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Iron (III) Selective Electrode Based on S-Methyl N-(Methylcarbamoyloxy) Thioacetimidate as a Sensing Material

Vinod Kumar Gupta[1,*], *Bhavana Sethi*[2], *Niraj Upadhyay*[3], *Sunita Kumar*[2], *Rakesh Singh*[4], *Lok Pratap Singh*[5]

[1]Department of Chemistry, Indian Institute of Technology, Roorkee, Uttarakhand, 247667-India
[2]Department of Chemistry, M.K.P. (P.G.) College, Dehradun, Uttarakhand, India
[3]Lovely Professional University, Jalandhar, Punjab, India
[4]Department of Chemistry, D.B.S degree college, Dehradun, Uttarakhand, India
[5]Central Building Research Institute, Roorkee, Uttarakhand, India
[*]E-mail: vinodfcy@gmail.com

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The construction, performance characteristics and application of a novel iron(III) membrane sensor based on a new S-methyl N-(methylcarbamoyloxy) thioacetimidate are reported in this paper. The designed sensor exhibited a wide linear response with a slope of 21.2 mV per decade over the concentration range of $9.1\text{x}10^{-6}$-$1.0\text{x}10^{-1}$ M. The potentiometric response is independent on the pH of the solution in the range of 3.2–4.8. The electrode shows a response time of 20 s. The proposed electrode can be used for at least two months without any considerable divergence in potentials. It exhibits very good selectivity relative to a wide variety of alkali, alkaline earth, transition and heavy metal ions. The developed sensor was used for the quantitative determination of Fe(III) in tap and mineral water samples. The electrode assembly was also used as an indicator electrode in the potentiometric titration of Fe^{3+} with EDTA.

Keywords: PVC Membrane, iron(III), sensor, potentiometry, S-methyl N-(methylcarbamoyloxy) thioacetimidate

1. INTRODUCTION

Iron is the most abundant trace mineral in the body and is one of the most important elements in the biological systems, playing a significant role in the oxygen transport, storage and in the electron transport [1, 2]. Enzymes involved in the making of amino acids, hormones, and neurotransmitters require iron. In the foods ingested during a day, approximately 10-15 mg of iron is present and studies indicate that normal subjects absorb ten per cent of iron in the food [3]. The absence of iron in the organism causes anemia, the result of decreased red blood cell content. However, if present in excess, iron accumulates in the heart, liver, and other vital organs [4, 5] and this surplus iron cannot be removed naturally by the body, and it puts the organs at risk for serious damage [6]. Some of the iron compounds are suspected to possess carcinogenic activity. Hence, there is a need for iron ion determination in clinical, medicinal, environmental and different industrial samples.

Presently, various sophisticated techniques, viz. atomic absorption spectroscopy (AAS), inductively coupled plasma (ICP), etc. are employed for the determination of trace amount of iron. However, these methods are disadvantageous in terms of cost and unsuitability for routine analysis of large number of samples [7, 8]. On the other hand, although the potentiometric methods of analysis with ion-selective electrodes are simple, cheap, convenient, fast and applicable to real samples and a lot of work has been done on ISEs in determination of cations[9-19], anions[20-22] and drug molecules[23-36] but there are only a few reports of selective electrodes for Fe(III) ions [37–50]. Hence, the development of highly sensitive and rapid methods for determination of trace amounts of iron is of considerable interest.

1.1. Choice of Ionophore

S-methyl N-(methylcarbamoyloxy) thioacetimidate (**I**, figure 1) was chosen as the ligand in the membrane electrode. It is a broad spectrum insecticide, commonly named as Methomyl. This compound was selected due to its tendency to form stable chelates with heavy metal ions of environmental concern and to its negligible affinity towards alkali and alkaline earth metal ions typically present in real samples. The chelates are formed due to the tendency of the compound to undergo keto-imine tautomerization. The hydroxyl oxygen resulted due to this tautomerization and imine carbon present in methomyl forms six membered stable chelate rings (figure 2). Hydroxyl oxygen of methomyl act as hard base while imine carbon act as soft base. Due to the complementary behavior of both chelating sites methomyl is found most suitable for iron and manganese like ions.

