17°, or in about sixty minutes at 20°. The fact that this salt is resolvable indicates that its complex ion is quite stable. The results in Table I show that the nickel atom in the complex ion exchanges at a measurable rate with the simple nickel ion in water solution. No attempt was made to establish the rate of this exchange under varying conditions. The observed interchange indicates that racemization of the optical isomers may be due to partial dissociation of the complex ion. This exchange of the nickel atom in the dipyridyl complex is interesting because Ruben, et al.,[5] found a slow exchange of iron atoms between ferrous ion and ferrous α,α'-dipyridyl ion, although the latter is diamagnetic so that no exchange was predicted.

Acknowledgments.—The authors wish to thank Dr. Truman P. Kohman who made helpful suggestions, Dr. J. L. McKibben who built the counting apparatus and operated the electrostatic generator for the preparation of the radionickel and Mr. Dave Frisch who also operated the generator. This work was supported in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

Summary

1. The nickel exchange of ten nickel coördination compounds was studied using Ni^{63} as the tracer. In the main the results, which are discussed in detail, show a satisfactory correlation with predictions of bond type based on other criteria.

2. bis-Methylbenzylglyoxime nickel, bis-methyl-n-butylglyoxime nickel, bis-N,N-di-n-propyldithiocarbamate nickel, bis-N,N-di-iso-amyldithiocarbamate nickel and bis-salicylaldehyde-ethylenediamine nickel was found not to exchange under the experimental conditions used in accordance with expectation based on the magnetic and other structural evidence for strong covalent bonds. The two dithiocarbamate compounds of nickel did, however, show exchange with nickel perchlorate in the presence of ammonia.

3. bis-Salicylaldehyde nickel and tris-ethylenediamine nickel chloride were found to exchange as predicted.

4. bis-Salicylaldoxime nickel and bis-salicylaldimine nickel, although diamagnetic in the solid state, were found to exchange. This is believed to be evidence that these compounds exhibit a change of bond type when dissolved in methyl cellosolve.

5. Although tris-α,α'-dipyridyl nickel chloride heptahydrate has been resolved into its optical isomers and was not therefore expected to exchange, it did exchange at a measurable rate. This may be connected with the racemization observed for this compound.

Reaction of Ferrous and Ferric Iron with 1,10-Phenanthroline. I. Dissociation Constants of Ferrous and Ferric Phenanthroline

By T. S. Lee, I. M. Kolthoff and D. L. Leussing

The intensely red colored complex of divalent iron and phenanthroline is used extensively for the colorimetric determination of iron and as an oxidation–reduction indicator. The dissociation constants of ferrous and ferric phenanthroline have hitherto not been determined, nor has a systematic study been made of the effect of acid on the dissociation of these complexes. Moreover, no study has been made of the kinetics of the formation and the dissociation of either complex. Such information is of general and especially of analytical interest.

The present paper is divided into three parts: (1) the basic strength of phenanthroline, (2) dissociation of "ferroin" (the ferrous phenanthroline complex) and (3) the dissociation of "ferriin" (the ferric phenanthroline complex).

In a subsequent paper the kinetics of formation and dissociation of ferroin and ferriin will be discussed.

Experimental

Materials Used.—1,10-Phenanthroline ("ortho-phenanthroline") monohydrate was obtained from the G.

Frederick Smith Chemical Co. The phenanthroline content of several different samples of this compound was found by conductometric titration with acid to be 100 ± 1% of theoretical. Standard solutions of phenanthroline and phenanthrolium chloride were prepared by dissolving the calculated amount of phenanthroline in water or in standard hydrochloric acid.

Standard solutions of the following compounds were prepared from analytical reagent chemicals and standardized by accepted procedures: ferrous sulfate, sulfuric acid, hydrochloric acid, ceric sulfate and potassium chloride.

Potentiometric Titration of Phenanthroline with Hydrochloric Acid.—One-hundredth M phenanthroline solution in water was titrated at room temperature with 0.2 N hydrochloric acid. The pH was measured with a glass electrode (Leeds and Northrup pH Meter, Model No. 7661).

Determination of pH of Mixture of Phenanthrolium Chloride and Phenanthroline.—Solutions were prepared which were 0.0200 M in phenanthroline, 0.0100 M in hydrochloric acid, and 0.001, 0.010, 0.100, 0.500 or 1.00 M in potassium chloride. The pH of these solutions was measured at 25 ± 0.1° with the apparatus described above.

