Int. J. Electrochem. Sci., 5 (**2010**) 29 - 38

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

An Imidazol Based Novel Potentiometric PVC Membrane Sensor for Aluminium(III) Determination

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Received: 1 November 2009 / *Accepted:* 1 December 2009 / *Published:* 1 January 2010

A new aluminum-selective liquid membrane electrode based on a neutral carrier 2-(4,5-dihydro-1,3-imidazol-2-yl)phenol(L) in a poly(vinyl chloride) (PVC) matrix is described. The sensor exhibits a Nernstian response for Al(III) over a wide concentration range ($1x10^{-6}$ M – $1x10^{-1}$ M) and detection limit of ($7x10^{-7}$ M). The best performance was obtained with a membrane composition of PVC (33%), ortho-nitrophenyloctyl ether (o-NPOE)(64%), ionophore (L) (2%) and sodium teraphenyl borate (NaTPB)(1%). The sensor exhibits the advantages of fast response time (10 seconds), operational lifetime (120 days), mixed solvent media tolerance upto (20%) and good selectivity co-efficient for Al(III) over an alkali, alkaline earth and transition metal ions. The electrode was used as indicator electrode in potentiometric titration of Al(III) with ethylenediaminetetraacetic acid (EDTA).

Keywords: Liquid membrane; Al(III) selective sensor; selectivity coefficient; potentiometry;

1. INTRODUCTION

Aluminium, the third most abundant element in the earth's crust, is the second most widely used metal in the world after iron, for the manufacture of automobiles, packaging materials, electrical equipments, machinery food additives, clinical drug, water purification and building construction etc. [1-2]. Aluminum, despite its wide applications in our daily life, has been found to be a non-essential element for living systems. It involved in causing dialysis dementia in patients who are unable to eliminate Al(III) because of renal dysfunction and also affect the central nervous system to cause different diseases like amyotropic lateral sclerosis [3–7]. Besides, aluminium toxicity causes microcytic hypochromic anemia, Al-related bone disease (ARBD), encephalopathy and also has the potential to produce some neurobehavioral and neuropathologic changes that are similar to those seen in Alzheimer's disease [8]. Therefore, liquid membrane type ion selective electrodes provide one of the most versatile sensing methods because it is possible to exhibit an extremely high sensing selectivity owing to the binding selectivity of an embedded lipophilic ionophore. Based on advances in host-guest chemistry of Al(III) selective ionophores there is a need of aluminium-selective sensors for the potentiometric monitoring of Al(III) ion in chemical, biological, industrial and environmental samples.

Some chromatographic and spectrophotometric techniques have been developed for the detection of aluminium, however, most of these methods involve using the hazardous chemicals such as fluorides, chloroform etc. Also, these analytical procedures are interfered easily by the variation in pH of the solution and the coexistence of interferential ions [9-11]. Further, the detection of Al(III) has always been a challenge due to the lack of spectroscopic characteristics, weak coordination ability in comparison with transition metal ions [12]. Therefore, there is a need of alternate options for detecting the trace of Al(III). In search of new metal ion quantification techniques, the potentiometric membrane sensor is an inexpensive and convenient method, provided acceptable sensitivity and selectivity for the target metal ion is achieved [13-21]. Because of these advantages, few aluminium selective sensors have been reported using neutral carriers [22-25]. However, the reported sensors exhibited some important limitations like low response time, narrow working activity range and some interference to Cu(II), Cd(II), Hg(II) and Fe(III). Keeping the above facts in view, the present work deals with the development an aluminium (III)-selective PVC membrane electrode using 2-(4,5-dihydro-1,3-imidazol-2-yl)phenol (L) as an ionophore and *o*-nitrophenyloctyl ether as a plasticizer.

2. EXPERIMENTAL PART

2.1. Reagents

The ionophore 2-(4,5-dihydro-1,3-imidazol-2-yl)phenol (L) was synthesized and purified, as described earlier [26]. Analytical grade *o*-nitrophenyloctyl ether (*o*-NPOE), dibutylphthalate (DBP), dioctylphthalate (DOP), bis-2-ethylsebcate (BES), tetrahydrofuran (THF), acetophenone (AP) and high molecular weight poly(vinyl chloride) (PVC) were used as received from Sigma-Aldrich. The nitrate salts of all metal ions were procured from Merck and were used as such after vacuum drying over P_2O_5. Triply distilled de-ionized water is used throughout.