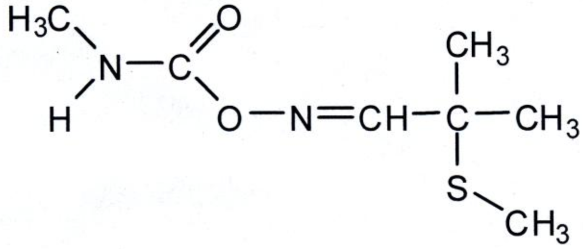

Figure 1. Structure of S-methyl N-(methylcarbamoyloxy) thioacetimidate (**I**).

Preliminary studies [51] show that the ionophore shows very strong interaction towards Fe (III), Mn(II), Cu(II) metal ions. The complex formed through that interaction with Fe (III) is stable above 900°C. The ionophore (**I**) was also studied by U.V–vis spectroscopy to see the effect of other transition metal ions. A 10^{-4} M amount of cations like Ni^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+}do not affect the absorption spectrum of the ionophore taken at the same concentration (10^{-4} M).

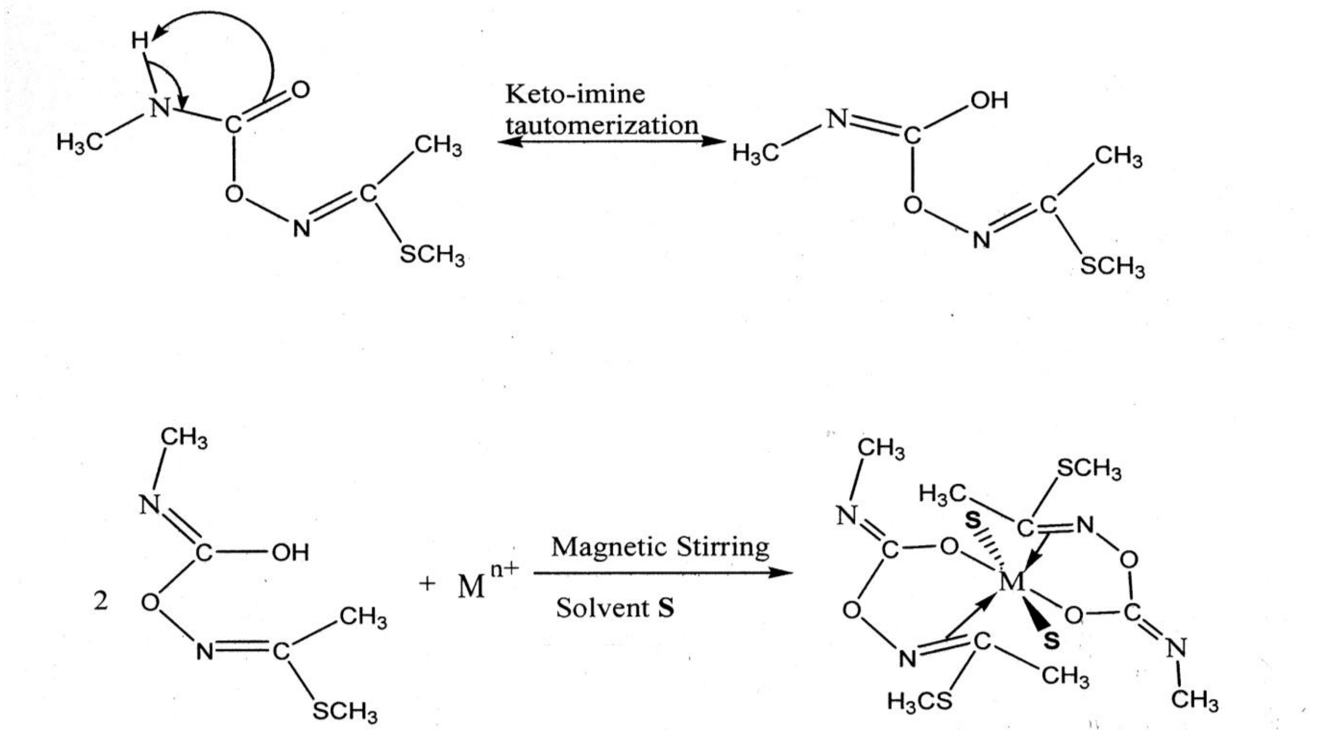

Figure 2. Tautomerization scheme of ionophore, **I** and mechanistic pathway of its metal complexation. (S = Solvent, M = Metal ion and n = charge on the metal ion).

Recent reviews on ionophore-based chemical sensors and research papers provide an intensive survey of literature. It reveals that S-methyl N-(methylcarbamoyloxy) thioacetimidate has not been used as an ionophore in making ion selective electrodes.

