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Talanta 64 (2004) 1048–1052
Talanta
www.elsevier.com/locate/talanta

A novel ion selective membrane potentiometric sensor for direct determination of Fe(III) in the presence of Fe(II)

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Received 21 January 2004; received in revised form 3 April 2004; accepted 7 May 2004
Available online 2 July 2004

Abstract

A new PVC membrane potentiometric sensor that is highly selective to Fe(III) ions was prepared by using 2-[(2-hydroxy-1-propenyl-buta-1,3-dienylimino)-methyl]-4-*p*-tolylazo-phenol [HPDTP] as a suitable carrier. The electrode exhibits a linear response for iron(III) ions over a wide concentration range (3.5×10^{-6} to 4.0×10^{-2}) with a super Nernstian slope of 28.5 (±0.5) per decade. The electrode can be used in the pH range from 4.5 to 6.5. The proposed sensor shows fairly a good discriminating ability towards Fe^{3+} ion in comparison to some hard and soft metals such as Fe^{2+}, Cd^{2+}, Cu^{2+}, Al^{3+} and Ca^{2+}. It has a response time of <15 s and can be used for at least 2 months without any measurable divergence in response characteristics. The electrode was used in the direct determination of Fe^{3+} in aqueous samples and as an indicator electrode in potentiometric titration of Fe(III) ions.

Keywords: Fe(III); Iron; Ion selective electrode; PVC membrane; Potentiometry; Schiff base

1. Introduction

Iron is widely distributed in nature and is one of the most important elements in biological systems. Biologically, iron plays roles in the transport and storage of oxygen and also in electron transport, and it is safe to say that, with only a few possible exceptions in the bacterial world, there would be no life without iron [1]. If iron concentration exceeds the normal level it may become potential health hazard. Iron deficiency leads to anaemia. Excess iron in the body causes liver and kidney damage (haemochromatosis). Some iron compounds are suspected carcinogens. Hence the need for iron ion determination in clinical, medicinal, environmental and different industrial samples has led to a number of methods for the measurement of this analyte [2–8]. However, despite the urgent need for Fe-selective sensors for the potentiometric monitoring of Fe^{3+} ions, there have been only limited reports on Fe^{3+} ion selective electrodes in the literature [9,10]. A few examples for the use of solid-state ISEs for Fe(III) were reported [11–15]. Also ionophore-free ion exchanger electrodes for iron complexes, such as tetracholoroferrate(III) or iron(II)-1,10-phenantroline, were described and may find applications in special cases, but the selectivity arising from complexation in the aqueous solution is in neither of these two cases fully satisfactory [16,17].

The Schiff bases derived from salicylaldehyde (salens) polydentate ligands are known to form very stable complexes with transition metal ions [18–20]. The resulting salen complexes have attracted increasing attention, mainly due to their peculiar properties [19] and their reactivity mainly in the area of binding small molecules [18,20]. As is known, Schiff bases are reagents, which are becoming increasingly important in the pharmaceutical, dye and plastic industries as well as for liquid-crystal technology and mechanistic investigations of the drugs used in pharmacology, biochemistry and physiology [23]. In addition, they are potential applications as metallomesogens and their use in development of photonic devices [21]. However, despite extensive scientific reports on the synthesis, characterization and crystalline structure of the transition metal-salen complexes, there have been only limited reports on the use of salen molecules as ionophore in ion-selective studies [22–27].

We have recently reported the successful use of some mercapto compounds and Schiff bases in con-

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doi:10.1016/j.talanta.2004.05.005

struction of poly vinyl chloride powder (PVC)-based membrane selective sensors for Ni^{2+}, Co^{2+}, Hg^{2+} and Cd^{2+} ions [28–34]. In the present work, we used 2-[(2-hydroxy-1-propenyl-buta-1,3-dienylimino)-methyl]-4-*p*-tolylazo-phenol [HPDTP] recently synthesized in our laboratory [35] as an excellent neutral ion carrier in construction of a novel Fe^{3+}-PVC membrane electrode.

