

Determination of Stability Constants of Iron(II) Complexes of *as*-Triazines Containing Ferriin-Yielding Chromogens

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Abstract

With the aim of determining stability constants of iron(II) complexes of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (PDT), 3-(2-pyridyl)-5,6-bis(*p*-methoxyphenyl)-1,2,4-triazine (PBMPT) and 3-(2-pyridyl)-5,6-bis(4-biphenyl)-1,2,4-triazine (PBBT), these organic reagents were prepared from commercially available relatively cheaper reactants. The absorptiometric characteristics of iron(II) complexes of these organic compounds; λ_{\max} and molar absorptivity (ϵ_{\max}) were determined. The composition and stability constants of these iron(II) complexes were determined by both molar ratio and Job's continuous variation methods. The mean logK values for iron(II) complexes of PDT, PBMPT and PBBT were found 16.48, 17.48 and 15.54 respectively reflecting the formation of very stable complexes. These are well comparable with the reported values for the iron(II) complexes of 2,2'-bipyridine, 1,10-phenanthroline, Ferrozine and Ferene. Higher sensitivity and stability constant values reflects the possibility of application of these compounds as promising chromogenic reagents for iron determination.

Keywords: Spectrophometric reagents, UV-visible Spectrophotometer, stability constant.

I. Introduction

Organic reagents play significant roles in determination of different metal ions spectrophotometrically because of their superiority over inorganic reagents which include sensitivity and selectivity. These reagents find many applications in the analytical chemistry of many inorganic species^{1,2}. The stability constant values of metal complexes are required for their application in different situations with high reliability. Examples of consideration of the stability constant values of complexes are the fields of meal extraction, nuclear energy industry, environmental, and industrial research etc³. Application of coordination compounds in medical science e.g. gadolinium-DTPA complex in MRI contrast enhancement requires stability constant data. The large stability constant value of this complex ensures the negligible concentration of free Gd^{3+} since it is very toxic. In designing metal ion buffers for use in biological systems and standardizing ion-selective electrodes stability constant data is required⁴.

The organic compounds containing ferriin functional group⁵ are widely used for the trace level determination of iron(II). 1,10-Phenanthroline is one of the well-known example and widely used for the determination of iron (II) ($\epsilon = 11,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 510 nm). The reported value of the stability constant (logK) for iron(II) complex of 1,10-Phenanthroline is 20.2-21.5^{6,7}.

Case and his co-workers⁸⁻¹¹ have reported the preparation of some *as*-triazines containing ferriin functional group. Schilt¹² has evaluated them as spectrophotometric reagents. Of these *as*-triazines, 3-(2-py)-5,6-diphenyl-*as*-triazine (PDT) has gained a great deal of popularity as a chromogenic reagent for the determination of iron despite the fact that its iron(II) chelate has comparatively lower molar absorptivity of 24000 at 555 nm¹³ compared to PPDT [3-(4-phenyl-2-py)-5,6-diphenyl-*as*-triazine]. However, the

stability constant of its (PDT) complex with iron (II) has not been reported yet.

A sulphonated derivative of PDT has been reported by Stookey¹⁴ which is readily soluble in water. Since its introduction in 1970, 3-(2-py)-5,6-bis(4-phenylsulphonic acid)-*as*-triazine, monosodium salt, monohydrate assigned the trivial name, Ferrozine, is being widely for iron determination. Gibbs¹⁵ has reported the details of synthesis of ferrozine, its purification and conditional formation constant of its iron(II) complex. Smith *et al.* have reported the synthesis of a very sensitive ferriin-yielding chromogen; 3-(2-py)-5,6-bis[2-(5-furylsulphonic acid)]-*as*-triazine disodium salt, dihydrate, assigned the trivial name, Ferene and the spectral characteristics of its iron(II) chelate. Ferene forms a tris-chelate with iron(II) in aqueous medium having absorptivity of $34,500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 593 nm. The reported value of the stability constant (logK) for Ferene-iron(II) complex is 14.9¹⁶.