2. EXPERIMENTAL

2.1. Reagents and Apparatus

All reagents used were of analytical reagent grade and were used without further purification. High molecular weight poly(vinyl chloride) (PVC) was obtained from Sigma Aldrich, USA; Sodium tetraphenylborate (NaTPB), BDH, England; dibutylphthalate (DBP) and dioctylphthalate (DOP), Reidel India; dibutyl (butyl) phosphonate (DBBP), Mobil, USA, 1-chloronaphthalene (CN), E.Merck, Germany; *o*–nitrophenyl octyl ether (*o*-NPOE), Fluka, Switzerland; tetrahydrofuran (THF) was obtained from Ranbaxy, India. Methomyl (40%), trade name Lannate® was obtained from Du Pont, India. Sodium nitrate, potassium nitrate, rubidium chloride, ammonium nitrate, cadmium nitrate, cobalt nitrate, ferric nitrate, nickel nitrate, zinc nitrate, lead nitrate, manganese nitrate, copper nitrate were obtained from Merck, India. Metal (nitrates and chlorides) solutions prepared were standardized according to appropriate methods.

2.2. Ionophore Synthesis

Methomyl is not available in the market in the pure form. It is exorbitantly costly and is available in very small amounts only. Also, due to its highly toxic nature, it cannot be conveniently synthesized under normal laboratory conditions. Therefore, methomyl was extracted from Lannate (DuPont, India) by simple laboratory techniques.

Breifly, 10 gm of Lannate was extracted with 50 mL of chloroform. After mechanical stirring for five minutes, the suspension was filtered and the residue thus obtained was extracted again with the same volume of the solvent as used earlier and the process was repeated 5-6 times with the residue left after each step. All the extracts were combined together and dried in a vacuum rotatory evaporator. The dry mass of the extracted, recrystallized carbamate was dissolved in a minimum volume of acetone and adsorbed on a column packed with silica gel. It was eluted with 1:3 acetone-chloroform mixture with an average flow rate of 2.0 mL/min. The column was run for 2 hours. The colored band obtained, if any, was discarded and the remaining eluate was collected. It was evaporated to dryness (using vacuum rotatory evaporator till minimum possible volume and then dried at room temperature) and residue was collected and recrystallized in 1:4, chloroform, petroleum ether ratio. For the safety reasons all operations were carried out in a fume hood equipped with high power exhaust. Melting point of purified compound was found to be in agreement with the pure compound (79ºC). Also, the spectroscopic data obtained for the extracted compound completely agreed with the values obtained from sigma-aldrich.

2.3. Membrane preparation

The PVC-based membranes were prepared by the method of Craggs et al. [52]. 1% of ionophore **(I)** and 32-36% of PVC were dissolved in 20 ml THF. The anion excluder, NaTPB (1%) and solvent mediators, DBP, DOP, DBBP, *o*-NPOE and CN (62-66%) were also added in some cases to get membranes of different compositions. The solution thus obtained, after complete dissolution of the various components, was poured into acrylic rings placed on a smooth glass plate and allowed to evaporate at room temperature. After 24h, transparent membranes of 0.5 mm thickness were obtained. A 5 mm diameter piece was cut out and glued to one end of a Pyrex glass tube [53-65]. The membranes prepared above were equilibrated in 1.0 M $Fe(NO_3)_3$ solution for two days and used further for potential measurement studies. Composition of the membranes, which gave best performance, is listed in Table 1 along with other characteristics.

2.4. Potential measurements

Potentiometric measurements were carried out at 25 ± 0.1 °C on a Mettler Toledo pH/ion analyser (model MA235) by setting up the following cell assembly:

Internal reference electrode | Internal solution | Membrane | Test solutions | External reference electrode

Table1. Composition and response characteristics of the PVC-based S-methyl N (methylcarbamoyloxy) thioacetimidate (**I**).

