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Pyridine Thioamides as Analytical Reagents for Iron[1]

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Abstract. Thiopicolinamide and pyridine-2, 6-dithioamide were investigated as spectrophotometric reagents for iron. Both reagents form soluble blue colored species with iron (II) ion in basic solutions. The tris-thiopicolinamide-iron (II) complex exhibits a wavelength of maximum absorption at 615 mμ with a molar absorptivity of 13,600. The bis-pyridine-2, 6-dithioamide-iron (II) complex exhibits a wavelength of maximum absorption at 600 mμ with a molar absorptivity of 21,000. A sensitive method for the determination of iron based upon the latter complex is proposed.

INTRODUCTION

Compounds containing the ferrous grouping, -N-C-C-N-, have been widely used as reagents for the spectrophotometric determination of iron. The 2,2' - bipyridines and 1,10 - phenanthrolines have been especially useful for iron in solutions of pH 2 to 10 (8).

Among the phenanthroline derivatives, only Snyder's reagent, 4,7-dihydroxy-1, 10-phenanthroline, appears to be suitable for use in solutions having a pH greater than 10(6). This reagent forms a red complex with iron (II) even in solutions saturated with sodium hyroxide. However, color development is slow in solutions less than three molar in hydroxyl ion. Methyl-2-pyridyl-ketoxime has been found to form an intensely colored complex with iron (II) in strongly alkaline solutions (1). This 3:1 complex is red-violet in color, characteristic of iron (II) chelates with ligands containing the ferroin grouping. Although the complex forms immediately and is stable for more than 24 hours, cyanide, cooper (II), nickel (II), cobalt (II) and manganese (II) ions interfere seriously. Phenyl-2-pyridyl ketoxime also contains the ferroin grouping and forms a soluble red complex with iron (II) in alkaline solutions (7, 9). Aqueous solutions of the complex are unstable, however, and sensitive to strong light and variation in pH. Stable solutions may be obtained by a single quantitative extraction with isoamyl alchol, providing that a small amount of ethanol is added (9). In this case, however, the aqueous solution should not be less than two molar in hydroxyl ion concentration.

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While the pyridine thioamides may be considered as also containing the ferroin grouping, Hartkamp (2) found that alkaline solutions of thiopicolinamide and iron (II) are not red, but deep blue in color. Alternatively, pyridine thioamides may be thought of as having the same functional grouping found in dithiooxamide and its N-substituted derivatives, -N=C—C=S (7). Although the dithiooxamides have been studied extensively as reagents for copper, nickel and cobalt, very little attention has been given to the reactions with iron (II), especially in alkaline solutions. Nilsson (4) has reported that dithiooxamide gave a distinct blue color with iron (II) in solutions greater than one molar in hydroxyl ion concentration.

This study was concerned with the formation and stability of the iron (II) complexes of the pyridine thioamides. Pyridine-2, 6-dithioamide apparently has not been studied previously as a reagent for metal ions. The possibility of using pyridine-2, 6-dithioamide as a reagent for the spectrophotometric determination of iron in strongly alkaline solutions was investigated.

Experimental

Reagents and Apparatus. Thiopicolinamide, a yellow crystalline solid, was prepared from 2-cyanopyridine, ammonia and hydrogen sulfide, according to the procedure of Karrer and Schukri (3). The crude material obtained was recrystallized from absolute ethanol and had a melting point of 137°-138°C. (lit. 137 C.).

Pyridine-2, 6-dithioamide, the dithioamide of pyridine-2, 6-dicarboxylic acid, was obtained from K & K Laboratories (121 Express St., Engineers Hill, Plainview, N. Y.) and was used without further purification. This reagent darkened at 170°C when heated, and decomposed at 242-4°C.

