



A Novel Chemosensor for Fe^{3+} Based on 2-(aminoquinolin-3-yl) methylene-4-nitrobenzohydrazide

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Abstract: New fluorescent chemosensor (E)-N''-((2-aminoquinolin-3-yl) methylene)-4-nitrobenzohydrazide the Schiff base ligand (SBL) have been designed and synthesized. The obtained SBL was characterized by spectroscopic techniques. The spectrophotometric titrations of SBL were investigated in acetonitrile (CH_3CN). The results showed that only Fe^{3+} ion show changes in spectra over other competing ions Al^{3+} , Cd^{2+} , Ca^{2+} , Co^{2+} , Cu^{2+} , Fe^{3+} , Fe^{2+} , Hg^{2+} , Pb^{2+} , Ni^{2+} , Mg^{2+} , Na^+ , K^+ and Mn^{2+} . After titration well defined isosbestic point is obtained which confirms formation of complex. The complex formation between SBL Fe^{3+} was found to be 1:2. This outcome is obtained on the basis of Job's plot. Thus SBL acts as good chemosensor for Fe^{3+} ion with high sensitivity and selectivity.

Keywords: Schiff base ligand, quinoline, colorimetric, chemosensor, iron

I. Introduction

In recent years the design and synthesis of chemosensor capable for recognition of metal ions or anion is an emerging field of research [1-4]. Transition metal ions play an important role in biological, physiological and environmental process. Out of these metal ions, iron is the most abundant heavy metal ion present in human body [5]. Large number of basic and essential biological processes in living organisms is depending on iron [6]. Haemoglobin contains an iron which carries transportation of oxygen to all the body parts. It is also present as part of a many catalytic site in several enzymes [7]. It is also observed that iron is actively involved in a number of physiological processes such as signal transduction, enzymatic reactions, respiration and oxygen transport in biological systems relying on its ability to activate molecular oxygen [8]. While the deficiency of iron leads to anaemia. Many reports suggested that either the deficiency or excess of iron produce various disorders. Research shows that high concentration of Fe^{3+} can causes neurodegenerative diseases including hemochromatosis, liver damage, Alzheimer's, Menkes and Parkinson's disease [9-11].

Hence, it is essential to develop precise Fe^{3+} selective sensors that can distinguish from other transition metal ions. Reports in literature reveals that numerous methods are available for detection of iron but these methods suffer through difficulty in synthesis and require laborious multistep organic preparations. Much attention is given for selective and sensitive determination of Fe^{3+} , but yet a huge demand for new sensor with improved properties, lower cost with high efficiency is needed. It is still remained a challenging field to develop chemosensor for selective and sensitive detection of Fe^{3+} in trace amount.

The current work focuses on recognition of Fe^{3+} ion and various analytical methods have been developed for its detection. Among all these methods, colorimetric method has attracted much attention due to its straight forward, fast measurement and less expensive instruments [12-16]. For detection of ions the receptor molecule requires a coordination sphere with donor atoms like N, S and O. It is also observed that coordination depends on the nature of metal ion and complexation ability of ligand in presence of other species having ability to form complex. For this purpose, we have designed and synthesized a schiff base from 2-amino quinoline 3-carbaldehyde and 4 nitro benzohydrazide.

Schiff base is a class of compound containing azomethine group which acts as good coordinating ligand. It shows convenient, fast and easy method for preparation and wide range of complexation with various metal ions [17-25]. The synthesized Schiff base, SBL, has coordination sphere which shows $-\text{NH}_2$ and carbazide group as binding site in quinoline and benzohydrazide molecule respectively. Whereas nitro group in the benzohydrazide acts as a chromophore. Thus introduction of these groups in SBL might be advantageous for recognition of Fe^{3+} ion. The sensing behavior of SBL was observed in CH_3CN . In the absence of metal ion the absorbance spectrum

of SBL shows band at 258 nm, 315 nm and 383 nm. By performing the titration of SBL with FeCl_3 in CH_3CN , the absorption band was remarkably changed. After titration well defined isosbestic point is obtained which confirms formation of complex between SBL and Fe^{3+} . The performed Job's plot of absorbance for SBL- Fe^{3+} system in CH_3CN clearly demonstrates a formation of 1:2 metal ligand stoichiometries. Thus SBL acts a good fluorescent sensor for Fe^{3+} ion with good sensitivity and selectivity over the other metal ions.

