Spectrophotometric, Solvent Extraction and Chelate Formation Study of Divalent Iron with Triazine in Presence of Large Excesses of Trivalent Iron.

I.H. HASHMI, I. ARAIN AND M. HANIF MEMON

Institute of Chemistry, University of Sind, Jamshoro, Pakistan.

(Received 7th April, 1981)

Summary: A comparative study of 4 substituted derivatives of symmetrical and unsymmetrical triazines as chromogenic reagents of the ferroin type has established 3-(2-pyridyl)-5, 6-diphenyl-1,2,4-triazine (PDT), as a highly sensitive and selective reagent for divalent iron present in association with large amount of iron (III). The ease with which the highly coloured metal ions can be extracted into immiscible solvent to give stable solution, makes this reagent useful for the determination of traces of Iron (II) present in a mixture of Iron(II) and Iron(III).

Introduction

The precise determination of iron(II) in microgram quantities present in association with relatively large amount of iron(III) has practical importance not only in steel corrosion investigation but also in the treatment of waste-waters from mining and steel industries.

The use of 4,7-diphenyl-1, 10-phenanthroline(batho) as a reagent for the determination of iron(II) in iron(II) and Iron(III) mixture has been proposed[1,2,3,4] with or without a masking agent (phosphate[3], pyrophosphate[4]) for iron(III). Fluoride has also been reported as a masking agent for iron(III) following a modification of the 1, 10-phenanthorline method[5], but this addition has not been widely accepted perhaps for the fear of interference by the fluoride[6]. However the use of fluoride for masking iron(III) by choosing proper working condition permits the convenient determination of iron(II) in a mixture of iron(II) iron(III)[7]

An attempt has been made to find a well characterised superior chromogenic reagent that costs substantially less than batho. Among the common extractable iron(II) spectrophoto metric reagents 2,4,6-tris-(2-pyridyl)-1,3,5-triazine(TPTZ), 3-(4-phenyl-2-pyridyl)-5,6-diphenyl-1,2,4-triazine(PPDT), 3-(2-Pyridyl)-5,6-(diphenyl)-1,2,4-triazine(PDT), and 2,4-bis(5,6-diphenyl-1,2,4-triazine-3yl)-pyridine were selected to evaluate their suitability as reagents for iorn(II) in presence of iron (III). Their advantages includes low cost, high sensitivity and applicability in a wide range of solutions[8]. The method described, provides the determination of 0.5 μg to 2.5 μg of iron(II) in presence of large excesses of iron(III).

Experimental.

Apparatus and Reagents.

All absorption spectra and absorbance measurments were recorded using SP 500 spectrophotmeter and silica cells of 1.0 cm optical path.

For all pH measurements a Pye Unicam model 292 pH meter, equipped with a glass-calomel electrode system was used.

Separating funnels of Squibb-type, made of boro silicate glass and of 100 ml capacity, preferably with 3.0 cm stems and less than 1.0 cm in outer diameter were used.

All chemicals were of AnalaR grade unless otherwise stated.

Standard iron(II) solution.

A stock solution containing 100 ug of iron(II) per ml was prepared by dissolving 0.3921 gram of ammonium iron(II) sulphate, $Fe.So_4\ (NH_4)_2\ SO_4.6H_2O$

(BDH) in 100 ml of water previously acidified with 2.0 ml of concentrated sulfuric acid, and diluted with water to 500 ml. Standard solutions containing 0.5 and 2.5 μg of iron(II) per ml were prepared by diluting 2.5 and 12.5 ml respectively of the stock solution to 500 ml with water containing 2.0 ml of concentrated sulfuric acid. Cover of carbon dioxide was maintained during further dilution as mentioned by Clark[2].

Ammonium fluoride solution 2.0 M.

It was prepared by dissolving 18.5 gram of ammonium fluoride in water, making the total volume upto 250 ml.

Chloroform.

Reagent grade, boiling range 60°C to 62°C.

Spectrophotometric reagents solutions.

These reagent grade chemicals were obtained from G.F. Smith Chemical Co., Columbus, Ohio, except TPTZ which was from BDH. It was essential to bubble carbon dioxide through the solution for 5 minutes. A cover of carbon dioxide was maintained above the solution.

TPTZ, 0.01%(w/v).

