A Novel Iron(III) Selective Membrane Electrode Containing a Tripodal Polycatacholamine as Sensor

Rati Kanta Bera,* Suban K Sahoo,† Minati Baral,‡ and B. K. Kanungo

Department of Chemistry, Sant Longowal Institute of Engineering & Technology, Longowal-148 106, Punjab, India
*E-mail: rati_bera@rediffmail.com
†Department of Applied Chemistry, SV National Institute of Technology, Surat-395 007, Gujrat, India
‡Department of Chemistry, National Institute of Technology, Kurukhestra-136 119, Haryana, India
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A novel poly(vinylchloride)-based membrane sensor using N^1,N^3,N^5-tris(2-(2,3-dihydroxybenzylamino)-ethyl)cyclohexane-1,3,5-tricarboxamide (CYCOENCAT, L) as ionophore has been prepared and explored as Fe^{3+} selective electrode. The membrane electrode composed of ionophore, poly(vinylchloride) and *o*-nitro-pheyloctyl ether in the optimum ratio 4:33:63 gave excellent potentiometric response characteristics, and displayed a linear log[Fe^{3+}] *versus* EMF response over a wide concentration range of 1.0×10^{-5} - 1.0×10^{-1} M with super nernstian slope of 28.0 mV/decade and the detection limit of 8.0×10^{-6} M. The proposed ion selective electrode showed fast response time (< 15 s), wide pH range (3.0-7.0), high non-aqueous tolerance (up to 20%) and adequate long life time (120 days). It also exhibited very good selectivity for Fe^{3+} relative to a wide variety of alkali, alkaline earth, transition and heavy metal ions. Further, the analytical applicability of the sensor was tested as an indicator electrode in the potentiometric titration of Fe^{3+} with EDTA.

Key Words : PVC membrane, Tripodal, Iron(III), Ion-selective electrode, Potentiometry

Introduction

Iron is widely distributed in nature and it is one of the most important elements in environmental and biological systems. Iron plays a crucial role in a variety of cellular events and indeed no life form is possible without this element with a few possible exceptions in bacterial world.[1,2] Though it is an essential element for all living systems, the gradual accumulation of iron leads to a number of diseases.[3] Excess of iron in body causes liver and kidney damage (haemochromatosis), whereas its deficiency adversely affects the health leading to anaemia. Moreover, iron compounds are also potential carcinogens. Therefore, there is of high importance for the development of novel techniques for the selective and accurate determination of iron ion in different clinical, medical, environmental and industrial samples.[4-11]

Among the existed metal ion sensing techniques, the potentiometric sensors particularly ion selective electrodes (ISEs) provide a simple, selective, precise and economical method for online monitoring of the target analyte without any pretreatment of the sample. During the past two decades, a large number of ionophores have been developed and applied extensively in potentiometric and optical sensors for the determination of metal ions.[12-18] However, despite the outstanding development in the field of ISEs, only few Fe^{3+}-selective sensors have been reported so far.[4,19-27] This may be due to the limited availability of strong stable iron chelators. Among the various iron chelators reported till date, sidero-phores are the naturally occurring powerful iron(III) chelat-ing agents produced by microorganisms and present unique chemical and physiochemical properties.[28] They can be differentiated based on the chemical nature of their binding functionalities *i.e.* catecholate, hydroxamate, or hydroxy-pyridonate. One of the most studied siderophore for the designing of biomimic synthetic chelators for iron(III) is enterobactin, which produced and excreted by bacteria in iron deficient media in order to bind and assimilate extra-cellular iron.[29,30] It contains three catechol groups appended to a tripodal cyclic L-serine unit through amide linkage and reported to be the best iron-chelating agent with highest formation constant (log K = 52).[31,32]

Keeping in view of the above importance of the tris-(catacholate) in the iron chelation, in this work a tripodal biomimetic tris(catacholate) ligand N^1,N^3,N^5-tris(2-(2,3-di-hydroxybenzylamino)ethyl)cyclohexane-1,3,5-tricarboxamide (CYCOENCAT, L) has been used as an ionophore for the development of a PVC-based membrane electrode for the selective and accurate determination of the Fe^{3+} ion.

