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Spectral, thermal and electrochemical investigation of carbohydrazone derived ionophore as Fe(III) ion selective electrode

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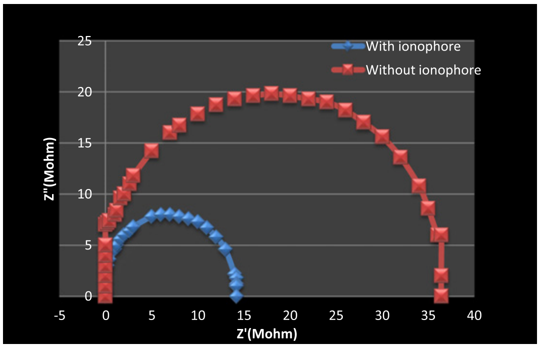
HIGHLIGHTS

- ▶ Carbohydrazone derivative as ionophore has been synthesized and characterized.
- ▶ It has been explored as Fe(III) ion selective electrochemical sensor.
- ▶ The reaction mechanism was discussed in the view of UV and EI Spectroscopy.

GRAPHICAL ABSTRACT



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ABSTRACT

Dibenzoylmethane bis(carbohydrazone) (BMBC) has been synthesized and structurally characterized on the basis of IR, ^{1}H NMR, mass, UV spectra and thermogravimetric analyses. BMBC has been analysed electrochemically and explored as new N, N Schiff base. It plays the role of an excellent ion carrier in the construction of iron(III) ion selective membrane sensor. This sensor shows very good selectivity and sensitivity towards iron ion over a wide variety of cations, including alkali, alkaline earth, transition and heavy metal ions. The response mechanism was discussed in the view of UV-spectroscopy and Electrochemical Impedance Spectroscopy (EIS). The proposed sensor was successfully used for the determination of iron in different samples.

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Introduction

The development of selective chemical sensors has received widespread attention during the past two decades because of their possible use in clinical and environmental monitoring [1–5]. Potentiometric detection based on ion-selective membrane electrodes, as a simple method, offers several advantages such as fast response, easy preparation, simple instrumentation, wide linear dynamic range, relatively low detection limit, reasonable selectivity, application in colour and turbid solutions and low cost. As a result of extensive research in this area, a number of Ion Selective Electrodes (ISEs) mainly for alkali, alkaline earth and some heavy and transition metal ions are now commercially available [6–9]. ISEs have found wide spread use for the direct determination of ionic species in complex samples [10]. In the early days, their selectivity was often the limiting factor in determining low levels of analyte ions. In unbuffered samples, the current polymer

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membranes ISEs show lower detection limits that are much, typically in the micromolar range [11].

Based on above considerations, the aim of the present work is to synthesize a neutral Schiff base ligand dibenzoylmethane bis(carbohydrazone) (BMBC) and characterize it on the basis of spectral and thermal techniques. The ion receptor characteristics of BMBC were evaluated by its application as the potentiometric sensor of iron ions [12].

The Schiff base BMBC was used to construct iron(III) ion selective sensor. A deficiency of iron limits oxygen delivery to cells, resulting in fatigue, poor work performance, and decreased immunity [13–17,18]. On the other hand, excess amounts of iron can result in toxicity and even death [19]. High levels of iron are associated with an increased risk of cancer, heart disease and other illnesses such as haemochromatosis [20–22]. Therefore, there is an urgent need to design such compounds which can monitor the level of iron in the environment.

Experimental

Materials

Analytical reagent grade chemicals and doubly distilled water were used. Dibenzoyl methane, carbohydrazide, high molecular weight poly (vinylchloride) powder (PVC), dibutyl phthalate (DBP), diisooctyl sebacate (DOS), tributyl phthalate (TBP) and tetrahydrofuran (THF) were obtained from Sigma. Potassium tetrakis(4-chlorophenyl)borate and 2-nitrophenyl octyl ether (NPOE) were obtained from Fluka. Salts of metal nitrates or chlorides and solvents like methanol, ethanol, diethylether, acetonitrile, nitric acid and hydrogen peroxide (all from Merck) were of the highest purity available and used without any further purification. All the metal nitrate solutions were freshly prepared by accurate dilution from their stock solution of 1 M, with distilled, de-ionized water.

Synthesis of ionophore dibenzoylmethane bis(carbohydrazone) (BMBC)

An aqueous ethanolic solution of carbohydrazide (0.02 mol, 1.80 g) was treated with 1 ml glacial acetic acid followed by slow addition of a solution of dibenzoylmethane (0.01 mol, 2.24 g) in 20 ml ethanol. The resulting mixture was heated under reflux for about 6 h. On cooling overnight at 0 °C, white crystalline precipitate of BMBC was separated out, which was filtered, washed with cold ethanol and dried under vacuum. Yield 81%, m.p. 182–185 °C. Elemental analysis: $C_{17}H_{20}N_8O_2$, Found (Calc.) C: 55.44 (55.13), H: 5.43 (5.08), N: 30.43 (30.17).

Fabrication of electrodes with ionophore BMBC

For analytical application, the membranes have been fabricated as suggested by Craggs et al. [23] and others [24]. The PVC-based membranes have been prepared by dissolving appropriate amounts of BBC, anionic additive and plasticizers, DBP, *o*-NPOE, DOS, TBP and PVC in THF (~5 ml). The components were added in terms of weight percentages. The homogeneous mixture was obtained after complete dissolution of all the components, concentrated by evaporating THF and it has been poured into polyacrylate rings placed on a smooth glass plate. The viscosity of the solution and solvent evaporation was carefully controlled to obtain membranes with reproducible characteristics and uniform thickness otherwise the response of the membrane sensors have shown a significant variation. The membranes of 0.4-mm thickness were removed carefully from the glass plate and glued to one end of a “Pyrex” glass tube. The membrane was studied under polarized optical microscope (Fig. 1).

Equilibration of membrane and potential measurement

The time of contact and concentration of equilibrating solution were optimized so that the sensors generated stable and reproducible potential at relatively short response time.

The polymeric membrane electrode was equilibrated for ~2 days in 1.0×10^{-1} M $Fe(NO_3)_3$ solution. The potentials were measured by varying the concentration of $Fe(NO_3)_3$ in test solution in the range 1×10^{-9}–1.0×10^{-1} M. Standard $Fe(NO_3)_3$ solutions were obtained by gradual dilution of 10^{-1} M $Fe(NO_3)_3$ solution.