2. Experimental

2.1. Reagents

Analytical reagent grade chemicals and doubly distilled water were used for preparing all aqueous solutions. High molecular weight poly vinyl chloride powder, dioctyl phthalate (DOP), dibutyl phthalate (DBP), dimethyl sebacate (DMS) and tetrahydrofuran (THF) were obtained from Aldrich. Sodium tetraphenyl borate (NaTPB) and 2-nitrophenyl octyl ether (NPOE) were obtained from Fluka. Salts of metal nitrates or chlorides (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5. Ligand 2-[(2-hydroxy-1-propenyl-buta-1,3-dienylimino)-methyl]-4-*p*-tolylazo-phenol was synthesized and purified as described elsewhere [35]. All the metal nitrate solutions were freshly prepared by accurate dilution from their stock solution of 0.1 M, with distilled de-ionized water. The concentration of solutions was checked by an atomic absorption spectrophotometer Model AA-760 (Shimadzu, Japan).

2.2. Apparatus

All potentiometric measurements were made with a pH/mV meter (Zag Chimi, Iran) using proposed sensor in conjunction with a double junction Ag/AgCl reference electrode. Atomic absorption spectrophotometric measurements were made on Shimadzu AA-760 spectrometer under the recommended conditions by user's manual of instrument.

2.3. Electrode preparation

The membranes were constructed by combining various components with ratios as detailed in Table 1. The sensor materials were dissolved in 2 ml of THF. The resulting mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly at room temperature until an oily concentrated mixture was obtained. A Pyrex or Teflon tube (3–5 mm i.d. on top) was dipped into the mixture for about 10 s so that a transparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 1 h. The tube was then filled with internal filling solution (1×10^{-3} M $Fe(NO_3)_3$). The electrode was finally conditioned for 24 h by soaking in a 1×10^{-3} M solution of ferric nitrate. A silver/silver chloride electrode was used as an internal reference electrode.

2.4. Preparation of sample solution

Raricap-haematinic tablet weighing 1.157 g containing 25 mg iron as ferrous calcium citrate was dissolved in 1 ml concentrated nitric acid by heating for 5 min. The solution was mixed with 10 ml water and boiled to remove excess acid. The resulting solution was diluted to 500 ml in a volumetric flask. Standard solutions were prepared by appropriate dilution of the stock solution with water.

2.5. Electrode system and emf measurement

All emf measurements were carried out with the following cell assembly:

Ag/AgCl | 10^{-3} M $Fe(NO_3)_3$ | electrode membrane | sample solution | Ag/AgCl.

All measurements were carried out in a 50 ml double-walled glass cell, with constant magnetic stirring of the test solution. The performance of the electrodes was investigated by measuring the emf of ferric nitrate solutions prepared with a concentration range of 10^{-1} to 10^{-7} M by serial dilution. Activities were calculated according to the modified Debye–Hückel equation:

$$\log \gamma = -0.511\, Z^2 \left[\frac{\mu^{12}}{(1 + 1.5\mu^{12})} - 0.2\mu \right]$$

where μ is the ionic strength and Z the valency. All measurements were carried out at 25 ± 0.1 °C.

3. Results and discussion

The structure of compound examined as ferric ion selective ionophore is presented in Fig. 1. Theoretical studies show that the ionophore is a three dentate ligand and form stable complexes with some transition metals including iron(III). The stochiometry of complex form between Fe^{3+} and this ionophore is ML_2 [36]. The key ingredient of such plasticized PVC membranes is the incorporated carrier that defines the selectivity of the electrodes via selective complex formation with the cation of interest. Due to its sufficient insolubility in water and the presence of donating nitrogen

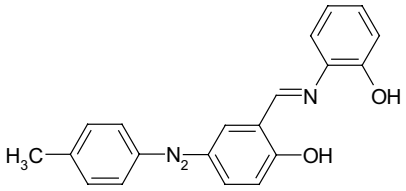

Fig. 1. Structure of ionophore 2-[(2-hydroxy-1-propenyl-buta-1,3-dienylimino)-methyl]-4-*p*-tolylazo-phenol.