Experimental

Reagents and Apparatus. The ionophore N^1,N^3,N^5-tris(2-(2,3-dihydroxybenzylamino)ethyl)cyclohexane-1,3,5-tricarbox-amide (CYCOENCAT, L) was synthesized and characteriz-ed as described earlier.[33] Plasticizers *viz.*, dibutylphthalate (DBP), bis-2-ethylsebcate (BES), *ortho*-nitrophenyloctyl-ether (*o*-NPOE), and high molecular weight PVC were purchased from Aldrich Chemical Company. Analytical reagent grade nitrate or chloride salts of the metal ions were obtained from Merck and used as such after vacuum drying over P_2O_5. Aqueous salt solutions were prepared by dis-solving appropriate salt in triply distilled de-ionized water.

Table 1. Optimization of composition for PVC-based membrane of CYCOENCAT and their performance as Fe^{3+}-selective electrode

Electrode no.	Components of the membrane (% w/w)			Slope (mV/decade)	Working concentration range(M)	Detection limit (M)
	L	PVC	Plasticizer			
1	2	33	65 (*o*-NPOE)	7.3	5.0×10^{-5} - 1.0×10^{-1}	5.0×10^{-6}
2	3	33	64 (*o*-NPOE)	6.9	1.0×10^{-4} - 1.0×10^{-1}	6.0×10^{-5}
3	4	33	63 (*o*-NPOE)	28	1.0×10^{-5} - 1.0×10^{-1}	8.0×10^{-6}
4	4	33	63 (BES)	12	5.0×10^{-5} - 1.0×10^{-1}	5.0×10^{-5}
5	4	33	64 (DOP)	7.6	5.0×10^{-4} - 1.0×10^{-1}	5.0×10^{-5}
6	4	33	64 (DBP)	9.9	1.0×10^{-4} - 1.0×10^{-1}	2.0×10^{-5}

All the solvents used in the investigation were of analytical reagent grade and purified before use. A Thermo Orion 720A⁺ pH/ISE meter was used for the measurement of the electrode potential.

Membrane and Electrode Preparation. The procedure adopted to prepare the PVC membrane was to mix PVC, plasticizers and ionophore thoroughly in 5 mL THF in the composition as detailed in Table 1. After complete dissolution of all the components and thorough mixing, the resulting homogeneous mixture was transferred into a glass dish of 30 mm diameter. THF was allowed to evaporate at room temperature; after 24 h, a transparent membrane was obtained. The prepared membrane was removed from the glass plate, and a circular piece of 1.25 cm diameter was cut and mounted on the ground end of the Pyrex glass tube with araldite. Membrane was conditioned for 24 h by soaking in 1 $\times 10^{-2}$ M $Fe(NO_3)_3$ solution.

The EMF Measurements. All the EMF measurements were carried out using the above mentioned apparatus, at the room temperature ($25 \pm 0.1°C$) with the following cell assembly:

SCE | 0.1 M Fe^{3+} || Membrane || Fe^{3+} test solutions | SCE

The potential was measured for test solutions by varying the concentration in the range 1.0×10^{-8} to 1×10^{-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 Fe^{3+} ion activity. The activities of metal ions were based on activity coefficient (γ). The activity coefficients of metal ions have been calculated from the modified form of the Debye-Hückel approximations,[34] which is applicable to any ion:

$$\log \gamma = -0.511 Z^2 \left[\frac{\mu^{1/2}}{(1 + 1.5\mu^{1/2})} - \mu \right]$$

Where, Z and μ represent the valency and the ionic strength respectively.

Results and Discussion

Complexation of CYCOENCAT with Metal Ions. The novel enterobactin analog, CYCOENCAT (L) derived from cyclohexane based triamine acts as a good iron(III) chelator with a calculated stability constant of log $\beta_{FeL} = 34.61$ and pFe (pFe = −log [Fe^{3+}]) value of 24.76 at pH = 7.4.[33] The ligand L showed the presence of intramolecular H-bonding between the *ortho*-hydroxy protons of catechol units and the adjacent nitrogen atoms of amine in the molecule, which provides a rigid tripodal framework for complexation (Fig. 1). The presence of amine and catcholate groups makes the ligand more pre-organized and provides either a tris(amino-catecholate) or a tris(catecholate) compartment for the encapsulation of metal ion.

