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# Electrochemical sensing of iron (III) by using rhodamine dimer as an electroactive material

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ABSTRACT

The voltammetric and potentiometric sensors based on a novel electroactive rhodamine dimer (RD) have been developed for the determination of Fe (III) ions. The RD exhibits two anodic peaks at 0.5 V and 0.7 V vs. $Ag/Ag^+$ within the potential range of 0.2–1.2 V, which on addition of Fe (III) ions get converted to single anodic peak with a shift toward more positive potential of 0.9 V vs. $Ag/Ag^+$ due to the formation of Fe (III)–RD complex. The voltammetric sensor has been found to work well in the concentration range of $1.5 \times 10^{-5}$–$3.5 \times 10^{-4}$ M with the detection limit of $3.3 \times 10^{-6}$ M. Further, the potentiometric response of proposed PVC based solid contact coated graphite electrode (CGE-1) was linear for Fe (III) ions in the concentration range of $1.0 \times 10^{-1}$–$1.0 \times 10^{-7}$ M. The electrode showed a slope of 18.8 mV/decade with a detection limit of $4.68 \times 10^{-8}$ M for Fe (III) ions. Both of the sensors revealed good selectivity towards Fe (III) ions in comparison to various diverse metal ions. The analytical utility of the proposed sensors has been confirmed by the estimation of the Fe (III) content in different sample matrices.

## 1. Introduction

Recently, the interest of scientific community is aimed at the design and development of electrochemical sensors for selective and specific detection of environmentally and biologically relevant metal ions. One of such metal ions, iron plays a critical role for all living organisms by participating in a wide diversity of metabolic processes, including oxygen transport, DNA synthesis, and electron transport [1,2]. Its deficiency causes anemia, low blood pressure, and decreased immunity [3,4]. Whereas, its excess amount in cells can trigger the formation of reactive oxygen species (ROS) through the Fenton reaction which further leads to several serious diseases such as Alzheimer's and Parkinson's diseases [5–7]. When iron containing chemical enter into the environment they persists and most of time affects the eco-balance. So, the quantitative determination of Fe (III) ions is important both from biological as well as environmental point of view. Electrochemical sensors can be used to detect a wide range of analytes and capable of being incorporated into robust, portable, miniaturized devices, thus enabling tailoring for particular applications [8,9]. However, there have been relatively very small number of electrochemical sensors for selective detection of Fe (III) ions therefore, their designing is still a challenge and interest [10–13]. Currently, the voltammetry and potentiometry techniques provide a crucial analytical tool for the selective determination of various metal ions. In potentiometry, the conventional PVC based polymeric membrane electrodes (PMEs) which include the inner reference solution of analyte ion has been replaced by the solid contact ion selective electrodes which showed better electrode response characteristics as compared to traditional PMEs [14–16]. Hence, in the present work, we also decided to construct solid contact (graphite surface) PVC based coated graphite electrodes (CGEs) to obtain the better electrode response characteristics.

Recently, the rhodamine derivatives have received great interest due to its chemosensing property. The distinct color and fluorescent changes due to spirolactum ring opening make these derivatives more important for the sensing of a variety of metal cations. Interestingly, various photometry or fluorometry based sensors specific for detection of Fe (III) have been reported [17–20]. But till now, there are no text reports concerning the rhodamine dimer based electrochemical sensors for iron (III) ions. In sight of the importance of selective determination of Fe (III) ions, we have made an attempt to develop the voltammetric as well as potentiometric sensors for selective recognition of Fe (III) ions based upon new electroactive rhodamine dimer, which undergoes electrochemical changes in the presence of Fe (III) ions. The proposed voltammetric and potentiometric sensors have been effectively applied to detect the Fe (III) ions content in various sample matrices. The obtained results were compared with atomic absorption spectroscopy (AAS) and were found in good agreement with each other.

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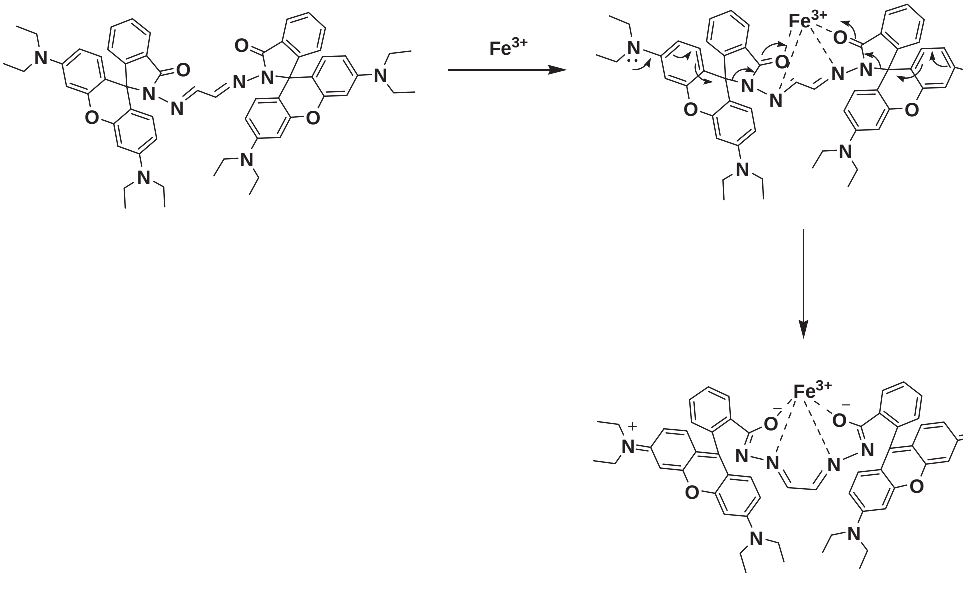