Conductometric Titration of Phenanthroline with Hydrochloric Acid.—One hundredth M phenanthroline solution in water was titrated with 0.2 N hydrochloric acid. The titration was carried out at room temperature in a titration conductance cell with freshly platinized elec-

trodes. The conductance bridge used was model RC-1B, Industrial Instruments, Inc.

Conductometric Determination of the Acid Dissociation Constant of Phenanthrolium Ion.—The equivalent conductances of the following solutions were determined: (1) 0.00100 M in phenanthroline and 0.00100 M in hydrochloric acid, (2) 0.0060 M in phenanthroline and 0.00100 M in hydrochloric acid and (3) 0.00100 M hydrochloric acid. The temperature of the solutions was maintained at 25 ± 0.1°. The cell constant was determined with 0.01 M hydrochloric acid using the value 412.0 for the equivalent conductance of this solution.[1]

Determination of Ferroin in Equilibrium Mixtures of Phenanthroline, Ferrous Sulfate and Sulfuric Acid.—Equilibrium mixtures were prepared by pipetting the appropriate quantities of reagent solutions into volumetric flasks and diluting to the mark. The reaction mixtures were allowed to stand in a thermostat at 25 ± 0.1° for one or two days, after which time equilibrium had been established. A portion of the solution was removed and the extinction of the solution was measured at 500 mμ with a Beckman Model DU Spectrophotometer. The concentration of ferroin was found by comparing the extinction with that on a calibration curve determined with known concentrations of ferroin. The extinction of ferroin was found to be unaffected by ionic strength, at least up to a value of 1 M (sodium sulfate used as the electrolyte).

Measurement of E. m. f. of the Cell $Au|Fe^{++}$, Fe^{+++}, $H_2SO_4|FePh_3^{++}$, $FePh_3^{+++}$, $H_2SO_4|Au$ **(Ph denotes phenanthroline).**—One of the half cells consisted of a gold electrode immersed in a solution $2.5 \cdot 10^{-3}$ M in ferrous sulfate, $2.5 \cdot 10^{-3}$ M in ferric sulfate and a M in sulfuric acid. The other half cell consisted of a gold electrode and a solution $2.5 \cdot 10^{-3}$ M in ferrous phenanthroline sulfate, $2.5 \cdot 10^{-3}$ M in ferric phenanthroline sulfate and a M in sulfuric acid. This solution was prepared by adding ferrous phenanthroline sulfate to the calculated quantity of ceric sulfate (of known sulfuric acid content) and sulfuric acid solution. The two half cells were connected by a bridge containing a M sulfuric acid. The concentrations, a, of sulfuric acid used in different experiments were 0.05, 0.5, 1, 2 and 8 M. The temperature of the cell was maintained at 25 ± 0.1° by means of a thermostat. The Leeds and Northrup instrument mentioned above was used to measure the E. m. f. The E. m. f. of the cell was found to vary with time due to the slow dissociation of ferroin and ferriin in the acid solution. The E. m. f. of the cell at zero time (time of addition of ferroin to sulfuric acid and ceric sulfate) was found by plotting E. m. f. against time and extrapolating to zero time.

Acid Strength of Phenanthrolium Ion.—Although the phenanthroline molecule possesses two basic nitrogen atoms it was found to combine with only one proton in acid solution The reason for this is that the nitrogen atoms are separated by a distance of only about 2.5 Å. and occupy such positions in the molecule that electrostatic or steric forces or both prevent two protons from combining with the phenanthroline (see Fig. 1).

The experimental points obtained in a potentiometric titration of phenanthroline with hydrochloric acid are plotted in Fig. 2. A relatively large change in pH occurs in the region corresponding to approximately one mole of acid per mole of phenanthroline. Little change in pH occurs in the region corresponding to approximately two moles of acid per mole of phenanthroline. The drawn curve in Fig. 2 is the theoretical curve calculated for the titration of phenanthroline with acid assuming that phenanthroline is a mono-acid base

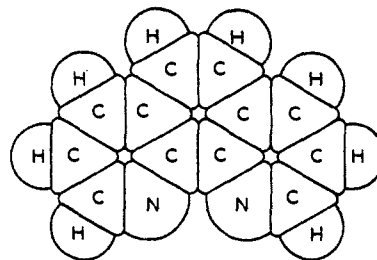(1) T. Shedlovsky, THIS JOURNAL, **54**, 1411 (1932).

