Aluminium (III) Selective PVC Membrane Sensor Based on Zinc Complex of Thiophenealdehyde Thiosemicarbazone as an Ionophore

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ABSTRACT

A new sensitive and selective PVC-based membrane sensor for Al(III) ion was constructed by employing Zinc(II) complex of Thiophenealdehydethiosemicarbazone [Zn(LL2)$_2$]Cl$_2$ as ionophore material. The best performance was recorded with a membrane having a composition of PVC: DBP: Ionophore: NaTPB as 30: 63: 2.8: 4.2 (w/w %). The sensor shows a Nerstian response for Al(III) ion over a wide concentration range of 1.0×10^{-7} to 1.0×10^{-1} M with the slope of 19.8 ± 0.1 mV/per decade. The detection limit found was 6.7×10^{-9} M. It has relatively fast response time of <10 s and can be used for 3 mon without any considerable changes in potentials. The proposed sensor provides relatively good selectivity and high sensitivity for Al(III) over other mono, di and trivalent cations and could be used in a pH range of 2.4-9.5. It was used successfully as an indicator electrode in potentiometer determination of Al^{3+} with EDTA.

Keywords: Chemical sensors, Al (III) electrode, Schiff base, Ion- selective electrode

INTRODUCTION

The construction of sensitive and precise devices based on electrochemical sensors, which are capable of detecting and identifying the concentration of polluting substances in different ecosystems, has been the subject of growing interest in recent years [1-4]. Polymeric membrane Ion Selective Electrode (ISEs) provides one of the most powerful sensing tool because it is possible to select various electroactive materials according to the charge and size of the target ion in clinical and environmental testings [5-8]. Membrane based Ion Selective Electrodes (ISE) are appropriate for this purpose because they are highly selective for inorganic ions and they are easy to develop. A large number of schiff base imines are reported to form strong complexes with a specific ion due to geometric factor [9,10].

Aluminium is the third most abundant element in the earth's crust and the second most widely used metal in the world, for the manufacture of automobiles, electrical equipments, as packaging materials, machinery food additives, clinical drug, in water purification and building constructions etc. [11,12]. Aluminum, despite its wide applications in our daily life, has been found to be a non-essential element for living systems. Aluminium is inert in the body. In spite of this, injuries to the pulmonary system and fibrosis have been found in animals exposed to prolonged inhalation of heavy concentration of aluminium dust. It is believed that aluminium plays important roles in the pathology of Parkinson's Disease (PD), Alzheimer's Disease (AD) and diseases of dialysis [13-17]. Aluminium toxicity also causes microcytic hypochromic anemia disease, Al-related Bone Disease (ARBD), encephalopathy and in higher concentration produces some neurobehavioral and neuropathologic changes that are similar to those seen in AD [18]. Therefore, liquid membrane type ion selective electrodes provide one of the most versatile sensing methods with 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.

The available methods for monitoring the aluminum ion 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 determing aluminum in samples. All these methods are either time consuming, involving multiple sample manipulations, or too expensive to afford in most analytical laboratories. Therefore, there is a need of alternate options for detecting the trace of Al(III). 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 [19-26]. Numerous ISEs based on Polyvinylchloride (PVC) membrane were reported for many inorganic ions [27], but very little was published on PVC-based trivalent ions such as Cr(III), Bi(III), Au(III) and Al(III) [28]. 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) ions.

In the present study, we reported a PVC membrane based on Zinc(II) complex of thiophenealdehydethiosemicarbazone [Zn(LL2)$_2$]Cl$_2$ as an ionophore and dibutyl pthalate (DBP) as a plasticizer. This PVC membrane sensor shows better potentiometric response as compared to the previously reported Al(III) sensors with low detection limits and wider pH range of 2.4-9.5.

MATERIALS AND METHODS

Experimental

All the chemicals used were of Analytical Grade (AR) and of the highest purity available. Thiophene-2-aldehyde (CDH), Thiosemicarbazide (CDH) and metal salts were purchased from E. Merck and were used as received. Dioctylphthalate (DOP), Tributyl Phosphate (TBP), Dibutylphthalate (DBP), Sodium Tetraphenyl Borate (NaTPB) were purchased from E. Merck and used without any purification. High molecular weight PVC powder and Tetrahydro Furan (THF) were purchased form Sigma-Aldrich. Standard solutions of metal salts were freshly prepared in double distilled dionized water.