**Scheme 1.** Structure of rhodamine dimer (RD) and its co-ordination mechanism with Fe (III) ions.

## 2. Experimental

### 2.1. Materials

All reagents used were of analytical grade. The electroactive rhodamine dimer (RD) (Scheme 1) has been synthesized as reported elsewhere [21]. Various plasticizers such as bis(2-ethylhexyl) sebacate (DOS), 2-nitrophenyl octyl ether (NPOE), bis(2-ethylhexyl) phthalate (DOP), tributylphosphate (TBP) and high molecular weight poly(vinyl chloride) (PVC) were used as received from Fluka. Anion excluder, sodium tetraphenylborate (NaTPB) was obtained from Merck while metal perchlorates, electrolyte tetrabutylammonium perchlorate (TBAP) and graphite rods ($3 \times 150\ mm^2$) were received from Sigma-Aldrich and were used without any further purification. Samples for analytical application i.e. the ferric dextran injection (Ciron drugs & pharmaceutical Pvt. Ltd., Mumbai, India) and ferric sucrose injection (Apothecon pharmaceutical Pvt. Ltd., Vadodara, India) were obtained from the local market of India.

### 2.2. Electrochemical measurements

The cyclic voltammetric and differential pulse voltammetric measurements were carried out with an electrochemical workstation (CH Instruments, Austin, TX, USA) Model 660D with a three-electrode cell, including a Pt working electrode (round disk, diameter 2 mm), Pt wire as the counter electrode and $Ag/Ag^+$ (0.1 M $AgNO_3$ in $CH_3CN$) as the reference electrode, separated from the solution by a plug. The CV and DPV studies were conducted in the rhodamine-dimer ($1.0 \times 10^{-4}$ M) solution within the potential range of 0.2–1.2 V vs. $Ag/Ag^+$ at a scan rate of 50 mV/s, pulse amplitude of 50 mV, pulse width of 0.05 s and pulse period of 0.08 s. Prior to measurements, the surface of the working electrode was polished with 0.05-micron alumina, and residual alumina particles were thoroughly removed by placing the working electrode in an ultrasonic cleaner for 15 min., dried and washed with pure acetonitrile. Acetonitrile was used as the solvent and 0.01 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte for all the voltammetric measurements.

For the potentiometric studies, PVC based coated graphite ion-selective membrane electrodes (CGEs) were constructed by the same procedure as reported earlier [22,23]. The potentiometric measurements were carried out using the following electrochemical cell assembly:

| | | | | |
|---|---|---|---|---|
| Graphite surface | PVC membrane | Test solution | 3.0 M KCl | $Ag/Ag^+$ |

The potentiometric measurements were carried out in double distilled water by using the Equip-tronics model EQ-602 potentiometer. The pH measurements were made using an Elico LI model-120 pH meter. The stock solutions ($1.0 \times 10^{-1}$ M) of metal ions were prepared from their metal nitrate salts and test solutions of desired concentration were obtained by successive dilution of the stock solution with double distilled water. The pH adjustments were performed by using conc. nitric acid and hexamine solution. The detection limits of the potentiometric measurements were calculated by a similar way as per recommended by IUPAC [24]. All the voltammetric and potentiometric experiments were performed in triplicate at $25 \pm 1$ °C.

## 3. Results and discussion

### 3.1. Voltammetric studies

The electrochemical behavior of rhodamine dimer (RD) ($1.0 \times 10^{-4}$ M) toward different metal ions were investigated using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in acetonitrile containing 0.01 M TBAP as the supporting electrolyte at a scan rate of 50 mV/s. As predicted, the CV scan of pure RD exhibits two anodic peaks at a potential of 0.5 V and 0.7 V vs. $Ag/Ag^+$ in the potential range of 0.2–1.2 V as shown in Fig. 1 (curve a). The anodic peak at 0.5 V is due to oxidation of the imine group while that at 0.7 V corresponds to the oxidation of the amide group of spirolactum ring [25].

