

Coated-wire iron(III) ion-selective electrode based on iron complex of 1,4,8,11-tetraazacyclotetradecane

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Abstract

The work described here comprises the determination of Fe(III) by ion selective potentiometry using a coated-wire ion-selective electrode (CWISE) based on iron–cyclam complex. Linear Nernstian response for this electrode was obtained over the total Fe(III) concentration range of 1×10^{-2} to 1×10^{-6} M in 0.05 M HNO₃, H₂SO₄, HClO₄, HCl, KNO₃ and KCl media, with a slope of 60 ± 5 mV per decade change. Working pH range of the electrode was found to be 1.3–3.5. Selectivity coefficients of some mono- and divalent metal ions were determined. Analysis of alloys, electroplating bath solutions and pharmaceutical samples have been carried out using this CWISE and the results are found to be comparable with those obtained by using conventional methods.
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1. Introduction

During the past few decades, a large number of ionophores, specially a wide variety of neutral macrocyclic polyethers based on nitrogen and sulphur, has been synthesized and found widespread applications in potentiometric sensors for the determination of respective ions in environmental, industrial and clinical samples [1]. Status of ion sensors and their applications in clinical chemistry is summarized by Bakker et al. [2]. Very few Fe(III) ion selective electrodes have been reported so far [1,3–7]. Scibona et al. had developed liquid anion membrane electrodes selective to multivalent metal ions [8]. Ionophore-free ion exchanger electrodes for iron complexes such as tetrachloroferrate(III) [1], and a ferroin membrane sensor, both for batch and flow-injection determination of Fe(II) and Fe(III) [9], have been

developed. FeCl₄[−] selective liquid membrane electrodes were prepared using triphenylpyrilium, phenylbenzopyrilium and cetylpyridinium tetrachloroferrates as solvent [10]. During our study on complexation of various metal ions in mixed solvents [11], using competitive potentiometry it was found that the stability constant of iron–1,4,8,11-tetraazacyclotetradecane (iron–cyclam) complex is reasonably good ($\log K = 8.9$ in 90% (v/v) DMSO + water using silver ion as a probe) to be used as an ionophore. After the successful fabrication and application of coated-wire silver(I) [12] and copper(II) [13] and chromium(III) [14] ion selective electrodes, an attempt has been made to develop a coated-wire iron(III) ion-selective electrode based on iron complex of cyclam. The substitution of sulphur and/or nitrogen atom for the ether oxygen in the coronand ring reduces the affinity of the ligand for alkali and alkaline earth metal ions. PVC membranes were prepared using dibutyl phthalate, diethyl phthalate and dibutyl maleate plasticizer. The membrane having electroactive material, dibutyl phthalate or diethyl phthalate with PVC in the optimum ratio 5:62:33 (w/w) gave better results as noticed before [15]. The linear working range was 1×10^{-2} to 1×10^{-6} M with

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a slope of 60 ± 5 mV per decade of activity and a detection limit of 5×10^{-7} M in the pH range 1.3–3.5. The selectivity coefficients (K_{ij}) of Na(I), K(I), Ag(I), Ca(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II), Hg(II), Cr(III) and Mg(II) interfering ions were also determined and it was found that the electrode shows good selectivity for Fe(III) ions over these mono- and divalent ions. The selectivity coefficient of Fe(II) was found to be more, with respect to the other metal ions.

2. Experimental

2.1. Reagents and standard solutions

Nitrates of iron(III), sodium(I), potassium(I), cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), lead(II), silver(I), mercury(II), tetrahydrofuran (THF), diethyl phthalate, dibutyl phthalate, dibutyl maleate, potassium nitrate, potassium chloride, nitric acid, perchloric acid, sulphuric acid and hydrochloric acid were analytical grade chemicals purchased from S.D. Fine Chem Ltd. (India) and were used as such. Calcium and magnesium perchlorates were prepared by general methods described elsewhere [16]. Chromium(III) perchlorate, polyvinyl chloride (PVC) and 1,4,8,11-tetraazacyclotetradecane (cyclam) were purchased from Fluka (Switzerland) and used as such. Standard solutions of metal salts were prepared in double distilled deionised water; working solutions were prepared as required by suitable dilution with the same water. The pH of the solutions was adjusted with 0.1 M nitric acid.

