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THE SUBSTITUENT EFFECT IN TRANSITION METAL COMPLEXES OF 1, 10-PHENANTHROLINE

by

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INTRODUCTION

The stability constants of metal-ligand complexes can, in a number of instances, be related in a linear manner to the stability constant of the corresponding proton-ligand complex, such that small structural variations in the ligand will result in linear changes in the respective stability constants. The existence of such linear relationships is of paramount importance to the analytical chemist, as it enables him to predict approximate values of the stability constant of a particular metal with a ligand when the constants of this metal have been measured for other, similar ligands. Of equal importance are relationships or empirical trends of the variation in stability of a series of metals with a particular ligand. An example is the Irving-Williams Series (1), which states that, for most ligands, the stability of the metal complexes will parallel the second ionization potential of the metal. In agreement with this generalization, the stability of a ligand with the following metals exhibits the following order for ions of equal charge: $Zn < Cu > Ni > Co > Fe > Mn$.

In addition, it has been demonstrated in selected cases (alkali metals, alkaline earths, and rare earths) that the stability of the complex with a given ligand is a function of e^2/r, the charge squared divided by the metal ionic radius. There are relatively sound theoretical reasons (2) for expecting the stabilities of complexes to be proportional to ionization potentials and electrostatic potentials, but these serve only as first approximations because of the various other effects that must necessarily play a significant part in the overall stability of a given complex. It is just these additional effects that must be recognized, interpreted, and separated, if possible, in order that one may feel justified in applying the theoretical generalizations to all complex compounds. Such is the case with the Irving-Williams Series. The sequence seems to hold for too many varied ligands to reject the correlation, but there are notable exceptions which prove the rule. The 1,10-phenanthroline complexes are an example of such an exception, the most obvious deviation being the fact that the stability of the tris(1,10-phenanthroline) iron(II) complex and the tris(1,10-phenanthroline) nickel(II) complex are both greater than the stability of the corresponding copper(II) complex, while for most ligands, the reverse would be true. This exceptional behavior alone would justify a serious study directed toward its explanation, but the 1,10-phenanthroline complexes themselves have many additional properties of interest. The iron(II) and copper(I) complexes of the 1,10-phenanthrolines exhibit an intense color formation, leading to their widespread use as a means for analysis. Several metals react kinetically slowly with 1,10-phenanthrolines (3), a fact which has lent itself to analytical separations of a unique nature, and which poses interesting problems in the interpretation of chelate reaction mechanisms.

While a great deal of attention has been given to 1,10-phenanthroline complexes in the literature (4), only recently, with the exception of the iron complexes, has there been any attempt to systematically measure stabilities of transition metal complexes with 1,10-phenanthroline (5), and even less work has been done with the complexes of substituted 1,10-phenanthrolines. If nothing else, it is hoped that the present work will contribute toward this goal.

The distant object in mind, however, is to attempt to establish the linearity, and the constants for the linear equation relating the stability of the metal complexes to the stability of the proton complexes, for a series of substituted 1,10-phenanthrolines. This equation then represents the substituent effect for a given metal relative to an arbitrary standard cation, the proton. The substituent effect can be measured for various transition metals. Then the question arises: Is there any relation between the substituent effects as the metal is varied? What can one expect this relation to be from theoretical considerations? It would be valuable, indeed, to have these primary questions answered.

THE SUBSTITUENT EFFECT IN METAL COMPLEXES

Review of Literature

Attempts to establish the linearity of the substituent effect date from as early as 1934 (6). In this case, the silver-ammine complexes were cited as possessing a definite linear stability relationship to the basic strength of the amines. While this was disputed by later workers (7), it now has been fairly well established that when ligands of sufficient structural similarity are used in the comparison, linearity seems to be the rule (8). Thus, the primary, secondary, tertiary, and aromatic amines each make a linear family. These data are reproduced in Figure 20. Bjerrum has extended the data on this system (9), and has included the mercury(II) complexes also. Schwarzenbach et al. studied the stability of the alkaline earth metals with aminopolycarboxylic acids, obtaining linear relationships (10). Van Uitert et al. (11) recently performed an extensive study of the β-diketone complexes with divalent transition metals and alkaline earths, and linear relations seem to be the rule. Even more recently a very similar study (12), with increased attention given to the symmetry of the β-diketones used, also showed linear relationships, with the exception of some anomalous points, which have been attributed tentatively to solvation effects. Linear relationships have also been reported for the 1,10-phenanthroline complexes of iron(II) (13), zinc (II) (14) and nickel(II) (15). Calvin and Wilson (16) were among the first to establish the linearity in the case of copper(II) chelates of enolate ligands, and to show the importance of resonance effects on the stabilities of these chelates.

There have been exceptions to the linearity rule, but, in general, these are peculiar to only a few compounds in which a known or expected property could account for the deviation. For example, 2-methyl-1,10-phenanthroline complexes fall far below their expected stability on the basis of the basic strength of the ligand (5), but it was expected that the methyl group would interfere greatly in the attainment of the same geometrical configuration as the other 1,10-phenanthrolines. Substituted malonate complexes of copper show not only an absence of linearity, but a reverse or anomalous dependence on the acid constants of the ligands (17). The reasons for the highly anomalous behavior in this case have not been proposed, although it appears that steric or solvation factors may account for some of the deviation from the general rule. This work deserves to be confirmed, and entropy data would be very useful for interpretation. Irving and Rossotti (18) have illustrated quite well the effect of steric hindrance on the stabilities of substituted oxines. The unhindered oxines gave linear substituent effects with copper(II), magnesium(II), and uranyl ion. As the steric effects are quite marked, minor deviations can be attributed to the fact that oxine is unsymmetrical with respect to its donor groups, and substituents cannot be expected to act equally upon them.

Little attention has been given to the variation in substituent effect from metal to metal. It has been pointed out by some authors (19, 12) that the substituent effect seems to parallel the order of stabilities in those systems when several metals have been considered. Thus, in the β-diketone system, the substituent effects fall in the order Cu(II), Ni(II), Ba(II), as do the stabilities of the complexes with any given β-diketone. Other authors (8, 20 p. 180) have observed that a particular metal seemed to have a low sensitivity to substituent changes, without proposing reasons. Irving and Rossotti (21) were the first to seriously propose the use of graphical correlations of the nature of those under discussion for their prophetic value in Analytical Chemistry, and have discussed the thermodynamic equations underlying each of the correlations they propose. In this work, they attempt to show that the substituent effects for two closely related metals should approach a theoretical equality, and cite the data for nickel(II) and copper(II) with a wide variety of ligands. It appears, however, that the data are better fit by assigning a larger substituent effect to the copper complexes, a result which is in accord with the previous observation that the substituent effects are related to the stabilities.

General Considerations

It would be useful to derive the thermodynamic relations which express the dependence of metal-complex stabilities on the stabilities of the proton-ligand complex, in order to have a better basis for discussion of the factors influencing the substituent effect.

Consider the reaction

$$M + HL \rightleftharpoons ML + H \quad , \qquad (1)$$

which represents the formation of the 1:1 complex, ML, of a metal ion, M, with a monobasic ligand L. The charges and solvent on the various species will be omitted for simplicity.

Let K_{ML} represent the thermodynamic dissociation constant of ML and K_{HL} the thermodynamic dissociation constant of the proton complex. From the definitions of these constants, and the thermodynamic relation

$$\bar{F} - \bar{F}^{o} = + RT\ln a \quad ,$$

where $\bar{F}^{o}$ is the partial molal standard free energy of a particular species in solution, and a is the activity of that species, one may easily derive the relation

$$\ln K_{ML} = \ln K_{HL} - \frac{1}{RT}(\bar{F}^{o}_{M} - \bar{F}^{o}_{ML} - \bar{F}^{o}_{H} + \bar{F}^{o}_{HL}) \quad . \qquad (2)$$

If now a substituent s were added to the ligand to give the ligand L_s, such that the primary effect of the substituent is the alteration of the nucleophilic character of the donor groups on the ligand, without any change in the stoichiometry or stereochemistry of the reaction in Equation 1, then the stability relationship for the reaction would read

$$\ln K_{ML_s} = \ln K_{HL_s} - \frac{1}{RT}(\bar{F}^o_M - \bar{F}^o_{ML_s} - \bar{F}^o_H + \bar{F}^o_{HL_s}) \ . \qquad (3)$$

The difference in Equation 2 and Equation 3 can be expressed as

$$\underset{s}{\Delta}\, pK_{ML} = \underset{s}{\Delta}\, pK_{HL} - \frac{1}{2.3RT}(\underset{s}{\Delta}\, \bar{F}^o_{HL} - \underset{s}{\Delta}\, \bar{F}^o_{ML}) \ , \qquad (4)$$

where $p = -\log_{10}$, and $\underset{s}{\Delta}$ is understood to mean the difference upon substitution of substituent s on ligand L, as, for example,

$$\underset{s}{\Delta}\, \bar{F}^o_{HL} = \bar{F}^o_{HL_s} - \bar{F}^o_{HL} \ .$$

The linear relation between two points (pK_{ML}, pK_{HL}) and (pK_{ML_s}, pK_{HL_s}) is

$$pK_{ML} = \frac{\underset{s}{\Delta}\, pK_{ML} pK_{HL}}{\underset{s}{\Delta}\, pK_{HL}.} + B \ . \qquad (5)$$

It can be derived from Equation 4 that the slope of this equation is

$$\underset{s}{\Delta} pK_{ML} / \underset{s}{\Delta}\, pK_{HL} = \frac{\underset{s}{\Delta}\, \bar{F}^o_{ML} - \underset{s}{\Delta}\, \bar{F}^o_L}{\underset{s}{\Delta}\, \bar{F}^o_{HL} - \underset{s}{\Delta}\, \bar{F}^o_L} \ . \qquad (6)$$

The condition that the substituent effect is truly linear is that the slope as expressed by Equation 6 be constant for any number of substituents. However, for the stated purpose of comparing the relative substituent effects as the metal is varied, the condition of linearity for all substituents is not essential. It is desirable only because more points could be provided to fix the slope accurately, thus minimizing errors in the individually measured pK_{ML} values. It is essential, however, that the stoichiometry of the complex formation and the steric factors depend neither on the variation in metal or substituent on the ligand. Furthermore, it is important that, if only two substituents are used, the stability constants be accurately measured.

Each $\Delta_s \bar{F}^o$ term in Equation 4 may be separated into its enthalpy and entropy components, since

$$\Delta_s \bar{F}^o = \Delta_s \bar{H}^o - T \Delta_s \bar{S}^o \,.$$

It is a reasonable assumption to interpret $\Delta_s \bar{H}^o_{ML}$ as representing primarily the difference in M-L bond energy between two complexes differing only in the substituent, and $\Delta_s \bar{S}^o_{ML}$ as representing primarily the difference in solvation between these two complexes. For the present discussion, the entropy terms shall be neglected. It will be seen that in the silver ammines (Appendix I), where it might be expected that solvation differences would be appreciable, the entropy terms contribute only a fraction of the overall substituent effect. The relative substituent effects for two metals will be approximated by bond energy terms, namely

$$\frac{\underset{s}{\Delta}\, pK_{M_1L}}{\underset{s}{\Delta}\, pK_{M_2L}} \approx \frac{\underset{s}{\Delta}\, \bar{H}^{o}_{M_2L}}{\underset{s}{\Delta}\, \bar{H}^{o}_{M_2L}} \approx \frac{\underset{s}{\Delta}\, E_{M_1-L}}{\underset{s}{\Delta}\, E_{M_2-L}} \quad . \tag{7}$$

A quantitative theoretical interpretation of changes in bond strength as both metal and ligand are varied is not possible, but a qualitative picture, based on what is known about the behavior of sigma bonds, from either the molecular orbital concepts or the electrostatic theory of bonding, leads to interesting conclusions which conform to observation.

Van Uitert and Fernelius (22) have used electrostatic theory concepts in discussing the variations in substituent effect observed for the β-diketone chelates. Briefly the interpretation is as follows: The free energy change of complex formation can be considered to be some function of (a) the product of the effective metal ion hybrid bond electronegativity, X_m, and the effective ligand donor atom hybrid bond electronegativity, X_c, (b) the dipole character of the bond due to differences in the effective electronegativities, $X_m - X_c$, and (c) a nuclear repulsion term. The nuclear repulsion term depends on the shielding of the respective nuclei by the electrons in the bond between them, and should increase as the electron density in the bond decreases. An indirect analysis of chelate compounds in general shows that X_c varies in a predictable manner, namely, that the electronegativities increase in the following order of ligand functional groups:

$-\mathrm{N}\begin{smallmatrix}\diagup\\ \diagdown\end{smallmatrix}$, $\begin{smallmatrix}\diagdown\!\!\diagdown\\ \diagup\end{smallmatrix}\mathrm{N}$, $-\mathrm{N}=\mathrm{N}-$, $\equiv\mathrm{N}$ and $-\mathrm{O}^-$, ${}^{\diagdown}\mathrm{O}^{\diagup}$, $=\mathrm{O}$

or, for the same functional group, X_c would increase in the following order of substituent groups:

$-NO_2$, Hal- , H- , $-CH_3$, $-OCH_3$.

Similarly, the metal hybrid bond electronegativity X_m, should approximate the reverse order of the ionization potentials for the ions as follows:

Cu(II), Ni(II), Co(II), Fe(II), Mn(II).

In Figure 1 the above picture is illustrated in terms of energy levels E_M and E_L placed in the same order as the electronegativities. The difference $E_{ML} - E_L$ represents the additional stabilization of the donor electrons due to sigma bond formation. Two levels each of E_M and E_L are drawn to illustrate the effect on $E_{ML} - E_L$ as each is varied separately in the hypothetical case. As E_M and E_L approach each other, the magnitude of the stabilization becomes greater. According to the molecular orbital theory, the orbital mixing, as measured by the overlap integral (23) increases as the individual orbital energies become alike in magnitude. Or, as before, the nuclear repulsion term decreases, permitting more profound attraction of the nuclei, as the electronegativities of the

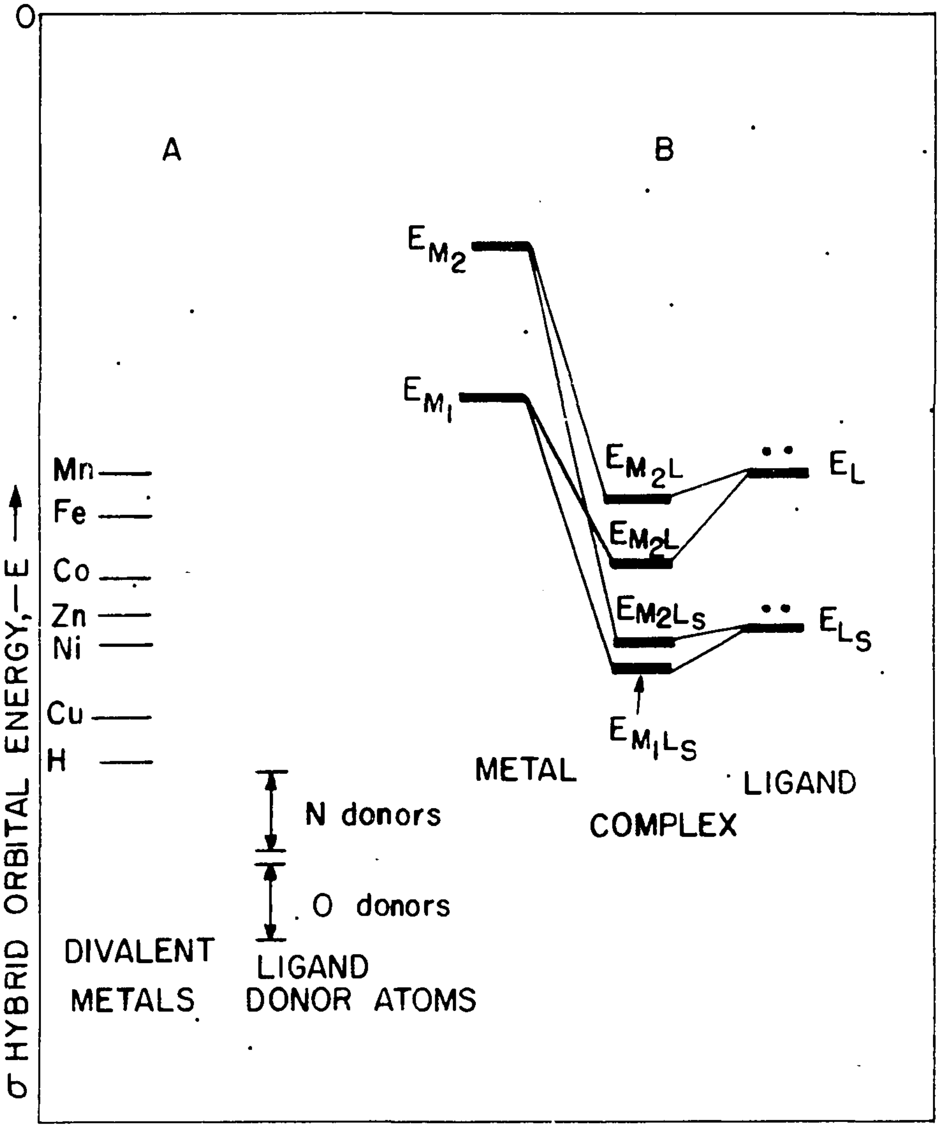


Figure 1. Schematic representation of covalent bonding in divalent metal complexes

A. Relative hybrid orbital energies of metals, based on the second ionization potentials, and ligands

B. Illustration of the effect of orbital mixing for metals and ligands of different hybrid orbital electronegativities as the basis for variations in the substituent effect combining atoms become so alike as to center the shared electrons between them.

It becomes evident from these considerations, that one would expect the ratio

$$\frac{(E_{M_2L_s} - E_{L_s}) - (E_{M_2L} - E_L)}{(E_{M_1L_s} - E_{L_s}) - (E_{M_1L} - E_L)} = \frac{\underset{s}{\Delta} E_{M_2L} - \underset{s}{\Delta} E_L}{\underset{s}{\Delta} E_{M_1L} - \underset{s}{\Delta} E_L} \approx \frac{\underset{s}{\Delta}\, pK_{M_2L}}{\underset{s}{\Delta}\, pK_{M_1L}} \qquad (8)$$

would be less than one. The subscripts are the same as those in Figure 1. Thus, the substituent effect for different metals would be expected to follow the ionization potentials and, because there is a correlation between the ionization potentials and the stabilities of a single ligand with a series of metals, a correlation should be found in this direction also.

A good illustration of the preceding arguments can be found on page 190 of Martell and Calvin (2). Correlations of the second ionization potential of the transition metals with the stabilities of various chelating agents show that the dependence of the stability of chelates formed from nitrogen donors is much greater than if the donor atom is oxygen. This indicates the nitrogen donors form stronger covalent bonds more profoundly, as the metal electronegativity is increased, than oxygen donors. Since, in general, nitrogen donors are less electronegative than oxygen donors, these facts are in agreement with the interpretation.

The relative changes in the substituent effect when the possibility of pi-bonding exists between the metal and ligand are not so easily predicted as in the case of sigma-bonding alone. The 1,10-phenanthroline complexes offer the possibility of comparing substituent effects between metals which seem to have normal covalent bonds, and iron(II), which is strongly suspected of double bonding with the 1,10-phenanthrolines in the 3:1 complex. It would seem that a nitro substituent would enhance double bond character, since pi-electrons would be drawn from the 3d orbitals of iron(II) and be donated to the ligand. Furthermore, this process would act to decrease the electron-withdrawing action on the nitrogen electrons, and thus the sigma bonds might be stronger than would be predicted from the decreased base strength of the 1,10-phenanthroline.

APPARATUS AND REAGENTS

Absorbancy measurements were made with a Beckman DU quartz spectrophotometer, a Cary Model 12 recording spectrophotometer, and a Cary Model 14 recording spectrophotometer. The measurement of pH was performed with Beckman Model G and GS pH meters. All work was performed at a thermostatically controlled room temperature of 25°C. All glassware used was of Class A specification.

The 1,10-phenanthrolines used were as follows: 1,10-phenanthroline, 5-methyl-1,10-phenanthroline, and 5-nitro-1,10-phenanthroline were obtained from the G. F. Smith Chemical Company; 5-bromo-1,10-phenanthroline was prepared by R. Fullerton, and 5-chloro-1,10-phenanthroline was prepared by R. V. Smith. Each of the 1,10-phenanthrolines was recrystallized from benzene-petroleum ether mixture until the crystals appeared white (pale yellow in the case of 5-nitro-1,10-phenanthroline), and melted sharply at the melting points listed in the literature for the anhydrous compounds. The solids were stored in a vacuum desiccator until ready for use. Solutions of the 1,10-phenanthrolines were prepared by weight, with acid added to convert the free base to the 1,10-phenanthrolium ion. It was noted that over a period of one to four weeks, initially clear solutions of the 1,10-phenanthrolines tended to become yellowish in appearance, particularly if they were exposed to light. As photochemical decomposition is indeed a likely possibility (24), the stock solutions were stored in flasks painted black, and were kept in the dark until used. This procedure seemed to prevent yellowing, and the absorption spectra of these solutions remained quantitatively the same over periods of six months.

Vanadium(IV) was prepared from vanadium pentoxide, which was first purified by several recrystallizations as ammonium vanadate, followed by ignition to the oxide. A slurry of the oxide in perchloric acid was electrolyzed. After the solution became an intense blue, the remaining slurry was filtered, and the solution was further electrolyzed until the absorbancy of the solution at 410 mμ just reached a minimum. At this wave length, both V(V) and V(III) absorb, while V(IV) does not absorb appreciably. Cacotheline was also used as a test for the presence of V(III).

A manganese(II) stock solution was prepared from reagent-grade $MnCl_2 \cdot 4H_2O$ and a cobalt(II) stock solution was prepared from reagent-grade $CoCl_2 \cdot 6H_2O$. Zinc chloride was prepared from "Bunker Hill" zinc metal, electrolytic, 99.99+ per cent pure, by dissolving it in hydrochloric acid. A solution of ethylenediaminetetraacetic acid, commonly termed EDTA, was standardized against this zinc solution; the EDTA was then used to standardize the manganese solution, using Eriochrome Black T, (25), and the cobalt solution, using 1-naphthylazoxine (26).

Iron(II) chloride solutions were prepared from electrolytic iron wire reported to be 99.85 per cent pure, by dissolving a weighed amount in hydrochloric acid. After dilution, iron wire was added to the solution to counteract oxidation by air. The solution was analyzed prior to use by dichromate titration, using barium diphenylamine as the indicator. A nickel(II) chloride solution was prepared from $NiCl_2 \cdot 6H_2O$ and standardized gravimetrically with 1,2-cycloheptanedionedioxime (27).

Copper(II) chloride was prepared by dissolving reagent-grade copper oxide, 99.8 per cent pure, in hydrochloric acid. The solution was analyzed iodometrically.

All other aqueous solutions were prepared from reagent-grade materials; these included potassium chloride solutions for adjusting ionic strength, and various buffers, all prepared by weight.

For the partition studies, the extractive solvent was 2-ethyl-1-hexanol. Commercial grade solvent was purified by fractional distillation under vacuum. The criterion for purity was that the absorbancy in the ultraviolet fall below one absorbancy unit in a five-centimeter cell at 250 mμ. This criterion permits quantitative spectrophotometry at wave lengths higher than 250 mμ. Two gallons of 2-ethyl-1-hexanol were received from Union Carbide and Carbon which met the ultra-violet spectra requirements and was not further purified.

THE DETERMINATION OF STABILITY CONSTANTS OF 1,10-PHENANTHROLINE-METAL COMPLEXES

Introduction

The determination of the stability constants of metal complexes is a matter of widespread concern in the literature, and attempts by Martell and Calvin (2, p. 76) and Sullivan and Hindman (28) have been made to summarize the approaches that have been used. The success with which any of these methods may be applied to a particular metal complex system, is greatly a function of that system, and it is one of the purposes of this thesis to show how several of these methods may be applied to the 1,10-phenanthroline complexes, and the limitations of such applications.

For the present, let us consider only the generalizations concerning these particular methods. The specific derivations for each method are entered in those sections where the method is used, and the form of the equations shall then be limited to describe only the system under consideration.

For a solution of a metal, M, and ligand, L, in which the system of complexes may be described by the reactions

$$\begin{aligned} &\text{a)}\quad H + L \rightleftharpoons HL \\ &\text{b)}\quad M + L \rightleftharpoons ML \\ &\text{c)}\quad ML + L \rightleftharpoons ML_2 \qquad (9) \end{aligned}$$

. . .

. . .

. . .

$$d)\ ML_{i-1} + L \rightleftharpoons ML_i \qquad (9)$$

The stability constants may be defined as follows:

$$K_i = k_1k_2k_3 \cdot \cdot \cdot k_i = (M)(L)^i/(ML_i) = 1/\beta_i \qquad (10)$$

$$k_i = (ML_{i-1})(L)/(ML_i) \qquad (11)$$

$$K_a = (H)(L)/(HL) \qquad (12)$$

The various constants may be named as follows: K_i is the overall dissociation constant for the i-th complex, β_i is the overall formation constant of the i-th complex, k_i is the stepwise dissociation constant of the i-th complex, and K_a is the acid dissociation constant for the ligand.

Expressions for the known analytical concentrations of the metal and ligand may be given as follows:

$$(M)_T = (M) + \sum_i (ML_i) \qquad (13)$$

$$(L)_T = (L) + (HL) + \sum_i i(ML_i)\ , \qquad (14)$$

where T refers to "total". Upon substitution of the corresponding values from the stability equations for (ML_i) and (HL), these equations become

$$(M)_T = (M)(1 + \sum_i \beta_i(L)^i\ ) \qquad (15)$$

$$(L)_T = (L)(1 + (H)/K_a) + (M)\sum_i i\beta_i (L)^i \qquad (16)$$

The concentration of free metal ion, (M), may be eliminated from Equations 15 and 16 to yield an expression which is defined as the formation function, $\bar{n}$, as follows:

$$\bar{n} = \frac{(L)_T - (L)(1 + (H)/K_a)}{(M)_T} = \frac{\sum_i i\beta_i (L)^i}{1 + \sum_i \beta_i (L)^i} \qquad (17)$$

The term $\bar{n}$ represents the average number of ligands bound to the metal per metal ion in the solution. It is evident from Equation 17 that i well chosen experimental determinations of $\bar{n}$, (L) pairs will suffice to determine all the constants, β_1 through β_i. The concept of $\bar{n}$ is a particularly useful one if more than one complex exist simultaneously, although there are other functions which are equally useful, in particular instances, for the graphical determination of stability constants.

Methods of Approach

Spectrophotometry

Because of the quantitative relation of absorbancy to concentration, spectrophotometry is a particularly useful means of determining stability constants. This is so especially for metal complexes for which a wave length can be found where the various metal complex species absorb appreciably, but the ligand absorption is negligible. An example is the 1,10-phenanthroline complexes of iron(II). The iron complexes absorb in the visible region of the spectra to an appreciable extent, while the ligand, 1,10-phenanthroline, absorbs only in the ultraviolet. However, most of the transition-metal complexes of the 1,10-phenanthrolines exhibit absorption bands which are only slightly changed from the ligand bands. In cases like these, it is convenient to determine stability constants if one can be assured that only two species, the ligand and one of the complexes ML_i, exist in a given solution. This condition can generally, but not always, be met if an excess of metal is used over the ligand, thus assuring the formation of only the 1:1 complex. This fact proved useful in the determination of the 1:1 formation constants of the copper and zinc complexes with the 1,10-phenanthrolines. The constants for the 2:1 and 3:1 complexes are easily obtained only if the successive step-wise formation constants differ by a factor of a hundred or more, in other words, if each of these complexes forms exclusive of the others in a given set of solution compositions. As this condition is seldom true in the transition-metal 1,10-phenanthroline complexes, a tedious technique of successive approximations with data that must be very good indeed must be employed. Such a method was used by McClure (29) in the study of the zinc(II)-1,10-phenanthroline complexes, and his results, in the light of more recent work, bear out the inadequacy of this spectrophotometric method for such systems.