2.2. Electrode preparation

The PVC membranes were prepared according to the following general procedure. Different membranes were prepared by dissolving 100mg of a mixture of ionophore, plasticizer and PVC (as given in Table 1) in approximately 5 mL of THF. After complete dissolution of all the components and thorough mixing, the resulting homogeneous mixture was poured into a glass dish of 30 mm diameter. THF was allowed to evaporate at room temperature, after ~24 h, transparent membranes were obtained. The prepared membranes were removed from the glass plate and circular pieces of 1.25 cm diameter were cut and mounted on the ground end of the Pyrex glass tube with araldite. Membranes were equilibrated for two days in a 1.0X10^{-2} M metal nitrate solution. The ratio of ionophore and the different additives in the membrane was optimized so that it should give good response in terms of Nernstian slope, working concentration range, detection limit etc.

2.4. The EMF measurements

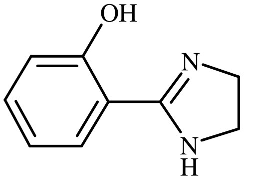
All the emf measurements were carried out at the room temperature (25±0.1° C) with the following cell assembly:

$$\text{SCE}\,|\,0.1\text{M Al}^{3+}\,||\,\text{Membrane}\,||\,\text{Al}^{3+}\text{ test solution}\,|\,\text{SCE}$$

The potential was measured for test solutions by varying the concentration in the range 1.0X10^{-8} to 1.0X10^{-1} M. Variation in the EMF were recorded after the stabilization and the values obtained were plotted as a function of the logarithm of the Al^{3+} ion activity. The activities of metal ions were based on activity coefficient (γ) and the data calculated from the modified form of the Debye-Hückel approximations.

3. RESULTS AND DISCUSSION

The ligand 2-(4,5-dihydro-1,3-imidazol-2-yl)phenol (L) has the coordinating sites *i.e.,* an hydroxyl group and a ternary N atom, similar to the family of the 8-Hydroxyquinoline ligands, which are extensively used in analytical chemistry for aluminium detection [27]. Recently, the ligand (L) has been investigated successfully as fluorescent sensor for the detection of aluminium(III) [28]. Further, the sufficient insolubility in water and ability to complex Al(III) selectively encourage us to use L as ionophore *i.e.,* an ion carrier in the PVC membranes. In preliminary investigation, the suitability of the ionophore (L) as an ion carrier was checked by its utilization in the fabrication of the PVC-membrane-ISEs for a wide variety of metal ions including alkali, alkaline earth and transition metal ions. The potential response of the membrane electrodes to various metal ions is shown in Fig. 1. As it can be observed, among the different tested cations, Al(III) presents the most sensitive response and seems to be suitably determined with the membrane electrode based on ionophore (L). This observation was clearly attributed both to the selective behavior of the ionophore against the Al(III) with respect to the other metal ions and also the rapid exchange kinetics of the resulting L-Al(III) complex. Therefore, the ionophore L can be used as suitable sensor material for the detection of Al(III).



2-(4,5-dihydro-1,3-imidazole-2-yl)phenol (L)

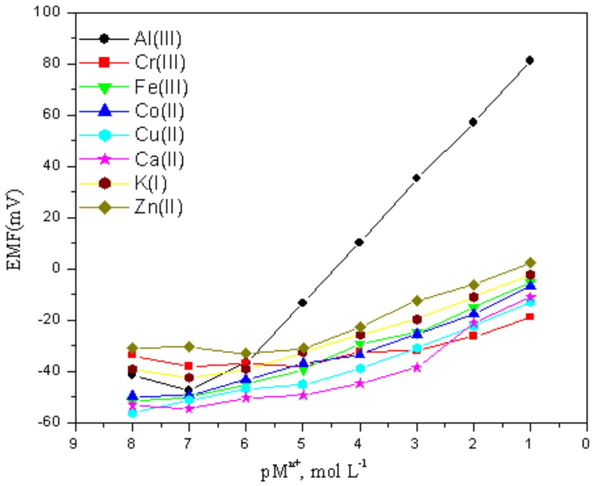


Figure 1. The potential response of various ISEs based on the following membrane composition: 33% PVC, 64% o-NPOE, 1% NaTBP and 2% L.

