Fabrication of Highly Selective Sensor for the Determination of Iron

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Abstract: *A ligand named, ((E) - 2 - ethoxy - 6 ((pyren - 1 - ylimino) methyl) phenol) has been synthesized and scrutinized to fabricate iron (III) – selective sensor. The addition of sodium tetraphenyl borate and various plasticizers, viz… chloronaphthalene (CN), 2 - nitrophenyloctyl (NPOE), benzyl acetate (BA), and dibutylphalate (DBP) has been used to substantially improve the performance of the sensor. The membrane of various compositions of the ligand were investigated and it was found that the best performance was obtained for the membrane of the composition (I) (5mg): PVC (75mg): chloronaphthalene (100mg): sodium tetraphenyl borate (4mg). the sensor showed a linear potential response to iron (III) over wide concentration range 6.8×10^{-6} to 1.0×10^{-1} M (detection limit 5.0×10^{-6} M) with Nernstian slope (20.0 mV/decade of activity) between pH 2.5 and 5.5 with a quick response time of 20 s. The potentiometric selectivity coefficient values as determined by match potential method (MPM) indicate excellent selectivity for iron ions over interfering cations. The sensor exhibits adequate life of 2 months with good reproducibility. The sensor could be used in direct potentiometry.*

Keywords: Schiff base ligand, Iron (III) – selective sensor, Chemical sensor, Potentiometry

1. Introduction

Iron is widely distributed in nature and a well - known essential nutrient which is vital to the process by which cell generates energy. Iron has a fundamental structure of hemoglobin, myoglobin, and many cofactors involved in enzyme activities. It is well known that an iron deficiency is the most common cause of anemia. On the other hand, too much iron can cause a several health problems. High levels of iron are associated with an increased risk for cancer, heart disease, and other illnesses such as hemochromatosis [1 - 3]. The fact that too little or too much of a nutrient is detrimental seems particularly apropos for iron. Thus, the need for quantification of iron in clinical, medicinal, environmental and industrial samples has led to a number of methods for its measurement and one of these methods which offers simple, rapid and reliable tool is ion - selective sensors. a large number of PVC membrane electrodes for diverse ions such as iron were reported by researchers [4 - 19]. We have therefore looked at the possibility of using Schiff base as ionophore for preparing Fe^{3+} sensor. For this purpose, we have explored a number of Schiff bases reported in the literature as ionophore for preparing Fe^{3+} - selective sensor. Our results have indicated that PVC - based membrane of ((E) - 2 - ethoxy - 6 ((pyren - 1 - ylimino) methyl) phenol) ligand works as good Fe^{3+} sensor and the results are reported in the present manuscript.

2. Experimental

2.1. Reagents

Analytical grade Reagents, sodium tetraphenylborate (NaTPB), dibutylphthalate (DBP), *o* - nitrophenyloctyl ether (*o* - NPOE), chloronaphthalene (CN) and tri - *n* - butylphosphate (TBP) were procured from E. Merck (Mumbai, MH, India). benzyl acetate (BA), Tetrahydrofuran (THF), hydrochloric acid and sodium hydroxide (Ranbaxy, India), high molecular weight Polyvinyl chloride (PVC) and metal salts were obtained from CDH (Pvt) Ltd (New Delhi, India). Stock solutions (0.1M) of metal salts were prepared in double distilled water and then used to prepare dilute solutions of various concentrations.

2.2 Apparatus and potential measurements

All potentiometric measurements were made at 25± 0.1ºC with a pH/mV meter [ESICO INTERNATIONAL Digital Potentiometer Model - 118] using proposed sensor in conjugation with a double junction Ag/AgCl reference electrode. pH measurements were made on a digital pH meter [ESICO INTERNATIONAL Digital pH meter Model - 101]. Atomic Absorption Spectrometer (Perkin Elmer - 3100) was used for the analysis of real samples. CHN determinations of the ligands were carried out micro analytically using CHNS Elementar vario EL III. Infrared spectra of the ligands were recorded as KBr discs on a FTIR, Nexus, Thermo Nicolet in the range 4000 - 650 cm - 1 and in Nujol mull over 650 - 200 cm - 1 range. The ^{1}H NMR spectra were recorded on a Bruker DRX 500 MHz NMR Spectrometer at the Institute Instrumentation Centre, Indian Institute of Technology, Roorkee.

The electrode potential (EMF) measurement were performed at 25 ^{0}C using the following electrochemical cell system.

Ag|AgCl (3.0M KCl) | Test solution |membrane| internal solution|Ag|AgCl (3.0M KCl)

Metal salt solution (1.0×10^{-1} M) was taken as internal solution and all standard or test solutions (1.0×10^{-6} to 1.0×10^{-1}M) were prepared by successive dilution. The performances of electrodes were accessed by measuring the potentials of the test solutions from low (1.0×10^{-6} M) to high (1.0×10^{-1} M) concentration or vice versa, stirred with magnetic stirrer.

