

PREPARATION AND CHARACTERIZATION OF LANTHANUM (III)
SELECTIVE ELECTRODE BASED ON 1,10-DIAZA-4,7,13,16-TETRAOXA-
CYCLOOCTADECANE-N,N'-DIACETIC ACID AS AN IONOPHORE

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Abstract

The Preparation and characterization of lanthanum (III) ion selective electrode based on the 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane-N,N'-diacetic acid as ionophore was studied. The electrode was prepared with an inner solution system in a membrane composition that contained active DACDA ionophore, the anionic side of KTCPB, the plasticizer of NPOE and a PVC matrix support. The good response was obtained with a slope of 19.53 ± 1.62 mV/decade and a good correlation between potential and lanthanum(III) concentration. Electrode could response with a detection limit of 3.92×10^{-6} M and range measurement between 10^{-5} M to 10^{-1} M. Electrode is steady at pH 4-9 and the best condition of inner solution concentration at 10^{-3} M. Response time was 27,1 seconds and their life time was 50 day.

Keywords: Lanthanum ion-selective-electrode, PVC membrane,
1,10-Diaza-4,7,13,16-tetraoxacyclooctadecane-N,N'-diacetic acid.

Telah dilakukan pembuatan dan karakterisasi elektroda selektif ion lantanum(III) dengan menggunakan ionofor senyawa 1,10-diaza-4,7,13,17-tetraoksasiklooktadekan-N,N'-diasetat. Elektroda yang dibuat dengan sistem larutan dalam dengan membran dengan komposisi bahan aktif membran ionofor DACDA, anion tanding KTCPB, pemlastis NPOE dan matrik pendukung PVC. Respon yang bagus diperoleh dengan nilai slope $19,53 \pm 1,62$ mV/dekade dan korelasi yang bagus antara potensial dengan konsentrasi ion lantanum(III). Elektroda dapat merespon ion lantanum hingga batas deteksi $3,92 \times 10^{-6}$ M dan rentang pengukuran antara 10^{-5} M - 10^{-1} M. Elektroda stabil pada pH 4-9 dan kondisi terbaik diperoleh pada konsentrasi larutan dalam 10^{-3} M. Waktu respon adalah 27,1 detik dan waktu hidup elektroda sampai 50 hari.

Kata kunci: elektroda selektif ion lantanum, membran PVC,
1,10-diaza-4,7,13,17-tetraoksasiklooktadekan-N,N'-diasetat

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INTRODUCTION

Rare earth elements are known as important inorganic compounds, because of their properties, especially their strong magnetic property. One of the important elements is lanthanum. The available methods for low level determination of rare earth ions in solution include, ICPMS, ICPAES, and X-ray fluorescence spectrometry, etc (Houk et al., 1980). These methods are either time consuming, involving multiple sample manipulation and too expensive for most analytical laboratories.

Ion selective electrode (ISE) in potentiometry is one method of analysis that is simpler and inexpensive but can be used as a good method. Ion selective electrodes with neutral carriers were developed for some elements especially for alkali, earth alkali and transition elements. They are successful methods for analysis (Morf and Simon 1978). For rare earth elements, a very little work on the system has been done by some researchers. Only a few reports are found in the literature on the preparation of rare earth ion selective electrodes (Choudhury, Obata and Kamato, 1996). For this reason, we tried to prepare an ion selective electrode for rare earth elements, especially for lanthanum.

Macrocyclic compounds have properties to form complex compounds with some metals. In this case, macrocycles function as ligands. For example, crown ethers with alkali and earth alkali metal ions to form very specific complex compounds. Macrocycles with N (nitrogen) element usually form complex compounds with transition elements. Chang C.A. and Ochaya (1986) synthesized the macrocyclic compound lariat diaza-18-C-6 (1,10-diaza-4,7,13,16-tetraoxacyclo-octadecane-N,N'-diacetic acid and 1,7-diaza-4,10,13-trioxacyclo-octadecane-N,N'-diacetic acid) and studied complexation with rare earth elements. They concluded that these compounds are selective reagents for lanthanide ions. For this reason, we tried to make an ion selective electrode for lanthanum with the compound lariat diaza-18-C-6. We focused on 1,10-diaza-4,7,13,16-

tetraoxacyclo-octa-decane-N,N'-diacetic acid compound with structure given in figure 1 (Zolotov, 1997).