A 0.01% solution of TPTZ was prepared by dissolving weighed amount in water previously acidified with a few drops of concentrated sulfuric acid.

PDT, 0.01%(w/v).

The solution of this reagent was prepared by adding two drops of concentrated sulfuric acid to the required amount of the compound, followed by the addition of ethanol.

PPDT, 0.01%(w/v).

The solution of this chromogenic reagent was prepared by adding a few drops of sulphuric acid to the appropriate weighed compound followed by ethanol.

DTYP, 0.01%(w/v).

The solution was prepared by dissolving the required amount and adding a few drops of hydrochloric acid followed by ethanol.

Experimental.

Tests were conducted under ordinary laboratory conditions. The prepared solutions and the extracts were kept at room temperature and exposed to normal light. Clark's method[2] was used to prevent air oxidations of iron(II).

Identical results were obtained on comparing all the four ferroin reagents under similar conditions. They are discussed in generalized form and true for all the four cases.

Preliminary experiments revealed that no immediate colour reaction takes place at room temperature when an aliquot portion of the iron(II) present in association with relatively large excesses of iron(III) was mixed with an excess of ferroin reagent and ammonium fluoride. An intense colour appeared on prolonged standing, or such more rapidly when the reactants were treated with a few drops of ammonium hydroxide. Significant increase in the absorption was observed when varying amounts of sulfuric acid were added. However the absorbance remained constant where 1.0 ml or more of the 4.0 *M* sulfuric acid was added. The wave length of maximum absorbance and molar absorptivity values of chloroform solution, table-1, of the four complexes are not significantly different from those obtained in aqueous solutions in the total determination of iron.

When chromogenic reagent solution is added to a mixed solution of iron(II) and iron(III) without masking iron(III) with fluoride, the colour intensity increases with time. However, if the same reaction is carried out in complete darkness a very insignificant increase in the intensity of the resulting complex was observed even for more than 30 minutes. From that it appears that the increase in the intensity of the resulting complex is due to the photo reduction of iron(III) chelate. But the presence of fluoride is seen to stabilize the colour for more than an hour under diffused sunlight even at 1000 ug concentration of iron(III) per ml. The colour inten-

Table 1. Maximum wave length and molar absorptivity for four complexes of Iron(II) in Chloroform.

Reagent	λ Max/nm	Molar absorptivity/1 $mol^{-1}cm^{1}$
TPTZ	594 (593)	22,000 (22,100)
PDT	555 (555)	24,000 (24,500)
PPDT	560 (561)	28,500 (28,000)
DTYP	563 (565)	32,000 (32,000)

Values obtained in aqueous solution are given in parenthesis.

sity, however, increased with time when an old solution of chromogenic reagent was used. It is, therefore, advisable to prepare fresh solution of chromogenic reagent every week.

Effects of variables.

A systematic investigation was carried on variables like pH, excess of chromogenic reagent, strength and choice of masking agent, amount and concentration of acid, prior treatment of the iron(II) samples regarding their effect on the rate and completeness of formation of iron(II) complexes of above mentioned chromogenic reagents in presence of iron(III) ion in aqueous solution. This was done by preparing a series of solutions in which all but one variable were kept constant. The conditions used for colour development were those recommended in the standard procedure.

For these experiments 10.0 ml of iron(II) solution containing 1.0 μg of iron(II) per ml was mixed with necessary reagents. In all the experiments performed, the overall volume was maintained between 20-25 ml. 10 ml chloroform was used for extraction.

The data obtained for several of the variables is summarized in figure-1. Each curve merely indicates the completion of complex formation, due to any of the variable, since the procedure followed was not same throughout the process.

The optimum pH range for fast quantitative formation of complexes is 3.0 to 5.0, under the conditions of the method recommended Reactions at the more acidic pH 3.0 advantageously prevents hydrolysis of iron (III). If the pH is less than 3.0, the development of the colour proceeds very slow. However, variation in pH between 3.0 to 5.0 do not influence the intensity or hue of the coloured product produced.

