



Design and construction of new potentiometric sensors for determination of Al^{3+} ion based on (Z)-2-(2-methyl benzylidene)-1-(2,4-dinitrophenyl) hydrazine



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ABSTRACT

(Z)-2-(2-methyl benzylidene)-1-(2,4-dinitrophenyl) hydrazine (L) was used as an active component of PVC membrane electrode (PME), coated graphite electrode (CGE) and coated silver wire electrode (CWE) for sensing Al^{3+} ion. The electrodes exhibited linear Nernstian responses to Al^{3+} ion in the concentration range of 1.0×10^{-6} to 1.0×10^{-1} M (for PME, LOD = 8.8×10^{-7} M), 5.5×10^{-7} to 2.0×10^{-1} M (for CWE, LOD = 3.3×10^{-7} M) and 1.5×10^{-7} to 1.0×10^{-1} M (for CGE, LOD = 9.2×10^{-8} M). The best performances were observed with the membranes having the composition of L:PVC:NPOE:NaTPB in the ratio of 5:35:57:3 (w/w; mg). The electrodes have a response time of 6 s and an applicable pH range of 3.5–9.1. The sensors have a lifetime of about 15 weeks and exhibited excellent selectivity over a number of mono-, bi-, and tri-valent cations including alkali, alkaline earth metal, heavy and transition metal ions. Analytical utility of the proposed sensor has been further tested by using it as an indicator electrode in the potentiometric titration of Al^{3+} with EDTA. The electrode was also successfully applied for the determination of Al^{3+} ion in real and pharmaceutical samples.

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1. Introduction

Aluminum is the most abundant metal in the Earth's crust. It is a major constituent of a large variety of volcanic and metamorphic rocks [1]. Known uses of aluminum are in cans, pots and pans, airplanes, and foil. Aluminum compounds are used in different products such as antacids, astringents, buffered aspirin, food additives, and antiperspirants. In most of the natural waters, the concentration of aluminum has been reported to be low because of the limited solubility at the pH of fresh water. It is too difficult to reveal the complete distribution of aluminum compounds in natural waters due to the formation of large number of compounds. Total concentration of aluminum is ranged from a few $\mu\text{g L}^{-1}$ in transparent neutral waters to mg L^{-1} in brownish water with low pH and the presence of organic and other substances [2, 3]. In biology, aluminum is considered as an essential element in the nutrition of animals, plants and humans. It acts as a co-factor in numerous enzymes and plays an important role in protein synthesis and cell

division [4]. It also plays an important role in the maintenance of cell membrane stability and in the function of the immune system. It also constitutes an active ingredient in medical products intended for tropical applications. Some studies on humans have shown that aluminum plays important roles in the pathology of Parkinson's disease, Alzheimer's disease, and diseases of dialysis [5–8]. Therefore, considering its widespread uses, its determination becomes important in view of its toxic effects. Although a number of methods such as spectrophotometry [9] spectrofluorimetry [10] graphite furnace atomic absorption spectrometry (GF-AAS) [11] inductively coupled plasma atomic emission spectrometry (ICP-AES) [12] and high performance liquid chromatography (HPLC) [13] have been reported for determination of aluminum in samples, their applications are restricted due to the complicated process of operating or expensive instrumentation. Ion-selective electrodes (ISEs) are useful tools for determination of an ion in the presence of other ions, offering interesting advantage such as fast response, simplicity, low cost and wide concentration range [14–19]. However, there have been only a few aluminum(III) selective sensors reported [20–29]. In this work, we used a recently synthesized (Z)-2-(2-methyl benzylidene)-1-(2,4-dinitrophenyl) hydrazine (L, Fig. 1) for the preparation of novel polymeric membrane electrode (PME), coated graphite electrode (CGE) and coated silver wire electrode (CWE) for highly selective and sensitive determination of Al^{3+} ion.

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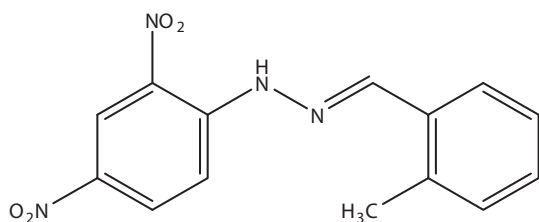


Fig. 1. Structure of ligand (L).

2. Experimental

2.1. Reagents

Reagent grade nitrophenyl octyl ether (NPOE), dibutyl phthalate (DBP), Benzylacetate (BA), tetrahydrofuran (THF) and high relative molecular weight PVC call from Merck were used as received. Nitrate salts of all cations used purchased from Merck were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5 . Triply distilled deionized water was used throughout.

2.2. Synthesis of ligand

A mixture of 2,4 dinitrophenylhydrazine (0.01 mol), 2-methyl benzaldehyde (0.01 mol) and a catalytic amount of PTSA was refluxed in ethanol (100 mL) for 4 h. Then the solvent was evaporated to 40 mL. After cooling to room temperature, the product was obtained as red crystals.