Membrane No.	**% Composition (w/w) of various components in membranes**								**Working Concentration Range**	**Slope (mV per decade of activity)**	**Response time (s)**
	I(%)	PVC	NaTPB	DBBP	DOP	DBP	CN	*o*-NPOE			
1	1	99	-	-	-	-	-	-	2.5 x 10^{-4} - 1.0 x 10^{-1}	16.8	40
2	1	33	1	65	-	-	-	-	6.3 x 10^{-5} - 1.0 x 10^{-1}	23.3	28
3	1	33	1	-	65	-	-	-	9.1 x 10^{-6} - 1.0 x 10^{-1}	21.2	20
4	1	33	1	-	-	65	-	-	2.5 x 10^{-5} - 1.0 x 10^{-1}	22.4	32
5	1	33	1	-	-	-	65	-	3.9 x 10^{-5} - 1.0 x 10^{-1}	22.8	38
6	1	33	1	-	-	-	-	65	1.0 x 10^{-4} - 1.0 x 10^{-1}	24.5	35
7	1	34	-	-	65	-	-	-	2.3 x 10^{-5} - 1.0 x 10^{-1}	23.0	33
8	1	32	1	-	66	-	-	-	9.8 x 10^{-6} - 1.0 x 10^{-1}	21.8	24
9	1	34	1	-	64	-	-	-	1.6 x 10^{-5} - 1.0 x 10^{-1}	22.1	26
10	1	35	1	-	63	-	-	-	1.2 x 10^{-5} - 1.0 x 10^{-1}	22.4	28
11	1	36	1	-	62	-	-	-	1.9 x 10^{-5} - 1.0 x 10^{-1}	22.3	31

A fixed concentration of Fe^{3+} was taken as internal solution (0.1 M) and a saturated calomel electrode was used as a reference electrode. The performance characteristics of the electrodes was examined by measuring potentials of the primary ion solutions with a concentration range of 10^{-6} to 10^{-1} M. Selectivity values ($K^{Pot}_{A,B}$) were evaluated using the 'Fixed Interference Method' [66-95]. The initial concentration for the interfering ions in FIM was 10^{-2} M.

3. RESULTS AND DISCUSSION

3.1. Potentiometric Response

The main ingredient of plasticized PVC membranes is the incorporated carrier i.e the ionophore **(I)** that defines the selectivity of the electrodes by selectively forming a complex with the ion of interest. In preliminary experiments, the ionophore **(I)** was used as a neutral carrier to prepare PVC-based membrane electrodes containing DOP as the plasticizer and NaTPB as anion excluder, for a variety of alkali, alkaline and transition metal ions. The potentiometric response curves obtained for individual metal ions with ionophore under identical conditions are given in Figure 3. Among these cations, Fe^{3+} with the most sensitive response seems to be suitably determined and the EMF responses obtained for all the other cations are much different as predicted by the Nernst equation.

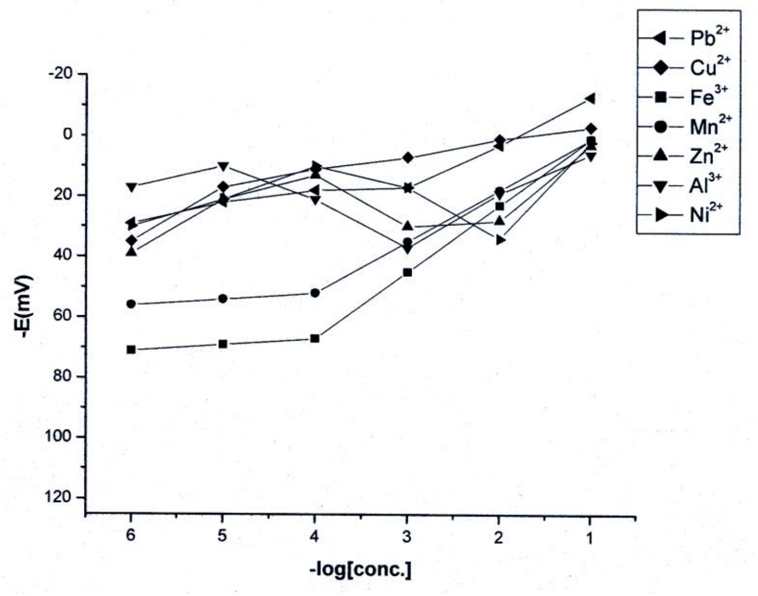

Figure 3. Potentiometric response curves of PVC-based electrodes containing **I** as ionophore towards various metal ions.