Table 1
Optimization of membrane ingredients

	Components in membranes (%)				Slope (mV dec^{-1})	Dynamic range (M)
	HPDTP	PVC	NaTPB	Plastisizer		
1	–	34.0	–	DBP, 66.0	3	1.2×10^{-5} to 1.8×10^{-4}
2	3.3	33.5	–	DBP, 63.2	28.5	3.5×10^{-6} to 4.0×10^{-2}
3	3.4	62.9	–	DBP, 33.7	12.5	2.2×10^{-5} to 3.5×10^{-3}
4	3.2	29.5	3.5	DBP, 63.8	34.3	1.5×10^{-6} to 5.4×10^{-3}
5	3.3	32.0	–	DOP, 64.7	17	5.3×10^{-6} to 1.5×10^{-3}
6	3.2	31.7	–	NPOE, 65.1	12	4.5×10^{-5} to 2.5×10^{-3}
7	3.3	32.1	–	DMS, 64.6	31	6.5×10^{-6} to 5.5×10^{-2}

and oxygen atoms in its structure, ligand HPDTP was expected to act as a suitable ion carrier in the PVC membranes with respect to special transition and heavy metal ions of proper size and charge. Thus, in preliminary experiments, it was used as a neutral carrier to prepare PVC-based membrane electrodes for a variety of metal ions. The potential responses of the most sensitive electrodes, prepared under the same experimental conditions (except for 24 h conditioning in a 0.01 M of the corresponding cations) are shown in Fig. 2. As it can be seen, among different tested cations, Fe^{3+} with the most sensitive response seems to be suitably determined with the PVC membrane based on HPDTP and the emf responses obtained for all other cation-selective electrodes are much lower than that predicted by the Nernst equation. This is probably due to both the selective behavior of the ionophore against Fe^{3+} in comparison to some other metal ions and the rapid exchange kinetics of the resulting HPDTP-Fe^{3+} complexes [37].

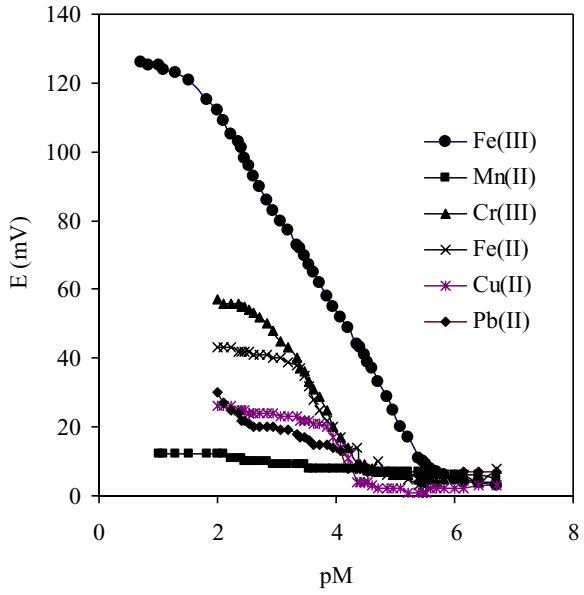

Fig. 2. Potential response of various ion-selective electrodes based on ligand HPDTP. Conditions: membrane ingredients 3.3% ionophore; 33.5% PVC; and 63.2% DBP; internal solution, 1.0×10^{-3} M of each cation used. The electrodes have been conditioned in 1.0×10^{-2} M of the corresponding cation for 24 h.

It is well known that the sensitivity and selectivity obtained for a given ion-selective electrode depends not only on the nature of ionophore used, but also significantly on the membrane composition and the properties of the plasticizer employed [28–32]. Thus, the influences of the membrane composition and the nature of plasticizer on the response characteristics of Fe^{3+} ion-selective electrode based on HPDTP were investigated and the results summarized in Table 1. The nature and amount of plasticizer on the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of ligand largely affect the response characteristics of ion-selective electrodes [37–39]. As can be seen in Table 1 among the four different plasticizers often used with PVC-membrane electrodes including NPOE, DOP, DBP and DMS, the best calibration parameters and mechanical characteristics of the membranes were observed in the case of DBP; hence, this plasticizer was used in further studies. This indicates the solvent medium of DBP is probably recognized in providing the best complexation environment between ferric ions and carrier.The results thus obtained indicate that the best sensitivity and linear range are obtained for membrane number two with a PVC:DBP:HPDTP percent ratio of 33.5:63.2:3.3 resulting in the best behavior of the membrane electrode.