3.1. Optimization of the membrane composition

Some important features of the PVC membranes such as the plasticizer properties, the plasticizer/PVC ratio, the nature and the amount of the ionophore and in particular, the nature and the amount of the additives used etc. are significantly influenced the sensitivity and selectivity of the ISEs [29-35]. Therefore, the performance characteristics *viz.,* measurement concentration ranges, slope of the calibration curve, detection limit are examined with several membranes having ingredients of different proportions (as listed in Table 1). Usually, the lower plasticizer loading leads to the distortion of the electrode characteristics. Therefore, in all electrodes, a typical polymer:plasticizer ratio in membrane formation is approximately 1:2 and this ratio was kept constant. The nature of the plasticizer also influenced the dielectric constant of the membrane phase and the mobility of the ionophore molecules and its complexes [36] and therefore, it is expected to play fundamental role in determining the selectivity of electrode characteristics. As it can be observed from the Table 1, among different plasticizer examined, the best performance characteristics are obtained with the membrane having *o*-NPOE as plasticizer. It penetrate between polymer strands and essentially neutralize their polar groups with its own polar groups due to this the distance between the polymer strands increases and reduce the strength of the intermolecular forces acting between them and this leads to stable liquid membrane in the PVC matrix. The sensor number 2 with the L:NaTPB:PVC:*o*-NPOE ratio of 2:1:33:64 exhibits a Nernstian slope of 19.3 mV/decade over a wide concentration range of 1.0X10^{-6}-1.0X10^{-1} M. The detection limit of the proposed sensor is ~7.2X10^{-7} M obtained from the intersection of the two extrapolated segments of the calibration graph (Fig. 2).

Table 1. Optimization of membrane ingredients

Sensor No.	**Percentage (w/w) of various ingredients**				**Working Concentration range (M)**	**Slope (mV/decade)**
	L	**PVC**	**Plasticizer**	**NaTBP**		
1	1	33	65(*o*-NPOE)	1	$5.0X10^{-5}$-$1.0X10^{-1}$	24.6
2	2	33	64(*o*-NPOE)	1	$1.0X10^{-6}$-$1.0X10^{-1}$	19.3
3	2	33	64(DOB)	1	$1.0X10^{-4}$-$1.0 X 10^{-1}$	14.1
4	2	33	64(DOP)	1	$7.0X10^{-5}$-$1.0 X 10^{-1}$	15.7
5	2	33	64(BES)	1	$8.0X10^{-5}$-$1.0 X 10^{-1}$	16.2
6	2	32	64(AP)	1	$7.0X10^{-5}$-$1.0 X 10^{-1}$	17.3

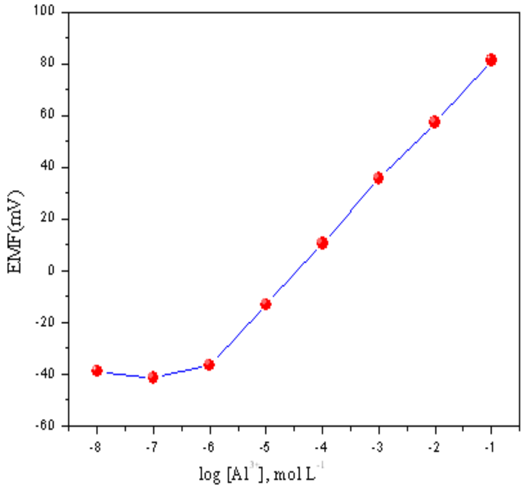


Figure 2. The calibration curve of the proposed Al(III)-ion selective electrode (sensor no.2).

3.2. Internal solution concentration and non-aqueous effect

The influence of the concentration of internal solution on the potential response of the proposed electrode was studied. The concentration was varied from $1.0X10^{-1}$ M to $1.0X10^{-3}$ M and the potential response of the electrode was obtained. It was found that the variation of the concentration of the internal solution does not cause any significant changes in the potential response of the electrode, except for an expected change in the intercept of the resulting Nernstian plots. The best results in terms of slope was obtained with internal solution of activity $1.0X10^{-2}$ M and thus, this concentration of internal solution is quite appropriate for smooth functioning of the proposed electrode.

The functioning of the electrode was also investigated in a partial non-aqueous media using 5-20% (*v/v*) water-methanol, water-ethanol and water-acetonitrile mixtures (Table 2). The sensor is worked satisfactory up to 15% (*v/v*) of non-aqueous content, and above this both working concentration ranges and slope decreases.

