proton and carbon nuclear magnetic resonance spectrum (<sup>1</sup>HNMR, and <sup>13</sup>CNMR), and molecular mass spectrum (Masspec).

#### 3.2. Preparation of HPMBP-Nd membrane system

The sensing membrane was prepared by immersing PTFE membrane in a 1.5 - 2.0% w/v HPMBP solutions in chloroform for 24 hours. After that the membrane was dried at room temperature, than attached to tubular type electrode body made of Teflon with 10 cm length, 1.5 cm diameter and 0.5 cm hole. The electrode body which has been equipped by membrane and Ag/AgCl internal reference electrode then was filled with internal solution consist of KCl and Nd<sup>3+</sup> with certain ratio. Finally HPMBP-Nd electrode was ready to investigate.

#### 3.3 Determination of HPMBP-Nd membrane potential

First, measurement of potential of the electrode was carried out to optimize pH of the analyte which are performed by adjusting the pH of the solution using HCl and NaOH. Base on the solubility product constant, *K<sub>sp</sub>*, value of the Nd(OH)<sub>3</sub>, the pH optimization was varied not more then pH 7. The Nd(III) selective membrane electrode potential was evaluated based on the Nernst equation[25].

$$E_{Nd^{3+}} = K + \frac{2,303RT}{zF} \log[Nd^{3+}] \quad (1)$$

Where, K = constant

R = 8,314 j,mole<sup>-1</sup>.K<sup>-1</sup>

F = Faraday constant (96,485 coulomb.mole<sup>-1</sup>)

T = temperature (K)

z = ionic charge

At room temperature, the Nernst equation can be simplified into:

$$E_{Nd^{3+}} = K + \frac{0,05916}{3} \log[Nd^{3+}] \quad (2)$$

The electrode potential of a series of Nd<sup>3+</sup> standard solutions with concentrations of 10<sup>-6</sup> to 10<sup>-2</sup>M can be mentioned to be Nernstian if the slope of the linear curve or its sensitivity satisfies the following equation:

$$S = \frac{0,05916}{3} = 19.72 \text{ mV/decade} \quad (3)$$

#### 3.3. Influence of the pH and the Ionic Strength Adjuster (ISA)

A series of standard solutions of 10<sup>-6</sup> to 10<sup>-2</sup>M Nd<sup>3+</sup> were prepared using the KCl as ISA with its concentrations varied 10<sup>-4</sup>M, 5 x 10<sup>-4</sup>M, 10<sup>-3</sup>M, 5x10<sup>-3</sup>M, 10<sup>-2</sup>M, 5x10<sup>-2</sup>M and 10<sup>-1</sup>M, and its pH varied for each sequence concentrations of 1, 2, 3, 4, 5, 6 and 7.

#### 3.4 Range of Concentration and Limit of Detection

The range of concentration and limit of ESI-Nd detection with HPMBP as ionophore was carried out by measuring the electrode potential in a solutions of Nd<sup>3+</sup> with concentration range of 10<sup>-6</sup>M to 10<sup>-2</sup>M. From the linear curve of electrode potential versus the Nd<sup>3+</sup> concentration, one can determine the slope (sensitivity), intercept (electrode constant) and linearity (*R*<sup>2</sup>) of the curve.

#### 3.5 Response Time and Life Time

The response time of the HPMBP-Nd electrode is determined by measuring the potential of the electrode from initially it immersed in solution studied until the time taken a stable potential.

Life time of the electrode are determined since the first time of application of the electrode for measurement until the time which the electrode no longer provides a slope that qualifies Nernstian.

### 3.6 Determination of Potentiometric Selectivity Coefficient ( $K_{ij}^{pot}$ )

The potentiometric selectivity coefficient ( $K_{ij}^{pot}$ ) of the HPMBP-Nd membrane electrode was determined by separate match potential methods (SMPM). In principle, one made a measurement of electrode potential in solution contain only  $Nd^{3+}$  ( $E_i$ ) and in solution contain only interfering ions ( $E_j$ ). The concentration of respective ion was  $10^{-6}$  M to  $10^{-2}$  M. The  $K_{ij}^{pot}$  was calculated from the concentration of measuring and interference ion at same electrode potential. If it suppose that response of the electrode has same sensitivity (slope), the calculation of potentiometric selectivity coefficient of the HPMBP-Nd electrode was performed by following equation:

