

Al³⁺-Selective PVC Membrane Sensor Based on Newly Synthesized 1,4-bis[o-(pyridine-2-carboxamidophenyl)]-1,4-dithiobutane as Neutral Carrier

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A new sensitive and selective poly(vinyl chloride)-based membrane sensor for aluminum ions was prepared by employing on 1,4-bis[o-(pyridine-2-carboxamidophenyl)]-1,4-dithiobutane (PCD) as a neutral ion carrier and investigated as a selective membrane sensor. The electrode exhibits a near Nernstian response (19.4 ± 0.3 mVdecade⁻¹) for Al³⁺ ions over a wide concentration range from 1.0×10^{-6} to 1.0×10^{-2} mol L⁻¹ with a limit of detection of 6.3×10^{-7} mol L⁻¹ in a pH range of 2.0–4.2. The best performance was obtained with membrane composition 30% poly(vinyl chloride), 66% nitrobenzene, 2% sodium tetrphenylborate and 2% ionophore PCD. It has relatively fast response time (~5 s) and can be used at least for 2 months without any considerable divergence in potentials. This sensor revealed a great enhancement in selectivity coefficients for aluminum(III) ions in comparison with the previously reported aluminum(III) sensors. It was used as an indicator electrode in potentiometric titration of Al³⁺ with EDTA.

Keywords: Sensors, PVC membrane, Ion-selective electrode, Potentiometry

1. INTRODUCTION

Aluminium (or aluminum) is a chemical element in the boron group with symbol Al and atomic number 13. Aluminum is a soft and lightweight metal. It has a dull silvery appearance, because of a thin layer of oxidation that forms quickly when it is exposed to air. Aluminum is nontoxic (as the metal) nonmagnetic and non-sparking. Aluminum is the third most abundant element (after oxygen and silicon), and the most abundant metal, in the Earth's crust. Although aluminum is the most abundant metal in the earth's crust, it is never found free in nature. All of the

earth's aluminum has combined with other elements to form compounds. Two of the most common compounds are alum, such as potassium aluminum sulfate ($KAl(SO_4)_2 \cdot 12H_2O$), and aluminum oxide (Al_2O_3). About 8.2% of the earth's crust is composed of aluminum. Aluminum is remarkable for the metal's low density and for its ability to resist corrosion due to the phenomenon of passivation. Structural components made from aluminum and its alloys are vital to the aerospace industry and are important in other areas of transportation and structural materials. The most useful compounds of aluminum, at least on a weight basis, are the oxides and sulfates. Aluminum is almost always alloyed, which markedly improves its mechanical properties, especially when tempered. For example, the common aluminum foils and beverage cans are alloys of 92% to 99% aluminum. The main alloying agents are copper, zinc, magnesium, manganese, and silicon (e.g., duralumin) and the levels of these other metals are in the range of a few percent by weight. Aluminum is usually alloyed – it is used as pure metal only when corrosion resistance and/or workability is more important than strength or hardness. A thin layer of aluminum can be deposited onto a flat surface by physical vapour deposition or (very infrequently) chemical vapour deposition or other chemical means to form optical coatings and mirrors [1-3].

The available methods for the aluminum ion monitoring in solution include graphite furnace atomic absorption spectrometry (GF-AAS), spectrophotometry, inductively coupled plasma atomic emission spectrometry (ICP-AES), high performance liquid chromatography (HPLC) and spectrofluorimetry have been reported for determination aluminum in samples. These methods are either time consuming, involving multiple sample manipulations, or too expensive for most analytical laboratories. Ion selective electrodes have proven to be very useful devices due to their unique characteristics including ease of use and selectivity over many common interfering ions [4-19]. A literature survey revealed that very little work have been reported on the development of aluminum(III) ion selective electrode[20-23].

Recently we have used various ionophores in fabrication of PVC-based membrane sensors for different cations [24-29]. The aim of this research is the fabrication of a greatly selective and sensitive Al^{3+} membrane sensor, based on 1,4-bis[o-(pyridine-2-carboxamidophenyl)]-1,4-dithiobutane (PCD) (Fig. 1) as a suitable ionophore for the potentiometric measurement of the Al^{3+} ion amounts for a certain concentration range.

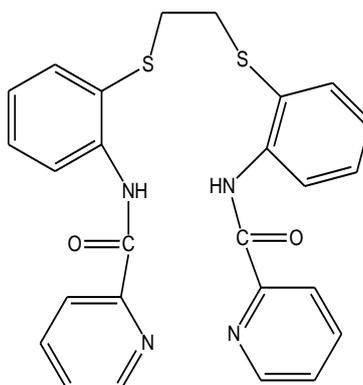


Figure 1. Chemical structure of PCD.