In the CV measurements, when 3.0 equivalent of Fe (III) ions is added to $1.0 \times 10^{-4}$ M RD solution, both the anodic peaks get transformed to a single anodic peak, which shift towards a more positive potential of 0.9 V vs. $Ag/Ag^+$ (Fig. 1 (curve b)). Simultaneously, the color of RD gets changed from light pink to wine (inset Fig. 1) which indicates the formation of RD–Fe (III) complex.

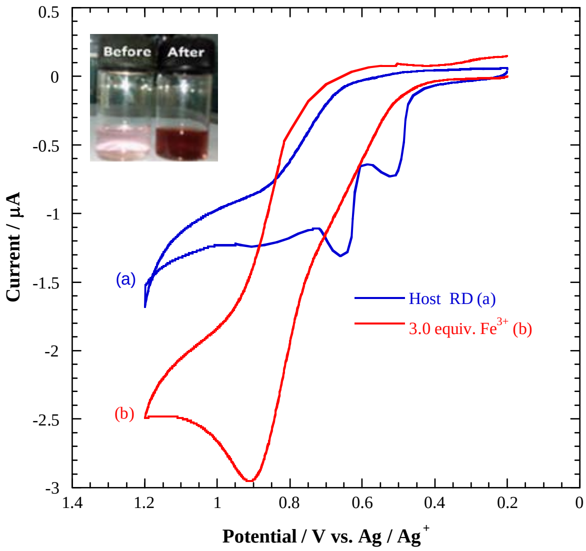

**Fig. 1.** Cyclic voltammogram (CV) of (curve a) the pure RD ($1.0\times10^{-4}$ M) and (curve b) after the addition of 3.0 equivalent of Fe (III) in $CH_3CN$; electrolyte 0.01 M TBAP; scan rate 50 mV/s within the potential range of 0.2–1.2 V vs. Ag/Ag$^+$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

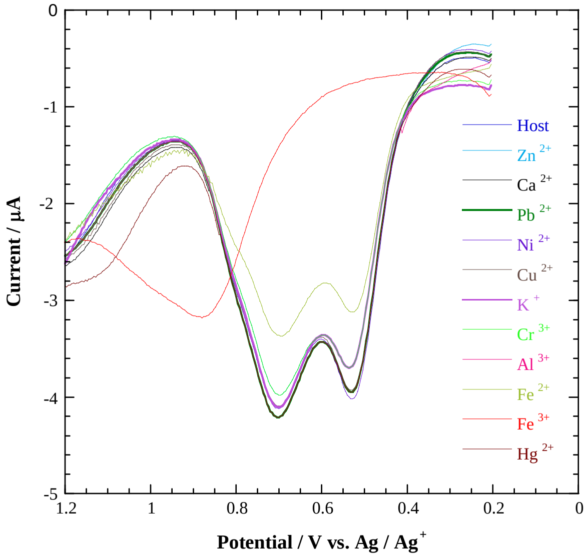

**Fig. 2.** Differential pulse voltammogram (DPV) of $1.0\times10^{-4}$ M RD (host) in the absence and presence (3.0 equivalent each) of the various metal ions in $CH_3CN$; electrolyte, 0.01 M TBPA; pulse amplitude, 50 mV within the potential range of 0.2–1.2 V vs. Ag/Ag$^+$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The binding of Fe (III) ion with the spirolactum rings of RD results in the ring opening reaction and transforms the RD to its spirolactum ring-opened form, which is most likely to be responsible for the potential shift observed in anodic peaks of RD (Scheme 1) on addition of Fe (III) ions [21,26,27]. The conjugated imine group and amide group of spirolactum ring act as redox active centers as well as binding sites.

