Spectrophotometric Studies of the Nature of Several Iron-Pyridinecarboxylic Acid Complexes

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Weidel[1] and Skraup[2] first studied the coloring reaction between iron and pyridinecarboxylic acids. The determination of iron based on this reaction has since been reported by several workers[3-7]. We ourselves have previously reported[5-7] on the 1 : 2 complex formed in the solution by the interaction of metal

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[1] H. Weidel, *Ber.*, **12**, 1989 (1886).

[2] Z. H. Skraup, *Monatsh. Chem.*, **7**, 212 (1886).

[3] K. Shinra, K. Yoshikawa, T. Kato and Y. Nomizo, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **75**, 44 (1954).

[4] A. K. Majumdar and S. P. Bag, *Anal. Chim. Acta*, **21**, 324 (1959); **22**, 549 (1960).

[5] I. Morimoto, H. Oida and T. Hayashi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **82**, 203 (1961).

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[7] I. Morimoto and S. Tanaka, *Anal. Chim.*, **35**, 141 (1963).

ions with 2, 6-pyridinedicarboxylic acid or 2, 4, 6-pyridinetricarboxylic acid. Shinra et al.[3] and Rây and Banerjee[8] have suggested the formation of a 1 : 3 complex between the metal ions and 2-pyridinecarboxylic acid, while Majumder and Bag[4] have found a ratio of 1 : 2 for 2-pyridinecarboxylic acid or 2, 3-pyridinedicarboxylic acid. These are also some discrepancies among the conclusions reached by various workers on the composition of the complexes formed in solution by ferrous ions and pyridinecarboxylic acid. Also, the composition of the complexes formed by the iron with 2, 4-pyridinedicarboxylic acid or 2, 5-pyridinedicarboxylic acid is still obscure. For the present work, studies were made of the composition of the complexes formed in solution by the reaction between ferrous ions and several pyridine-2-carboxylic acids in the presence or absence of potassium cyanide and pyridine.

Experimental

Apparatus.—A Hirama photoelectric colorimeter was employed with 1 cm. cells for optical density measurement at room temperature. A Horiba-Hitachi model 3 pH meter was used for all pH determinations.

Iron Solution.—A standard solution was prepared by dissolving ferrous ammonium sulfate in twice-distilled water. Weaker solutions were prepared by diluting the standard solution.

Buffer Solution.—A Michaelis buffer solution and a 35% sodium acetate solution were used for the regulation of the pH value.

Hydroxylamine Hydrochloride Solution. — Ten grams of hydroxylamine hydrochloride were dissolved in 100 ml. of distilled water.

Reagent Solution. — 2-Pyridinecarboxylic acid, 2, 3-pyridinedicarboxylic acid, 2, 4-pyridinedicarboxylic acid, 2, 5-pyridinedicarboxylic acid, 2, 6-pyridinedicarboxylic acid, and 2, 4, 6-pyridinetricarboxylic acid were used. A 1/100 molar solution of each pyridinecarboxylic acid was used. 2, 5-Pyridinedicarboxylic acid was dissolved in 1 ml. of ammoniac water, and the solution was diluted with aliquots of water. Pyridine and a 0.1 N solution of potassium cyanide were used.

Procedure.—Aliquots of a standard ferrous solution were taken in 25 ml. flasks. To each flask, 1 ml. of the hydroxylamine hydrochloride solution, several milliliters of the reagent solution, a potassium cyanide solution or pyridine, a buffer solution, and water were added to make up the volume. The absorbance of the solution was measured at 420 and 460 mμ respectively.

Results and Discussion

Absorbance Curves. — The absorbance curves for the iron complexes in the ultraviolet range and in the visible range are shown in Figs. 1 and 2. In Fig. 1, curves 1, 2, 2′, 3, 4 and 4′ represent the absorbance of the colored complexes formed by 16 p. p. m. of iron in the absence of potassium cyanide; curve 5 represents the value with 8 p. p. m. of iron in the absence of potassium cyanide. Each of the solution of the complexes of pyridinecarboxylic acids has a maximum at 265∼280 mμ. These maxima of absorption may be the absorption of pyridinecarboxylic acids. In Fig. 2, curves

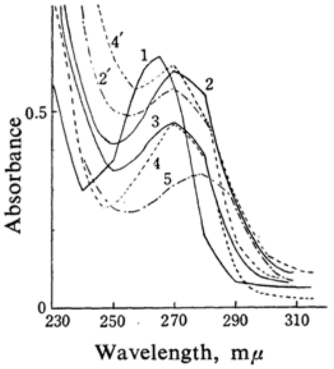

Fig. 1. The ultraviolet absorption spectra of the iron complexes.