$$a_{Nd} = K_{Nd/j}^{pot} \cdot a_j \quad (4)$$

But, if each response potential has different sensitivity (slope), the  $K_{Nd/j}^{pot}$  can be determined by following some of the following equations:

$$E_{Nd} = K_{Nd} + \frac{2,3 RT}{z_{Nd} F} \log a_{Nd} = K_{Nd} + S_{Nd} \log a_{Nd} \quad (5)$$

and the solvent-containing solution alone used the equation:

$$E_j = K_j + \frac{2,3 RT}{z_j F} \log K_{Nd/j}^{pot} a_j^{z_{Nd}/z_j} = K_j + S_j \log K_{Nd/j}^{pot} a_j^{z_{Nd}/z_j} \quad (6)$$

if  $E_{Nd} = E_j$ ,

$$K_{Nd} + S_{Nd} \log a_{Nd} = K_j + S_j \log K_{i/j}^{pot} a_j^{z_{Nd}/z_j} \quad (7)$$

$$S_j \log K_{i/j}^{pot} a_j^{z_{Nd}/z_j} = (K_i - K_j) + S_{Nd} \log a_{Nd} \quad (8)$$

and simplified to be,

$$K_{Nd/j}^{pot} a_j^{z_i/z_j} = 10^{\frac{(K_{Nd} - K_j) + S_{Nd} \log a_{Nd}}{S_j}} \quad (9)$$

or

$$K_{Nd/j}^{pot} = \frac{10^{\frac{(K_{Nd} - K_j) + S_{Nd} \log a_{Nd}}{S_j}}}{a_j^{z_{Nd}/z_j}} \quad (10)$$

$K_{Nd/j}^{pot}$  = potentiometric selectivity coefficient

$K_{Nd}$  = intercept of Nernst equation for  $Nd^{3+}$ .

$K_j$  = intercept of interference

$S_{Nd}$  = sensitivity of  $Nd^{3+}$ .

$S_j$  = sensitivity of interference

$a_{Nd}$  = activity of  $Nd^{3+}$

$a_j$  = activity of interference

$z_{Nd}$  = ionic charge of  $Nd^{3+}$

$z_j$  = ionic charge of interference

The interference which have been studied were,  $Ce^{3+}$ ,  $La^{3+}$ , and  $Th^{4+}$  in the same concentration.

### 3.7 Use of HPMBP-Nd Electrode in real samples (Monazite)

Finally, the HPMBP-Nd electrode fabricated has been used to analyze the concentration of  $Nd^{3+}$  in the solution resulted from the treatment of monazite sand from Bangka. The result then to be compared with the concentration of  $Nd^{3+}$  in the same sample resulted by standard method.

## 4. Results and discussion

### 4.1 Synthesis and characterization of HMPBP

The HMPBP synthetic was a yellow powder and the yield was 9.0037 g. The powder is easily soluble in chloroform resulting, a yellow solution. Figure 1 show the stoichiometric synthesis reaction of HPMBP from PMP and benzoyl chloride as reactants in presence of  $Ca(OH)_2$  as catalyst and chloroform as solvent.