1H NMR (500 MHz, DMSO- d_6): 8.85 (s, 1H, CH), 8.31 (m, 1H, CH), 8.12 (s, 1H, CH), 7.15–7.65 (m, 4H), 6.95 (s, 1H, CH), 4.07 (s, 1H, NH), 2.37 (s, 3H, CH₃).

^{13}C NMR (125 MHz, DMSO- d_6): 149.2 (C–NH), 145.1 (C=N), 139.0 and 137.6 (C–NO₂), 135.2–118.3 (10, CH aromatic), 18.5 (CH₃).

Anal. Calcd for C₁₇H₁₂N₄O₃: C, 56.00; H, 4.03; N, 18.66; O, 21.31; found: C, 55.87; H, 4.21; N, 18.46; O, 21.46.

2.3. Preparation of electrodes

Membrane solution was prepared by thoroughly dissolving 5 mg of ligand, 35 mg of powdered PVC, 3 mg of additive and 57 mg of plasticizer in 5 mL of THF. The resulting clear mixture was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3 mm o.d. on top) was dipped into the mixture for about 10 s so that a nontransparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 1 h. The tube was then filled with an internal filling solution (1.0×10^{-3} M Al³⁺ ion). The electrode was finally conditioned for 20 h by soaking in a 1.0×10^{-2} M Al³⁺. A Silver/Silver chloride electrode was used as the internal reference electrode.

To prepare the coated graphite electrodes (CGEs), spectroscopic grade graphite rods of 10 mm long and 3 mm in diameter were used. A shielded copper wire was glued to one end on the graphite rod, and the electrode was sealed into the end of a PVC tube of about the same diameter with epoxy resin. The working surface of the electrode was polished with fine alumina slurries on a polishing cloth, sonicated in distilled water and dried in air.

The polished graphite electrode was dipped into the membrane solutions mentioned above, and the solvent was evaporated. A membrane was formed on the graphite surface, and the electrode was allowed to stabilize overnight and was finally conditioned by soaking in a 1.0×10^{-2} M solution of Al³⁺ ion for 48 h.

2.4. Emf measurements

The emf measurements with the polymeric membrane electrodes (PMEs) and CGE were carried out with the following cell assemblies:

Ag–AgCl|KCl (3 m)| internal solutions, 1.0×10^{-3} M Al³⁺ ion | PVC membrane | test solutions | Hg–Hg₂Cl₂, KCl (sate) (PME)

Hg–Hg₂Cl₂ (satd) | test solutions | membrane | graphite surface (CGE).

The emf observations were made relative to a double-junction saturated calomel electrode (SCE, Philips) with the chamber filled with ammonium nitrate solutions. A double-junction Silver/Silver chloride electrode (Metrohm) containing a 3 M solution of KCl was used as the internal reference electrode. Activities were calculated according to the Debye–Hückel procedure.

3. Results and discussion

Ligands used as ionophores in Al³⁺ ion-selective sensors should ideally fulfill certain conditions. It should interact selectively with Al³⁺ over other metal ions. It should have rapid exchange kinetics and should be sufficiently lipophilic to prevent leaching of the ligand into solutions surrounding the membrane sensor. The existence of donating nitrogens in the ligand L is expected to increase the stability of its aluminum complex over the other metal ions, especially alkali and alkaline earth cations [26,27,30].

3.1. Complexation study

In preliminary experiments, the complexation of L with a number of alkali, alkaline earth, transition metal and rare earth metal ions has been investigated conductometrically in acetonitrile solutions in order to obtain a hint about the stoichiometry of the resulting complexes at 25 ± 0.05 °C. For this purpose, 25 mL of 1.0×10^{-4} M cation solution was titrated against a 1.0×10^{-2} M ionophore solution in acetonitrile media. The conductance of the solution was measured after each addition of ionophore until the titration plot showed a break which corresponds to the 1:1 stoichiometry of the complexes. The conductometric titration data was further used to calculate the stability constant of the various ion–ionophore complexes formed [31,32] and the results are summarized in Table 1. As can be seen from Table 1, stability of the Al–L complex is higher than other cations tested. Thus, L with the most stable

Table 1
The formation constants of L–Mⁿ⁺ complexes at 25.0 ± 0.1 °C.

Ion	Log K _f
Al ³⁺	4.35 ± 0.02
Ag ⁺	2.95 ± 0.05
Fe ²⁺	2.11 ± 0.04
Ba ²⁺	2.09 ± 0.04
K ⁺	2.05 ± 0.06
Ca ²⁺	2.01 ± 0.03
Mg ²⁺	1.96 ± 0.03
Be ²⁺	1.91 ± 0.05
Fe ³⁺	2.03 ± 0.07
Pb ²⁺	2.20 ± 0.04
Zn ²⁺	1.85 ± 0.03
Cd ²⁺	1.80 ± 0.04
Na ⁺	1.77 ± 0.06
Tl ⁺	1.74 ± 0.05
Sr ²⁺	1.69 ± 0.06
Co ²⁺	1.61 ± 0.10
Ce ²⁺	1.51 ± 0.04
Cu ²⁺	1.49 ± 0.03
Ni ²⁺	2.00 ± 0.05
Hg ²⁺	2.41 ± 0.06

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