2.2. Synthesis of Ionophore

The Ligand ((E) - 2 - ethoxy - 6 ((pyren - 1 - ylimino) methyl) phenol) (**I**) was synthesized from 3 - ethoxy salicylaldehyde

and 1 - aminopyrene [15] according to Scheme 1, and a good yield was obtained under reflux conditions using ethanol as a solvent. The products were re - crystallized via the slow evaporation of the solvent at room temperature.
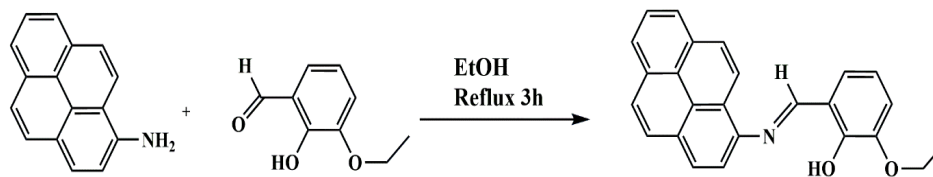
Scheme 1. Synthesis pathway of I

2.4 Membrane preparation

The method reported by Craggs et al. was adopted for the preparation of membranes [16]. A number of membranes incorporating ligand, anion excluder and plasticizer in different compositions in PVC matrix were fabricated. Varying amounts of the ligand and an appropriate amount of PVC were dissolved in a minimum amount of THF. The solutions thus obtained, after complete dissolution of various components, were poured into acrylic rings placed on a smooth glass and allowed to evaporate at room temperature. After 24 h, transparent membranes of 0.5 mm thickness were obtained which were then cut to size and attached to a Pyrex tube with Araldite. Further, the membranes were equilibrated with corresponding metal salt solution for which the membrane is selective. The ratio of various membrane ingredients, time of contact and the concentration of equilibrating solution were optimized first so that the membranes develop reproducible, stable and noiseless potentials. Besides these, some membranes containing only PVC (blank membranes) were also prepared in order to account for any background potential being generated because of the binder. During non - usage, membranes were stored in 0.1 M salt solution to avoid drying, cracking and poisoning.

2.5 Sample preparation

E - ZIF capsules were dissolved in concentrated nitric acid by gentle warming and filtered off. The resulting solution was diluted to 500 mL in a volumetric flask. Standard solutions were prepared by appropriate dilution with double - distilled water.

3. Results and discussion

3.1 Potentiometric response

The nature of plasticizers strongly influences the sensor's performance characteristics. Therefore, membrane of different plasticizers: CN, BA, DBP, o - NPOE and TBP were prepared and investigated. The main factors that improve sensor's performance characteristics are dielectric constants of the membrane and the mobility of ionophore and its complexes [20 - 22] and binding properties of used plasticizers.

The different dielectric constants (ε) of different plasticizers: CN (ε = 5.0), BA (ε= 5.0), DBP (ε=6.4), o - NPOE (ε=24), TBP (ε=8.0) and PVC (ε=3.9) shows different effect on the sensor's performance characteristics, working range, detection limit response time and slope. The various membrane fabricated with different plasticizers, viz., BA, DBP, o - NPOE, TBP and CN have been prepared and studied their response characteristics to see the effect of these plasticizers. The optimum composition with response characteristics of these membrane are shown in Table 1. It is observed that membrane which contain only the ligand (I) and anion excluder NaTPB in PVC matrix (Sensor No.1) in the ratio 5: 75: 6 (I: PVC: NaTPB, w/w, mg) showed a working concentration range of 1.0×10^{-4} to 1.0×10^{-1}M of Fe^{3+} with super Nernstian slope of 30.0 mV/decade of activity. It is well verifiable that plasticizers are used also selectivity and sensitivity of the sensors. Therefore, various membranes prepared with different plasticizers. The addition of plasticizers showed a marked able improvement in the concentration range of the sensor except BA. The working

Table 1: Composition and response characteristics of Schiff base ligand (I) based membrane electrodes selective to Fe^{3+}