Fig. 1.—Fisher-Hirshfelder-Taylor steric model of 1,10-phenanthroline. All atoms of the phenanthroline molecule lie in the same plane.

and that the dissociation constant of the phenanthrolium ion is 1.1×10^{-5} (see below). It is seen that the calculated curve agrees with the experimental data.
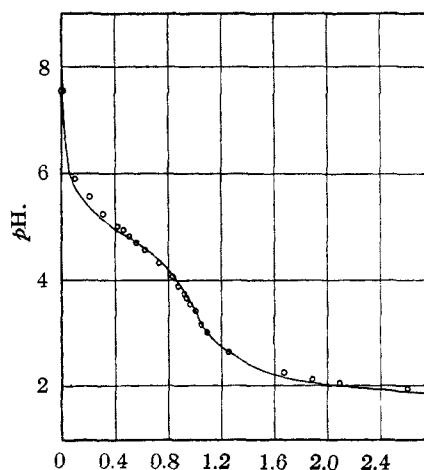

Fig. 2.—Potentiometric titration of phenanthroline with hydrochloric acid (curve is calculated, dots are experimental points).

The acid constant of the phenanthrolium ion K_A was determined potentiometrically by measuring the paH (hydrogen ion activity) of solutions which were 0.01 M in phenanthroline and 0.01 M in phenanthrolium chloride, and which contained potassium chloride at various concentrations. The results are given in Table I.

TABLE I

DEPENDENCE OF HYDROGEN ION ACTIVITY OF 0.01 M PHENANTHROLINE–0.01 M PHENANTHROLIUM CHLORIDE BUFFER ON IONIC STRENGTH

Concentration of KCl, M	Observed paH	Total ionic strength, μ	γ_{PbH^+}
0.001	4.81	0.011	0.91
.010	4.83	.020	.87
.100	4.91	.11	.73
.500	5.03	.51	.55
1.00	5.12	1.01	.45

In Figure 3 the observed values of paH are plotted against the square root of the ionic
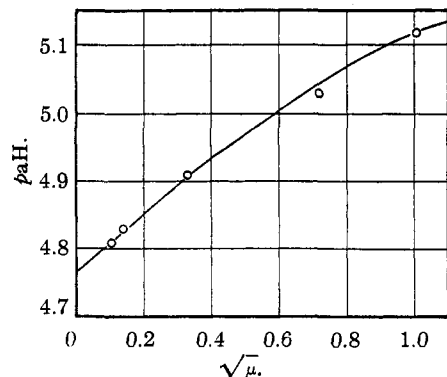
Fig. 3.—Dependence of hydrogen ion activity of phenanthrolium chloride–phenanthroline solution on ionic strength.

strength. It is seen that the curve is nearly linear at low ionic strengths and extrapolates to a value of $p a$H of 4.77 at zero ionic strength. This value corresponds to a hydrogen ion activity of 1.7 × 10^{-5}, hence the acid dissociation constant K_A of the phenanthrolium ion is about 1.7 × 10^{-5} at 25°. The data of Table I involve a small error due to the liquid junction potential between the saturated potassium chloride solution in the salt bridge and the potassium chloride, phenanthrolium chloride solution under investigation.

For use in calculations described below approximate activity coefficients of the phenanthrolium ion were calculated. The equation employed was

$$\gamma_{\text{PhH}^+} = \frac{a_{\text{H}^+}\gamma_{\text{Ph}}(\text{Ph})}{K_A(\text{PhH}^+)} \quad (1)$$

where γ represents activity coefficient, a represents activity, and parentheses indicate molar concentrations. The values of γ_{PhH^+} given in Table I are subject to an error due to liquid junction potential.

Figure 4 shows the results of the conductometric titration of 0.01 M phenanthroline with 0.2 N hydrochloric acid. (The conductivity of the solution was corrected for the small change in volume which occurred during the titration.) It is seen that phenanthroline behaves as a mono-acid base. Only one mole of hydrogen ion combines with one mole of phenanthroline.

