Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1102087

57 (2016) 18120–18130
August

Taylor & Francis
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Construction and performance characteristics of polymeric membrane electrode based on $^{i}Pr_2Ph$-DAD for the selective determination of Fe^{3+} ion

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Received 23 January 2015; Accepted 23 August 2015

ABSTRACT

A new PVC membrane potentiometric sensor for Fe(III) ions was prepared using N,N´-bis (2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene) ($^{i}Pr_2Ph$-DAD) as a suitable carrier. The best performance was observed for the membrane composition including 33.0% PVC, 66.0% DOS, and 1.0% ionophore. The electrode displayed a linear potential response over a concentration range from 1.0×10^{-6} to 1.0×10^{-2} M with a detection limit of 4.5×10^{-7} M and a Nernstian slope of 19.9 ± 0.3 mV/decade. The sensor response is pH independent in the range of 2.1–6.0 and has a fast response time of 7 s. It also shows good selectivity to Fe(III) ion over many alkali, alkaline earth, transition, and heavy metal ions. The lifetime of the electrode was two months. It has been observed that the developed sensor satisfactorily works in partially non-aqueous media up to 10% (v/v) content of methanol, ethanol, and acetone. The proposed electrode could be used to quantify Fe^{3+} ion in some different synthetic and real samples with satisfactory results. It can also be used as an indicator electrode in potentiometric titration of Fe^{3+} ion with EDTA.

Keywords: Fe^{3+}; PVC-membrane; Ion-selective electrode; Potentiometry; Ionophore

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1. Introduction

Iron is a prominent element that is present in a variety of aspects of human life ranging from environment and industry to medical physiology and biology. Biologically, iron plays a significant role in the oxygen transport, storage, and in the electron transport [1]. It is widely accepted that the presence of iron, alone or in combination, has beneficial or deleterious effects on the properties of many substances and the nature of various biological systems. On the one hand, iron provides a fundamental structure of haemoglobin, myoglobin, haem enzymes, and many cofactors involved in enzyme activities. On the other hand, if the iron concentration exceeds the normal level in the body, iron and its compounds can lead to serious problems, including depression, rapid and shallow respiration, coma, convulsions, and cardiac arrest [2–4]. Thus, it is important to monitor the concentration of iron in clinical, medicinal, environmental, and industrial samples. A number of instrumental techniques such as energy dispersive X-ray fluorescence [5], neutron activation analysis [6], inductively coupled plasma mass spectrometry (ICP-MS) [7], electrothermal atomization atomic absorption spectrometry [8], cathodic stripping voltammetry [9–11], luminescence [12], and spectrophotometry [13],

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are available for its estimation. These methods provide accurate determination of Fe^{3+} ion content but require large infrastructure backup and support of expertise. However, ion-selective electrodes have proven to be the very promising devices. Among the available analytical techniques, the application of carrier-based ion-selective electrodes (ISEs) has become a well-established routine analytical technique. ISEs containing polymeric membranes, such as poly(vinyl chloride) (PVC), which are assumed to behave as organic liquids of high viscosity, are by far the most versatile and widely studied class of ISEs. They are eco-friendly techniques, providing easy construction and manipulation, present good selectivity in a wide concentration range of operability and relatively low detection limit, show fast response and non-destructive analysis, and can be used as very useful tools for clinical, chemical, and environmental analysis [14,15]. During the last few decades, although some ISEs for the estimation of Fe^{3+} concentration have also been reported [16–30], a more sensitive and selective electrode with good performance parameters for Fe^{3+} ion quantification is required and needs to be developed.

To develop a good ISE, a selective ionophore is required. 1,4-Diaza-1,3-diene (DAD) ligands are an important class of ligands and are well established as highly versatile ligands for nearly every element in the periodic table [31]. The π-acceptor capacity of certain 1,4-diaza-1,3-diene ligands such as ^{t}BuN=CHCH=N^{t}Bu is about twice as high as that of the traditionally used 2,2´-bipyridine. Several research groups pay attention to the preparation of metal complexes of DAD ligands and study the coordination mode of the DAD ligand to metals [32–37]. However, the behavior of these compounds as ion carriers in ion-selective membrane electrodes has received no attention yet. Therefore, in the present study, 1,4-diaza-1,3-butadiene type ligand N,N´-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene) ($^{i}Pr_2$Ph-DAD) (Fig. 1) was used as an excellent neutral ion carrier in the construction of a novel Fe^{3+}-PVC membrane electrode.

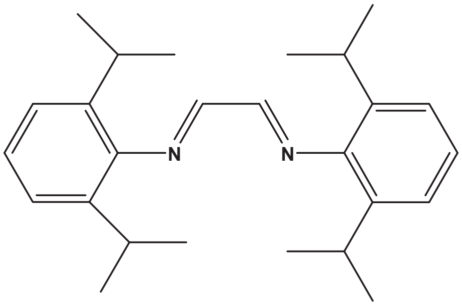

Fig. 1. The structure of N,N´-bis(2,6-di-isopropylphenyl)-1,4-diaza-1,3-butadiene) ($^{i}Pr_2$Ph-DAD).