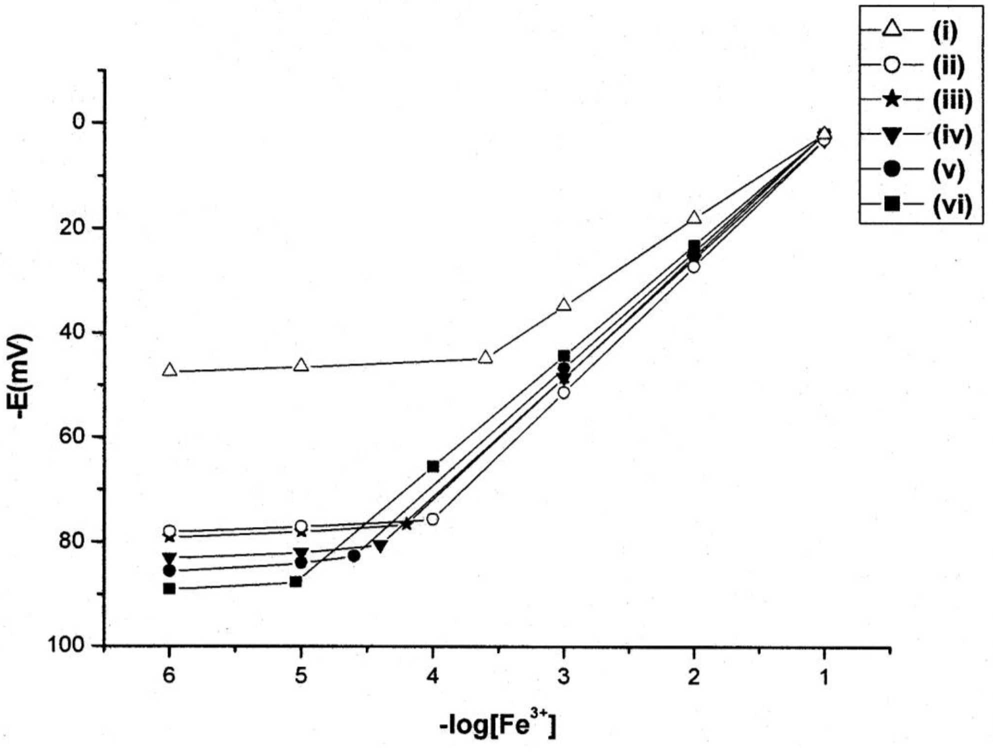

Figure 4. Variation of cell potential with activity of Na^+ ions of PVC based membranes of I with different plasticizers. (i: without plasticizer; ii: *o*-NPOE, iii: DBBP, iv: CN; v: DBP; vi: DOP).

3.2. Working Concentration range and slope

The performance characteristics like slope, response time etc. for all membrane electrodes are recorded in Table 1. The membranes of different compositions exhibited linearity in the concentration range as shown in Figure 4. In order to achieve perm-selectivity it is essential that no significant amount of counter ion should enter to the membrane phase. Lipophilic salt (Sodium tetraphenylborate, NaTPB) was added to reduce the anionic interference and to lower the electrical resistance of the membrane.

These lipophilic salts also exhibit ion-exchange properties and participate in the selective charge transport process if insufficient amount of ionophore is present. Addition of appropriate amount of plasticizer leads to optimum physical properties and ensures high mobility of ions in the membrane. These solvent mediators strongly influence the working concentration range of the sensors. The lipophilicity, polarity, viscosity and dielectric constant of solvent mediators play a significant role in the optimization of the membrane ingredients so as to ensure long and stable response by the sensor assembly [96-100]. The addition of solvent mediator DBP ($\varepsilon \sim 6.4$), DOP ($\varepsilon \sim 5.1$), DBBP($\varepsilon \sim 4.6$), CN($\varepsilon \sim 5$), *o*-NPOE ($\varepsilon \sim 24$) to the membrane, exhibited the enhanced working concentration range of 2.5×10^{-5} - 1.0×10^{-1} M, 9.1×10^{-6}-1.0×10^{-1} M, 6.3×10^{-5} - 1.0×10^{-1} M, 3.9×10^{-5} - 1.0×10^{-1} M, 1.0×10^{-4} - 1.0×10^{-1} M with an improved slope of 22.4, 21.2, 23.3, 22.8, 24.5 mV per decade, respectively (Fig. 4). The effect of addition of various solvent mediators to the membrane is presented in Table 1. Among all the membrane electrodes prepared, the best performance was obtained with the membrane having DOP as the plasticizer. The best performance of DOP among other plasticizers can be attributed to the polarity of DOP ($\varepsilon \sim 5.1$), which can be estimated from the interaction of charged species with a continuum of given dielectric constant. The DOP concentration was also examined. The membrane electrodes (No. 3 and 8) with 65 wt% and 66 wt% DOP show the better properties (slope and linear range) than that of membrane electrodes with 62, 63, 64 wt% DOP. Thus, membrane composition with 65 wt% DOP was chosen for further experiments.