1	2-Pyridinecarboxylic acid (pH 5.3)
2, 2′	2,4-Pyridinedicarboxylic acid (pH 3.9, pH 2.6)
3	2,3-Pyridinedicarboxylic acid (pH 5.1)
4, 4′	2,5-Pyridinedicarboxylic acid (pH 5.2, pH 2.9)
5	2,4,6-Pyridinetricarboxylic acid (pH 5.3)

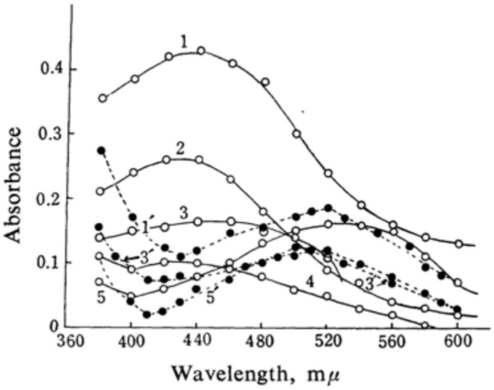

Fig. 2. The visible absorption spectra of the iron complexes.

----	In the presence of potassium cyanide
——	Without potassium cyanide
1, 1′	2-Pyridinecarboxylic acid (pH 5.3, pH 6.5)
2	2,3-Pyridinedicarboxylic acid (pH 5.1)
3, 3′	2,4-Pyridinedicarboxylic acid (pH 6.8, pH 6.4)
4	2,5-Pyridinedicarboxylic acid (pH 5.2)
5, 5′	2,4,6-Pyridinetricarboxylic acid (pH 5.3, pH 6.4)

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[8] P. Rây and B. Banerjee, *J. Indian Chem. Soc.*, 35, 297, 493 (1958).

1, 2 and 3 represent the absorbance, in the absence of potassium cyanide, of the colored complexes formed by 16 p.p.m. of iron; curves 1′, 3′ and 5′ represent the values obtained in the presence of potassium cyanide with 11 p.p.m. of iron. The complexes of pyridinecarboxylic acid have a maximum at 430∼530 mμ. In the presence of potassium cyanide, these complexes have a maximum at 500∼520 mμ.

Effect of Pyridine.—The authors frequently observed that the absorbance of the iron complexes was increased considerably by the addition of a small drop of pyridine⁹⁾. The results are shown in Fig. 3. In Fig. 3, curves 1, 2, 3 and 4 show the values obtained at pH 5.9 in the presence of 2 ml. of pyridine and 11 p. p. m. of iron.

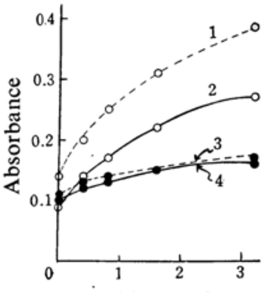

Fig. 3. The effect of pyridine on the iron complexes.
---- 2, 5-Pyridinedicarboxylic acid
—— 2, 4-Pyridinedicarboxylic acid
1, 2 at 372 mμ 3, 4 at 460 mμ

Nature of the Complexes in Solution. — The empirical formulas of the ferrous iron complexes were established by three independent methods: the continuous variation method of Job¹⁰⁾ modified by Vosburgh and Cooper¹¹⁾, the mole ratio method of Yoe and Jones¹²⁾, and the slope ratio method of Harvey and Manning¹³⁾. The results of these experiments are shown in Figs. 4—12. For Job's method, an equimolar solution (1/200 mol.) of iron and the reagent were taken in different quantities (total, 4 ml.) in 25 ml. flasks. The iron solution was mixed with 1 ml. of hydroxylamine hydrochloride, and the necessary amount of the reagent, 5 ml. of potassium cyanide, a buffer solution (pH 6.2∼6.3), and water were added to make up the volume. Curves 1 and 1′ in Figs. 4, 5 and 6 represent the results on the 2-pyridinecarboxylic acid and 2, 3-pyridinedicarboxylic acid, 2, 4-pyridinedicarboxylic acid, 2, 5-pyridinedicarboxylic acid, 2, 6-pyridinedicarboxylic acid and 2, 4, 6-pyridinetricarboxylic acid complexes systems respectively. Curves 3 and 3′ represent the results on each pyridinecarboxylic acid complex system without potassium cyanide. Curves 2 and 2′ represent those