It is apparent from fig-1, that the rate of the complex formation increases with the amount of chromogenic reagent added. The curve is seen to reach its maximum, at a chormogenic reagent to iron(II) ratio of about 25. to 1. The recommended 5 ml of ferroin reagent used in the standard procedure supplies a ratio of 30 to 1, when the sample contains 2.5 μg of iron(II) per ml and 150 to 1 for 0.5 μg of iron(II) per ml. This quantity is several times higher if iron(III) was not present. It is probably due to the formation of colourless mixed complexes of iron(III) with fluoride and ferroin reagent.

Several masking agents for iron(III) other than ammonium fluoride and dihydrogen phosphate were investigated. These includes acetates, citrates, tartarates and disodium EDTA, but none of these reagents seemed as effective as ammonium fluoride and dihydrogen phosphate at about pH 3.0. Fluoride was chosen for its

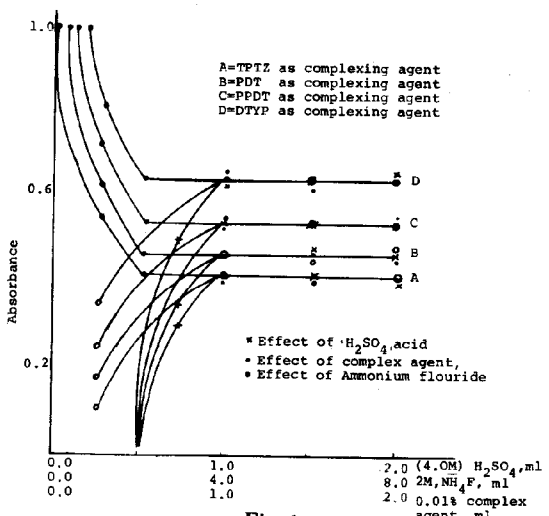


Fig. 1

higher solubility. A large excess of the fluoride has no effect on the colour development of the complexes (Fig. 1). This indicates that TPTZ, PDT, PPDT and DTYP chelates of iron(II) are quite stable towards fluoride substitutions.

It is seen from Fig. 1 that the intensity of the resulting complexes increases with the amount of sulfuric acid added. However the absorbance remains constant for an addition of 1.0 ml or more of 4.0 *M* sulfuric acid.

The effect of iron(III) ion on the system was studied by adding a solution of iron(III) to a sample containing 0.5 μg iron(II) per ml and developing according to the standard procedure. It is observed that the addition upto 1000 μg of iron(III) per ml has no effect on the determination of iron(II). If iron(III) concentration is higher than 1000 μg per ml then large quantities of acid, fluoride and complexing reagent needs to be added. The calibration curve however is not effected by the presence of iron(III) if proper conditions are used. The toleraence to iron(II) was considered as the maximum concentration which caused an error not greater than 0.005 in the absorbance reading of the sample.

Standard Procedure.

Transfer accurately measured aliquot of sample solution of appropriate strength (containing 0.5 to 2.5 μg of iron(II) and 1000 μg of iron(III) per ml) into 100 ml separatory funnel. Add 1.0 ml of sulfuric acid (4.0 *M*), 0.5 ml of ammonium fluride and 5.0 ml of spectrophotometric reagent. Add the reagents in the above order and swirl the solution after addition of each reagent. Insert a small piece of Congo red indicator paper into the solution and add dropwise concentrated ammonium hydroxide until the paper becomes raddish blue. The adjusted pH should be approximately 3.0.

Extract the solution with 10.0 ml of chloroform, immediately shake for one to two minutes at moderate rate, allow two layers to separate and become clear, withdraw chloroform layer into 10 ml volumetric flask and make the extract to 10.0 ml with ethanol. Measure the absorbance of the resulting solution in a 10 mm cell at wave length of their maximum absorbance against the reagent blank. Determine the iron(II) concentration from a calibration curve.

Order of the addition of reagents.

when fluoride is added before the spectrophotometric reagent, it helps to stabilize iron(III) against the complexing with PDT as well as it helps to keep iron(III) in aqueous phase. However, if the determination is carried out without fluoride, a higher value of abosorbance is obtained. This is probably due to the photo reduction of iron(III) chelate with PDT to iron(II) chelate. the effect of the time of exposure to direct sun light is shown in table-2. It is, therefore, advantageous to add the reagents as described in the standard peocedure.

Range and precision.