The emf measurements with the polymeric membrane electrode were carried out on digital potentiometer at 25 ± 1 °C using saturated calomel electrode (SCE) as reference electrode with the following cell assemblies:

$Hg–Hg_2Cl_2$, KCl (sat.) ||internal solution 1.0×10^{-1} M Fe^3 |test solution|| $Hg_2Cl_2–Hg$, KCl (sat.)

Physical measurements

IR spectra (KBr pellets) were recorded in the region 4000–400 cm^{-1} on a FT–IR spectrum BX-II spectrophotometer. ^1H NMR spectrum was recorded with a model Bruker Advance DPX-300 spectrometer operating at 300 MHz using DMSO-d_6 as a solvent and TMS as an internal standard. Electron impact mass spectrum was recorded on JEOL, JMS, DX-303 mass spectrometer. Electronic spectra were recorded on Shimazdu UV mini-1240 spectrophotometer using DMSO as a solvent. Elemental analyses were carried out on a Carlo-Erba EA 1106 analyzer. The emf measurements with the polymeric membrane electrode were carried out on digital potentiometer (Equiptronic Model No. EQ-609) at 25 ± 1 °C using saturated calomel electrode (SCE) as reference electrode. Electrochemical impedance measurements were carried out using a potentiostat/galvanostat instrument (Autolab PGSTAT 302).

Results and discussion

The analytically pure ligand BMBC was readily synthesized with very good yield (81%) by Schiff base condensation of dibenzoylmethane with two equivalents of carbohydrazide in water–ethanol. The ligand may show keto–enol tautomerism because it contains the amide bonds (Fig. 2). The IR spectrum does not show a υ(OH) band at ca. 3550 cm^{-1} but shows the bands at 3395 and 3212 cm^{-1} corresponding to υ_{as}(NH) and υ_s(NH), indicating that in solid state, the ligand exists in the keto form. However, the ^1H NMR spectrum of ligand exhibits a sharp singlet at υ 8.1 ppm due to enolic —OH which indicates that the amide groups are transformed into iminol groups in solution.

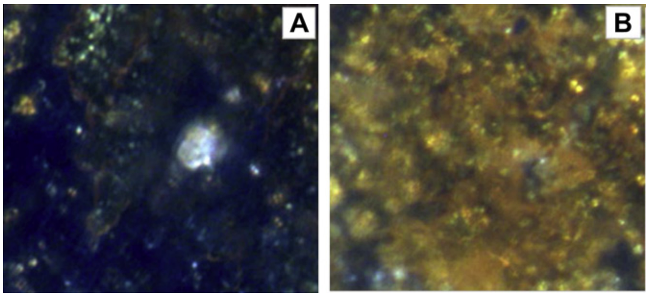


Fig. 1. Membrane picture under polarized optical microscope (A) before use and (B) after use.

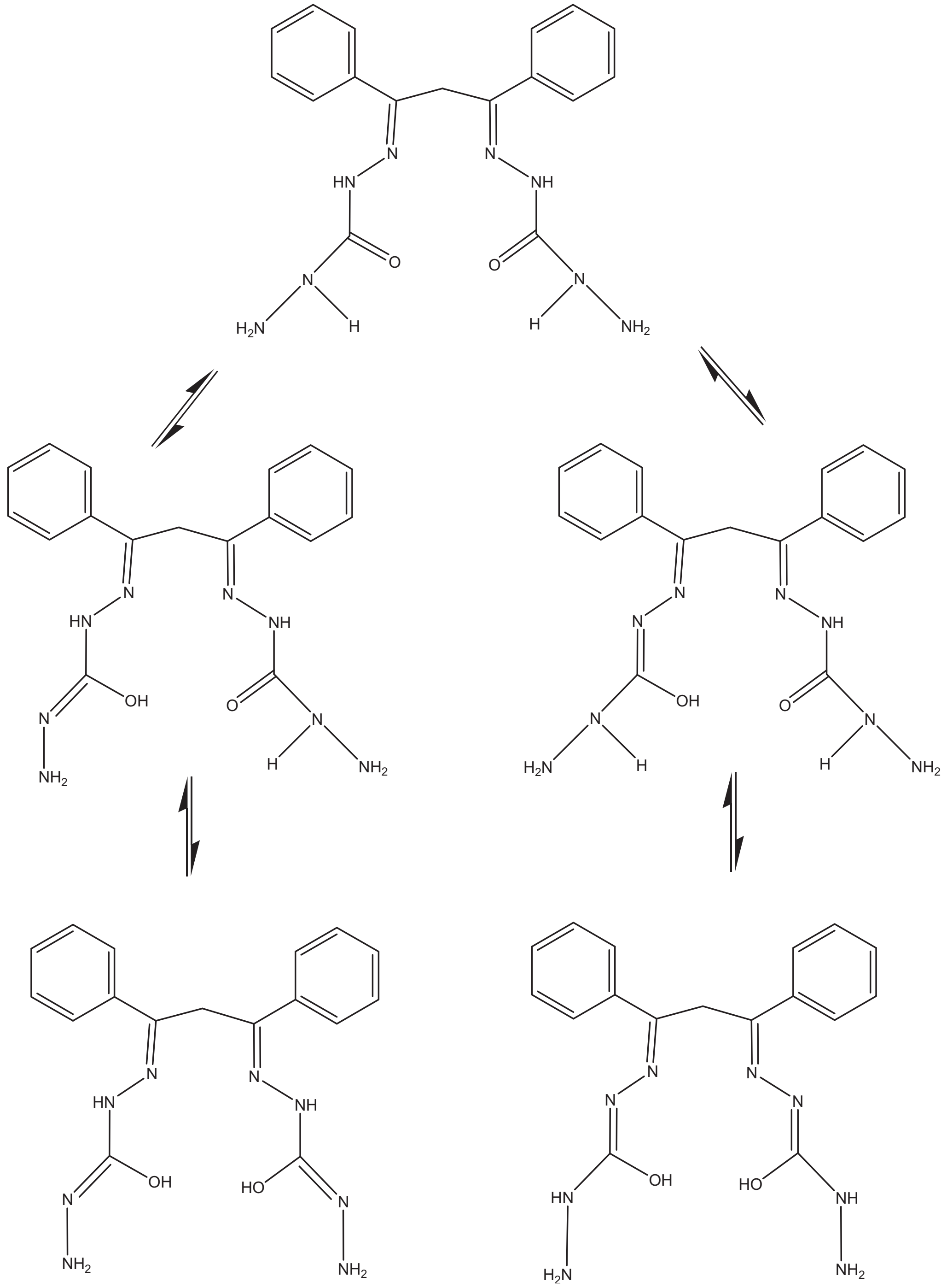


Fig. 2. Five possible isomeric forms of ligand BMBC.

