ORIGINAL ARTICLE

Assessment of Al^{3+} Ion Selectivity Coefficient (Kij) in Polyurethane Membranes Derived from Castor Oil (*Ricinus communis*. L) via Separated Solution Method

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Abstract

The influence of foreign ions on the response of Al3+ ISE-based polyurethane membranes from castor oil has been determined using SSM. The results showed that the presence of the foreign ions tested did not affect the sensitivity and response of Al3+ ISE. The influence of foreign ions Na^+, K^+, Li^+, Pb^{2+}, Ca^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Cr^{3+}, and Fe^{3+} on the selectivity of ion-selective electrodes (Al^{3+} ISE) in the concentration range $1x10^{-9}$ – $1x10^{-4}$ M has been performed using separate methods. The results show that the presence of foreign ions does not affect the performance of Al^{3+} ISE with a Kij value < 1. The selectivity sequence of foreign ions is $Fe^{3+} > Cr^{3+} > Pb^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Ca^{2+} > Li^+ > Na^+ > K^+$ respectively.

Introduction

Aluminum (Al) is one of the most abundant elements in the earth's crust and is found in water, air, and soil [1]. This metal has been employed for water treatment, packaging, food additives, pharmaceuticals, and cosmetics [2]. Even though Al is widely used, excessive levels of Al can be dangerous for the environment and human life [3–5]. The average concentration of Al exposure in the human body is approximately 65 mg. Al is available in the liver, brain, lungs, kidneys, and thyroid. The body excretes excess through urine, feces, and sweat [1]. The accumulation effect in the human body causes various diseases, such as colic, rickets, Alzheimer's, and Parkinson's [6–9]. Hence, determining Al using a simple method is still needed. Available method to determine the Al^{3+} ions has been established, such as atomic absorption spectroscopy (AAS), atomic emission spectroscopy (AES), and inductively coupled plasma mass spectroscopy (ICP-MS). However, this method requires complicated sample preparation, time-consuming, and sophisticated instrumentation [2]. Therefore, a simple and quick method is still needed to determine the Al^{3+} ion. The potentiometric method is simple, accurate, and precise. Therefore, using the ion-selective electrodes (ISE) as a working electrode is more favorable for obtaining accurate results [10].

The membrane is part of the ISE compartment, which is sensitive to the measured analyte. The selective membrane for the ISE construction contains ionophores. Polyurethane (PU) is one of the membranes that can be employed as a matrix in ISE working systems, and it can be synthesized from polyol material such as castor oil (*Ricinus communis L.*). Our previous research has succeeded in optimizing Al^{3+} ISE manufacturing using the same membrane. The results show that the polyurethane membrane from castor oil has suitable characteristics for the ISE construction. This study focuses on the ISE performance on the influence of foreign ions at various concentrations on the ISE response.

The ISE response determines the accuracy of measurement results greatly influenced by the presence of foreign ions. It is necessary to evaluate their presence affects the response. In this study, the influence of foreign ions Na^{+}, K^{+}, Li^{+}, Pb^{2+}, Ca^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Cr^{3+}, and Fe^{3+} has been investigated on the sensitivity of +1, +2 and +3 cation valence ions.

Materials and Methods

Materials

All chemical salts used in this research were cations valences of I, II and III as listed: $Al(NO_3)_3.9H_2O$, $NaNO_3$, $Pb(NO_3)_2$, $Ca(NO_3)_2$, KNO_3, $LiNO_3$, $Co(NO_3)_2.6H_2O$, $Cu(NO_3)_2.3H_2O$, $NiSO_4.6H_2O$, $Cr(NO_3)_3.9H_2O$, and $FeCl_3$ (Sigma-Aldrich, St. Louis, MO, USA). 1,10-phenanthroline, acetone and toluene diisocyanate (TDI) were purchased from (Merck) were us to synthesize polyurethane membrane., a commercial castor oil was obtained from local company PT. Rudang Jaya (Medan, Indonesia). The Swallow Globe agar was obtained from a local market.