Table 2. Performance of Al(III)-ion selective sensor in partially non-aqueous media

Non-aqueous content (%, v/v)	**Working concentration range (M)**	**Slope (mV/decade)**
0	$1.0X10^{-6}$-$1.0X10^{-1}$	19.3
Methanol		
5	$1.0X10^{-6}$-$1.0X10^{-1}$	19.3
10	$1.0X10^{-6}$-$1.0X10^{-1}$	19.3
15	$7.0X10^{-6}$-$1.0X10^{-1}$	16.9
20	$4.0X10^{-4}$-$1.0X10^{-1}$	12.7
Ethanol		
5	$1.0X10^{-6}$-$1.0X10^{-1}$	19.8
10	$1.0X10^{-6}$-$1.0X10^{-1}$	19.6
15	$8.0X10^{-6}$-$1.0X10^{-1}$	17.0
20	$7.0X10^{-4}$-$1.0X10^{-1}$	12.2
Acetonitrile		
5	$1.0X10^{-6}$-$1.0X10^{-1}$	19.8
10	$1.0X10^{-6}$-$1.0X10^{-1}$	19.2
15	$6.0X10^{-6}$-$1.0X10^{-1}$	16.3
20	$8.0X10^{-4}$-$1.0X10^{-1}$	10.9

3.3. Effect of pH

The potential respond of the proposed electrode for the two test solution of Al(III) ion with concentration $1.0X10^{-2}$ M and $1.0X10^{-3}$ M was examined by varying the pH between 1.0 to 10.0 (Fig. 3). From Fig. 3, it is cleared that the potential respond is almost independent of pH in the range of 3.0–8.0, and the same can be taken as the working pH range of the proposed electrode. Above pH ~8.0, a gradual reduction in the potential was observed may be due to the formation of some Al(III)-hydroxo complexes in the solution. On the contrary, at lower pH values, the potentials increased, indicating the membrane sensor response to hydrogen ions.

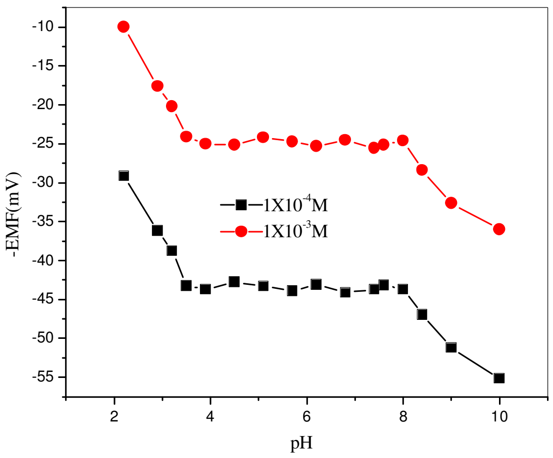


Figure 3. Effect of pH on the potential response of the proposed electrode (sensor no. 2).

3.4. The life time

The lifetime and stability of the proposed electrode are tested over a period of 120 days by taking four identical electrodes and it was found that the potential response characteristics remain unaltered. During this time period, the electrode works without any significant change in the response time (< 10 s), slope and working concentration ranges. However, a slight gradual decrease in slope was observed after this period due to some leaching of the plasticized PVC membrane components.

3.5. Potentiometric selectivity

The selectivity behavior is obviously one of the most essential characteristics of an ISE, which determined the feasibility of a reliable measurement in the target sample. To investigate the membrane electrode selectivity, its potential response was monitored in the presence of different interfering foreign cations viz., Li^+, Na^+, K^+, Cd^{2+}, Ca^{2+}, Mg^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Ag^+, Fe^{3+}, Cr^{3+} and Hg^{2+} with the help of the matched potential method (MPM) [37,38].In compared to the previous method that based on the Nicolski-Eisenman equation for the determination of potentiometric selectivity coefficients, MPM is able to get rid of some important limitations like non-Nernstian behavior of interfering ions, inequality of charged and activity dependence of potential values. According to MPM, the selectivity coefficients $K_{A,B}^{Pot}$ are calculated by the equation: $K_{A,B}^{Pot} = (a_A - a_A^/)/a_B$, where a known activity ($a_A^/$) of the primary ion solution is added to a reference solution that contains fixed activity (a_A) of primary ion and the potential change is recorded. Secondly, a solution of interfering ions (a_B) is added to the primary ion solution until the same potential change is observed. In the present studies a_A (1.0X10^{-3} M Al^{3+}), $a_A^/$ (1.0X10^{-2} M Al^{3+}) and a_B (1.0×10^{-2} M interfering ion) were taken to determine the selectivity coefficients. The resulting values of $K_{A,B}^{Pot}$ are summarized in Table 3. They are in the order of 10^{-2} or lower for almost all diverse metal ions examined indicating their non-interferences with the functioning of the proposed Al^{3+} selective sensor [22,24,26]. The high selectivity of the membrane electrode for aluminium ions over above metal ions probably arises due to the strong affinity of the L for Al^{3+}.