IR Spectra

The assignments of the main IR absorption bands of the ligand are shown in Fig. 3. The IR spectrum of the free ligand displays the bands at 3395 and 3212 cm^{-1}corresponding to the $\upsilon_{as}(NH_2)$ and $\upsilon_s(NH_2)$ stretching vibrations, respectively, which suggests the presence of free NH_2 groups in the ligand. The spectrum exhibits the IR bands at 1630 and 1617 cm^{-1} 1500 cm^{-1} which may be assigned to the amide I [υ (C=O)], amide II [υ (C=N) + υ (NH)] and amide III stretching vibrations, respectively, due to the presence of the amide groups in the ligand [25,26].

^{1}H NMR spectra

The ^{1}H NMR spectrum of ligand was recorded in deuterated DMSO (DMSO-d_6) at 300 MHz. The spectrum (Fig. 4) shows that the different non-equivalent protons resonate at different values of applied field. A singlet at δ 1.6 ppm appears due to the two protons of methylene group. A distorted singlet at δ 4.0 ppm appears in the spectrum which is assigned to the four protons of two amino groups. The appearance of signal as a broad peak may be due to the nuclear quadrupole broadening by nitrogen [27]. Another distorted singlet at δ 5.8 ppm corresponding to the 2H is appeared due to the amide protons. The spectrum

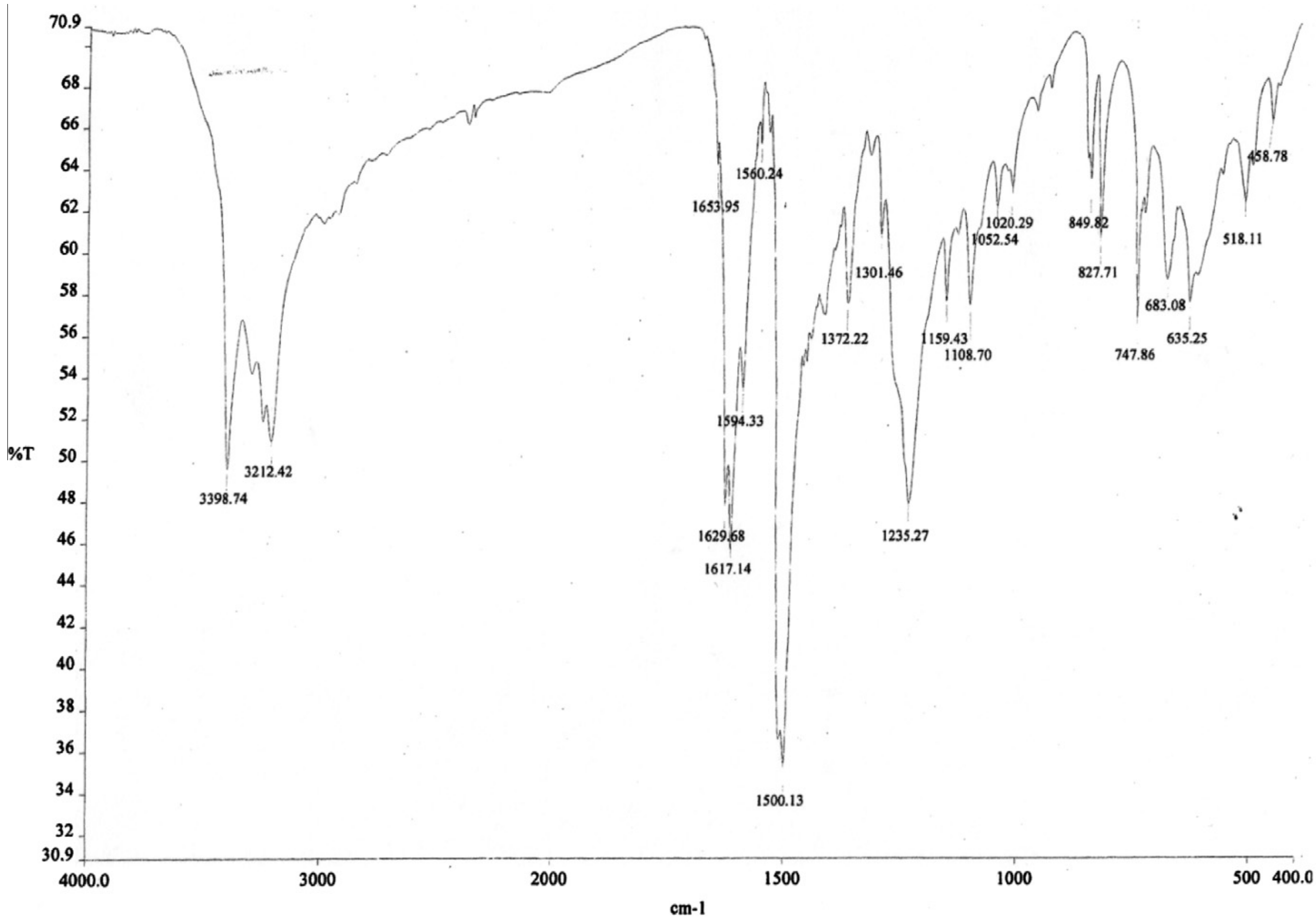
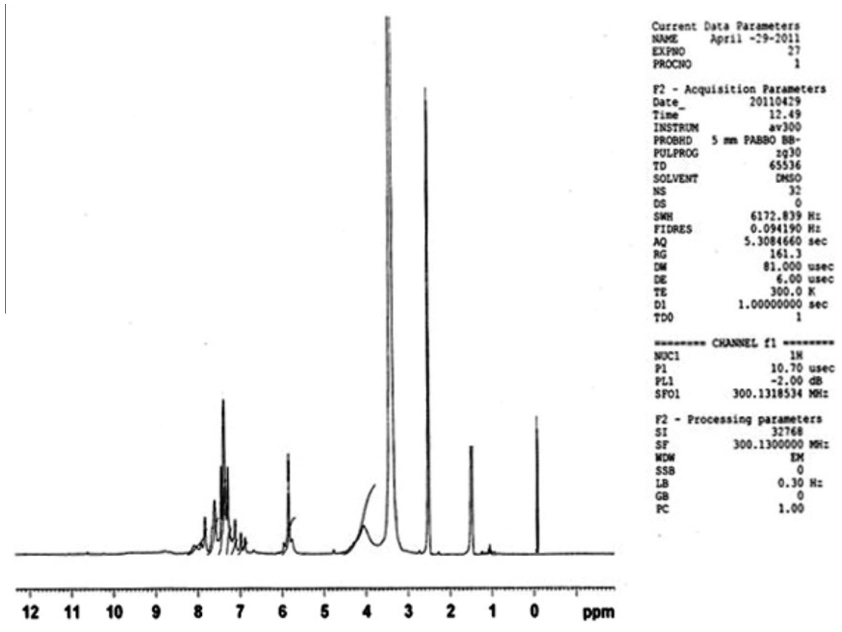