2. Materials and methods

2.1. Reagents

Ionophore $^{i}Pr_2$Ph-DAD was synthesized according to the procedures described in the literature [38]. The materials used to prepare the polymeric membrane were of analytical reagent grade. 2-Nitrophenyloctyl ether (*o*-NPOE) and potassium tetrakis (4-chlorophenyl-borate) (KT*p*ClPB) were purchased from Fluka. Dibutyl phthalate (DBP), dioctyl phthalate (DOP), dioctyl sebacate (DOS), sodium tetraphenylborate (NaTPB), tetrahydrofuran (THF) (dried by sodium and distilled prior to use), and poly(vinylchoride) (PVC) of high molecular mass were obtained from Shanghai Chemical Company. Nitrate and chloride salts of all metals as well as hydrogen peroxide (30%, 8.82 M) were also purchased from Shanghai Chemical Company and used without further purification. Double-distilled water was used for the preparation of metal salt solutions by diluting stock solution of 0.1 M.

2.2. Preparation of electrodes and potentiometric measurements

Various membrane ingredients viz. ionophore, PVC, plasticizers (DOS, DBP, DOP and *o*-NPOE), and anionic excluders (NaTPB and KT*p*ClPB) were used for the fabrication of the membranes. These ingredients were dissolved in various amounts in 5 mL of THF. They were mixed vigorously with a glass rod. The solution was poured into an 18-mm diameter glass ring and the solvent was allowed to evaporate at room temperature for two days. The resulting membrane was cut into small diameter disks and was sealed onto the end of the Ag/AgCl electrode barrel with a 5% THF solution of PVC (wt%). By varying the relative amounts of membrane ingredients, a number of membranes with different compositions were prepared and studied. Prior to potentiometric measurements, the electrodes were conditioned in a 0.01 M Fe^{3+} solution for 24 h.

Potentials and pH values were measured using an ion meter of model pXSJ-216 (Leici Instruments Corporation, Shanghai) and a pH meter of model 6071 (JENCO Electronics, Ltd, Shanghai), respectively. All potentials were measured relative to an Hg/Hg_2Cl_2 double junction reference electrode with 0.1 M lithium acetate in the outer compartment and saturated potassium chloride in the inner compartment. The potentiometric measurements were made with the following electrochemical cell:

$Hg/Hg_2Cl_2/KCl$(saturated)/0.1 M LiAc/sample solution//PVC membrane//0.01 M $FeCl_3$ /Ag/AgCl.

The performance of each electrode was investigated by measuring its potential in Fe(III) solutions prepared in the range of 1.0×10^{-8} to 1.0×10^{-1} M by serial dilution of 0.1 M stock solution. The solutions were stirred and potential readings were recorded when they reached steady state values. All measurements were carried out at 25 ± 0.1℃.

2.3. Spectrophotometric titrations

Standard stock solutions of ligand (5.0×10^{-4} M) and Fe^{3+} ion (1.0×10^{-3} M) were prepared for investigation of the interaction of ligand with iron(III) cation by spectrophotometric method. The exactly weighed (with an accuracy of 0.0001 g) pure solid compound was dissolved in a 25.0 mL volumetric flask and diluted up to mark with acetonitrile. Working solutions were prepared by appropriate dilution of the stock solutions. Titration of the ligand solution (1.0×10^{-5} M) was carried out by the addition of microliter amounts of a concentrated standard solution of iron(III) ion (1.0×10^{-3} M) using a pre-calibrated microsyringe. The absorbances were measured on a UV–vis spectrophotometer (Model TU-1900, Purkinje General).

3. Results and discussion

3.1. Complexation investigation of $^{i}Pr_2$Ph-DAD with metal ions

Ligand use as an ionophore in a Fe^{3+} ion-selective electrode should be selective for Fe^{3+} over other metal ions and should be sufficiently lipophilic to prevent leaching of the ligand into the solutions surrounding the membrane electrode. Ligand $^{i}Pr_2$Ph-DAD is insoluble in water and can form a stable complex with Fe^{3+} ion in non-aqueous media.

Preliminary experiments are made to review the complexation properties of $^{i}Pr_2$Ph-DAD in acetonitrile solution (5.0×10^{-5} M) with several metal ions by the spectrophotometric method. The UV–vis spectrum of the ligand $^{i}Pr_2$Ph-DAD is recorded initially in the absence of metal ions. The absorption spectrum given in Fig. 2 exhibits one significant absorption band at 215 nm, which is attributed to the π–π* transition of $^{i}Pr_2$Ph-DAD. Upon addition of metal ions to the solution of $^{i}Pr_2$Ph-DAD, a shift in the peak at 215 nm was observed and a new absorbance band at 375 nm appears. The band at 375 nm is assigned to the electronic transition associated with hydrogen ion, because HNO_3 was added to metal ion solutions to prevent hydrolysis. What is noteworthy is that the UV–vis spectrum of ligand undergoes a clear change after the addition of Fe^{3+} ion. Three new bands showed up at 265, 375, and 465 nm. The enhancement in the intensity of the principal band (215 nm) caused significant hyperchromic and bathochromic with the increasing absorbance. These changes indicated that the iron(III)–$^{i}Pr_2$Ph-DAD complex was formed.