Optimization of the Membrane Composition. It is well known that the sensitivity and selectivity obtained for a given ion-selective electrode depend not only on the nature of ionophore used, but also significantly on the membrane composition and the properties of the plasticizer employed. The effect of composition on the response of the electrode was investigated. For this purpose, the performance characteristics like slope of the calibration curve, measurement range and detection limit were studied and are summarized in Table 1. The membrane having 4% ionophore (w/w) exhibited the best result (Electrode no. 3, Table 1). This composition gave reproducible super-nernstian response with slope 28.0 mV/decade in the concentration range of 1.0×10^{-5} to 1.0×10^{-1} M and response time of 15 s. The detection limit of the proposed sensor is 8.0×10^{-6} M, which was obtained from the intersection of two straight-line portions of the calibration curve (Fig. 2). The effect of the nature of the plasticizer on the Fe^{3+} response was studied on electrodes containing four different types of plasticizers having different dielectric constants namely, *o*-NPOE, DOP, DBP and BES. It is clear from Table 1 that *o*-NPOE is more effective in solvent medium than DBP and BES in preparing the Fe^{3+} ion-selective electrode, most probably due to the
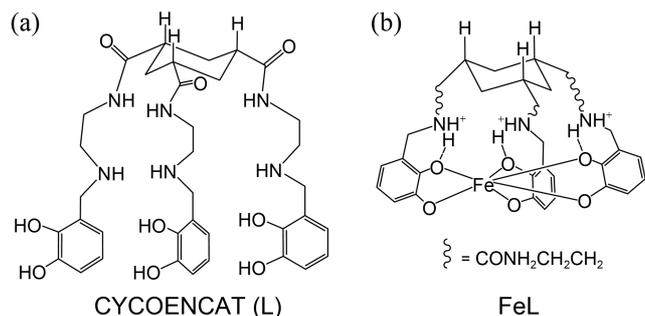
Figure 1. Structure CYCOENCAT and its complexation mode with Fe^{3+}.
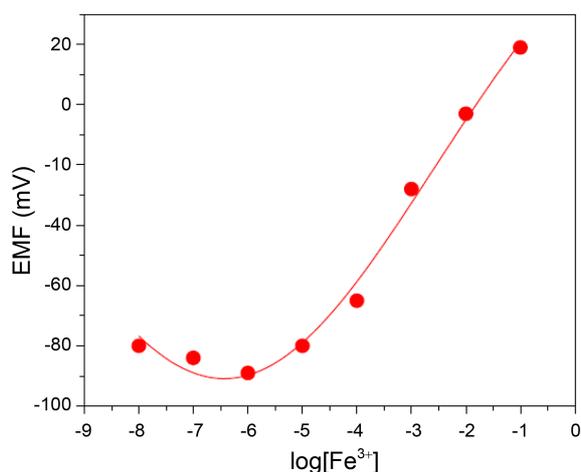
Figure 2. Calibration curve of Fe^{3+} ISE based on CYCOENCAT.

Figure 3. Effect of pH on the response of Fe^{3+} ion-selective electrode at two different Fe^{3+} ion concentrations.

better solubility of ionophore L in it. The nature of the plasticizer not only affects the dielectric constant of the membrane phase but also in the mobility of the ionophore molecules. Thus, the optimized composition ionophore: PVC:*o*-NPOE::4:33:63 was chosen for all further study. The reproducibility of this electrode was evaluated by preparing five electrodes with the above composition and the response of these electrodes to Fe^{3+} was measured. The average of slopes, detection limits, and linear dynamic ranges of these five electrodes were 28 ± 0.3 mV/decade, $8(\pm 0.2) \times 10^{-6}$ M, and $1(\pm 0.4) \times 10^{-6}$ to $1(\pm 0.2) \times 10^{-5}$ M respectively.

Effect of Internal Solution. The internal solution may affect the electrode response when the membrane internal diffusion potential is appreciable. Therefore, the influence of the concentration of the internal solution on the potential response of the proposed electrode was studied. The concentration was varied from 1.0×10^{-1} to 1.0×10^{-3} M and the potential response of the electrode was obtained. Variation in the concentration of the internal solution did not cause any significant difference in the EMF, except for an expected change in the intercept of the resulting plots. The concentration of internal $Fe(NO_3)_3$ solution was selected as 1.0×10^{-3} M.