Fig. 3. IR Spectra of ligand BMBC.



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NS                    32
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FIDRES          0.094190 Hz
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RG                 161.3
DW                81.000 usec
DE                  6.00 usec
TE                 300.0 K
D1            1.00000000 sec
TD0                    1

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PL1                -2.00 dB
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F2 - Processing parameters
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GB                     0
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Fig. 4. ^{1}H NMR Spectra of ligand BMBC.

exhibits a multiplet between δ 6.8 and δ 7.9 ppm equivalent to the 10H of two phenyl groups. The spectrum displays a sharp singlet at δ 8.1 ppm equivalent to 2H represents the enolic protons of ligand in solution [28].

Mass spectra

The mass spectrum of ligand is given in Fig. 5. The spectrum shows the molecular ion peak (M$^+$) at m/z = 368 (78%) and a weak

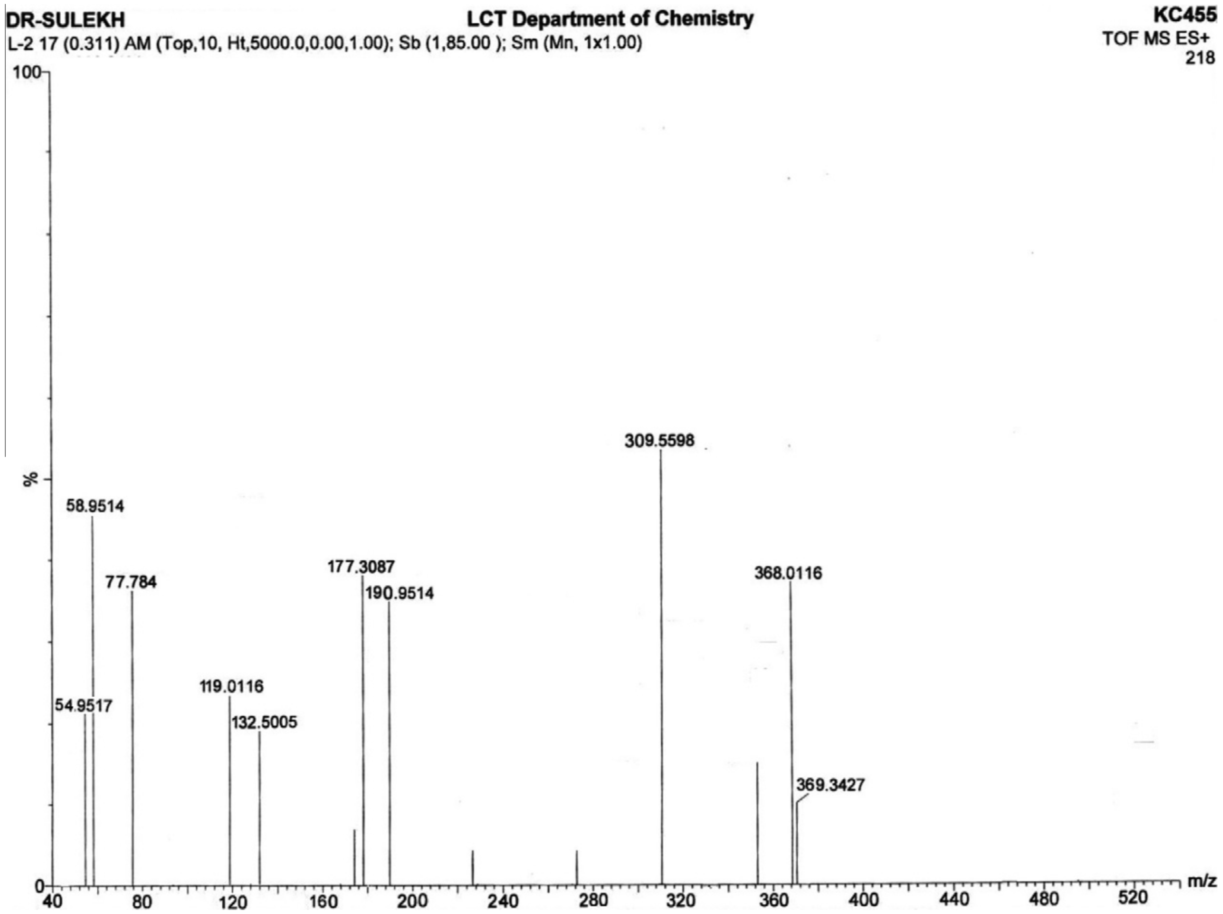

Fig. 5. Mass spectra of ligand BMBC.

peak at $m/z = 369$ due to ^{13}C isotope. The amide characteristic peak appears at $m/z = 59$ and the moderate high intense peak (81%) at $m/z = 177$ appears in the spectrum due to the six member cyclic positive ion which results from γ δ C—C bond cleavage and followed by cyclisation. The other different ions give the peaks of different mass numbers like 309, 190.9, 132, 119 and 55. The intensities of peaks are in accordance with the abundance of the ions [29]. The fragmentation path of ligand is given in Fig. 6.