The pH dependence of the membrane sensors, tested over the pH range 3–8 at a 1.0×10^{-4} mol dm^{-3} Fe^{3+} ion concentration, and a typical plot for electrode (2) are shown in Fig. 3. The potentials are fairly constant in the pH range 4.5–6.5. 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 probably protonated, and unable to complex readily with iron(III). Furthermore, the sensor may also be exhibiting an interference effect due to hydrogen ions [28]. At elevated pH, the iron(III) in solution is dramatically reduced through the formation of iron(III) hydroxo complexes, and the magnitude of the voltage change should be reconciled with iron(III) speciation calculations in solution.

The proposed membrane electrode was also examined with different concentrations of the inner reference solution from 1.0×10^{-2} to 1.0×10^{-5} M. Functioning of the membrane sensor with reference solutions of various $Fe(NO_3)_3$ concentration was found only a slight effect on the potential

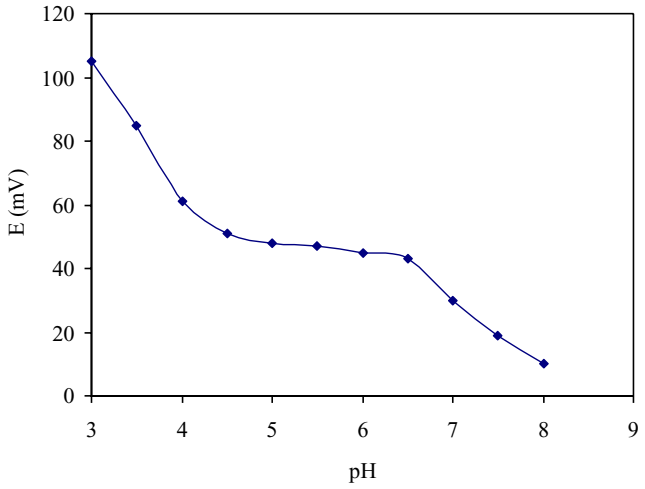

Fig. 3. Effect of pH of test solutions on the response of Fe^{3+} selective electrode based on HPDTP.

response of the electrode. A 1.0×10^{-2} M concentration of the reference solution is quite appropriate for smooth functioning of the membrane electrode system. Optimum conditioning time for the membrane electrode in a 0.01 M ferric nitrate solution is 24 h. It then generates stable potentials when placed in contact with Fe^{3+} solutions.

We measured the average time required for the Fe^{3+} ion-selective electrode to reach a potential within ±1 mV of the final equilibrium value after successive immersion in a series of ferric ion solutions, each having a 10-fold difference in concentration. The static response time of the membrane electrode thus obtained was ∼15 s and potentials stayed constant for ∼10 min, after which only a very slow divergence within the months without any measurable change in response time, slope, or detection limit. The performance characteristics of the membrane remained unchanged when the potentials recorded either from low to high concentrations or vice versa. This means that the response was rapid and reversible. The membrane electrode prepared could be used for about 2 mounts without observing any change in response characteristics (week-to-week tested). The standard deviation of ten replicate measurements with one membrane within 6 weeks was 5.0%. The membranes were stored in 0.01 M Fe^{3+} solution or dry when not in use. If the membrane was stored dry, it must be conditioned in a 0.01 M ferric nitrate solution for 24 h.

To evaluate the reproducibility of this electrode, a series of membranes (five) with similar composition (No 2) prepared and the response of these electrodes to Fe^{3+} ion concentration were tested. The results show that the average of slopes, detection limits and linear dynamic ranges were 28 ± 1 mV/decade, 2.5 (±0.2) $\times 10^{-6}$ M and (4.0 (±0.2) $\times 10^{-2}$ to 3.5 (±0.3) $\times 10^{-6}$ M), respectively. The standard deviation of measurements of 1.0×10^{-5} M of Fe^{3+} solution with these five electrodes was ±1.5 mV.