Standard procedure was adopted for obtaining the magneta iron(II) complex, which gave reproducible absorbance values for replicate iron(II) samples. A plot of absorbance v/s concentration in which the amount of iron(II) was varied from 0.5 to 2.5 μg of iron(II) per ml, gave a straight line passing through the origin.

The precision of the method was checked by studying values from 25 of the samples, all which had a final concentration the value of which is at near the cnetre of the optimum range. A standard deviation of 0.005 absorbance unit was obtained. This study was an attempt to measure the inherent precision of the method and was performed under recommended and non variant conditions.

Conclusion.

Although the results obtained for all the four chromogenic reagents are identical, the preparation of 0.01% solution of DTYP is tedious and time consuming due to its poor solubility in water or in any organic solvent. In case of TPTZ as complexing agent, two layers (i.e.aqueous and chloroform) takes fairly long time for separation. In addition TPTZ is hitherto[9] reported to form 2:1 and 3:1 complexes under certain restricted conditions. If these conditions are not maintained, which are difficult to maintain, then the formation of both type of the complexes takes place at a time. It is seen that PDT and PPDT are much more reliable and suitable reagents for the determination of iron(II) in presence of iron(III).

Table 2. Effect of the time to sun light before the addition of fluoride on the absorbance obtained.

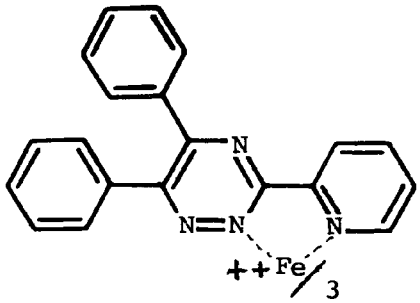
(Volume 10 ml, 2.5 ug Fe^{+2}, 1000 ug Fe^{+3})

S. No.	Time (In minute)	Absorbance for Iron (II) chelate of TPTZ	PDT	PPDT	DTYP
1.	0	0.228	0.234	0.288	0.325
2.	5	0.312	0.334	0.352	0.387
3.	10	0.398	0.405	0.424	0.456
4.	15	0.524	0.611	0.727	0.795

The tris(PDT)-iron(II) complex is highly soluble in water, ethanol, ethnol-water and propylene carbonate, whereas the perchlorate salt of the complex is soluble in chloroform, 1,1,1-trichloroethane, isoamyl alcohol and nitromethane. Since the coloured species is highly soluble in water and non-extractable into organic solvents, it was inferred that it is probably ionic in nature, and on the basis of its formula and spectral characteristic the $Fe(DPT)_3^{+2}$ ion probably has a structure very similar to that of the tris(2,2-bipyridine)-iron(II) ion, with three planer bidentate ligands coordinate to the iron ion, each with two nitrogen atoms bound to iron to form a five membered ring, and with all six nitrogens are in octahedral configuration about the central metal ion. In the case of PDT, the two most reasonable donor atoms for steric-free chelation are the pyridyl N-atom and the N-atom in the position 6 of the triazine ring. The intense absorptivity of the complex indicates that electron delocalization in the complex is pronounced, suggestive of a planer conformation for each ligand to provide electronic conjugation among its various rings. Thus the structure of $Fe(PDT)_3^{+2}$ may be depicted in abbreviated fashion as follows

Applications:

The spectrophotometric method described in this work was used to determine μg quantities of iron(II) in oxidation product from corrosion of iron and its alloys. Iron(II) was determined in chemical reagents. The procedure has also been applied in analysis of magnetite and other iron oxides.



References

1. Lee G.F. and Stumn W., *J.Am. Water Works Ass.*, 52, 1567 (1960).
2. Clark, L.J. *Anal. Chem.*, 34, 348. (1962).
3. Pollock, E.M. Ibid, 34, 394. (1962).
4. Mizuno, T. *Talanta*, 19, 369. (1972).
5. Verbeck, R. *Bull. Soc. Chem. Belg.*, 70, 423. (1960).
6. APHA, AWWA, WPCF, Standard Methods. 13th edn. p. 433, APHA. New York, 1971.
7. Tamura, K. Gots, K. Kotsuyanagi T. and Nagayama, M. *Talanta*, 21, 314(1974).
8. Hashmi, I.H. *Pak. J. Sci.*, 29, 91. (1977).
9. Hashmi, I.H. Ph. D Thesis, University of Exeter, (1977).