Membrane/ Sensor no.	Composition of the membrane (w/w, mg)								Working Concentration Range (M)	Slope mV/ decade of Activity	Response time (s)
	I	PVC	CN	BA	DBP	NPOE	TBP	NaTPB			
1.	5	75	-	-	-	-	-	6	1.0×10^{-4} to 1.0×10^{-1}	30.0	60
2.	5	75	100					6	1.8×10^{-4} to 1.0×10^{-1}	29.0	32
3.	5	75		100	-	-	-	6	1.0×10^{-4} to 1.0×10^{-1}	33.0	40
4.	5	75		-	100	-	-	6	8.9×10^{-5} to 1.0×10^{-1}	25.0	35
5.	**5**	**75**		**-**	**-**	**100**	**-**	**6**	6.8×10^{-6} to 1.0×10^{-1}	**21.0**	**20**
6.	5	75		-	-	-	100	6	5.2×10^{-5} to 1.0×10^{-1}	26.0	15

concentration range is widened to 8.9×10^{-5} to 1.0×10^{-1}, 6.8×10^{-6} to 1.0×10^{-1}, 5.2×10^{-5} to 1.0×10^{-1}M with the addition of CN, DBP, NPOE and TBP. While there is no change in the concentration range with the addition sf BA. The potential is determined as a function of Fe^{3+}ions in test solution (fixed concentration 1.0×10^{-1}M) were plotted against the logarithm of the activity of ferric ions as shown in Fig.1. The limit of detection for sensor no.5 is calculated and

is found to be 5.0×10^{-6} M. Since the best working concentration range and slope were showed for the membrane with plasticizers NPOE (Sensor No.5), the same was chosen for further studies. This sensor gave a standard deviation of ±0.1mV in the observed values of potential in working concentration range.
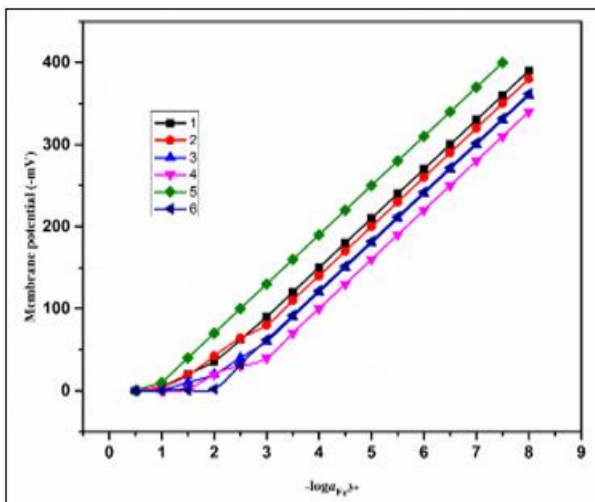
Figure 1: Variation of membrane potential of PVC – based membranes of (I) with varying concentrations of Fe^{3+} ions (1) without plasticizers; (2) with CN; (3) BA; (4) DBP; (5) NPOE; (6) TBP.

3.2 Response and lifetime

Dynamic response time is the most important factor for a sensor. In this manuscript, the practical response time was recorded by the changing concentration of Fe^{3+} ion in solution, over a concentration range from 1.0×10^{-6} to 1.0×10^{-2} M, and the result shown in Fig.2. It is apparent that over whole concentration response time is 20s. the life time of Fe^{3+} membrane sensor was tested and record 60days.
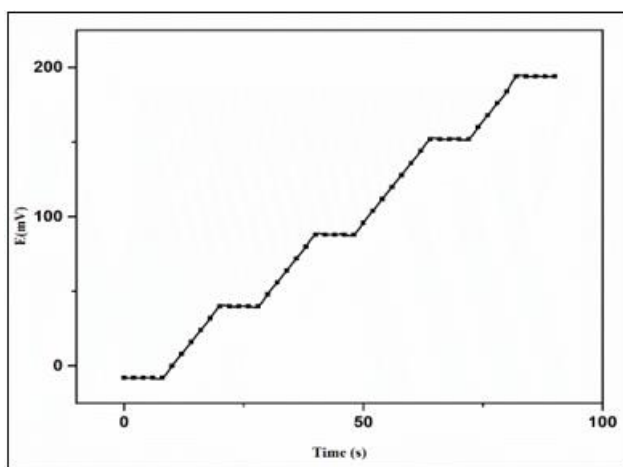

Figure 2: Dynamic response time of the iron electrode.

3.3 Potentiometric selectivity

The response characteristics of the sensors were examined in presence of various foreign ions in order to examine the selectivity. The match potential method (MPM) of Gadzekpo and Christian [23] was used to determine the potentiometric selectivity of the sensor. Potentiometric selectivity coefficients were determined graphically using the expression.

$$K_{Fe.B}^{Pot} = \frac{\Delta a_{Fe}}{a_B} = \frac{a_{Fe}' - a_{Fe}}{a_B}$$

where Δa_{Fe} is the chang in the activity of the reference solutions and a_B is the activity of the interfering ion.

The seltivity coefficient values determined for variuos interfering ions are presented in Table 2. It is clear from Table 2 that the proposed sensor is selective for Fe^{3+} over many mono, di – and trivalant cations.