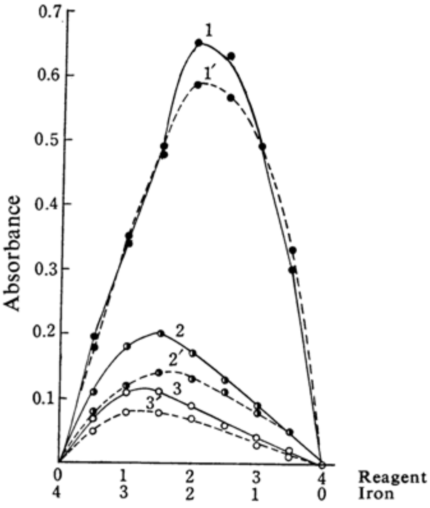

Fig. 4. The continuous variation method applied to the iron complexes at 460 mμ.
—— 2-Pyridinecarboxylic acid
---- 2, 3-Pyridinedicarboxylic acid
1, 1′ In the presence of potassium cyanide
2, 2′ In the presence of pyridine
3, 3′ In the absence of potassium cyanide

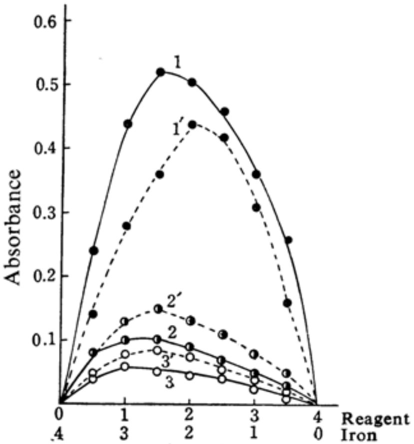

Fig. 5. The continuous variation method applied to the iron complexes at 460 mμ.
—— 2, 4-Pyridinedicarboxylic acid
---- 2, 5-Pyridinedicarboxylic acid
1, 1′ In the presence of potassium cyanide
2, 2′ In the presence of pyridine
3, 3′ In the absence of potassium cyanide

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9) I. Morimoto and K. Furuta, *Anal. Chem.*, **34**' 1033 (1962).

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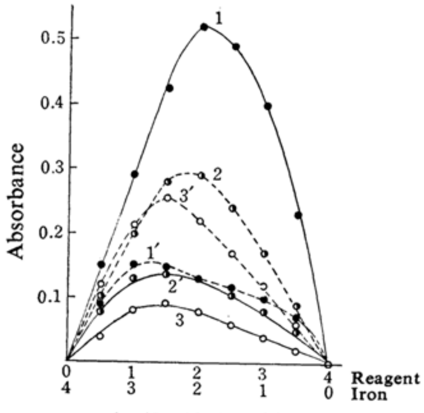
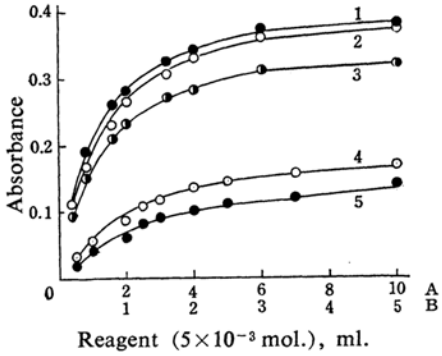


ml. (5×10^{-3} mol.)

Fig. 6. The continuous variation method applied to the iron complexes at 460 mμ.
—— 2, 6-Pyridinedicarboxylic acid
---- 2, 4, 6-Pyridinetricarboxylic acid
1, 1′ In the presence of potassium cyanide
2, 2′ In the presence of pyridine
3, 3′ In the absence of potassium cyanide

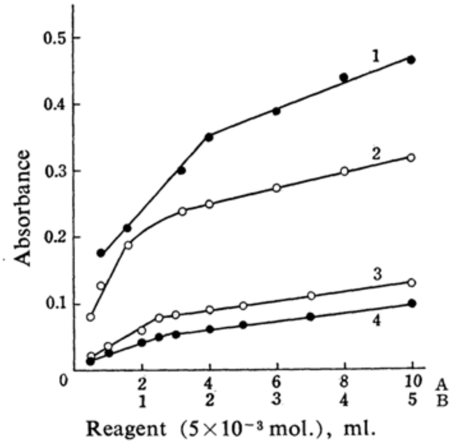
of pyridinecarboxylic acid in the presence of pyridine (2 ml.). 2, 4-Pyridinedicarboxylic acid is an exception. From the curves it can easily be inferred that, in the presence of potassium cyanide, the metal forms a 1 : 1 complex with these acids, whereas without cyanide and in the presence of pyridine, the ratio is always 1 : 2.