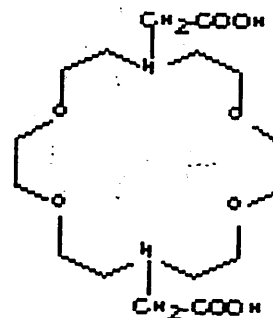


Figure 1: Structure of the 1,10-diaza-4,7,13,16-tetraoxacyclo-octadecane-N,N'-diacetic acid

1. EXPERIMENTAL

2.1. Reagent

Stock solutions (10^{-1} M) of lanthanum(III) were prepared by dissolving $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ (99.9 % purity, Merck, Germany) in distilled water. Ionophore 1,10-Diaza-4,7,13,16-tetraoxacyclo-octadecane - N, N' - diacetic acid was purchased from ACROS ORGANIC, New Jersey, USA. The plasticizer o-nitro phenyl octyl ether (NPOE) and anionic side potassium tetrakis (4-chlorophenyl) borate (KTCBPB) were purchased from Fluka Chemie AG, Switzerland. Tetrahydrofuran (THF) used for dissolving the membrane components was purchased from Merck. All other chemicals used in analytical determinations were guaranteed reagent grade purity.

2.2. Membrane and electrode preparation

The membrane solution was prepared by dissolving 10.0 mg 1,10-Diaza-4,7,13,16-tetraoxacyclo-octadecane-N,N'-diacetic acid, 45 mg PVC, 90 mg NPOE and 5 mg KTCBPB in 3 mL of THF. The solution was evaporated on the glass with square $1.5 \times 4 \text{ cm}^2$. The electrode was prepared by gluing the tube electrode to the membrane. The inner electrode reference Ag/AgCl and inner solution (mixture $\text{KCl } 10^{-3} \text{ M}$ and $\text{La}^{3+} 10^{-3} \text{ M}$) is set in the tube and connected to the cable. The electrode was conditioned before potentiometry measurement by immersing it in

10^{-3} M LaCl_3 solution for 24 hour. The shape of the electrode can be seen in figure 2.

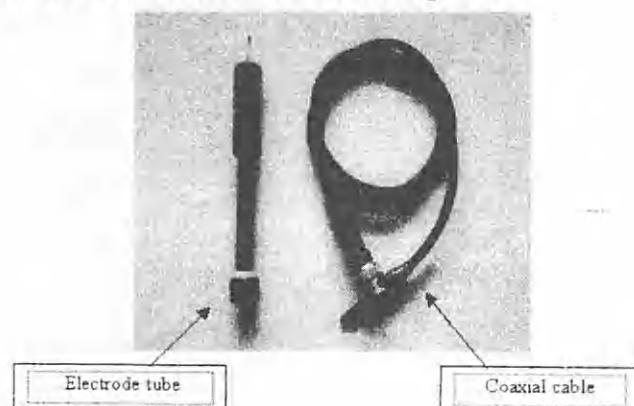


Figure 2. Shape of membrane electrode

2.3. Electrode system and *emf* measurement

Cell configuration used for potentiometry measurement were of the type:

$\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{KCl}(\text{sat}): 3 \text{ M KCl} :: \text{Sample solution} \parallel \text{membrane} \parallel \text{internal filling solution} / \text{AgCl}/\text{Ag}$

Emf measurement were carried out with calomel electrode (ORION) coupled with ORION pH/Ion-meter 420A. The concentration of lanthanum (III) ion in the sample solution was varied from 10^{-1} to 10^{-8} M in stirred solution. The *emf* value were recorded when the reading ion-meter became stable. The pH value of the sample solution were adjusted with NaOH and HCl/ HNO_3 and measured with pH-meter. The activity of metals ion were based on their activity coefficient, γ , as calculated from the modified Debye Huckel equation:

$$\text{Log } \gamma = -0,511 Z^2 \left[\frac{\sqrt{\mu}}{1+1,5 \sqrt{\mu}} - 0,2 \mu \right]$$

Where μ is ionic strength and Z is valence of the concerned ion. All the *emf* measurement we performed at 25 ± 3 °C. The scheme of *emf* measurement can be seen in figure 3.