Pyridine-2, 6-dithioamide was also prepared in this laboratory. A 25 g. sample (0.15 moles) of pyridine-2, 6-dicarboxylic acid was reflexed for 15 hours with 80ml. (1.1 moles) of thionyl chloride. Volatile material was removed by distillation and the white, solid acid chloride was dissolved in 200 ml. of dry ether. Dry ammonia gas was bubbled through the solution for 30 minutes and the insoluble diamide (M.P. 236-238°C) was removed by filtration. Six grams (0.036 moles) of the diamide was heated at 70°C for three hours with 35 ml. of pyridine (0.44 moles) and 5 ml. of phosphorus oxychloride (0.05 moles). After removal of pyridine by distillation, the residue was neutralized with aqueous sodium carbonate and the reaction product, 2, 6-dicyanopyridine, was extracted into chloroform. The chloroform extract was evaporated to dryness and the dicyano compound

was recrystallized from absolute ethanol. An ammoniacal solution of 2, 6-dicyanopyridine in methanol was treated with hydrogen sulfide gas for 30 minutes. The insoluble dithioamide was removed by filtration and recrystallized from acetone as an amorphous yellow solid.

Methyl cellosolve, 2-methoxyethanol, was purified by distillation from anhydrous calcium sulfate. The fraction boiling at 122°C was collected and used.

A stock solution of iron was prepared by dissolution of pure iron wire in hydrochloric acid. The solution was standardized titrimetrically with standard potassium dichromate solution.

Deionized water, used exclusively throughout this study, was prepared by passing distilled water through a Barnstead Bantam dimineralizer equipped with a standard 0802 Cartridge. All other chemicals used were of reagent grade quality.

Absorptimetric studies were made with a Cary Model 14 recording spectrophotometer. One centimeter matched silica cells were used for all measurements. Measurements of pH were made with a Beckman pH meter equipped with standard glass-calomel electrodes.

Preliminary Studies. The solubility of the reagents in a variety of solvent systems was investigated. Solubility was tested in most common water miscible organic solvents as well as in aqueous solutions at various pH values.

The reactivity of the reagents toward a series of transition metal ions was investigated. Aqueous solutions (25% by volume of methyl cellosolve) were prepared and analyzed spectrophotometrically. Each solution was 1.2×10^{-4} *M* in the specific metal ion and 6.0×10^{-4}*M* in the particular reagent.

Iron (II) *Complexes.* The iron (II) complexes of thiopicolinamide and of pyridine-2, 6-dithioamide were studied in great detail. The effects of the following variables were determined: concentration of reactants, pH, solvent, reducing agent, time, and diverse ions.

A mole ratio study was carried out on a series of solutions, 3.00×10^{-5}*M* in iron (II) and 1.0 - 24.0 x 10^{-5}*M* in thiopicolinamide. Each solution of 25 ml. volume contained 12 volume per cent of methyl cellosolve, 2.0 ml. of 0.5 M sodium hydroxide and 30 mg. of ascorbic acid. Solutions were measured spectrophotometrically at 615 mμ, the wavelength of maximum absorption. A similar series of solutions containing pyridine-2, 6-dithioamide as reagent was prepared and measured spectrophotometrically at 600 mμ.

The conformance of solutions of the iron complexes to Beer's

law was determined. A series of solutions 6.0 x $10^{-4}M$ in thiopicolinamide and 1.0 x 8.0 x $10^{-5}M$ in iron II, was prepared and analyzed spectrophotometrically. A similar series of solutions, 8.00 x 10^{-4} in pyridine-2, 6-dithioamide and 0.597 - 3.58 x $10^{-5}M$ in iron (II), was prepared and measured. Each 25 ml. volume of solution contained 3 ml of methyl cellosolve, 2 ml. of 0.5 *M* sodium hydroxide and 40 mg of ascorbic acid.

The pH dependence of the iron (II) complex of thiopicolinamide was determined on solutions containing 4.00 x 10^{-5} moles/liter iron (II), 6.00 x 10^{-4}moles/liter reagent, 30 mg ascorbic acid and 2 - 8 x 10^{-2}moles/liter sodium hydroxide. A second series of solutions, 3.58 x $10^{-5}M$ in iron (II) and 8.00 x $10^{-4}M$ in pyridine-2, 6 dithioamide, was prepared with sodium hydroxide concentrations of 0.02 - 1.0*M*. All solutions contained equivalent amounts of methyl cellosolve and ascorbic acid and were measured spectrophotometrically at regular intervals for a period of 36 hours.