Physical measurement

The percentage composition of C, H, N and S were analyzed on a Vario Micro Cube elemental analyzer, Model Vario-III. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker, Model DPX-300 NMR spectrophotometer using dimethyl sulfoxide (DMSO) as solvent. Chemical shift are given in ppm relative to tetra methylsilane as reference. The IR spectra were recorded on a Perkin Elmer FT-IR spectrophotometer, Model No. BX-2. A Perkin-Elmer Atomic Absorption Spectrophotometer (AAS) of Model 3100 was used.

Syntheses of ionophore (LL2)

Hot ethanolic solution (20 ml) of thiophene-2-aldehyde (1.12 g, 0.01 mmol) was mixed with equivalent amount of thiosemicarbazide (0.91 g, 0.01 mmol) in a beaker with few drops of acetic acid with constant stirring. The mixture was refluxed at ~80°C for 2 h. On cooling, a chreme-white coloured compound was separated out. It was filtered, washed several times with 50% ethanol, dried and recrystallized from methanol (Figure 1).
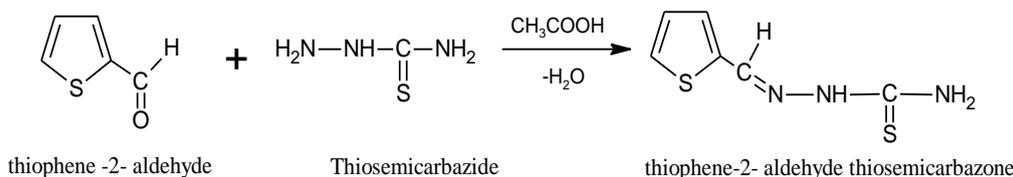

Figure 1: Synthesis of ionophore (*LL2*)

Thiophenealdehydethiosemicarbazone (LL2)

Yield (75.0%), M.P: 160°C, Anal. calc. for (%)=C$_6$H$_7$N$_3$S$_2$: C, 38.89%; H, 3.81%; N, 22.68%; and Found (%): C, 41.35%; H, 3.68%; N, 24.05%; FT-IR (KBr)/cm^{-1}: υ(NH$_2$) 3452 (b), υ(NH) 3295 (b), υ(C=N) 1454, υ(C=S) 1241, δ (C=S) 802; ^{1}H NMR (DMSO-D6, 300 MHz): δ/ppm=7.2 (H,s,- NH); 6.1-6.45 (Ar-H); 6.9 (H,s,-N=CH); 2.8 (2H,s,-NH$_2$).

Synthesis of complex [Zn(LL2)$_2$]Cl$_2$

A hot aqueous ethanolic solution (20 ml, 1:1 v/v) of thiophenealdehydethiosemicarbazone (0.37 g, 0.02 mmol) and a hot aqueous solution (20 ml) of zinc chloride (0.068 g, 0.01 mmol) were mixed with constant stirring. The mixture was refluxed for about 4 h on water bath. On cooling a light yellow coloured precipitate was separated out. The same was filtered, washed with 50% ethanol and and recrystallized from methanol (Figure 2).
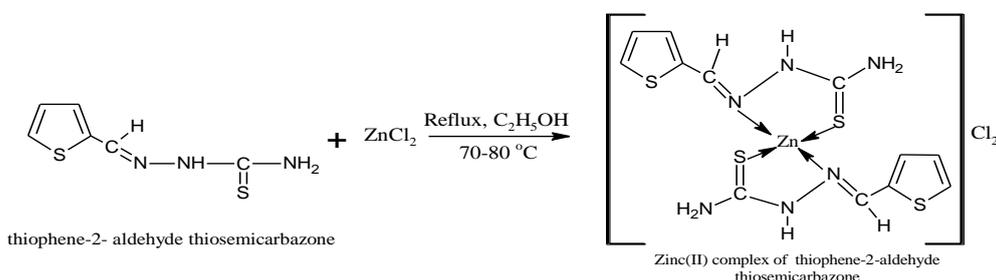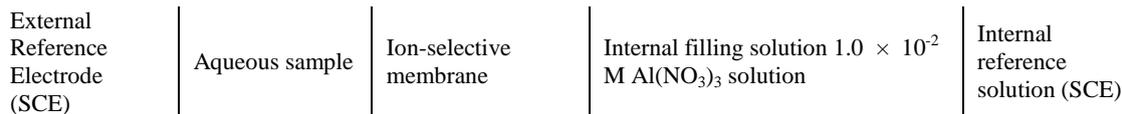