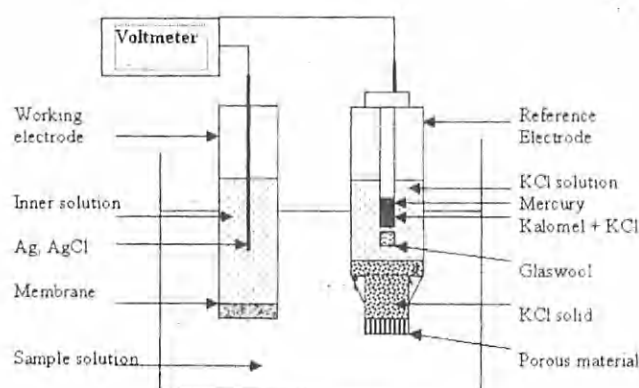


Figure 3. Potential measurement with potentiometry system

3. RESULTS AND DISCUSSION

3.1. Response characteristics of La(III)-selective electrode

The potential response of the electrode was affected by the composition of the membrane electrode. For this reason we varied the composition of the membrane to result in a good potential response. The variation of the membrane electrode can be seen in table 1.

Table 1. Composition of the membrane electrode and their Nernstian response

No	PVC (mg)	NPOE (mg)	DACDA (mg)	KTCPB (mg)	Slope
1	44.6 (32.32%)	83.0 (56.42%)	14.4 (9.79%)	5.7 (3.47%)	12.27±1.51
2	45.3 (30.54%)	82.5 (55.63%)	10.2 (6.87%)	10.3 (6.95%)	18.51±1.11
3	45.5 (30.11%)	90.2 (59.69%)	10.0 (6.62%)	5.4 (3.57%)	19.53±1.62
4	49.4 (32.93%)	90.1 (60.06%)	5.2 (3.47%)	5.3 (3.53%)	21.50±1.72
5	50.0 (33.67%)	90.2 (60.74%)	5.1 (3.43%)	3.2 (2.15%)	34.19±3.06
6	50.2 (34.15%)	90.2 (61.36%)	5.0 (3.40%)	1.6 (1.09%)	33.03±0.76

From the data, it can be seen that the composition with 6.87 % ionophore DACDA and 3.57 % KTCPB gave a Nernstian response with a slope of 19.53 mV/decade.

3.2. Correlation of potential response and lanthanum concentration

To see the correlation between potential and lanthanum(III) concentration, we varied lanthanum concentration from 10^{-1} M to 10^{-8} M. The potential of each solution measure with lanthanum electrode and result can be seen in figure 4.

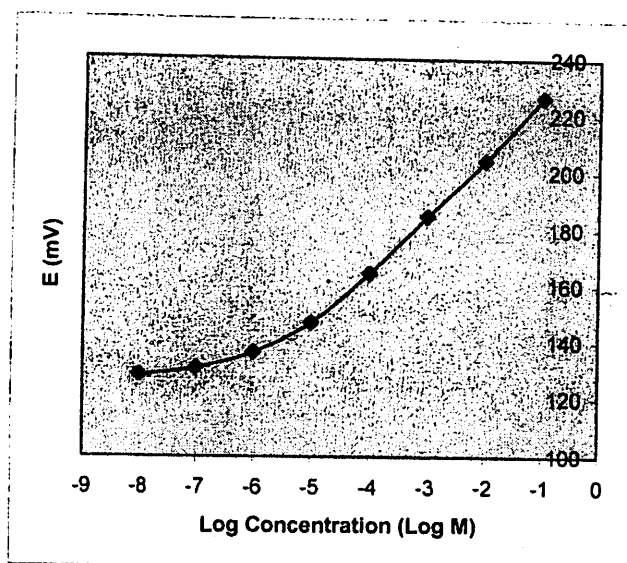


Figure 4. Correlation of concentration of La(III) with potential response

The correlation between potential and lanthanum(III) concentration are linear at concentration from 10^{-1} M to 10^{-5} M with coefficient correlation 0,99. So that the linear range measurement is at concentration between 10^{-1} M to 10^{-5} M. From the data we can calculate the detection limit of lanthanum measurement. The value of detection limit is 3.92×10^{-6} M.