2. EXPERIMENTAL

2.1. Reagents and materials

Analytical reagent grade dibutyl phthalate (DBP), benzyl acetate (BA), acetophenon (AP), nitrobenzene (NB), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) and high relative molecular weight PVC were purchased from the Merck and the Aldrich Chemical Companies. The ligand PCD was synthesized as described elsewhere [30]. The nitrate and chloride salts of all cations used (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying. Doubly distilled and deionized water was used throughout.

2.2. Preparation of membrane

The viscous solution that was used for the formation of the membrane was prepared by the mixing 30 mg of powdered PVC, 66 mg of NB and 2 mg of NaTPB in 3 mL of THF, and 2 mg of PCD. The resulting low-viscosity mixture was thoroughly mixed and transferred into a glass dish of 2 cm diameter and then its solvent was slowly evaporated to gain an oily concentrated mixture. The membrane was then formed on the tip of a Pyrex tube of (3-5 mm o.d.) and by dipping the tube into the mixture for about 10 s, a transparent membrane of about 0.3 mm thickness was formed [31-34]. Then, the tube was removed from the mixture, kept at room temperature for 12 h and then filled with an internal solution (1.0×10^{-3} mol L⁻¹ AlCl₃). The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} mol L⁻¹ aluminum chloride solution. A silver/silver chloride electrode was used as an internal reference electrode.

2.3. Apparatus and emf measurements

All electromotive force was carried out with the membrane sensor using the following cell assembly:

Ag–AgCl | KCl, 3 mol L⁻¹ | internal solution, 1.0×10^{-3} mol L⁻¹ AlCl₃ | PVC membrane | test solution | Hg–Hg₂Cl₂, KCl (satd.)

A Corning ion analyzer (250 pH/mV meter) was used for the potential measurements at 25.0 °C. The emf observations were made relative to a double junction saturated calomel electrode (SCE) with the chamber filled with an ammonium nitrate solution. The reference electrodes was obtained from Azar Electrode Company (Urmia, Iran). The activities were calculated according to the Debye-Hückel procedure [35].

3. RESULTS AND DISCUSSION

3.1. Potential response of the sensor

In order to check the suitability of PCD as a sensing ionophore for Al³⁺ and other metal ions, it was used to prepare PVC membrane sensor for a wide variety of cations including alkali, alkaline

earth, and transition metal ions. The potential responses for the ions are depicted in Figure 2. With the exception of Al^{3+} ions, all the tested cations showed relatively weak responses in the concentration range 1.0×10^{-6} to 1.0×10^{-2} mol L⁻¹, due to their weak interactions with the ionophore.

3.2. The membrane composition

Taking into consideration that the sensitivity and selectivity of a given ion carrier depends radically on the membrane ingredients as well as the nature of the solvent mediator and the nature and the amount of the used additives [36-38], the membrane composition influences on the potential responses of the Al(III) sensor were investigated. The results are summarized in Table 1. It can be observed that the ionophore amount increase up to a value of 2%, in the presence of 2% NaTPB and 66% of polar solvent (NB), results in the best sensitivity (membrane no. 6). The influence of the nature of plasticizer on the Al^{3+} response was studied on sensors containing four types of plasticizers having different dielectric constants, namely, AP, DBP, BA and NB. As shown in Table 1, NB results in the best potential responses. It should be noted that the nature of the plasticizer affects not only the dielectric constant of membrane phase but also the mobility of ionophore molecules [37-40]. It is well established that the addition of lipophilic anions to cation-selective membrane electrodes not only diminishes the ohmic resistance and enhances the response behavior and selectivity, but also in cases where the extraction capability is poor, increases the sensitivity of the membrane electrodes [39, 40]. As it can be seen from Table 1, without the additive NaTPB, sensor (no. 4) do not respond properly toward the expected Nernstian value. However, the addition of 2% NaTPB increases the sensitivity of the electrode response considerably, so that the membrane sensor (no. 6) demonstrates a nice Nernstian behavior.

Table 1. Optimization of the membrane ingredients.