3.3. Response and lifetime

The practical response time of the sensor was calculated by measuring the time required to achieve 95% of the equilibrium potential from the moment of addition of 1.0×10^{-5} M Fe^{3+} solution. Figure 5 gives the plot of EMF against time and it was found that the practical response time was 20 s. The practical reversibility required for the Fe^{3+} sensor to reach a potential within ±1 mV of the final equilibrium value was measured by successive immersion in a series of the sodium ion solutions, each having a 10-fold difference in concentration. This dynamic response is plotted as EMF versus time and is shown as Figure 6. The potentials remained constant for about 1.2 min. The sensing behaviour of the membrane remained unchanged when potentials were recorded either from low to high concentrations or vice versa.

The membranes were used over a period of two months without significant change in potentials. Whenever a drift in potential was observed, membranes were re-equilibrated with 1.0 M Fe^{3+} for 2-3 days. The membranes were stored in 0.1 M Fe^{3+}solution when not in use.

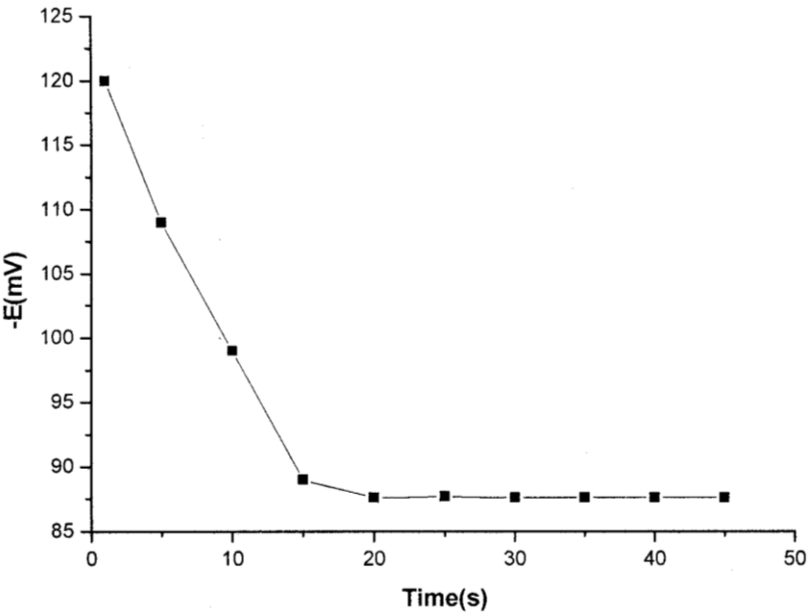

Figure 5. Practical response time of the sensor from the point of addition of Fe^{3+} ($1x10^{-5}M$) solution.

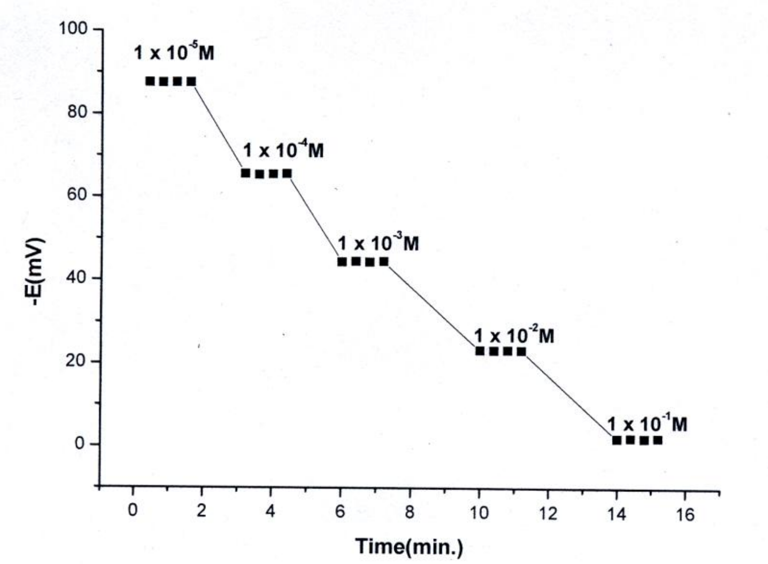

Figure 6. Dynamic response time of the sensor for reversibility with step changes in concentration of Fe^{3+} ($1x\ 10^{-5}$ to $1x10^{-1}$ M).