### Figure 1. Stoichiometric reaction of HPMBP synthesis

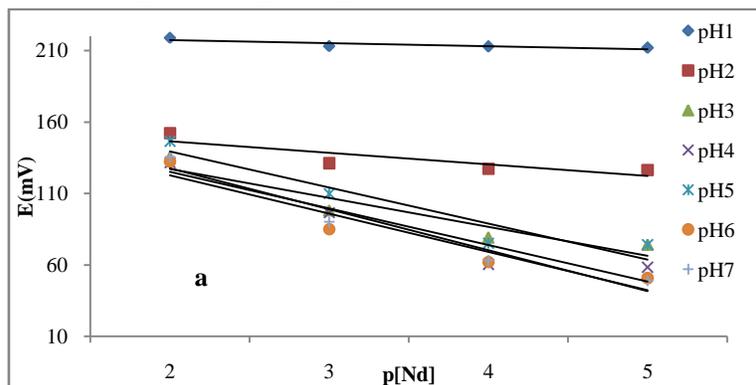
Based on the stoichiometric of reaction, theoretically the product resulted as much as 16.0000 gram. Experimentally, the results obtained was 9.0070g or 56.27% of its rendement. The melting point of the solid obtained in the form of enol, was 92 - 94<sup>0</sup>C. The characterization by infrared spectroscopy show a vibration weak band on  $\bar{\nu}=3053.32\text{cm}^{-1}$  originally from C-H aromatic stretching. The strong and sharp band of  $\bar{\nu}=1598.99\text{cm}^{-1}$  came from the C = C aromatic vibration and  $\bar{\nu}=1560.41\text{cm}^{-1}$  was the vibration of C = O. The C-N vibration band of the pyrazolone ring appear at the wave number  $\bar{\nu}=1496.76\text{cm}^{-1}$  and reappears at  $\bar{\nu}=1192.01\text{cm}^{-1}$ . The C-H vibration band of the methyl group (-CH<sub>3</sub>) appears at wave number  $\bar{\nu}=1444.88\text{cm}^{-1}$  and the vibration band O-H occurs at  $\bar{\nu}=1362.10\text{cm}^{-1}$  and  $\bar{\nu}=1145.72\text{cm}^{-1}$ , whereas the peak of the pyrazolone skeleton appears at  $\bar{\nu}=947.05\text{cm}^{-1}$ . Determination of molecular mass of the compound by mass spectrophotometer is 278.1 z/e (C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>).

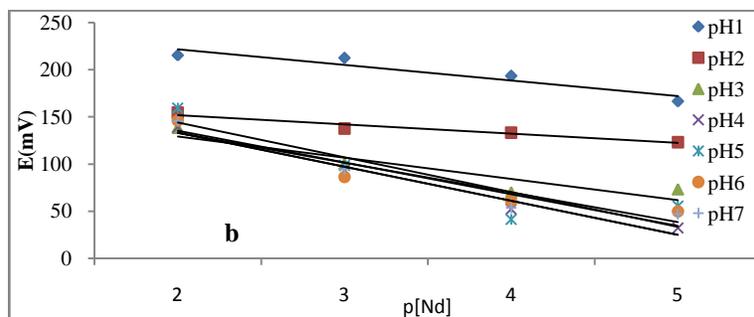
The <sup>1</sup>H NMR spectrum showed a singlet with chemical shift  $\delta_{\text{H}} = 2.11\text{ppm}$  of the -CH= group, proton at C<sub>4</sub> of benzene give triplet signal and indicate 1 proton at  $\delta_{\text{H}} = 7.30 - 7.33\text{ppm}$ . The triplet signal show indicate the 2 protons on C<sub>3</sub> and C<sub>5</sub> atoms of the benzene ring at  $\delta_{\text{H}} = 7.47 - 7.50\text{ppm}$ . The pyrazolone framework appear at  $\delta_{\text{H}} = 7.51 - 7.54\text{ppm}$ . Triple signal with 1 protons of C<sub>4</sub> from the pyrazolone detected at position  $\delta_{\text{H}} = 7.58 - 7.61\text{ppm}$ . Doublet signal with 2 protons on C<sub>2</sub> and C<sub>6</sub> of the benzene ring appear at  $\delta_{\text{H}} = 7.65 - 7.66\text{ppm}$  and from the pyrazolone at  $\delta_{\text{H}} = 7.89 - 7.90\text{ppm}$ . The <sup>13</sup>C NMR analysis the C carbonyl signals at C<sub>4</sub> and C<sub>5</sub> at  $\delta_{\text{C}} = 191.96\text{ppm}$  and  $147.94\text{ppm}$ . C<sub>1</sub> signal from methyl at  $\delta_{\text{C}} = 15.84\text{ppm}$ . The C<sub>2</sub> and C<sub>3</sub> signals of the pyrane ring are at  $\delta_{\text{C}} = 161.50\text{ppm}$  and  $103.60\text{ppm}$ . C<sub>1</sub> - C<sub>6</sub> atomic signals from benzene ring at  $\delta_{\text{C}} = 127.75 - 128.41\text{ppm}$  and C<sub>1</sub> - C<sub>6</sub> from the pyrazolone framework at  $\delta_{\text{C}} = 129.12\text{ppm} - 137.60\text{ppm}$ .