Effect of pH and Life Time. The effect of pH on the performance of the electrode was studied over the pH range of 1.2-10.0 using two different Fe^{3+} concentrations, 1.0×10^{-3} and 1.0×10^{-4} M. The desired pH of the test solution was adjusted by using 0.1 N HCl or 0.1 N NaOH.

The potential of the proposed sensor was determined as a function of pH, and the results are shown in Fig. 3. The potential remains constant over the pH range of 3.0-7.0, which may be employed as the working pH range of the sensor. Beyond this range, a gradual drift was observed. The observed drift could be explained by the fact that at low pH values the donor atoms in the chelating ionophore are protonated, and unable to complex readily with iron(III). Furthermore, the sensor may also be affected due to interference of the hydrogen ions.[35] At the elevated pH, the iron(III) concentration in solution was dramatically reduced, which may be due to the formation of iron(III) hydroxo complexes, and the magnitude of the voltage change can be reconciled with iron(III) speciation calculations in solution.

The life time of the proposed electrode was about four months and the sensing behavior of the electrode remained reasonably constant during this time. After this period, drift in the potential was observed because the membrane became mechanically weak and swelled up; and resulted in the leaching of ions took place from the membrane phase. During non-usage, the electrodes were stored in 0.1 M $Fe(NO_3)_3$ solution to avoid any change in iron ion concentration in the membrane phase.

Effect of Partially Non-aqueous Medium on the Working of Fe^{3+} Electrode. The utility of the sensor system was also investigated in partial non-aqueous medium using 10%, 20% and 30% methanol-water, ethanol-water and acetone-water mixtures. The membrane electrodes did not

Table 2. Comparison of the proposed Fe^{3+}-selective electrode with recently reported electrodes

Sl . No.	Reference	Working concentration range (M)	Slope (mV/decade)	pH range	Response time (Second)	Life time (months)
1	[4]	3.5×10^{-6} - 1.0×10^{-2}	28.5	4.5-6.5	< 15	2
2	[21]	5.0×10^{-5} - 1.0×10^{-1}	20.0	-	-	1
3	[26]	1.0×10^{-6} - 1.0×10^{-1}	51.0	1.0	30	2
4	[27]	6.3×10^{-6} - 1.0×10^{-1}	20.0	3.5-5.5	15	2
5	This work	1.0×10^{-5} - 1.0×10^{-1}	28.0	3.0-7.0	15	4

Table 3. Effect of partial non-aqueous medium on the working of Fe^{3+} ion selective electrode

Non-aqueous content	Volume/ Volume (%)	Slope (mV/decade)	Working concentration range(M)
Nil	-	28.0	1.0×10^{-5} to 1.0×10^{-1}
Methanol : water	10:90	28.0	1.0×10^{-5} to 1.0×10^{-1}
	20:80	27.3	1.0×10^{-5} to 1.0×10^{-1}
	30:70	20.1	1.0×10^{-3} to 1.0×10^{-1}
Ethanol : water	10:90	28.0	1.0×10^{-5} to 1.0×10^{-1}
	20:80	27.5	1.0×10^{-5} to 1.0×10^{-1}
	30:70	18.6	5.0×10^{-4} to 1.0×10^{-1}
Acetone : water	10:90	28.0	1.0×10^{-5} to 1.0×10^{-1}
	20:80	27.1	1.3×10^{-5} to 1.0×10^{-1}
	30:70	19.4	8.0×10^{-4} to 1.0×10^{-1}

Table 4. Potentiometric selectivity coefficient by FIM Method

Metal ions	Selectivity coefficient
Na^+	-1.5
K^+	-1.8
Ag^+	-1.8
Ca^{2+}	-2.1
Mg^{2+}	-2.3
Sr^{2+}	-2.2
Fe^{2+}	-1.6
Cu^{2+}	-1.8
Ni^{2+}	-1.9
Cd^{2+}	-2.3
Hg^{2+}	-1.6
Co^{2+}	-2.0
Zn^{2+}	-2.2

show any appreciable change in working concentration range or slope in the mixture up to 20% (v/v) non-aqueous contents (Table 3), but above 20% non-aqueous content, the performance of the electrode was affected, resulting a decrease in the working concentration range and slope. Above 20% non-aqueous content the membrane degrades due to leaching of the ionophore from the PVC matrix. Accordingly, the electrode assembly can only be used in non-aqueous medium when its content is not more than 20%.