Instruments

Moreover, during the analytical performance of the ISE Al^{3+}, we used potentiometer Orion model with a serial name Thermo Orion Scientific Star A2115 (Waltham, MA, USA) and a hand-made Ag/AgCl reference electrode.

Dope Membrane Solution Preparation

The dope solution was prepared using 3.5 grams of commercial castor oil of the Ricinus communis L. mixed with 10 mg of 1,10-phenanthroline in a 50 mL Beaker glass and stirred for 3 hours until homogeneous solution obtained and then reacted with 1.75 grams of TDI followed by heating for 15 minutes at 60°C. The solution obtained is a clear yellowish dope solution. The same results have also been reported by [11].

Preparation Polyurethane Membrane

After the dope solution was obtained from the previous experiment, the mixed solution was then sonicated using a sonicator (Krisbow Brand). During sonication, as much as ±4 grams of acetone was added and then poured onto a glass plate. The membrane was flattened and left to dry for 48 hours in an oven at 25°C until a thin layer or film was obtained. The membrane was then removed from the glass plate.

Fabrication Ion Selective Electrode

The PU membrane was cut to a diameter of 2 cm and attached to the electrode body, then soaked in a 0.1 M $Al(NO_3)_3$ solution for one night. Slowly fill an internal solution containing KCl 0.1 M + $Al(NO_3)_3$ 0.1 M through the top of the electrode body and insert with an Ag/AgCl reference electrode to cover the electrode body as illustrated in the Figure 1.

An Ag/AgCl Reference Electrode Preparation

The Ag/AgCl reference electrode contained 2% agar and 0.1 M Li acetate. The design of the Ag/AgCl reference electrode as presented in Figure 1.

Al^{3+} ISE Sensitivity Determination

Potential measurements to determine the ISE sensitivity were carried out by measuring the potential of Al^{3+} standard solutions at concentrations of 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6}, 10^{-7}, 10^{-8}, 10^{-9}, and 10^{-10}.

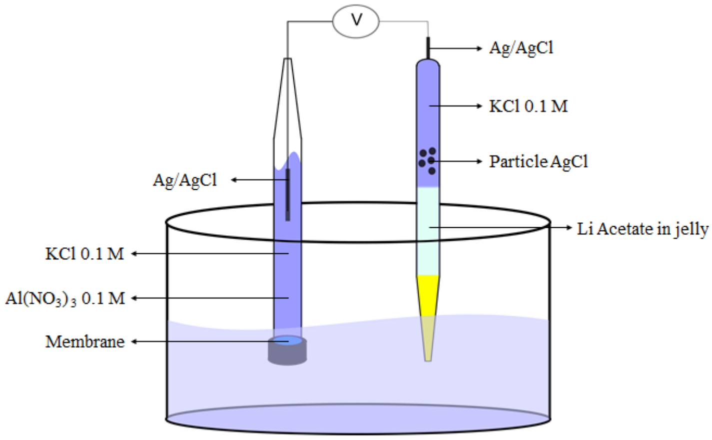

Figure 1. A schematic of Al3+ ISE potentiometric measurement.

Selectivity Coefficient (Kij)

Determination of selectivity coefficients for the Al^{3+} ion and interfering ions namely Na^{+}, K^{+}, Li^{+}, Pb^{2+}, Ca^{2+}, K^{+}, Li^{+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Cr^{3+}, and Fe^{3+} with concentrations of 10^{-4}, 10^{-5}, 10^{-6}, 10^{-7}, 10^{-8}, and 10^{-9} M through potential measurements (mV) using Separate Solution (SSM) method. Each Al^{3+} ion solution and interfering ions were measured at concentrations of 10^{-4}, 10^{-5}, 10^{-6}, 10^{-7}, 10^{-8}, and 10^{-9} M. The potential of Al^{3+} ion and interfering ions were used to calculate the Kij values using equation 1.