Thermogravimetric analyses

BMBC was studied by thermogravimetric analyses from ambient temperature to 700 °C in nitrogen atmosphere. The TG curve was redrawn as % mass loss versus temperature (TG) curve. Typical TG curve is presented in Fig. 7. Thermal techniques, such as thermogravimetric analysis (TG and DTG), has been successfully employed for the study of the energetic of interactions of metal cations with biological species, such as amino acids [30]. The weight loss profiles are analysed the amount or percent of weight loss at any given temperature, and the temperature ranges of the degradation process were determined. Thermal stability domains, melting points, decomposition phenomena and their assignments for the BMBC are summarized below. The overall loss of mass from the TG curves is 100% for BMBC. The compound is stable up to the temperature 300 °C. The compound undergoes first step decomposition with weight loss exp. 4.335–4.658%, between 130 and 168 °C due to the loss of NH_2 moiety. Delta H for the degradation is 112.082 J/g. DTG maximum temperature is 202.16 °C and it shows an endo peak.

Complexation study

The interactions between the ionophore (L) and different transition metals were tested. Thus, the complexation behaviour of L with different cations was measured conductometrically in acetonitrile solution, at room temperature in order to establish the stability and sensitivity of the resulting complexes. The 1:1 binding of the cations with the ionophore can be expressed by the following equilibrium

$$\mathrm{M}^{n+} + \mathrm{L} \rightleftharpoons \mathrm{ML}^{n+} \tag{1}$$

The complex formation constant, K_f were evaluated by the molar conductance mole ratio data obtained by using the equations given below:

$$K_f = \frac{[\mathrm{ML}^{n+}]}{[\mathrm{M}^{n+}][\mathrm{L}]} \times \frac{f_{(\mathrm{ML}^{n+})}}{f_{(\mathrm{M}^{n+})} f_{\mathrm{L}}} \tag{2}$$

$$K_f = \frac{[\mathrm{ML}^{n+}]}{[\mathrm{M}^{n+}][\mathrm{L}]} = \frac{\Lambda_{\mathrm{M}} - \Lambda_{\mathrm{obs}}}{(\Lambda_{\mathrm{obs}} - \Lambda_{\mathrm{ML}})\mathrm{L}} \tag{3}$$

$$K_f = C_{\mathrm{L}} - \frac{C_{\mathrm{M}}(\Lambda_{\mathrm{M}} - \Lambda_{\mathrm{obs}})}{\Lambda_{\mathrm{obs}} - \Lambda_{\mathrm{ML}}} \tag{4}$$

where $[\mathrm{ML}^{n+}]$, $[\mathrm{M}^{n+}]$ and [L] represents equilibrium molar concentration of complexes, free cation and free ligand respectively. Λ_{M} is the molar conductance of the cation before addition of the ligand, Λ_{M} is the molar conductance of the complex, Λ_{obs} molar conductance of the solution during titration and Λ is the analytical concentration of the ionophore. The complex formation constant K_f and the

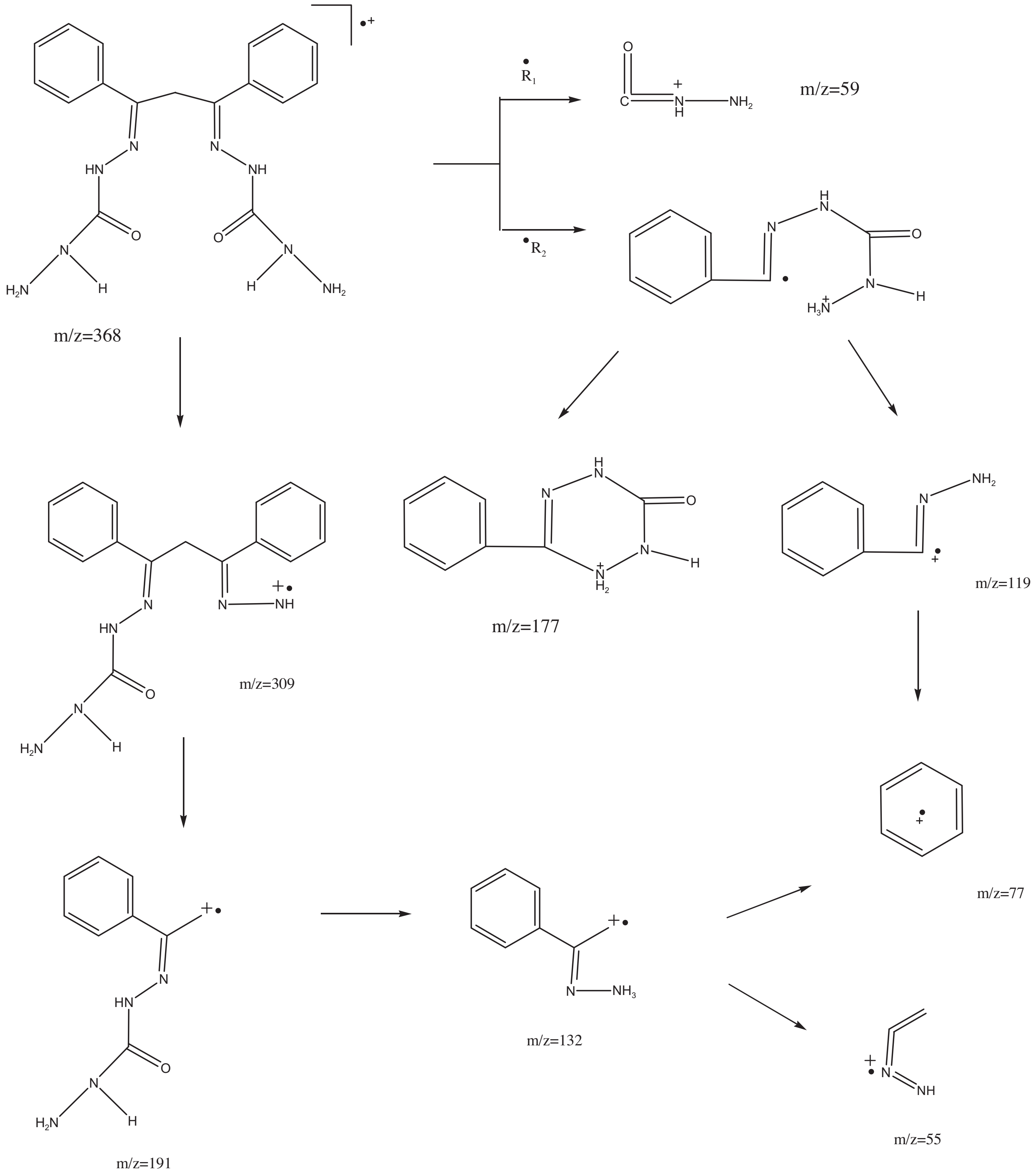

Fig. 6. Mass fragmentation pattern of ligand BMBC.

molar conductance of the complexes were obtained by using a non-linear least square program KINFIT [31]. In this experiment, the ligand to cation mole ratio was equal to 1 in all cases. The formation-constant values (log $K_f = 5.92 \pm 0.12$) of the resulting 1:1 complexes in Table 1 show the high selectivity of the proposed ionophore to Fe^{3+} ions. The suggested structure of Fe^{3+} complex with BMBC is shown in Fig. 8.

