



Selective sensing ability of ferrocene appended quinoline-triazole derivative toward Fe (III) ions



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ABSTRACT

Selective electrochemical sensors based on newly synthesized ferrocene appended quinoline-triazole (FAQT) derivative for Fe (III) ions have been developed. The cyclic voltammetry (CV) of FAQT exhibited reversible voltammogram corresponding to ferrocene/ferrocenium redox process in the potential range of -0.4 to 0.6 V vs Ag/Ag⁺. The CV of FAQT undergoes electrochemical perturbation on addition of Fe (III) ions and results in the shift of voltammogram toward more positive potential (anodic shift) which ascribed the formation of FAQT-Fe (III) complex. The binding behavior and 1:1 stoichiometry of FAQT-Fe (III) complex was further confirmed by employing fluorescence and UV-visible techniques. The high binding constant (1.82×10^3 M⁻¹) and negative free energy change (-18.6 kJ mol⁻¹) indicates the stability and feasibility of FAQT-Fe (III) complex. The voltammetric sensor works within the concentration range of 1.0×10^{-4} – 5.0×10^{-6} M with detection limit of 2.33×10^{-7} M. The potentiometric solid contact electrode exhibits the Nernstian slope of 18.7 mV decade⁻¹ for Fe (III) ions in concentration range of 1.0×10^{-1} – 1.0×10^{-7} M with the detection limit of 2.94×10^{-8} M. These proposed sensors showed high selectivity toward Fe (III) ions and therefore, used for quantification of Fe (III) ions in different sample matrices.

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1. Introduction

The importance of electrochemical sensors in biological and environmental systems has recently gained much scientific interest and hence, their development is one of the most active areas of analytical research. In past few years, the detection of metal ions which play an important role in human health and ecosystem has drawn immense interest. Among various metal ions, iron is the most abundant and essential metal ion in human and its adequate quantity in body regulate many biological processes, such as cellular metabolism, oxygen transport, electron transport, and DNA synthesis [1,2]. However, its overdosage causes serious health problems including convulsions or cardiac arrest, severe cell damage, respiration irregularity and organ dysfunction through abnormal production of reactive oxygen species (ROS) [3,4]. In our day-to-day life, the speedy urbanization and growth of industries has increased iron content in the environment which ultimately possess adverse effects on the structure and function of ecosystem [5]. Thus, the monitoring of iron by using the reliable sensing methods in various sample matrices is now considered crucial. The most commonly used analytical methods for the qualitative and quantitative

determination of Fe (III) ions are atomic absorption spectroscopy (AAS), inductively coupled plasma-mass spectroscopy (ICP-MS), colorimetry and fluorometry [6–9]. However, the tedious sample preparation, requirement of trained analyst and the use of sophisticated and expensive instrumentation limited their analytical applications. Relatively electrochemical techniques (voltammetry/potentiometry) proved as the superior and potential analytical tool for selective detection of various analytes due to their low production cost, portability, fast analysis, close to real analysis, no-external pretreatment, accuracy and ease of operation [10,11]. The design and development of innovative and practical electrochemical sensors that offer promising advancement for the selective detection of Fe (III) ions is still a great challenge. The ferrocene appended receptors are well known for their considerable contribution in the field of electrochemical sensors [12–15]. These receptors consist of one or more ferrocene redox unit which behaves like functional antenna whose redox properties got perturbed by coordination of analytes in its close proximity. Several electrochemical sensing systems were designed by assembling ferrocene unit with different binding motifs [16–18]. Among them, 1,2,3 triazole motif has proved to be an efficient binding unit for recognition of various cations as well as anions [19,20]. Recently, the combination of ferrocene unit (signaling unit) with triazole (binding unit) proved as an efficient electrochemical sensing platform for the detection of various analytes and therefore, this mingle system has huge

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analytical value and applications in the field of electrochemical sensing [21,22]. In extension to our recent efforts [23–25], the present study elucidates the construction of new electrochemical (voltammetric/potentiometric) sensors for selective Fe (III) ions determination based on newly synthesized ferrocene appended quinoline-triazole (FAQT) as electroactive receptor. To the best of our knowledge, the ferrocene (electroactive antenna), triazole (binding unit) and quinoline (optical antenna) assembly has been used for the very first time as an electrochemical/optical multi-signaling receptor system for selective detection of Fe (III) ions. In the present work, our primary aim is mainly focused on to explore the FAQT as a potential electroactive material for developing Fe (III) ion selective electrochemical sensors. However, the fluorescence/UV-visible techniques have been employed to confirm the binding behavior of Fe (III) ion toward FAQT. The developed voltammetric and potentiometric sensors have also been successfully applied to determine the Fe (III) ion content in various medicinal, agricultural and environmental samples matrices. The results obtained from developed sensors were compared with atomic absorption spectroscopy (AAS) and were found to be in good agreement. The smart analytical performance, simplicity, low cost, portability and reproducibility made these electrochemical sensors a promising analytical tool for quick, selective and onsite analysis of Fe (III) ions in various applications.