2.2. Preparation of membrane

Equal volumes of equimolar solutions of 1,4,8,11-tetraazacyclotetradecane and $\text{Fe}(\text{ClO}_4)_3$ were mixed in ethanol and kept for some time for precipitation. The reddish colour precipitate obtained was filtered washed and dried at room temperature to obtain the ionophore.

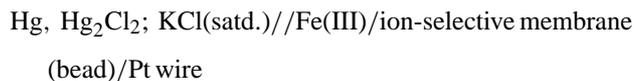
2.3. Preparation of electrode

Slurries of 1.5%, 3%, 5% (w/w) ionophore, 36.5%, 35%, 33% (w/w) PVC, respectively and 62% (w/w) plasticizer (dibutyl phthalate/dibutyl maleate/diethyl phthalate) were made in tetrahydrofuran. To prepare the electrode platinum wire was coated by dipping it several times in the slurry until a bead was formed and was kept for drying in air for 24 h. Before using, the electrode was dipped in distilled water for 10 min and after every 5 days it was conditioned with 0.01 M $\text{Fe}(\text{NO}_3)_3$ for 30 min.

2.4. Apparatus and e.m.f. measurements

All solutions were prepared using a digital single-pan balance (Mettler Toledo AB204, Switzerland). A Cyber-Scan 2500 pH meter (Eutech Instruments, Singapore) hav-

ing ± 0.1 mV accuracy with a SCE as reference electrode and KNO_3 salt bridge was used for potential measurements. All measurements were carried out at 25°C with cell of the type:



The performance of the electrode was investigated by measuring the e.m.f. of iron(III) solutions over the range of 1×10^{-1} to 1×10^{-8} M. To check for Nernstian response, standard solutions of $\text{Fe}(\text{NO}_3)_3$ in 0.05 M HNO_3 , 0.05 M HClO_4 , 0.05 M H_2SO_4 and 0.05 M HCl were prepared. The standard solutions of $\text{Fe}(\text{NO}_3)_3$ containing 0.05 M HNO_3 and 0.01 M $\text{KNO}_3/0.01$ M KCl were also prepared for calibration of the electrode. The e.m.f. were noted after every 15 s. It was found that the reading was stable to ± 1 mV after 30–55 s depending upon the medium and the plasticizer. The selectivity coefficients (K_{ij}) were calculated by mixed solution method [17]. A constant concentration of the interfering ions M(I) and M(II) was kept at 1×10^{-2} M.

2.5. Sample preparation

Samples from copper and nickel electroplating baths were diluted by 50% with 0.02 M KNO_3 before measuring the potentials. In case of zinc plating bath solutions measurements were done directly. The alloy sample was treated with aqua regia and boiled to near dryness. The resulting solution was diluted by 0.05 M HNO_3 and was used for analysis. Pharmaceutical samples analyzed were 'VitaminZ' capsules (Okasa Pharma Ltd., India) and 'Mumfer' (Glenmark Pharma Ltd., India). In addition to iron(II) fumarate 'VitaminZ' contained Vitamins A–C, E, calcium pantothenate and manganese sulphate, sodium selenate, and chromium(III) chloride whereas Mumfer tablets contained folic acid and some vitamins in addition to iron(III) hydroxide polymaltose. Each sample was treated with HNO_3 , HClO_4 and/or H_2O_2 to