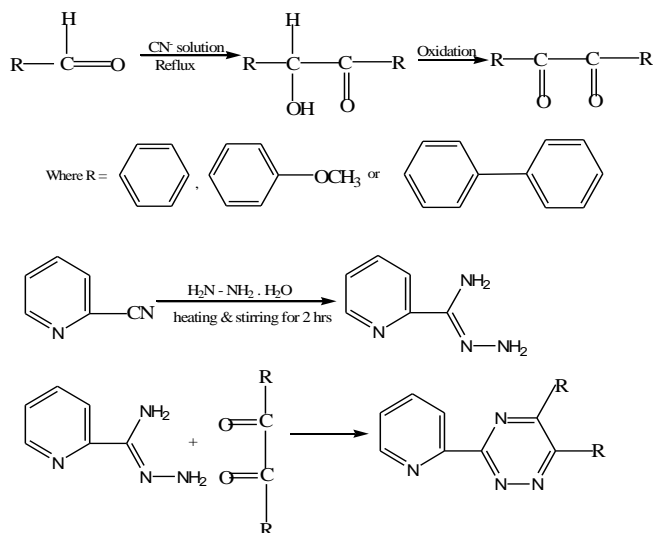
Searching for superior chromogenic reagents, Stephen and Islam¹⁷ have reported fourteen new *as*-triazines incorporating various appropriate substituents at 3-, 5- and 6- positions along with the chromophoric enhancement of the ferriin functional group due to different substituents at 5- and 6- positions of *as*-triazines. Recently three among the fourteen *as*-triazines have been successfully utilized for the determination of Fe(II) in different water samples spectrophotometrically¹⁸. However, the stability constants of iron(II) complexes of these *as*-triazines have not been reported by Stephen and Islam. Literature survey so far revealed that there is no report on the stability constant of iron(II) complexes of those *as*-triazines. Thus, there appears the scope of finding the stability constants of iron(II) complexes of these new promising spectrophotometric reagents. In this study, the conditional formation constants (stability constants) of iron(II) complexes of some *as*-triazines have been determined along with their composition and other spectrophotometric characteristics.

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II. Experimental

Preparation of 3,5,6-trisubstituted *as*-triazines

Three *as*-triazines; 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (PDT), 3-(2-pyridyl)-5,6-bis(*p*-methoxyphenyl)-1,2,4-triazine (PBMPT) and 3-(2-pyridyl)-5,6-bis(4-biphenyl)-1,2,4-triazine (PBBT) were prepared from commercially available relatively cheaper reagents following methods described in Vogel's text book of practical organic chemistry¹⁹ and of Stephen and Islam¹⁷ according to the following the reaction scheme.



Schematic diagram for synthesis of *as*-triazines.

Spectrophotometric examination of reaction of *as*-triazines with iron(II)

Reagents

Stock iron(II) solution

A standard stock iron(II) solution was prepared by dissolving 3.51 g of analaR grade Mohr's salt in small volume of distilled water and 5-mL concentrated H₂SO₄ was added before dilution to 500-mL with distilled water.

Iron(II) complexing reagent

A typical stock solution (0.005 M) of the organic reagents were prepared by dissolving required amount of PDT, PBMPT and PBBT in small volume of ethanol into three different 250-mL volumetric flasks respectively. The solutions were then diluted to required volume with ethanol. Further dilutions of the stock solutions were made for the required concentration of the reagents for spectrophotometric examinations.

Buffer solution

A buffer solution of pH 4.76 was prepared in a 500-mL volumetric flask by mixing of 250-mL 2M CH₃COOH solution and 250-mL 2M CH₃COONa solution.

Reducing agent

A 10% (w/v) solution of pure hydroxylamine hydrochloride was prepared by dissolving 25 g of the material in 250-mL volumetric flask with distilled water.