In the rest of the voltammeric experiments, differential pulse voltammetry (DPV) was employed instead of CV to get the improved resolution of waves under identical conditions. The complexation behavior of RD towards diverse metal cations such as alkali, alkaline earth and transition metals was investigated by DPV at Pt working electrode in TBAP/acetonitrile solution (0.01 M). As per Fig. 2, the DPV of the host RD ($1.0\times10^{-4}$ M) shows two anodic peaks at 0.5 V and 0.7 V vs. Ag/Ag$^+$ in the potential range of 0.2–1.2 V vs. Ag/Ag$^+$. On the addition of 3.0 equivalent of Fe (III) ions to RD solution, both the anodic peaks get completely converted to single anodic peak and get shifted to more positive potential of 0.9 V vs. Ag/Ag$^+$, which indicates the formation of RD–Fe (III) complex. On the other hand, the addition of 3.0 equivalent of various metal ions such as $K^+$, $Ca^{2+}$, $Zn^{2+}$, $Pb^{2+}$, $Ni^{2+}$, $Cr^{3+}$, $Cu^{2+}$, $Hg^{2+}$, $Al^{3+}$, $Ag^+$ and $Fe^{2+}$ into $1.0\times10^{-4}$ M RD solution (Fig. 2) shows no significant change in any of the anodic peaks of the host RD, under similar conditions (no potential shift observed). Furthermore, the color of the host also remained unchanged (light pink) in the presence of these metal ions. These finding suggest that the RD is very much selective to Fe (III) ions as compared to other metal ions in the potential range of 0.2–1.2 V vs. Ag/Ag$^+$. Also, the host RD can behave as a colorimetric probe for the selective detection of Fe (III) ions, due to the fact that the color change can be distinguished by naked eyes. Further, when a mixture containing 3.0 equivalent of $K^+$, $Ca^{2+}$, $Zn^{2+}$, $Pb^{2+}$, $Ni^{2+}$, $Cr^{3+}$, $Cu^{2+}$, $Hg^{2+}$, $Al^{3+}$, $Ag^+$ and $Fe^{2+}$ was added to the solution of RD–Fe (III) complex; the anodic shift of RD–Fe (III) complex remains approximately the same (Fig. S1 of Supporting information). Results indicate that RD preferentially coordinates with Fe (III) without any interference from closely related metal ions.

The electrochemical behavior of RD for Fe (III) ions was further explored by performing the voltammetric titration of RD with the increasing amount of Fe (III) ions. A constant volume (15 μL) of Fe (III) ions was injected sequentially into RD solution ($1.0\times10^{-4}$ M) to give a final concentration range of 0.5–3.5 equivalent of Fe (III) in the solution. Fig. 3 shows the effect of increasing concentration of Fe (III) ion on the peak current of RD. On the addition of 0.50 equivalent of Fe (III) ions in RD solution, both the anodic peaks get vanished, and converted to single anodic peak which get shifted at 0.9 V within the potential range of 0.2–1.2 V vs. Ag/Ag$^+$. On the successive addition of Fe (III) ions (0.5–3.5 equivalent) in RD solution, the anodic peak at 0.9 V gets quenched with a decrease in the peak current which gradually reaches to lower value at about 3.5 equivalent of Fe (III) ions. The inset of Fig. 3, shows that the peak current has good linear relationship with the concentration of Fe (III) ions. The linear regression equation of Fe (III) is $I_p = -6.142 + 0.011[\text{Fe (III)}]$, ($R = 0.9902$ and confidence limit of

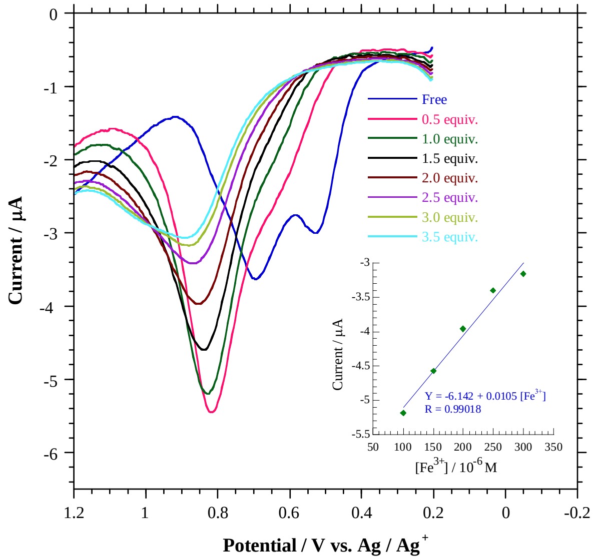

**Fig. 3.** DPV of $1\times10^{-4}$ M of RD in the presence of increasing amount of Fe (III); electrolyte, 0.01 M TBAP; pulse amplitude, 50 mV within the potential range of 0.2–1.2 V vs. Ag/Ag$^+$. Inset: corresponding calibration plot.

95%) ($I_p$: μA) within the concentration range of $1.5\times10^{-5}$–$3.5\times10^{-4}$ M and detection limit ($S/N=3$) of $3.3\times10^{-6}$ M.

The relative standard deviation (% R.S.D., $N=10$) for $1.0\times10^{-5}$ M of Fe (III) ions under identical conditions was ±3.5%, which confirmed the reproducibility of the proposed voltammetric sensor.