The degree of hydrolysis, h, of the phenanthrolium ion in 0.001 M phenanthrolium chloride solution was determined by means of the relation

$$h = (\Lambda_1 - \Lambda_2)/(\Lambda_3 - \Lambda_2) \quad (2)$$

where Λ_1 is the equivalent conductance of 0.001 M phenanthrolium chloride, Λ_2 is the equivalent conductance of 0.001 M phenanthrolium chloride in the presence of an excess of phenanthroline (to repress hydrolysis), and Λ_3 is the equivalent conductance of 0.001 M hydrochloric acid. The value of Λ_1 was found to be 136.0 at 25°, and the value of Λ_2 104.5. Taking the value of Shedlovsky[1] of 421.4 for the equivalent conductance of 0.001 M hydrochloric acid at 25°, we find that h
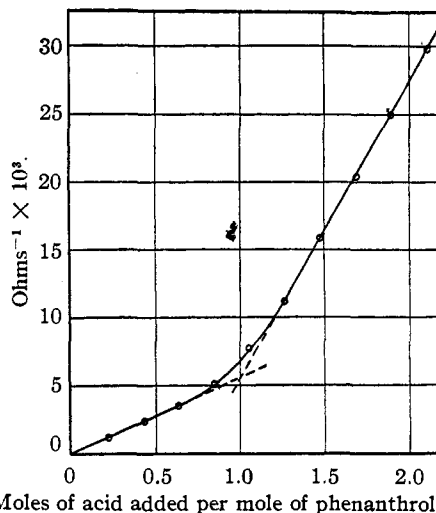

Fig. 4.—Conductometric titration of phenanthroline with hydrochloric acid.

for 0.001 M phenanthrolium chloride is 1.0 × 10^{-1}. From this value the acid dissociation constant of the phenanthrolium ion is calculated to be 1.1 × 10^{-5}. The computation involves the assumption that the activity coefficient of phenanthrolium ion is equal to that of the hydrogen ion in a solution of an ionic strength of 0.001 M. From the value of the acid constant, 1.1 × 10^{-5} at 25°, it is found that the ionization constant of the base phenanthroline in water is about 9 × 10^{-10} at 25°.

Dissociation of Ferroin.—It is known that in ferroin the iron is joined to three phenanthroline molecules.[2,3] The formula may be represented by $\text{FePh}_3{}^{++}$. Gould and Vosburgh[4] found that complexes with one and with two phenanthroline molecules per iron atom do not exist in spectrophotometrically detectible amounts in neutral aqueous mixtures of ferrous iron and ferroin. As will be described in a subsequent paper we found evidence that the complexes FePh^{++} and $\text{FePh}_2{}^{++}$ exist in acid solutions at appreciable concentrations if the iron concentration is very high. However, for the present purposes only $\text{FePh}_3{}^{++}$ need be considered.

In acid solutions with a pH of 3 or less phenanthroline is present chiefly as the phenanthrolium ion rather than as free phenanthroline, and the equilibrium between ferroin and a strong acid may be represented by

$$\text{FePh}_3{}^{++} + 3\text{H}^+ \rightleftarrows \text{Fe}^{++} + 3\text{PhH}^+ \quad (3)$$

The value of the equilibrium constant, K_c', of reaction (3) was found by determining the concentration of ferroin in equilibrium with known concentrations of ferrous sulfate and sulfuric acid. The results are given in Table II.

(2) F. Blau, Monatsh., 19, 666 (1898).
(3) Smith and Richter, "Phenanthroline and Substituted Phenanthroline Indicators," G. Frederick Smith Chemical Co., Columbus, Ohio, 1944.
(4) Gould and Vosburgh, This Journal, 64, 1630 (1942).

TABLE II

EQUILIBRIUM OF FERROUS IRON WITH PHENANTHROLINE IN ACID SOLUTIONS

Reaction mixture	Initial concn. of H_2SO_4, M	Initial concn. of $FeSO_4$, $M \times 10^5$	Initial concn. of phen., $M \times 10^5$	Concn. of ferroin found, $M \times 10^5$	Concn. of Fe^{++} calcd., $M \times 10^5$	Concn. of PhH^+ calcd., $M \times 10^5$	Concn. of H^+ calcd., M	Concn. equilib. const. $K_c' \times 10^7$	Activity equilib. const.[a] $K' \times 10^7$
1	0.00536	10.4	9.97	1.63	8.8	5.08	0.0089	9.7	8.4
2	.0511	10.3	99.7	6.42	3.9	80.4	.0687	9.7	5.2
3	.505	10.3	1000	5.80	4.5	983	.572	39	5.2
4	.501	253	100	0.790	252	97.6	.584	15	2.0
5	.502	253	200	4.75	248	186	.584	17	2.3
6	.512	239	199	4.16	234	187	.595	17	2.1
7	.502	496	200	7.70	487	164	.584	14	1.8

[a] In calculating the activity equilibrium constant from the concentration equilibrium constant the values 0.87, 0.71 and 0.47 were used for the activity coefficients of phenanthrolium ion in mixtures 1, 2, and 3-7, respectively. The values 0.92, 0.85 and 0.92 were used for the activity coefficients of hydrogen ion in reaction mixtures 1, 2, and 3-7, respectively.