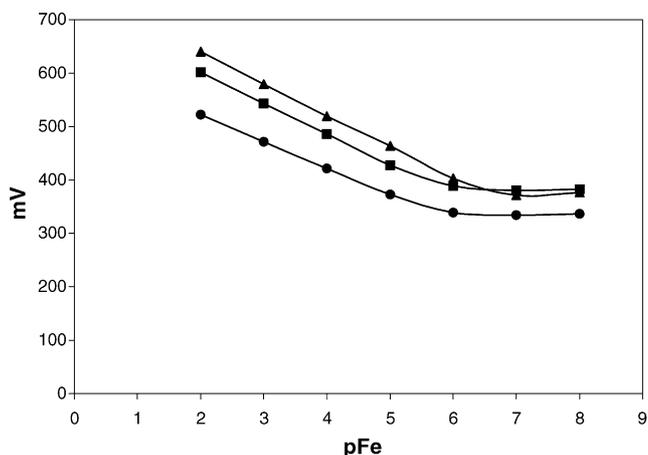


Fig. 1. Plot of e.m.f. vs. iron(III) concentration: (\blacktriangle) Nernstian response using dibutyl phthalate plasticizer; (\blacksquare) Nernstian response using diethyl phthalate plasticizer; (\bullet) Nernstian response using dibutyl maleate plasticizer.

Table 1
Comparison and properties of present Fe(III) ISEs with different plasticizers in various media during the first month