Apparatus

Ultraviolet-visible spectra were recorded in a double beam UV-1800, UV-visible Spectrophotometer, SHIMADZU, Japan. Rectangular glass cells of path length 1 cm were used throughout this investigation. A digital pH meter Mi 151, pH/ORP/Temperature Bench Meter, U.S.A was used for pH measurements in this research work.

Colour development procedure of iron(II) complexes of organic reagents

The iron(II) complexes of PDT, PBMPT and PBBT were prepared for spectrophotometric examination following general procedure:

5.0-mL of iron(II) solution was pipetted to a 25-mL volumetric flask and 2-mL of 10% (w/v) hydroxylamine hydrochloride, 5-mL of the organic reagent solutions, and 5-mL buffer solution of pH 4.76 were added. The contents of the flask were diluted to volume by adding ethanol. Spectra of all solutions were recorded against similarly prepared reagent blanks in the appropriate solvents.

The wavelengths of maximum absorbance, (λ_{\max}) of PDT-iron(II) and PBMPT-iron(II) and PBBT-iron(II) complexes were recorded. Specific absorptivity (a) and molar absorptivity (ϵ) of different iron(II) complexes at the wavelength of maximum absorbance calculated from the linear regression coefficient in terms of absorbance versus concentration were determined.

Determination of compositions and the conditional formation constants (stability constant) of iron(II) complexes of *as*-triazines

In this study, the stability constant and metal to chelates ratio were determined spectrophotometrically by both mole ratio and Job's continuous variation methods.

Mole ratio method

In this method, two types of runs were carried out. In the first, the concentrations of organic reagent were varied keeping the iron(II) concentration constant, and in the second, the conditions were reversed.

In the series in which the concentration of the organic reagent was varied, to each of 50-mL volumetric flasks 5.0-mL of standard iron(II) solution (keeping the concentrations of iron(II) constant at 4.475×10^{-5} M and 2.148×10^{-5} M), 2-mL of 10% hydroxylamine hydrochloride solution, 5-mL of buffer solution, followed by a varying amount (1-28-mL) of stock organic reagent solutions (5.0×10^{-4} M) were added in turn and then diluted to volume with ethanol. In the second run where the concentration of iron(II) was varied, to each series of 50-mL volumetric flasks were added in turn; 5.0-mL of reagent solutions keeping the

concentrations of organic reagents constant (at two different values) 2-mL of 10% hydroxylamine hydrochloride solution, 5-mL of buffer solution, followed by a varying amount (1-30-mL) of stock iron(II) solution (1.79×10^{-4} M) and then diluted to volume with ethanol. The absorbances of the different series of solutions were recorded at corresponding wavelengths of maximum absorbance (λ_{\max}). The absorbances were plotted against molar ratio of metal: 1/3 ligand or ligand: metal.

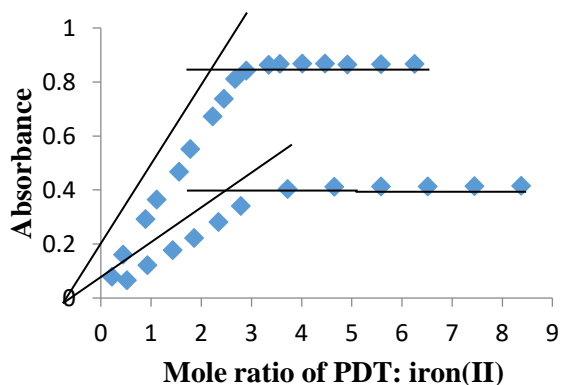


Fig. 1. Variation of PDT concentrations with iron concentration held constant at 4.47×10^{-5} M and 2.14×10^{-5} M.