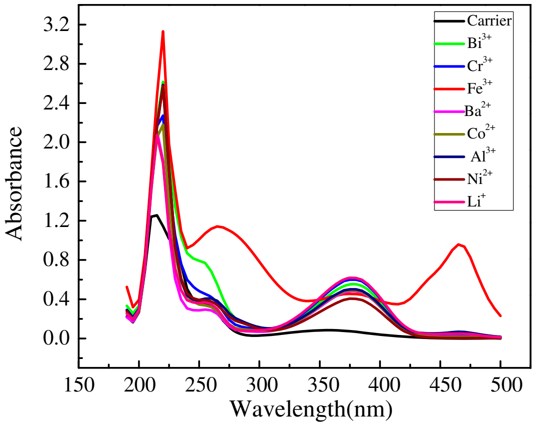

Fig. 2. Spectral changes of $^{i}Pr_2$Ph-DAD acetonitrile (5.0×10^{-5} M) with different metal ions.

In order to determine the stoichiometry and stability of the resulting $^{i}Pr_2$Ph-DAD complex with Fe^{3+} ion in acetonitrile solution, the spectra of a series of solutions containing a constant concentration of ligand (1.0×10^{-5} M) and varying amounts of Fe^{3+} ion were

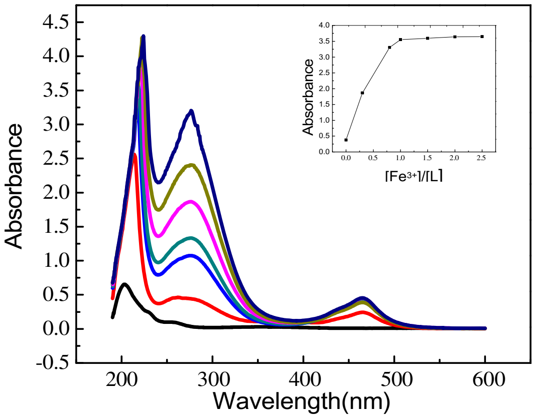

Fig. 3. Electronic absorption spectra of ligand ($^{i}Pr_2$Ph-DAD) in acetonitrile (1.0×10^{-5} M) in the presence of increasing concentration of Fe^{3+} ion. Mole ratio plot at 215 nm is shown in the inset. The corresponding $[Fe^{3+}]/[L]$ mole ratios from low to high values are: 0, 0.3 0.8, 1.0, 1.5, 2.0 and 2.5.

obtained and the result is shown in Fig. 3. The obtained mole ratio plot (absorbance vs. $[Fe^{3+}]/[L]$) at wavelength 215 nm is shown in the inset of Fig. 3. The absorption-mole ratio plot revealed a level off at $[Fe^{3+}]/[L]$ molar ratio of 1, indicating the formation of 1:1 (metal to ligand) complex in solution. The formation constant of the complex between Fe^{3+} and ligand, evaluated from computer fitting of the absorbance-mole ratio data, was found to be $2.83 \times 10^5\ M^{-1}$. The high stability constant for complexation makes $^iPr_2Ph$-DAD suitable for the preparation of a new Fe^{3+} ion-selective electrode.

3.2. Investigation of membrane composition

The response of the membrane is determined by partition of cations between two phases, water and membrane. Thus, the membrane composition is important on the selectivity and sensitivity of the electrode [39,40]. Thus, some different compositions of the Fe^{3+} selective membrane based on $^iPr_2Ph$-DAD were optimized and the results are given in Table 1.

The properties of plasticizer can affect the dielectric constant of the membrane phase and the mobility of the carrier. Several solvent mediators, such as *o*-NPOE ($\varepsilon \sim 24$), DOP ($\varepsilon \sim 5.1$), DBP ($\varepsilon \sim 6.4$), and DOS ($\varepsilon \sim 4.8$) were tested as potential plasticizers for preparing the membranes. As shown in Table 1, the electrode based on DOS exhibited a Nernstian response towards Fe(III) ions than the other plasticizers. Therefore, the membrane with DOS revealed the best physical properties with maximum sensitivity and wide linear dynamic range for Fe(III) ions. It is most probably due to the fact that DOS has a good ability for extraction–complexation of Fe(III) ions into the bulk of PVC membrane [41]. Contrarily, the membrane plasticized by other plasticizers having the large dielectric constant produced super-Nernstian response slopes. This may be due to the formation of ion-pairs between complexed cations (Fe^{3+}) and anion X^- (NO_3^- or Cl^-) in these membranes, which influence the slope of the response function [41]. In this study, predominantly divalent species (FeX^{2+}) take part in the phase transfer equilibrium and/or occur in the membrane, a slope characteristic of divalent ions was obtained. Furthermore, in this study, a plasticizer/PVC ratio of nearly 2 was found to be the most suitable ratio.

In addition, the response mechanism of neutral carrier-based sensors depends mainly on the extraction equilibrium at the vicinity of the interface between the membrane and aqueous layer, as well as concentration of the ionophore in the PVC membrane [41,42]. Therefore, different amounts of ionophore in PVC membranes were tested. As can be seen, the best response of the electrode towards Fe^{3+} ion was observed with 1.0 wt% ionophore. The performance of the PVC membranes was deteriorated on decreasing or increasing the amount of ionophore. This deviation in electrode response is due to the loss of selectivity or enhanced interference of the lipophilic counter ions of the test solution as presumed in the phase boundary potential model of carrier based ISEs [43].