#### 4.2 Influence of pH

The investigation was performed by measuring a series of 10<sup>-3</sup> M of Nd<sup>3+</sup> solutions with a with its pH varied between 1 to 7, that was adjusted using HCl and NaOH. The PTFE membrane as supporting sensing material was performed to determine the pH of analyt solution provide a Nernstian potential response of the electrode. The optimal pH conditions used for the next potential electrode measurements in the varied concentration of Nd<sup>3+</sup> solution, obtained meet Nernst requirements. The results of the influence of pH on the potential response of the electrode which have Nernstian value was obtained at pH 4, and 6. But the pH used for the next analysis parameter was pH 4, because Nd<sup>3+</sup> are very easy to settle at pH more then 6 that can disturb the measurement. Figure 2a and 2b show influence of pH on the response of potential of two HMPBP-Nd membrane electrodes prepared by the same procedure.

Figure 2a. Influence of pH on response potential offirst HPMBP-Nd electrode (code-1).



**Figure 2b. Influence of pH on response potential of second HPMBP-Nd electrode (code-2).**

Meanwhile, Table 2a and 2b show the influence of pH on regression's equation resulted by two HPMBP-Nd membrane electrodes prepared by the same procedure.

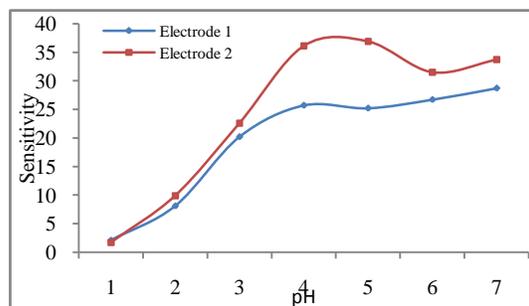
**Table 2a. Influence of pH on potential response of first HPMBP-Nd electrode**

pH	Equation of regression	R <sup>2</sup>
1	$E = 219.5 + 2.1 \log [\text{Nd}^{3+}]$	0.7547
2	$E = 154.5 + 8.1 \log [\text{Nd}^{3+}]$	0.7434
3	$E = 147.3 + 20.2 \log [\text{Nd}^{3+}]$	0.8886
4	$E = 150.8 + 25.7 \log [\text{Nd}^{3+}]$	0.9073
5	$E = 164.4 + 25.2 \log [\text{Nd}^{3+}]$	0.8985
6	$E = 149.3 + 26.7 \log [\text{Nd}^{3+}]$	0.9167
7	$E = 156.2 + 28.7 \log [\text{Nd}^{3+}]$	0.9434

**Table 2b. Influence of pH on potential response of second HPMBP-Nd electrode**

pH	Equation of regression	R <sup>2</sup>
1	$E = 238.4 + 1.7 \log [\text{Nd}^{3+}]$	0.9013
2	$E = 161.8 + 9.9 \log [\text{Nd}^{3+}]$	0.9470
3	$E = 151.8 + 22.6 \log [\text{Nd}^{3+}]$	0.8476
4	$E = 169.4 + 36.1 \log [\text{Nd}^{3+}]$	0.9727
5	$E = 180.9 + 36.9 \log [\text{Nd}^{3+}]$	0.8066
6	$E = 164.5 + 31.5 \log [\text{Nd}^{3+}]$	0.8883
7	$E = 169.2 + 33.7 \log [\text{Nd}^{3+}]$	0.9156

At pH 1 to pH 4 the sensitivity and constant of both electrodes increase significantly, and practically constant at pH 4 to pH 7. Based on the above table, the influence of pH on the potential response of the electrode which have Nernstian value was obtained at pH 4, and 6. But the pH, used for the next parameter investigation was pH 4. At pH 6,  $\text{Nd}^{3+}$  is very easy to settle and consequently the measurement at pH 6 and more will disturb by hydroxide of the Nd(III). The limit of the concentration can be predicted based on the  $K_{sp}$  of the hydroxide of Nd(III). In general the value of REE's  $K_{sp}$  lie between  $1.0 \times 10^{-22}$  to  $9.4 \times 10^{-27}$ , means that REE's ions will precipitate at pH 6. More clearly the influence of pH on the sensitivity of the two HPMBP-Nd electrodes prepared by same procedure can be seen in Figure 3 below.