Table 2: Selectivity coefficient $K_{A,B}^{Pot.}$ values for Fe (III) – selective sensor obtained match potential method (MPM) for various interfering ions

Interfering ion (B)	Selectivity Coefficient $K_{A,B}^{Pot.}$
Na^+	3.4
Ag^+	3.8
Ca^{2+}	3.7
Mg^{2+}	3.2
Cu^{2+}	2.5
Hg^{2+}	3
Zn^{2+}	3.1
Cr^{3+}	2.7
Ni^{2+}	3.6

3.4. Effect of pH and non – aqueous solution

The pH of the sensor tasted over the range 1.5 – 6.5 for 1.0×10^{-4} M Fe^{3+}. The pH was adjusted with hydrochloric acid and sodium hydroxide, Fig.3. shows that the pH dependence of the sensor is good in the range of pH 2.5 – 5.5. The performance of the sensor was also investigated in non – aqueous content which contained partially non – aqueous solution of methanol, ethanol and acetonitrile in water were added to the proposed sensor no.5. The membranes do not show any appreciable change in working concentration range or slope in mixtures up to 15% (v/v) non - aqueous contents (Table 3). Above this, developed potential showed an erratic behaviour. This may be due to leaching of the ionophore in organic medium.
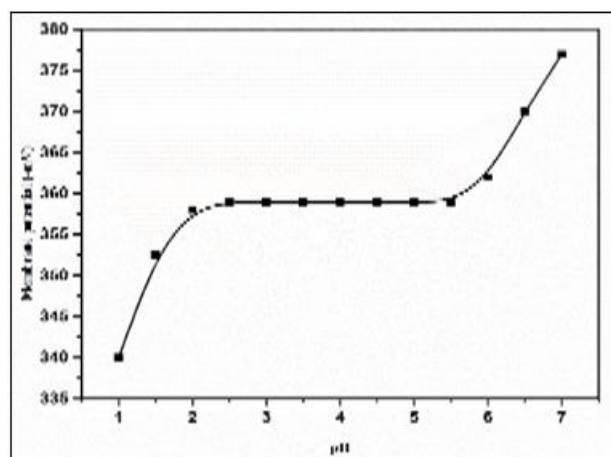

Figure 3: Effect of pH on potential; $[Fe^{3+}] = 1.0 \times 10^{-4}$ M for sensor no.5.

Table 3: Performance of Fe^{3+} - selective sensor (no.5) in aqueous media.

Non - aqueous Content (%, v/v)	Slope (mV/decade)	Working concentration range (M)
0	21.0	6.8×10^{-6} to 1.0×10^{-1}
Methanol		
10	21.0	6.8×10^{-6} to 1.0×10^{-1}
15	21.0	6.8×10^{-6} to 1.0×10^{-1}
20	27.7	8.8×10^{-6} to 1.0×10^{-1}
Ethanol		
10	21.0	6.8×10^{-6} to 1.0×10^{-1}
15	21.0	6.8×10^{-6} to 1.0×10^{-1}
20	15.0	1.8×10^{-5} to 1.0×10^{-1}
Acetonitrile		
10	21.0	6.8×10^{-6} to 1.0×10^{-1}
15	21.0	6.8×10^{-6} to 1.0×10^{-1}
20	22.3	3.8×10^{-6} to 1.0×10^{-1}

4. Analytical applications

The proposed Fe^{3+} ion – selective electrode was found to work well in real samples. The sensor was applied to detection of iron ions in mineral and wastewater samples. The found amount were measured from the calibration curve of iron ions in the range of 6.8×10^{-6} to 1.0×10^{-1} M. the results are given in Table 4 and compared with those obtained by atomic absorption spectrophotometry (AAS). It is clear that resulting data of the fabricated sensor were in satisfactory agreement with those of AAS.

Table 4: Determination of Fe (III) in water samples

Sr. No.	Sample	Proposed sensor (mg/L)	AAS (mg/L)
1	Mineral water 1	1.8	1.6
2	Mineral water 2	1.6	1.3
3	Waste water 1	4.6	4.2
4	Waste water 1	4.8	4.5

5. Conclusion

It may be concluded that a potentiometric PVC – based membrane sensor based on ((E) - 2 - ethoxy - 6 ((pyren - 1 - ylimino) methyl) phenol) as an excellent Fe^{3+} - selective membrane sensor with a wide concentration range of 6.8×10^{-6} to 1.0×10^{-1} M and Nernstian slope, fast response time 20s in entire concentration range. It could be used for the determination of this ion in the presence of the considerable concentrations of common interfering ions. Applicable pH range, lower detection limit and potentiometric selectivity coefficients of the proposed sensor make it as a suitable device for the determination of iron ions.

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