$$K_{i,j}^{pot} = \frac{10^{\Delta E/\pm \text{slope}} . ai}{a_j^{zi/\,zj}} \quad (1)$$

Results and Discussion

Determination of Selectivity Foreign Ion Valency 1

The selectivity coefficient (Kij) is the important parameter for the ISE response. This work determined the selectivity coefficient using the SSM. Selectivity data was obtained by measuring the potential of the Al^{3+} ion and foreign ions (Na^{+}, Ca^{2+}, Pb^{2+}, K^{+}, Li^{+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Cr^{3+}, and Fe^{3+}) at concentrations of 10^{-9} M - 10^{-4} M. The Kij is necessary because the amine group of PU also has an affinity for other foreign ions [12]. The influence of each foreign ion on the Al^{3+} ISE response has been determined based on various charges of foreign ions I, II, and III. The Nerst equation provides information on how the kij value can contribute to the ISE response.

Equation 2 shows that Kij <1 will not affect the ISE response. Conversely, if Kij > 1, then the ISE response is influenced by foreign ions. The greater the Kij value, the more foreign ions play a role in the resulting potential [13].

Influence of foreign ion valence I on the Kij values

The valence I foreign ions measured in this study were Na^{+}, K^{+}, and Li^{+}. The measurement results can be seen in Table 1.

Table 1. Influence of foreign ion valence I on the Al^{3+}ISE response.

Ions [10^{-4} - 10^{-9}] (M)	Sensitivity (mV/decade)	LOD (M)	LOQ (M)	R^2
Al^{3+}	18.53 ± 0.34	$10^{-9.11}$	$10^{-8.83}$	0.996
Na^{+}	3.37 ± 1.98	3.23	1.12	0.361
K^{+}	3.99 ± 1.00	1.003	0.49	0.157
Li^{+}	0.99 ± 0.30	194.98	3.09	0.096

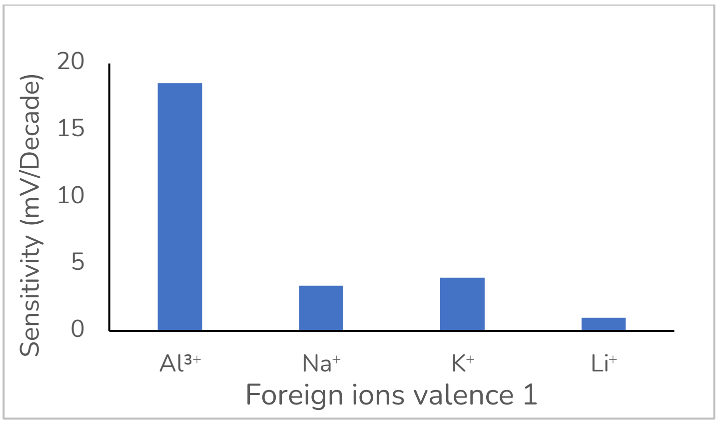

Figure 2. Sensitivity profile of Al3+ ISE on foreign ions valence 1.

A plot potential versus Al^{3+} concentration without foreign ions showed a closed Nernstian sensitivity value of 18.12 mV/decade (19.6 mV/decade). The sensitivity value again of Al^{3+} ISE on foreign ions Na^{+}, K^{+}, and Li^{+} showed deviations from the theoretical Nernst value (Figure 2). These results mean that the Al^{3+} ISE has a higher response to Al^{3+} ions than Na^{+}, K^{+}, and Li^{+} ions. It is also proven by the lower determination coefficient (R^2) values that indicate the Al^{3+} ISE does not respond to foreign ions linearly. Also, its LOD and LOQ values are much smaller when compared to the tested foreign ions.