Medium	Ionophore (%)	PVC (%)	Response time (s)	Working range (M)	Slope (mV per decade)
Plasticizer used: dibutyl phthalate					
0.05 M HNO ₃	1.5	36.5	45	1×10^{-2} to 1×10^{-4}	58 ± 2
	3.0	35.0	40	1×10^{-2} to 1×10^{-5}	60 ± 2
	5.0	33.0	30	1×10^{-2} to 5×10^{-6}	60 ± 2
0.05 M HClO ₄	1.5	36.5	45	1×10^{-2} to 1×10^{-4}	58 ± 2
	3.0	35.0	40	1×10^{-2} to 1×10^{-5}	58 ± 2
	5.0	33.0	35	1×10^{-2} to 5×10^{-6}	58 ± 2
0.05 M H ₂ SO ₄	1.5	36.5	45	1×10^{-2} to 1×10^{-4}	50 ± 2
	3.0	35.0	40	1×10^{-2} to 5×10^{-5}	52 ± 2
	5.0	33.0	40	1×10^{-2} to 5×10^{-5}	52 ± 2
0.05 M HCl	1.5	36.5	45	1×10^{-2} to 1×10^{-4}	58 ± 2
	3.0	35.0	40	1×10^{-2} to 1×10^{-5}	58 ± 2
	5.0	33.0	35	1×10^{-2} to 5×10^{-6}	60 ± 2
0.01 M KCl	1.5	36.5	30	1×10^{-2} to 1×10^{-4}	58 ± 2
	3.0	35.0	30	1×10^{-2} to 1×10^{-5}	62 ± 2
	5.0	33.0	25	1×10^{-2} to 5×10^{-6}	62 ± 2
0.01 M KNO ₃	1.5	36.5	35	1×10^{-2} to 1×10^{-4}	60 ± 2
	3.0	35.0	25	1×10^{-2} to 1×10^{-5}	62 ± 2
	5.0	33.0	25	1×10^{-2} to 5×10^{-6}	62 ± 2
Plasticizer used: diethyl phthalate					
0.05 M HNO ₃	1.5	36.5	45	1×10^{-2} to 1×10^{-4}	56 ± 2
	3.0	35.0	40	1×10^{-2} to 1×10^{-5}	57 ± 2
	5.0	33.0	30	1×10^{-2} to 1×10^{-6}	58 ± 2
0.05 M HClO ₄	1.5	36.5	50	1×10^{-2} to 1×10^{-4}	55 ± 2
	3.0	35.0	45	1×10^{-2} to 1×10^{-5}	57 ± 2
	5.0	33.0	45	1×10^{-2} to 1×10^{-6}	57 ± 2
0.05 M H ₂ SO ₄	1.5	36.5	55	1×10^{-2} to 1×10^{-4}	45 ± 2
	3.0	35.0	40	1×10^{-2} to 5×10^{-5}	47 ± 2
	5.0	33.0	40	1×10^{-2} to 5×10^{-5}	52 ± 2
0.05 M HCl	1.5	36.5	55	1×10^{-2} to 1×10^{-4}	55 ± 2
	3.0	35.0	50	1×10^{-2} to 1×10^{-5}	56 ± 2
	5.0	33.0	40	1×10^{-2} to 5×10^{-5}	56 ± 2
0.01 M KCl	1.5	36.5	30	1×10^{-2} to 1×10^{-4}	57 ± 2
	3.0	35.0	30	1×10^{-2} to 1×10^{-5}	60 ± 2
	5.0	33.0	25	1×10^{-2} to 1×10^{-6}	60 ± 2
0.01 M KNO ₃	1.5	36.5	35	1×10^{-2} to 1×10^{-4}	58 ± 2
	3.0	35.0	25	1×10^{-2} to 1×10^{-5}	60 ± 2
	5.0	33.0	25	1×10^{-2} to 1×10^{-6}	60 ± 2
Plasticizer used: dibutyl maleate					
0.05 M HNO ₃	1.5	36.5	45	1×10^{-2} to 1×10^{-4}	58 ± 2
	3.0	35.0	40	1×10^{-2} to 1×10^{-5}	60 ± 2
	5.0	33.0	40	1×10^{-2} to 5×10^{-6}	60 ± 2
0.05 M HClO ₄	1.5	36.5	45	1×10^{-2} to 1×10^{-4}	58 ± 2
	3.0	35.0	40	1×10^{-2} to 1×10^{-5}	60 ± 2
	5.0	33.0	40	1×10^{-2} to 5×10^{-6}	60 ± 2
0.05 M H ₂ SO ₄	1.5	36.5	55	1×10^{-2} to 1×10^{-4}	45 ± 2
	3.0	35.0	40	1×10^{-2} to 5×10^{-4}	47 ± 2
	5.0	33.0	40	1×10^{-2} to 5×10^{-5}	52 ± 2
0.05 M HCl	1.5	36.5	45	1×10^{-2} to 1×10^{-4}	58 ± 2
	3.0	35.0	45	1×10^{-2} to 1×10^{-5}	60 ± 2
	5.0	33.0	40	1×10^{-2} to 5×10^{-6}	60 ± 2
0.01 M KCl	1.5	36.5	30	1×10^{-2} to 1×10^{-4}	58 ± 2
	3.0	35.0	30	1×10^{-2} to 1×10^{-5}	58 ± 2
	5.0	33.0	25	1×10^{-2} to 1×10^{-6}	60 ± 2
0.01 M KNO ₃	1.5	36.5	35	1×10^{-2} to 1×10^{-4}	58 ± 2
	3.0	35.0	25	1×10^{-2} to 1×10^{-5}	58 ± 2
	5.0	33.0	25	1×10^{-2} to 1×10^{-6}	60 ± 2

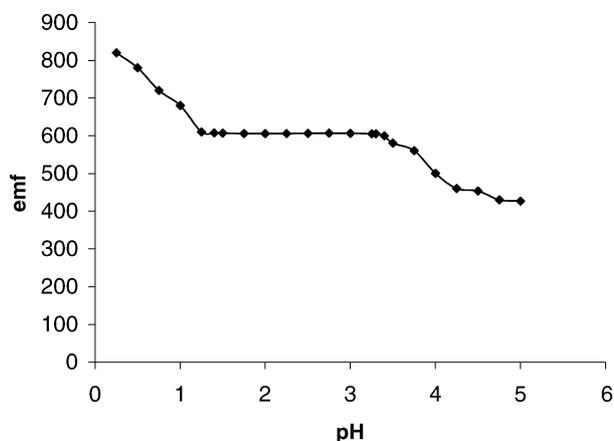


Fig. 2. Plot of e.m.f. vs. pH.

decompose the organic component and to convert Fe(II) to Fe(III).