The concentration equilibrium constant

$$K_c' = \frac{(Fe^{++})(PhH^+)^3}{(FePh_3^{++})(H^+)^3} \qquad (4)$$

where parentheses represent concentrations, was calculated for each of the reaction mixtures. The concentration of phenanthrolium ion was calculated from the expression

$$(PhH^+) = (Ph)_t - 3 \times (FePh_3^{++}) \qquad (5)$$

where $(Ph)_t$ represents the total initial concentration of phenanthroline. The concentration of ferrous iron was calculated from the relation

$$(Fe^{++}) = (Fe^{++})_t - (FePh_3^{++}) \qquad (6)$$

where $(Fe^{++})_t$ represents the total initial concentration of iron. The concentration of hydrogen ion was estimated by assuming that the first hydrogen ion of sulfuric acid is completely dissociated and that the second dissociation constant is 0.012.[5] The calculated value of the hydrogen ion concentration depends on the values used for the activity coefficients of hydrogen ion, hydrogen sulfate ion, and sulfate ion. These activity coefficients were estimated by the individual ion activity coefficient method.[6] This method involves the assumption that the activity coefficients of potassium ion and chloride ion are equal in any given solution, and that the activity coefficient of an individual ion depends on the nature of the ion and on the total ionic strength of the solution but does not depend on the nature of electrolyte.

In evaluating the activity constant

$$K' = a_{Fe^{++}}a^3_{PhH^+}/a_{FePh_3^{++}} \, a^3_{H^+} \qquad (7)$$

it was assumed that $\gamma_{Fe^{++}} = \gamma_{FePh_3^{++}}$ where γ denotes activity coefficient. The values for γ_{PhH^+} were taken from Table I.

In experiments 1–3 of Table II the total concentration of iron was held constant and the acid and phenanthroline concentrations were varied. The values of K' were nearly the same in the three experiments. In experiments 4 and 5 the acid and iron concentrations were held constant and the phenanthroline concentration was varied. In ex-

periments 6 and 7 the acid and phenanthroline concentrations were held constant and the iron concentration was varied. The total variation in K' was from 1.8 to 8.4 $\times 10^{-7}$. Considering the uncertainty in activity coefficients, especially in 0.5 M sulfuric acid, the reported values of K' may be considered as reasonably constant. The average value of K' at 25° is 4 $\times 10^{-7}$. In view of the fact that the hydrogen ion concentration was varied by a factor of 100 in these experiments and that the hydrogen ion activity occurs in equation (7) as a cube power it may be stated that the experimental data confirm the validity of equation (7) over the range of concentrations studied.

Equilibrium "constants" for the hypothetical reaction

$$FePh_3^{++} + 6H^+ = Fe^{++} + 3PhH_2^{++} \qquad (8)$$
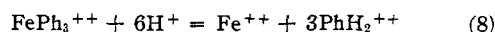
were also calculated from the data of Table II. The "constant" calculated for reaction (8) changes by a factor of about one million when the sulfuric acid concentration is changed from 0.005 to 0.5 M. This result substantiates the conclusion given in the previous section that phenanthroline is a mono-acid base.

The constant for the dissociation of ferroin, represented by the equations

$$FePh_3^{++} = Fe^{++} + 3Ph \qquad (9)$$
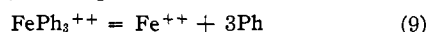
$$K_{diss. ferroin} = a_{Fe^{++}}a^3_{Ph}/a_{FePh_3^{++}} \qquad (10)$$

can be calculated from the equilibrium constant K' of reaction (7) and the acid constant of the phenanthrolium ion. The relation is $K_{diss. ferroin} = K'K_A^3$. The values 4 $\times 10^{-7}$ and 1.1 $\times 10^{-5}$ for K' and K_A, respectively, give a value of 5 $\times 10^{-22}$ for $K_{diss. ferroin}$ at 25°. In a subsequent paper it will be shown that this value is in agreement with a value determined by an entirely independent method.

Knowledge of the nature of the dissociation of ferroin in acid solution (equation 3) and of the value of K' can be applied to the colorimetric determination of iron. The quantitative conversion of ferrous iron to ferroin is dependent on the ratio of phenanthroline to acid. If the colorimetric determination of iron is carried out at relatively high acidity, the concentration of excess

(5) W. Hamer, THIS JOURNAL, **56**, 860 (1934).