II. Experimental

A. Reagents and apparatus

All the reagents for the preparation of compound 3 (scheme 1), solvents and metal salts were purchased from Sigma-Aldrich and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker Avance II spectrometer operating at 400 MHz with chemical shifts in ppm in DMSO- D_6 and TMS as an internal standard. Mass spectra were obtained on water Q-TOF micro mass (LC-MS). Fluorescence spectra were recorded on Perkin Elmer model LS45 fluorescence spectrophotometer. UV-Vis spectra were recorded on Shimadzu UV 2450 spectrophotometer at room temperature using a quartz cuvette of 1cm path length and 5 nm slit width. Cyclic voltammetry measurements of the compounds in CH_3CN were conducted K_Lyte 1.2 series electrochemical analyser at room temperature. The electrolytic cell comprises three electrodes, the working electrode was a Pt, and the auxiliary electrode was Pt mesh and Ag/AgCl as reference electrode.

B. Synthesis and Characterization of *N'*-((2-aminoquinolin-3-yl) methylene)-4-nitrobenzohydrazide

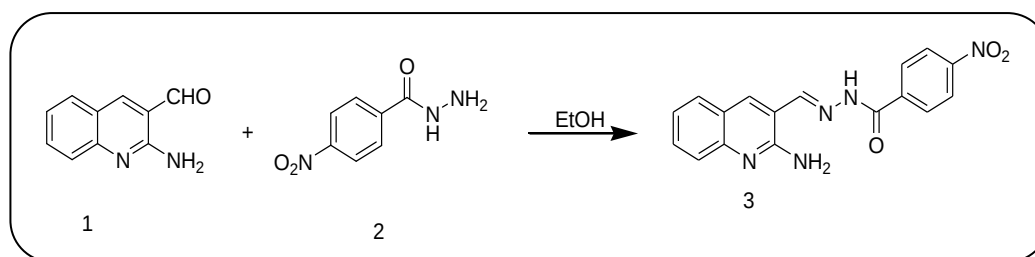
Compound 1 was obtained by following the reported procedure [26, 27]. Compound 2 was purchased from Sigma Aldrich and used as received. 2-amino quinoline 3 carbaldehyde (1mM) was dissolved in dry ethanol and then 4 nitro benzohydrazide (1mM) dissolved in dry ethanol was added to above solution. Reaction mixture was refluxed and confirmed by TLC. A yellow colored precipitate was obtained after 9 hr. The precipitate was then filtered and washed with hot ethanol and dried under vacuum to obtain (E)-*N'*-((2-aminoquinolin-3-yl) methylene)-4-nitrobenzohydrazide. The synthesis for compound 3 is represented in scheme 1. The product obtained was characterized by ^1H NMR, ^{13}C NMR and mass spectrometry. These recorded spectra are provided as a supplementary data.

(SBL)Yield 88.53% (Yellow powder).

^1H NMR (400 MHz, DMSO- d_6): 7.2(dt,1H,-CH), 7.5(dd,2H,-CH), 7.7(d,1H,-CH), 7.7(s,2H,-NH₂), 8.14(s,1H,-CH), 8.23(d,2H,-CH), 8.38(d,2H,-CH), 8.65(s,1H,-NH), 12.5(s,1H,-CH).

^{13}C NMR (400 MHz, DMSO- d_6): 161.49, 155.06, 149.35, 149.05, 147.81, 141.47, 138.57, 130.93, 129.21, 128.19, 124.91, 123.69, 122.27, 121.71 and 114.88.

LC-MS m/z calc. For $\text{C}_{17}\text{H}_{13}\text{N}_5\text{O}_3$:335, found: 336.1044



Scheme 1: Synthesis of Schiff base ligand "*N'*-((2-aminoquinolin-3-yl) methylene)-4 Nitrobenzohydrazide.

C. Testing and Calculating methods

a. UV-vis absorption

To determine the sensing properties of SBL, it was dissolved in dimethyl sulphoxide and then diluted with acetonitrile (99:1) to form 1mM solution. The solution of various metal ions like Al^{3+} , Cd^{2+} , Ca^{2+} , Co^{2+} , Cu^{2+} , Fe^{3+} , Fe^{2+} , Hg^{2+} , Pb^{2+} , Ni^{2+} , Mg^{2+} , Na^+ , K^+ and Mn^{2+} were prepared from its chloride salts in CH_3CN solvent of 1mM concentration. Working solutions of SBL and metal ions were freshly prepared from the stock solution of required concentration. All the UV-Vis experiments were carried out in CH_3CN solution. Any changes in the UV-vis spectra of SBL were recorded after the addition of chloride metal salts while the ligand concentration was kept constant in all experiments.