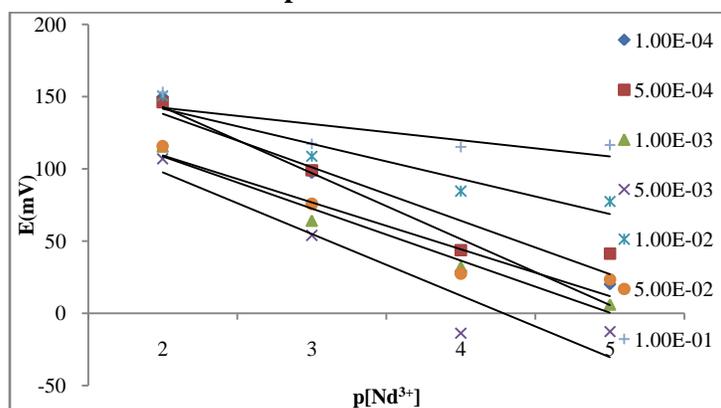
**Figure 3. The influence of pH on sensitivity of two HPMBP-Nd electrodes prepared by same procedure**

At pH 1 to pH 4, the sensitivity of both electrode increase significantly and practically constant at pH 5. The  $\text{Nd}^{3+}$  concentration could be predicted from the solubility of hydroxide of Nd(III). This prediction can be proved that, although the precipitate appear, both electrodes show the potential response to  $\text{Nd}^{3+}$  concentration, and this is the limitation of performance of HPMBP-Nd electrode.

#### 4.3 Influence of ISA concentration

Beside influence of pH on the performance of the membrane electrodes, it will be important to investigate the influence of the stability and ionic strength of the solution. The ionic strength and ions stability determined by the ionic strength adjuster (ISA) which serves to maintain ionic strength in solution at various concentrations. According to the Debye-Huckel equation, ionic strength is defined as  $I = 1/2 \sum C_i z_i^2$  and  $a_i = \gamma_i C_i$ , where  $\gamma_i$  is the activity coefficient obtained from the equation  $-\log \gamma_i = 0.5 z_i^2 \sqrt{I}$ . In this study, ISA of the solution was maintained by KCl with a concentration of  $10^{-4}\text{M}$  to  $10^{-1}\text{M}$ . The ISA should not react with the analyte and should not affect the measurement (non interfering). The measurement of the electrode potential response of ion selective electrode is then carried out at pH 4 with a concentration variation of ISA solution from  $10^{-4}\text{M}$  to  $10^{-1}\text{M}$ . The curve of HPMBP-Nd electrode potential measurement can be seen in Figure 4. Performance of the electrode is showed by regression equation's parameters.

**Figure 4. The HPMBP-Nd electrode potential curve at various ISA KCl concentrations.**



**Table 3. Regression equation of HPMBP-Nd electrode response at various concentrations of ISA KCl**

KCl (M)	Regression equation	R <sup>2</sup>
$1 \times 10^{-4}$	$E = 188.55 \text{ mV} + 45.7 \text{ mV/decade } \log [\text{Nd}^{3+}]$	0.9331
$5 \times 10^{-4}$	$E = 175.10 \text{ mV} + 37.0 \text{ mV/decade } \log [\text{Nd}^{3+}]$	0.9088
$1 \times 10^{-3}$	$E = 144.65 \text{ mV} + 36.1 \text{ mV/decade } \log [\text{Nd}^{3+}]$	0.9746
$5 \times 10^{-3}$	$E = 140.25 \text{ mV} + 42.7 \text{ mV/decade } \log [\text{Nd}^{3+}]$	0.8943
$1 \times 10^{-2}$	$E = 166.15 \text{ mV} + 24.4 \text{ mV/decade } \log [\text{Nd}^{3+}]$	0.9078
$5 \times 10^{-2}$	$E = 141.85 \text{ mV} + 32.5 \text{ mV/decade } \log [\text{Nd}^{3+}]$	0.9197
$1 \times 10^{-1}$	$E = 153.60 \text{ mV} + 11.2 \text{ mV/decade } \log [\text{Nd}^{3+}]$	0.6160

From Fig. 4. and Table 3 .its can be seen that a good ISA concentration is  $10^{-2}\text{M}$ , as it gives a sensitivity of 24.4mV/decade. The sensitivity of the electrode obtained is upper Nernstian, but practically close to the Nernstian factor (19.71mV/decade). For the next, the ISA concentrations used is  $10^{-2}\text{M}$  of KCl. This decision to be taken based on the calculations of ionic strengths, that with ISA concentrations smaller than  $10^{-2}\text{M}$  did not provide significantly changes in ionic activity of  $\text{Nd}^{3+}$ .