### 3.2. Potentiometric studies

In the preliminary experiments, different PVC-based coated graphite electrodes (CGEs) membrane sensors were prepared using PVC (40.0 mg), DOS as plasticizer (80.0 mg), NaTPB as an additive (2.0 mg), and rhodamine dimer (RD) as an ionophore (4.5 mg). The membrane sensors so prepared were conditioned in $1.0\times10^{-2}$ M solution of different ions for 48 h. To determine the potential response of the electrodes towards different metal ions, the potential values of each electrode were noted against solutions of respective metal nitrate within the concentration range of $1.0\times10^{-1}$–$1.0\times10^{-9}$ M. The results signify that, except the Fe (III) ions, no electrode shows any potentiometric response for other metal ions such as $Co^{2+}$, $Pb^{2+}$, $Cd^{2+}$, $Cu^{2+}$, $Ag^{+}$, $Ca^{2+}$, $K^{+}$, $Zn^{2+}$, $Na^{+}$ and $Fe^{2+}$. Fig. S2 (Supporting information) represents the potential response curves obtained for the different ion selective electrodes investigated for their potential selectivity. Consequently, we can say that RD has preferable affinity toward Fe (III) ions and can be employed as a potential ionophore for the growth of Fe (III) ion selective coated graphite electrodes (CGEs).

Based on the results obtained from the preliminary investigation on RD, we decided to prepare Fe (III) ion selective electrodes by incorporating RD as an ionophore. The potentiometric response curve for CGE-1 based on the ionophore RD has been shown in Fig. 4 whose compositions and response characteristics are given in Table 1. The CGE-1 exhibited the Nernstian slope of 18.8 mV/decade over the concentration range of $1.0\times10^{-1}$–$1.0\times10^{-7}$ M for Fe (III) ions with the lower detection limit of $4.68\times10^{-8}$ M ('X' in Fig. 4).

Incorporation of an additional membrane component is known to affect the perm-selectivity, Ohmic resistance and response behavior of the PVC based membrane electrodes [28]. Moreover, it increases the membrane sensitivity of the ionophores whose extraction capacity is poor and thus catalyzes the exchange kinetics [29]. In this work, NaTPB was incorporated as an additional membrane component to construct the coated graphite electrodes (CGEs). The response characteristics for the CGE-1, CGE-2 and CGE-3 incorporating the different amounts of NaTPB are given in Table 1. The optimum NaTPB content for the preparation of proposed CGE-1 was worked out to be 2.0 mg, which may be suitable for charge compensation of the counter ion present in the proposed membrane and additionally, it may assist the process of ion charge transduction. Whereas, CGE-3 contains no lipophilic additive in the membrane showed non-Nernstian slope of 8.6 mV/decade.

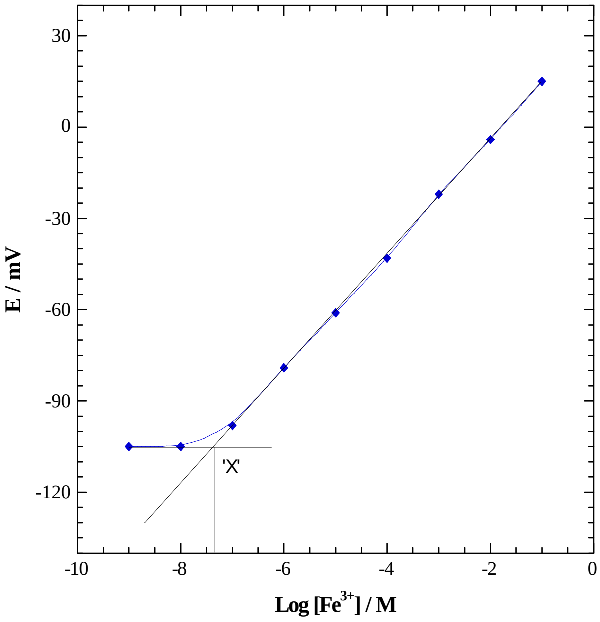

**Fig. 4.** Potentiometric response curve of CGE-1 based on RD toward Fe (III) ions.

The effect of ionophore (RD) content on the response characteristics of Fe (III) ion CGE-1 was studied by preparing membrane electrodes consisting of different amounts of RD as an ion carrier. The coated graphite electrodes CGE-1 (4.5 mg), CGE-4 (2.5 mg) and CGE-5 (6.5 mg) were prepared by varying the amount of RD. It is clear from Table 1, out of these three electrodes, the CGE-1 possessing 4.5 mg RD gives the best response characteristics.