2. Experimental

2.1. Chemicals

All reagents used were of analytical grade and used without any further purification. Various plasticizers such as 2-nitrophenyl octyl ether (2-NPOE), bis(2-ethylhexyl) sebacate (DOS), 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, metal nitrates ($M^{n+} = K^+, Ca^{2+}, Fe^{2+}, Fe^{3+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+}, Pb^{2+}, Zn^{2+}$ and Hg^{2+}), electrolyte tetrabutylammonium perchlorate (TBAP), graphite rods (3 mm × 150 mm) and conducting polymer (Baytron P) were received from Sigma–Aldrich. The iron tablets (Limited Biotech Pvt. Ltd., New Delhi), iron injection (Aquatic Formulation India Ltd., Mumbai, India) and mix micronutrients fertilizer (Redox Industries Ltd., Ahmedabad, India) were obtained from local market of India whereas the steel industrial waste water (outlet) was obtained from Jai Bharat Steel Pvt. Ltd., Nalagarh, India for analysis of Fe (III) ions.

2.2. Electrochemical measurements

All electrochemical 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 counter electrode and Ag/Ag⁺ (0.1 M AgNO₃ in CH₃CN) as reference electrode, separated from the solution by a plug. The cyclic voltammetric (CV) and differential pulse voltammetry (DPV) measurements were carried out at a scan rate of 0.05 V s⁻¹, pulse amplitude of 0.05 V, pulse width of 0.05 s and pulse period of 0.08 s in the potential range of -0.4 to 0.6 V vs Ag/Ag⁺. 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 CH₃CN. The CH₃CN was used as the solvent and 0.01 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte for all the voltammetric measurements.

For the potentiometric studies, PVC based solid contact coated graphite ion-selective membrane electrodes (SC-CGEs) were constructed by same procedure as reported earlier [26,27]. The potentiometric measurements were carried out using the following electrochemical cell assembly:

Graphite	PEDOT/PSS	PVC	Test	Ag/AgCl,
Surface	Thin layer	Membrane	Solution	3M KCl

The potentiometric measurements were carried out in double distilled water by using the Equiptronics model EQ-602 potentiometer. The pH measurements were made using Elico LI model-120 pH meter. All the voltammetric and potentiometric experiments were performed in triplicate at 25 ± 1 °C.

2.3. Spectroscopic measurements

The emission and absorption spectra were recorded on Hitachi F-4600 and Shimadzu 1601 spectrophotometers, respectively. The emission spectra of ferrocene appended quinoline-triazole (FAQT) was recorded in the range of 370–500 nm at an excitation wavelength of 340 nm using an excitation emission slit width of 5 nm. The UV-vis. spectra were recorded in the range of 250–900 nm. All the fluorescence and UV-vis titrations were performed on 1.0 × 10⁻⁵ M and 3.0 × 10⁻⁵ M solution of FAQT in CH₃CN-H₂O, (9:1, v/v) buffered with HEPES, pH = 7.0, respectively. Each time a 3 mL solution of FAQT was filled in quartz cuvette (path length, 1 cm) to record each spectrum. The spectroscopic titrations were carried out in a manner similar to that of electrochemical measurements. All the spectroscopic experiments were performed in triplicate at 25 ± 1 °C.

2.4. Synthesis of FAQT

The synthesis of FAQT is depicted in Scheme 1a. The precursor 4-Azido-7-chloroquinoline **2**, was prepared by applying the method described by de Souza et al. [28], whereby 4, 7-dichloroquinoline was reacted with 2 equivalents of NaN₃ in anhydrous DMF at 65 °C for 6 h. Cu-promoted click chemistry of **2** with propargyl bromide afforded the corresponding 4-(4-bromomethyl-[1,2,3]triazol-1-yl)-7-chloro-quinoline **3** in good yields. Treatment of **3** with sodium azide in dry DMF at 60 °C led to the isolation of another click chemistry precursor 4-(4-azidomethyl-[1,2,3]triazol-1-yl)-7-chloro-quinoline **4**. Azide-alkyne cycloaddition reaction of **4** with ethynyl-ferrocene gave the desired 7-chloro-4-(4-[1,2,3]triazol-1-ylmethyl-[1,2,3]triazol-1-yl)-quinolin-ferrocene **5** in 88% yields. Yellow Solid; Yield: 88%; m.p. 187–189 °C. ¹H NMR (300 MHz, DMSO-d₆): δ 4.04 (s, 5H, Ferrocene-H); 4.30 (s, 2H, Ferrocene-H); 4.73 (s, 2H, Ferrocene-H); 5.88 (s, 2H, -CH₂); 7.77 (d, J = 9.0 Hz, 1H, H³); 7.86 (d, J = 4.2 Hz, 1H, H²); 7.99 (d, J = 9.0 Hz, 1H, H⁴); 8.28 (s, 1H, triazole-H); 8.30 (s, 1H, triazole-H); 8.94 (s, 1H, H⁵); 9.15 (d, J = 4.5 Hz, 1H, H¹); ¹³C NMR (500 MHz, DMSO) δ: 49.2, 71.8, 73.6, 74.8, 77.0, 122.0, 125.1, 125.8, 130.5, 131.1, 133.7, 134.0, 141.1, 146.0, 148.2, 151.5, 155.2, 157.3. HRMS calculated for C₂₄H₁₈ClFeN₇ [M+1]⁺ 496.0695 found 496.4100; Anal. Calcd (%) C, 58.15; H, 3.66; N, 19.78; Found: C, 58.05; H, 3.72; N, 19.86. The original spectra are given in S2–S5 of ESI†.

3. Results and discussion

3.1. Voltammetric sensing

The electrochemical properties of ferrocene appended quinoline-triazole (FAQT) have been investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in

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