Figure 2: Synthesis of complex [Zn(LL2)$_2$]Cl$_2$

Zinc(II) Thiophenealdehydethiosemicarbazone complex [Zn(LL2)$_2$]Cl$_2$

Yield (90%), M.P: 230°C, Anal calc. for (%)=C$_{12}$H$_{14}$N$_6$S$_4$ZnCl$_2$: C,28.44; H,2.78; N,16.58; S,25.31; Found: (%): C,28.15; H,2.76; N,16.47; S,24.98; FT-IR(KBr)/cm^{-1}: υ(NH$_2$) 3452 (b), υ(NH) 3295 (b), υ(C=N) 1454, υ(C=S) 835.

Potential measurements

The PVC membranes were equilibrated for 48 h in 1.0 × 10^{-2} M Al(NO$_3$)$_3$ solution. Membrane electrode potentials have been measured at room temperature by varying the concentration of Al(NO$_3$)$_3$ in the test solutions by using digital pH meter, potentiometer (ELICO L1-10, India) and Saturated Calomel Electrodes (SCE) as a reference electrode with the following electrochemical cell assembly:

External Reference Electrode (SCE)	Aqueous sample	Ion-selective membrane	Internal filling solution 1.0×10^{-2} M $Al(NO_3)_3$ solution	Internal reference solution (SCE)

Fabrication of PVC membrane and electrodes

The general procedure for preparing the ion selective membranes was used given by Craggs et al. [29,30]. For the preparation of PVC membrane, appropriate amounts of PVC; Plasticizer; Ionophore; Excluder was thoroughly dissolved in THF (10 ml). The homogeneous mixture was obtained by evaporating the solvent THF at room temperature until a sticky and oily mixture was obtained. After this mixture was poured into a glass dish and 5 mm diameter Pyrex tubes were dipped into this mixture for some time to obtain a 0.3 mm thick non-transparent membrane. One end of this Pyrex tube was fixed with the help of Araldite. After getting dried for 4 h, this tube was filled with 1.0×10^{-2} M $Al(NO_3)_3$ as internal filling solution and conditioned for atleast 2 days in $Al(NO_3)_3$ solution. It is well known [31-33], that the sensitivity, linearity and selectivity obtained for the given ionophore depends significantly on the membrane composition and the nature of plasticizer used. Therefore, the ratio of membrane components, contact time and concentration of equilibrating solution were optimized after a good deal of experimentation with various membranes of different compositions. The PVC membranes, which generate reproducibe and stable potentials, have been studied. The blank membrane having only PVC as membrane ingredients was also fabricated and studied for potential. The membrane with PVC and plasticizer only, were generated small potentials with slope of ~ 9 mV/decade.

RESULTS AND DISCUSSION

Response of the cation

Various PVC-membranes ion-selective electrodes with the synthesized ionophore were prepared and tested for different metal ions. The potential responses of ions were plotted as the negative *log* of concentration against the potential values (E/mV) obtained as shown Figure 3. It has been observed that the best response was shown by PVC membrane with Al^{3+} ion as compared to the other cations over a linear concentration range $(1.0 \times 10^{-7}\text{-}1.0 \times 10^{-1}$ M).
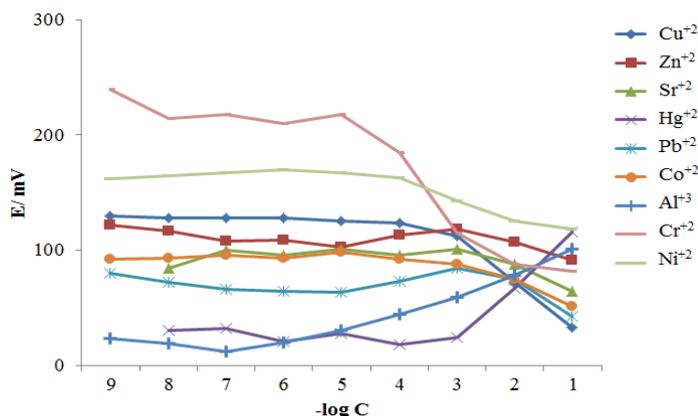