Plasticizers are known to influence the dielectric constant of membrane, mobility of ionophore molecules and the state of ionophore [30,31]. The response characteristics of an ion selective electrode are thus affected by the nature of plasticizer. In order to study the effect of plasticizer on the potential response of Fe (III) ion selective electrode, different plasticizers like DOS (4.6), NPOE (20), TBP (3.5) and DOP (5.1) of varying dielectric constant ($\epsilon$) were used for membrane preparation. The composition and electrode characteristics for the coated graphite electrodes CGE-1, CGE-6, CGE-7 and CGE-8 containing DOS, NPOE, TBP and DOP as plasticizers respectively have been given in Table 1. Out of different plasticizers employed for membrane preparation, the CGE-1 containing DOS as a plasticizer shows the Nernstian slope of 18.8 mV/decade to Fe (III) ions over wide concentration range of $1.0\times10^{-1}$–$1.0\times10^{-7}$ M with lower detection limit of $4.68\times10^{-8}$ M, whereas, the CGE-6 containing 2-NPOE as plasticizer exhibited super Nernstian response of 26.9 mV/decade over concentration range of $1.0\times10^{-1}$–$1.0\times10^{-6}$ M for Fe (III) ions with lower detection limit of $2.04\times10^{-6}$ M. In addition, CGE-7 and CGE-8 containing TBP and DOP as plasticizers exhibit sub-Nernstian slopes of 13.1 and 16.7 mV/decade over the concentration ranges of $1.0\times10^{-3}$–$5.0\times10^{-7}$ M and $1.0\times10^{-2}$–$1.0\times10^{-6}$ M with lower detection limits of $7.24\times10^{-6}$ M and $1.07\times10^{-5}$ M respectively for Fe (III) ions. The comparative evaluation of the electrode characteristics properties for CGE-1, CGE-6, CGE-7 and CGE-8 from Table 1 makes it apparent that DOS is the most appropriate plasticizer for the preparation of Fe (III) coated graphite electrodes containing RD as an ionophore.

It is well known that characteristics of an ion selective electrode are significantly affected by the pH of the working solution. The pH dependence of the proposed CGE-1 was investigated at concentration of $1.0\times10^{-2}$ M of the Fe (III) ion. The pH of the solution was varied using concentrated nitric acid and hexamine. The effect of pH variation on the potential response of Fe (III) ion selective electrode CGE-1 has been shown in Fig. S3 (Supporting information). It is clear from Fig. S3, that potential response of electrode CGE-1 remains constant within pH range of 2.0–6.0 and this can be taken as the working pH range for CGE-1. The observed deviation in potential at the lower end of the pH range may be attributed to the interference from $H^{+}$ ions and potential deviation observed at the higher end of the pH range may be credited to the formation of some hydroxyl complexes of Fe (III) ions in solution from the hydrolysis of iron (III) nitrate salt.

The formation of thin water layer in between the PVC membrane and its solid contact (graphite here) might decrease the potential stability of proposed electrode; hence the stability of the proposed CGE-1 need to be checked by using the protocol developed by Fibbioli et al. [32]. The proposed Fe (III) CGE-1 was immersed into the $1.0\times10^{-2}$ M $Fe(NO_3)_3$ solution in the

**Table 1**
Composition and response characteristics of RD based Fe (III)-coated graphite electrodes (CGEs).

| S. no. | PVC (mg) | Plasticizer (mg) | NaTPB (mg) | Ionophore (mg) | Linear range (M) | Detection limit (M) | Slope (mV/decade) |
|---|---|---|---|---|---|---|---|
| CGE-1 | 40.0 | 80.0 (DOS) | 2.0 | 4.5 | $1.0\times10^{-1}$–$1.0\times10^{-7}$ | $4.68\times10^{-8}$ | 18.8 |
| CGE-2 | 40.1 | 80.2 (DOS) | 1.0 | 4.6 | $1.0\times10^{-1}$–$1.0\times10^{-6}$ | $2.51\times10^{-6}$ | 16.3 |
| CGE-3 | 40.0 | 79.9 (DOS) | 0.0 | 4.5 | $1.0\times10^{-1}$–$1.0\times10^{-6}$ | $1.01\times10^{-6}$ | 8.6 |
| CGE-4 | 40.3 | 79.5 (DOS) | 2.1 | 2.5 | $1.0\times10^{-1}$–$5.0\times10^{-6}$ | $6.02\times10^{-6}$ | 13.3 |
| CGE-5 | 40.0 | 80.0 (DOS) | 2.2 | 6.5 | $1.0\times10^{-1}$–$5.0\times10^{-7}$ | $3.16\times10^{-7}$ | 24.4 |
| CGE-6 | 39.9 | 80.1 (2-NPOE) | 2.0 | 4.6 | $1.0\times10^{-1}$–$1.0\times10^{-6}$ | $2.04\times10^{-6}$ | 26.9 |
| CGE-7 | 40.6 | 79.8 (TBP) | 2.0 | 4.4 | $1.0\times10^{-3}$–$5.0\times10^{-7}$ | $7.24\times10^{-6}$ | 13.1 |
| CGE-8 | 39.8 | 80.1 (DOP) | 2.2 | 4.5 | $1.0\times10^{-2}$–$1.0\times10^{-6}$ | $1.07\times10^{-5}$ | 16.7 |