In order to examine the influence of concentration of lipophilic anionic sites added to the membrane phase on the working parameters of electrode, a series of membranes are studied using lipophilic additives KT*p*ClPB and NaTPB. Compared with the response behavior of the electrodes without lipophilic additives, the addition of KT*p*ClPB and NaTPB causes a super-Nernstian response towards Fe^{3+} ion. This could be due to the formation of FeL^{3+}T*p*ClPB or FeL^{3+}TPB ion pairs in the membrane. These ion pairs diffused from

Table 1
Composition and performance of PVC membrane Fe^{3+}-selective electrodes based on $^iPr_2Ph$-DAD

Membrane composition % (w/w)						
Ionophore	Plasticizer	PVC	Additive	Slope (mV/decade)	Linear range (M)	Detection limit (M)
0.99	DOS, 65.99	33.02	0	19.9 ± 0.3	1.0×10^{-2}–1.0×10^{-6}	4.5×10^{-7}
1.02	DBP, 65.98	33.00	0	31.0 ± 0.3	1.0×10^{-2}–1.0×10^{-6}	1.7×10^{-7}
0.99	DOP, 65.99	33.02	0	37.8 ± 0.3	1.0×10^{-2}–1.0×10^{-6}	2.9×10^{-7}
0.99	*o*-NPOE, 65.98	33.03	0	33.0 ± 0.4	1.0×10^{-2}–1.0×10^{-6}	5.2×10^{-7}
0.51	DOS, 66.34	33.15	0	36.6 ± 0.3	1.0×10^{-2}–1.0×10^{-6}	3.8×10^{-7}
1.49	DOS, 65.67	32.84	0	50.5 ± 0.4	1.0×10^{-2}–1.0×10^{-6}	3.6×10^{-7}
0.98	DOS, 65.99	32.98	NaTPB, 0.05	61.1 ± 0.4	1.0×10^{-2}–1.0×10^{-5}	4.3×10^{-6}
0.99	DOS, 65.94	32.98	NaTPB, 0.09	64.2 ± 0.3	1.0×10^{-2}–1.0×10^{-5}	5.6×10^{-6}
0.99	DOS, 65.96	33.00	KTpClPB, 0.05	45.9 ± 0.5	1.0×10^{-2}–1.0×10^{-5}	4.9×10^{-6}
0.99	DOS, 65.93	32.99	KTpClPB, 0.09	55.8 ± 0.3	1.0×10^{-2}–1.0×10^{-5}	2.7×10^{-6}

organic phase to the organic/liquid phase interface. The ion pair then was slightly dissociated which results in increasing concentration of Fe^{3+} ion at the surface regions. Thus, we obtained super-Nernstian potential responses [44,45].

The results obtained indicate that the best performance was observed with the membrane comprising the percent ratio as 0.99:33.02:65.98 (%, w/w) for $^{i}Pr_2Ph$-DAD:PVC:DOS constituents, respectively. The best sensor composition showed a linear response towards the activity of Fe(III) ions in the range of 1.0×10^{-6}–1.0×10^{-2} M (Fig. 4), with a slope of 19.9 ± 0.3 mV/decade. The lower limit of detection, determined by extrapolating two segments of the calibration graph [41], was estimated to be 4.5×10^{-7} M.

3.3. Selectivity coefficients

The potentiometric selectivity coefficients, which reflect the relative response of the membrane sensor towards the primary ion over other ions present in solution, are perhaps the most important characteristics of an ion-selective electrode. In this work, the selectivity coefficients of the proposed membrane selective electrode were determined against a number of different cations using the matched potential method (MPM) [46,47] and the fixed interference method (FIM) [48].

According to the MPM, the activity of Fe^{3+} was increased from $a_{Fe^{3+}} = 1.0 \times 10^{-5}$ M as reference solution to $a'_{Fe^{3+}} = 6.0 \times 10^{-5}$ M, and the corresponding changes in potential (ΔE) were measured. In a separate experiment, different activities a_B, in the range 5.0×10^{-5} to 1.0×10^{-4} M, was successively added to an identical reference solution until the same potential change (ΔE) was recorded. a_B was experimentally determined. The selectivity factor, $K^{pot}_{Fe^{3+},B}$, for each interference was calculated using the following equation:

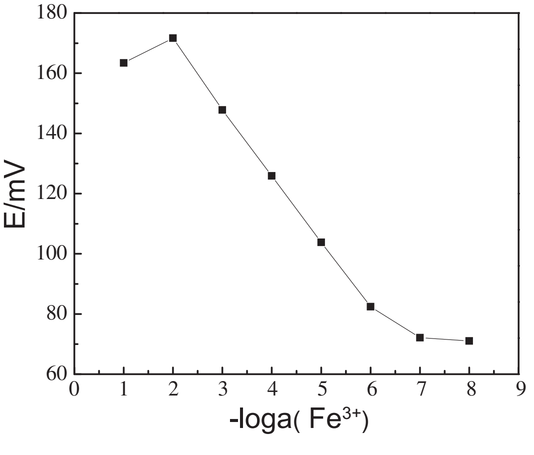

Fig. 4. Potentiometric responses of PVC membrane electrode with optimum composition to Fe^{3+}.

$$K^{pot}_{Fe^{3+},B} = \frac{\Delta a_{Fe^{3+}}}{a_B} = \frac{a'_{Fe^{3+}} - a_{Fe^{3+}}}{a_B} \quad (1)$$