Figure 3: Potential response of various ion selective electrodes based on zinc complex of thiophenealdehyde thiosemicarbazone (ZTATS) as an ionophore

Optimization of the membrane composition

These sensors exhibit the wide working concentration range of $1.0 \times 10^{-7}\text{-}1.0 \times 10^{-1}$ M with a slope of 19.8 ± 0.1 mV/decade for Al(III) ions with the detection limit of 6.7×10^{-9} M. Further the influence of the membrane composition on the potential response of the membrane electrode was studied. Some characteristic features of the PVC membranes such as the plasticizer properties, the plasticizer/PVC ratio, the nature and the amount of the ionophore added and the nature of the additives used etc. are significantly influenced the sensitivity and selectivity of the proposed ISEs [34-36]. Therefore, the performance characteristics *viz.,* measurement of concentration ranges, slope of the calibration curve, detection limits are examined with several membranes having ingredients of different proportions (Table 1).

Table 1: Composition of PVC membrane of zinc complex of thiophenealdehyde thiosemicarbazone as an ionophore and performance characteristics of Al^{3+} selective sensors based on them

Sensor No.	Composition of membranes (w/w %)				Working conc. range (M)	Slope ($\pm$ mV/decade)
	ZTATS	PVC	NaTBP	Plasticizer		
1	3.8	33	4.5	-	$1.0 \times 10^{-7}\text{-}1.0 \times 10^{-1}$	15.2
2	2.8	30	4.2	DBP, 63	$1.0 \times 10^{-7}\text{-}1.0 \times 10^{-1}$	19.8
3	3.3	30	4.7	DOP, 62	$1.0 \times 10^{-5}\text{-}1.0 \times 10^{-3}$	19.6
4	4.2	27	3.8	TBP, 65	$1.0 \times 10^{-5}\text{-}1.0 \times 10^{-1}$	16.0
5	3.2	31	4.8	DBP, 61	$1.0 \times 10^{-6}\text{-}1.0 \times 10^{-2}$	16.4

Optimization studies of the PVC-membranes for Al^{3+} selective electrode is reported in Table 1. It has been observed (Figure 3), that the membrane without plasticizer (sensor no.1) shows linear response to Al^{3+} in the concentration range 1.0×10^{-7}-1.0×10^{-1} M with a slope of 15.2 mV/decade. The nature of plasticizer in membrane influences the dielectric constant, the mobility of the ionophore molecules and state of compound [37], which plays a key role for the ion-selective characteristics of electrode. Response characteristics of the membrane electrode were investigated by using different plasticizers of variable polarities including Dibutylphthalate (DBP), Di(2-ethylhexyl)phthalate (DOP) and Tert-butylphenol (tBP). Results in Table 1, shows that the membranes prepared with a plasticizer: PVC ratios of about 2.1 with DBP were found to have the best sensitivity and the widest linear range. It is obvious from Table 1, membrane number 2 with PVC; DBP; Ionophore; NaTPB in percent ratio of 31: 64: 3.2: 1.8 shows the Nernstian behavior of the proposed membrane electrode over a wide concentration range. The Nernstian slope was found to be 19.8 ± 0.1 mV/decade of activity for this sensor.