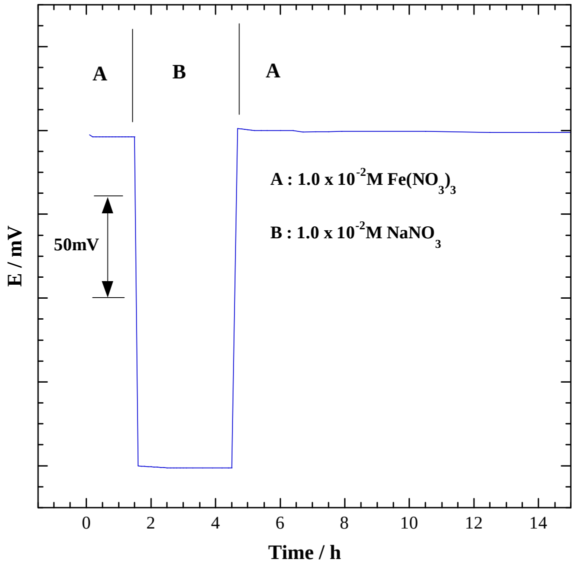

**Fig. 5.** Water layer test for Fe (III) CGE-1 recorded in (A) $1.0\times10^{-2}$ M of $Fe(NO_3)_3$ and (B) $1.0\times10^{-2}$ M $NaNO_3$.

beginning. After 1.5 h (approx.) the solution was then altered to $1.0\times10^{-2}$ M $NaNO_3$ solution (diverse ion). After 3 h diverse ion solution was replaced again by $1.0\times10^{-2}$ M $Fe(NO_3)_3$ solution. It is obvious from Fig. 5 that no potential drift was observed for Fe (III) CGE-1 upon changing the analyte in the sample solution from primary ions to the diverse ions and again to primary ions. The results revealed that no aqueous layer was formed in between CGE-1 membrane and solid contact (graphite surface).

For analytical applications, the response time of an ion selective electrode is a significant issue. The response time of an electrode indicates the time required by an ion selective electrode to achieve a steady-state potential (within ±1 mV), when it is dipped in successive analyte ion solution each having the tenfold divergence in concentration. The dynamic response time of CGE-1 for step changes in the concentration of Fe (III) ions has been given in Fig. S4 (Supporting information). It is evident from Fig. S4 that the time taken for the electrode to achieve 95% of the stable potential is less than 10 s (approx.) and response time remains constant up to 5 min. The lifetime of projected CGE-1 was at least 3 months. During this time, the response characteristics of CGE-1 such as concentration range ($1.0\times10^{-1}$–$1.0\times10^{-7}$ M), detection limit ($4.68\times10^{-8}$ M) and Nernstian slope (18.8 mV/decade) remained almost constant. After this time period, the electrochemical behavior of CGE-1 gradually deteriorates, that may be due to leaching of ionophore (RD) from membrane of CGE-1.

The most vital characteristic of an ion selective electrode is its relative response for the primary ion over various diverse ions present in the solution, which is expressed in terms of logarithmic selectivity coefficient ($\log K^{\text{Pot.}}_{A,B}$). In this work, the $\log K^{\text{Pot.}}_{A,B}$ of proposed Fe (III) CGE-1 was determined using the fixed interference method (FIM) based on the semi-empirical Nikolsky–Eiseman equation [33] at $1.0\times10^{-2}$ M concentration of various diverse ions (B). The values of logarithmic selectivity coefficients ($\log K^{\text{Pot.}}_{Fe^{3+},B}$) obtained by FIM for CGE-1 are shown in Table 2, where the pattern of selectivity coefficient values clearly indicates that CGE-1 is very much selective for Fe (III) ions over other diverse ions. Among all the diverse ions, Fe (II) ion has the highest selectivity coefficient (−2.05) but it did not interfere in the normal functioning of proposed Fe (III) CGE-1 up to a concentration of $1.0\times10^{-2}$ M. Above this concentration, the Fe (II) ions show the interference in the normal functioning of Fe (III) CGE-1.

**Table 2**
Selectivity coefficients of various diverse ions (B) for RD based Fe (III) coated graphite electrode (CGE-1).

| Diverse ions (B) | $\log K^{\text{Pot.}}_{Fe^{3+},B}\pm SD$[a] | Diverse ions (B) | $\log K^{\text{Pot.}}_{Fe^{3+},B}\pm SD$[a] |
|---|---|---|---|
| $Co^{2+}$ | $-4.25\pm0.02$ | $Mg^{2+}$ | $-3.28\pm0.03$ |
| $Pb^{2+}$ | $-3.12\pm0.06$ | $Ag^{+}$ | $-2.39\pm0.08$ |
| $Cd^{2+}$ | $-3.94\pm0.05$ | $Li^{+}$ | $-2.89\pm0.09$ |
| $Cu^{2+}$ | $-3.58\pm0.07$ | $Ca^{2+}$ | $-3.30\pm0.08$ |
| $Zn^{2+}$ | $-4.25\pm0.05$ | $K^{+}$ | $-3.52\pm0.03$ |
| $Fe^{2+}$ | $-2.05\pm0.05$ | $Na^{+}$ | $-3.36\pm0.06$ |
| $NH_4^{+}$ | $-3.20\pm0.07$ | $Hg^{2+}$ | $-2.57\pm0.03$ |

[a] Mean value ± standard deviation (three measurement).