Electrochemical sensor

Response of electrode based to Fe^{3+} ions

The existence of nitrogen and oxygen as donor atoms in the ligand with high lipophilic character seems to form strong complexes with transition metal ions [25,26,29]. In order to study the potential response and selectivity of the ionophore for different

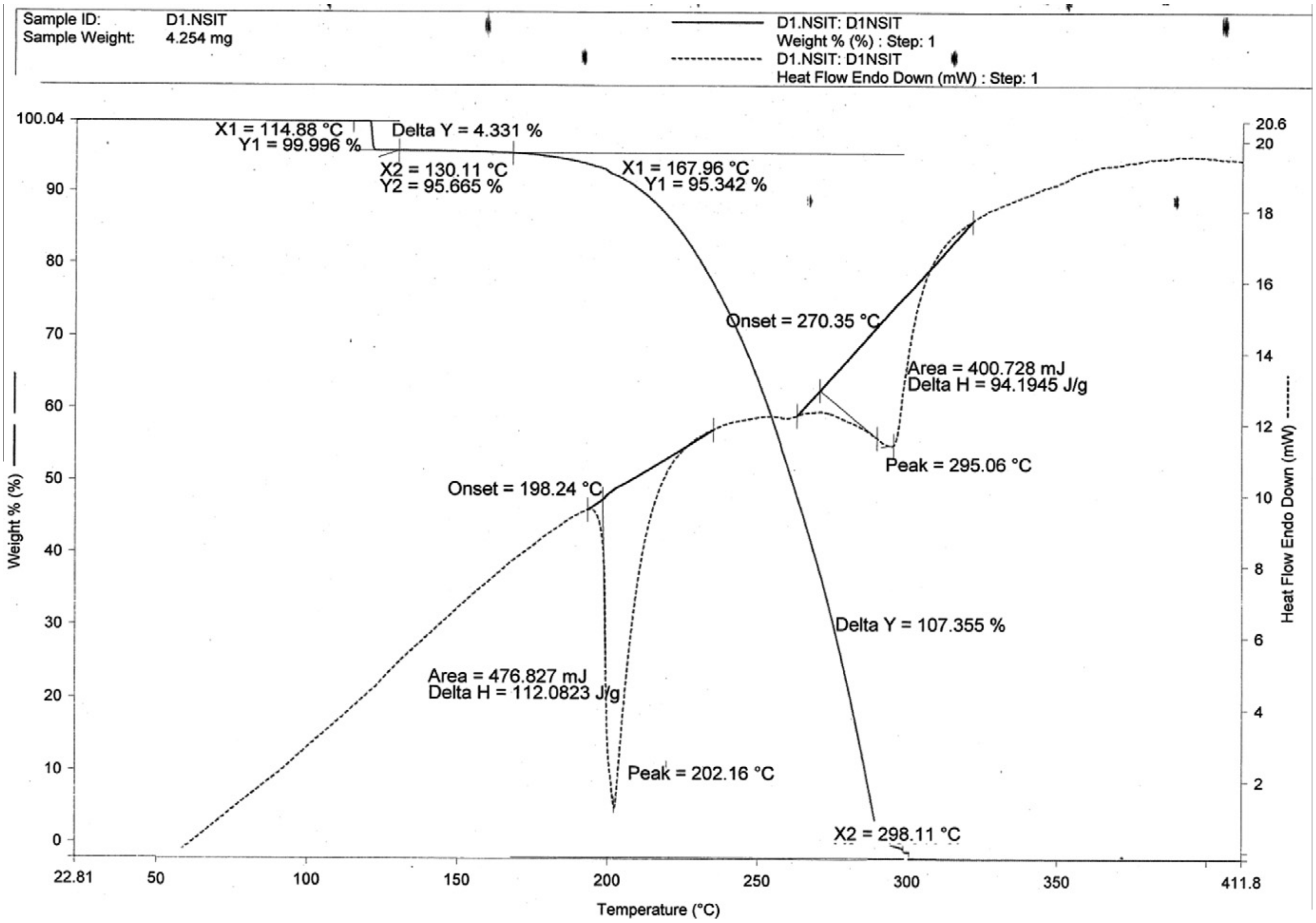

Fig. 7. TGA/DTA curve for ionophore BMBC.

Table 1
Stability formation constants of different metal ions with BMBC.

Metal	log K_f	Metal	log K_f
Fe^{3+}	5.92 ± 0.2	Hg^{2+}	1.49 ± 0.03
Zn^{2+}	1.47 ± 0.04	Co^{2+}	2.57 ± 0.07
Cr^{3+}	3.45 ± 0.03	Ni^{2+}	1.98 ± 0.08
La^{3+}	2.98 ± 0.03	Cu^{2+}	3.45 ± 0.02
Mn^{2+}	2.12 ± 0.04	Ag^{+}	1.99 ± 0.02
Pb^{2+}	1.14 ± 0.02	Cd^{2+}	2.12 ± 0.05
Fe^{2+}	3.42 ± 0.01	Bi^{3+}	2.35 ± 0.02

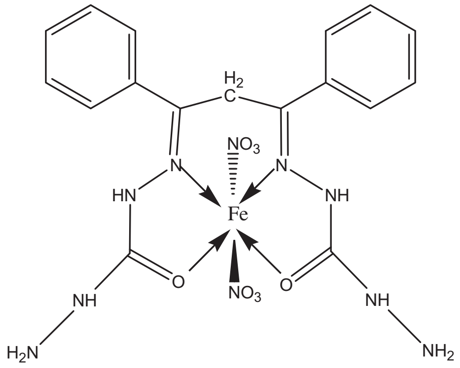

Fig. 8. Suggested structure of Fe(III) complex of BMBC.

metal ions, BMBC was used as a neutral carrier to prepare PVC based membrane electrodes for a variety of metal ions including alkali, alkaline earth, transition and heavy metal ions. The potential responses obtained are shown in Fig. 9. The sensitivities and selectivites obtained for a given membrane depend significantly on the membrane ingredients and the nature of plasticizer and additives used. Therefore, 10 membranes of different compositions (Table 2) have been prepared and their response characteristics were evaluated according to the IUPAC recommendations [32].