For the mole ratio method, the absorbance of the solution was obtained by adding various amounts of the organic acids and a fixed amount of potassium cyanide to a constant amount of iron; the results are shown in Figs. 7 and 8. Curves 4 and 5 in Fig. 7 and curves 3 and 4 in Fig. 8 were obtained by adding different amounts of the reagent (5×10^{-3} mol.) to 2 ml. of an iron solution of the same molarity and by adjusting the pH to 6.2, without adding cyanide. Curves 1, 2 and 3 in Fig. 7, and 1 and 2 in Fig. 8 were obtained by adding different amounts of the reagent (5×10^{-3} mol.) to 2 ml. of an iron solution of the same molarity and to 5 ml. of potassium



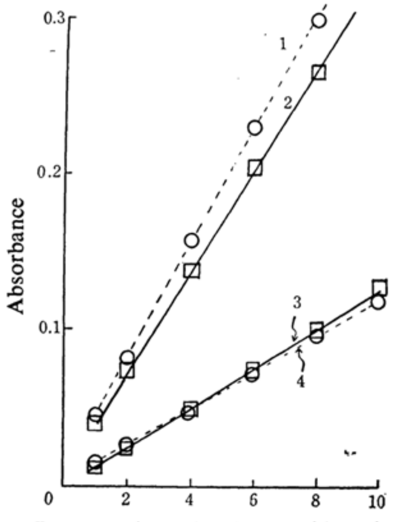
Reagent (5×10^{-3} mol.), ml.

Fig. 7. The mole ratio method applied to the iron complexes.
Axis A Without potassium cyanide
Axis B In the presence of potassium cyanide
2, 4 2-Pyridine carboxylic acid
1, 5 2, 3-Pyridinedicarboxylic acid
3 2, 6-Pyridinedicarboxylic acid
1, 2, 3 In the presence of potassium cyanide



Reagent (5×10^{-3} mol.), ml.

Fig. 8. The mole ratio method applied to the iron complexes.
Axis A Without potassium cyanide
Axis B In the presence of potassium cyanide
1, 4 2, 4-Pyridinedicarboxylic acid
2, 3 2, 5-Pyridinedicarboxylic acid
1, 2 In the presence of potassium cyanide
3, 4 Without potassium cyanide



Reagent, iron (1×10^{-3} mol.), ml.

Fig. 9. The slope-ratio method applied to the iron complexes at 420 mμ.
---- 2-Pyridinecarboxylic acid
—— 2, 3-Pyridinedicarboxylic acid
1, 2 Excess reagent
3, 4 Excess iron

cyanide and by adjusting the pH to 6.2~6.3. From these curves it can easily be inferred that, in the presence of potassium cyanide, the metal forms a 1 : 1 complex with 2-pyridinecarboxylic acid, 2, 3-pyridinedicarboxylic acid, 2, 5-pyridinedicarboxylic acid, and 2, 6-pyridinedicarboxylic acid, whereas without cyanide the ratio is always 1 : 2.

For the slope ratio method, two series of solution were used. In one series various amounts of a 5×10^{-4} mol. reagent solution were added to a constant amount of iron solution (2 ml. of 5×10^{-3} mol.), while in the other series, the amount of iron solution (5×10^{-4} mol.) was varied and that of the reagent solution was kept constant (5 ml. of 5×10^{-3} mol.). The results are shown in Figs. 9—12. The ratio of the slope of two straight lines supports the view that the complex formed without potassium cyanide contains the metal and the reagent in the ratio of 1 : 2. In the presence of potassium cyanide, the complex contained the metal and the reagent in the ratio of 1 : 1. In the case of 2, 4-pyridinedicarboxylic acid, the complex formed in the presence of potassium cyanide contains the metal and the reagent in the ratio of 1 : 2, while without potassium cyanide, it contains the metal and the reagent in the ratio of 1 : 3.