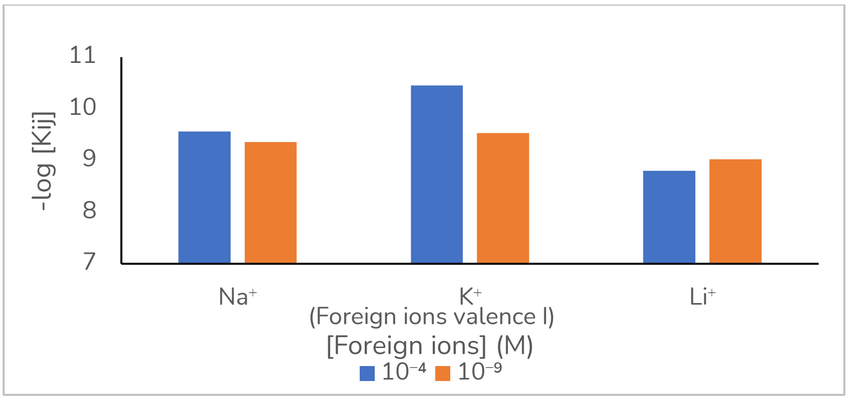

Figure 3. Kij value of foreign ions valence I.

The sequence of Kij values obtained from measurements is $K^{+} < Na^{+} < Li^{+}$ **(**Figure 3**)**. This order is determined by the electronegativity properties of $Li^{+} > Na^{+} > K^{+}$. Thus, Li^{+} ions attract electrons strongly on the N atom in the 1,10-phenanthroline structure compared to K^{+} and Na^{+} ions. This result is due to the electronegativity of an element decreasing within a group [14].

Influence of foreign ion valence II on the Kij value

The II valence foreign ions measured in this study were Ni^{2+}, Ca^{2+}, Pb^{2+}, Co^{2+}, and Cu^{2+}. Table 2 displays the results of sensitivity, LOD, and LOQ measurements. It indicates a significant deviation of the sensitivity of each valence II foreign ion from the theoretical Nernst factor value. The Figure 4 showed that deviations indicate that the Al^{3+} ISE is not sensitive to the valence II metal ions tested. The order of foreign ions sensitivities tested as presented in Figure 5 is $Co^{2+} > Ca^{2+} > Cu^{2+} > Pb^{2+} > Ni^{2+}$. Apart from sensitivity, the linear response of Al^{3+} ISE to valence II ions is also determined by the linearity of the ISE response at various foreign ion concentrations. Table 2 also shows that linearity coefficients are not directly proportional to the foreign ion concentrations, and the Al^{3+} ISE does not respond linearly to foreign ions. Then, the LOD and LOQ values (Table 2) obtained for the Al^{3+} ion was smaller than those for ions. As with valence I ions, the Kij value is influenced by the type of ion and electronegativity. The order of interference properties of valence II ions based on the Kij value is $Pb^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Ca^{2+}$.

Table 2. Influence of foreign ion valence II on the ESI response of Al^{3+}.

Ions [10^{-4} - 10^{-9}] (M)	Sensitivity (mV/decade)	LOD (M)	LOQ (M)	R^2
Al^{3+}	18.02 ± 0.62	$10^{-9.11}$	$10^{-8.83}$	0.997
Ni^{2+}	0.60 ± 0.14	3.24	1445.43	0.076
Ca^{2+}	3.2 ± 1.61	0.43	0.70	0.486
Pb^{2+}	1.03 ± 0.45	1.04	4.69	0.053
Co^{2+}	3.52 ± 0.56	0.29	1.17	0.805
Cu^{2+}	2.42 ± 0.50	1.06	5.62	0.248