3.4 Effect of pH

The dependence of electrode potential response on pH was tested over the range 2.0 – 8.0 for $1.0x10^{-3}$ and $1.0x10^{-4}$ M Fe^{3+} ions [101-120] (Figure 7) . The operational range was studied by varying the pH of the test solutions with nitric acid and sodium hydroxide. Figure 7 shows that potential is independent of pH in the range 3.2 to 4.8. The variations in potentials above and below this pH range may be due to the hydrolysis of Fe^{3+} ion and H^+ ions co-transport respectively.

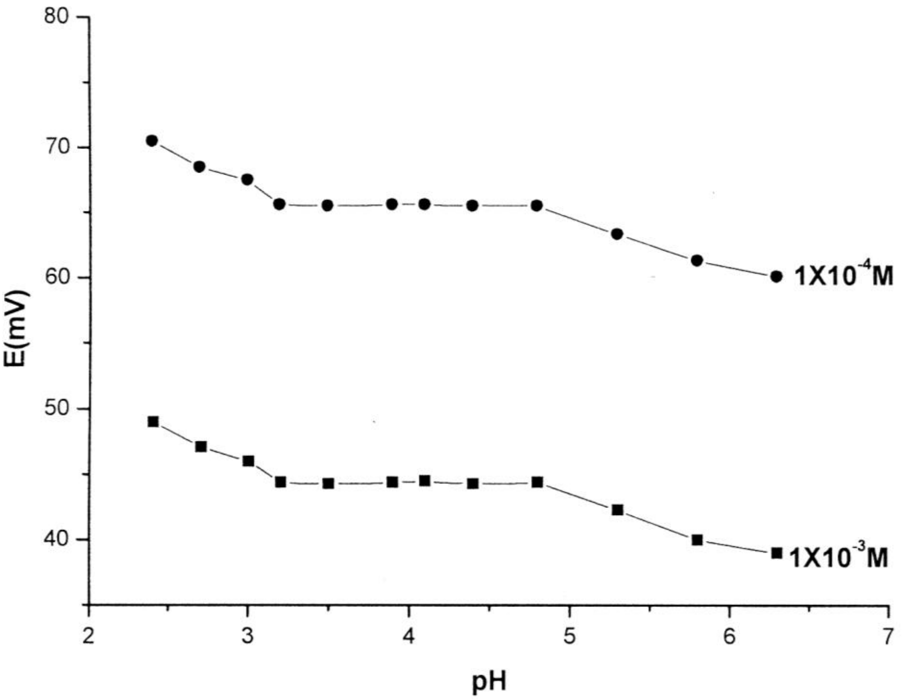

Figure 7. Effect of pH on the potential response of the optimized Fe^{3+} selective electrode.

3.5 Potentiometric selectivity

The potentiometric selectivity coefficient, ($K_{A,B}^{Pot}$) of an ISE is commonly used as a quantitative expression of the ability of the electrode to respond to primary ion in the presence of interfering ions. In the present study it has been evaluated using fixed interference method at $1x10^{-2}$ M concentration of interfering ions.

Table 2 gives potentiometric selectivity coefficient data of S-methyl N-(methylcarbamoyloxy) thioacetimidate **(I)** based Fe(III) ion selective electrode for interfering cations related to Fe^{3+}.

As can be seen, for all cations used, the selectivity coefficients are in the order of 10^{-3} or lower emphasizing that they would not significantly disturb the functioning of the Fe^{3+} selective membrane. Thus, it is clear that the proposed Iron(III) electrode is highly selective with respect to other common cations.

4. ANALYTICAL APPLICATIONS

4.1. Fe(III) ions detection in tap and mineral water

The proposed sensor was also applied to the Fe^{3+} detection in tap water and drinking mineral water samples.10 ml water sample was treated with 5 ml of H_2O_2 solution (IN) and 5 ml of HNO_3 solution (IN) to oxidize Fe(II) ions to Fe(III) ions. Then, the resulting solution was diluted with distilled water in a 100 mL volumetric flask.

Table 2. Selectivity coefficient values for Iron (III) selective membrane electrode for various interfering ions (B) using the Fixed Interference Method (FIM).