Competition

Irving and Mellor (30) have recently used the ability of various metals to compete with iron for 1,10-phenanthroline, thus reducing the absorbancy of the iron complex at the 510 mμ band, to measure portions of the formation curve. The formation curve, it should be pointed out, is the plot of $\bar{n}$ against the logarithm of the ligand concentration, and is expressed analytically by Equation 17. In principle, the method consists of the following steps:

1. A solution of known iron(II) concentration and known 1,10-phenanthroline concentration is prepared, and the absorbancy is read.
2. A known amount of a second metal is added to this solution. The absorbancy will be lowered, indicating dissociation of the iron complex due to competition.
3. 1,10-Phenanthroline is added to the solution until the original absorbancy is again attained. It is assumed that no volume change occurs in these steps, and that the acidity does not change.

Because the absorbancy of the initial and final solutions is the same, it is known that the amounts of iron complexes must be the same, and therefore, that the free 1,10-

phenanthroline concentration is also the same in these solutions. Since the stability constants for the iron complexes are known, the free base concentration can be calculated. It follows also, that the 1,10-phenanthroline added in step 3, must necessarily react completely with the second metal added in step 2. The ratio of these two amounts is seen to be $\bar{n}$, and thus, one point of the formation curve has been determined. Other points may be obtained by starting with different initial absorbancies, the iron concentration being held constant, however. The most important limitation of this method is that only a limited portion of the formation curve of the second metal with 1,10-phenanthroline can be obtained, specifically, that portion lying between free base 1,10-phenanthroline concentrations of $2x10^{-8}$ and $2x10^{-7}M$. This portion has little usefulness for calculating stability constants except under very specific conditions. The range of free ligand concentrations should permit only one complex to be formed, and the stepwise stability constant must be of the order of magnitude of the ligand concentrations specified above. As neither of these conditions are met in the transition-metal 1,10-phenanthroline complexes, the data obtainable by this method serve principally to verify or supplement data obtained by other methods.

Partition

Partition methods, as applied to the measurement of stability constants of metal complexes, have been discussed by Irving and Williams (31) and applied to the 1,10-phenanthroline systems by Kolthoff et al. (32), Irving and Mellor (5) and Grimes (33). While this method tends to become unduly complex if more than one species distributes itself significantly between the chosen solvents, it is particularly useful if only the ligand tends to distribute. Such is the case with the transition-metal-1,10-phenanthroline complex systems. The metal ion, and the complexes, being charged, show no tendency to extract into solvents of low dielectric. The free base 1,10-phenanthroline, however, being uncharged, and of relatively low dipole moment, favors the nonaqueous media. The partition coefficient for the free base can be measured independently, and its value serves to establish the free base concentration in solutions of metal complexes by simply measuring the equilibrated free base in the extractive solvent. The amount of ligand complexed is easily found from the total number of moles of ligand, the amount of ligand in the extractive solvent, the partition coefficient, and the pH of the metal complex solution. Since both the free base concentrations and $\bar{n}$ are established by this procedure, it is possible to obtain the entire formation curve by varying the total number of moles of free base in the system.

In practice, however, there are a number of limitations. The formation of ion pairs can seriously impair the interpretation of the data. Ion pairs are known to form between the 1,10-phenanthrolium ion and several anions (33), however, the experiments can be designed such as to minimize their formation. The partition coefficient is a function of both the ionic strength and the solubility of the neutral base in each phase. While the ionic strength can be controlled, the solubility considerations are a serious limitation because, in general, the higher concentrations of free base in the aqueous phase, if at all attainable, are subject to an error which is difficult to correct. Thus, for particularly weak metal complexes, the portion of the formation curve corresponding to the higher $\bar{n}$ values, may not be obtainable by this method. Another limitation may be the specifications required of the extractive solvent. In the case of the 1,10-phenanthrolines, which adsorb only in the ultraviolet, an important requirement is that the solvent have little or no absorption above 250 mμ. Trace impurities commonly found in solvents which, if absolutely pure, meet this requirement, tend to absorb in this region, however, and special pains must be taken to prepare and preserve a spectrally pure media. Chloroform, a solvent which has been used for 1,10-phenanthroline extractions, tends to decompose photochemically, producing acid, which upsets the pH balance of the aqueous solution, and free radicals or carbene, which apparently react with 1,10-phenanthroline, producing changes in spectra. As this decomposition occurs under various conditions, this solvent could be used only for special cases. Needless to say, the solvent choice also depended on its tendency to form emulsions, absence of side reactions, and availability.

In summary, it can be said that the partition method is the one method which offered the best chance of obtaining the entire formation curves of the transition-metal-1,10-phenanthroline complexes, but it was not without effort that the proper conditions were established.

pH measurements

The use of titrimetric pH measurements for the determination of the formation curves of metal complexes was first extensively employed by Bjerrum (34). Since then, titrimetric methods, and the concept of the formation function, have been very extensively employed in the determination of stability constants of complexes of all types. The method consists, in principle, of measuring the number of protons released by the ligand when it complexes the metal. With a knowledge of the proton-ligand stability constants, this is a measure of the amount of ligand complexed, and, therefore, $\bar{n}$ can be calculated. The free base ligand concentration is derivable from the known concentration of uncomplexed ligand and the pH of the solution. Experimentally, this is accomplished by titrating an acid solution of the ligand, of known concentration, with base, followed by a similar titration of the ligand with a known quantity of metal present in the solution. The difference in the number of moles of base required to reach the same pH value in the two titrations corresponds to the amount of ligand used in complexing the metal, provided the addition of the metal has not disturbed the degree of association of the proton with the ligand. The principal limitation of this method is the accuracy with which pH may be determined. For a very strong complex, the pH must be quite low to assure the condition necessary for any stability determination, namely, that the complex be only partially formed. In such cases, it frequently happens that the moles of protons released in the complexing reaction are of the same order of magnitude as the error in the determination of pH. Failure to recognize this fact can lead to quite erroneous results, as will be illustrated in the experimental sections of this thesis. Practically, this limitation prevents the determination of the 1:1 stability constants of the 1,10-phenanthroline complexes of virtually all the transition metals, and the higher complexes of especially strong complexes, such as cobalt and nickel.

The titrimetric method does have the important advantage over the other methods employed in this thesis (with the exception of partition methods), of being the most accurate for the determination of the upper portions of the formation curve, from which the 3:1 stability constants can be calculated. The titrimetric method is also quite rapid.

A variation of the commonly used experimental technique was used in the present work. Instead of titrating with base, a solution of ligand was titrated with the metal. This technique was made possible by the high sensitivity of the Beckman Model GS pH meter, which permits pH changes of as little as 0.003 unit to be determined. A smooth curve of pH against concentration of metal can thus be obtained, even though the maximum overall change in pH is 0.3 unit. The derivations of the equations pertinent to this technique as applied to 1,10-phenanthrolines are presented in the section on the copper(II)-1,10-phenanthroline complexes.

Kinetics

Several of the transition metals undergo kinetically slow reactions with 1,10-phenanthroline (3), a fact which has been utilized in analytical separations of these metals from iron, in the colorimetric determination of iron by formation of the 1,10-phenanthroline complex. The measurement of the rates of formation and dissociation of these complexes constitutes another means of obtaining their stabilities. This technique was utilized by Lee et al. (35) to measure the overall stability of the tris(1,10-phenanthroline)iron(II) complex, and by Margerum et al. (36) to study the nickel(II) system with 1,10-phenanthroline. While the mechanisms of these reactions raise interesting and perplexing questions, they are not of real importance as far as the determination of the stability of the complexes is concerned, as it was shown that the over-all stoichiometry is not affected.

The vanadium(IV)-1,10-phenanthroline system was studied extensively with respect to the rate of formation of the complexes, and while it cannot be said that the system is fully understood, it is believed that, with qualifications, the stability of the 1:1 complex can be obtained from the kinetic data. The reason for the qualifications is that, within a relatively small range of pH, three different formation reactions take place, only one of which has the same stoichiometry as comparable reactions of the 1,10-phenanthrolines with other transition metals. The data pertinent to the substituent effect have been presented elsewhere (15), and only the results will be presented in this thesis. A discussion of the vanadium(IV) system as a whole must await further research.

Mono(5-Substituted-1,10-Phenanthroline)Iron(II).

Experimental

The stability constant of the tris(1,10-phenanthroline) iron(II) complex has been measured by several authors in a variety of manners, and can be said to be well established within certain limits. The corresponding complexes of 5-nitro- and 5-methyl-1,10-phenanthroline have been studied by Brandt and Gullstrom (13). The stability of the mono(1,10-phenanthroline)iron(II) complex has been measured by Kolthoff et al. (37). The method of determination used in the latter paper was employed in this case to measure the stabilities of the 5-nitro-, 5-bromo-, 5-methyl- and 5-hydrogen-1,10-phenanthroline 1:1 complexes of iron(II). This method requires a knowledge of the stability of the corresponding 3:1 complex; these were taken to be the average of the literature values.

The stability constants of the 1:1 and 3:1 complexes may be written as follows:

$$K_1 = \frac{(\mathrm{Fe})(\mathrm{Ph})}{(\mathrm{FePh})} \tag{18}$$

$$K_3 = \frac{(\mathrm{Fe})(\mathrm{Ph})^3}{(\mathrm{FePh}_3)} \tag{19}$$

The charges have been omitted, and shall be omitted throughout this thesis, for simplicity, as it is understood that all metal ions used are divalent.

The 2:1 complex of iron(II) with 1,10-phenanthroline exists to a very small extent under optimum conditions for its formation. The only report on its stability indicates that it is 100 times weaker than the 1:1 complex (5). Thus it is a reasonable assumption to neglect the 2:1 complex of iron with any of the 1,10-phenanthrolines in calculating the stability of the 1:1 complex.

Equations 18 and 19 may be combined to give the expression

$$K_1 = (K_3)^{1/3} \frac{(FePh_3)}{(FePh)} \left[\frac{(Fe)}{(FePh_3)} \right]^{2/3} \qquad (20)$$

If a solution is prepared in which there is an excess of iron over 1,10-phenanthroline, one may then write

$$(Fe)_T = (Fe) + (FePh) + (FePh_3) \qquad (21)$$

and

$$(Ph)_T = (FePh) + 3(FePh_3) \qquad (22)$$

Because the 1:1 complex has been shown not to absorb appreciably at the wave length of maximum absorption of the 3:1 complex (37), we may write for the absorbancy, A, of this solution

$$A = ab(FePh_3) \qquad (23)$$

The molar absorptivity, a, has the units liters/mole-cm., and is determined from a solution in which there is quantitative conversion to the 3:1 complex. The cell length, b, has the units of centimeters. As can be seen from Equations 20, 21, 22, and 23, there is sufficient information to determine K_1, if K_3 is known independently.

The preparation of the iron(II) chloride and 5-substituted-1,10-phenanthroline stock solutions has been previously described. The composition of each of the solutions used for the stability determinations is indicated in Table 1. For any given 1,10-phenanthroline, two solutions were prepared.

Table 1. Data for the determination of the stabilities of the 1:1 complexes of iron(II) with 5-substituted-1,10-phenanthrolines

Substituent in 5-position	$(Ph)_T$ $M\times10^4$	$(Fe)_T$ $M\times10^4$	pH	A	λ, mμ	pK_1
H	9.57	0.957	4.00	1.050	510	5.85
H	2.87	56.6	4.00	.770	510	
H	2.87	56.6	4.00[a]	.760	510	
H	2.87	56.6	5.00[b]	.920	510	
NO_2	7.03	1.00	3.78	1.193	510	5.06
NO_2	3.00	44.7	3.78	.709	510	
CH_3	7.14	1.00	3.78	1.157	513	6.05
CH_3	3.00	58.4	3.78	.930	513	
Br	7.175	1.00	3.78	1.222	510	5.45[c]
Br	3.00	47.16	3.77	.876	510	

[a] No buffer present, pH adjusted with 0.1 N NaOH.

[b] HCl-NaOAc buffer, apparent hydrolysis occurred.

[c] pK_1 for the 5-Br-1,10-phenanthroline complex is estimated as described in the text.

One solution was prepared with three times as much 1,10-phenanthroline as there was iron in the second. In this manner, the amount by which the absorbancies of these two solutions differed was directly proportional to the amount of the 1:1 complex present in the solution with the excess iron (II). The molar absorptivity of the 3:1 complex can be calculated from the absorbancy of the solution that contained excess 1,10-phenanthroline. The pH of these solutions was maintained constant at a level which permitted an essentially complete reaction by a sodium formate buffer. The ionic strength in all solutions was 0.1, and was attained by adjusting the amounts of hydrochloric acid and sodium formate, as suggested by Bates (38). Two additional solutions were prepared to test the influence of the formate ion on the equilibria. The absorbancy difference between the solutions with and without formate was considered insignificant, the change being more likely due to the difference in ionic strength. An identical solution prepared with acetate ion instead of formate ion showed too high an absorbancy, undoubtedly due to hydrolysis and oxidation of the excess ferrous iron at the higher pH.

The spectra of all solutions were taken on the Cary Model 14, and the absorbancy was read at the wave length of maximum absorbancy on the Beckman DU quartz spectrophotometer. The data are presented in Table 1.

Discussion

The pK_1 values calculated from Equation 20 are listed in Table 1. The pK_3 values used for these calculations are 21.3 for the 5-hydrogen-1,10-phenanthroline iron(II) complex (an average of three values, 21.15, 21.3, and 21.5), 18.0 for the 5-nitro-1,10-phenanthroline iron(II) complex (an average of two values, 18.1 and 17.8), and 22.3 for the 5-methyl-1,10-phenanthroline iron(II) complex. The stability constant for tris(5-bromo-1,10-phenanthroline)iron(II) has not been reported. However, the relation

$$pK_1 = \frac{1}{3}\, pK_3 - 1.123 \qquad (24)$$

can be derived from the data and Equation 20. The constants in Equation 24 refer specifically to the 5-bromo-1,10-phenanthroline complexes of iron(II).

Using the acid dissociation constants, K_a, available in the literature, the plot of pK_3 against pK_a is a linear relationship. The equation of the best straight line is

$$pK_3 = 2.5\ pK_a + 9.15\ . \qquad (25)$$

Similarly, a straight line may be drawn through the points (pK_1, pK_a), the equation of which is

$$pK_1 = 0.596\ pK_a + 2.93 \qquad (26)$$

It is expected that the constants for the 5-bromo-1,10-phenanthroline iron(II) complexes should also obey Equation

25 and Equation 26. If this is true, then these two equations and Equation 24 may be solved simultaneously to yield values for the various constants, namely

$$pK_a = 4.2$$

$$pK_1 = 5.45$$

$$pK_3 = 19.7$$

These values are supported by an independent measurement of pK_a in another part of this thesis, and also by the close agreement of pK_a and pK_3 with the corresponding values measured by Brandt and Gullstrom (13) for the 5-chloro-1,10-phenanthroline system of complexes. The substituents Cl and Br have very similar inductive constants (39).

In Table 27 are presented all the constants for the iron (II) complexes of the 1,10-phenanthrolines.

The Copper(II)-1,10-Phenanthroline System

Spectrophotometric study

Experimental. The copper 1,10-phenanthroline system has been studied by Pflaum and Brandt (40) and Irving and Mellor (5). Pflaum and Brandt attempted to measure the formation curve for this system by pH measurements, and also studied the system by means of Job's method of continuous variations. The composition of the solutions as calculated from the stability constants they obtained, and the Job's plots did not agree, however. Their constant for the 1:1 complex differs from that obtained by Irving and Mellor by a factor of a thousand. Irving and Mellor's constants were determined by partition methods, but the work has not yet been published, a relative evaluation cannot be made, although their constants are more in agreement with Pflaum and Brandt's continuous variations results. It will be seen later on that Irving and Mellor's constants are verified in the present work.

The following experiments are a spectrophotometric study of the copper(II)-1,10-phenanthroline system for the purpose of determining the number of complexes formed, the molar absorptivities of each complex, and, if possible, the stabilities of each complex. The ultraviolet provides the best region of the spectrum to study the formation of the copper (II) complexes of 1,10-phenanthroline. The spectra of 1,10-phenanthroline at all pH values had been previously studied (36) and the molar absorptivities of the absorption bands are well defined. Thus changes in the ligand absorption band due to complexing are easily detected.

A series of solutions was prepared in which the total 1,10-phenanthroline concentration, $(Ph)_T$, was maintained constant, at 4.85×10^{-5}M, while the total copper concentration, $(Cu)_T$, was varied, such that the ratio $(Cu)_T/(Ph)_T$ varied from zero to 2.0. The absorption of the metal was negligible. The ionic strength in all solutions was determined by the total acid concentration, which was maintained at 10^{-3}M. The composition of each solution is presented in Table 2. The ultraviolet spectra, taken on the Cary Model 14 spectrophotometer, are shown in Figure 2, and the variation in absorbancy at several wave lengths with increasing $(Cu)_T/(Ph)_T$ ratio is shown in Figure 3. The isosbestic points in Figure 2 are well defined, appearing at 300, 284, 274, and 269 mμ. Maximum changes in absorbancy occur at 320, 293, and 272 mμ.

Table 2. Variation in absorbancy with changing ratio of copper(II) to 1,10-phenanthroline

$(Ph)_T = 4.78 \times 10^{-5}$M

$(Cu)_T$, Mx10^5	Cu_T/Ph_T	pH	A, 272 mμ	A, 293 mμ	A, 320 mμ
0.00	0.00	3.0	1.407	0.306	0.164
0.625	0.131	3.01	1.393	0.328	0.136
1.25	0.262	2.98	1.388	0.353	0.1155
1.87	0.392	2.99	1.391	0.371	0.093
2.50	0.524	2.99	1.407	0.388	0.080
3.12	0.653	3.00	1.422	0.402	0.069
4.36	0.912	2.96	1.487	0.425	0.064
5.00	1.045	2.98	1.496	0.4305	0.055
6.24	1.347	2.99	1.489	0.4295	0.059
9.35	1.955	2.97	1.494	0.4305	0.0565
15.6	3.26	2.96	1.495	0.4305	0.0552

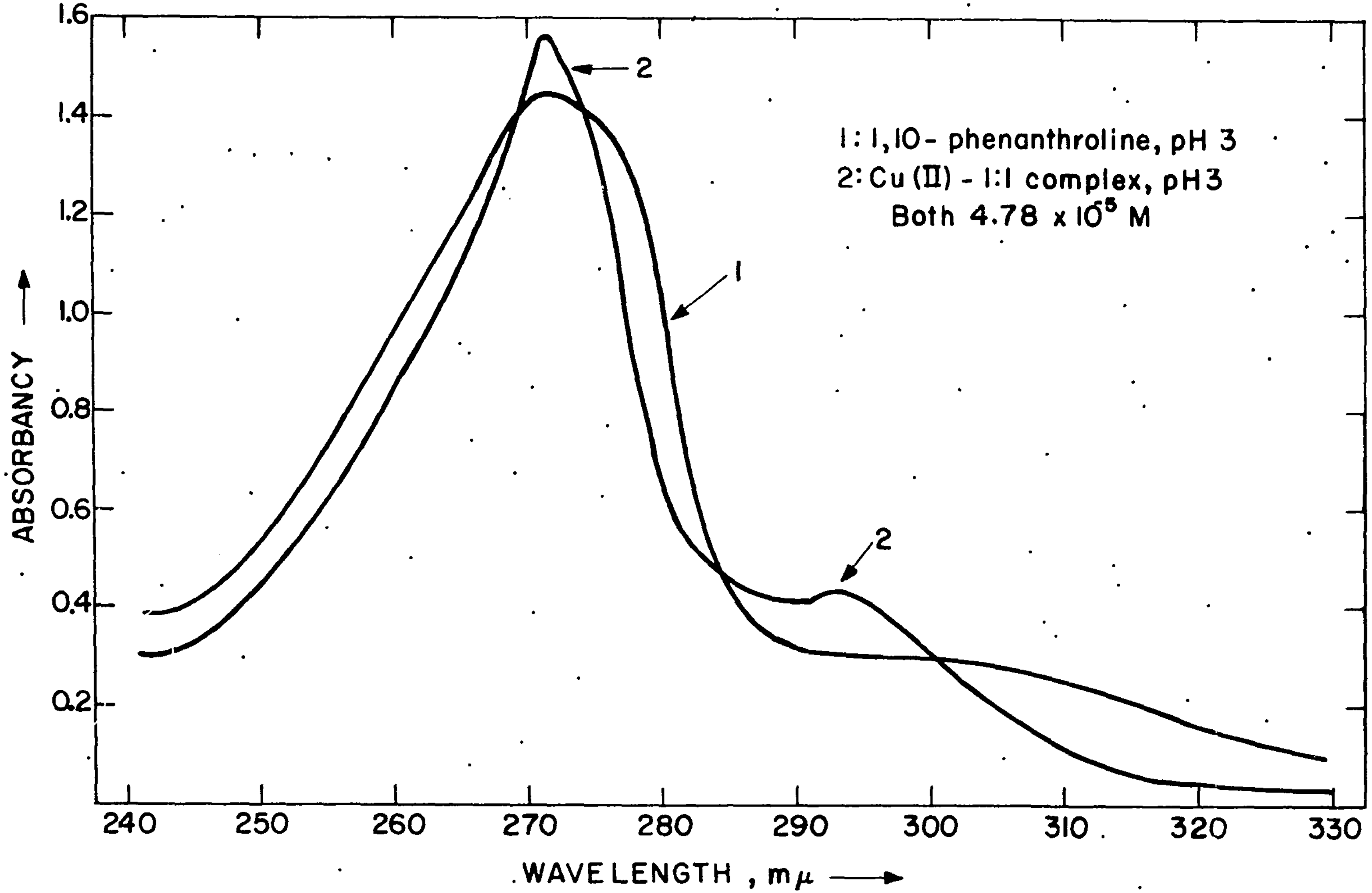


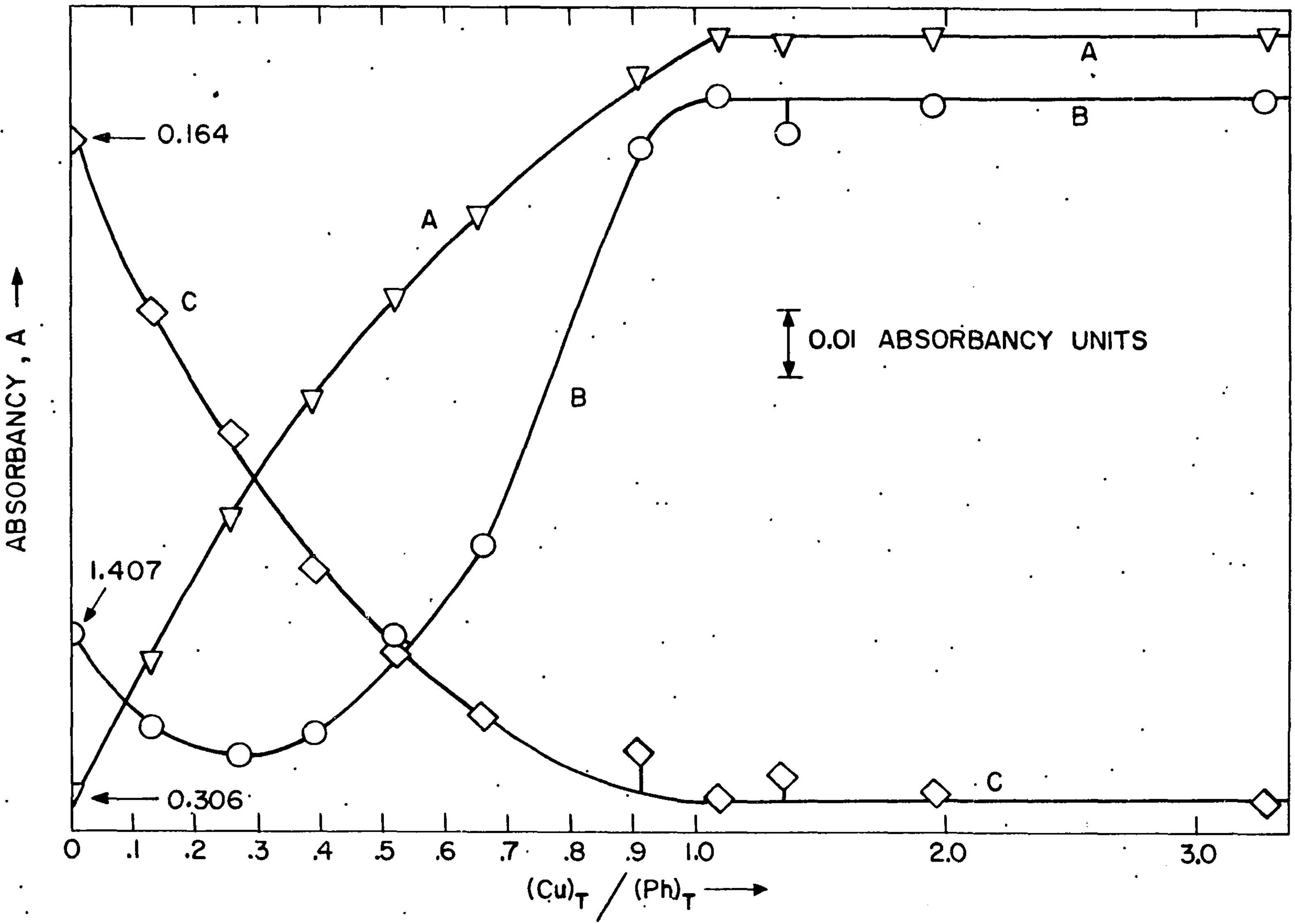
Figure 2. Absorption spectra of copper(II) with 1,10-phenanthroline

Figure 3. Variation in absorbancy with changing ratio of copper(II) to 1,10-phenanthroline

A. Data taken at 293 mμ

B. Data taken at 272 mμ

C. Data taken at 320 mμ


ABSORBANCY , A
0.164
1.407
0.306
A
B
C
0.01 ABSORBANCY UNITS
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
2.0
3.0
$(Cu)_T / (Ph)_T$

A second series of solutions was prepared in which the concentration of copper was held constant while the 1,10-phenanthroline concentration was varied. The pH, as in the first series, was maintained at 3.0, and the ionic strength was constant as determined by the hydrogen ion concentration. The absorbancy of these solutions was read in a 1-cm. cell on the Beckman Model DU spectrophotometer at the wave lengths of maximum absorbancy change, and at the 300 mμ isosbestic point, in order to check on errors in 1,10-phenanthroline concentration. These data are summarized in Table 3 and plotted in Figure 4.