3. Results and discussion

The coated Pt wire Fe(III) ISEs showed a linear far-Nernstian response (80 mV per decade change) for the first 2 weeks. Later they showed proper linear Nernstian response for more than 2 months (Fig. 1). Among all the ISEs prepared, the membrane containing plasticizer dibutyl phthalate and 5% ionophore gave best response with a slope of 60 ± 5 mV per decade in the activity range of 1×10^{-2} to 1×10^{-6} M in standard solutions of Fe(NO₃)₃ in 0.05 M HNO₃ medium over a period of 3 months (as shown in Table 1). After that, the sensitivity decreases (1×10^{-2} M to 1×10^{-5} M) and frequent conditioning was required. Being the best out of all the electrodes prepared, it was used for further studies.

The influence of pH on the response of the CWISE to various concentrations of Fe(III) is shown in Fig. 2. It was

Table 2
Selectivity coefficients of Fe(III) ISE

Serial no.	Interfering ion	Selectivity coefficient ($K_{Fe^{3+},M}$)
1	Na(I)	5.0×10^{-3}
2	K(I)	1.1×10^{-3}
3	Ag(I)	1.3×10^{-2}
4	Ca(II)	8.0×10^{-4}
5	Co(II)	1.59×10^{-3}
6	Ni(II)	6.3×10^{-3}
7	Cu(II)	1.26×10^{-3}
8	Zn(II)	1.99×10^{-3}
9	Cd(II)	1.25×10^{-3}
10	Pb(II)	1.0×10^{-3}
11	Hg(II)	4.9×10^{-3}
12	Cr(III)	5.1×10^{-3}
13	Mg(II)	4.8×10^{-3}
14	Fe(II)	3.1×10^{-1}

observed that above pH 3.5 the potential starts decreasing slowly, this may be because of the formation of ferric hydroxide in the solution at higher pH. At pH, lower than 1.3 the potential drastically increases, possibly due to the electrode response towards hydrogen ions.

The ISE response is attributed to the electron-exchange mechanism at the membrane–contact interface and ion exchange at the membrane–solution interface [17]. The monovalent response can be attributed to the Fe(III)/Fe(II) redox reaction at the membrane–contact interface. Monovalent response for Fe(III) ISEs has been observed by De Marco et al. [18] and Wang and Shih [19]. It is interesting to note that the electrode in our present work gave a quicker response time of 25–30 s and stable reading in the presence of 0.01 M KNO₃ medium (Table 1) as experienced by De Marco et al. [18]. The CWISE developed, works over a lower concentration range of iron(III) as compared to ISE developed for Fe(III) earlier [1, 10]. Because of its better response in 0.01 M KNO₃, this medium was used for the analysis of electroplating bath solutions. The selectivity coefficients ($K_{Fe^{3+},M}$) for some cations having a back ground concentration of 10^{-2} M