#### 4.4 Influence of internal solution

The composition of the internal solution should be adjusted to allow a complex equilibrium of ionophores on the inside of the membrane. The influence of internal solution compositions on the sensitivity and constant of HPMBP-Nd electrodes can be seen in Table 4. Performance of the electrode is showed by regression equation's parameters, R<sup>2</sup>, S and K.

**Table 4. Influence of internal solution composition on the HPMBP-Nd electrode performance**

Internal solution	Composition					
	1	2	3	4	5	6
KCl [M]	$2.5 \times 10^{-4}$	$3.3 \times 10^{-4}$	$5 \times 10^{-4}$	$6 \times 10^{-4}$	$6.7 \times 10^{-4}$	$7.5 \times 10^{-4}$
Nd <sup>3+</sup> [M]	$7.5 \times 10^{-4}$	$6.7 \times 10^{-4}$	$5 \times 10^{-4}$	$4 \times 10^{-4}$	$3.3 \times 10^{-4}$	$2.5 \times 10^{-4}$
R <sup>2</sup>	0.7868	0.8061	0.8037	0.7271	0.8302	0.8291
S	19.8	30.5	27.1	21.0	24.7	28.8
K	134.4	24.0	126.9	129.8	134.7	159.4

Based on Table 4. the respective concentration ratios between Cl<sup>-</sup> and Nd<sup>3+</sup> in internal solutions that provide a Nernstian sensitivity value are  $2.5 \times 10^{-4}$ M and  $7.5 \times 10^{-4}$ M or a volume ratio of 1: 3 in concentrations of  $10^{-3}$ M.

#### 4.5 Response time

The response time of the electrode is calculated as the HPMBP-Nd electrode begins to be dipped in the solution until a stable potential value is obtained on the analyte with a concentration range of  $10^{-7}$ M to  $10^{-2}$ M. The HPMBP-Nd electrodes are used measuring consecutively from small concentrations to large concentrations ( $10^{-7}$ ,  $10^{-6}$ ,  $10^{-5}$ ,  $10^{-4}$ ,  $10^{-3}$  and  $10^{-2}$ M). Results of HPMBP-Nd electrode response time determination can be seen in Table 4.

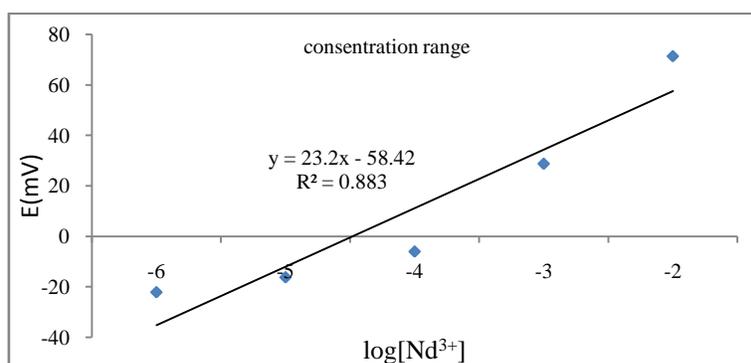
**Table 5. Response Time of HPMBP-Nd electrode**

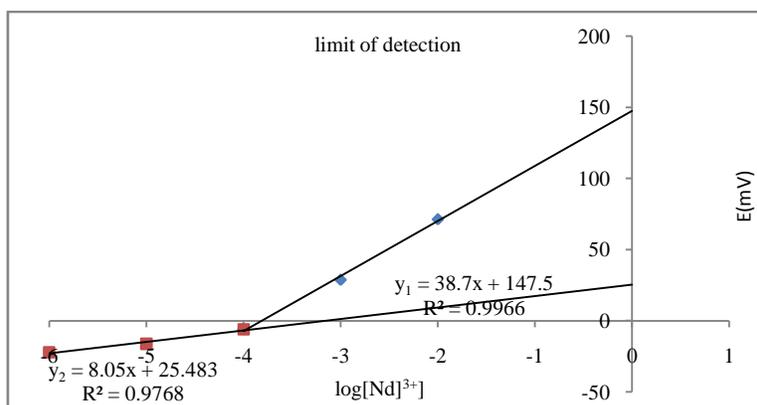
p[Nd <sup>3+</sup> ]	2	3	4	5	6	7	R	S	K
E(mV)	67.8	37.1	8.4	-10.3	-17.2	-23.3	0.9565	18.2	93.2
t(s)	18	18	34	16	25	21	Average 22 s		