Interference Studies. The selectivity behavior is obviously one of the most important characteristics of an ion selective electrode, determining whether a reliable measurement in the target sample is possible.[36] To ascertain the selectivity of the membrane electrode proposed, their potential response were investigated in the presence of various interfering foreign ions such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Sr^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Ag^+. Selectivity coefficients for the membrane electrode were determined by the fixed interference ion method (FIM) with a fixed concentration of the interfering ion (1.0×10^2 M) and varying the amounts of primary ion (Fe^{3+}). The EMF values are plotted against the logarithm of the primary ion. Fe^{3+} ion concentrations corresponding to the intersection of the extrapolated linear
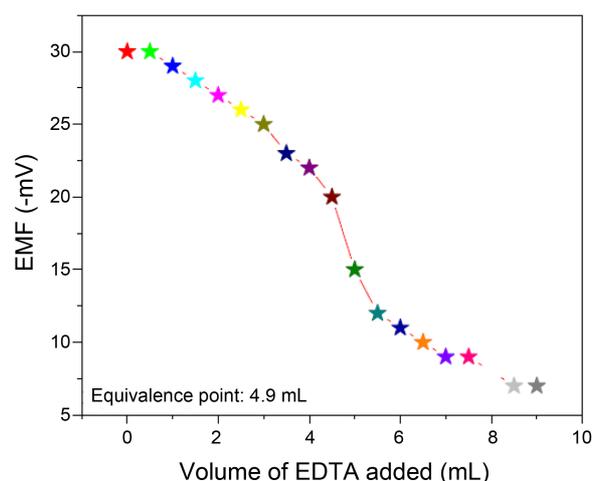
Figure 4. Potentiometric titration of 50 mL of Fe^{3+} (1.0×10^{-3} M) with EDTA solution (1.0×10^{-2}).

portions of the plots are used to calculate $K_{Fe^{3+},M}^{Pot}$ by applying the Nikolsky-Eisenmann equation[37-40]:

$$K_{Fe^{3+},M}^{Pot} = a_A/a_B(Z_A/Z_B)$$

Where, a_A and a_B are the activity of the primary ion (A) and the activity of interfering ion (B) respectively; Z_A and Z_B are the respective charges on (A) and (B). The resulting selectivity coefficients are summarized in Table 4. The selective coefficient values are in the order of 10^{-2} or lower for almost all examined divalent metal ions, which indicate that the functioning of the proposed Fe^{3+} selective sensor was not interfered by other metal ions even at a higher concentration levels. Further, to investigate the effect of anions, cell potentials were obtained using ferric nitrate, ferric chloride and ferric sulphate solutions and the response of the proposed sensor was found to be insensitive to the nature of these anions.

Potentiometric Titration. The practical utility of the proposed membrane sensor was tested by using it as an indicator electrode to determine the end point in the potentiometric titration of Fe^{3+} solution with EDTA. 50 mL of 1.0×10^{-3} M Fe^{3+} solution was titrated against 1.0×10^{-2} M EDTA solution after adjusting the pH at 5.0 and the resulting titration curve is shown in Figure 4. The curve shows sharp inflexion point at the titrant volume corresponding to the formation of 1:1 complex of iron ion with EDTA.

Conclusions

This PVC-based membrane sensor comprised of PVC, CYCOENCAT as an ionphore and *o*-NPOE as a plasticizer in the ratio of 4:33:63 can be used for the selective and accurate determination of Fe^{3+}. The electrode exhibited linearity over a wide concentration range, fast response time (15s), long life time (four months), high detection limit and selectivity over a number of cations. Also, the electrode

works well in a wide pH range of 3.0-7.0. The electrode was employed as an indicator electrode in the potentiometric titration of Fe^{3+} ions against EDTA. Further, the response characteristics of the proposed electrode are obtained in absence of any additive like lipophilic additives, which are generally used to enhance the response characteristics of the electrodes.

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