A variety of reducing agents including ascorbic acid, hydroxylammonium chloride, and sodium hydrosulfite (sodium dithionite) were studied with the iron complexes. The effectiveness of a reducing agent was determined from the stability of the color intensities of the colored systems.

The effects of methyl cellosolve and of diverse ions upon the iron complexes were determined. Solutions were prepared containing 12 to 32 volume per cent of the nonaqueous solvent. Each solution was measured spectrophotometrically versus a reference system containing all constituents with the exception of iron. Diverse ions, 2-200 p.p.m. were added to solutions of the iron complexes containing 2.59 p.p.m. of iron. The absorbance values of the resulting solutions were recorded at 600 and 615 mμ for the thiopicolinamide and pyridine-2, 6-dithioamide systems, respectively.

The Nature of the Iron Complexes. The chemical constitution of the iron (II) complexes was determined from continuous variations and ion migration studies. For the continuous variations studies, equimolar stock solutions (5.00 x $10^{-4}M$) of iron (II) and the particular ligand under consideration were used. Series of test solutions were prepared in the usual manner and absorption spectra obtained.

Ion migration studies were varied out with a modified Hittorf transference apparatus. A solution of the complex was placed in the center compartment and aqueous solutions of pH12 were placed in the electrode compartments. The center compartment was isolated from the electrode compartments by medium porosity sintered glass disks to minimize transference by

connection. An average current of 75 ma was applied for 1 hour. The tris-1, 10-phenanthroline-iron (II) complex was studied under identical conditions as a reference system. Migration of the colored iron complex in a direction opposite to that of the ferroin complex indicated an anionic complex.

Results and Discussions

Thiopicolinamide and pyridine-2, 6-dithioamide were found to be soluble in acetone, dimethylformamide, dioxane, ethanol, and methyl cellosolve. Both compounds are readily soluble in dilute sodium hydroxide, but undergo hydrolysis slowly, in basic solution.

Because of its ease of purification, methyl cellosolve was used for the preparation of all stock solutions of the reagents. Such solutions remain stable for at least one month. Solutions of the reagents are pale yellow in color and do not absorb light at wavelengths longer than about 550 mμ.

The two thioamides react with transition metal ions to yield colored complexes. The reactivity of the reagents is summarized in Table 1. Although several metal ions form soluble colored

Table 1. Reactivity of the Reagents with Transition Metal Ions

Reagent Concentration: 6.00 x $10^{-4}M$
Metal Ion Concentration: 1.20 x $10^{-4}M$
in 0.040M sodium hydroxide

	Reagent	
Metal	TPA	PDT
Iron (II)	blue	blue
Cobalt (II)	yellow	yellow
Nickel (II)	ppt.	orange
Chromium (III)	green	green
Manganese (II)	ppt.	orange
Copper (II)	ppt.	colorless
Copper (I)[a]	ppt.	ppt.

[a] ascorbic acid added

species, only the iron complexes are intensely colored and worthy of further study.

The Iron (II) - Thiopicolinamide System. Thiopicolinamide forms a soluble blue complex with iron (II) in basic solution. A 6:1 excess of reagent to metal ion is sufficient for maximum color development. Color development is independent of solvent and hydroxyl ion in the range of 0.02-0.08 molar sodium hyroxide. Complex formation is slow with a 1½ hour period required for maximum color development. In the pressure of ascorbic acid, color intensity remains constant for a period of 24 hours.

The blue iron (II) thiopicolinamide complex exhibits a wavelength of maximum absorption at 615 mμ and a molar absorptivity of 13,600. Solutions of the complex conform to Beers'

law over the concentration range studied, 1.00-8.00 x $10^{-5}M$ iron.