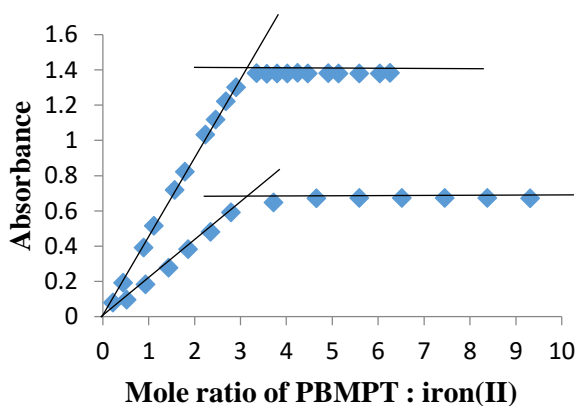


Fig. 2. Variation of PBMPT concentrations with iron concentration held constant at 4.47×10^{-5} M and 2.14×10^{-5} M.

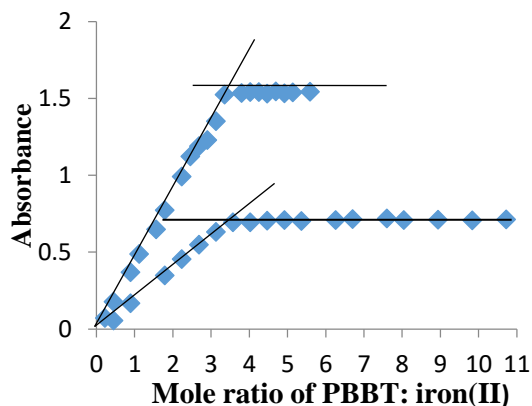


Fig. 3. Variation of PBBT concentrations with iron concentration held constant at 4.475×10^{-5} M and 2.237×10^{-5} M.

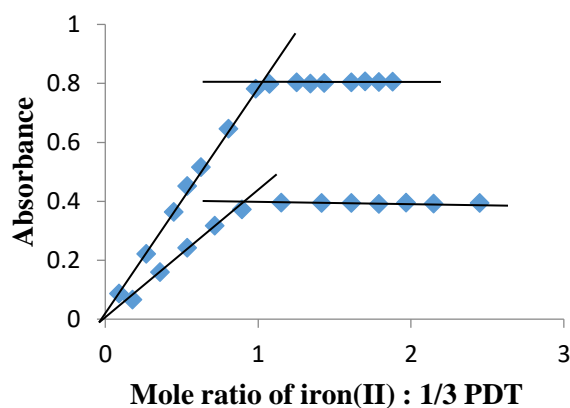


Fig. 4. Variation of iron concentration with PDT concentrations held constant at 1.20×10^{-4} M and 6.0×10^{-5} M

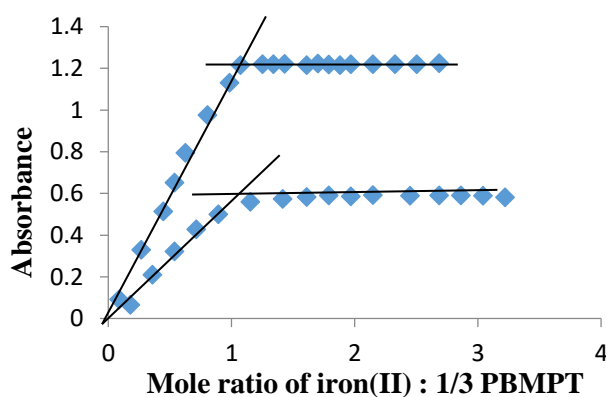


Fig. 5. Variation of iron concentration with PBMPT concentrations held constant at 1.20×10^{-4} M and 6.0×10^{-5} M.