In the FIM, the selectivity coefficient was evaluated from potential measurement in solutions containing a fixed concentration of interfering ion (1.0×10^{-2} M) and varying amount of Fe^{3+} ions. The emf values obtained were plotted vs. the logarithm of the activity of the primary ion. The intersection of the extrapolated linear portions of the plot indicates the value of a_A that is used to calculate $K^{pot}_{Fe^{3+},B}$ from the following equation:

$$K^{pot}_{Fe^{3+}} = \frac{a_A}{(a_B)^{Z_A/Z_B}} \quad (2)$$

where both Z_A and Z_B are the charges of Fe^{3+} ion and interfering ions, respectively. The resulting selectivity coefficient values are summarized in Table 2. A value of selectivity coefficient $\log K^{pot}_{Fe^{3+},B}$ equal to 0 indicates that the sensor responds equally to primary ion as

Table 2
Selectivity coefficients of the iron(III) ion electrodes

	$\log K^{pot}_{Fe^{3+},B}$	
Interfering ions (B)	FIM	MPM
NH_4^+	−4.13	−4.47
Li^+	−4.22	−4.53
K^+	−4.07	−4.24
Na^+	−4.32	−4.65
Ca^{2+}	−3.81	−4.33
Sr^{2+}	−4.01	−4.12
Zn^{2+}	−4.56	−4.36
Cu^{2+}	−3.71	−3.47
Ni^{2+}	−3.05	−3.15
Co^{2+}	−2.50	−2.38
Mn^{2+}	−0.85	−1.01
Cd^{2+}	−3.22	−3.32
Hg^{2+}	−1.48	−1.68
Ag^+	−1.21	−1.03
Pb^{2+}	−1.34	−1.23
Al^{3+}	−0.50	−0.30
Cr^{3+}	−0.43	−0.52
Bi^{3+}	−0.08	−0.18
La^{3+}	−3.52	−3.71
Ce^{3+}	−4.00	−3.84

Table 3
Comparison of the response characteristics of different Fe^{3+}-selective electrodes

Reference (electrode type)	Slope (mV/decade)	Detection limit (M)	Linear range (M)	pH range	Response time	Lifetime	Interfering ions $\log K^{\text{pot}}_{\text{Bi}^{3+},\text{M}} > -3$
This work (PVC-ME[a])	19.9	4.5×10^{-7}	1.0×10^{-2}–1.0×10^{-6}	2.1–6.0 (10^{-3} M, 10^{-4} M)	7 s	>2 months	Mn^{2+}, Hg^{2+}, Cr^{3+}, Pb^{2+}, Ag^{+}, Co^{2+}, Bi^{3+} By FIM and MPM method
Ref. [18] (PVC-ME[a])	28.5	2.5×10^{-6}	4.0×10^{-2}–3.5×10^{-6}	4.5–6.5 (10^{-4} M)	15 s	>2 months	Zn^{2+}, Cu^{2+}, Cr^{3+}, Ni^{2+}, Cd^{2+}, Ca^{2+} By SSM method
Ref. [19] (PVC-ME[a])	19.9	5.0×10^{-8}	1.0×10^{-1}–1.0×10^{-7}	3.0–6.3 (10^{-3} M, 10^{-5} M)	12 s	2 months	Co^{2+}, Zn^{2+}, Cu^{2+}, Al^{3+}, Mn^{2+}, Cr^{3+}, Ni^{2+} By FIM method
Ref. [20] (PVC-ME[a])	20.0	5.0×10^{-6}	1.0×10^{-1}–6.7×10^{-6}	3.5–5.5 (10^{-3} M)	15 s	2 months	Cr^{3+}, Co^{2+}, Cu^{2+} By MPM method
Ref. [21] (PVC-ME[a])	19.6	8.6×10^{-8}	1.0×10^{-2}–1.0×10^{-7}	1.6–4.3 (10^{-3} M)	10 s	9 weeks	–
Ref. [22] (CWISE[b])	60	5.0×10^{-7}	1.0×10^{-2}–1.0×10^{-6}	1.3–3.5	25–30 s	–	Na^{+}, K^{+}, Co^{2+}, Ag^{+}, Zn^{2+}, Cu^{2+}, Al^{3+}, Cd^{2+}, Cr^{3+}, Ni^{2+}, Hg^{2+}, Pb^{2+} By FIM method
Ref. [23] (PVC-ME[a])	19.9	3.9×10^{-7}	1.0×10^{-2}–6.9×10^{-7}	1.8–5.6 (10^{-4} M)	10 s	>2 months	Mn^{2+}, Hg^{2+}, Cr^{3+}, Pb^{2+}, Ag^{+}, Bi^{3+}, Pb^{2+}, La^{3+}, Ce^{3+}, Al^{3+}, Zn^{2+}, Ca^{2+}, Ni^{2+},Co^{2+} By MPM method
Ref. [24] (PVC-ME[a])	19.4	4.8×10^{-8}	1.0×10^{-2}–1.0×10^{-7}	2.3–3.5 (10^{-4} M)	10 s	10 weeks	Cr^{3+}, Na^{+} By MPM method
Ref. [25] (PVC-ME[a])	51	1.0×10^{-6}	1.0×10^{-1}–1.0×10^{-6}	2.2–4.8	30 s	2 months	Ag^{+}, Cu^{2+}, Pb^{2+} By FIM method
Ref. [26] (PVC-ME[a])	21.2	9.1×10^{-6}	1.0×10^{-1}–9.1×10^{-6}	3.2–4.8 (10^{-3} M, 10^{-4} M)	20 s	2 months	Mn^{2+} By FIM method
Ref. [27] (PVC-ME[a])	19.6	1.4×10^{-7}	1.0×10^{-1}–6.7×10^{-7}	2.0–5.0 (10^{-3} M)	13 s	5 weeks	La^{3+} By FIM method
Ref. [28] SP ISE[c]	19.2	1.6×10^{-7}	2.5×10^{-2}–1.0×10^{-6}	3.0–7.5 (10^{-3} M, 10^{-4} M)	7–10 s	>6 months	Co^{2+}, Sr^{2+}, Hg^{2+}, Zn^{2+}, Cu^{2+}, Al^{3+}, Mg^{2+}, Mn^{2+}, Cd^{2+}, Li^{+}, Ca^{2+}, Ba^{2+}, Cr^{3+}, Ni^{2+} By FIM method