Table 3. Absorbancy of solutions of copper(II) and 1,10-phenanthroline in which Ph_T is varied
All solutions:
$(Cu)_T = 2.231 \times 10^{-5}M$
$pH = 3.00$

$(Ph)_T$, $M \times 10^5$	Ph_T/Cu_T	A, 272 mμ	A, 293 mμ	A, 320 mμ	A, 300 mμ
0.855	0.38	0.303	0.0825	0.010	0.0525
1.71	0.76	0.536	0.151	0.020	0.100
2.565	1.14	0.796	0.226	0.032	0.154
3.08	1.37	0.932	0.265	0.0425	0.186
3.42	1.53	1.030	0.287	0.0525	0.208
3.76	1.68	1.122	0.313	0.060	0.226
4.28	1.91	1.269	0.348	0.071	0.255
4.79	2.14	1.410	0.385	0.085	0.286
5.13	2.29	1.503	0.407	0.095	0.305

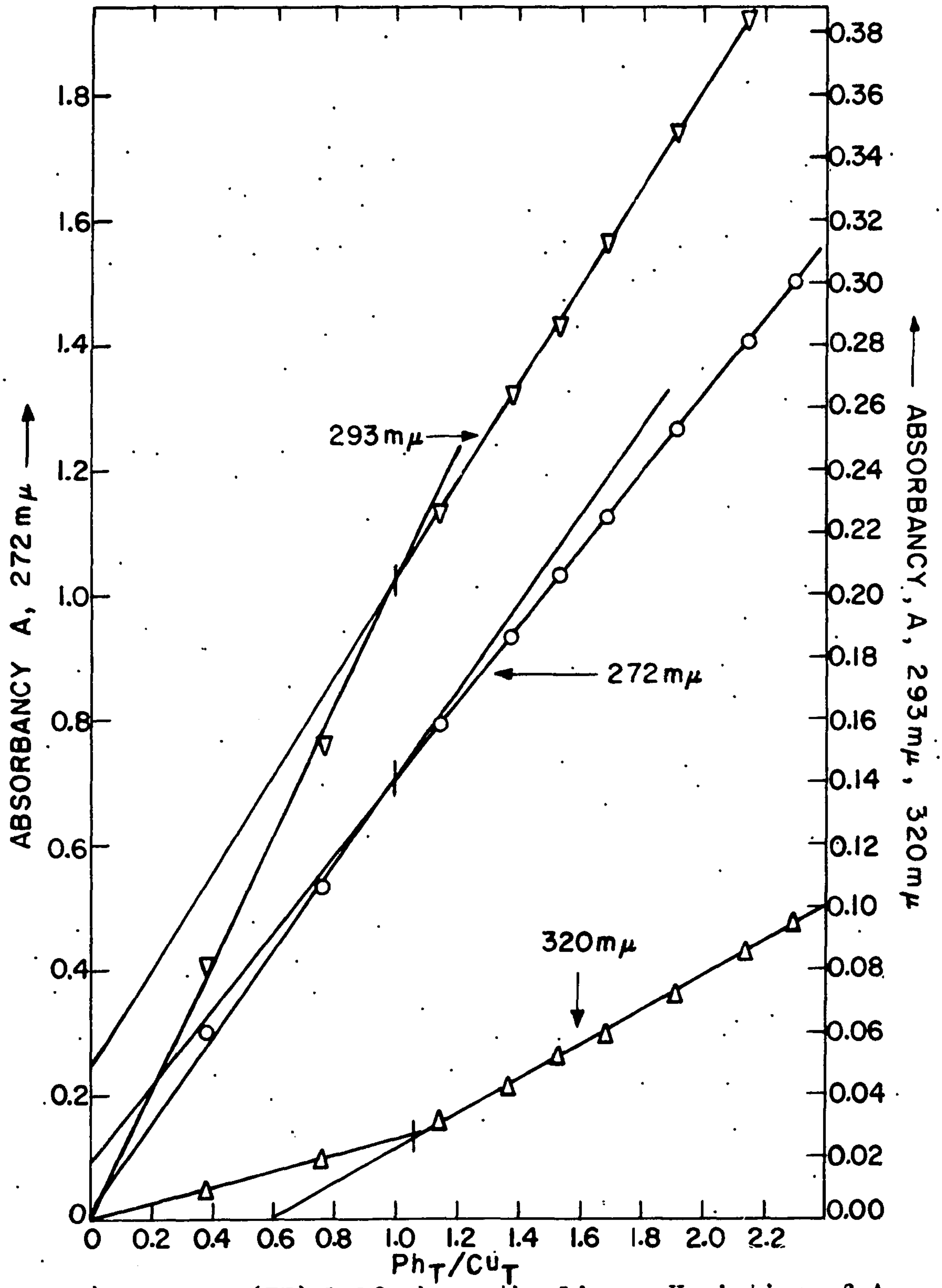


Figure 4. Copper(II)-1,10-phenanthroline. Variation of A with $(Ph)_T$

Discussion. The data in Figure 3 show a definite trend upon changes in the $(Cu)_T/(Ph)_T$ ratio. The break in the curves, at all wave lengths, at a composition corresponding to the 1:1 complex is quite pronounced, and, indeed, as the copper concentration is further increased, the absorbancy remains constant, indicating that the formation of this complex is complete. At least at 272 mμ, the absorbancy plot appears to break at a $(Cu)_T/(Ph)_T$ ratio of 0.33, which corresponds to the 3:1 complex. At the other wave lengths, however, no definite breaks occur between the ratios of 0 and 1.

The interpretation of this plot must be reserved. There can be no doubt of the existence of the 1:1 complex, and the molar absorptivities for this complex may be calculated to be

$$a\ (272\ m\mu) = 32000$$
$$a\ (293\ m\mu) = 9200$$
$$a\ (320\ m\mu) = 1170$$

The molar absorptivities for the 1,10-phenanthrolium species, PhH, as calculated from the absorbancy in the absence of copper, is seen to be

$$a\ (272\ m\mu) = 30100$$
$$a\ (293\ m\mu) = 6500$$
$$a\ (320\ m\mu) = 3500\ .$$

While the nonlinearity of the plots in Figure 3, between the ratios of 0 and 1, is sufficient evidence for the existence of a 2:1 species, the evidence in Figure 4 is more convincing.

As the ratio of 1,10-phenanthroline to copper increases, the absorbancy increases. A definite break occurs at the ratio corresponding to the 1:1 complex, and the initial slope is proportional to the molar absorptivity of the 1:1 complex. After this break, the absorbancy continues to increase linearly, but with a slope which is significantly different from that which would be predicted by the molar absorptivity of the 1,10-phenanthrolium ion. This is true at all three wave lengths. Assuming the absence of 3:1 complex in these solutions, one may calculate the molar absorptivities for the 2:1 species to be

$$a\ (272\ m\mu) = 54200/\alpha$$
$$a\ (293\ m\mu) = 14100/\alpha$$
$$a\ (320\ m\mu) = 5020/\alpha\ ,$$

where α is the degree of association of the 2:1 complex, defined as

$$\alpha = (CuPh_2)/(Cu)_T\quad .$$

With the knowledge of the magnitude of the stepwise stability constants, determined in another section of this thesis, it may be asserted that α , for the above solutions, is about 0.9.

Because of the evidence that the molar absorptivity of the 2:1 species is less than twice that of the 1,10-phenanthrolium ion species, it cannot be stated from the data of Figure 3 alone, that the break at $(Cu)_T/(Ph)_T = 0.33$ is evidence for a 3:1 species existing in solutions having a $(Cu)_T/(Ph)_T$ ratio lower than this value. The shape of this curve can result from the presence of only the 1:1 and 2:1 species in solutions of ratios 0 to 1. This point, made with the hindsight that all three complex species do exist, and a knowledge of their stabilities, illustrates the limitations of the application of the mole ratio method. This method, when applied to the determination of compositions of solutions in which several complexes may exist, is inadequate if there is no means to detect one species exclusive of the rest. The same limitation is pertinent to applications of Job's method of continuous variations; the data and conclusions drawn depend on the concentration level of the components.

Spectrophotometric determination of stability

Experimental. A series of solutions was prepared in which there was a constant twofold excess of copper(II) to 1,10-phenanthroline. The concentrations were so designed, that if the stability of the 1:1 complex was 10^8 to 10^9, the complex would be only partially formed. The pH of each of these solutions was 3.0 and the total copper and 1,10-phenanthroline concentrations were in the order of 10^{-6} and were varied a factor of six. The spectra of these solutions were recorded in 10-cm. cells, and the absorbancies were read at 272 mμ and 293 mμ. The maximum absorbancy of the most concentrated solution did not exceed 0.4. In the first preparation of this series, the absorbancy results were highly erratic. It was found that the cause was ultraviolet absorbing impurities in the water used for diluting these solutions, and these were traced to a leaching of the polyethylene or tygon tubing used for siphoning this water. Further series of solutions were prepared from water distilled from alkaline permanganate, and stored in all glass systems.

Discussion. In spite of the additional precautions, results calculated from the data obtained were still erratic, although the data were fairly precise. The reason for this is ultimately that the difference in the molar absorptivities of the 1:1 complex and the 1,10-phenanthrolium ion is a small enough fraction of the molar absorptivity of either species, that a 1 per cent error in both will result in as much as a 30 per cent uncertainty in the difference. The degree of association of the 1:1 complex, α , is determined from the formula

$$\alpha = \frac{A - a_{HPh}\,(Ph)_T}{a_{CuPh} - a_{HPh}}$$

where A is the absorbance of the solution, $(Ph)_T$ is the equivalent total molar concentration of 1,10-phenanthroline in the solution, and a is the molar absorptivity of the species indicated by the subscript. As the terms in the numerator are subject to the same experimental error as those in the denominator, it can be seen that α must be subject to a large uncertainty. The average result, however, indicated that α must be in the order of 1 ± 0.2, which means that the formation of the complex must be almost complete. If this is so, it could be ascertained that the formation constant must be greater than 5×10^8, and that the determination of this constant could not be accomplished by this method. As the spectrophotometric determination of the formation constants of the 2:1 and 3:1 complexes depends, in part, on a knowledge of the 1:1 constant, this method was not further applied to their determination. These data have not been entered here because they do not serve to illustrate any more than has been already stated, and no constant could be calculated from them.

pH measurements, a titrimetric method

Derivation of equations. The principle of the present titration method, the equations of which are to be derived here, has been discussed in another section of this thesis. It is desired to titrate a solution of 1,10-phenanthroline, of known pH, with a metal ion solution, of known pH, and from the resultant changes in pH, derive the formation curve. Let the subscript 1 refer to the solution of 1,10-phenanthroline before the addition of metal ion titrant, and 2, to the solution after the addition of $V_2 - V_1$ milliliters of titrant. The subscripts T and M will refer to "Total", and "Metal ion titrant solution", respectively. The concentrations of the various species shall be indicated by parentheses, (), and the symbols Ph, HPh, M, and MPh_i shall be used to represent the free base 1,10-phenanthroline, the protonated 1,10-phenanthroline, the metal ion, and the i-th complex of the metal, respectively. From definition, then, we may write (see Equations 13 and 14)

$$\begin{aligned} &\text{a)}\quad (H)_1 + (HPh)_1 = (H)_{T1} \\ &\text{b)}\quad (H)_2 + (HPh)_2 = (H)_{T2} \\ &\text{c)}\quad (Ph)_1 + (HPh)_1 = (Ph)_{T1} \\ &\text{c)}\quad (Ph)_2 + (HPh)_2 = (Ph)_{T2} - \sum_i i(MPh_i)_2 \end{aligned} \qquad (26)$$

The concentration acid dissociation constant is defined as in Equation 12. The term $\sum_i i(MPh_i)_2$ may be solved for in terms of $(H)_1$, $(H)_{T1}$, $(H)_2$, $(H)_{T2}$, and K_a by appropriate substitutions, and by considering the effect of dilution, namely

$$(Ph)_{T1} = (Ph)_{T2}\, V_2/V_1 \; .$$

The result is

$$\sum_i i(MPh_i)_2 = \left[(H)_{T1} - (H)_1 - K_a + \frac{K_a(H)_{T1}}{(H)_1}\right]\frac{V_2}{V_1} - \left[(H)_{T2} - (H)_2 - K_a + \frac{K_a(H)_{T2}}{(H)_2}\right] . \qquad (27)$$

If one defines

$$\alpha = (H)_M/(H)_1 \; ,$$

and recognizes that the mole balance of protons during the titration is expressed by

$$(H)_{T1}\, V_1 = (H)_{T2}\, V_2 - (V_2 - V_1)(H)_M \;,$$

one may simplify the expression for the concentration of complexed 1,10-phenanthroline to be

$$\sum_i i(MPh_i)_2 = (H)_2 - (H)_1\left[\alpha + \frac{V_1}{V_2}(1 - \alpha)\right] + \frac{K_a(H)_{T2}}{(H)_1(H)_2}\Big[(H)_2 - (H)_1\Big] - K_a\left(1 - \frac{V_1}{V_2}\right)(1 - \alpha)\;. \qquad (28)$$

On the right of this equation, all terms can be measured, and thus, $\bar{n}$ is easily obtained from Equation 17, restated as

$$\bar{n} = \frac{\sum_i i(MPh_i)_2}{(M)_{TM}\dfrac{V_2 - V_1}{V_2}}\;. \qquad (29)$$

The free base 1,10-phenanthroline concentration can be obtained at any pH from Equation 16, which can be restated as

$$(Ph)_2 = \frac{(Ph)_{T1}\dfrac{V_1}{V_2} - \sum_i i(MPh_i)_2}{1 + (H)_2/K_a}\;. \qquad (30)$$

It is to be noted that if care is taken to make the pH of the titrant and the 1,10-phenanthroline solution equal prior to the titration, then $\alpha = 1$ in Equation 28. This is an important consideration, if calculations are to remain simple. If volume changes are neglected, Equation 28 reduces to exactly the difference in hydrogen ion concentrations of the initial and titrated solution, plus a correction term for the change in the equilibrium of Equation 9a.

It may be noted that the hydrogen ion concentrations in this method must be derived from the pH, and therefore the activity coefficient of the proton must be known.

Determination of the formation curve. Several considerations must be made in designing the concentrations to be used for the metal ion titrant method. First of all, the extent of hydrolysis of the metal must be known, either from known hydrolysis constants or a direct measurement. It is, of course, preferable that no hydrolysis occur in the pH range of the titration. Secondly, in order for a change in pH upon complexing to be observed, the major portion of the 1,10-phenanthroline should initially exist as the 1,10-phenanthrolium ion species. This requirement fixes the upper limit of the initial pH at the magnitude of pK_a. Thirdly, the total concentration of 1,10-phenanthroline must be of the same order as the initial hydrogen ion concentration, in order that an optimum change in (H), as measured by $\Delta pH/pH$, may be obtained. If $(Ph)_T > (H)_1$, the second condition above is not met sufficiently. If, however, the 1,10-phenanthroline concentration is much less than the initial hydrogen ion concentration, the change in pH will be too small to measure accurately. Thus the concentration levels are predetermined quite strongly by the optimum conditions for the titrations, namely, $(Ph)_T \leqslant (H)_1 \cong K_a \cong (H)_M$. The titrant concentration is best dictated by the desire to keep the total volume change at a minimum, and by the accuracy of the buret.

Considering the above conditions, and the fact that copper(II) hydrolyzes extensively at pH = 5, which is the magnitude of pK_a for 1,10-phenanthroline, it was necessary to first measure the extent of hydrolysis at pH values less than 5.

The activity coefficient of hydrogen ion, γ_H, at an ionic strength of 0.1 in potassium chloride was measured as follows: solutions of hydrochloric acid of analytically known concentration, in the order of 10^{-4}M, and potassium chloride, exactly 0.1M were prepared. The paH of these solutions were read relative to a pH 4 buffer prepared according to National Bureau of Standards specifications (38) using a glass-calomel electrode system. The Beckman GS meter permitted the paH to be read to ± 0.003 units, although the accuracy was determined by the accuracy of the buffer, which is ± 0.01 unit. The ratio of the measured to the known concentration of hydrogen ion was calculated to be 0.80 ± 0.01, which agrees well with the value for γ_H, 0.805, in the tables of Latimer (41). It is understood that this value includes changes in the liquid junction potential, but under the conditions, this potential should be constant, and was assumed to be.

A solution of 10^{-2}M $CuCl_2$, 0.1 M in potassium chloride, was titrated with 0.100 M sodium hydroxide under an inert atmosphere of helium, after first having been flushed of CO_2 with this gas. The pH was read every 0.05 ml. A plot was made of pcH, calculated from the data and the activity coefficient measured above, against the milliliters of sodium hydroxide added. On the same graph, a curve representing the titration curve if no copper were present was plotted. The one assumption for the calculation of this curve was that, at pH 3.3, the initial point, there was no hydrolysis of copper occurring. The difference in the two curves at the same pH was proportional to the moles of base consumed by the copper. In this way it was determined that at pH 4, the amount of hydrolysis was small enough not to interfere seriously with the titration which follows.

The titration for the determination of the formation curve of the copper-1,10-phenanthroline system was performed as follows: a solution of 4.78×10^{-4} M 1,10-phenanthroline, 5×10^{-4} hydrochloric acid, and 0.1 M potassium chloride was prepared. The pH of this solution was measured to be 4.14. The copper titrant was prepared by diluting appropriate amounts of 0.1978 M $CuCl_2$, 1.0 M potassium chloride and 0.1 M sodium hydroxide to give a solution 0.989×10^{-2}M in Cu(II), an ionic strength of 0.1 and a pH of approximately 3.8. Duplicate titrations were performed, and the curves were reproduced to within the 0.01 pH unit. Before and after each titration, the buffer, and the proton concentration standard ($5x10^{-4}$ M hydrochloric acid) were read several times. Table 4 contains the data for one of the titrations and the calculations to obtain $\bar{n}$ and (Ph), the free base concentration.

Table 4. Determination of the formation curve of the copper (II)-1,10-phenanthroline system by pH measurements

V_1 = 40 mls.
$(Ph)_{T1} = 4.78x10^{-4}M$
$(H)_{T1} = 5.0x10^{-4}M$
ionic strength = 0.1
$K_a = 1.0x10^{-5}$

Titrant:
$(Cu)_{TM} = 0.989x10^{-2}M$
ionic strength = 0.1
$(H)_M = 2.05x10^{-4}M$
$\alpha = 2.28$

V_2-V_1, mls.	pH	(H), $Mx10^4$	$\sum_i i(CuPh_i)_2$, $Mx10^4$	$\bar{n}$	(Ph), $Mx10^5$
0.0	4.145	0.90	0.00	—	6.3
0.10	3.956	1.390	0.683	2.77	2.75
0.20	3.817	1.914	1.304	2.65	1.71
0.30	3.703	2.490	1.932	2.62	1.09
0.40	3.621	3.005	2.475	2.53	0.728
0.50	3.557	3.48	2.972	2.44	0.490
0.65	3.491	4.045	3.553	2.25	0.278
0.80	3.445	4.508	4.014	2.07	0.146
1.00	3.415	4.830	4.340	1.66	0.0656
1.10	3.411	4.876	4.37	1.65	0.057
1.20	3.408	4.908	4.414	1.53	0.045

Calculations and conclusions. The Equations 28, 29 and 30 are used in the calculation of $\bar{n}$ and (Ph) values; the values for α, K_a, and γ_H used in these calculations are stated in Table 4. The formation curve is presented in Figure 5. Several points must be considered to understand the validity of this curve for purposes of calculating stability constants. First, the precision of the individual points taken is a function of the magnitude of the pH change observed. Toward the end of the titration, pH increments become smaller because almost all of the protons in the solution have been released by the 1,10-phenanthroline. In this case, $\bar{n}$ can be measured quite accurately, since it becomes $(Ph)_T/(Cu)_T$, but (Ph) acquires a large uncertainty. This uncertainty is indicated by the vertical bars about the points in Figure 5. The second consideration is the value of K_a. Grimes[1] has noted that in solutions in which the total 1,10-phenanthroline and proton concentrations are about equal, there exist significant quantities of species in which more than one 1,10-phenanthroline are associated with a proton. The strongest of these compounds, Ph_2H, is 10^3 times less stable than the mono-protonated-1,10-phenanthroline, specifically,

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[1] Grimes, P. G., Ames, Iowa. Evidence for the existence of Ph_1H^+ species in solution. Private communication. 1957.

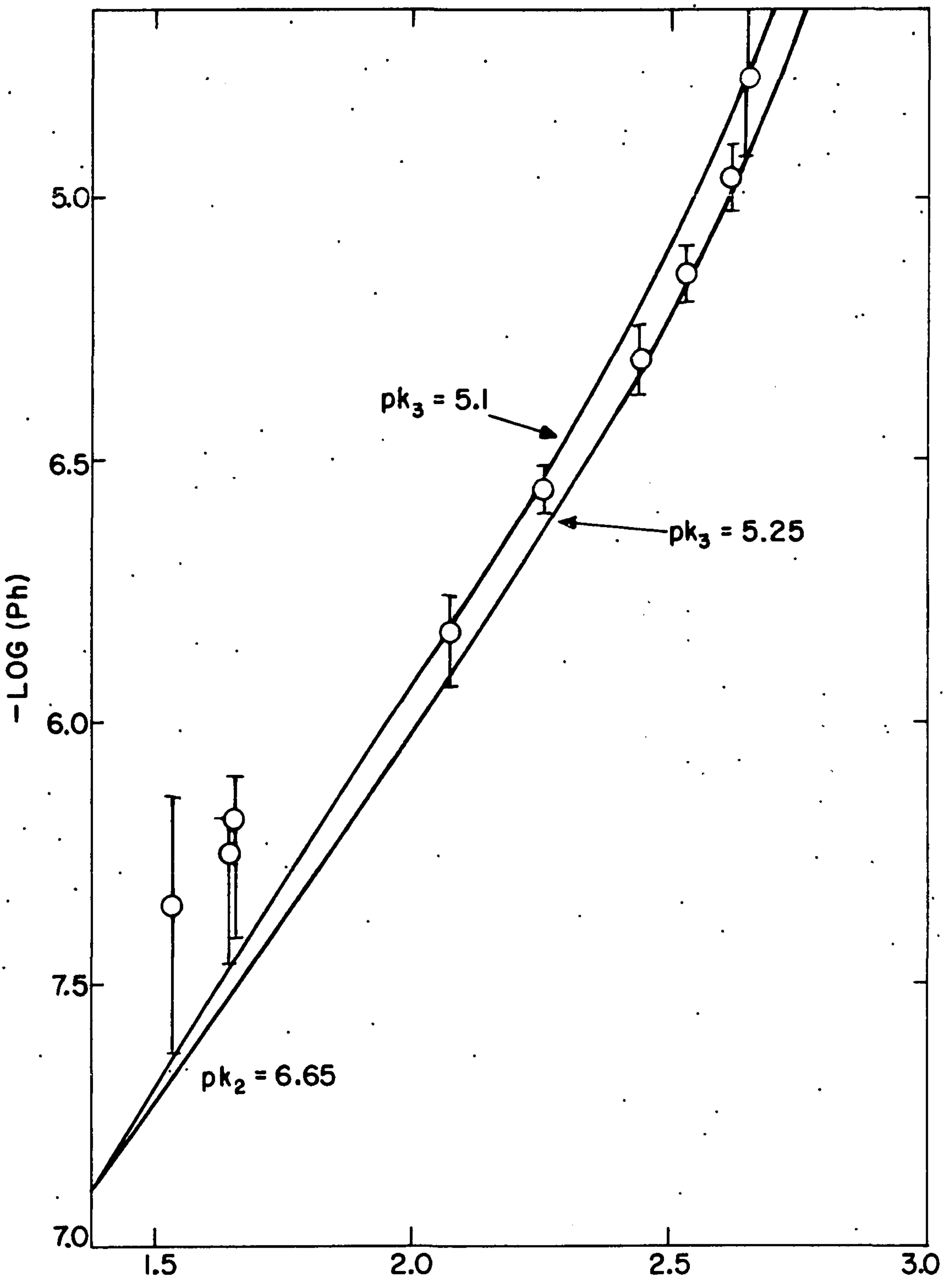


Figure 5. The formation curve of the copper(II)-1,10-phenanthroline system from pH measurements

$$K_{a2} = \frac{(HPh)(Ph)}{(Ph_2H)} = 1.6 \times 10^{-2}$$

The value of K_a (Equation 12) has been determined in a variety of manners in the literature, and the existence of these species undoubtedly can explain the lack of agreement in many cases. The best value for K_a, taken from data in which the other species can be taken in account or their effect minimized, seems to be about 1.0×10^{-5}, at 0.1 M ionic strength. It will be noted that one can use the pH of the 1,10-phenanthroline solution in Table 4 to calculate an "apparent" K_a value, as follows

$$K_a' = \frac{(H)(Ph)}{(HPh)} = \frac{(H)\left[(Ph)_T-(H)_T+(H)\right]}{(H)_T - (H)} =$$

$$\frac{0.85 \times 0.63 \times 10^{-4}}{(5.0 - 0.85)} = 1.29 \times 10^{-5} .$$

But $K_a' = K_a + K_aK_{a2}(Ph)$. Solving for K_a, one obtains 1.19×10^{-5}, which is closer to the value stated above. Presumably, if one considers additional species, the correct K_a, as defined, will result. A systematic study of these additional 1,10-phenanthroline species was not undertaken in this thesis, although their existence serves to explain several observations, notably in the partition studies, which could not be explained otherwise. The importance of additional species in the present case is that the free 1,10-phenanthroline concentration calculated by means of Equation 30 will be slightly high because they were not considered in the derivation. A third point, which is discussed on pages 130-132, is the little understood behavior of the 1,10-phenanthrolines with glass surfaces. Because a glass electrode was being used in the present titration, it might be expected that the overall potentials representing the pH would be affected by glass adsorption phenomena. Drifting potentials, and "wrong" potentials have been observed, but in the present case erratic behavior of this type was not observed, and the pH at the beginning and end of the titration were within experimental error of the theoretical value.

As the complete formation curve was not obtained by this method because of the inherent limitations, it was necessary to resort to partition methods to obtain the remainder, before stability constants could be calculated.

Application of the partition method

Derivation of equations. Since the application of partition methods to the measurement of formation curves has been discussed more generally elsewhere (31) the present equations shall be derived to apply to a system in which only the free base ligand, 1,10-phenanthroline, is distributed between an aqueous phase and some organic phase. Since all other species are charged, an ion pair mechanism is necessary for them to distribute. The extraction of 1,10-phenanthrolium ions by means of ion pair formation with several anions has been studied (33) and the conditions necessary for this process to be significant are understood, and can be avoided. The extraction of metal complexes, on the other hand, would become obvious from the spectrum of the organic phase, and in no case was this observed in the present work. With these points in mind, the equations that follow will be derived.

The moles of a particular species shall be indicated by the symbol for the species, as, for instance, Ph. As before, parentheses indicate concentration in moles per liter, V, the volume in liters, the subscripts o and w, the organic and aqueous (water) phases, respectively, and subscript T refers to the total in the system (both phases).

From a mole balance of a system containing both a 1,10-phenanthroline and a metal M, it follows that

$$(Ph)_T = (Ph)_o + (Ph)_w + (HPh)_w + \sum_i i(MPh_i)_w \qquad (31)$$

From the definition of the acid dissociation constant K_a and $\bar{n}$ (Equation 17) and Equation 31, the equation

$$Ph_T = (Ph)_o V_o + (Ph)_w V_w (1 + (H)/K_a) + \bar{n} M_T \qquad (32)$$

can be derived. The partition coefficient for the free base 1,10-phenanthroline may be defined as

$$K_D = (Ph)_o/(Ph)_w \qquad (33)$$

and may be substituted in Equation 15, giving

$$Ph_T - \bar{n}M_T = \left[K_D V_o + V_w(1 + (H)/K_a)\right](Ph)_w = Q(Ph)_w , \qquad (34)$$

where, for convenience, the symbol Q has been substituted for the term in brackets.

It is evident that Equations 33 and 34 are sufficient for the calculation of $\bar{n}$ and $(Ph)_w$, for all other terms are known or separately measurable quantities.

Determination of the formation curve. The partition coefficient of 1,10-phenanthroline for the chloroform-water system has been measured by Kolthoff et al. (32) and by Grimes (33) who studied this system in much greater detail. The value of this coefficient as defined in Equation 33 is 1040. This value was used in the subsequent work.

The concentrations of the reagents used in each solution, from which data were to be taken to obtain an $\bar{n}$, (Ph) pair, were carefully calculated in advance, so as to insure maximum accuracy theoretically available in the method. A reasonable set of stability constants was assumed for the complex system and a formation curve calculated from these by means of Equation 17. From the curve, pairs of $\bar{n}$, (Ph) values were taken in a systematic manner, and using these values, the amounts of Ph_T and M_T that would have to be used if one-half of the total 1,10-phenanthroline were to remain in the organic phase at equilibrium. In other words, from Equation 34

$$Ph_T - \bar{n}M_T = \tfrac{1}{2}Ph_T = Q(Ph)_w .$$

The composition of the solutions prepared are presented in Table 5. The concentration of acid in the aqueous phase was so designed to (1) be high enough to assure the absence of hydrolysis of the copper, (2) maintain the ionic strength of the various solutions constant, and (3) be low enough that extraction of ion pairs would be negligible.

The following procedure was followed in preparing these solutions: In a 100 ml flask, the appropriate carefully measured amounts of hydrochloric acid, stock 1,10-phenanthroline solution, stock copper(II) chloride solution, and redistilled water were added, in that order, such that the final volume was exactly 25 mls. Then exactly 25 mls. of water-saturated chloroform were added by pipet, with the tip of the pipet below the water surface. The flask was stoppered and shaken vigorously on a mechanical shaker for one hour. After the phases had separated, aliquots of the chloroform phase were withdrawn by pipet for analysis. It was found that if a portion of the aqueous phase was first taken up in the pipet, loss of chloroform by evaporation due to the reduced pressure in drawing the aliquot could be eliminated.