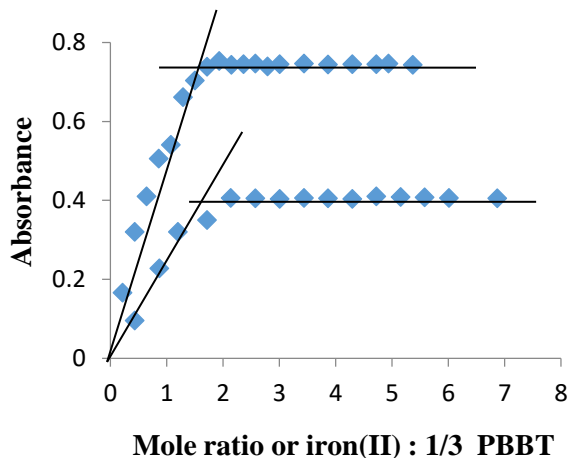


Fig. 6. Variation of iron concentration with PBBT concentrations held constant at 5.0×10^{-5} M and 2.5×10^{-5} M.

Job's Continuous variations method

This method was carried for the determination of compositions and stability constants of iron(II) complexes of different organic reagents. Various volumes of iron(II) and organic reagents solutions of equal molarity were mixed in a series of 50-mL volumetric flasks maintaining the total concentration at 1.79×10^{-4} M. The absorbances of these series of solutions were plotted against the corresponding mole fraction of iron(II). Results of this study are given in Figs. 7-9.

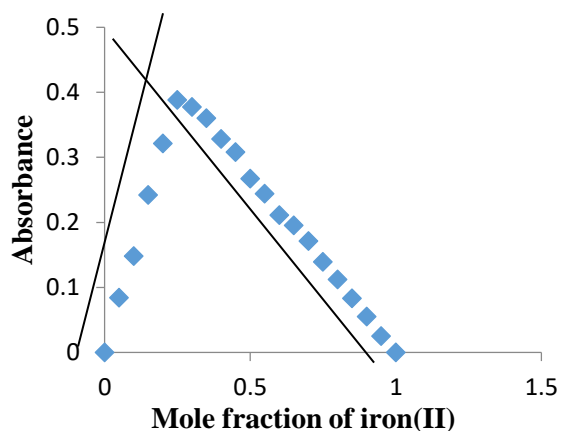


Fig. 7. Continuous variations of PDT and iron(II) concentrations keeping a constant value of 1.79×10^{-4} M.

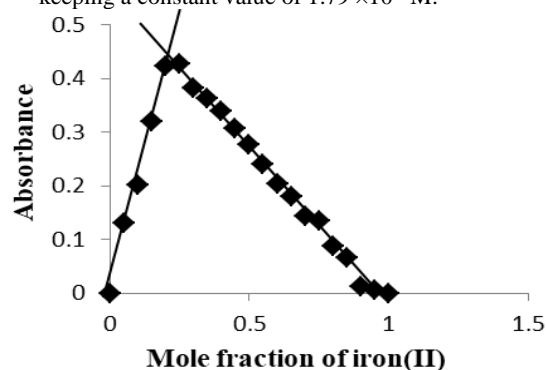


Fig. 8. Continuous variation of PBBT and iron(II) concentrations keeping constant total concentration of 1.79×10^{-4} M.

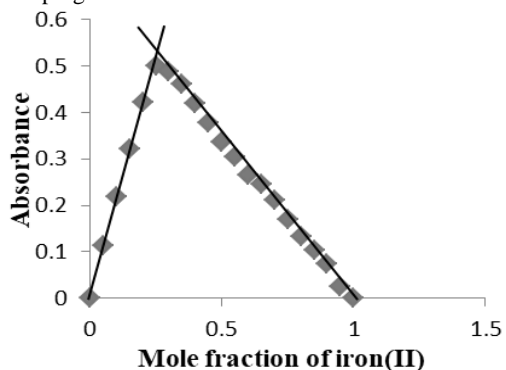


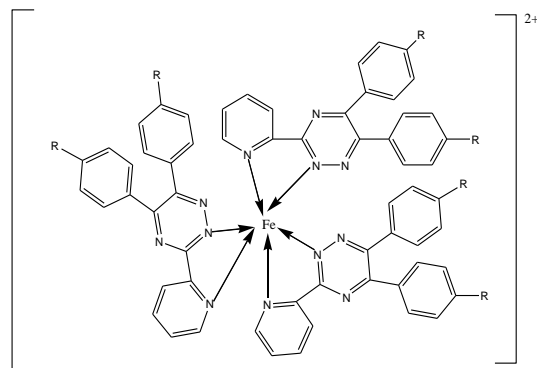
Fig. 9. Continuous variations of PBMPT and iron(II) concentrations keeping a constant value of 1.79×10^{-4} M.