Effect of pH

The influence of pH on Al(III) selective electrode was tested at 1.0×10^{-4} M Al^{3+} ion concentration over the pH range of 2.4-9.5 and results are shown in Figure 4. The pH of the solutions was adjusted by adding 0.1 N HCl or NaOH solutions. Results shows that the potentials remain constant in the pH range 2.4-9.5, which is useful as the working pH range for the proposed electrode. However, at higher pH values potential decreses and at lower pH below 3, a sharp rise in potential is recorded which probably due to the hydrolysis of Al^{3+} and disruption of H^+ ions from the test solution, respectively. The working pH range is 2.4-9.5.
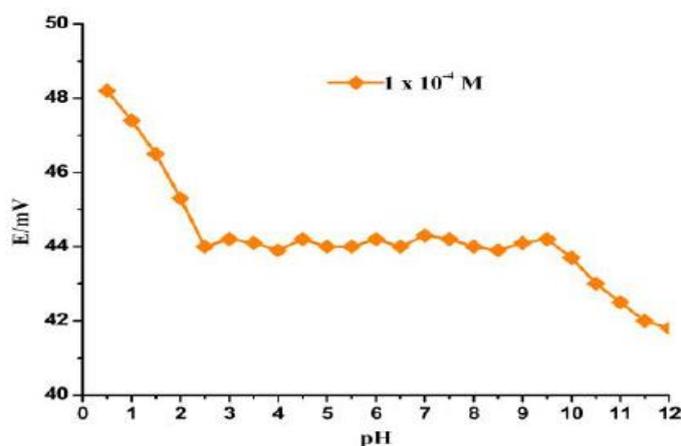

Figure 4: Effect of pH variations on potential (E/mV) for the Al^{3+} ISE

Non-aqueous effect

The performance of the proposed sensor was also investigated in partially non-aqueous medium. For this methanol-water, ethanol-water and acetone-water mixtures were taken. Results are summarized in Table 2, which shows that the membrane worked satisfactorily in non-aqueous medium up to 20% (v/v) and the working concentration range as well as slope remained unaffected. However with non-aqueous content of more than 20% (v/v), slope and working concentration range was reduced.

Table 2: Effect of partially non-aqueous medium on the working of Al^{3+} selective sensor (sensor no. 2)

Non-aqueous content (v/v, %)	Working concentration range (M)	Slope (± 0.1 mV/decade of activity)
Methanol		
10	1.0×10^{-7}-1.0×10^{-1}	19.8
20	1.0×10^{-7}-1.0×10^{-1}	19.5
30	1.0×10^{-6}-1.0×10^{-1}	19.1
Ethanol		
10	1.0×10^{-7}-1.0×10^{-1}	19.6
20	1.0×10^{-7}-1.0×10^{-1}	19.5
30	1.0×10^{-7}-1.0×10^{-1}	19.2
Acetone		
10	1.0×10^{-7}-1.0×10^{-1}	19.7
20	1.0×10^{-7}-1.0×10^{-1}	19.3
30	1.0×10^{-7}-1.0×10^{-2}	19.1

Selectivity of ion sensing membranes

The selectivity is one of the most important characteristic of a membrane sensor that determines the utility of sensor device for the estimation of analyte ion in the presence of other ions and in real sample measurements. In order to determine the selectivity of the proposed electrode fixed interference method (FIM) was employed [38-40]. The selectivity coefficient values (K_{sel}) are calculated and summarized in Table 3. The potential (E) of a cell composed of an ion-selective electrode and a reference electrode is measured with solutions containing a fixed concentration of interfering ions, a_B and by varying the activity of Al^{3+} ion, a_A. The potential values obtained were then plotted against the activity of the aluminium ion. The intersection of the extrapolated linear portions of this curve will give the value of activity of Al^{3+} ion a_A, which is to be used to calculate selectivity coefficient values ($K_{A,B}^{Pot}$) from the equation:

$$K_{A,B}^{pot} = \frac{a_A}{(a_B)^{z_A/z_B}} \qquad (2)$$

Where z_A and z_B are charge on the primary ion A (Al^{3+}) and on interfering ion, B; a_A and a_B are the activities and K_{sel} is the selectivity coefficient for the primary ion A against the interfering ion, B. The charges on the ions z_A and z_B have the same signs, either positive or negative. Value of selectivity coefficient equal to 1.0 indicates that the proposed sensor responds equally to primary ion as well as for interfering ions. However, a smaller value less than 1.0 indicates that membrane sensor is responding more to primary ion compared to the interfering ion. Further, smaller is the selectivity coefficient, higher is the selectivity order. It is found that the selectivity coefficient values in Table 3 are sufficiently smaller than 1.0 for the proposed sensor, which indicates that the proposed electrode is highly selective to Al^{3+} over all the interfering ions. Thus it can be used to estimate aluminium in presence of other ions by direct potentiometry.