The best performance was obtained with a membrane composition of 31% poly (vinyl chloride), 64% DOS, 3.5% BMBC and 2% Potassium tetrakis(4-chlorophenyl)borate. The electrode exhibits a Nernstian behaviour (with slope of 19.7 mV per decade) over a

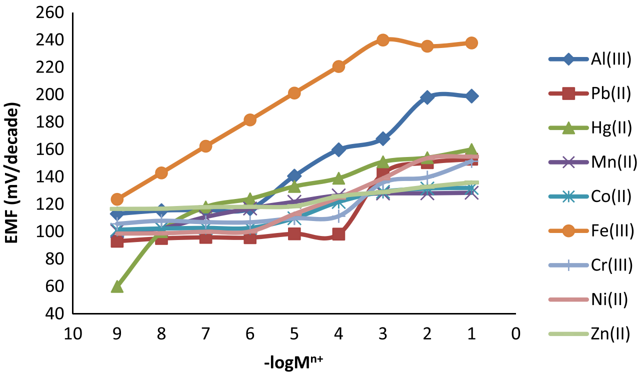

Fig. 9. Potential response of ligand BMBC to M^{n+} ion.

very wide concentration range 1.0×10^{-3}–1.0×10^{-9} M with a detection limit of 3.2×10^{-9} M. This sensor shows very good selectivity and sensitivity towards iron ion over a wide variety of cations, including alkali, alkaline earth, transition and heavy metal ions. In this work, the selectivity coefficient of the sensor towards different cationic species (M^{n+}) was evaluated by using the fixed interference method (FIM) [33,24]. In FIM, the selectivity coefficient was evaluated from potential measurement on solutions containing a fixed concentration of interfering ion (1.0×10^{-2} M) and varying amount of Fe^{3+} ions. It is given by the expression

$$\log K^{pot}_{Fe^{3+},B} = \log(a_{Fe^{3+}}) - \log(a_B)^{Z_{Fe^{3+}}/Z_B}$$

where Z^{3+}_{Fe} and Z_B is the charge on Fe^{3+} ion and interfering ion.

The resulting $K^{pot}_{Fe^{3+},B}$ values are summarized in Table 3 and shows that BMBC sensor is highly selective to iron ions in presence of various ions.

The effect of pH of the test solution on the response of the membrane electrode was examined at two Fe^{3+} ion concentrations. As illustrated in Fig. 10, the potentials remained constant from pH 2.6 to 6.6. However, outside this range the electrode responses at pH < 2.6 seems ascribable to the competitive binding of proton to the ligand at the surface of the membrane electrode, while the diminished potential at higher pH (>6.6), the potential change may be due to the hydroxylation of Fe^{3+} ions.

Dynamic response time is an important factor for any ion-selective electrode. In this study, the practical response time was recorded by immediately changing the Fe^{3+} ion concentration from 1.0×10^{-9} to 1.0×10^{-3} M. In the whole concentration range, the sensor reaches the equilibrium response in a very short time (~9 s).

To evaluate the reversibility of the electrode, a similar procedure in the opposite direction was adopted. The measurements have been performed in the sequence of high-to-low from (1.0×10^{-3}–1.0×10^{-9} M) sample concentrations. The results showed that, the potentiometric response of the electrodes was reversible; although the time needed to reach equilibrium values (40 s) were longer than that of low-to high sample concentrations.

The high lipophilicity of ionophore and plasticizer ensure table potentials and longer lifetime [24] for the membrane. Hence, the lifetime is dependent upon the components of the solution and the measured specimens. 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^{-3}–1.0×10^{-9} M Fe^{3+} solutions. The experimental results showed that the lifetime of the present sensor was over 95 days. During this time, the detection limit and the slope of the electrode remained almost constant. Afterwards, the electrochemical behaviour of the electrode gradually deteriorated, which may be due to ageing of the polymer (PVC), the plasticizers, and leaching of the ionophore. Therefore, the electrode can be used for at least 3 months without a considerable change in their response characteristic towards Fe^{3+}. This sensor has potential applications in a variety of fields. We successfully applied the ionophore electrode as an indicator electrode in the potentiometric titrations as well as determination of iron(III) ion in various water samples and in ferric tablets. The results obtained were in good agreement with atomic absorption spectroscopy results shown in Table 4.

Table 3
Potentiometric selectivity coefficient $\left(\log K^{pot}_{Fe^{3+},B}\right)$ for interfering ions.

Interfering ion	$\log K^{pot}_{Cd^{2+},B}$	Interfering ion	$\log K^{pot}_{Cd^{2+},B}$
K^+	−2.65	Cr^{3+}	−3.32
Ba^{2+}	−3.47	Zn^{2+}	−2.38
Cs^+	−2.21	Pb^{2+}	−3.51
Ni^{2+}	−2.98	Sr^{2+}	−3.27
Cu^{2+}	−3.03	Hg^{2+}	−2.82
Co^{2+}	−2.87	Ce^{3+}	−3.19
La^{3+}	−3.32	Ca^{2+}	−3.84
Fe^{2+}	−2.34	Mg^{2+}	−3.59

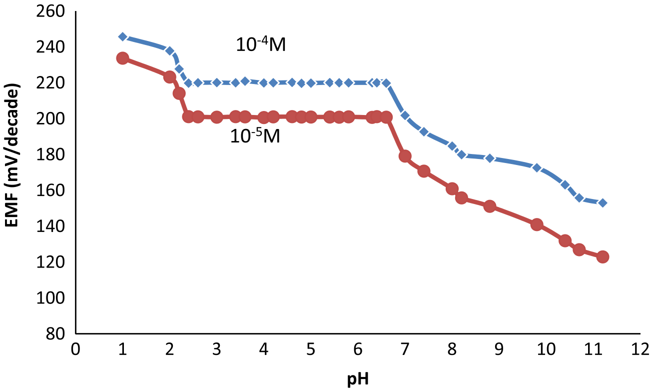

Fig. 10. pH effect on the response of Fe^{3+}-ISE.