III. Results and Discussion

The visible absorption spectrum of the iron(II) complexes of PDT, PBMPT and PBBT showed a single sharp peak with a maximum absorbance at 556, 561 and 566.5 nm respectively. The molar absorptivities of iron(II) complexes of PDT, PBMPT and PBBT at the wavelength of maximum absorbance in aqueous ethanol medium are $24,126 \text{ Lcm}^{-1}\text{mol}^{-1}$, $31,807 \text{ Lcm}^{-1}\text{mol}^{-1}$ and $31,800 \text{ Lcm}^{-1}\text{mol}^{-1}$ respectively. The spectral characteristics found in this investigation i.e., λ_{max} and molar absorptivity (ϵ_{max}) are almost similar to those of the reported values of Stephen and Islam¹⁷.

The stoichiometry of the iron(II) complexes of *as*-triazines; PDT, PBMPT and PBBT were determined by both molar ratio and Job's continuous variation methods. The results of this study are given in Figures 1-9. It is clear from these Figures that these ligands PDT, PBMPT and PBBT forming a tris-complex with iron(II) acting as a bidentate ligand.

Since excess reagents were required for complete complex formation it was possible to evaluate K, the stability constant values of iron(II) complexes by straightforward means. The stability constants values ($\log K$) of iron(II) complexes of PDT, PBMPT and PBBT were calculated following the methods of calculation of Gibbs¹⁵ and are summarized in Tables 1 – 3 respectively.



Schematic representation of the complex $[\text{FeL}_3]^{2+}$

Table. 1. Stability (conditional formation) constant for the tris(PDT)-iron(II) complex $[\text{FeL}_3]^{2+}$.

Conditions	$\text{Fe}^{2+}:\text{L}$ ratio	$[\text{FeL}_3^{2+}]^a$ (M)	$[\text{Fe}^{2+}]^b$ (M)	$[\text{L}]^c$ (M)	$\text{Log}_{10}K^d$
$[\text{Fe}^{2+}]$ constant at 4.475×10^{-5} M, $[\text{L}]$ varied	1:3	3.54×10^{-5}	9.30×10^{-6}	4.78×10^{-8}	16.54
$[\text{Fe}^{2+}]$ constant at 2.148×10^{-5} M, $[\text{L}]$ varied	1:3	1.62×10^{-5}	5.22×10^{-6}	3.92×10^{-6}	16.71
$[\text{L}]$ constant at 1.2×10^{-4} M, $[\text{Fe}^{2+}]$ varied	1:3	3.29×10^{-5}	1.52×10^{-7}	2.13×10^{-5}	16.35
$[\text{L}]$ constant at 6.0×10^{-5} M, $[\text{Fe}^{2+}]$ varied	1:3	1.61×10^{-5}	9.92×10^{-7}	1.20×10^{-5}	15.97
Continuous variations Both $[\text{Fe}^{2+}]$ and $[\text{L}]$ varied	1:3	1.60×10^{-5}	1.29×10^{-6}	5.70×10^{-6}	16.82

Mean value of the stability constant = 16.48

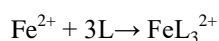
Table 2. Stability (conditional formation) constant for the tris(PBMPT)-iron(II) complex $[\text{FeL}_3]^{2+}$.