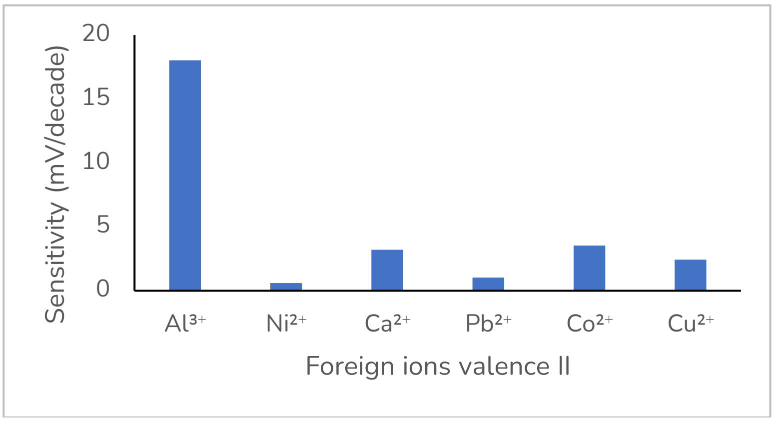

Figure 4. The influence of Al^{3+} ISE to foreign ions valence II.

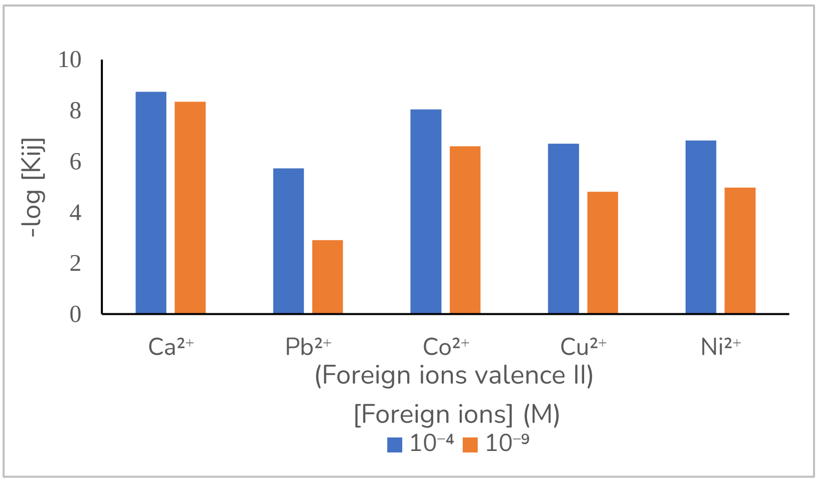

Figure 5. Kij value of foreign ions valence II.

Overall, the Kij value tested for foreign ions with valence II at various concentrations $10^{-4} – 10^{-9}$ M <1 (Figure 5). This means that the valence II ions Ni^{2+}, Ca^{2+}, Pb^{2+}, Co^{2+}, and Cu^{2+} do not affect the Al^{3+} ISE response.

Effect of foreign ions of valence III on the Kij value

The foreign ions of valence III measured in this study were Cr^{3+} and Fe^{3+}. The measurement results as presented in Table 3.

Table 3. Influence of foreign ions of valence III on the Al^{3+}ESI response.

Ions [10^{-4} -10^{-9}] (M)	Sensitivity (mV/decade)	LOD (M)	LOQ (M)	R^2
Al^{3+}	18.03±0.59	$10^{-9.11}$	$10^{-8.83}$	0.994
Cr^{3+}	2.94±0.25	1.25	2.34	0.304
Fe^{3+}	4.55±1.80	1.18	1.74	0.326

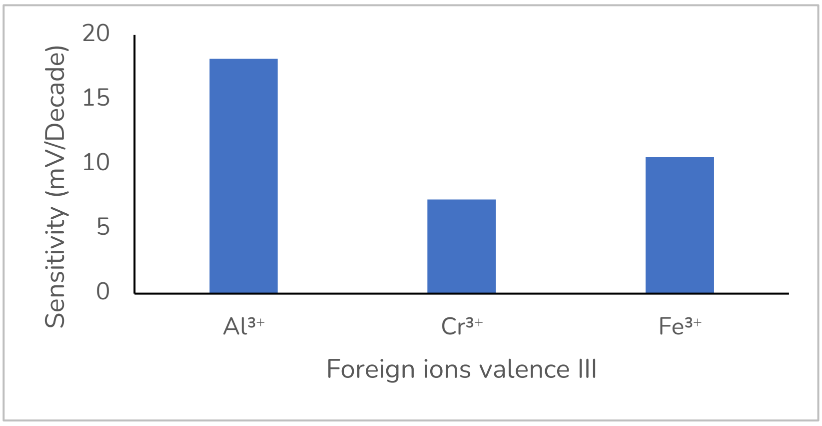

Figure 6. The effect of Al^{3+} ISE sensitivities on foreign ions valence III.