[a] PVC-based membrane electrode.

[b] Coated-wire ion-selective electrode.

[c] Screen-printed ion-selective electrode.

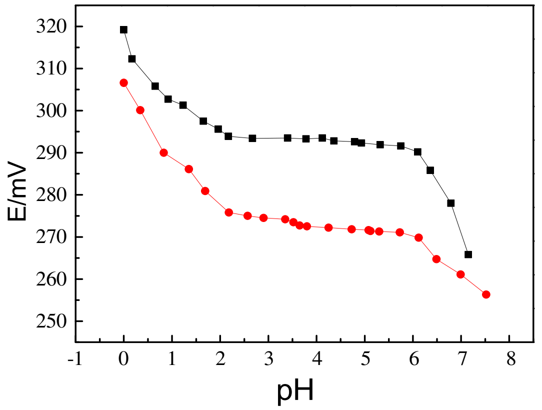

Fig. 5. Plot showing the variation of membrane potentials with pH for the electrode at 1.0×10^{-3} (■) and 1.0×10^{-4} M (●) Fe^{3+} ion concentration based on $^{i}Pr_2Ph$-DAD.

well as interfering ion. However, a value smaller than 0 indicates that membrane sensor is responding more to primary ion than interfering ion and in such a case the sensor is said to be selective to primary ion over interfering ion. Further, the smaller the selectivity coefficient is, the higher the selectivity order. A perusal of Table 2 shows that the most values of selectivity coefficient are much smaller than 0 indicating that the electrode is significantly selective over many transition metal cations and cations of the first and second groups ions listed in Table 2. Thus, it is possible to determine Fe(III) in the presence of interfering ions at a concentration level smaller or slightly higher than the Fe(III) concentration. However, Mn^{2+}, Al^{3+}, Cr^{3+}, and Bi^{3+} cations slightly interfere with the determination of Fe^{3+}. 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 vs. pFe^{3+} plots were observed, indicating that these anions (NO^{3-}, Cl^{-} and SO_4^{2-}) do not cause any interference.

The high selectivity of the membrane electrode for Fe^{3+} cation over other ions probably arises due to the strong affinity of the ionophore to Fe^{3+} cation. Table 3 shows the main analytical features of the some pervious iron(III)-selective electrodes [18–28] for comparing with this new Fe^{3+} ISE. As can be seen from this table, linear range, potentiometric selectivity, and pH range of the proposed sensor are suitable and comparable with the literature data. Lower selectivity compared with Refs. [24–27] may be related to lower stability constants obtained in this study and stoichiometric factors of the formed complexes between different ionophore and Fe^{3+} [41]. The Nernstian slope of the new Fe^{3+} selective electrode in some cases is much better than those reported in previous works [18,22,25,26]. The feature to mark is the response time of the proposed membrane electrode. Shorter response time of this electrode makes it more applicable for flow injection analysis methods [49].

3.4. Effect of pH and non-aqueous solvents

The effect of pH of the test solutions on the electrode potentials was studied. The pH was adjusted using HNO_3 or NaOH to the test solutions of 1.0×10^{-3} and 1.0×10^{-4} M. For each pH value, the potential was recorded and thus the potential–pH curves for two Fe(III) concentrations were constructed

Table 4
Solvent effect of the electrodes based on $^{i}Pr_2Ph$-DAD

Non-aqueous content (%, v/v)	Slope (mV/decade)	Linear range (M)	Detection limit (M)
Methanol			
10	22.1	1.0×10^{-2}–1.0×10^{-6}	4.3×10^{-7}
20	15.2	1.0×10^{-2}–1.0×10^{-6}	6.9×10^{-7}
30	12.7	1.0×10^{-2}–1.0×10^{-5}	7.9×10^{-6}
Ethanol			
10	22.5	1.0×10^{-2}–1.0×10^{-6}	5.6×10^{-7}
20	17.6	1.0×10^{-2}–1.0×10^{-6}	2.4×10^{-7}
30	12.7	1.0×10^{-2}–1.0×10^{-5}	2.7×10^{-6}
Acetone			
10	21.9	1.0×10^{-2}–1.0×10^{-6}	4.7×10^{-7}
20	14.2	1.0×10^{-2}–1.0×10^{-6}	3.1×10^{-7}
30	12.1	1.0×10^{-2}–1.0×10^{-5}	8.9×10^{-6}