3.3. Effect of pH on the potential response

We prepared a series of solutions of La^{3+} with the pHs ranged from 1 to 10, by adding HCl and NaOH solutions. The pH variation are applied to some lanthanum(III) concentration (10^{-2} M – 10^{-6} M). Solution potentials were measured by the cell system and the results can be seen in figure 5.

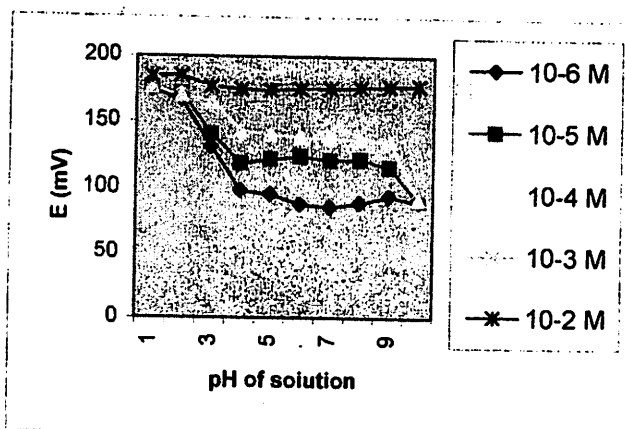


Figure 5: Effect of pH on the potential response

Figure 5 shows that potential responses were relatively constant at pH 4 to 9 but then dropped to 10. At the low pH, the high ion H^+ can shift of equilibrium DACDA. This is because DACDA can be ionisation as this reaction below:

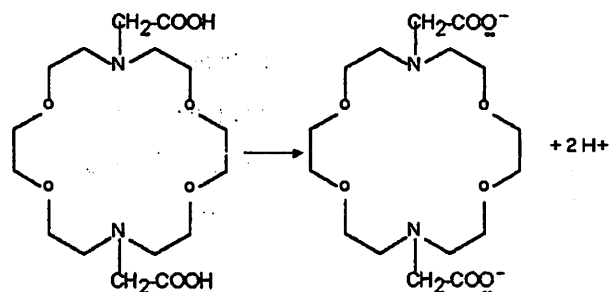


Figure 6: The ionisation of DACDA

At the pH 10 the potential are dropped, this is because the lanthanum ion was precipitated to form metal hydroxide. So, we worked at pH 4.5. This results are relative same with some researcher that pH is constant at 3 – 9 (Bakker et al., 1997, Choudhury et al., (1996), and Ganjali, 2004).

3.4. Effect of inner solution concentration

The effect of inner solution concentration of ion selective electrode was studied some researcher (Mittal, Kumar and Sharma, 2003). For this system we varied

concentration of lanthanum(III) in inner solution from 10^{-2} M to 10^{-5} M. The potential response from this electrode for measurement of lanthanum(III) in the solution that has concentration between 10^{-1} M to 10^{-8} M, can be seen in figure 7.