From Table 5. the response time of the HPMBP-Nd electrode at various concentrations of the solution averaged 22 seconds, while the determination of response time with a fixed concentration of  $10^{-3}$ M and repeated measurements obtained faster response time ie less of 20 seconds.

#### 4.6 Concentration range and detection limit

The concentration range of the HPMBP-Nd electrode is performed using multiple electrodes. The concentration range is known from curves that still follow Nernst's law while the detection limit is determined from the intersection of two straight lines of Nernstian and non-Nernstian[28]. The measurement range values and the detection limit of the electrodes can be seen in Figure 5.

**Figure 5. Concentration range and detection limit of HPMBP-Nd electrode**



Determination of HPMBP-Nd electrode detection limit is done by joining the two equations of curves in Figure 7. as follows. with

$$y_1 = 38.7x + 147.5$$

$$y_2 = 8.1x + 25.4$$

if  $y_1 = y_2$  will be obtained;

$$38.7x + 147.5 = 8.1x + 25.5$$

or

$$38.7x - 8.1x = 25.5 - 147.5$$

than,

$$30.6x = -122$$

so

$$x = -122/30.6 = -3.99$$

$$\log [x] = 10^{-3.99} [x] = 1.02 \times 10^{-4}M$$

Then the limits of HPMBP-Nd electrode detection to the concentration of  $Nd^{3+} = 1.02 \times 10^{-4}M$  solution.

#### 4.7 Test of realibility

After the optimum condition of HPMBP-Nd potential measurement is obtained then determined the toughness of the electrode. By using several electrodes, the calculation of each parameter as in Table 8. follows.

**Table 8. Potential for determination of toughness of HPMBP-Nd electrode**

p[Nd]	Electrode								Aver age	SD
	1	2	3	4	5	6	7	8		
5	-71.9	-66.9	-68.8	-66	-67.3	-67.3	-52.1	-75.4	-67.0	6.33
4	-73	-65.9	-64.5	-56.8	-66.3	-72.6	-63	-66.3	-66.1	4.86
3	-14.1	-5.8	-6.2	-11.6	-11.3	-13.3	-12.1	-14.1	-11.1	3.09
2	47.3	53.1	53.2	46.3	45.1	47.4	50.8	38.8	47.8	4.43
R	0.9400	0.9468	0.9535	0.9601	0.9459	0.9291	0.9018	0.9654	0.9428	0.0188
S	41.65	42.01	42.43	38.21	39.22	40.34	35.96	39.48	39.91	2.03
K	117.85	125.66	126.93	111.71	112.32	114.74	106.76	108.93	115.61	6.93

In Table 8. HPMBP-Nd electrode toughness value can be calculated. If the average value of  $R^2$  is 0.9428 and the average sensitivity is 39.91mV/decade and the mean value of the intercept is 115.61mV. The  $R^2$  toughness test of the following measurements;

$$\overline{R^2} = 0.9428 \quad \text{and} \quad SD = 0.019 \text{ then,}$$

$$\Delta R = \frac{SD \times t_{90}}{\sqrt{n}} = \frac{0.019 \times 1.86}{\sqrt{8}} = \frac{0.03534}{2.8284} = 0.01$$

So the toughness of the correlation coefficient is:

$$\mu R^2 = \overline{R} \pm \Delta R = 0.9428 \pm 001$$

then performed calculation of toughness test of sensitivity of electrode with data:

$\bar{S} = 39.91$  mV/decade and  $SD = 2.03$  than,

$$\Delta S = \frac{SD \times t_{90}}{\sqrt{n}} = \frac{2.03 \times 1.86}{\sqrt{8}} = \frac{3.7758}{2.8284} = 1.33$$