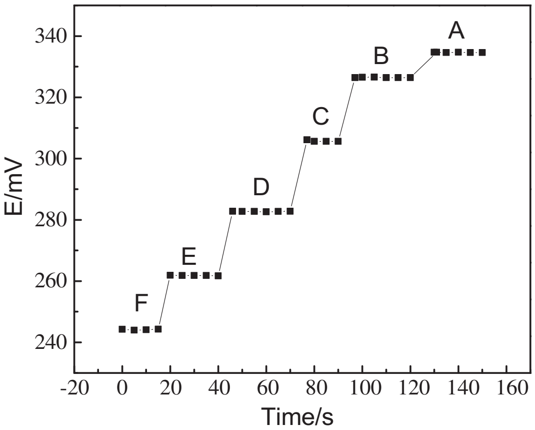

Fig. 6. Dynamic response time of Fe^{3+}-ISE for stepwise addition of the Fe^{3+} concentration: (A) 1.0×10^{-7} M, (B) 1.0×10^{-6} M, (C) 1.0×10^{-5} M, (D) 1.0×10^{-4} M, (E) 1.0×10^{-3} M, and (F) 1.0×10^{-2} M.

(Fig. 5). Obviously, the potential remained fairly constant in the pH range of 2.1–6.0. 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). At higher pH, the iron(III) in solution is dramatically reduced through the formation of iron(III) hydroxyl complexes, and the magnitude of the voltage change should be reconciled with iron(III) speciation calculations in solution.

Sometimes, in real situations, the real sample may contain non-aqueous content. In this study, the function of the proposed electrode was investigated in partially non-aqueous media using acetone–water, methanol–water, and ethanol–water mixtures, and the obtained results are presented in Table 4. No significant change in the working concentration range and slope was observed up to 10% (v/v) non-aqueous content. Beyond this value, non-aqueous content caused a significant interference in the slope. This probably appears due to leaching of ionophore in higher organic content. Hence, the proposed sensor can be used in non-aqueous medium when its content is not more than 10%.

3.5. Response time and the electrode lifetime

To measure the dynamic response time of the proposed sensor, the concentration of the test solution has been successively changed from 1.0×10^{-7} to 1.0×10^{-2} M. The time needed to reach a potential within ±0.5 mV of the final equilibrium value after successive immersion of a series of Fe^{3+} ions, each having a 10-fold difference in concentration, is 7 s (Fig. 6). This is most probably due to the fast exchange kinetics of complexation–decomplexation of Fe^{3+} ions with the ionophores at the test solution–membrane interface.

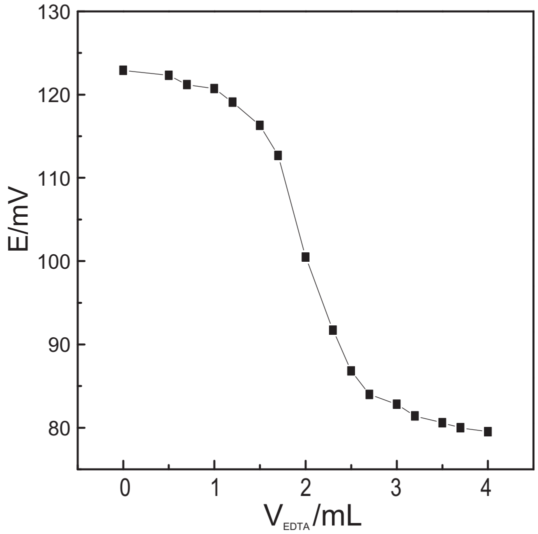

Fig. 7. Potentiometric titration curve of 20 mL of 1.0×10^{-3} M Fe^{3+} solution with 1.0×10^{-2} M EDTA using the proposed membrane sensor as an indicator electrode.

The lifetime of the electrode was determined by performing calibrations periodically with standard solutions and calculating the slopes over the concentration ranges of 1.0×10^{-6}–1.0×10^{-2} M Fe^{3+} solutions. The experimental results showed that the lifetime of the present sensor was over two months. This lifetime is comparable with those previously reported [18–20,23,25,26] and is higher than the other reported electrode [27]. Subsequently, the electrochemical behavior of the electrode gradually deteriorated. This is attributed to aging of the polymer (PVC) and the decrease in the amount of the plasticizer and ionophore in PVC membrane. 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 Fe^{3+} solution for 24 h before use.