Interaction mechanism on the basis of UV spectroscopy

The interaction mechanism of Fe^{3+} ion with the ionophore was discussed on the basis of UV–visible spectrophotometry. Thus, in order to investigate such mechanism of UV–visible spectra of carrier without and with iron ions were recorded. A UV–visible spectrum of BMBC of 0.001 M concentration dissolved in DMSO was recorded first. It was then used for the quantitative complexation

Table 4
Determination of Fe(III) in different samples.

Samples	Proposed sensor (ppm)	AAS (ppm)
Tap water1 (Dwarka, New Delhi)	5.9 ± 0.1	5.7 ± 0.2
Tap water2 (Ajmeri gate, New Delhi)	3.3 ± 0.2	3.5 ± 0.2

Table 2
Optimization of membrane composition.

S. No.	PVC (wt.%)	Plasticizer (wt.%)	Ionophore (wt.%)	KTpClPB (wt.%)	Slope (mV/decade)	Detection limit (M)	Linear range (M)
1	33	66(DOS)	1.0	–	9.6	1.0×10^{-5}	1.0×10^{-3}–1.0×10^{-5}
2	33	65(DOS)	1.5	0.5	13.2	1.6×10^{-5}	1.0×10^{-2}–1.0×10^{-5}
3	33	65(DOS)	1.0	1.0	18.1	6.0×10^{-5}	1.0×10^{-3}–1.0×10^{-6}
4	31	64(DOS)	3.0	2.0	19.7	3.2×10^{-9}	1.0×10^{-3}–1.0×10^{-9}
5	33	63(DBP)	3.0	1.0	13.5	5.0×10^{-7}	1.0×10^{-1}–1.0×10^{-7}
6	31	65(NPOE)	3.0	2.0	11.3	1.0×10^{6}	1.0×10^{-4}–1.0×10^{-7}
7	32	65(TBP)	2.0	1.0	13.7	5.0×10^{-6}	1.0×10^{-3}–1.0×10^{-7}
8	33	64(NPOE)	1.0	2.0	25.4	1.0×10^{-5}	1.0×10^{-1}–1.0×10^{-6}
9	34	64(NPOE)	2.0	2.0	24.6	3.2×10^{-8}	1.0×10^{-1}–1.0×10^{-8}
10	31	66(DBP)	1.0	1.0	15.6	3.0×10^{-5}	1.0×10^{-4}–1.0×10^{-7}

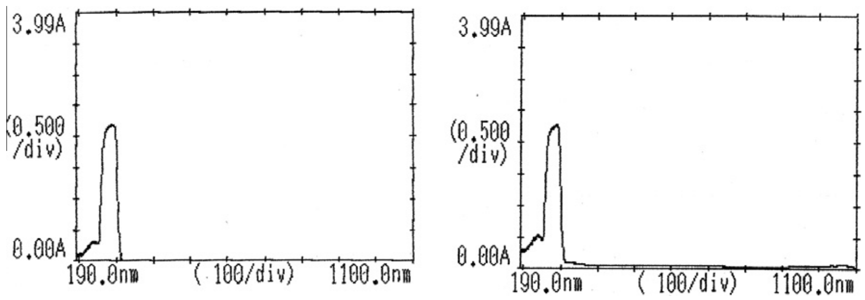

Fig. 11. UV–visible interaction mechanism of (a) BMBC (1×10^{-3} M) in DMSO and (b) BMBC with Fe^{3+} (1×10^{-3} M) in DMSO.

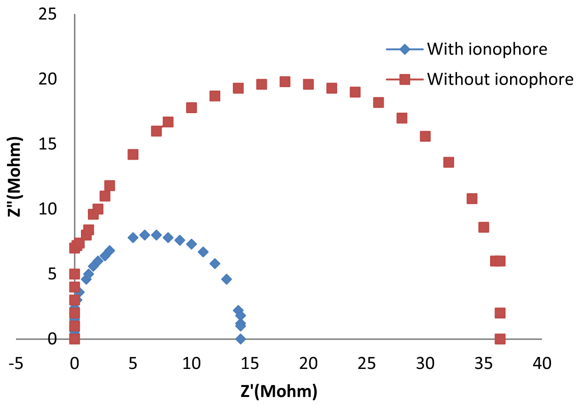

Fig. 12. Complex plan plots of the membrane with and without ionophore.

with Fe^{3+} ion by adding increasing amount of the Fe^{3+} ion up to 0.001 M concentration. The spectra of the ionophore BMBC show the absorption bands at 290 nm (Fig. 11a). In Fig. 11b shift in the peaks was observed and the new peaks were observed at 1035 and 1072 nm with increased absorptivity when Fe^{3+} ion interacted with the carrier, which shows that the size of the complex increases on interaction of Fe^{3+} with the carrier. The absorption intensity changes as a function of molar ratio $[Fe^{3+}]/[BMBC]$ [34].

Electrochemical impedance spectroscopy

Impedance measurements were carried out on the membrane with and without ionophore, and 1.0×10^{-3} and 1.0×10^{-4} M solutions of ferric nitrate as the internal and external solutions of the electrode were used, respectively. Finally their complex plan plots were generated and compared. As shown in Fig. 12, the charge transfer resistance of the membrane without ionophore (36.431 Mohm) is more than that of the membrane with ionophore (14.215 Mohm). These results can be attributed to increasing the electrical conductivity with the available ionophore that can reduce a charge transfer resistance (R_{ct}). This explanation confirms the results obtained from the UV–visible and potentiometric studies.

Conclusion

On the basis of IR, ^{1}H NMR and mass spectra, dibenzoylmethane bis(carbohydrazone) (BMBC) has been characterized, thermally analysed and explored as a iron(III) ion selective electrode. The interaction mechanism is explained by the UV-spectroscopy and electron impedance spectroscopy. The ionophore BMBC based membrane exhibits a linear stable response over a wide concentration range with a near Nernstian response of 19.7 mV/decade. The sensor was used for the direct determination of iron ion in different samples with reproducible results.

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