The electrode shows a linear response to the activity of Fe^{3+} ion in the range 3.5×10^{-6} to 4.0×10^{-2} M (Fig. 2). The slopes of the calibration plots were 28 ± 1 mV per decade of ferric ion activity change at 25 °C. The limit of detection was 2.5 (±0.1) $\times 10^{-6}$ M, as determined from the intersection of the two extrapolated segments of the calibration graph. The standard deviation of 10 replicate measurements was ±0.5 mV.

The selectivity behavior is obviously one of the most important characteristic of an ion selective electrode, determining whether a reliable measurement in the target sample is possible. To investigate the selectivity of the membrane electrode proposed, their potential response were investigated in the presence of various interfering foreign ions. Fig. 2 clearly shows the selective behavior of the PVC membrane electrode based on HPDTP for Fe^{3+} ion over other cationic species. The selectivity coefficients of the proposed membrane selective electrode were determined against a number of different cations by using separate solution method (SSM) [40].

According to the SSM, the potentiometric selectivity coefficients were determined using 1×10^{-4} M test solution of different ions at pH ∼ 5 and utilizing the equation:

$$\log K^{\text{pot}}_{\text{Fe(III),M}} = (E_j - E_i)/S - \log a_j^{Z_i Z_j} + \log a_i$$

Where E_j and E_i are the measured emf for the solutions of interfering and Fe^{3+} ions, respectively; Z_i and Z_j are the charges of Fe(III) and interfering ion. S is the calibration slope of the sensor and a_i and a_j are the activity of Fe(III) and interfering ion, respectively.

The resulting selectivity coefficients are summarized in Table 2. They are in the order of 10^{-3} or lower for almost all diverse ions tested. Hence, these cations are not expected to interfere with the functioning of the proposed Fe^{3+} selective sensor even at high concentration levels. Moreover, to investigate the effect of anions on the electrode's potential responses, the cell potentials were obtained using ferric nitrate, ferric sulfate and ferric chloride. No significant change in the emf versus pFe plots were observed, indicating that these anions (NO_3^-, Cl^- and SO_4^{2-}) do not cause any interference.The proposed Fe^{3+} ion selective electrode based on ionophore HPDTP was found to work under laboratory con-

Table 2
Selectivity coefficients of various interfering ions for Fe(III) ion-selective electrode based on HPDTP

Interfere ion	$-\log K^{\text{pot}}_{\text{Fe(III),M}}$
Mn^{2+}	4.5
Cd^{2+}	No-response
Ca^{2+}	No-response
K^+	3.1
Zn^{2+}	2.5
Fe^{2+}	3.0
Cu^{2+}	2.3
Co^{2+}	3.2
Pb^{2+}	3.3
Ni^{2+}	2.1
Cr^{2+}	3.1

Table 3
Determination of the concentration (mg ml^{-1}) of iron(III) in different samples by use of the proposed electrode and comparison with the atomic absorption spectrometry (AAS)

Sample	Fe(III) added	Found by AAS	Found by the proposed method[a]
Tap water	0.0	0.35	0.34 (0.05)
	0.5	0.84	0.86 (0.05)
Waste water	0.0	2.2	2.2 (0.1)
	1.5	3.7	3.65 (0.08)
River water	0.0	1.2	1.3 (0.4)
	1.0	2.2	2.4 (0.4)
Iron tablet	0.0	23 mg per tablet	24 (1.0) mg per tablet

[a] Values in parentheses are RSDs based on five replicate analyses.

ditions. It was successfully applied as indicator electrode in the potentiometric titration of Fe^{3+} ion with NaOH. This electrode was also successfully applied to the direct determination of iron in different water samples and the results are given in Table 3. As can be seen, the accuracy of iron determination in different water samples is almost quantitative. Moreover, the iron content of Raricap-haematinic tablet (25 mg) determined by the proposed electrode was in good agreement with data obtained by AAS method (Table 3).

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