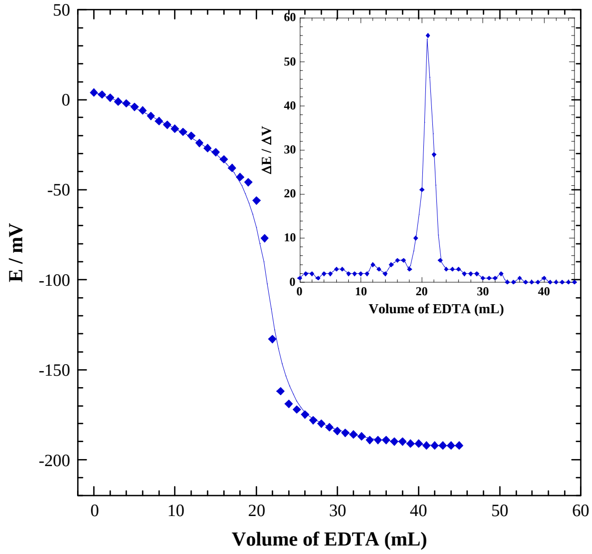

**Fig. 6.** Titration plot of Fe (III) ions vs. EDTA using proposed CGE-1 as an indicator electrode.

**Table 3**
Estimation of Fe (III) ions in different samples matrices by the proposed sensors.

| Sample | Fe (III) content in different samples ± SD (M)[a] | | | | |
|---|---|---|---|---|---|
| | Voltammetric method | Potentiometric method (CGE) | Atomic absorption method (AAS) | Percentage compatibility with voltammetry | Percentage compatibility with potentiometry |
| Synthetic water (1) | $(3.91 \pm 0.04) \times 10^{-6}$ | $(3.88 \pm 0.06) \times 10^{-6}$ | $(4.01 \pm 0.02) \times 10^{-6}$ | 97.50 ± 0.06 | 96.76 ± 0.03 |
| Synthetic water (2) | $(7.81 \pm 0.02) \times 10^{-6}$ | $(7.86 \pm 0.08) \times 10^{-6}$ | $(7.66 \pm 0.05) \times 10^{-6}$ | 101.96 ± 0.05 | 102.61 ± 0.03 |
| Venofer iron injection | $(8.79 \pm 0.06) \times 10^{-5}$ | $(8.70 \pm 0.05) \times 10^{-5}$ | $(8.58 \pm 0.06) \times 10^{-5}$ | 102.45 ± 0.06 | 101.40 ± 0.07 |
| Iron dextran injection | $(4.84 \pm 0.05) \times 10^{-5}$ | $(4.79 \pm 0.09) \times 10^{-5}$ | $(4.63 \pm 0.02) \times 10^{-5}$ | 101.04 ± 0.02 | 103.45 ± 0.08 |

[a] Mean value ± standard deviation (three measurement).

## 4. Analytical applications

The practical significance of the proposed CGE-1 was tested by using it as an indicator electrode for monitoring the potentiometric titration of ferric nitrate vs. EDTA and the corresponding titration plot is shown in Fig. 6. Before the end point, potential shows usual sigmoid change with the increase in the volume of titrant, while the potential response remains almost constant after the end point due to low concentration of free Fe (III) ions in solution.

To evaluate the applicability and feasibility of the proposed voltammetric and potentiometric sensors, these were employed to determine the concentration of Fe (III) ions in real sample matrices such as synthetic water, ferric dextran and ferric sucrose injections. All samples were prepared in the same way reported earlier [23]. The results obtained from voltammetric and potentiometric sensors were compared with those obtained by an atomic absorption spectrophotometer (AAS) (Table 3). Table 3 reveals that there is no significant difference between the results obtained by the proposed electrochemical methods and AAS, suggesting the reliability and proper functioning of the proposed sensor.

## 5. Conclusions

In this work, new electrochemical (voltammetric and potentiometric) sensors based on rhodamine dimer (RD) as an electroactive material have been designed for the detection of Fe (III) ions. In voltammetry, the addition of Fe (III) ions led to the complete transformation of both the anodic peaks of the RD to a single anodic peak appearing at more positive potential due to formation of Fe (III)–RD complex. The proposed electrochemical sensors exhibited excellent selectivity and sensitivity towards Fe (III) ions without any interference from the diverse ions. Both electrochemical sensors have been effectively applied for the determination of Fe (III) in various sample matrices with good precision and accuracy. Hence, the proposed electrochemical sensors can prove beneficial for the analysis of Fe (III) ions for various applications.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.04.034.

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