The 1,10-phenanthroline in the chloroform phase was analyzed in two ways: The spectra was either taken in the chloroform solution, or, the chloroform was evaporated completely, the residue of 1,10-phenanthroline then being dis-

Table 5. The copper(II)-1,10-phenanthroline system. Partition between chloroform and water

Ph_T moles x 10^6	Cu_T moles x 10^6	A, 271 $m\mu$[a]	$(Ph)_o$[b] M x 10^4	$(Ph)_w$ M x 10^8	$\bar{n}$[c]
17.7	5.90	4.675	1.550	14.9	1.5
5.9	2.46	1.640	0.547	5.25	1.14
2.36	1.18	0.600	0.200	2.0	1.00
0.59	0.421	0.080	0.0264	0.25	1.04
0.295	0.295	0.0484	0.016	0.153	0.685

[a] Obtained through the evaporation technique. The absorbancy here is in reference to a 1 cm. cell length, and dilution factors are taken in account.

[b] The aqueous molar absorptivity of the 1,10-phenanthrolium ion, a_{HPh} = 30,100, is used to obtain $(Ph)_o$ from the formula $(Ph)_o = A/a_{HPh}$.

[c] Calculated using Q = 59.0. See text.

solved in a measured volume of 0.1 M hydrochloric acid, and the spectra recorded. The calculations and results using these two methods are recorded in Table 5.

Calculations and conclusions. The experimental points are plotted in Figure 6, along with the data from the titrimetric technique. A best smooth curve drawn through these points must be the formation function defined in Equation 17. The constants are found by successive approximations. The step-wise constants can be assumed to be equal to the free base 1,10-phenanthroline concentrations at half-integer $\bar{n}$

Figure 6. The formation curves of the copper(II)-5-nitro-1,10-phenanthroline and copper(II)-1,10-phenanthroline systems

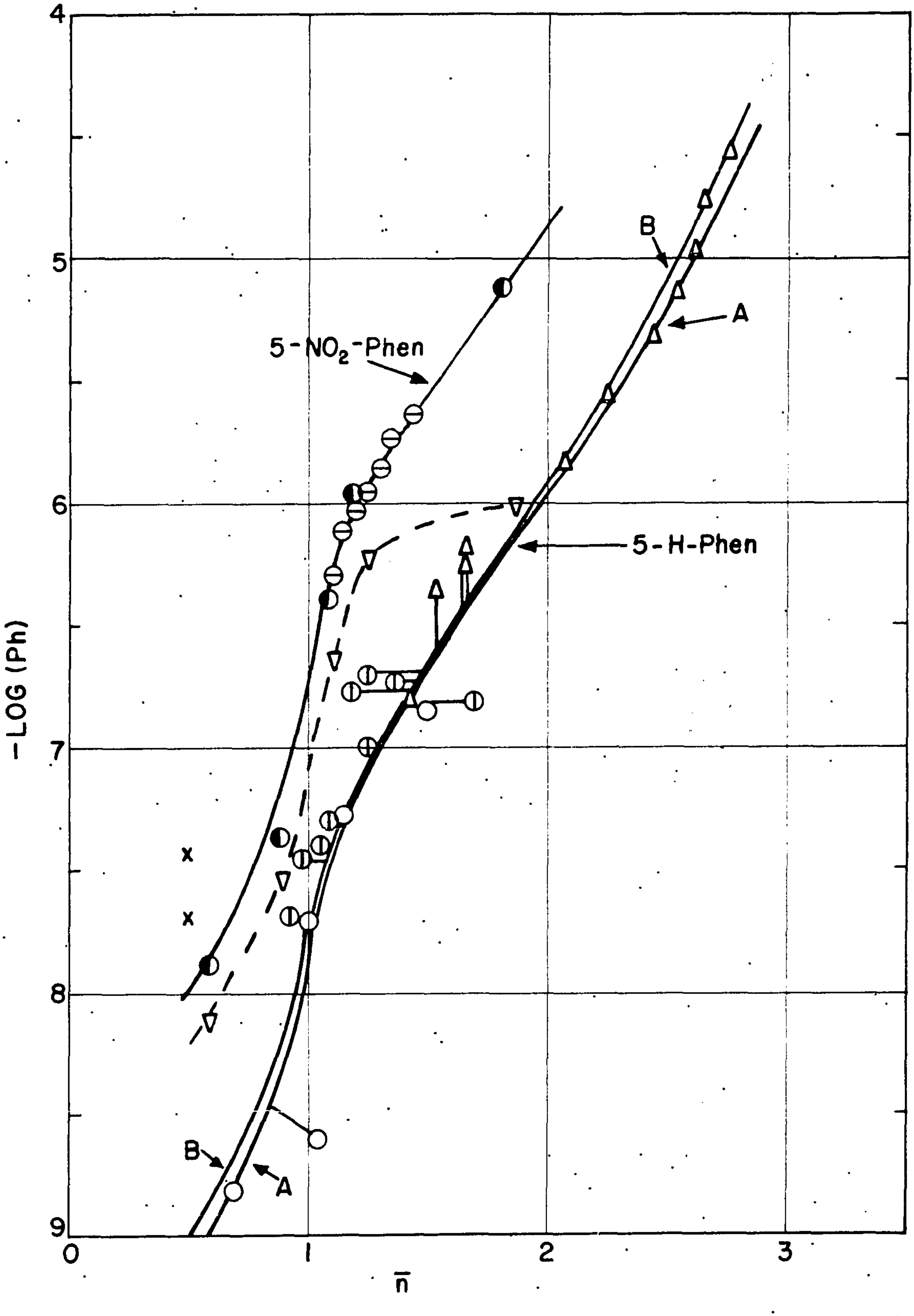
The points show are:

- ✗ Spectrophotometric determination of pk_1 for the 5-nitro-1,10-phenanthroline complex
- ⊖ Results of the competition method for 5-nitro-1,10-phenanthroline
- ◐ Results of the partition method for 5-nitro-1,10-phenanthroline using $K_D = 1700$
- ▽ Results of the partition method for 5-nitro-1,10-phenanthroline using $K_D = 3070$
- △ Results of pH measurements for 1,10-phenanthroline
- ○ Results of the partition method for 1,10-phenanthroline
- ⦶ Results of the competition method for 1,10-phenanthroline from the data of Irving and Mellor (30)

Curves shown are:

A. Formation curve calculated for 1,10-phenanthroline using $pk_1 = 9.15$, $pk_2 = 6.65$, and $pk_3 = 5.25$

B. Formation curve calculated for 1,10-phenanthroline using $pk_1 = 9.0$, $pk_2 = 6.7$, and $pk_3 = 5.1$


-LOG (Ph)
n̄
4
5
6
7
8
9
0
1
2
3
5-NO₂-Phen
5-H-Phen
A
B
B
A
x
x

values as the first approximation. A formation curve is then calculated using this set of constants, and compared to the experimental data. If a good fit is not obtained over the entire range of the curve, the appropriate constants are adjusted and a new formation curve calculated. In Figure 6, two calculated curves are drawn, to illustrate the sensitivity of the formation curve to the constants chosen. Both curves fit the experimental points within the margin of error. It should be pointed out that only one experimental point is obviously not given weight, that is No. 4 in Table 5. The location of this point is unreasonable if all the others are correct, and it is likely that an undetected gross error, such as overheating on evaporation occurred.

The best values of the constants are $pk_1 = 9.15$, $pk_2 = 6.65$, $pk_3 = 5.25$. These compare favorably with the constants quoted by Irving and Mellor (5), $pk_1 = 8.82$, $pk_2 = 6.57$, and $pk_3 = 5.02$, but not with those of Pflaum and Brandt (40), which are $pk_1 = 6.3$, $pk_2 = 6.15$, and $pk_3 = 5.5$. In reviewing the data of Pflaum and Brandt, who used the titrimetric method of Bjerrum, it is apparent that too much was asked of the data, for the change in pH due to complexation is within the reading error. This is particularly true for the data which affects pk_1. Insufficient points were taken to accurately pin down values for pk_2 and pk_3. The data of Irving and Mellor is not yet available for close examination.

The Copper(II)-5-Nitro-1,10-Phenanthroline System

There is no reference in the literature to work with complexes of 5-nitro-1,10-phenanthroline other than those of iron(II) and nickel(II). Preliminary spectrophotometric investigations, similar to those carried out with 1,10-phenanthroline, indicated that copper(II) behaves similarly regardless of the substituent in the 5-position. The system in the present work was studied by competition with the iron(II)-5-nitro-1,10-phenanthroline complexes in the manner described by Irving and Mellor (30), and by competition with the protonated species, utilizing the ultraviolet spectra.

Application of the competition method

The principle behind the present method has already been described, and for details of development the reader is referred to Irving and Mellor's paper (30). The overall stability of the 3:1 iron(II) complex with 5-nitro-1,10-phenanthroline has been measured by Brandt and Gullstrom (13) as pK_3 = 18.1, from rate data, and 17.9 from equilibrium data. The average, 18.0, and the measured value for pk_1, 5.06, can be used to calculate the formation curve for the iron(II) system, by means of Equation 17. It is assumed that the 2:1 complex is non-existent. At the absorption maximum of the 3:1 iron(II) complex, neither the 1:1 iron(II) complex or the copper(II) complexes absorb at the concentration levels used in the following work. Thus it is possible to validly derive absorbancy relations as follow:

$$A = ab(\mathrm{FePh}_3) ,$$

and

$$A_{max} = ab(\mathrm{Fe})_T . \qquad (35)$$

From the definition of the formation constants and Equation 35, it is then apparent that

$$A/A_{max} = (\mathrm{Fe})(\mathrm{Ph})^3/(\mathrm{Fe})_T$$

$$= \beta_3(\mathrm{Ph})^3/\left[1 + \beta_1(\mathrm{Ph}) + \beta_3(\mathrm{Ph})^3\right] . \qquad (36)$$

Equation 36 is used to calculate the curve in Figure 7. Thus, the free 1,10-phenanthroline concentration can easily be found if the absorbancy of a 1,10-phenanthroline solution, containing a known amount of iron(II), is measured, regardless of other metals present.

Now consider two 1,10-phenanthroline solutions, both of which contain the same concentration of iron(II), $(\mathrm{Fe})_T$, but one also contains a known concentration of a second metal, $(\mathrm{M})_T$, which competes for 1,10-phenanthroline. The absorbancies and pH of these solutions are equal. The mole balance equations for each solution would read

$$(\mathrm{Ph})_{T1} = (\mathrm{Ph}) + (\mathrm{HPh}) + \sum_i i(\mathrm{FePh}_i) + \sum_i i(\mathrm{MPh}_i), \text{ and}$$

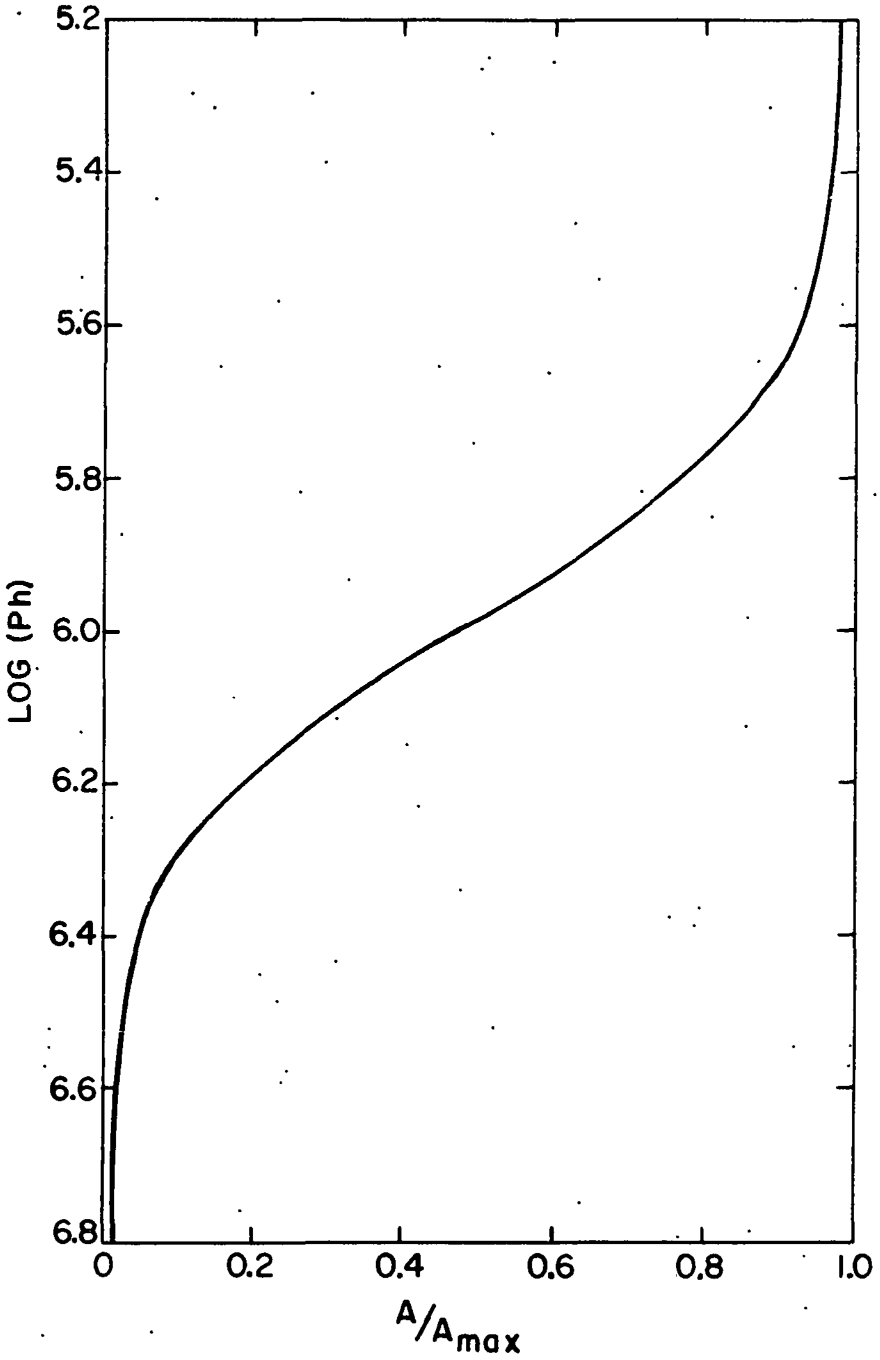


Figure 7. Graphical determination of the free base concentration in the competition method. Curve calculated from Equation 36 using the constants, $pK_1 = 5.06$, $pK_3 = 18.0$, for the iron(II)-5-nitro-1,10-phenanthroline system

$$(Ph)_{T2} = (Ph) + (HPh) + \sum_i i(FePh_i) \ .$$

Because of the fact that at equal absorbancy, the free 1,10-phenanthroline concentrations in these two solutions must be equal, it is apparent that the difference in total 1,10-phenanthroline concentrations between these two solutions must be equal to $\sum_i i(MPh_i)$ or $\bar{n}(M)_T$, by definition. Practically, a series of solutions are prepared, in which the pH and iron(II) concentration are constant. For each series, a constant amount of the second metal is added, and the 1,10-phenanthroline concentration is increased until the absorbancy reaches a maximum as determined by the iron concentration. The absorbancy data are plotted as in Figure 8. Each curve represents a line of constant $(M)_T$. The $\bar{n}$ values are easily calculated at constant absorbancy by means of the equation

$$\bar{n} = \left[(Ph)_{T1} - (Ph)_{T2}\right] / \left[(M)_{T1} - (M)_{T2}\right] \qquad (37)$$

and (Ph) is read from Figure 7. The composition of the solutions used in the application of this method to copper(II) is shown in Table 6. The ionic strength and pH were maintained constant at 0.1 and 4.0, respectively, by addition of calculated amounts of potassium chloride, hydrochloric acid, and sodium formate, as suggested by Bates (38). The iron(II) added was analyzed immediately prior to the solution preparation. The data were taken at 510 mμ with the Cary Model 14 spectrophotometer. The results of calculations are shown in

Figure 8. Absorbancy of solutions of iron(II) and 5-nitro-1,10-phenanthroline as the copper(II) concentration is increased

A. $(Cu)_T = 0.0$

B. $(Cu)_T = 0.989 \times 10^{-5}M$

C. $(Cu)_T = 4.95 \times 10^{-5}M$

D. $(Cu)_T = 9.89 \times 10^{-5}M$

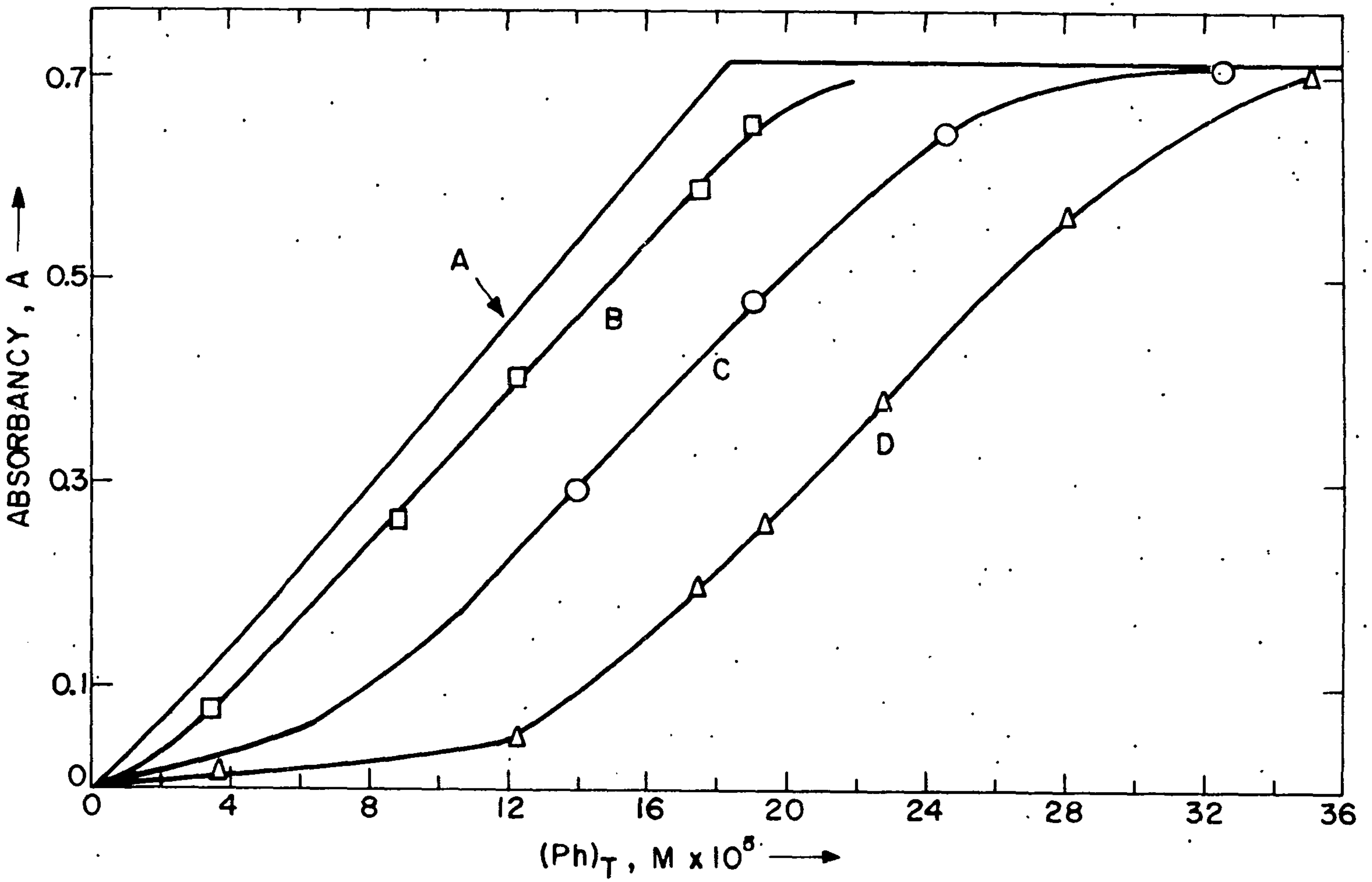

ABSORBANCY , A
0.7
0.5
0.3
0.1
0
A
B
C
D
0
4
8
12
16
20
24
28
32
36
(Ph)$_T$, M x 10^5

Table 6. Composition of solutions and data for the determination of the formation curve of the copper(II)-5-nitro-1,10-phenanthroline system by the competition method

All solutions:
ionic strength = 0.1
$(KCl)_T$ = 0.0381 M
$(HCl)_T$ = 0.0381 M
$(HCOONa)_T$ = 0.1 M
$(Fe)_T$ = 6.19×10^{-5} M

No.	$(Ph)_T$ M x 10^5	$(Cu)_T$ M x 10^5	A, 510 mμ
1	35.15	0.00	0.717
2	3.517	0.989	0.068
3	8.77	0.989	0.264
4	12.30	0.989	0.400
5	17.57	0.989	0.588
6	19.30	0.989	0.651
7	35.17	0.989	0.715
8	14.05	4.95	0.288
9	19.30	4.95	0.475
10	24.60	4.95	0.647
11	32.50	4.95	0.711
12	3.69	9.89	0.012
13	12.30	9.89	0.048
14	17.57	9.89	0.200
15	19.30	9.89	0.262
16	22.80	9.89	0.381

Table 6. (Continued)

No.	$(Ph)_T$ M x 10^5	$(Cu)_T$ M x 10^5	A, 510 mμ
17	28.10	9.89	0.551
18	35.17	9.89	0.699

Table 7. The resulting formation curve is shown in Figure 9. The uncertainty in the curve is indicated, and is the result of the large dependence of $\bar{n}$ on the uncertainty in A/A_{max} as this ratio approaches either zero or one.

It is evident that only a small portion of the formation curve for this system is obtained. The calculation of pk_2 from this portion is, at best, an estimate, unless it can be shown that the 1:1 complex is completely formed before the 2:1 begins to form. There should be only a negligible con-

Table 7. Calculation of the formation curve for the copper (II)-5-nitro-1,10-phenanthroline system from the data of Table 6

$A/A_{max.}$	(Ph) M x 10^{-6}	$\bar{n}$
0.91	2.35	1.44
0.84	1.86	1.35
0.70	1.39	1.304
0.56	1.13	1.245
0.42	0.93	1.203
0.28	0.76	1.15
0.21	0.49	1.12

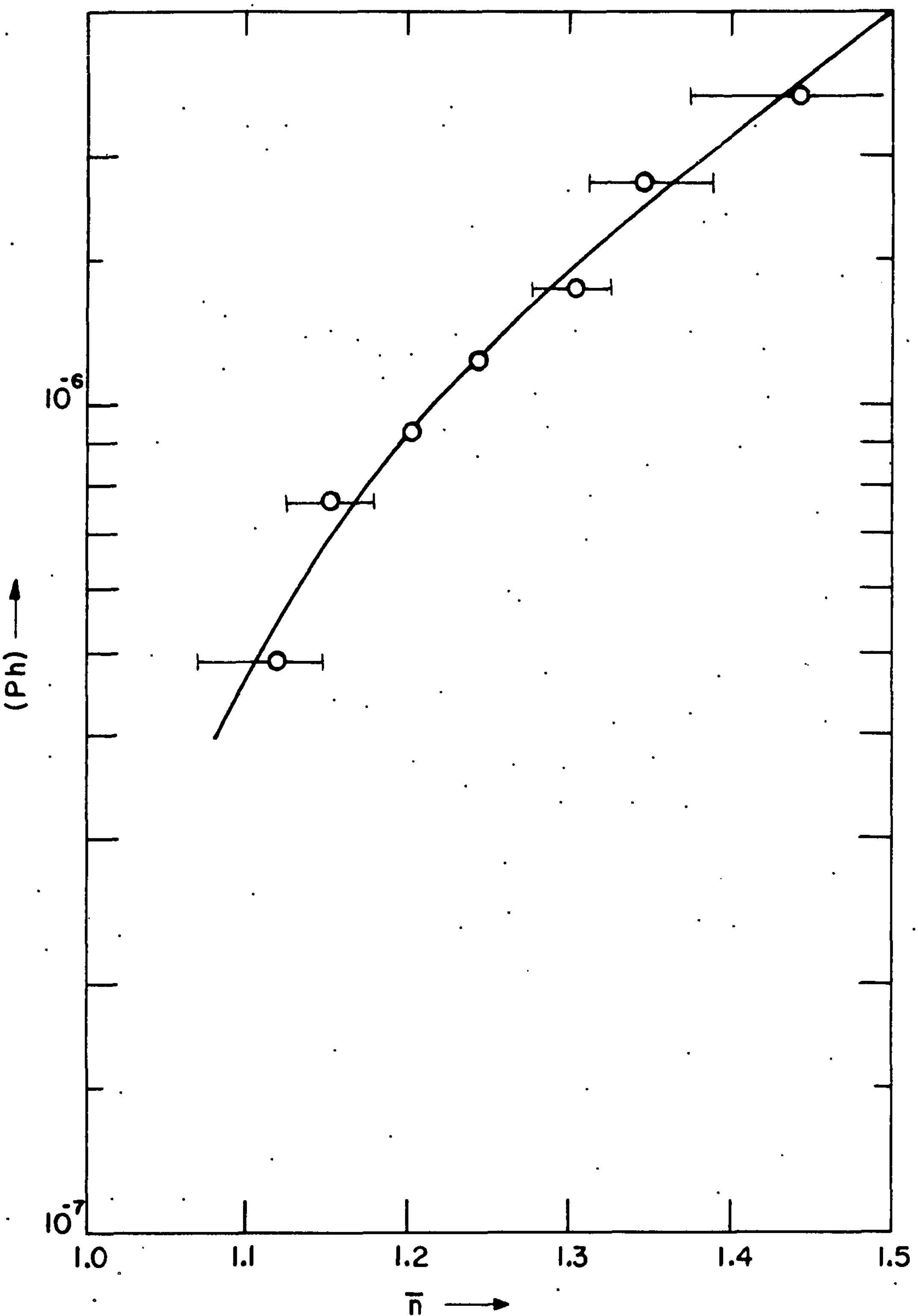


Figure 9. Formation curve for the copper(II)-5-nitro-1,10-phenanthroline system from the competition method

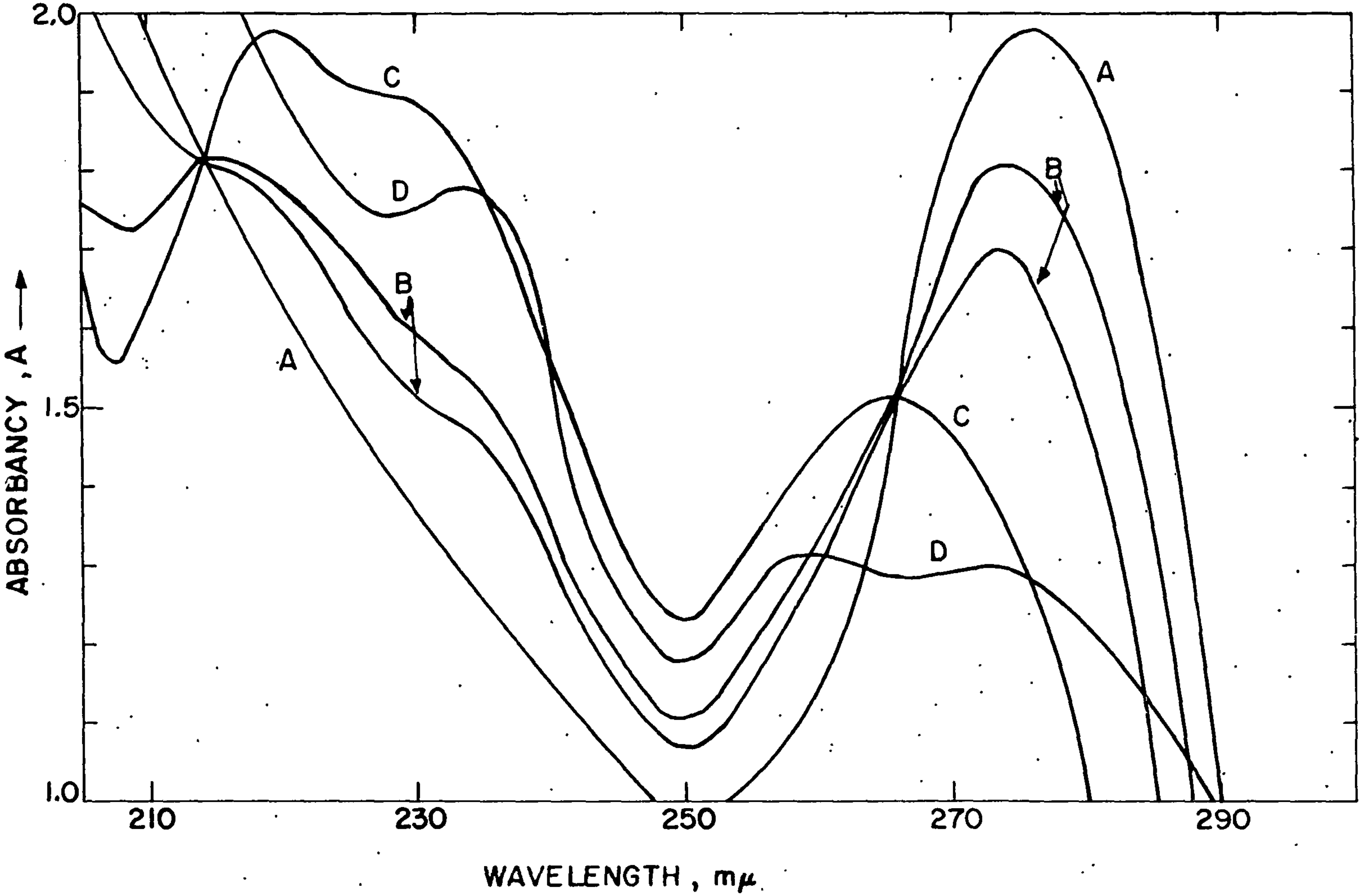
tribution of the 3:1 complex to $\bar{n}$, if the system parallels that of the copper(II)-1,10-phenanthroline at all. The calculation of the constants is presented in the section on the measurement of the formation curve of the copper(II)-5-nitro-1,10-phenanthroline system by means of partition methods.