b. Calculation of binding constant

Binding constant was calculated according to the Benesi-Hildebrand equation¹. K_a was calculated following the equation stated below.

$$1/(A-A_0) = 1/\{K(A_{\text{max}}-A_0)[M]_n\} + 1/[A_{\text{max}}-A_0]$$

Here, A_0 is the absorbance of receptor in the absence of metal ions, A is the absorbance recorded in the presence of added metal ion and A_{max} is absorbance in presence of added $[M]_{\text{max}}$ and K is the association constant (M^{-1}). The plot between $1/(A-A_0)$ versus $1/[M]_n$, is a straight line and the slope obtained gives the value of the association constant (K_a). The association constant (K_a) was determined by UV-vis titration method for sensor with Fe^{3+} .

III. Results and Discussions

A. The response of UV-Vis absorption spectra

The chemosensing behaviour of receptor 3 with 14 metal ions (chlorides): Al^{3+} , Cd^{2+} , Ca^{2+} , Co^{2+} , Cu^{2+} , Fe^{3+} , Fe^{2+} , Hg^{2+} , Pb^{2+} , Ni^{2+} , Mg^{2+} , Na^+ , K^+ and Mn^{2+} was primarily investigated by using UV-vis and fluorescence measurements in acetonitrile solvent. SBL showed three peaks at 258 nm, 315 nm and 383 nm in absence of metal ions. As shown in Fig.1., after the addition of 1 equiv. of each metal ion, only Fe^{3+} ion show an increase in absorbance near 340 nm while other metal ions show negligible changes in the absorption spectra. These results show that SBL is highly sensitive and selective to Fe^{3+} in CH_3CN .

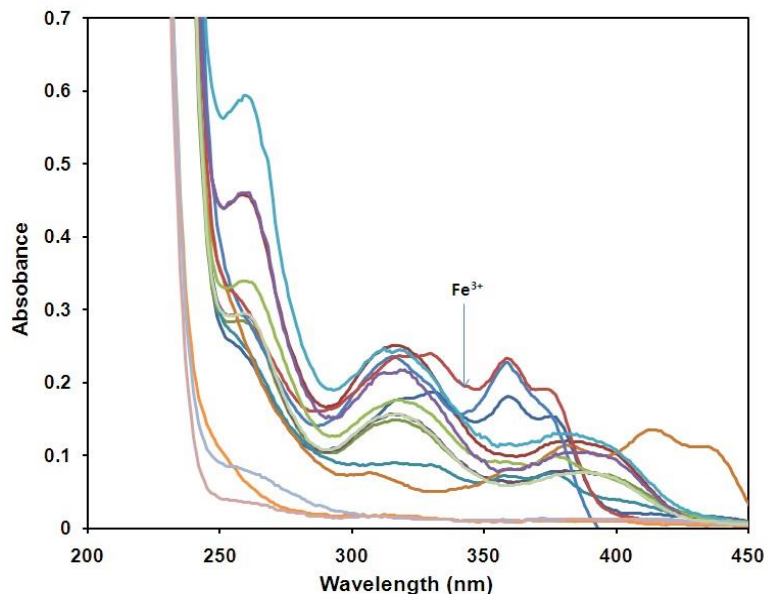


Figure 1. UV-vis absorption spectra of SBL ($1 \times 10^{-5}\text{M}$) in the presence of 5 equiv. of various cations ($1 \times 10^{-4}\text{M}$) in CH_3CN (9:1, v: v) solution at room temperature

To determine further the interaction between sensor SBL and Fe^{3+} , UV-Vis absorption spectra of SBL in CH_3CN was studied with addition of Fe^{3+} with various concentrations (0 to 100 equivalents). As shown in Figure 2a, a sharp increase in absorbance was observed at 365 nm. Three isosbestic points are observed at 342 nm, 382 nm and at 404 nm with increasing concentration of Fe^{3+} . This clearly indicates that SBL forms a highly stable complex with Fe^{3+} . The association constant for SBL- Fe^{3+} with Fe^{3+} was determined by UV-Vis method and found to be $2.080 \times 10^2 \text{ M}^{-1}$ (Fig.2b).