No.	Composition of the membrane (wt %)					Slope (mV decade ⁻¹)
	PVC	Plasticizer	PCD	NaTPB	Linear range (mol L ⁻¹)	
1	30	DBP, 66	2	2	1.0×10^{-2} - 1.0×10^{-5}	10.6±0.3
2	30	BA, 66	2	2	1.0×10^{-2} - 1.0×10^{-6}	11.7±0.3
3	30	AP, 66	2	2	1.0×10^{-2} - 1.0×10^{-5}	16.8±0.5
4	30	NB, 68	2	0	1.0×10^{-2} - 1.0×10^{-5}	23.7±0.8
5	30	NB, 67	2	1	1.0×10^{-2} - 1.0×10^{-5}	22.1±0.4
6	30	NB, 66	2	2	1.0×10^{-2} - 1.0×10^{-6}	19.4±0.3
7	30	NB, 65	2	3	1.0×10^{-2} - 1.0×10^{-5}	19.2±0.5
8	30	NB, 67	1	2	1.0×10^{-2} - 1.0×10^{-5}	17.5±0.2
9	30	BA, 65	3	2	1.0×10^{-2} - 1.0×10^{-6}	21.8±0.6

3.3. Calibration curve

The emf response of the PVC membrane at varying concentrations of aluminum ions (Figure 2) indicates a rectilinear range from 1.0×10^{-6} to 1.0×10^{-2} mol L⁻¹. The slope of the calibration curve was

19.4 ± 0.3 mV decade⁻¹ of Al³⁺ ions activity. The detection limit, as determined from the intersection of the two extrapolated segments of the calibration curve, was 6.3×10^{-7} mol L⁻¹. The standard deviation of ten replicate measurements is ± 0.6 mV. The membrane electrode prepared could be used for at least 2 months without any measurable divergences in the responses.

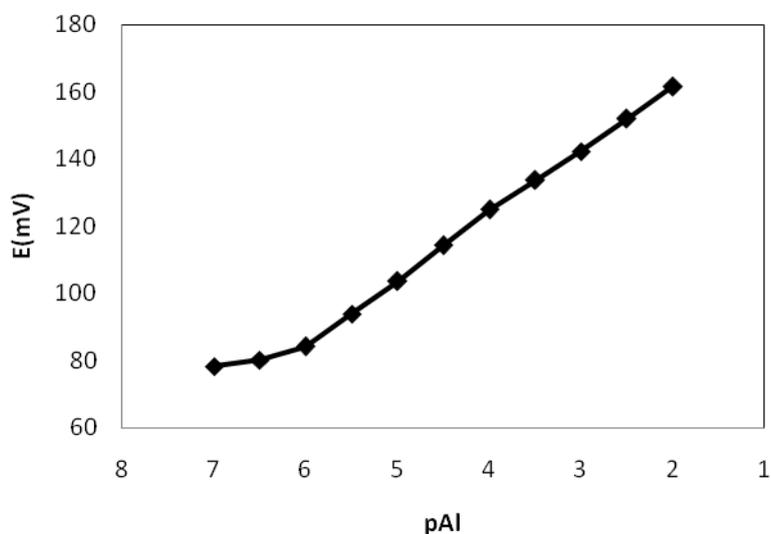


Figure 2. Calibration curves of the PCD-based Al³⁺ sensor.

3.4. The pH influence on membrane electrode response

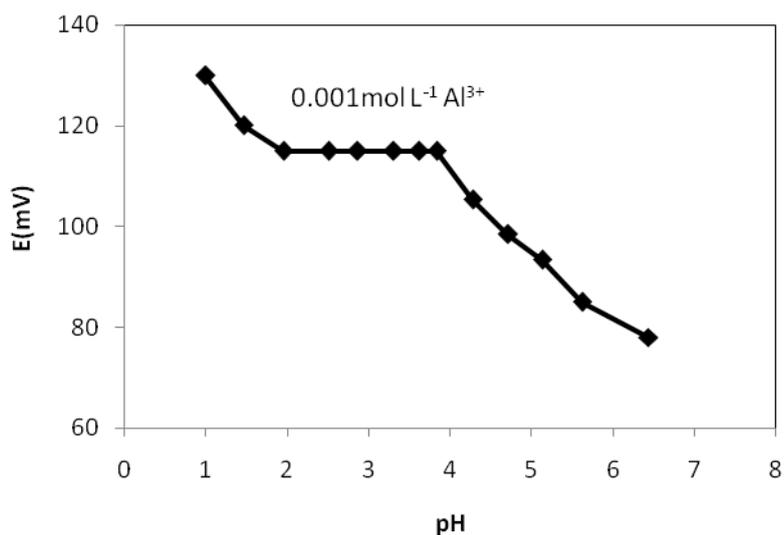


Figure 3. pH effect of the test solution (1.0×10^{-3} mol L⁻¹ of Al³⁺) of the Al³⁺ sensor based on PCD.