The acid dissociation constant of 5-nitro-1,10-phenanthroline

A series of solutions in which the 5-nitro-1,10-phenanthroline concentration was constant while the pH was varied were prepared. The ionic strength was adjusted to 0.1 with potassium chloride in all solutions, and the pH was varied by adding appropriate amounts of hydrochloric acid or potassium hydroxide. The spectra of these solutions are shown in Figure 10. Table 8 lists the data taken, and the calculations to obtain the acid dissociation constant. The data are plotted in Figure 11 as the molar absorptivity against pH. The constant is calculated assuming 5-nitro-1,10-phenanthroline acts as a monobasic acid, and does not interact appreciably with potassium. The constant obtained, 4.7×10^{-4}, is a factor of two greater than that obtained by Brandt and Gullstrom (13), 2.6×10^{-4}. Their value was measured by extrapolation from water-dioxane solutions, but as the data were not published, it is difficult to judge the probable accuracy of his result. The present value, it is recognized, is subject to reinterpretation if two unstudied factors,

Figure 10. Absorption spectra of 5-nitro-1,10-phenanthroline at various pH values

A.	pH 1.0	The phenanthrolium species
B.	pH 3 - 4	Mixture of the free base and the phenanthrolium species
C.	pH 5 -10	The free base
D.	pH 11	Addition of OH^- on the substrate


2.0
1.5
1.0
ABSORBANCY , A
210
230
250
270
290
WAVELENGTH , mμ
A
B
C
D
C
D
B
A
C
D
B
A

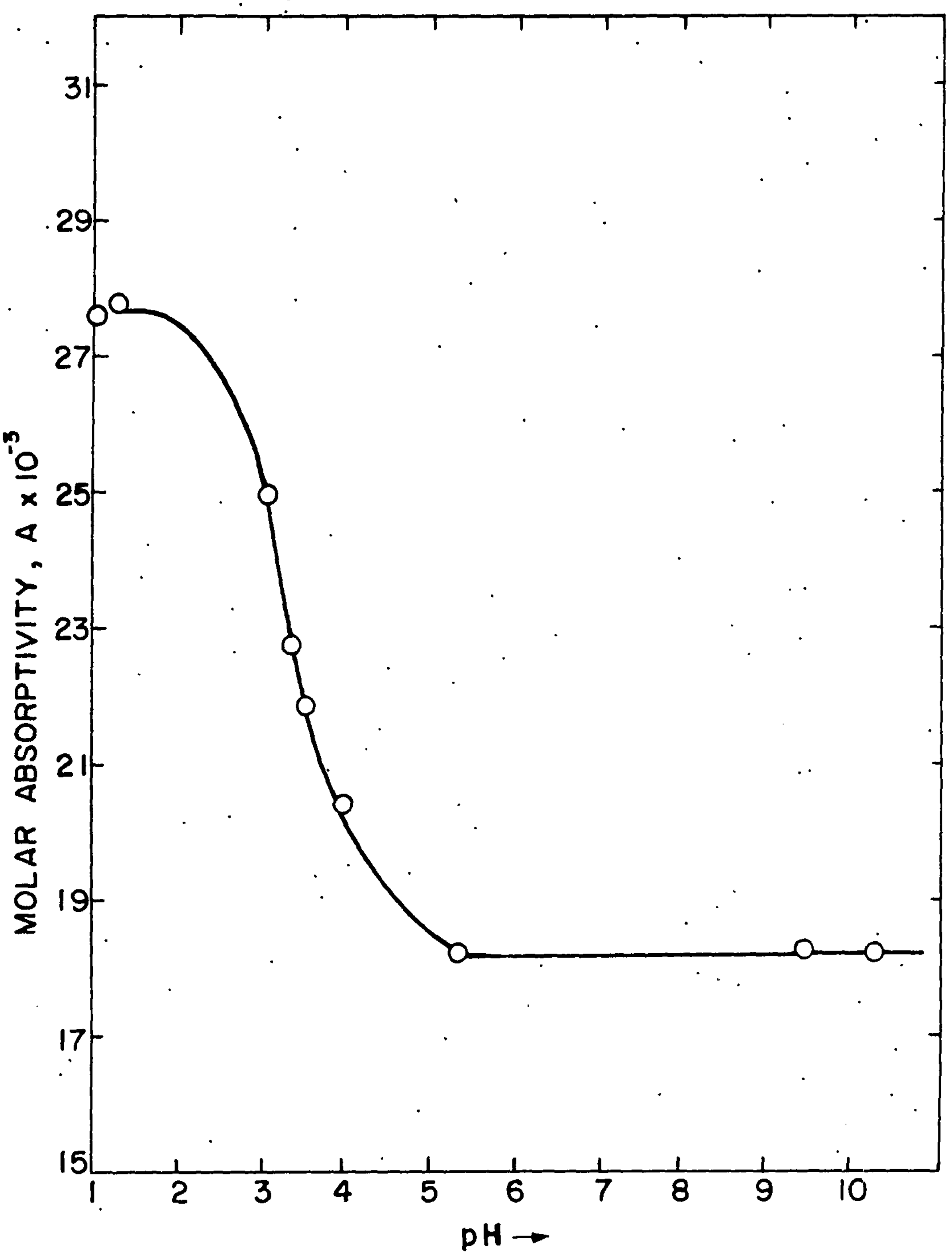


Figure 11. Molar absorptivity of 5-nitro-1,10-phenanthroline as a function of pH at 276 mμ

Table 8. Spectrophotometric determination of pK_a of 5-nitro-1,10-phenanthroline.

$(Ph)_T = 7.03 \times 10^{-5} M$
cell length = 1 cm.
ionic strength = 0.1

No.	pH	A,276 mμ	a(276 mμ)	α[a]	$K_a \times 10^4$ [b]
1	1.01	1.940	27800	-	
2	1.31	1.955	27580	-	
3	3.03	1.756	24960	0.71	4.5
4	3.19	1.660	23600	0.57	4.7
5	3.33	1.600	22750	0.48	5.1
6	3.53	1.538	21860	0.38	4.9
7	3.93	1.435	20400	0.23	3.8
8	5.29	1.280	18200	-	
9	9.42	1.285	18270	-	
10	10.31	1.282	18220	-	
11	11.76	1.285	18270	-	
				av. K_a	$(4.7 \pm .6) \times 10^{-4}$

[a] $$\alpha = \frac{a - 18230}{9350} = \frac{(HPh)}{(Ph)_T} .$$

[b] Defined as: $$K_a = \frac{(Ph)(H)\gamma_H}{(HPh)} = \frac{a_H(1 - \alpha)}{\alpha} .$$

namely, the presence of other 1,10-phenanthroline species, and the adsorption of 1,10-phenanthroline on glass, are taken into consideration. Disagreements of this magnitude have precedent in the 1,10-phenanthroline constants obtained by different methods (37). In Figure 10, attention should be drawn to the spectrum of 5-nitro-1,10-phenanthroline in strongly basic solutions (D). The radical departure from the spectrum of the free base (C) indicates that another species is formed. Qualitative evidence indicates that this species tends to remain in aqueous solutions on partition with chloroform more than does the free base. Because it was suspected that base was attaching itself reversibly to the 1,10-phenanthroline, in a manner similar to the behavior of many other nitro compounds (42), a sample of 5-nitro-1,10-phenanthroline was titrated non-aqueously with triethylammonium hydroxide. The reaction was quantitative with the addition of one mole of OH^-, and a color change was observed at the endpoint[1]. As the 6-position is most activated by the nitro group, it is postulated that this is the position of addition. The other substituted 1,10-phenanthrolines apparently do not undergo this reaction.

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[1] Moye, A. J., Ames, Iowa. Information and data on the addition of base to nitro-aromatic compounds. Private Communication. 1957.

Spectrophotometric determination of stability

The stability of 1:1 complexes can be measured by maintaining an excess of the metal ion to the 1,10-phenanthroline, provided of course, that the stabilities of the 2:1 and 3:1 complexes are small enough that neither of them form. Since this is true for the copper and zinc complexes of the 1,10-phenanthrolines, the present method is satisfactory. An important limitation arises if the metal itself absorbs at the concentration levels used, as this requires a precise correction to be made. The stability constant may be expressed in terms of the degree of association:

$$k_1(1 + (H)/K_a) = (Ph)_T \frac{((M)_T/(Ph)_T - \alpha)(1 - \alpha)}{} , \quad (38)$$

where α can be obtained from the absorbance data at a particular wave length as

$$\alpha = \frac{A - a_{Ph}b\,(Ph)_T}{(a_{MPh} - a_{Ph})b(Ph)_T} . \quad (39)$$

The absorbancies in Equation 39 are of solutions in which the 1,10-phenanthroline concentrations, $(Ph)_T$, are all the same, while the metal ion concentration is varied.

The composition of the solutions used in the present study, and the absorbancy data at the wave length of maximum absorption of the 1:1 complex are listed in Table 9.

Table 9. Spectrophotometric determination of K_1 for the copper(II)-5-nitro-1,10-phenanthroline system

$(Ph)_T = 2.81 \times 10^{-6}$M
(H) = 0.022 M, pH = 1.73
ionic strength = 0.1
cell length = 10 cm.

$(Cu)_T$, Mx10^6	A, 275 mμ	A corr.[a]	α	k_1[b] x10^8	k_1[c] x10^8
0.00	0.883	0.883			
2.960	0.848	0.847	0.61	2.0	1.1
4.94	0.842	0.839	0.74	2.5	1.4
6.92	0.842	0.837	0.78	3.3	1.9
9.89	0.844	0.836	0.80	4.7	2.6
14.83	0.840	0.832	0.86	5.0	2.8
247.0	0.971	0.824			
			av.	3.5±1.0	2.0±0.8

[a] Correction applied for free Cu(II) absorption.

[b] Calculated using $K_a = 4.7 \times 10^{-4}$.

[c] Calculated using $K_a = 2.6 \times 10^{-4}$.

It is seen that the constant is very subject to small errors in absorbancy. The absorbancy of the solution which contained a large excess of copper required a significant correction for copper ion absorbance. The other solutions were also corrected approximately, although the correction was small. The constant is calculated using both the K_a

measured in this work, and that measured by Brandt and Gullstrom (13). These values are indicated in Figure 6 by small crosses.

The partition coefficient of 5-nitro-1,10-phenanthroline for the chloroform-water system

Considerable difficulty was encountered in the use of chloroform as an extractive solvent for 5-nitro-1,10-phenanthroline, but it is believed that qualitative reasons for the difficulty are sufficiently understood to be able to state the qualifications on the data taken using this system.

The partition coefficient, defined in Equation 33, was measured by simply equilibrating a weighed amount of the 5-nitro-1,10-phenanthroline between equal volumes of chloroform and water. The aqueous phase was 0.1 M in potassium chloride to maintain ionic strength, and various amounts of hydrochloric acid or potassium hydroxide were added to adjust the pH. The molar absorptivity of 5-nitro-1,10-phenanthroline in chloroform was measured to be 22,500 at the 266 mμ absorption maximum, which is identical in appearance to the spectra of the free base in water (Figure 10). The molar absorptivity of the 5-nitro-1,10-phenanthroline in water at 266 mμ is 21,300, and as this wave length is an isosbestic point, it is a particularly useful one at which to measure the total 5-nitro-1,10-phenanthroline concentration, since the pH cannot be easily controlled. The free base 5-nitro-1,10-phenanthroline concentration in the water can then be obtained from the pH and the K_a previously measured. Since there was some doubt about the exact value of K_a, and to avoid the potential ion pair extraction in acid solutions, it was decided to work at pH values which allow minimum correction for the HPh species in water, namely, $pH > pK_a$. Solutions No. 1-6 in Table 10 state the results of a series of such measurements of K_D.

Further study of this system unveiled the following interesting points. The aqueous spectra of 5-nitro-1,10-phenanthroline, which has been equilibrated with chloroform, in many cases, is different from that in pure water. The ratios of absorbancies taken at various wave lengths are not the same for any two different solutions. A study in detail indicates the appearance of another species with a spectra similar to 5-nitro-1,10-phenanthroline, but with an absorption maximum at 272 mμ to 280 mμ . Attempts to calculate the pH of the solution by means of the absorbancies at 276 mμ and 266 mμ and the relation of molar absorptivities to pH in Figure 11, result in a vast disagreement with the measured pH (as much as 2 pH units). This species is not due to base attack, because the spectra is distinctly different (Figure 10 (D)), and the solutions are still somewhat acidic. The latter species does appear in highly basic solutions in con-

Table 10. Measurements of K_D of 5-nitro-1,10-phenanthroline between chloroform and water

$V_o = V_w = 50$ mls.
ionic strength = 0.1

No.	Ph_T moles x 10^6	pH	$(Ph)_{T,w}$ M x 10^5	$(Ph)_o$ M x 10^4	K_D [a]	
					$K_a = 2.6 \times 10^{-4}$	$K_a = 4.7 \times 10^{-4}$
1	552.0	3.52	2.06	110.0	1110	854
2	27.2	3.98	0.0705	5.45	1070	940
3	85.8	5.00	0.206	17.2	864	850
4	186.0	4.12	0.466	37.2	1025	924
5	257.0	4.99	0.545	51.4	976	960
6	107.0	4.17	0.324	21.4	825	754
7	1.405	1.88[b]	0.97	5.61	2900	1600
8	0.352	1.88[b]	0.217	3.515	3240	1790
9	0.176	1.88[b]	0.114	1.76	3080	1700

[a] $$K_D = \frac{(Ph)_o}{(Ph)_{T,w}} \cdot (1 + a_{H}/K_a) \;.$$

[b] Ionic strength = 0.0132; $(H)_T = 0.0132$ M.

tact with chloroform, and appears to be more soluble in water than the free base or the offending species. Similar shifts in spectra occur even in more highly acid solutions if the chloroform solution is heated, however, the new aqueous absorption band in this case appears at 285 $m\mu$, which is reasonable if one assumes a 1,10-phenanthrolium ion formation.

In light of the apparent activation of the 1,10-phenanthroline structure by the nitro group to nucleophilic attack, it seems likely that chloroform is attacking, with catalysis by light, heat, or base, possibly as carbene, $:CCl_3$.

Solutions No. 7-9 in Table 10 are measurements of K_D with chloroform and an acidic aqueous solution. The values of K_D are reproducible, and the spectra in both phases well-behaved. It is believed that the large value of this constant as compared to the average of the values measured at higher pH, is probably due in part to the species HPh_1^+, existing in the latter solutions. As these species would be more water soluble than the free base, the apparent partition coefficient would be smaller than the true value.

Application of the partition method

The method used here is identical with that described in the corresponding section on the copper(II)-1,10-phenanthroline system. The composition of each of the solutions, the data, and results are listed in Table 11, and the

Table 11. The copper(II)-5-nitro-1,10-phenanthroline system. Partition between chloroform and water

$V_o = V_w = 25$ mls.
(H) = 0.0132
a (266 mμ, $CHCl_3$) = 22,500

Ph_T moles x 10^6	Cu_T moles x 10^6	A^a, 266 mμ	$(Ph)_o$ Mx10^4	$(Ph)_w^b$ Mx10^8	$\bar{n}^b$	$(Ph)_w^c$ Mx10^8	$\bar{n}^c$
5.315	8.31	0.494	0.219	1.29	0.57	0.71	0.58
13.59	12.66	2.095	0.931	5.48	0.89	3.03	0.89
44.36	25.32	14.96	6.65	39.0	1.08	21.7	1.12
98.62	43.50	41.4	18.4	108.0	1.19	59.9	1.25
216.16	77.14	67.5	30.0	177.0	1.81	97.7	1.86

[a] Includes dilution factors.

[b] Calculated using $K_D = 3070$, $K_a = 2.6 \times 10^{-4}$

[c] Calculated using $K_D = 1700$, $K_a = 4.7 \times 10^{-4}$

points are recorded in the formation curve in Figure 6, along with the results of the competition method.

It should be pointed out that the data used here are those taken from absorbancy readings in chloroform media, and therefore, are not to be weighed in the same manner as the points of the 1,10-phenanthroline system, which were taken by the evaporation technique. The evaporation technique is undoubtedly better because it avoids the large absorption blank correction due to chloroform, but in the present case of 5-nitro-1,10-phenanthroline, the application of this technique resulted in reaction of the chloroform with 5-nitro-1,10-phenanthroline, as evidenced by the appearance of a new absorption band.

Results

The formation curve was calculated using the K_D values of 1700 and 3070, as measured in Table 10. It is evident from Figure 6, that the formation curve calculated from the former value corresponds closely with the data from the competition method, while two points calculated from the latter do not agree well at all. This is considered to be supporting evidence for the K_a value measured in this thesis, for the difference in the two K_D values depends on the choice of K_a.

The stability constants that can be calculated from the best smooth curve through all the data are as follows:

$pk_1 = 8.0$
$pk_2 = 5.47$
$pk_3 = 4.2$

Zinc(II) and the 5-Substituted-1,10-Phenanthrolines

The stability constants of the zinc(II)-1,10-phenanthroline system have been measured by Kolthoff et al. (32), Irving and Mellor (5), Yasuda et al. (14) and McClure (29). The former two used partition methods, while Yasuda used the titrimetric technique of Bjerrum, and McClure, the spectrophotometric pH method. The constants are summarized in Table 27, along with the constants measured in the present work. In the above work, some zinc(II) constants with 5-methyl-, 4,7-dimethyl-, and 2-methyl-1,10-phenanthroline were also measured.

In the present work, the spectrophotometric techniques already described were used for the measurement of the 1:1 complex stabilities of the 5-nitro- and 5-chloro-1,10-phenanthroline with zinc(II). The data are shown in Tables 12 and 13, and the results of the calculations, using Equations 38 and 39, are also shown. The constants, calculated using the pK_a values measured in this thesis are shown in Table 27.

The titrimetric technique used for the copper(II)-1,10-phenanthroline system was applied to the zinc(II)-1,10-phenanthroline system. The data and calculations are presented in Table 14, and the formation curve is shown in Figure 12. It was possible to obtain constants for all three complexes, even though part of the formation curve could not be measured. In Table 27 it can be seen that these constants compare favorably with those obtained by others, although pk_3 does seem to be too large. It must be pointed out that there is some question as to the first decimal place in pk_2 and pk_3 as measured by Kolthoff, and by Yasuda, since it ap-

Table 12. Spectrophotometric measurements of pK_1 of zinc(II)-5-nitro-1,10-phenanthroline

$(Ph)_T = 3.517 \times 10^{-5} M$
$(H) = 0.0112$ M
ionic strength = 0.1
cell length = 1 cm.

No.	$(Zn)_T$ M x 10^4	$\lambda_{m\mu}$	A	α	$K_1(1 + (H)/K_a)$ x 10^4
1	0.00	300	0.288		
		275	0.950		
		231	0.640		
2	668.7	300	0.204		
		275	0.892		
		231	0.748		
3	1.486	300	0.241	0.560	1.17
		275	0.917	0.568	1.13
		231	0.706	0.611	0.95
4	2.97	300	0.229	0.702	1.26
		275	0.907	0.741	1.04
		231	0.721	0.750	0.99
5	4.46	300	0.220	0.810	1.05
		275	0.900	0.896	0.52
		231	0.731	0.845	0.82
					av. 1.0 ± 0.1

pears that the values were taken from half-integer $\bar{n}$ values, which is only a first approximation in the case of the zinc complexes. Mixtures of complexes exist at these values.

Attempts were made to study the 5-chloro- and 5-nitro-1,10-phenanthroline complexes of zinc(II) by the titrimetric technique. All of these attempts were uniformly unsuccessful.

Table 13. Spectrophotometric measurements of pK_1 of zinc(II)-5-chloro-1,10-phenanthroline

$(Ph)_T = 3.72 \times 10^{-5}$ M
(H) = 0.022 M
ionic strength = 0.1
cell length = 1 cm.

No.	$(Zn)_T$ M x 10^4	$\lambda_{m\mu}$	A	α	$K_1(1+(H)/K_a)$ x 10^4
1	0.00	215	0.929		
		230	0.853		
		274	1.217		
2	668.7	215	0.695		
		230	1.178		
		274	1.400		
3	29.72	215	0.726	0.867	4.87
		230	1.130	0.852	
		274	1.374	0.858	
4	14.86	215	0.749	0.769	4.51
		230	1.104	0.772	
		274	1.356	0.760	
5	10.4	215	0.767	0.692	4.92
		230	1.068	0.661	
		274	1.342	0.683	
6	7.43	215	0.783	0.623	4.85
		230	1.047	0.597	
		274	1.326	0.596	
7	4.46	215	0.827	0.435	4.97
		230	1.020	0.514	
		274	1.301	0.459	
8	2.97	215	0.838	0.389	5.07
		230	0.970	0.360	
		274	1.283	0.361	
9	1.486	215	0.875	0.231	4.52
		230	0.932	0.243	
		274	1.265	0.262	
					av. 4.8 ± 0.1

Figure 12. Formation curve of the zinc(II)-1,10-phenanthroline from pH measurements. The curve shown is calculated using Equation 17 and $pk_1 = 6.36$, $pk_2 = 5.64$, $pk_3 = 5.2$. Data taken by Kolthoff et al. (32) and Yasuda et al. (14) are also shown

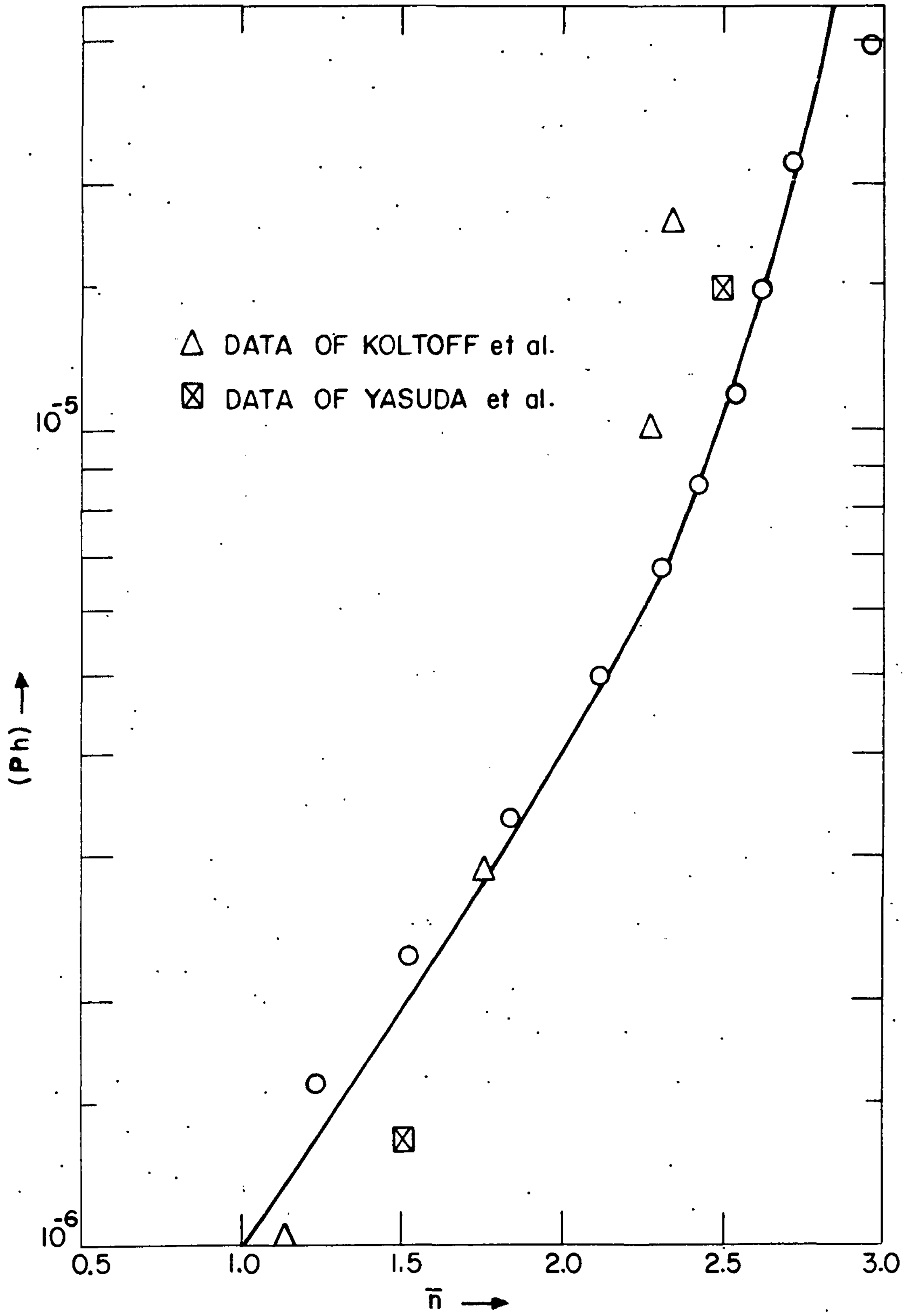

△ DATA OF KOLTOFF et al.
⊠ DATA OF YASUDA et al.
10^{-5}
10^{-6}
(Ph) →
0.5
1.0
1.5
2.0
2.5
3.0
$\bar{n}$ →

Table 14. Determination of the formation curve of the zinc (II)-1,10-phenanthroline system by pH measurements

V_1 = 50 mls.
$(Ph)_{T1} = 4.78 \times 10^{-4} M$
$(H)_{T1} = 5.0 \times 10^{-4} M$
ionic strength = 0.1
$K_a = 1.0 \times 10^{-5}$

Titrant:
$(Zn)_{TM} = 0.929 \times 10^{-2} M$
ionic strength = 0.1
$(H)_M = 1.183 \times 10^{-4} M$
$\alpha = 1.25$

$V_2 - V_1$ mls.	pH	(H) $M \times 10^4$	$\sum_i i(ZnPh_i)_2$ $M \times 10^4$	$\bar{n}$	(Ph) $M \times 10^5$
0.0	4.023	0.95	—	—	
0.1	3.876	1.33	0.532	2.96	2.96
0.2	3.765	1.718	1.004	2.71	2.07
0.3	3.673	2.12	1.460	2.63	1.48
0.4	3.602	2.50	1.872	2.54	1.10
0.5	3.548	2.83	2.227	2.42	0.854
0.6	3.505	3.126	2.537	2.30	0.675
0.8	3.444	3.60	3.030	2.06	0.451
1.0	3.408	3.91	3.346	1.84	0.334
1.35	3.373	4.24	3.684	1.51	0.223
1.75	3.35	4.45	3.89	1.24	0.159

The adsorption phenomenon which is discussed in more detail on pages 130-132, can account for this lack of success. It should be added that the free base 5-substituted-1,10-phenanthroline concentrations in these attempts were initially

10 to 100 times those used in the titrations with 1,10-phenanthroline. The effect of adsorption seems to be proportional to the free base concentration, and this may be the reason why the data of the copper(II) and zinc(II)-1,10-phenanthroline systems were not affected.