Table 3: Selectivity coefficient values for Al³⁺ ion selective sensor by fixed interference method

S. No.	Interfering ion (B)	Selectivity coefficients (K_{sel})
1	K^+	3.24×10^{-2}
2	Cd^{2+}	3.12×10^{-2}
3	Ca^{2+}	2.46×10^{-3}
4	Na^+	2.76×10^{-2}
5	Sr^{2+}	2.06×10^{-2}
6	Ba^{2+}	2.56×10^{-2}
7	Co^{2+}	3.61×10^{-2}
8	Ni^{2+}	2.36×10^{-2}
9	Zn^{2+}	3.55×10^{-3}
10	Cu^{2+}	2.94×10^{-2}
11	Cr^{3+}	4.10×10^{-2}
12	NH_4^+	3.72×10^{-2}
13	Hg^{2+}	2.58×10^{-2}
14	Pb^{2+}	3.07×10^{-2}
15	Ce^{3+}	2.65×10^{-2}

Response time of the proposed electrode

The response time is an important characteristic for any ISE to critically review its analytical application as a sensor [41]. This is defined as the average time required for the electrode to reach a potential within ± 1 mV of final equilibrium value after successive immersion of a series of Al^{3+} ion with minimum tenfold difference in concentrations [42]. The static response time of the proposed Al^{3+} sensor was found as <10 s. over the concentration range 1.0×10^{-1}-1.0×10^{-7} (Figure 5).
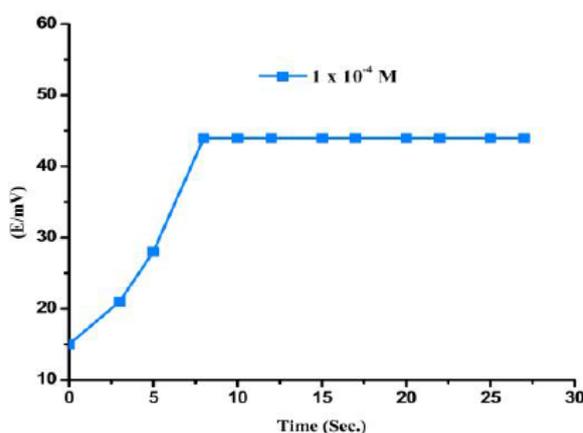
Figure 5: Static potential-time plots Al³⁺ concentration of 1.0×10^{-4} M

Lifetime of the proposed sensor

Lifetime of any sensor is a measure of sensor durability. The lifetime of the sensor (no. 2) was studied over a 4 mon period. It was seen that the proposed membrane electrode can be used for at least 3 mon, without any major changes in response time, slope, or selectivity. A 1.0×10^{-2} M solution of Al(III) ion is well appropriate for smooth functioning and storage of the membrane electrode.

Comparison study of the electrode

The response characteristics such that response times, slope, pH range, working concentration range and selectivity coefficients of the membrane electrode are compared with the previously reported Al(III) ion selective electrodes based on various ionophores by other researchers [43-48]. From the results summarized in Table 4, it is clear that the selectivity, linear range and pH range of the proposed Al(III) sensor is superior to the reported sensors for Al^{3+} ions.

At the same time, easy synthesis of a highly lipophilic ligand and open chain ionophore, using easily and economically available starting materials, makes the proposed sensor a better membrane electrode.

Table 4: Comparison of the potentiometric parameters of the proposed Al^{3+} sensor with the literature reported