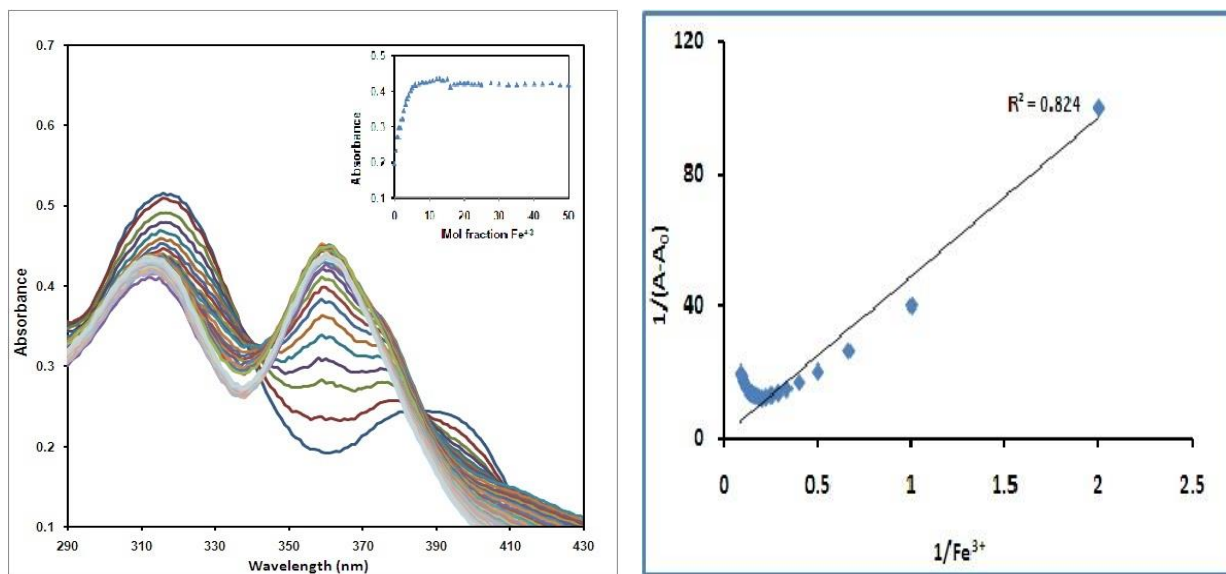


Figure 2 a) UV-vis spectral titration of SBL ($1 \times 10^{-5}\text{M}$) with Fe^{3+} (0 to 100 equivalents) in CH_3CN solution. Inset: absorption versus the mol fraction of Fe^{3+} added at 365 nm b) The relationship between the absorbance and the concentration of Fe^{3+} .

B. The response of fluorescence spectra

A fluorescence spectrum was further studied to know the interaction between sensor SBL and Fe^{3+} . By keeping SBL concentration constant Fe^{3+} ion solution was added from 0 to 20 equivalents and spectra was recorded. Figure 3 shows that addition of Fe^{3+} gradually decreases the fluorescence intensity. The maximum fluorescence intensity of the sensor decreased linearly with the increasing concentration of Fe^{3+} indicates strong complexation between SBL and Fe^{3+} .

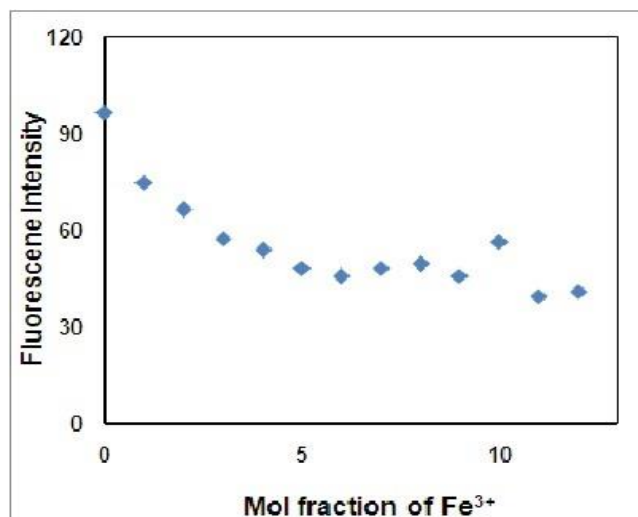


Figure 3. Fluorescence spectra of SBL (1×10^{-5} M, $\lambda_{\text{ex}}=220$ nm) after addition of increasing amounts of Fe^{3+} ion (0-20equiv.) at room temperature.