Interfering Ions (B)	Selectivity coefficient ($K^{Pot}_{A,B}$)	log $K^{Pot}_{A,B}$
Rb^+	5.4×10^{-5}	-4.26
Na^+	7.8×10^{-5}	-4.10
K^+	2.3×10^{-5}	-4.63
NH_4^+	8.2×10^{-4}	-3.08
Ca^{2+}	7.6×10^{-4}	-3.11
Mg^{2+}	7.0×10^{-4}	-3.15
Ba^{2+}	6.3×10^{-4}	-3.20
Mn^{2+}	3.4×10^{-3}	-2.46
Ni^{2+}	9.2×10^{-4}	-3.03
Co^{2+}	8.3×10^{-4}	-3.08
Zn^{2+}	5.7×10^{-4}	-3.24
Cd^{2+}	6.2×10^{-4}	-3.20
Pb^{2+}	4.4×10^{-4}	-3.35
Cu^{2+}	8.4×10^{-5}	-4.07
Al^{3+}	1.6×10^{-5}	-4.79
Cr^{3+}	3.2×10^{-5}	-4.49

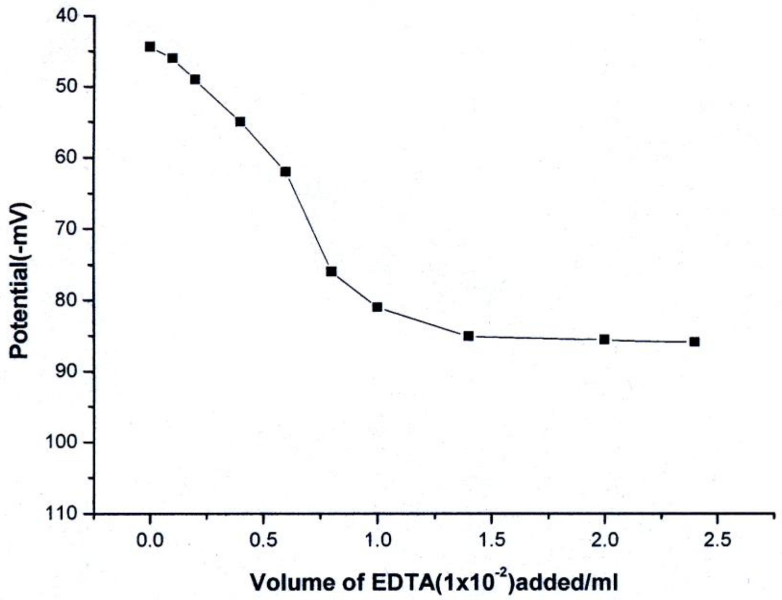

Figure 8. Potentiometric titration plot of 1.0×10^{-3} M Fe^{3+} solution (10 ml) with EDTA (1.0×10^{-2} M) using the developed sensor as an indicator electrode.

The potentials were then measured by using the electrode cell assembly and calibration plots were further employed to evaluate the concentration of Na^+ in these samples.

Table 3. Determination of Fe(III) in tap and mineral water samples.

Sample	Proposed Sensor (ppm)	AAS (ppm)
Tap water 1	4.7	4.4
Tap water 2	4.9	4.7
Mineral water 1	1.7	1.4
Mineral water 2	1.8	1.6

Table 3 shows that the values of Fe^{3+} obtained by the proposed sensor are in good agreement with those obtained by AAS. Thus, the proposed sensor can be used for the determination of Fe^{3+} in real samples.

4.2. Potentiometric titration

The analytical application of the electrode was tested by using it as an indicator electrode in the potentiometric titration of Fe^{3+} with EDTA. A 10 ml (1.0 x 10^{-3} M) solution was titrated with 1.0 x 10^{-2} M EDTA solution. The addition of EDTA caused the formation of Fe-EDTA complex and a decrease in Fe^{3+} concentration caused a decrease in potential. The plot given in Figure 8 is not of standard shape because of the interference caused by Na^+ as the sodium salt of EDTA was used. However, the end point corresponds to the stoichiometric formation of Fe-EDTA complex. Therefore, the membrane can be successfully used as an indicator electrode for determining Fe^{3+} by potentiometric titration.

5. CONCLUSION

The membrane assembly prepared using S-methyl N-(methylcarbamoyloxy) thioacetimidate as membrane ingredient with plasticizers (DOP) and anion excluder (NaTPB) exhibited linearity over a wide concentration range ($9.1x10^{-6}$-$1.0x10^{-1}$ M) with Nernstian slope (21.2 mV/decade of activity), fast response time (20s), long lifetime (two months) and selectivity (of the order of 10^{-4} and 10^{-5}) over a number of cations. The iron ion-selective electrode can be employed as an indicator electrode in potentiometric titration and the determination of iron ions in water samples.

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