The influence of the pH of a test solution on the potential response of the membrane was studied using a 20.0 mL portion of a 1.0×10^{-3} mol L⁻¹ solution of aluminum chloride. Its pH was adjusted by drop-wise addition HCl or NaOH, and the emf of the sensor was measured at each pH value, in a pH range of 1.0–6.5. The results are shown in Figure 3. As seen, the potential remained

constant from pH 2.0 to 4.2, beyond which the potential changed considerably. At lower pH than 2.0, an increasing in potential was observed. This is due to the response of the membrane to hydronium ion (protonation of nitrogen atoms in acidic media). At higher pH values than 4.2, a decreasing in potential, due to the formation of insoluble of aluminum hydroxide, was observed.

3.5. Dynamic response time

Dynamic response time is an important factor for any ion-selective sensor. In this work, the practical response time was recorded by changing the concentration of Al^{3+} solution in the range 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1} and the results are shown in Figure 4. As can be seen, in the whole concentration range the electrode reaches its equilibrium response in a very short time (~ 5 s).

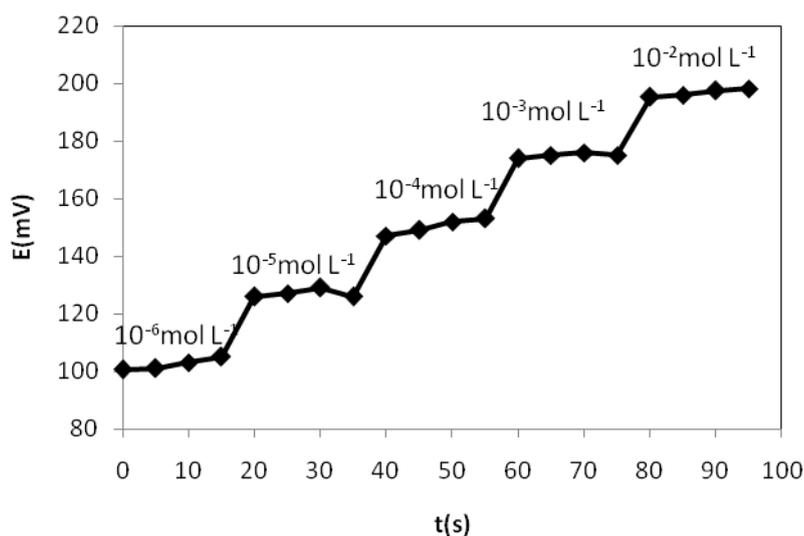


Figure 4. Dynamic response time of Al^{3+} sensor based on PCD.

3.6. Potentiometric selectivity of the Al^{3+} sensor

Selectivity is one of the most important characteristics of the ion selective electrodes. In order to assess the selectivity of the proposed Al^{3+} sensor over other interfering ions (B), the method of the matched potential method (MPM) was employed [41-44]. According to this method, the selectivity coefficient is defined as the activity (concentration) ratio of the primary ion (A) and the interfering ion, which gives the same potential change in a reference solution. Subsequently, the potential change should be measured upon changing the primary ion activity. Then, the interfering ion would be added to an identical reference solution until the same potential change would be obtained. The MPM selectivity coefficient, K^{MPM} , is then given by the resulting primary ion to the interfering ion activity (concentration) ratio, $K^{\text{MPM}} = a_A/a_B$. The resulting selectivity coefficients values are given in Table 2. From the data given in Table 2, it is immediately obvious that the proposed Al(III) sensor is highly selective with respect to most of cations. In the case of other lanthanide ions (i.e. Tb^{3+} , Er^{3+} , Ho^{3+} , Sm^{3+} and Nd^{3+}), the selectivity coefficients are equal or smaller than 2.7×10^{-3} , which seems to indicate

that the Al(III) ions can be determined in the presence of other lanthanides. As can be seen from Table 2, the selectivity coefficients for other metal ions tested (Pb^{2+} , Ni^{2+} , Co^{2+} , Cd^{2+} , Ca^{2+} , Mg^{2+} , K^+) are equal or smaller than 3.1×10^{-3} , indicating they would not significantly disturb the functioning of the proposed Al(III) membrane sensor. The surprisingly high selectivity of the membrane electrode for Al^{3+} ions over other cations used, most probably arises from the strong tendency of the carrier molecules for Al^{3+} ions.

Table 2. Selectivity coefficients ($K_{\text{Al}^{3+},\text{B}}^{\text{MPM}}$) of proposed Al^{3+} sensor.