The Acid Dissociation Constants of 5-Bromo- and 5-Chloro-1,10-Phenanthroline

The acid dissociation constants for the 5-bromo- and 5-chloro-1,10-phenanthrolines were measured in the manner described for 5-nitro-1,10-phenanthroline. The data and calculations are indicated in Tables 15 and 16, and plotted in Figures 13 and 14. The pK_a values are quite similar, as is expected, since the bromo and chloro groups have about the same electron withdrawing capacity.

The pK_a of 5-bromo-1,10-phenanthroline was also calculated from the data and substituent effect of the iron(II) complexes of the 1,10-phenanthrolines. It is interesting to note that the present measurement of pK_a lends support to the substituent effect constants measured for the iron(II) system.

The Partition Coefficient of 5-Nitro-1,10-Phenanthroline for the 2-Ethyl-1-Hexanol-Water System

Because chloroform was considered to cause side effects in partition studies, a search was made for a solvent which

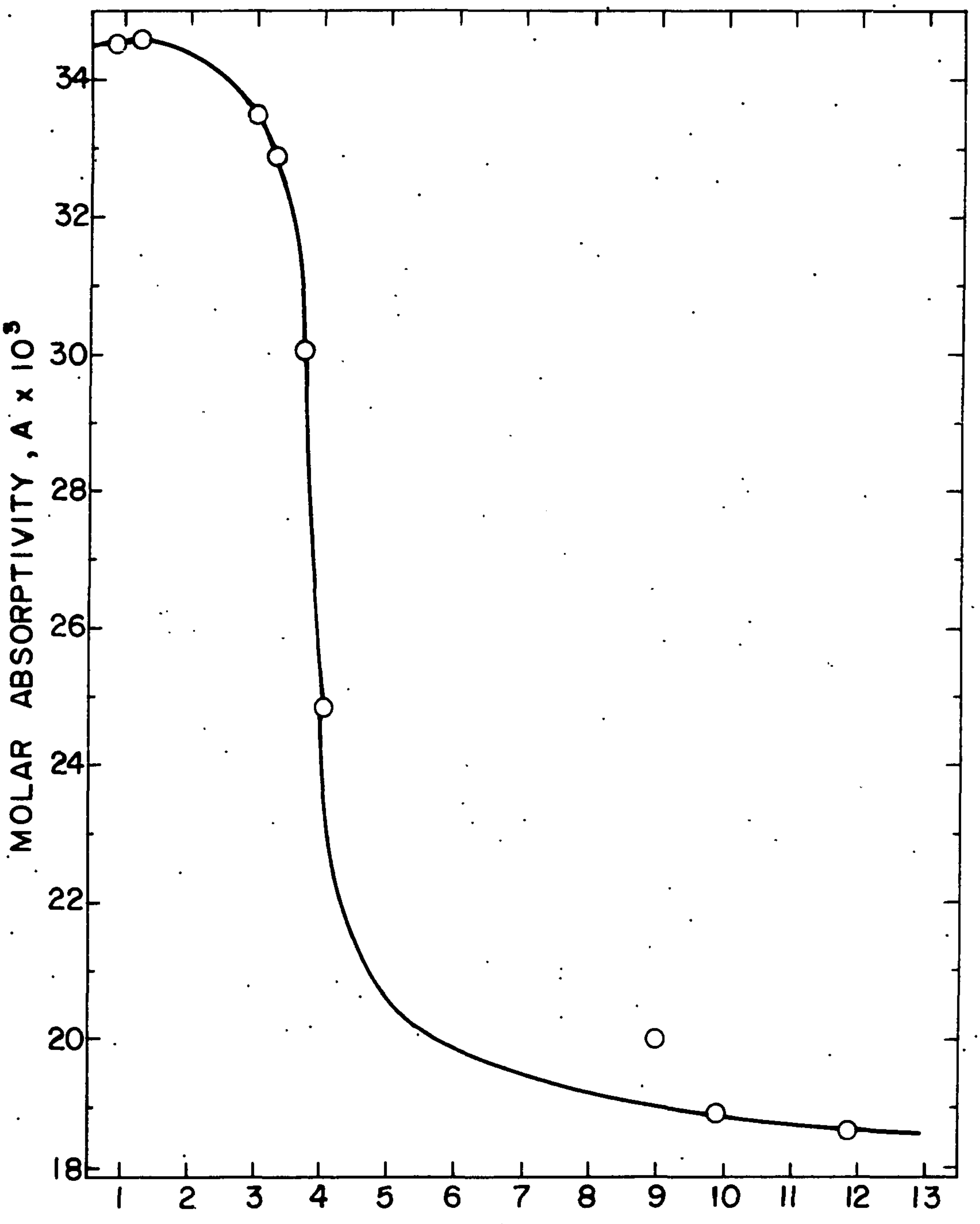


Figure 13. Molar absorptivity of 5-chloro-1,10-phenanthroline as a function of pH at 275.7 mμ

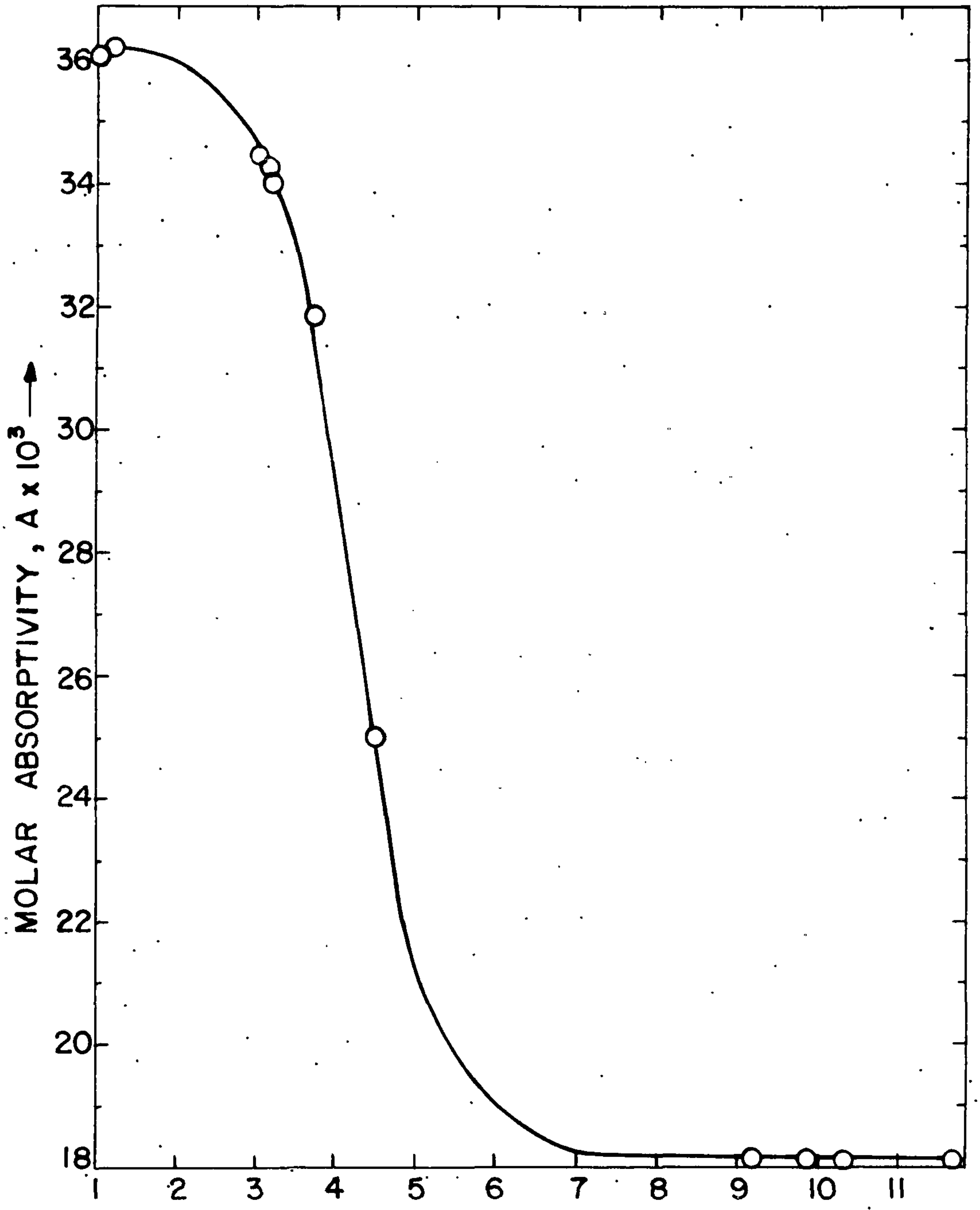


Figure 14. Molar absorptivity of 5-bromo-1,10-phenanthroline as a function of pH at 277.5 mμ

Table 15. Spectrophotometric determination of K_a for 5-chloro-1,10-phenanthroline

$(Ph)_T = 3.72 \times 10^{-5}M$
ionic strength = 0.1
cell length = 1 cm.

No.	pH	A, 275.7 mμ	a, 275.7 mμ	α	$K_a \times 10^5$
1	0.99	1.285	34510		
2	1.27	1.289	34620		
3	3.01	1.248	33520	.93	7.1
4	3.24	1.225	32900	.89	6.8
5	3.70	1.148	30830	.76	6.2
6	4.39	0.925	24840	.38	6.6
7	9.00	0.748	20090		
8	9.87	0.707	19000		
9	11.83	0.698	18750		

av. $K_a = (6.7 \pm 0.3)10^5$
$pK_a = 4.18$

was ultraviolet transparent, highly immiscible in water, sufficiently polar to extract 5-nitro-1,10-phenanthroline, and suitable otherwise for quantitative work. Of the higher alcohols investigated, 2-ethyl-1-hexanol was the most suitable, although it was found necessary to redistill this solvent

Table 16. Spectrophotometric determination of K_a for 5-bromo-1,10-phenanthroline

$(Ph)_T = 2.87 \times 10^{-5}M$
ionic strength = 0.1
cell length = 1 cm.

No.	pH	A, 277.5 mμ	a,(277.5mμ)	α	K_a x10^5
1	1.06	1.041	36230		
2	1.27	1.039	36230		
3	3.03	0.993	34600	0.91	9.2
4	3.24	0.978	34070	0.881	7.8
5	3.18	0.985	34310	0.895	5.6
6	3.68	0.915	31870	0.760	6.7
7	4.50	0.720	25080	0.385	5.2
8	9.22	0.520	18110		
9	9.83	0.520	18110		
10	10.36	0.520	18110		
11	11.76	0.520	18110		

av. $K_a = (6.3 \pm 0.9)10^5$

$pK_a = 4.20$

several times under vacuum in order to remove trace quantities of ultraviolet absorbing compounds.

The relatively small partition of 5-nitro-1,10-phenanthroline into 2-ethyl-1-hexanol compared to chloroform, made it necessary to work at higher pH values in order to observe significant extraction. Under these conditions, the spectra of the 5-nitro-1,10-phenanthroline in the 2-ethyl-1-hexanol appeared well-behaved, and the molar absorptivity at the wave length of maximum absorbancy, 266 mμ, was measured to be 24,100. The molar absorptivities of the 5-nitro-1,10-phenanthroline in water at various pH values, are shown in Figure 11. The partition coefficients were measured by weighing milligram quantities of the 5-nitro-1,10-phenanthroline, transferring this quantity to a 100-ml. volumetric flask, adding the two solvents and shaking the mixture on a mechanical shaker until the solid 5-nitro-1,10-phenanthroline had been dissolved completely for several hours. When both phases were clear, aliquots were withdrawn for spectrophotometric analysis. The compositions of each solution and the results are shown in Table 17. The partition coefficients are calculated using two values of K_a for the 5-nitro-1,10-phenanthroline to indicate the insensitivity of the data to pH at the levels used.

The accuracy of the partition coefficient, as defined, will depend on the possible existence of species other than the free base and the 5-nitro-1,10-phenanthrolium ion in these solutions.

Table 17. Measurements of K_D for 5-nitro-1,10-phenanthroline between 2-ethyl-1-hexanol and water

V_o = 25 mls.
V_w = 50 mls.
ionic strength = 0.1

Ph_T	$(Ph)_{T,w}$	$(Ph)_o$	pH	K_D	
moles x 10^5	$Mx10^5$	$Mx10^3$		$K_a = 2.6x10^{-4}$	$K_a=4.7x10^{-4}$
2.79	2.90	1.055	4.39	42	39.5
20.56	32.8	7.57	3.44	54.2	40.4
9.08	8.5	3.46	4.71	43.6	42.5
13.6	15.12	5.14	4.70	36.5	35.5
17.63	16.6	6.72	6.18	40.6	40.5
1.52	1.6	0.563	6.59	35	35
4.81	4.5	1.81	6.60	40	40
1.35	1.36	0.500	6.50	36.8	36.8
				41.1± 4.1	38.8± 2.2

The Cobalt(II)-5-Nitro-1,10-Phenanthroline System

There are in the literature no references to the preparation or to stability measurements with the cobalt(II) complexes of 5-substituted-1,10-phenanthrolines. The 1,10-phenanthroline system has been studied primarily as the hydrated crystal (4). Irving and Mellor (5) have measured the aqueous stabilities of the 1,10-phenanthroline complexes by partition methods.

In the present work, the formation curve for the 5-nitro-1,10-phenanthroline system was obtained by partition methods using 2-ethyl-1-hexanol as the extractive solvent for the free base. The equations used in calculations from the data have been presented elsewhere. The composition of each solution, the data, and the results are presented in Table 18. The

Table 18. Measurement of the formation curve of the cobalt (II)-5-nitro-1,10-phenanthroline system by the partition method, using 2-ethyl-1-hexanol

V_o = 25 mls.
V_w = 50 mls.
ionic strength = 0.1
K_D = 40

No.	Ph_T moles x 10^6	Co_T moles x 10^6	pH	$(Ph)_o$ $Mx10^4$	$(Ph)_w$ $Mx10^6$	$\bar{n}$
1	0.8765	0.86	4.50	0.178	0.426	0.48
2	2.63	1.27	4.85	0.535	1.28	0.964
3	5.4	1.8	4.80	1.116	2.68	1.37
4	11.0	2.76	4.75	2.317	5.56	1.78
5	24.5	4.9	4.60	5.32	12.74	2.14
6	34.58	15.15	4.6	2.70	6.75	1.80
7	56.6	15.15	4.6	8.63	21.6	2.27
8	64.06	8.08	4.6	16.58	41.3	2.68
9	66.4	15.15	4.6	11.37	28.4	2.45
10	107.7	20.2	4.6	21.86	54.7	2.54

techniques used are the same as those using chloroform. The formation curve is plotted in Figure 15. The curve drawn through the points was calculated using Equation 17 and the constants $pk_1 = 6.25$, $pk_2 = 5.41$, and $pk_3 = 4.63$.

A few solutions were also prepared using chloroform as the extractive solvent. The composition of these solutions, the data, and the results are shown in Table 19. The partition coefficient used was 1700, the same as that which gave the most consistent results with the copper(II) system. These points are also indicated in Figure 15.

The competition method described in detail for the copper(II) system was also applied to the cobalt(II) system.

Table 19. The formation curve of the cobalt(II)-5-nitro-1,10-phenanthroline system by the partition method, using chloroform

$V_o = V_w = 50$ mls.
ionic strength = 0.1
$K_D = 1700$
$5.0 > pH > 4.0$

No.	Ph_T moles x 10^6	Co_T moles x 10^6	$(Ph)_o$ Mx10^4	$(Ph)_w$ Mx10^4	$\bar{n}$
1	5.77	7.25	1.03	0.605	0.085
2	14.47	10.0	2.58	1.52	0.157
3	70.96	20.0	11.87	6.98	0.578
4	165.3	36.0	26.7	15.8	0.87
5	254.8	50.0	38.4	22.6	1.26

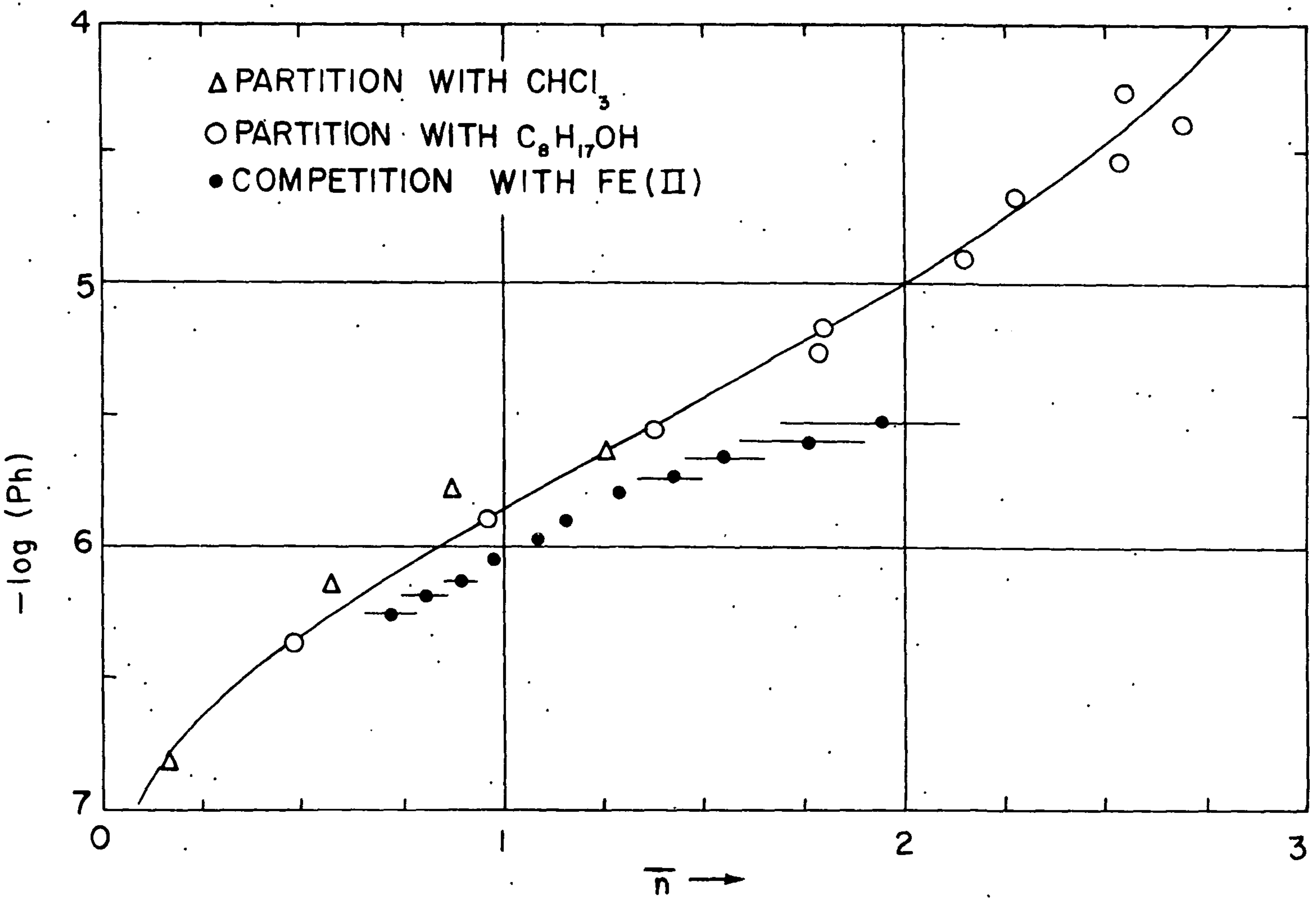


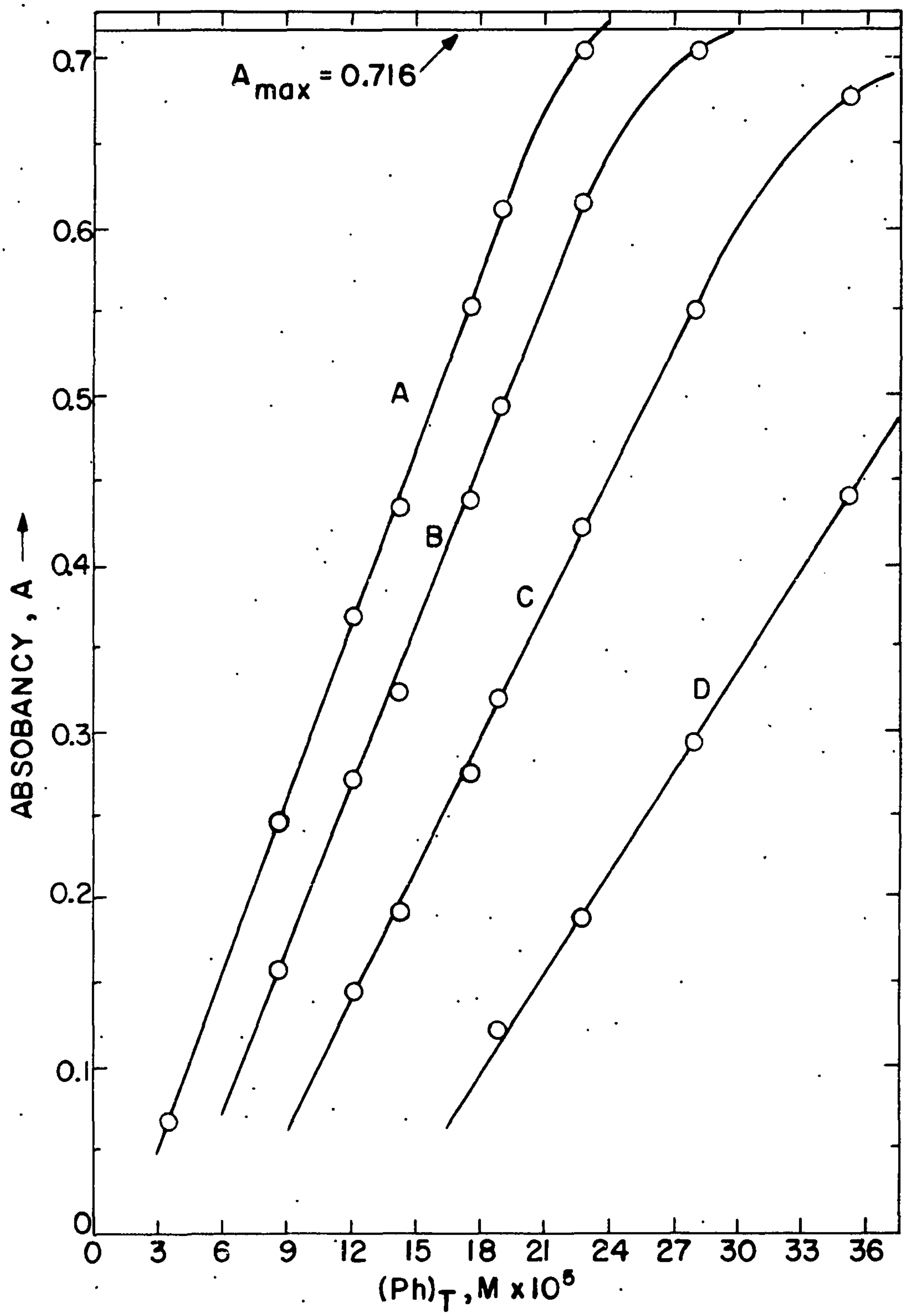
Figure 15. The formation curve of the cobalt(II)-5-nitro-1,10-phenanthroline system

Curve shown: $pK_1 = 6.25$, $pK_2 = 11.65$, $pK_3 = 16.28$

The composition of the solutions and the data are given in Table 20. The data are plotted in Figure 16 to illustrate the decrease in absorbancy as the cobalt concentration is raised. The results from this data are given in Table 21, and the formation curve is shown in Figure 17. The horizontal bars in this figure indicate the uncertainty in $\bar{n}$ at the various free base concentrations. The formation curve as measured by competition methods is also shown in Figure 15. It is apparent that the curve parallels that measured by partition methods, but are separated by more than the experimental error in each method. It is believed that the discrepancy can be explained by two considerations. The value of pK_3 for the tris (5-nitro-1,10-phenanthroline)iron(II) complex is uncertain to ± 0.2 units. The value 17.8 was obtained from a kinetic study, and if this represents an alternate value, the result is that the formation curves from competition methods should be raised by 0.06 $_p$(Ph) units. Secondly, if the value of K_D used in the partition method is too small as measured, as might be expected if additional species of 5-nitro-1,10-phenanthroline existed at the pH values where K_D was measured, then the formation curve from the partition method would be too high. A value of $K_D = 54$ would be sufficient to cause the curve to coincide with that from the competition method. As the measured value of the partition coefficient for the same 5-nitro-1,10-phenanthroline

Figure 16. Absorbancy of solutions of iron(II) and 5-nitro-1,10-phenanthroline as the cobalt(II) concentration is increased.