A continuous variations study of the Iron (II)-thiopicolinamide system is represented in Figure 1. An absorbing species

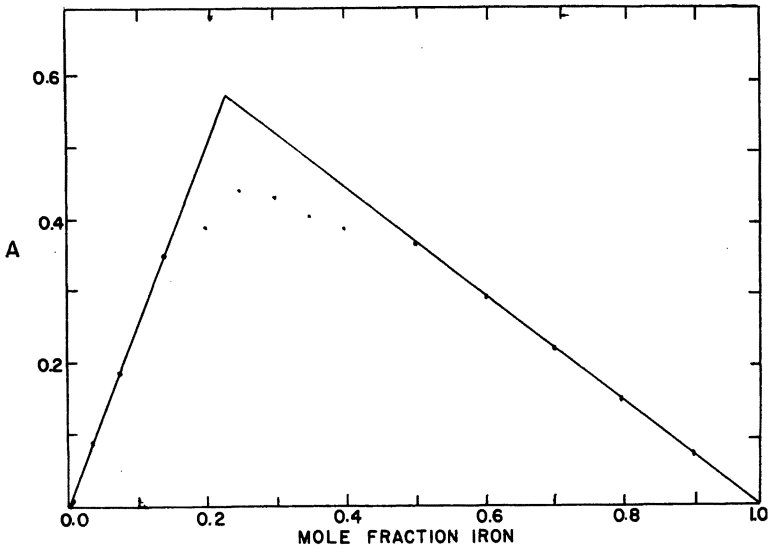

Figure 1. Continuous Variations Plot for the Iron (II); Thiopicolinamide System; Absorbance Values at 615 mμ

with a 3:1 ratio of ligand to metal ion is indicated from the continuous variations plot. It is expected that the metal ion would form a chelate complex with three molecules of the bidentate ligand. Since ion migration studies showed the complex to be negatively charged, it is assumed that the ligand enters the coordination sphere of the metal ion as a singly charged anion.

The Iron (II)-Pyridine-2, 6-Dithioamide System. Pyridine-2, 6-dithioamide reacts with iron (II) ion in basic solution to yield a soluble blue metal ion complex. In solutions of pH greater than 12, a 10:1 excess of reagent to metal ion is sufficient for maximum complex formation. Maximum color is developed within 15 minutes and is stable for a period of 2½ hours in the presence of ascorbic acid. Ascorbic acid appeared to be a more satisfactory reducing agent than sodium dithionite. Complex formation is independent of pH in the range of 11-14 and independent of methyl cellosolve concentration in the aqueous solutions. Methyl cellosolve was used to solubilize the difficulty soluble reagent.

The blue iron (II)-pyridine-2, 6-dithioamide complex exhibits

a wavelength of maximum absorption at 600 mμ with a molar absorptivity of 21,000. Absorption spectra of methyl cellosolve - water solutions of the complex are shown in Figure 2. Solutions of the complex conform to Beer's law over the concentration

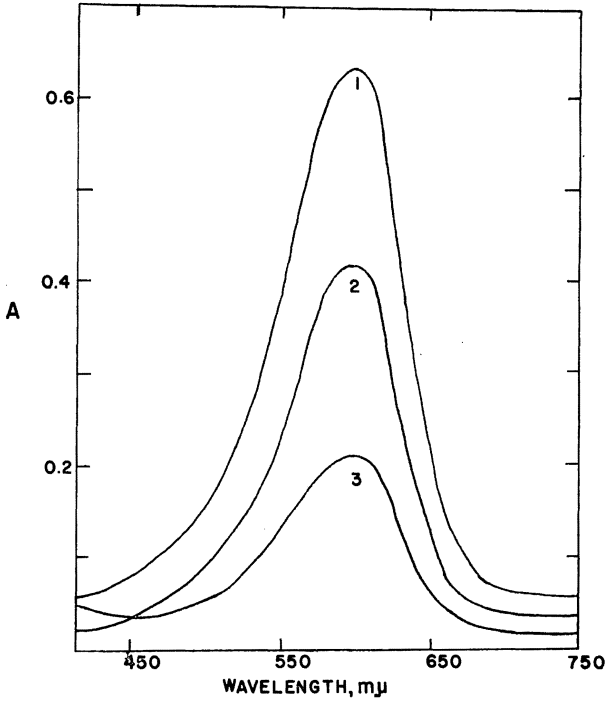

Figure 2. Absorption Curves of the Iron (II)- Pyridine-2, 6-Dithioamide Complex
Curve 1 3.00 x $10^{-5}M$ Fe (II)
2 2.00 x $10^{-5}M$ Fe (II)
3 1.00 x $10^{-5}M$ Fe (II)

range studied, .997 - 7.94 x $10^{-5}M$ iron.