Conditions	$\text{Fe}^{2+}:\text{L}$ ratio	$[\text{FeL}_3^{2+}]^a$ (M)	$[\text{Fe}^{2+}]^b$ (M)	$[\text{L}]^c$ (M)	$\log_{10}K^d$
$[\text{Fe}^{2+}]$ constant at $4.475 \times 10^{-5}\text{M}$, $[\text{L}]$ varied	1:3	4.34×10^{-5}	1.35×10^{-6}	4.05×10^{-6}	17.68
$[\text{Fe}^{2+}]$ constant at $2.148 \times 10^{-5}\text{M}$, $[\text{L}]$ varied	1:3	2.04×10^{-5}	1.04×10^{-6}	3.12×10^{-6}	17.81
$[\text{L}]$ constant at $1.2 \times 10^{-4}\text{M}$, $[\text{Fe}^{2+}]$ varied	1:3	3.84×10^{-5}	1.64×10^{-6}	4.92×10^{-6}	17.29
$[\text{L}]$ constant at $6.0 \times 10^{-5}\text{M}$, $[\text{Fe}^{2+}]$ varied	1:3	1.85×10^{-5}	1.50×10^{-6}	4.50×10^{-6}	17.13
Continuous variations Both $[\text{Fe}^{2+}]$ and $[\text{L}]$ varied	1:3	1.67×10^{-5}	1.20×10^{-6}	3.60×10^{-6}	17.47
Mean value of the stability constant = 17.48					

Table 3. Stability (conditional formation) constant for the tris(PBBT)-iron(II) complex, $[\text{FeL}_3]^{2+}$.

Conditions	$\text{Fe}^{2+}:\text{L}$ ratio	$[\text{FeL}_3^{2+}]^a$ (M)	$[\text{Fe}^{2+}]^b$ (M)	$[\text{L}]^c$ (M)	$\log K^d$
$[\text{Fe}^{2+}]$ constant at $4.475 \times 10^{-5}\text{M}$, $[\text{L}]$ varied	1:3	4.25×10^{-5}	2.29×10^{-6}	1.27×10^{-5}	15.96
$[\text{Fe}^{2+}]$ constant at $2.237 \times 10^{-5}\text{M}$, $[\text{L}]$ varied	1:3	1.98×10^{-5}	2.56×10^{-6}	1.06×10^{-5}	15.81
$[\text{L}]$ constant at $5.0 \times 10^{-5}\text{M}$, $[\text{Fe}^{2+}]$ varied	1:3	1.52×10^{-5}	2.71×10^{-6}	4.43×10^{-5}	15.65
$[\text{L}]$ constant at $2.5 \times 10^{-5}\text{M}$, $[\text{Fe}^{2+}]$ varied	1:3	1.02×10^{-5}	1.60×10^{-6}	2.65×10^{-5}	15.17
Continuous variation Both $[\text{L}]$ and $[\text{Fe}^{2+}]$ varied	1:3	1.34×10^{-5}	4.47×10^{-7}	1.34×10^{-5}	15.10
Mean value of the stability constant = 15.54					

A typical calculation is given below:



^aCalculated using ϵ_{max} ,

$$[\text{Fe}^{2+}]^b = [\text{Fe}^{2+}]_{\text{initial}} - [\text{FeL}_3^{2+}]^a,$$

$$[\text{L}]^c = [\text{L}]_{\text{initial}} - 3[\text{FeL}_3^{2+}]^a$$

$$K^d = [\text{FeL}_3^{2+}]^a / [\text{Fe}^{2+}]^b [\text{L}]^c$$

The mean $\log K$ values obtained for iron(II) complexes of PDT, PBMPT and PBBT were 16.48, 17.48 and 15.54 respectively. These values are very high reflecting the formation of very stable complexes. These are well comparable with the reported values for the iron(II) complexes of 2,2'-bipyridine, (16.4-17.6) and 1,10-phenanthroline (20.2-21.5)^{6,7}, Ferrozine-15.6¹⁵ and Ferene-14.9¹⁶. Ferrozine is widely used for the spectrophotometric determination of iron. Easier way of synthesis of PBMPT from commercially available relatively cheaper reactants, higher sensitivity and stability constant values reflects that it would be a better reagent for iron determination.

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