Table 3 and Figure 6 presented the sensitivity value of foreign ion valence III towards Al^{3+} ISE, and the values show closeness to the theoretical Nernst equation for trivalent cations. Then, sensitivity values for the III valence of foreign ions, namely Fe^{3+} and Cr^{3+} ions do not match the theoretical Nernst equation value. In addition, LOD and LOQ for Al^{3+} ions were much smaller than the foreign ions **(**Table 3**).** Therefore, the Al^{3+} ISE does not respond to foreign ions and this might be due to the nature of electronegativity. The periodic system Fe^{3+} is to the right of Cr^{3+}, and the ISE works system only produces potential equilibrium with Al^{3+} ion. Kij is influenced by the type of ion and its electronegativity, such as valence I and valence II.

Based on Figure 7. among valence metals I, II, and III, the metal that responds best to Al^{3+} ISE is metal ion valence III, namely Cr^{3+} and Fe^{3+} ions. The theory states that increasing the oxidation state increases the bond strength between the metal and the ligand [15]. The order of disturbance characteristics based on the measurement results is as follows: Fe^{3+} > Cr^{3+} > Pb^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Ca^{2+} > Li^{+} > Na^{+} > K^{+}.

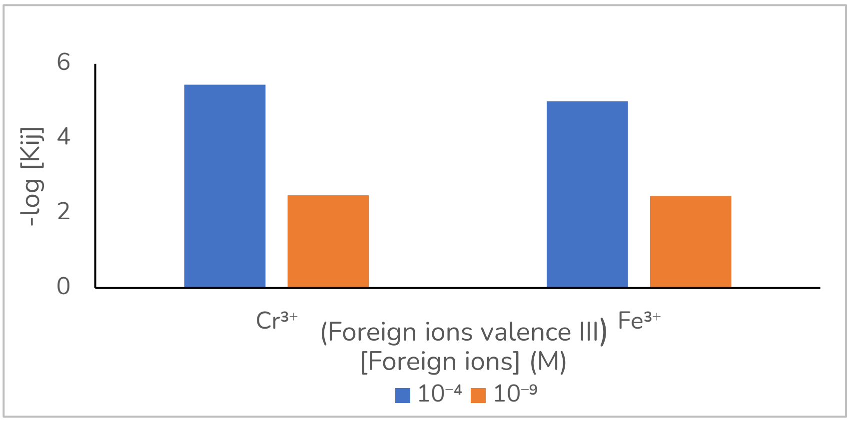

Figure 7. Kij value of foreign ions valence III.

Conclusions

The sensitivity response of Al^{3+} ISE to foreign ions of valences I, II, and III tested showed a deviation from the theoretical Nernst factor value, and the selectivity coefficient values for the three cation valences showed < 1. It indicates that the Al^{3+} ISE has not responded to foreign ions valence I, II, and III. The sequential order of selectivity represented by the -log Kij value for each ion is Fe^{3+} (2.46) > Cr^{3+} (2.48) > Pb^{2+} (2.91) > Cu^{2+} (4.81) > Ni^{2+} (4.97) > Co^{2+} (6.59) > Ca^{2+} (8.35) > Li^{+} (9.02) > Na^{+} (9.36) > K^{+} (9.53).

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Data Availability Statement: Not applicable.

Conflicts of Interest: All the authors declare that there are no conflicts of interest.

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