Table 3
Results obtained by direct potentiometry for synthetic samples

Serial no.	Composition	Observed content (M)
1	0.0010 M Fe(NO ₃) ₃ + 0.01 M NaNO ₃ + 0.01 M Co(NO ₃) ₂ + 0.01 M Pb(NO ₃) ₂	0.0011
2	0.0010 M Fe(NO ₃) ₃ + 0.01 M Mg(ClO ₄) ₂ + 0.01 M Cu(NO ₃) ₂ + 0.01 M Ni(NO ₃) ₂	0.0012
3	0.0010 M Fe(NO ₃) ₃ + 0.01 M AgNO ₃ + 0.01 M Cd(NO ₃) ₂ + 0.01 M KNO ₃	0.0009
4	0.0010 M Fe(NO ₃) ₃ + 0.01 M Cr(ClO ₄) ₃ + 0.01 M Zn(NO ₃) ₂ + 0.01 M Hg(NO ₃) ₂	0.0010
5	0.0010 M Fe(NO ₃) ₃ + 0.01 M Zn(NO ₃) ₂ + 0.01 M Hg(NO ₃) ₂ + 0.01 M FeCl ₂ + 10% H ₂ O ₂	0.0107
6	0.0010 M Fe(NO ₃) ₃ + 0.01 M Cr(ClO ₄) ₃ + 0.01 M Ca(ClO ₄) ₂ + 0.01 M Hg(NO ₃) ₂	0.0009
		Observed content (ppm)
1	100 ppm Fe(III) in 20% HCl solution	101
2	150 ppm Fe(III) in 20% HCl solution + 0.01 M KNO ₃	147
3	150 ppm Fe(III) in 80 g copper sulphate + 8 ml sulphuric acid in 1000 ml 0.01 M KNO ₃	146
4	150 ppm Fe(III) in 25 g nickel sulphate + 10 g boric acid + 13 g nickel chloride + 8 ml sulphuric acid in 1000 ml 0.01 M KNO ₃	154
5	150 ppm Fe(III) in 20 g zinc chloride + 10 g boric acid + 8 g KCl in 1000 ml 0.01 M KNO ₃	147
6	150 ppm Fe(III) in 80 g CrO ₃ + 1 ml sulphuric acid in 1000 ml 0.01 M KNO ₃	–
7	150 ppm Fe(III) in 25 g CrO ₃ + 1 ml sulphuric acid in 1000 ml 0.01 M KNO ₃	–
8	150 ppm Fe(III) in 2.5 g CrO ₃ + 1 ml sulphuric acid in 1000 ml 0.01 M KNO ₃	–

Table 4
Comparison of the present and conventional methods in real samples

Sample	Present method (ppm)	AAS method (ppm)
Electroplating bath solutions		
Copper plating solution 1	255	259
Copper plating solution 2	172	167
Zinc plating solution 1	249	254
Zinc plating solution 2	310	303
Nickel plating solution 1	251	250
Nickel plating solution 2	146	151
	ISE method (%)	Conventional method (%)
Alloy sample		
Stainless steel	63.5 ± 0.4 (n = 5)	63.2
	Observed content (mg)	Quoted content (mg)
Pharmaceutical samples		
VitaminZ capsules	26.89 ± 0.3 (n = 5)	30.5
Mumfer tablets	97.5 ± 0.3 (n = 5)	100.0

in 0.05 M HNO₃ were determined by the mixed-solution method (Table 2). Iron(III) was also determined in some artificial and real samples and results of the real samples were confirmed by conventional methods (Tables 3 and 4). Samples in the bottom half of Table 3 were prepared to resemble the iron impurities in acid pickling and electroplating bath solutions used in metal finishing industry. The CWISE did not work, or rather got spoiled even in diluted chrome solutions. This could be because of the strong oxidizing nature of hexavalent chromium, which can decompose the membrane/ionophore. Also, it was observed that, the membrane retained the orange colour of chromate, after removal from the chromium solution and washing the CWISE. However, no retention of blue/green colour was observed when the electrode was used in copper/nickel solutions, respectively. So, it is possible that, the chromate anions get adsorbed onto the membrane, rendering it useless for further measurements.

From the selectivity coefficients it was found that iron(II) presents some interference. As this could affect the real sample analysis, Fe(II) was oxidized to Fe(III) in the solutions with H₂O₂ and the total iron content was determined. Unlike other coated wire Fe(III) electrode [1], the present electrode can be used in presence of Hg(II). The ISEs thus prepared provide a means for rapid routine analysis of electroplating bath solutions, alloys and pharmaceutical samples (Table 4).

4. Conclusions

The platinum wire-coated ISE fabricated in the present work holds promise for the analysis of Fe(III) in various matrices as it shows appreciable selectivity towards Fe(III) ion in presence of most of the mono-, bi-, and trivalent metal

ions. The CWISE, so prepared can provide a means for rapid routine analysis of electroplating bath solutions, alloys and pharmaceutical samples.

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