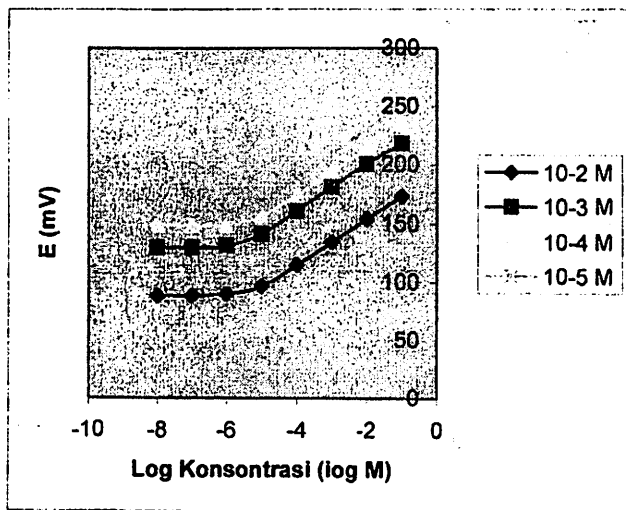


Figure 7: Electrode potential response with some inner solution concentration

Result show that the variation in the concentration (10^{-2} M to 10^{-5} M) of the internal solution give the same shape of the graph. But in different concentration give different potential value. The potential at 10^{-3} M, 10^{-4} M and 10^{-5} M has high potential, and at 10^{-2} M give smooth graph and slope value is nernstian.

3.5. Response time

Response time is the time taken for the potential of the cell to reach a value 1 mV from the final equilibrium potential. To find the time response of the lanthanum electrode, we use some electrode and to measure some concentration of lanthanum standard solution (10^{-3} M to 10^{-5} M). The time that need to measure some lanthanum standard solution for some electrode could be seen in table 2.

Table 2. Response time of lanthanum ion selective electrode

[La ³⁺](M)	Response time some electrode (second)	Mean
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	E-1	E-2	E-3	E-4	E-5	(second)
10^{-5}	23	32	28	22	32	$27,4 \pm 4,9$
10^{-4}	28	20	20	23	33	$24,8 \pm 5,8$
10^{-3}	35	23	21	28	39	$29,2 \pm 7,9$
Mean	28,7	25,0	23,0	24,3	34,7	$27,1 \pm 4,8$

From the result, the mean of time response is 27,1 second. The result is relatively same for all time response of membrane electrode that is usually has value about 30 second (Evan, A, 1997).

3.6. Life time

For ion selective electrode, the concentration decrease, if slow, would simultaneously occur at the membrane - inner filling solution interface, so that no net effect is expected in the measured potential, although the selectivity would still deteriorate. In contrast, solid contact ISE indeed show potential shifts due to leaching. With classical electrode, the critical concentration can be established on the basis of lose of selectivity and electrode slope (Bakker, Bulhman and Pretch (1997). In this research we measure the potential response electrode from time to time. Then, we monitored the slope value from calculation of the potential response data. The slope value of lanthanum electrode any time can be seen figure 8.

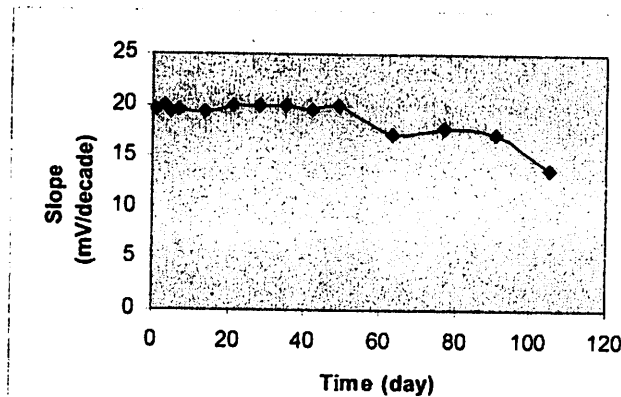


Figure 8. The slope value of lanthanum electrode as function of time

From the figure, show that lanthanum electrode has constant slope value (about 19 mV/decade) until 50 day. To get more long

time of life time we can change some active membrane with material that has more lifofil.

4. CONCLUSIONS

The electrode of ESI-La was success prepare from this research. The Preparation and characterization of lanthanum (III) ion-selective electrode based on the 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane-N,N'-diaetic acid as ionophore was studied. The good response was obtained with a slope of 19.53 ± 1.62 mV/decade. Electrode could response with a detection limit of 3.92×10^{-6} M and range measurement between 10^{-5} M to 10^{-1} M. Electrode is steady at pH 4-9 and the best condition of inner solution concentration at 10^{-3} M. Response time was 27,1 seconds and their life time was 50 day.

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