A. $(Co)_T = 2.02 \times 10^{-5} M$
B. $(Co)_T = 5.05 \times 10^{-5} M$
C. $(Co)_T = 1.01 \times 10^{-4} M$
D. $(Co)_T = 2.02 \times 10^{-4} M$


A$_{max}$ = 0.716
A
B
C
D
ABSOBANCY , A
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
3
6
9
12
15
18
21
24
27
30
33
36
(Ph)$_T$, M x 10^5

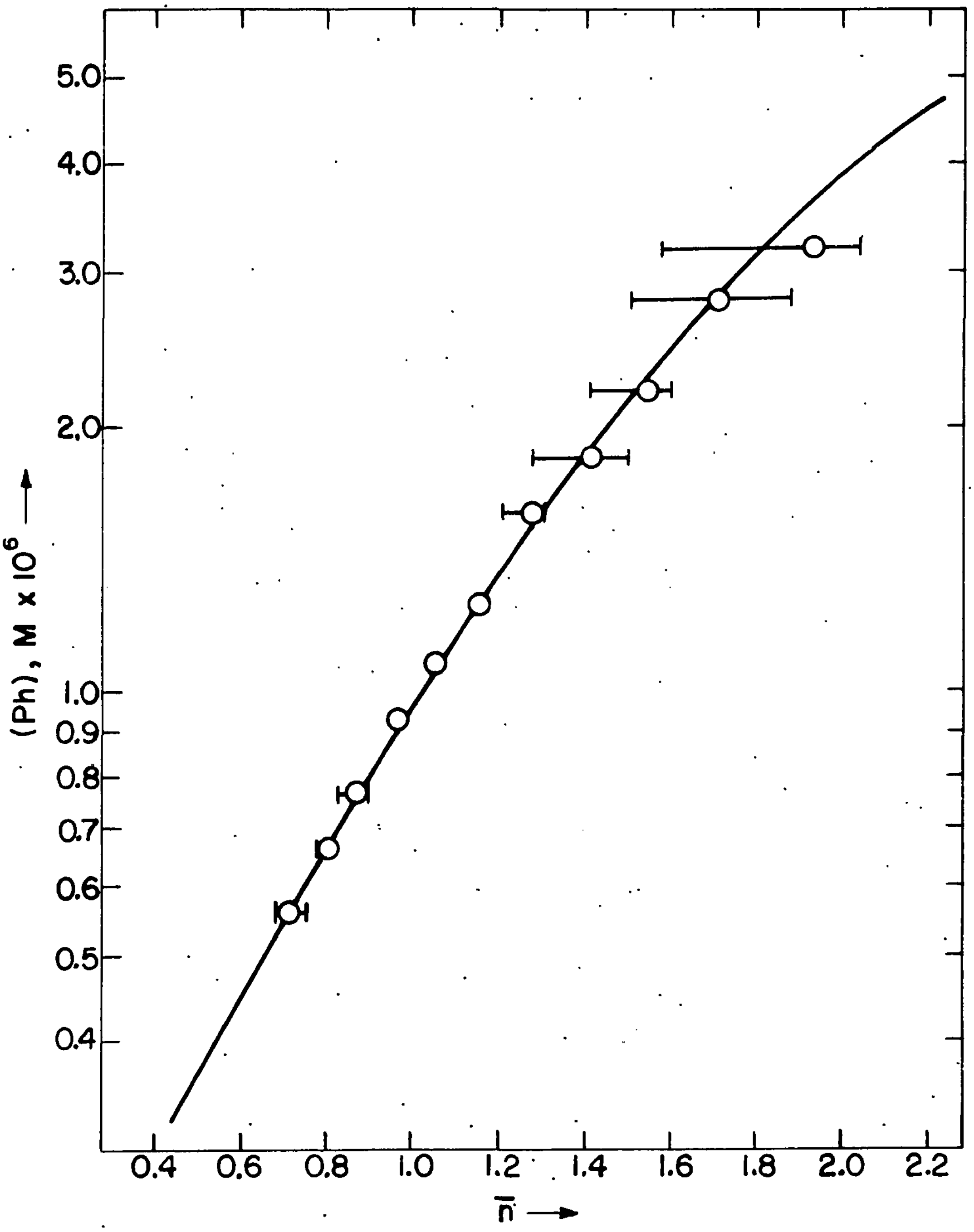


Figure 17. Formation curve of the cobalt(II)-5-nitro-1,10-phenanthroline system from the competition method

Table 20. The cobalt(II)-5-nitro-1,10-phenanthroline system. Application of the competition method

$(Fe)_T = 6.25 \times 10^{-5}M$, $A_{max.} = 0.717$
ionic strength = 0.1
$(HCl)_T = 0.381$ M
$(KCl)_T = 0.381$ M
$(HCOONa)_T = 0.1$ M

No.	$(Ph)_T$ $Mx10^5$	$(Co)_T$ $Mx10^5$	A, 510 mμ
1	3.52	2.02	0.064
2	8.78	2.02	0.245
3	12.29	2.02	0.365
4	14.05	2.02	0.433
5	17.55	2.02	0.553
6	19.32	2.02	0.612
7	22.84	2.02	0.707
8	8.78	5.05	0.159
9	12.29	5.05	0.266
10	14.05	5.05	0.324
11	17.55	5.05	0.435
12	19.32	5.05	0.488
13	22.84	5.05	0.603
14	28.10	5.05	0.706
15	12.29	10.1	0.142
16	14.05	10.1	0.188
17	17.55	10.1	0.275
18	19.32	10.1	0.322

Table 20. (Continued)

No.	$(Ph)_T$ $M\times10^5$	$(Co)_T$ $M\times10^5$	A, 510 mμ
19	22.84	10.1	0.423
20	28.10	10.1	0.550
21	35.17	10.1	0.680
22	19.32	20.2	0.121
23	22.84	20.2	0.186
24	28.10	20.2	0.291
25	35.17	20.2	0.437

Table 21. Calculation of the formation curve for the cobalt(II)-5-nitro-1,10-phenanthroline system from the data of Table 20

A/A_{max}	(Ph) $M\times10^6$	$\bar{n}$
0.961	3.25	1.93
0.943	2.8	1.716
0.891	2.19	1.54
0.838	1.85	1.42
0.768	1.59	1.28
0.629	1.25	1.15
0.524	1.075	1.056
0.419	0.93	0.9707
0.279	0.755	0.885
0.209	0.66	0.803
0.140	0.56	0.708

in the chloroform-water system shows a significant difference of this same order depending on the acidity of the aqueous solution, such an error is not unexpected. It is unfortunate that attempts to measure the partition coefficient in the 2-ethyl-1-hexanol-water system at lower pH were inconclusive. The discrepancy is not serious, however, and constants calculated from either curve will serve.

The Nickel(II)-5-Nitro-1,10-Phenanthroline System

A limited study of the nickel(II)-5-nitro-1,10-phenanthroline system was made using the partition method with 2-ethyl-1-hexanol as the extractive solvent. The only prior study of this system was performed by Margerum (15) who measured the stability of the 1:1 complex by the kinetic method and by spectrophotometric method. The pk_1 obtained by either method was 7.6 in solutions 0.5 M in acid. An acid dependence of the formation and dissociation reactions indicates the stability constant would appear to be less in less acid solutions. The 5-hydrogen-1,10-phenanthroline system of complexes was studied in more detail. The stabilities of the various complexes were measured spectrophotometrically to be $pk_1 = 8.6$, $pk_2 = 8.1$, and $pk_3 = 7.6$. The kinetic results for the 1:1 complex were in approximate agreement with the value of pk_1. Irving and Mellor (5) have also studied the 1,10-phenanthroline system by partition methods and obtained

$pk_1 = 8.0$, $pk_2 = 8.0$, and $pk_3 = 7.9$. The formation curves using both sets of constants are plotted in Figure 18, and can be considered to be in fair agreement. The exact conditions of the partition study are not known, but the spectrophotometric constants are generally subject to more error.

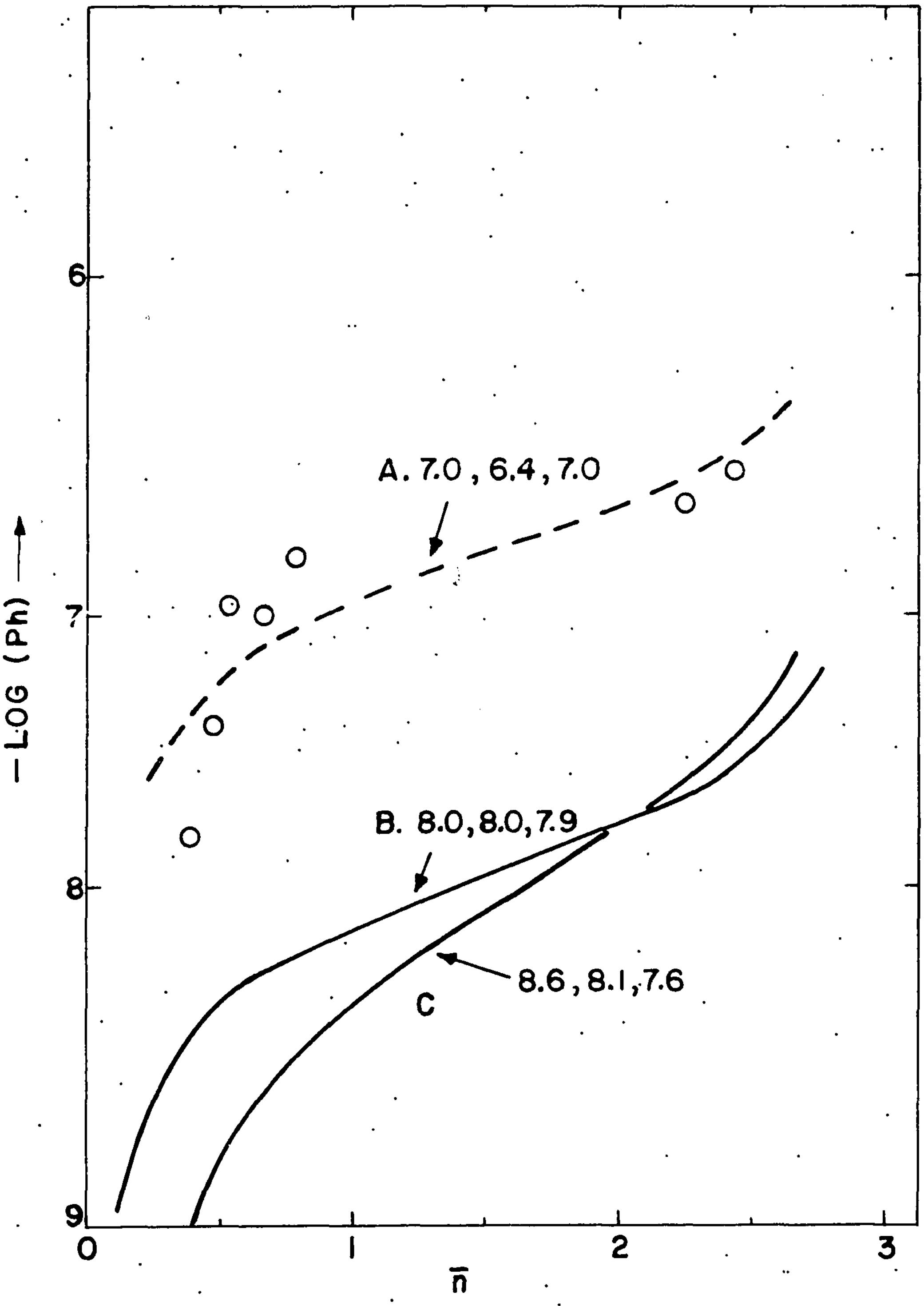
The present study, the data and results of which are shown in Table 22 and plotted in Figure 18, showed an abnormal amount of variation in the experimental points. Part of the difficulty may lie in insufficient equilibration, since the entire system is kinetically slow to form, but all solutions were equilibrated for 24 to 48 hours, and the pH was such as to permit the shortest half-life possible at the concentration levels necessary. Observations of the spectra of the organic phase suggest that some complex may have partitioned. Calculations were performed in which such an occurrence would be compensated, but the formation curve was little affected. The data shown are selected to be that least subject to large errors in the absorbancy of the organic phase. The formation curve drawn through the points in Figure 18 was calculated using the constants $pk_1 = 7.0$, $pk_2 = 6.4$, and $pk_3 = 7.0$. The constants indicate that the 2:1 complex is the weakest of the three. An exact fit of the experimental points is not warranted, but would indicate a smaller pk_2 and proportionately larger values of pk_1 and pk_3. These results indicate an increased relative stabilization of the 3:1 complex when the substituent group is highly electron-withdrawing.

Figure 18. Formation curves of the 1,10-phenanthrolines with nickel(II)

A. 5-nitro-1,10-phenanthroline. Curve calculated using $pk_1 = 7.0$, $pk_2 = 6.4$, $pk_3 = 7.0$

B. 1,10-phenanthroline. Curve calculated using the indicated constants of Irving

C. 1,10-phenanthroline. Curve calculated using the indicated constants of Margerum



6
7
8
9
0
1
2
3
— LOG (Ph) →
$\bar{n}$
A. 7.0, 6.4, 7.0
B. 8.0, 8.0, 7.9
C
8.6, 8.1, 7.6

Table 22. Measurement of the formation curve of the nickel(II)-5-nitro-1,10-phenanthroline system by the partition methods

ionic strength = 0.1
V_w = 30 mls.[a]
K_D = 40

a(266 mμ) = 24,100
cell length = 5 cm.
$4.26 < pH < 4.61$

No.	Ph_T moles x 10^7	Ni_T moles x 10^7	A, 266 m	$(Ph)_o$ $Mx10^6$	$(Ph)_w$ $Mx10^7$	Q	$\bar{n}$
1	0.505	0.916	0.073	0.606	0.151	1.04	0.38
2	0.835	0.916	0.187	1.552	0.388	1.04	0.47
3	1.67	0.916	0.543	4.50	1.12	1.06	0.53
4	1.67	0.916	0.482	4.0	1.0	1.06	0.67
5	2.51	0.916	0.800	6.64	1.66	1.08	0.78
6	5.05	0.916	1.263	10.48	2.62	1.14	2.25
7	6.68	1.145	1.594	13.23	3.31	1.18	2.43

[a] V_o varied from 25 to 30 mls. This variation is included in the calculation of Q.

The Manganese(II)-1,10-Phenanthroline System

The manganese(II) complexes of 1,10-phenanthroline have been studied by Miller and Brandt (43), who reported a maximum of three 1,10-phenanthroline molecules per manganese(II) ion in solution, although a 4:1 ratio was reported by Pfeiffer and Werdelmann (44) in the perchlorate salt. The 2:1 complex crystallized from solutions in which the predominant species is the 3:1 complex. The 2,2'-bipyridyl complexes apparently behave differently, as the solid 3:1 complex is known, but the third ligand is easily lost in aqueous solutions. The magnetic moment of the 3:1 complex indicates five unpaired electrons (45). Irving and Mellor (5) have measured the stability constants of both the 2,2'-bipyridyl and 1,10-phenanthroline complexes by partition methods and have obtained the constants as follows:

Ligand	pk_1	pk_2	pk_3
2,2'-bipyridyl	2.6	2.0	1.1
1,10-phenanthroline	4.8	4.1	5.4

It seems remarkable that the 3:1 complex of 1,10-phenanthroline is more stable than the 2:1 complex, particularly in light of the 2,2'-bipyridyl constants. The same order of stabilities, $pk_3 > pk_1 > pk_2$, is found for the iron (II) complexes.

In the present work, attempts were made to obtain the formation curves of the 5-nitro-, 5-chloro-, and 5-hydrogen-1,10-phenanthroline complexes of manganese(II), by means of the titrimetric method already described. The same solutions of the 1,10-phenanthrolines were used for the manganese titrations as were used for the zinc and copper titrations. The concentration of the manganese titrant was 0.01 M, and the pH of the titrant was the same as the pH of the 1,10-phenanthroline solution initially. Under these conditions, it was expected, that if Irving's constant could be assumed correct, virtually the entire formation curve would be obtained from the data. In other words, in the first increment of the titration, three protons should have been released by the 1,10-phenanthroline for every manganese(II) ion added. In the case of every 5-substitued-1,10-phenanthroline, at no point in the entire titration was the pH change observed sufficient to account for more than 0.5 protons released per manganese(II) ion added.

Such an unusual behavior can be easily accounted for in the case of 5-nitro-, and 5-chloro-1,10-phenanthroline titrations. The formation curves of zinc(II) with these 5-substituted-1,10-phenanthrolines were not obtainable by this method either. The 5-substituted-1,10-phenanthroline solutions which were titrated, however, were observed to affect the electrode system in the manner shown in the following section. The 5-hydrogen-1,10-phenanthroline results are more difficult to explain. In this case, stable pH readings of the 1,10-phenanthroline solution could be obtained. The

1,10-phenanthroline solution titrated with manganese was identical to that titrated with zinc, from which data a formation curve, in agreement with partition method results, was obtained. It seems that two possibilities exist: manganese (II) may behave differently from zinc(II) in its interactions with 1,10-phenanthroline and the adsorption process, or, the data may represent the actual condition of the solution. The latter possibility is a striking one, and calculations were performed to see if the implications were reasonable.

The data for the titration of 1,10-phenanthroline with manganese(II) are presented in Table 23. In Figure 19 the experimental $\bar{n}$ values are plotted against log(Ph). In the same figure are shown the formation curve obtained from Irving and Mellor's constants, and a curve representing the expected formation curve as measured by a pH technique if the only protons released by the 1,10-phenanthroline were those due to the formation of the 1:1 and 2:1 complexes. In other words, the assumption is that the principal 3:1 species exists as $Mn(Ph)_3H_3^{+5}$.

While it does appear that such a stoichiometry would tend to fit the observed data, the implication that a charged species is stabilized by the addition of more charge is difficult to conceive. It would appear that the possibility of double bonding in the 3:1 complex would help explain its unusual stability, and that such double bonding would tend to

Figure 19. Formation curves of the manganese(II)-1,10-phenanthroline system

A. Results of pH measurements
B. Curve calculated assuming the 3:1 species retains three protons per ion
C. The formation curve calculated from the constants given by Irving and Mellor (5), $pk_1 = 4.8$, $pk_2 = 4.1$, $pk_3 = 5.4$
D. Percentage of the total complexed 1,10-phenanthroline present as the 3:1 species

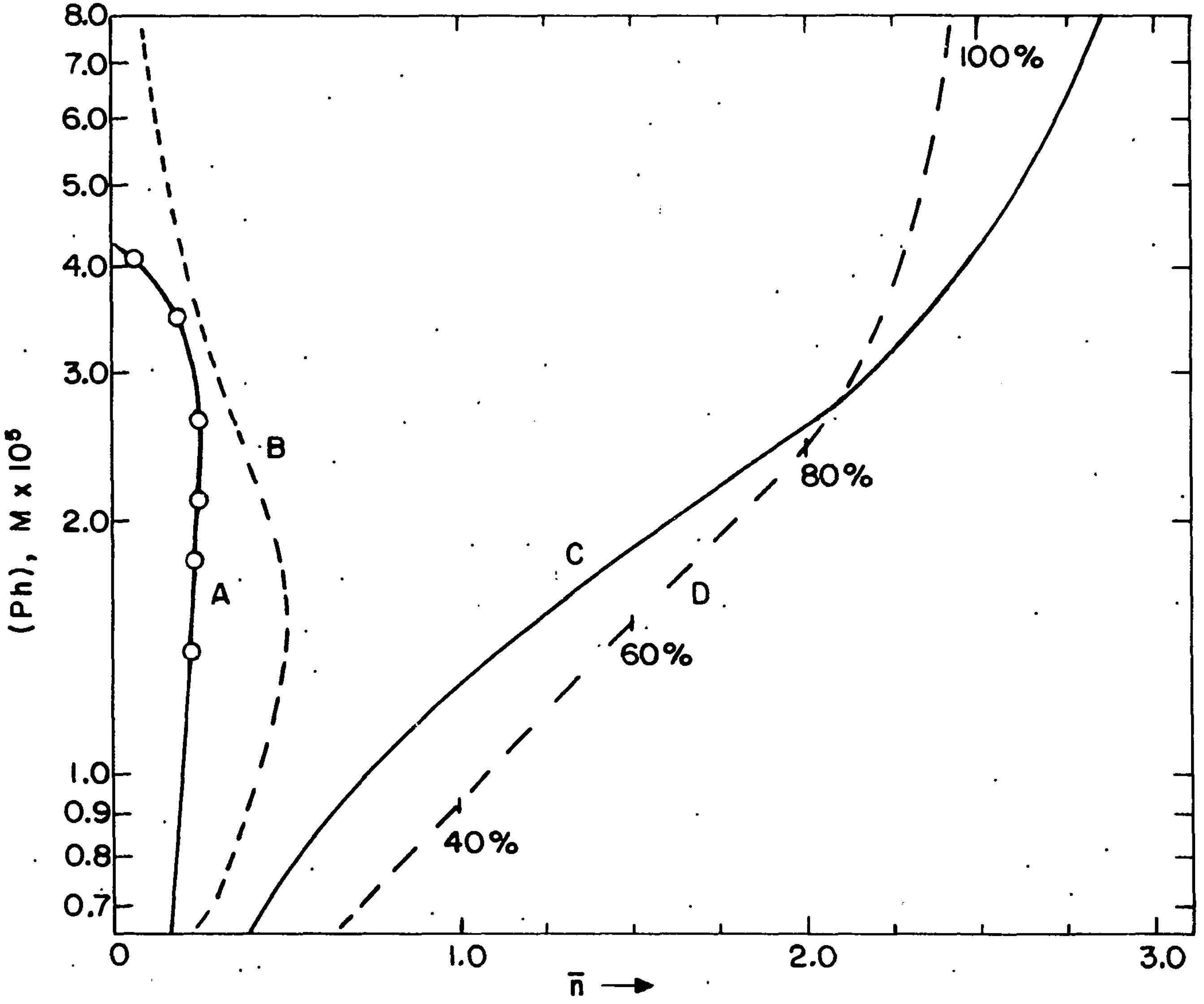

8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.9
0.8
0.7
(Ph), M x 10⁵
0
1.0
2.0
3.0
n̄ →
A
B
C
D
40%
60%
80%
100%

Table 23. Determination of the formation curve of the manganese(II)-1,10-phenanthroline system by pH measurements

V_1 = 50 mls.
$(Ph)_{T1} = 4.78 \times 10^{-4}M$
$(H)_{T1} = 5.0 \times 10^{-4}M$
ionic strength = 0.1
$K_a = 1.0 \times 10^{-5}$

Titrant:
$(Mn)_{TM} = 1.009 \times 10^{-2}M$
ionic strength = 0.1
$(H)_{TM} = 0.92 \times 10^{-4}M$
$\alpha = 1.02$

V_2-V_1 mls.	pH	(H) $M \times 10^4$	$\sum_i i(MnPh_i)_2$ $M \times 10^4$	$\bar{n}$	$(Ph)^a$ $M \times 10^5$	$(Ph)^b$ $M \times 10^5$
0.0	4.145	0.902	-	-	-	-
0.1	4.122	0.950	0.012	0.06	4.53	4.1
0.2	4.105	0.989	0.072	0.18	4.30	3.5
0.4	4.07	1.075	0.197	0.247	3.87	2.65
0.6	4.04	1.151	0.304	0.254	3.53	2.1
0.8	4.017	1.21	0.385	0.239	3.29	1.8
1.2	3.98	1.33	0.540	0.228	2.88	1.4
2.0	3.92	1.510	0.758	0.198	2.38	-
3.0	3.873	1.69	0.965	0.169	2.10	-
6.0	3.79	2.024	1.329	0.123	1.38	-
20.0	3.71	2.44	1.71	0.059	0.67	-

[a] Calculated from Equation 30.

[b] Calculated assuming $pk_1 = 4.8$, $pk_2 = 4.1$, $pk_3 = 5.4$, and Equation 17.

make peripheral positions on the 1,10-phenanthroline basic in character. Such considerations have been given weight with reference to the iron(II) complex, and there is chemical evidence that suggest this strongly. For example, diazotization of 1,10-phenanthroline as the 3:1 iron(II) complex proceeds vigorously compared to its reaction as the free base (46). Krumholz (47) has suggested protonated 3:1 iron(II) complexes would account for kinetic anomalies. The visible absorption band of the 3:1 complex has been assigned to an electron transfer process from the metal to the ligand by Jørgensen (48).

The strongest objection to such a highly protonated 3:1 manganese complex, plausible though these arguments may make it seem, is that the basicity of the peripheral positions would have to be of the same order as that of the nitrogens in 1,10-phenanthroline. Furthermore, a strong electron transfer band should be observed at wave lengths approaching the visible region. Miller and Brandt (43) report a molar absorptivity of only 100 at 390 mμ . Qualitative spectra of the 3:1 complex were run at pH 4 and 7, and while the spectra is partly masked by the excess 1,10-phenanthroline necessary, it appears that no radical change in spectra occurs, as might be expected if protons were removed from the complex in this pH interval. The problem certainly deserves further study. The possibility of a kinetically slow formation reaction for the 3:1 complex has not been considered, but would also account for the anomalous behavior. If the octahedral configuration involves d^2sp^3 (inner orbital) bonding, the energy requirements for the pairing of the 3d electrons in manganese (II) would cause the reaction to be slow.

The Vanadium(IV)-5-Substituted-1,10-Phenanthrolines

The vanadium(IV) complexes with the 1,10-phenanthrolines have been studied, but there is some doubt yet whether they parallel the other metal ion complexes in this thesis in stoichiometry. The kinetics of formation and dissociation of the 1:1 complex were studied spectrophotometrically, using the 1,10-phenanthrolium ion absorption maxima at 293 $m\mu$ and 272 $m\mu$, and the complex absorption band at 426 $m\mu$. Part of the data have been presented in detail by Margerum (15). The publication of new data must await a careful reevaluation, as it is now apparent that consecutive reactions take place in the formation reaction, and it is still uncertain which species are involved in the final equilibrium state. The initial formation reaction is first order with respect to both vanadium(IV) and 1,10-phenanthroline in the pH range 0.5 to 1.5. The formation rate constants are 3.9×10^4 min^{-1} for the reaction with 5-methyl-1,10-phenanthroline, 3.1×10^4 min^{-1} for the 5-hydrogen-1,10-phenanthroline, and 1.6×10^{-3} min^{-1} for the 5-nitro-1,10-phenanthroline reaction with vanadium(IV) in 0.3 M perchloric acid. There seems to be a much greater sensitivity to substituent changes in the vanadium(IV) rates of formation with 1,10-phenanthroline than with the iron(II) or nickel(II) reactions. On the other hand, the rates of dissociation appear to have little or no sensitivity to substituent changes. The values of these constants are 3.3×10^{-2} min^{-1}, 3.16×10^{-2} min^{-1}, and 3.1×10^{-2} min^{-1} for the 5-methyl, 5-hydrogen, and 5-nitro-1,10-phenanthroline complexes, respectively. It is not known if the zinc, which was used to compete with the vanadium(IV) for the 1,10-phenanthroline, participates in the dissociation reaction, perhaps to level the rates of reaction in some way.

The stability constants, calculated from the ratio of the rate of formation to the rate of dissociation, expressed as the logarithm, are 5.99, 5.99, and 4.72 for the 5-methyl-, 5-hydrogen- and 5-nitro-1,10-phenanthroline complexes with vanadium(IV). The value obtained by Trujillo and Brita (49) of the 1,10-phenanthroline 1:1 constant is 5.8. The pH measurement technique used in this case may have some merit.

THE SILVER(I)-AMMINES

The data of Bruehlman and Verhoek (8) are the only metal complex data in the literature where the temperature dependence of the stability constants is available for a variety of ligands. The data are especially amendable to a detailed look at the substituent effect. The enthalpy and entropy changes can be calculated from the data, and Equation 6 can be tested. The results can be interpreted in a manner which suggests the reason why the silver ion has a much lower sensitivity to changes in amine substituents than does the proton.

In Figure 20 the stability data of Bruehlman and Verhoek are plotted against the acid dissociation constants of the amines. The slopes of the lines are about 0.25 for the families of primary, aromatic, and secondary ammines. Only two points are available for the tertiary ammines, but the apparent slope is about 1. The secondary ammines lie below the primary and aromatic ammines in stability, while the tertiary ammines are even less stable.

In Table 24, the changes in enthalpy and entropy are calculated for both the formation of the proton-ammine and silver-ammine complexes. In Table 25, the data of Table 24 are used to calculate the slope, S, by means of Equation 6. It is seen that calculated slope and the slopes drawn through the points in Figure 20 agree as well as can be expected.

Figure 20. The substituent effect in the silver(I)-ammines. Reproduced from the data of Bruehlman and Verhoek (8)

A. Aromatic amines
B. Primary amines
C. Secondary amines
D. Tertiary amines

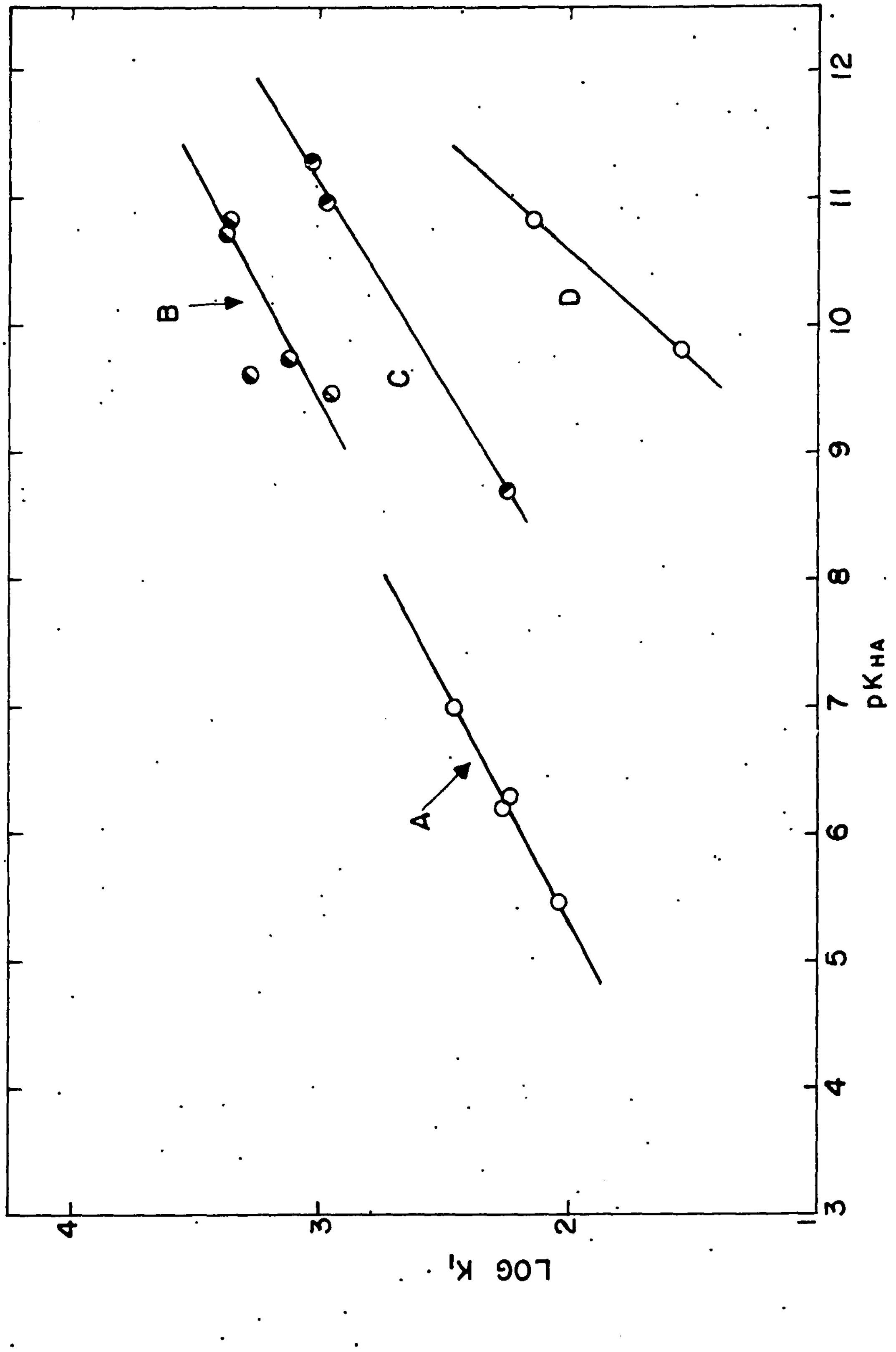

LOG K1
pKHA
1
2
3
4
3
4
5
6
7
8
9
10
11
12
A
B
C
D

Table 24. The substituent effect in silver(I)-ammines

No.	Amine	T(°C)	pK^a_{AH}	$-\Delta H_f$ (Kcal.)	ΔS(e.u.)	$-\log K^a_{AgA}$	$-\Delta H_f$ (Kcal.)	$-\Delta S$(e.u.)
1	Ethylamine	25	10.81	13.42	4.45	3.37	6.51	6.42
		35	10.48			3.21		
2	Isobutylamine	25	10.72	13.01	5.42	3.38	6.51	6.37
		35	10.40			3.22		
3	Ethanolamine	25	9.74	9.36	13.18	3.13	4.88	2.05
		35	9.51			3.01		
4	Pyridine	25	5.45	4.07	11.29	2.04	4.47	5.66
		35	5.35			1.93		
5	α-Picoline	25	6.20	4.88	12.00	2.27	4.47	4.61
		35	6.08			2.16		
6	γ-Picoline	25	6.26	4.88	12.28	2.24	4.07	3.40
		35	6.14			2.14		
7	2,4-Lutidine	25	6.99	5.29	14.24	2.47	4.47	3.69
		35	6.86			2.36		

[a] Data of Bruehlman and Verhoek (8), measured in solutions 0.525 M in potassium nitrate.