Ion	K^{MPM}
Er^{3+}	3.8×10^{-4}
Tb^{3+}	5.7×10^{-4}
Nd^{3+}	2.1×10^{-3}
Sm^{3+}	6.1×10^{-4}
Ho^{3+}	2.7×10^{-3}
Ca^{2+}	4.3×10^{-4}
Mg^{2+}	7.4×10^{-4}
K^+	1.8×10^{-4}
Pb^{2+}	8.7×10^{-4}
Ni^{2+}	3.1×10^{-3}
Co^{2+}	6.5×10^{-4}
Cd^{2+}	2.2×10^{-3}

Response times, detection limits, slope, pH range, dynamic ranges and interfering ions of this electrode are compared with those of the best previous Al^{3+} electrodes, reported in the literature by other researchers [20-23] and the resulting values are given in Table 3. Obviously, the proposed sensor not only in terms of response time and detection limit but also in terms of selectivity is superior to the previously reported Al^{3+} sensors.

Table 3. Comparison of different Al^{3+} electrodes.

Parameter	Ref. 20	Ref. 21	Ref. 22	Ref. 23	This work
LR (mol L^{-1})	1.0×10^{-6} - 1.0×10^{-1}	1.0×10^{-6} - 1.0×10^{-1}	9.0×10^{-6} - 1.0×10^{-1}	1.0×10^{-6} - 1.0×10^{-2}	1.0×10^{-6} - 1.0×10^{-2}
DL (mol L^{-1})	6.0×10^{-7}	6.3×10^{-7}	7.0×10^{-6}	1.3×10^{-7}	6.3×10^{-7}
Response time (s)	<10	~10	~9	~70	~5
pH range	3.0-8.5	3.0-6.0	2.5-4.0	0.5-3.0	2.0-4.2
Slope(mVdecade^{-1})	20.0	19.6	20.0	18.5	19.4
Log $K_{\text{sel}} > -2$	Ag, Ba, Hg, K, Na, NH_4	Ca	Mg, Co, Zn	Cu, Ba, Hg, Cd	-

3.7. Analytical application

The proposed membrane electrode for Al^{3+} ion was found to work well under laboratory conditions. The sensor was successfully applied as an indicator electrode in the titration of 25 mL Al^{3+} ($1.0 \times 10^{-4} \text{ mol L}^{-1}$) with a standard EDTA solution ($1.0 \times 10^{-2} \text{ mol L}^{-1}$). The resulting titration curve is shown in Figure 5, indicating that the amount of Al^{3+} can be accurately determined with the electrode.

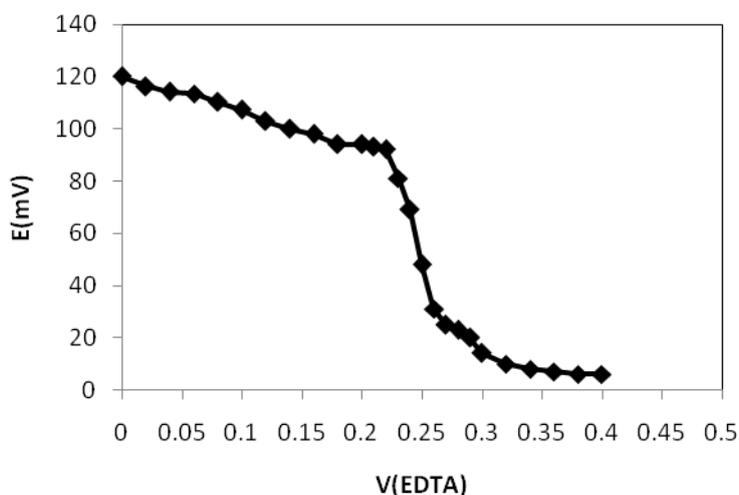


Figure 5. Potential titration curves of 25 mL $1.0 \times 10^{-4} \text{ mol L}^{-1} \text{ Al}^{3+}$ solution with $1.0 \times 10^{-2} \text{ mol L}^{-1}$ of EDTA.

4. CONCLUSION

The results obtained from the above-mentioned work revealed that a potentiometric PVC-based membrane sensor based on PCD functioned as a selective and sensitive Al^{3+} selective membrane sensor. The membrane with a composition containing 2% PCD as ionophore, 2% NaTPB as an anionic excluder, 66% NB as solvent mediator and 30% PVC showed the best potential response with a Nernstian behavior over a wide concentration range of 1.0×10^{-6} – $1.0 \times 10^{-2} \text{ mol L}^{-1}$ aluminum ions with a detection limit of $6.3 \times 10^{-7} \text{ mol L}^{-1}$. The developed electrode showed a fast response time ($\sim 5 \text{ s}$) and its potential responses were pH independent across the range of 2.0–4.2. The sensor exhibited aluminum selectivity with low interference from common alkali, alkaline earth, transition and heavy metal ions. The proposed sensor was used for the potentiometric titration of aluminum ions with EDTA.

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