(6) Lewis and Randall, "Thermodynamics," McGraw–Hill Book Co., Inc., New York, N. Y., 1923, p. 381.

phenanthroline must be correspondingly high. In order that the reaction be 99% complete, the ratio of excess phenanthrolium ion to hydrogen ion should be 0.035 or greater. Thus if the hydrogen ion concentration is 10^{-3} M, the concentration of excess phenanthrolium ion must be 3.5 $\times$ 10^{-5} M or greater.

Dissociation Constant of Ferriin.—The constant for the dissociation of ferriin (a reaction analogous to reaction 9) was calculated from the dissociation constant of ferroin and the equilibrium constant for the reaction of ferrous iron with ferriin

$$Fe^{++} + FePh_3^{+++} = Fe^{+++} + FePh_3^{++} \quad (11)$$
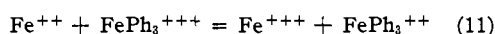
The equation expressing this relation is

$$K_{\text{diss. ferriin}} = \frac{a_{Fe^{+++}}a^3_{Ph}}{a_{FePh_3^{+++}}} = \frac{a_{Fe^{+++}}a_{FePh_3^{++}}}{a_{Fe^{++}}a_{FePh_3^{+++}}} K_{\text{diss. ferriin}} \quad (12)$$

The equilibrium constant K'' for the reaction of ferrous iron with ferriin was calculated by two different methods: (1) from the e. m. f. of the cell Au$|$Fe^{++}, Fe^{+++}, H$_2$SO$_4|$FePh$_3^{++}$, FePh$_3^{+++}$, H$_2$SO$_4|$Au, and (2) from the formal potentials of the ferroin-ferriin couple and of the ferrous–ferric couple. The former method is somewhat more direct and is thought to be more reliable. The experimental data for method (1) are given in Table III. The data for use in method (2) were taken from the literature.[7,8,9,10]

The values of the dissociation constant of ferriin calculated from the experimental data using equation (12) were found to be 8.0 $\times$ 10^{-15} in 0.05 M sulfuric acid, 2.5 $\times$ 10^{-15} in 0.5 M, 1.0 $\times$ 10^{-15} in 1 M, 2.9 $\times$ 10^{-16} in 2 M, and 7.5 $\times$ 10^{-21} in 8 M. In the calculations it is assumed that the activity coefficients of ferric and ferriin ions are approximately equal.

(7) Walden, Hammett and Chapman. This Journal, **55**, 2649 (1933).

(8) Hume and Kolthoff, ibid., **65**, 1895 (1943).

(9) Smith and Richter, Ind. Eng. Chem., Anal. Ed., **16**, 580 (1944).

(10) E. H. Swift, "System of Chemical Analysis," Prentice-Hall, New York, N. Y., 1939, p. 540.

Table III

EQUILIBRIUM CONSTANT FOR THE REACTION OF FERRIC IRON WITH FERROIN

Concn. of H$_2$SO$_4$, M	E. m. f. of cell, volts	K'' From e. m. f.	From formal potentials
0.05	0.425	1.6 10^7	....
0.5	.395	5.0 10^6	....
1	.373	2.1 10^6	4.4 10^6
2	.340	5.8 10^5	9.1 10^5
8	.110	1.5 10	2.3 10

The dissociation constant of ferriin appears to decrease with increasing sulfuric acid concentrations. This variation is opposite to that which would be expected if the effect were due merely to complexing of the ferric ion with sulfate. The variation is also opposite to that which would be expected if the activity coefficient of ferriin were greater than the activity coefficient of ferric ion. (The ferriin ion is larger and might be expected to have the larger activity coefficient.) The variation may be explained if it is assumed that the ferriin ion possesses a proton in solutions of high acidity, FeHPh$_3^{++++}$. This will be discussed in a subsequent paper.

Summary

1,10-Phenanthroline has been found to behave as a typical mono-acid base in aqueous solutions. The acid dissociation constant of the phenanthrolium ion is 1.1 $\times$ 10^{-5} at 25°.

The dissociation constants of ferrous and ferric phenanthroline have been evaluated. The constant of ferrous phenanthroline in various concentrations of sulfuric acid is 5 $\times$ 10^{-22} at 25° and that of ferric phenanthroline in 0.05 M sulfuric acid is 8 $\times$ 10^{-15} at 25°.