A continous variations study of the iron (II) - pyridine-2, 6-dithioamide complex is represented in Figure 3. It can be seen that the stoichiometry of the absorbing species is a 2:1 ratio of ligand to metal ion. The reagent therefore acts as a tridentate ligand toward the metal ion.

Ion migration studies indicated that the complex is negatively charged. If it is assumed that the reactive form of the ligand is the divalent anion, the complex likewise exists as the divalent anion. It is proposed that coordination involves the metal ion, the nitrogen atom of the pyridine nucleus and the two sulfur atoms of the ligand. Complexation therefore results in the formation of four five-membered chelate rings.

The bis pyridine-2, 6-dithioamide iron (II) complex and the

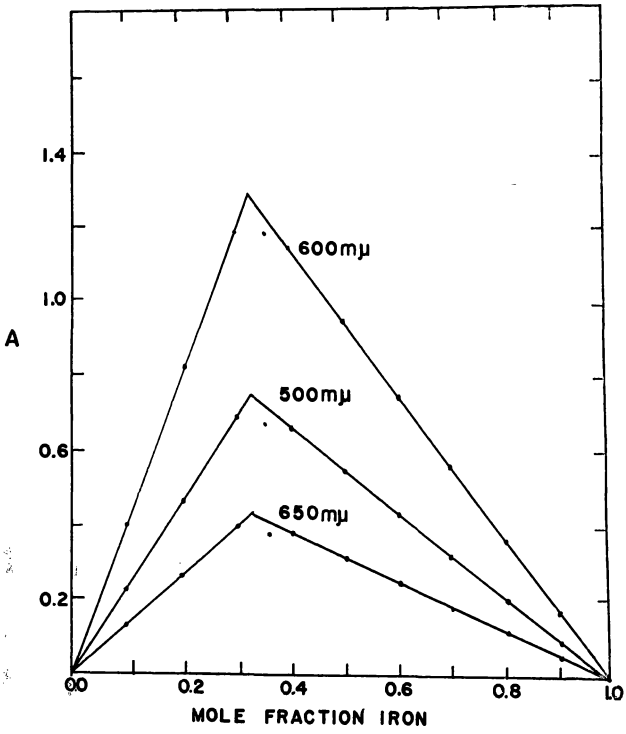

Figure 3. Continuous Variations Plots of the Iron (II)- Pyridine-2, 6-Dithioamide System

tristhiopicolinamide iron (II) complex are not extractable into non-aqueous solvents. The anionic complexes could not be extracted into isoamyl alcohol, ethyl acetate, chloroform, hexanol, or nitrobenzene even in the pressure of large amounts of tetramethylammonium bromide.

The iron (II)-pyridine-2, 6-dithioamide complex is not immune from the effects of diverse ions. The presence of other transition metal ions serves to bind reagent in the form of other complexes. Cyanide ion and reducible anions cause incomplete complex formations. The halide ions, citrate, perchlorate, phosphate, sulfate, tartrate, and thiocyanate ions do not interfere with the complex system.

Recommended Procedure for the Determination of Iron

Prepare a stock solution of the reagent by dissolving pyridine-2, 6-dithioamide in methyl cellosolve. The addition of a small amount of ascorbic acid will retard decomposition of the reagent.

To a liquid sample containing 10-100 micrograms of iron (II)

or iron (III) ion, add 50 millograms of ascorbic acid, 3 ml of 5 x $10^{-3}M$ reagent solution, and 2 ml. of 0.5 M sodium hydroxide solution. Dilute the resultant blue solution to 25 ml with deionized water. Measure the absorbance at 600 mμ versus a reference solution. The reference solution contains all components of the test solution with the exception of the sample aliquot. Calculate the amount of iron from a previously prepared calibration curve.

The results of analysis on selected samples are summarized in Table 2. The data show that the method is useful for the determination of small amounts of iron. The method is simple, sensitive, and exhibits a high degree of accuracy.

Table 2. Results of Iron Determination on Selected Samples

Sample	μg. Fe Taken	μg. Fe Found
S_1	13.6	13.4
S_2	41.0	42.0
S_3	68.4	69.4
S_4	95.8	96.8

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