Thus, the sensitivity limit of HPMBP-Nd electrode is obtained;

$$\mu S = \bar{S} \pm \Delta S = 39.91 \pm 1.33 \text{ mV/decade}$$

Then also performed toughness test intercept electrode with data as follows;

$\bar{K} = 115.61$  and  $SD = 6.93$  than,

$$\Delta K = \frac{SD \times t_{90}}{\sqrt{n}} = \frac{6.93 \times 1.86}{\sqrt{8}} = \frac{12.8898}{2.8284} = 4.56$$

So as to obtain the limit of toughness of the intercept of HPMBP-Nd electrode is;

$$\mu K = \bar{K} \pm \Delta K = 115.61 \pm 4.56 \text{ mV}$$

#### 4.8 Selectivity coefficient $K_{Nd/j}^{pot}$

Selectivity is the ability of the electrode to distinguish the major ions and the interfering ions present in a solution. The selectivity of the HPMBP-Nd electrode was determined by calculating the potential influence of the interfering metal ions  $La^{3+}$ ,  $Ce^{3+}$  and  $Th^{4+}$  against the  $Nd^{3+}$  potential ions.  $La^{3+}$  and  $Ce^{3+}$  ions are used to determine their effect on main  $Nd^{3+}$  ions that are similar in nature to being in the same group (lanthanides). While  $Th^{4+}$  ions besides having different oxidation numbers are also in other classes. The results of electrode selectivity analysis of the three disturbing ions can be seen in Table 9.

**Table 9. Selectivity of HPMBP-Nd electrode**

p [Nd]	$K_{Nd/j}^{pot}$		
	$La^{3+}$	$Ce^{3+}$	$Th^{4+}$
5	1.05	1.00	0.101
4	1.00	1.00	0.102
3	1.00	1.00	0.178
2	1.00	1.00	0.316
1	1.00	1.00	0.309

Based on the theory if the value of  $K_{Nd/j}^{pot} = 1$  then the electrode is not selective to the disturbing ion, whereas if the value  $K_{Nd/j}^{pot} < 1$  then the electrode is selective to the intruder ion [29]. The results of the calculations in the Table above are known, HPMBP-Nd electrodes are not selective against similar REE's ions such as  $La^{3+}$  and  $Ce^{3+}$  but are selective against  $Th^{4+}$  ions.

The use of HPMBP-Nd electrodes for the analysis of the real samples was performed on the monazite solution which was removed from  $Th^{4+}$  ions which results were compared with the monazite concentrations obtained from the measurements using ICP. Based on the analysis results obtained  $Nd^{3+}$  3378.56ppm or  $2.34 \times 10^{-2}M$ . By dilution of the sample 10 times the potential value of sample obtained compared to potential value of the standard curve as in Table 10.

**Table 10. Determination of standard and sample potentials**

p[ $Nd^{3+}$ ]	2	3	4	5	Sample
E(mV)	102.9	92.1	80.8	73.9	92.2

With the potential comparison of standard solutions and samples in Table 10. above we obtain  $Nd^{3+}$  concentrations with HPMBP-Nd electrode  $1.02 \times 10^{-2}M$  or close to  $2.32 \times 10^{-2}M$ . thus the HPMBP-Nd electrode can be used as one of the methods used for the analysis of  $Nd^{3+}$  ions in the sample.

#### 5. Conclusions

HPMBP compounds can be synthesized and used as ionophores in analysis especially neodymium selective electrodes using tubular Teflon electrodes and PTFE polymer as membranes. The HPMBP-Nd electrode gave a good response to the  $Nd^{3+}$  standard solution under pH 4 and ISA KCl  $10^{-2}M$  concentration and the internal solution composition of 3: 1 base volume of KCl and  $Nd^{3+}$   $10^{-3}M$  solutions.

Measuring range of electrode obtained  $10^{-6}$  to  $10^{-2}$ M with detection limit of  $1.02 \times 10^{-4}$ M with sensitivity  $39.91 \pm 1.33$ mV/decade with 22 second response time and 3 weeks usage period. The use of electrodes in the analysis of monazite solution samples obtained  $\text{Nd}^{3+}$  concentration of  $1.02 \times 10^{-2}$ M and selective against  $\text{Th}^{4+}$  ions but less selective against  $\text{Ce}^{3+}$  and  $\text{La}^{3+}$  ions.

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