3.6. Analytical applications

3.6.1. Potentiometric titration

The membrane electrode was successfully used as an indicator electrode in the potentiometric titration of Fe(III) with EDTA. 20.00 mL 1.0×10^{-3} M Fe^{3+} solutions was titrated against 1.0×10^{-2} M EDTA solution at pH 4. The addition of EDTA causes a decrease in potential as

Table 5
Determination of Fe(III) ions in mixtures of different ions

No.	Composition	Recovery %
1	0.0010 M $Fe(NO_3)_3$ + 0.01 M KNO_3 + 0.01 M $Pb(NO_3)_2$	100.7
2	0.0010 M $Fe(NO_3)_3$ + 0.01 M $Ca(NO_3)_2$ + 0.01 M $Ag(NO_3)_2$	110.5
3	0.0010 M $Fe(NO_3)_3$ + 0.01 M KNO_3 + 0.01 M $Hg(NO_3)_2$	98.9
4	0.0010 M $Fe(NO_3)_3$ + 0.01 M $Ni(NO_3)_2$ + 0.01 M $Co(NO_3)_2$ + 0.01 M $Mg(NO_3)_2$	106.4
5	0.0010 M $Fe(NO_3)_3$ + 0.01 M $Cr(NO_3)_3$ + 0.01 M $Co(NO_3)_2$	104.7

Table 6
Determination of the iron(III) ion concentrations in water samples ($n = 5$)

Sample	Added (M)	Found by ISE (M)	Found by AAS (M)
Tap water	2.00×10^{-2}	$(2.01 \pm 0.04) \times 10^{-2}$	$(2.03 \pm 0.03) \times 10^{-2}$
	1.00×10^{-4}	$(0.97 \pm 0.15) \times 10^{-4}$	$(1.01 \pm 0.13) \times 10^{-4}$
	3.00×10^{-6}	$(2.85 \pm 0.20) \times 10^{-6}$	$(2.79 \pm 0.19) \times 10^{-6}$
Pond water	2.00×10^{-2}	$(2.04 \pm 0.03) \times 10^{-2}$	$(2.03 \pm 0.03) \times 10^{-2}$
	1.00×10^{-4}	$(0.98 \pm 0.15) \times 10^{-4}$	$(1.08 \pm 0.14) \times 10^{-4}$
	3.00×10^{-6}	$(3.29 \pm 0.29) \times 10^{-6}$	$(3.28 \pm 0.20) \times 10^{-6}$

a result of the decrease in free Fe(III) ion concentration due to formation of a complex with EDTA (Fig. 7). The titration plot is found to be sigmoid shape and the inflexion point of the plot corresponds to 1:1 stoichiometry of Fe^{3+}–EDTA complex. The maintained stoichiometry of the titration may be due to no interference caused by Na^+ ions released from the titrant EDTA.

3.6.2. Determination of Fe(III) in some cationic mixtures

Due to the high selectivity of the proposed ISE, the applicability of the electrode was evaluated for monitoring the Fe(III) concentration ions in some cationic mixtures. The results summarized in Table 5 reveal that the recovery of the Fe(III) ions in all mixtures is satisfactory.

3.6.3. Determination of Fe(III) in pharmaceutical formulation and water samples

The proposed Fe^{3+} electrode has been used for the direct potentiometric determination of iron(III) in the ferrous sulfate tablets and two water samples (tap and pond water). Ferrous sulfate tablet (weighing 300 mg containing 60 mg iron) was obtained from Shanghai Huanghai Pharmaceutical Co., Ltd. To avoid problems with heterogeneity, five ferrous sulfate tablets were finely powdered. A certain amount of sample was weighted accurately and put in a glass beaker. The pond water samples were collected from the pond in our university and filtered. Then H_2O_2 and HNO_3 solution (1 M) were added in ferrous sulfate tablets sample and water sample solutions in order to oxidize Fe(II) to Fe(III). The resulting solutions were diluted with distilled water in the volumetric flasks and their pH values were adjusted to 4.0 using HNO_3. The Fe(III) concentration in the three samples were directly determined using the standard curve method. It can be seen from Tables 6 and 7 that the iron content in different samples determined by the proposed electrode was in good agreement with data obtained by AAS method.

Table 7
Determination of the iron(III) ion concentrations in ferrous sulfate tablets ($n = 5$)

	Stated content (mg)	Found (mg)	AAS (mg)
Sample 1	60	59.2 ± 0.3	59.7 ± 0.3
Sample 2	60	60.1 ± 0.4	60.5 ± 0.2
Sample 3	60	59.4 ± 0.3	59.8 ± 0.3

3.6.4. Determination of Fe(III) in spike

The weighted spike was dissolved in 20 mL of the mixture of concentrated sulfuric acid and nitric acid ($V_{H_2SO_4}:V_{HNO_3} = 1:1$). Then the solutions were transferred to a 250-mL volumetric flask and diluted with water. Then 1.0 mL of the resulting solution was transferred to a 250-mL volumetric flask, 12.5 mL of 2 M HNO_3 was added, and the solution was diluted with water again. The content of iron in spike was measured using the proposed electrode by the standard curve method and compared with the results from AAS. The result of $5.00 \times 10^{-3} \pm 0.1$ M obtained by the proposed electrode is in excellent agreement with $4.76 \times 10^{-3} \pm 0.1$ M determined by AAS.

4. Conclusions

This work revealed that the proposed PVC-membrane iron-selective electrode based on $^{i}Pr_2Ph$-DAD as neutral carrier exhibits good potentiometric performance. It responds to Fe^{3+} in a Nernstian fashion and presents a good selectivity over most of the cations. The electrode performs successfully in partially non-aqueous medium. The electrode could be used for the potentiometric determination of Fe^{3+} ions in tap and pond water samples, spike and pharmaceutical samples with good accuracy, as well as an indicator electrode in the potentiometric titration of Fe^{3+} against EDTA.

Acknowledgment

The authors gratefully acknowledge the financial support of this research proposal, provided by the Science and Technology Project of Henan Province (142102310336).

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