S. No.	Ionophore name	Woking concentration range (M)	Slope (mV/decade of activity)	pH range	Lifetime (month)	Ref.
1	2-(4,5-dihydro-1,3-imidazol- 2-yl)phenol	$1 \times 10^{-6} - 1 \times 10^{-1}$ M	19.3 ± 0.1	3-8	>3	[43]
2	6-(4Nitrophenyl) -2-phenyl-4-(thiophen-2-yl)-3,5-diaza-bicyclo[3.1.0]hex-2-ene	$1 \times 10^{-6} - 1 \times 10^{-1}$ M	19.6 ± 0.4	3-6	>3	[44]
3	1,4-bis[o-(pyridine-2-carboxamidophenyl)]-1,4-dithiobutane (PCD)	$1 \times 10^{-6} - 1 \times 10^{-2}$ M	19.4 ± 0.3	2-4.2	2	[45]
4	Salicylaldehyde salicyloyl hydrazone	$9 \times 10^{-6} - 1 \times 10^{-1}$ M	20.0 ± 0.2	2.5-4.0	3	[46]
5	Furil	$1 \times 10^{-6} - 1 \times 10^{-2}$ M	18.5 ± 0.7	0.5-0.3	2	[47]
6	1-Hydroxy-3-methyl-9-xanthen-9-one	$1.6 \times 10^{-6} - 1 \times 10^{-1}$ M	20.0 ± 0.2	3.0-8.5	3	[48]
7	ZTATS	$1.0 \times 10^{-7} - 1.0 \times 10^{-1}$ M	19.8 ± 0.1	2.4-9.5	3	This work

Analytical applications

Potentiometric titration of Al^{3+} ions with a standard EDTA solution

The proposed Al(III) membrane sensor was found to work well as an indicator electrode. The membrane sensor was successfully tested as an indicator electrode in the potentiometric titration of Al^{3+} with Ethylenediaminetetraacetic Acid (EDTA). For this 25 ml 1.0×10^{-4} M solution of Al^{3+} was titrated against a standard solution of EDTA of 1.0×10^{-2} M concentration. Results in Figure 6 shows that the amount of Al^{3+} in solution can be accurately determined with this membrane electrode.
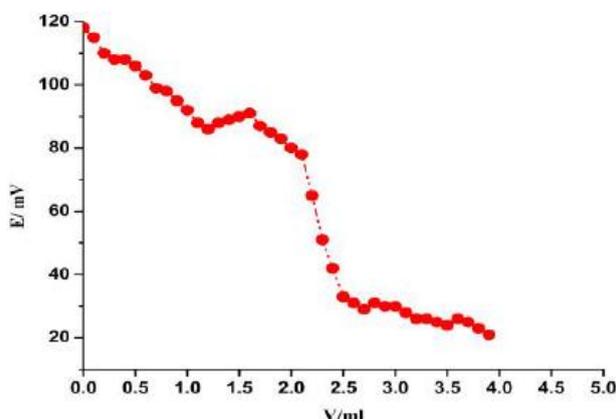
Figure 6: Potentiometric titration curve of 20 ml solution of 1.0×10^{-3} M Al^{3+} with 0.01 M EDTA at pH 7 by using the proposed sensor (no.2)

Determination of aluminium in water samples

The practical utility of the proposed Al^{3+} ion sensor was demonstrated through the analytical determination of Al^{3+} in tap water, ground water, mineral water and syrup by using potentiometry. The results observed for analysis were also compared with Atomic Absorption Spectrometry (AAS) and summarized in Table 5. It is seen that the values obtained were in good agreement with the results obtained by AAS method. Hence, the proposed sensor finds application for the estimation of aluminium ion in solution.

Table 5: Determination of Al^{3+} in real samples by proposed sensor electrode and atomic absorption spectrometry

Sample type	Al^{3+} found by proposed sensor (mgL^{-1})	Al^{3+} found by AAS (mgL^{-1})
Tap water	5.8	5.4
Ground water	12.2	12.0
Mineral water	9.8	9.6
Syrup	8.4	8.1

CONCLUSION

Based on the results discussed in this paper, Zn(II) complex of thiophenealdehyde thiosemicarbazone $[Zn(LL2)_2]Cl_2$ can be considered as a an ionophore for the construction of membrane based electrode for determining Al^{3+} ion in solution. The proposed membrane sensor was developed with a membrane composition of 30% PVC, 63% DBP as solvent mediator, 2.8% NaTPB as cation excluder and 4.2% $[Zn(LL2)_2]Cl_2$ as an ionophore.

The proposed electrode exhibits a Nernstian slope of 19.8 ± 0.1 mV decade^{-1} of activity, and a wide concentration range 1.0×10^{-7}-1.0×10^{-1} M. It was employed to determine Al^{3+} ions in various water samples with good accuracy. High selectivity, a wide linear range, a low detection limit, short response time, stable reading and long lifetime as well as a Nernstian slope were observed for the sensor. The life time of the electrode was 3 mon with a short response time of < 10 s.

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