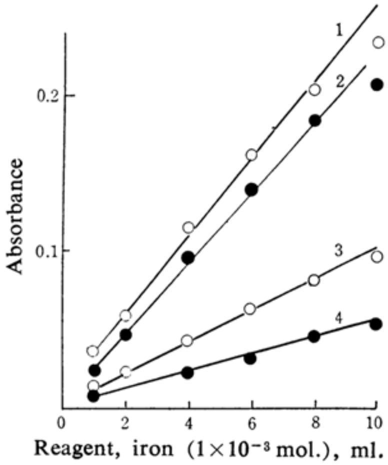


Fig. 10. The slope-ratio method applied to the iron complexes at 420 mμ.
1, 3 2, 5-Pyridinedicarboxylic acid
2, 4 2, 4-Pyridinedicarboxylic acid
1, 2 Excess reagent
3, 4 Excess iron

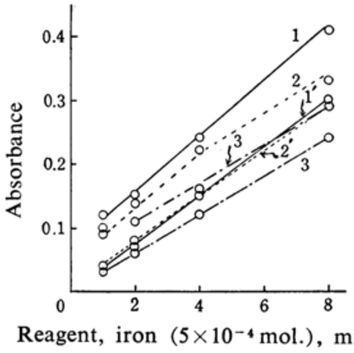


Fig. 11. The slope-ratio method applied to the iron complexes at 460 mμ.
—— 2-Pyridinecarboxylic acid
---- 2, 3-Pyridinedicarboxylic acid
·—· 2, 6-Pyridinedicarboxylic acid
1, 2, 3 Excess iron (2 ml. of 5×10^{-3} mol.)
1′, 2′, 3′ Excess reagent (5 ml. of 5×10^{-3} mol.)

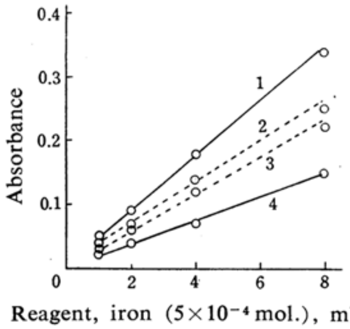


Fig. 12. The slope-ratio method applied to the iron complexes.
—— 2, 4-Pyridinedicarboxylic acid
---- 2, 5-Pyridinedicarboxylic acid
1, 3 Excess reagent (5 ml. of 5×10^{-3} mol.)
2, 4 Excess iron (2 ml. of 5×10^{-3} mol.)

With the exception of 2, 4-pyridinedicarboxylic acid, it was shown that, in the absence of potassium cyanide, iron in solution is associated with pyridine-2-carboxylic acids in a ratio of 1 : 2, while, in the presence of cyanide, the ratio is 1 : 1. The structure of the complexes, therefore, must be as shown in Fig. 13.

The degree of dissociation, α, and the stability constant, K, were calculated according to the equations of Harvey and Manning[12]. The degree of dissociation is given by $\alpha=(E_m-E_s)/E_m$, where E_m is the absorbance at

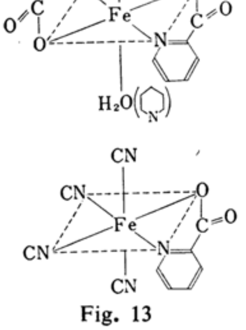


Fig. 13

TABLE I

Complex with	log K		
	With potassium cyanide (1/200 mol.)	Without potassium cyanide (1/200 mol.)	Without potassium cyanide (1/100 mol.)
2-Pyridinecarboxylic acid	3.3	3.8	3.4
2,3-Pyridinedicarboxylic acid	3.2	3.8	3.4
2,4-Pyridinedicarboxylic acid	5.0	4.9	4.5
2,5-Pyridinedicarboxylic acid	3.4	3.8	3.4
2,6-Pyridinedicarboxylic acid	3.3	3.6	3.0
2,4,6-Pyridinetricarboxylic acid	2.2	3.7	4.2

$15\pm2^\circ$C, $\mu=0.1$

460 mμ due to a given amount of metal ions being completely complexed with an excess of the reagent, and where E_s is the absorbance calculated for the same amount of the metal ions complexed with a stoichiometric amount of the reagent.

For 2-pyridinecarboxylic acid, the values for E_m and E_s are 0.377 and 0.276 for the complex with cyanide, and α is equal to 0.268; without cyanide, E_m and E_s are 0.197 and 0.055 respectively, and α is equal to 0.723.

The stability constant, K, of the complex is obtained by substituting the value of α in the equation $K=C(1-\alpha)/\alpha C(n\alpha C)^n$, where C is the concentration of the metal ions in moles per liter and n is the number of moles of the reagent required for complex formation with 1 mol. of the metal ions. Thus, for the complex with cyanide, $K=2.0\times10^3$, and for the complex without cyanide, $K=7.9\times10^3$. The results are given in Table I. From Table I, the value of log K for iron-pyridinecarboxylic acid complexes are concluded to be 3～5. When pyridinecarboxylic acids are used for the spectrophotometric determination of iron, it should be noted that the absorbance of the iron complexes is increased considerably by the presence of potassium cyanide.

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