C. Selectivity of SBL towards Fe^{3+}

For the superior chemosensor, high selectivity plays an important role. To confirm the selectivity of sensor SBL, (E)-N'-((2-aminoquinolin-3-yl) methylene)-4-nitrobenzohydrazide was examined by colorimetric method during the addition of different metal ions. The selectivity of SBL as a colorimetric sensor for Fe^{3+} was investigated in the presence of different metal ions such as Al^{3+} , Cd^{2+} , Ca^{2+} , Co^{2+} , Cu^{2+} , Fe^{3+} , Fe^{2+} , Hg^{2+} , Pb^{2+} , Ni^{2+} , Mg^{2+} , Na^+ , K^+ and Mn^{2+} . Interference of various cations was examined by treating SBL with 10 equivalent of Fe^{3+} in the presence of 10 equivalents of other metal ions. A careful inspection of Fig.4 reveals that, the response of compound SBL for Fe^{3+} is influenced by any other competing metal ion. Present study reveals that SBL had very high selectivity towards Fe^{3+} than any other metal ions and hence SBL could be an excellent chemosensor for detection of Fe^{3+} .

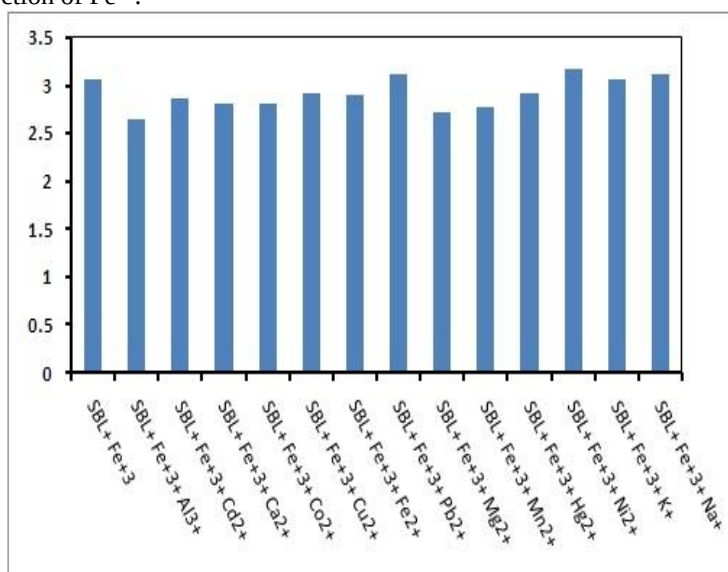


Figure 4. Competitive selectivity of SBL (1×10^{-5} M) toward Fe^{3+} (1×10^{-4} M) in the presence of other metal ions (1×10^{-4} M) (10 equiv.).

D. Electrochemical studies

To know electrochemical behavior of SBL after the titration of Fe^{3+} cyclic voltammetry was studied. The cyclic voltammogram of SBL + Fe^{3+} complex in CH_3CN solvent is depicted in Fig.5a the same voltammogram shows cathodic and anodic peak. As shown in Fig. 5a, oxidation peak potential of SBL increases from 0.759 V to 0.769

V and reduction peak potential decreases from -0.254 V to -0.301V respectively after the addition of Fe^{3+} (2.0 Equiv.). This confirms that after formation of complex SBL does not change its electrochemical structure and forms a stable complex with Fe^{3+} . Chemosensors forming reversible complexes is an important aspect in coordination chemistry. Electrochemical properties were studied by cyclic voltammetry to check the reversibility of SBL towards Fe^{3+} [28]. To know the reversibility of SBL towards Fe^{3+} , EDTA (1.0 mM, 2.0 Eq.) was added to complex of SBL+ 2 Eq. of Fe^{3+} . As shown in Fig. 5b, addition of EDTA generates the original spectra of SBL. This confirms removal of Fe^{3+} from coordination of SBL and indicating reversible complex formation.