Table 3: Potentiometric selectivity coefficients of Al(III)-ion selective electrode

Interfering ions (B)	**Logarithmic values of the selectivity coefficients ($K^{Pot}_{Al^{3+},B}$)**			
	This work	**Reported work**		
		[22]	[24]	[26]
Li^{+}	-3.02	-		-
Na^{+}	-3.17	-3.05	-2.76	-0.37
K^{+}	-3.18	-3.17	-3.00	-0.89
Cd^{2+}	-3.34	-3.12	-3.30	-2.30
Ca^{2+}	-2.46	-1.98	-	-3.00
Mg^{2+}	-2.57	-2.06	-	-2.81
Ba^{2+}	-2.72	-2.59	-	-
Mn^{2+}	-3.01	-2.51	-3.60	-2.65
Co^{2+}	-2.90	-	-3.61	-2.24
Ni^{2+}	-2.94	-3.01	-3.72	-2.36
Cu^{2+}	-2.94	-3.02	-3.92	-2.67
Zn^{2+}	-2.88	-2.01	-3.55	-2.26
Ag^{+}	-3.53	-	-	-0.99
Fe^{3+}	-2.61	-2.54	-2.60	-3.70
Cr^{3+}	-3.13	-3.07	-	-4.30
Ce^{3+}	-3.52	-2.67	-	-
Hg^{2+}	-2.90	-2.54	-4.00	-1.21
Pb^{2+}	-2.41	-2.73	-3.09	-2.34

3.6. Potentiometric titration

The practical utility of the proposed membrane electrode was investigated by using it as an indicator electrode for the titration of 50 ml of $1.0X10^{-3}$ M Al^{3+} ion solution against a standard $1.0X10^{-2}$ M EDTA solution. The obtained titration curve (Fig. 4) is of standard sigmoid shape, indicating the sufficient selectivity of the proposed electrode for Al^{3+} ions and sharp inflection point at the titrant volume corresponding to the 1:1 stoichiometry for Al^{3+}-EDTA complex.

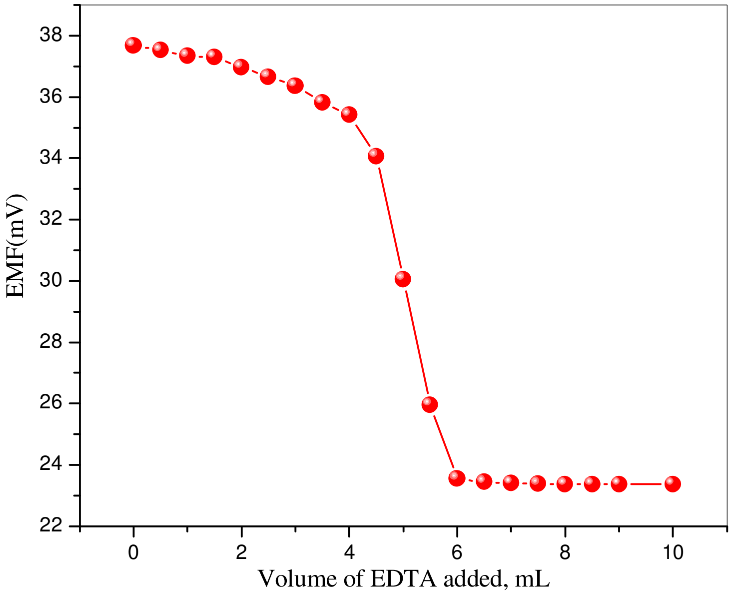


Figure 4. Potentiometric titration of 50 mL of Al^{3+} ($1.0X10^{-3}$ M) against EDTA solution ($1.0X10^{-2}$ M) using the proposed electrode as an indicator.

4. CONCLUSIONS

Based on the findings discussed in this paper, L could be used as an electro-active material to produce Al(III) ISEs with excellent electrode characteristics like linear response, sensitivity and selectivity with a number of common interfering ions. The electrode having a lifetime of 120 days with good reproducibility and can be used in non-aqueous media up to 15% (*v/v*) content. The electrode works well in a wide pH range of 3.0-8.0 and shows fast response time (< 10 s). This electrode was successfully employed as an indicator electrode in potentiometric determination of Al^{3+}.

ACKNOWLEDGEMENTS
The authors are thankful to Director, Thapar University, Patiala and Sant Longowal Institute of Engineering & Technology, Longowal for providing research facilities.

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