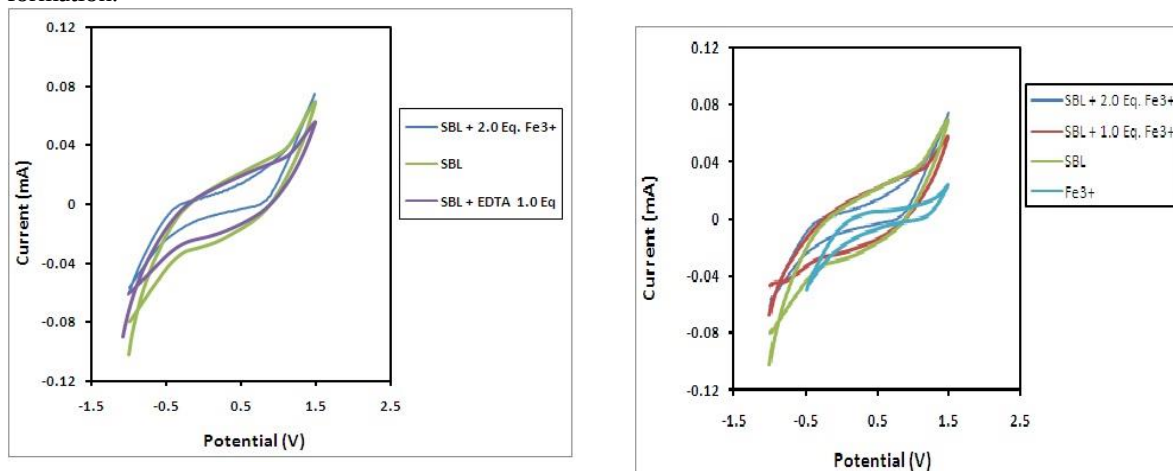
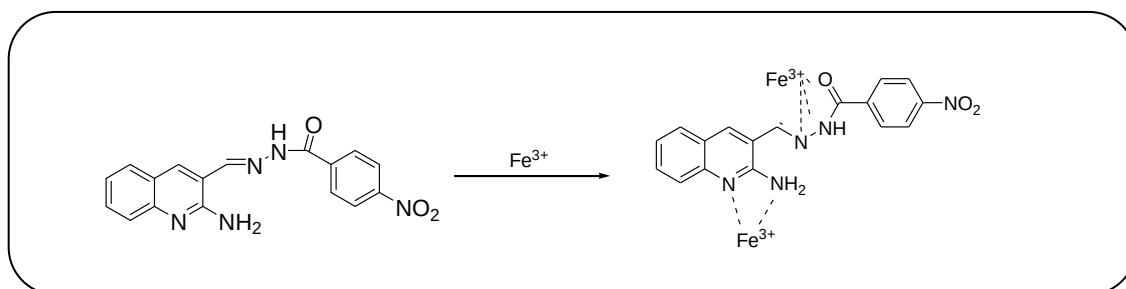


Figure 5. a) Titration of SBL with Fe^{3+} upto 2.0 equiv. using cyclic voltammetry and b) CV profiles of SBL, complex SBL+ 2 Eq. Fe^{3+} and SBL+ 2 Eq. Fe^{3+} with EDTA (2.0 Eq.) in CH_3CN solution.

E. Stoichiometry of complexation

Job's varian technique was used to determine the binding stoichiometry of complexation between SBL and Fe^{3+} [29, 30]. For Job's plot the sum of the concentration of Fe^{3+} and the receptor SBL was maintained and the mole fraction of Fe^{3+} varied from 0.1 to 0.9 then the absorbance spectra was obtained. (Fig. 6). Maximum absorbance was obtained at 0.4 mole fraction, indicating a 1:2 binding stoichiometry for the SBL- Fe^{3+} complex. The possible binding mode between SBL and Fe^{3+} is as shown below in Scheme 2.



Scheme 2. The possible binding model of SBL

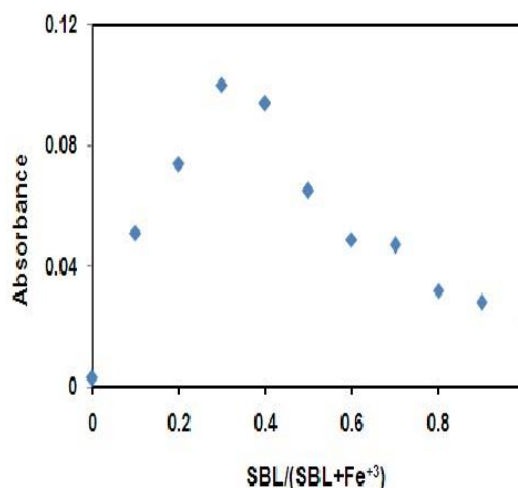


Figure 6. Job's plot between SBL and Fe^{3+} at 432 nm, indicating the 1:2 stoichiometry for SBL- Fe^{3+}

IV. Conclusions

In conclusion, a new Schiff base was designed and synthesized. Conformation of the synthesized compound is performed using ^1H NMR, ^{13}C NMR and mass spectrometry. The synthesized compound, SBL, shows high selectivity and sensitivity for Fe^{3+} and is able to detect this ion rapidly in CH_3CN solution. The 1:2 binding stoichiometry of SBL- Fe^{3+} complex was confirmed by the Job's plot analysis.

V. Acknowledgement

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VI. References

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