Table 25. The substituent effect in silver(I)-ammines

Difference taken between amines:	$\underset{s}{\Delta}(\Delta F_{AgA})$	$\underset{s}{\Delta}(\Delta F_{HA})$	S
(1)-(3)	-0.328	-1.46	0.225
(2)-(3)	-0.343	-1.337	0.256
(4)-(5)	0.313	1.026	0.305
(4)-(6)	0.273	1.105	0.248
(4)-(7)	0.587	3.10	0.190
(5)-(7)	0.274	1.078	0.255
(6)-(7)	0.01	0.994	0.01
		av.	0.212 ± .065
		av.	0.246 ± .026 neglecting (6)-(7)
		av. found	=0.268

One can separate the $\underset{s}{\Delta}\Delta F$ terms into $\underset{s}{\Delta}\Delta H - T\underset{s}{\Delta}\Delta S$ for a closer look at the magnitude of these terms. As representative samples, the differences between isobutylamine and ethanolamine, and γ-picoline and pyridine ((2)-(3), and (6)-(4) in Tables 24 and 25) can be taken. The slopes $\underset{s}{\Delta}\Delta F_{AgA}/\underset{s}{\Delta}\Delta F_{HA}$, respectively are expressed by

$$\frac{\underset{s}{\Delta}\Delta H_{AgA} - T\underset{s}{\Delta}\Delta S_{AgA}}{\underset{s}{\Delta}\Delta H_{HA} - T\underset{s}{\Delta}\Delta S_{HA}} = \frac{-1.6 + 1.3}{-3.6 + 2.3} \text{ and } \frac{+0.4 - 0.68}{-0.8 - 0.3},$$

where the individual values are in Kcals.

A close examination will reveal that the enthalpy substituent effect is more sensitive to a change from H to Ag than is the entropy substituent effect. This is interpreted to mean the silver-ligand bond strengths are less sensitive to substituent effects than the proton-ligand bond strengths.

This difference in bond strength sensitivity is more pronounced than differences in the entropy terms (sensitivity of the extent of solvation) between the silver- and proton-ammines.

This result means that the Ag-N bond is rather insensitive to substituents, and that this may be due to hydrogen bonding to the protons in the ammines enhancing the sensitivity of the proton-ligand bonds to substituent changes. It will be noted, in this light, that the slope in Figure 20 for the tertiary amines, where no hydrogen bonds can form, is close to unity, indicating equal sensitivities of the silver ion and proton.

GENERAL OBSERVATIONS ON THE EFFECT OF 1,10-PHENANTHROLINE ON GLASS SURFACES

Little mention is given to the interaction of 1,10-phenanthroline with glass surfaces in the literature. The effect is important enough to account for significant decreases in absorbancy in spectrophotometric work, and in the present work, is noted to affect the response of glass electrodes profoundly under certain conditions.

From the decrease in absorbancy of a 1,10-phenanthroline solution in contact with freshly cleaned silica absorption cell walls, Margerum (15) estimated that about 5 x 10^{-9} moles of 1,10-phenanthroline adsorbed per sq. cm. of surface. This order of magnitude is about right for a monolayer. The adsorption is evidenced by the inability of water to wet glass surfaces that have been in contact with 1,10-phenanthroline. Acids and several organic solvents remove adsorbed 1,10-phenanthroline readily. Desicote does not prevent the adsorption process. The 1,10-phenanthrolium ion shows little or no tendency to adsorb, but the rate and completeness of the adsorption process is some function of the concentration of free base 1,10-phenanthroline present. In Table 26, a series of pH readings taken with a glass-calomel electrode system and the Beckman Model GS pH meter with several solutions, including 5-chloro-1,10-phenanthroline, are recorded to illustrate the behavior in question. Both electrodes were

Table 26. Response of a glass-calomel electrode system to 1,10-phenanthroline-containing solutions

Solution	Scale reading	Comments
Buffer[a]	510	rapid equilibrium
Acid[b]	792	rapid equilibrium
Buffer[a]	510	rapid equilibrium
Phen[c]	ca. 840	first reading taken; immediate and rapid drift to lower values
	732	30 sec. after first reading; progressively slower drifting
	610	stable reading attained after 8 min. of standing; shorter time if stirred
Buffer[a]	575	first reading taken; a slow drift occurs
	555	after 30 sec.
	540	after 3 min.
	510	stable reading attained after 1 hr. of standing; or if the glass electrode is cleaned with acetone
Phen[c]	610	after sufficient time for equilibrium
add HCl	650	rapid equilibrium

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[a] pH 4 buffer, prepared to National Bureau of Standards specifications.

[b] Hydrochloric acid, exactly 1.11×10^{-3}M, 0.1 M in potassium chloride.

[c] 5-Chloro-1,10-phenanthroline solution, 1.8×10^{-3} M.

Table 26. (Continued)

Solution	Scale reading	Comments
Phen[c]	610	fairly rapid equilibrium
add base	537	rapid equilibrium
Buffer[d]	510	fairly rapid equilibrium
Buffer[a]	ca. 575	first reading, drifting to lower values
	510	after standing a long period

[d] Same buffer as in a., with a small amount of solid 5-chloro-1,10-phenanthroline added.

From the nature of the responses listed in Table 26, it seems that the coating process or the removal of the coat causes drifting potentials to be observed. The coat itself has little effect on the potential. The coat does not seem to impair the hydrogen electrode function of the glass electrode. It is probable that the application of pH measurements to the determination of the stabilities of metals with the 1,10-phenanthrolines did not succeed in some cases because the metal tended to remove the adsorbed 1,10-phenanthroline, causing erratic potentials to be observed. The entire phenomenon deserves further study.

DISCUSSION

In Table 27 is presented a compilation of all the stability constants of 1,10-phenanthroline, 5-nitro-, 5-bromo-, 5-chloro-, 5-methyl-, and 4,7-dimethyl-1,10-phenanthroline, which have been measured either in the literature or in this thesis, with the proton and the divalent metals, cadmium, zinc, copper, nickel, cobalt, iron and manganese. Both the stepwise and overall stability constants are given. The source of information and the general method used in determining the constants are also listed.

Variations in the constants are understood if the limitations of the methods used are considered. Generally speaking, pK values within 3 per cent of each other are considered to be in good agreement. Variations outside of this range are generally due to the difficulties in applying a specific method to the measurement of the constant. Examples of constants which are definitely out of line are as follows: pK_3 of zinc with 1,10-phenanthroline by the spectrophotometric method, pk_1 of copper with 1,10-phenanthroline by pH measurements, and pK_3 of manganese with 1,10-phenanthroline by the spectrophotometric method. The cadmium constants measured by polarographic methods do not agree with those by partition or pH measurements. In two cases, (14, 15), workers have obtained constants with three substituted 1,10-phenanthrolines and obtained linear substituent effects. In each case, the

Table 27. Stability constants of the transition metals with substituted 1,10-phenanthrolines

Ligand[a]	Metal	pk_1[b,c]	pk_2[b,c]	pk_3[b,c]	pK_2[d]	pK_3[d]
1,10-Phen	Cd(II)	5.17 C (5)	4.83 C (5)	4.26 C (5)	10.0	14.3
		-	5.2 A (14)	4.2 A (14)	13.2 G (52)	15.2 G (52)
pK_a = 4.77A(37)	Zn(II)	6.36 A	5.64 A	5.2 A	12.00	17.0
4.96H(37)		6.43 E (32)	5.72 C (32)	4.85 C (32)	12.15	17.0
4.857A(50)		6.6 C (32)				
5.02A(51)		6.47 B (29)	5.5 B (29)	1.1 B (29)	12.00	13.1
5.0 (5)		6.4 C (5)	5.63 C (5)	5.0 C (5)	12.03	17.0
		-	5.9 A (14)	4.8 A (14)	11.62 B (53)	
	Cu(II)	9.15 C	6.65 A,C	5.25 A	15.8	21.05
		9.0 C	6.7 A,C	5.1 A	15.7	20.9
		8.82 C (5)	6.57 C (5)	5.02 C (5)	15.4	20.4
		6.3 A (40)	6.15 A (40)	5.5 A (40)	12.4	17.9
	Ni(II)	8.6 B (15)	8.1 B (15)	7.55 B (15)	16.7	24.25
		8.0 C (5)	8.0 C (5)	7.9 C (5)	16.0	23.9
	Co(II)	7.02 C (5)	6.70 C (5)	6.38 C (5)	13.72	20.1

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[a] The symbolism indicates the substituent and position on 1,10-phenanthroline.

[b] Constants stated without a reference number are calculated from data in this thesis.

[c] The methods used are coded as follows: A - pH measurements, B - spectrophotometric equilibrium method, C - partition method, D - kinetic study, E - competition method, F - oxidation-reduction potential, G - polarographic method, H - conductometric method.

[d] References and methods are listed for direct measurements only.

Table 27. (Continued)

Ligand[a]	Metal	pk_1[b,c]	pk_2[b,c]	pk_3[b,c]	pK_2[d]	pK_3[d]
	Fe(II)	5.85 B				21.3 B (37)
		5.85 B (54)				21.5 D (35)
		5.85 C (5)	5.3 C (5)	10.0 C (5)	11.15	21.15 C (5)
						21.3 B (13)
						21.5 D (13)
						21.3 F (55)
	Mn(II)	4.8 C (5)	4.1 C (5)	5.4 C (5)	8.9	14.3
		4.0 A[e]				7.35B (43)
5-NO_2- 1,10-Phen	Zn(II)	5.6 B[f]	-	-	-	-
		5.4 B[g]	-	-	-	-
pK_a = 3.57A(13) 3.33B	Cu(II)	8.0 C	5.47 C,E	4.2 C	13.47	17.7
		7.8 B[f]	-	-	-	-
		7.6 B[g]	-	-	-	-
	Ni(II)	7.57 B (15)	-	-	-	-
		7.0 C	6.4 C	7.0 C	13.4	20.4
	Co(II)	6.25 C	5.41 C	4.63 C	11.65	16.3
		6.44 E[h]	5.60 E[h]	4.82 E[h]	12.0	16.8

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[e] Calculated from the data of Table 23, disregarding the first points taken.

[f] Calculated using the pK_a value of Brandt and Gullstrom (13).

[g] Calculated using the pK_a value measured in this thesis.

[h] Taken from a formation curve through the competition method data, and parallel to that through the partition method data.

Table 27. (Continued)

Ligand[a]	Metal	pk_1[b,c]	pk_2[b,c]	pk_3[b,c]	pK_2[d]	pK_3[d]
	Fe(II)	5.06 B	-	-	-	18.1 D (13) 17.8 B (13)
5-Br-1,10-Phen pK_a = 4.20B	Fe(II)	5.45 B[i]	-	-	-	19.7 B[i]
5-Cl-1,10-Phen pK_a = 4.26A(13) 4.18B	Zn(II)	5.85 B[f] 5.72 B[g]	- -	- -	- -	- -
	Fe(II)	-	-	-	-	19.7 D (13) 19.7 B (13)
5-CH_3-1,10-Phen pK_a = 5.26A(14) 5.23A(13)	Cd(II)	-	5.2 A (14)	4.3 A (14)	-	-
	Zn(II)	-	6.0 A (14)	5.0 A (14)	-	-
	Ni(II)	8.7 B (15)	-	-	-	-
	Fe(II)	6.05 B	-	-	-	22.3 B (13)
4,7-$(CH_3)_2$-1,10-Phen pK_a = 5.94A(14)	Zn(II)	-	6.3 A (14)	5.4 A (14)	-	-

[i] Computed indirectly using the substituent effect.

same method was used for all three 1,10-phenanthrolines. In the case of nickel(II), the substituent effect as measured by spectrophotometric methods agrees well with that obtained by partition methods, but the pK_1 values by the former method are 0.6 units greater than those measured by the latter. In the case of zinc(II), the pk_2 value of the 1,10-phenanthroline complex used in substituent effect comparisons is 0.3 units greater, on the average, than the constants obtained by other workers by other methods. These examples serve to point out that there are systematic errors connected with a particular method which may not have an appreciable effect on substituent effect comparisons, but cause appreciable variations in the absolute magnitude of the constants.

In Figure 21 the constants for the 1,10-phenanthroline and 5-nitro-1,10-phenanthroline complexes with nickel, cobalt, zinc, and iron are plotted against the corresponding constants for the copper complexes of the ligands. The slopes of lines drawn through the corresponding complexes of the same metal with the two ligands are a measure of the substituent effect. It should be pointed out that the size of the points is indicative of the uncertainty in the constants, and the slopes are the average of several that can be drawn. The slopes drawn through the zinc(II) points for the 2:1 and 3:1 complexes are estimated from the substituent effect measured by Yasuda et al. (14). On examination of the plot, several

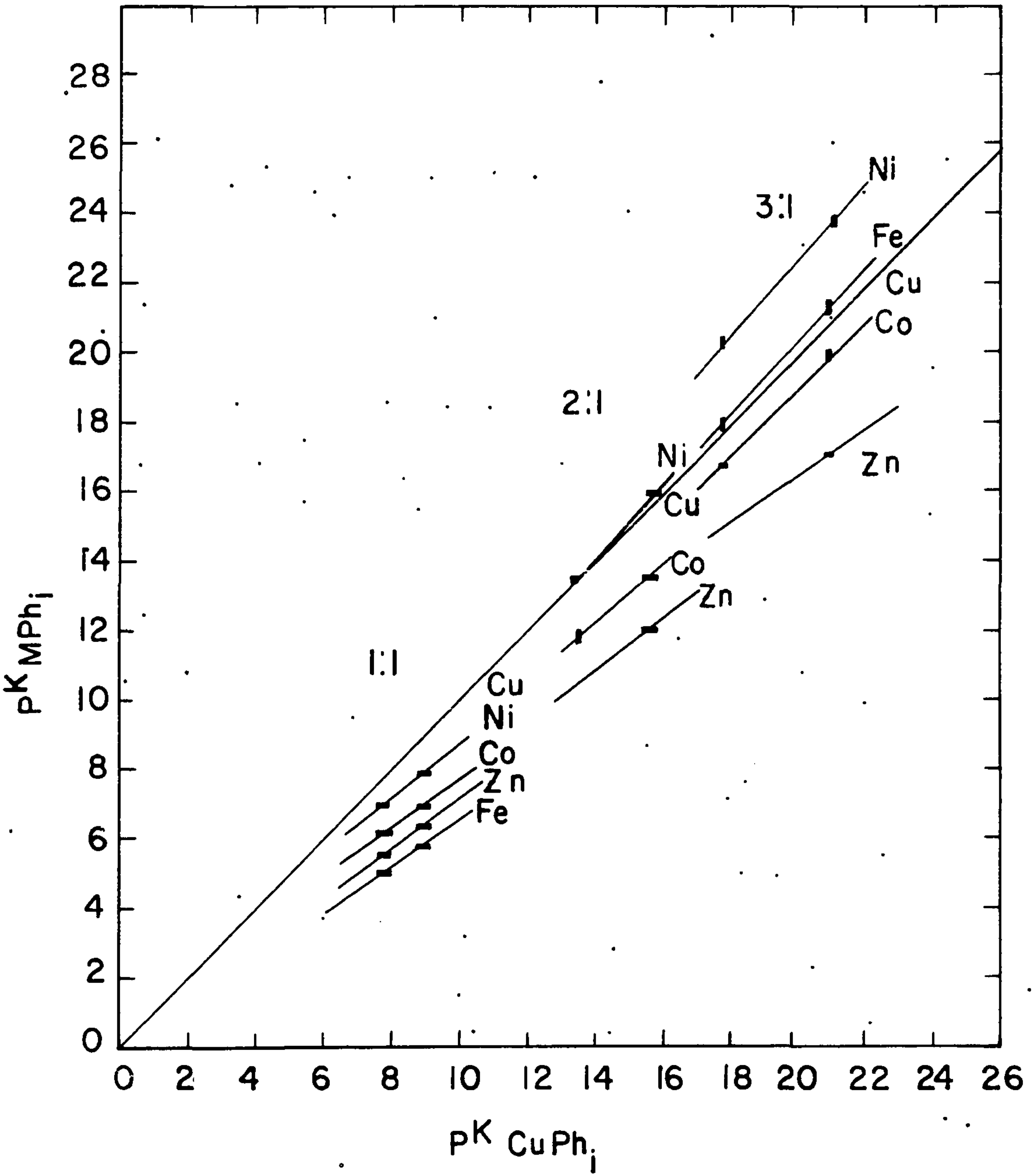

Figure 21. The substituent effect in transition-metal complexes of the 1,10-phenanthrolines

points become evident:

(1) The order of stabilities for the 1:1 complexes follow the Irving-Williams series, namely, Zn $<$ Cu $>$ Ni $>$ Co $>$ Fe.

(2) The order of stabilities for the 3:1 complexes is Ni $>$ Fe $\gtrsim$ Cu $>$ Co $>$ Zn, which does not follow the Irving-Williams series.

(3) The substituent effects for the 1:1 complexes fall in the same order as that of the stabilities, except that the effects with cobalt and iron are approximately equal. The substituent effects for the 3:1 complexes also follow the order of stabilities.

In Figure 22 the ratio of the stability of the 1,10-phenanthroline complexes of the above metals to the stability of the corresponding copper complex is plotted against the corresponding slopes of the lines in Figure 21. Even with the large degree of uncertainty indicated, it is apparent that there is some correlation between the relative stabilities and the relative substituent effects. This sort of correlation was anticipated in the first part of this thesis for 1:1 complexes. The correlation should also hold for higher complexes since the more general equation, similar to Equation 6 is

$$\frac{\underset{s}{\Delta}\, pK_{M_1L_i}}{\underset{s}{\Delta}\, pK_{M_2L_i}} = \frac{\underset{s}{\Delta}\, \bar{F}^{o}_{M_1L_i} - i\,\underset{s}{\Delta}\, \bar{F}^{o}_{L}}{\underset{s}{\Delta}\, \bar{F}^{o}_{M_2L_i} - i\,\underset{s}{\Delta}\, \bar{F}^{o}_{L}} \approx \frac{pK_{M_1L_i}}{pK_{M_2L_i}}$$

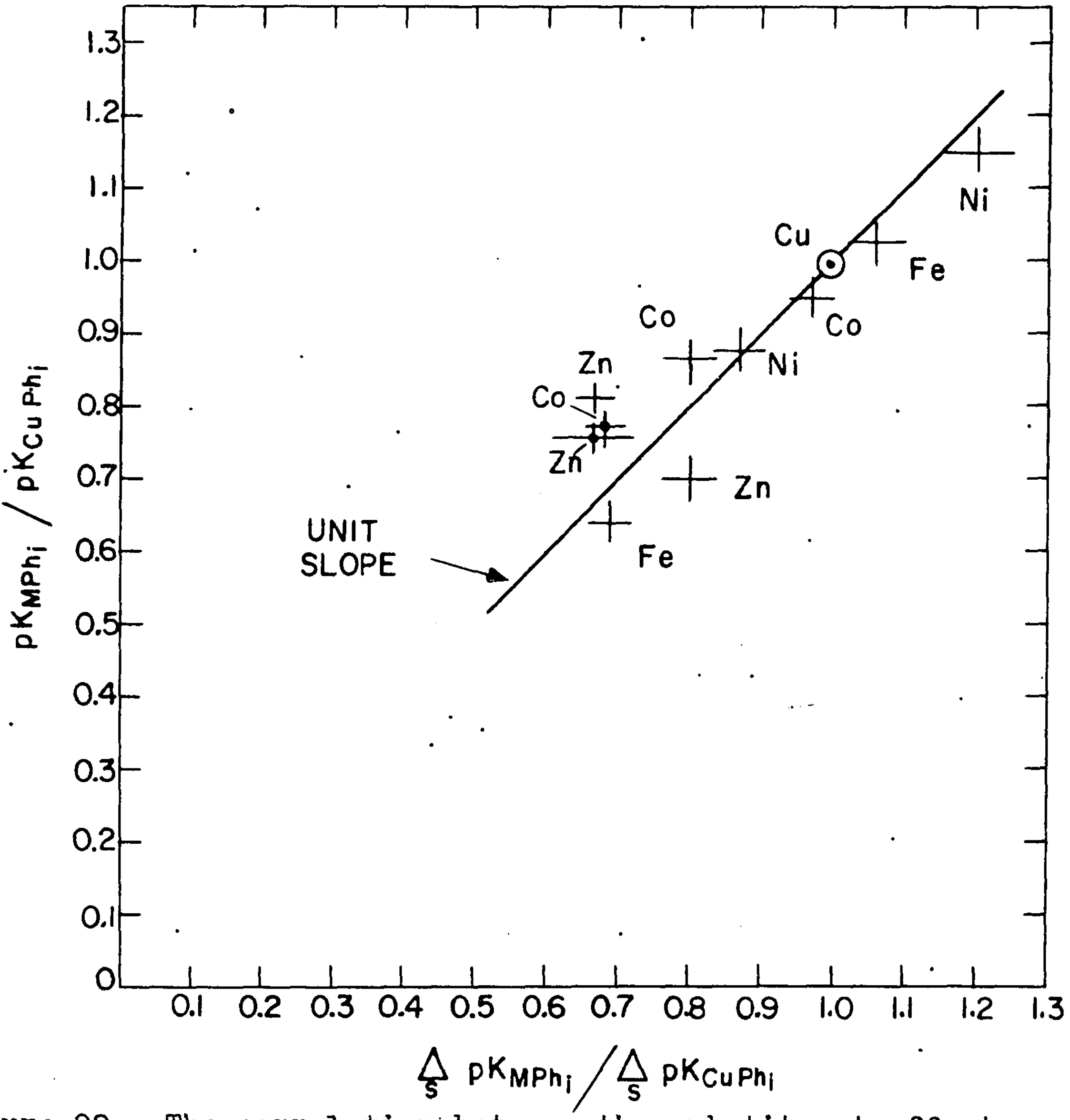

Figure 22. The correlation between the substituent effects for various transition metals complexed with the 1,10-phenanthrolines and the relative stabilities of these complexes

The same assumptions concerning the stoichiometry, the entropy term, and the relative order of the hybrid metal-orbital energies also apply in this case, of course.

As an empirical rule, useful in the approximate prediction of stability constants, it is roughly true that the lines in Figure 21 pass through the origin. A measure of the accuracy of this statement is the amount by which the points in Figure 22 depart from the line of unit slope. This rule arises from the fact that the intercepts are generally only a small fraction of the magnitude of the stability constants. Thus, if the stabilities of 5-substituted-1,10-phenanthrolines with one metal ion are known, and the stability of another metal with one of the 1,10-phenanthrolines is known, the stabilities of the second metal with the other 1,10-phenanthrolines can be predicted. Plots of pK_{MPh_1} against pK_a are also useful in this respect.

The reasons for the change in the order of stabilities of the complexes as the number of attached ligands is increased can be postulated if a few additional comparisons are made. In Table 28 the second ionization potential, and the gaseous ionic radii of the transition metals are compared to pK_1 and pK_3 of the 1,10-phenanthroline complexes of these metals. In Table 29, the pK_3 values are compared to hypothetical values based on a statistical decrease in pk for the successive complexes. The probability of attaching a ligand to

Table 28. Correlation of pK_1 and pK_3 values with the second ionization potential, E_2

Metal	Mn	Fe	Co	Ni	Cu	Zn
E_2 (e.v.)	15.7	16.6	17.3	18.2	20.34	17.89
pK_1	4.8	5.85	7.0	8.0	9.0	6.4
pK_3	14.3	21.3	20.1	24.0	21.0	17.0
ionic radii(Å)	.78	.76	.74	.73	.72	.72

Table 29. Comparisons of pK_3 values to statistically predicted values

Metal	Mn	Fe	Co	Ni	Cu	Zn
pK_1 (expt.)	4.8	5.85	7.0	8.0	9.0	6.4
pK_3 (theory)[a]	13.4	16.5	20	23	26	18.2
pK_3 (expt.)	14.3	21.3	20.1	24.0	21.0	17.0
pK_3 (expt.) - pK_3 (theory)	+0.9	+4.8	+0.1	+1.0	-5.0	-1.2

[a] pK_3 (theory) = $3pK_1 - 1$.

a metal should be proportional to the number of available positions on the metal (2, p. 80). The successive stepwise stability constants, for a bidentate ligand and an octahedral metal configuration, should decrease by a factor of 1/3, or 0.5 log units. Thus, pk_3 should be 1 log unit less than pk_1 if all metal orbitals were identical initially, and did not change with the presence of ligands on the metal. The third comparison to be made is to the ethylenediamine complexes with the same metals, as an example of another case of a bidentate ligand bonding through essentially covalent bonds. These data, taken from Martell and Calvin (2, p. 518) are presented in Table 30.

Table 30. Stability constants of the ethylenediamine complexes

Metal	Mn	Fe	Co	Ni	Cu	Zn
pK_1	2.73	4.28	5.89	7.66	10.72	5.92
pK_2	4.79	7.53	10.72	14.06	20.1	11.06
pK_3	5.66	9.52	13.82	18.61	19.0	12.9

The points to observe in these tables are as follows:

(1) The ionic radii of the transition metals do not vary sufficiently to be a significant factor in the strength of the bonds.

(2) The pK_1 values parallel the second ionization potentials when arranged according to the atomic number.

(3) The pK_3 values of iron and nickel appear larger than would be expected on the basis of the second ionization potential.

(4) Manganese, cobalt and nickel have pK_3 values which are approximately predicted on the basis of a statistical

decrease in the stepwise stability constants. Zinc has a value slightly smaller than predicted.

(5) The 3:1 complex of iron is very much more stable than would be predicted on the basis of the statistical factor, while the 3:1 complex of copper appears to be considerably weaker on the same basis.

(6) The 3:1 complex of copper with ethylenediamine is very unstable, while the corresponding nickel complex forms as easily as do the 3:1 complexes of manganese, iron, cobalt, and zinc.

(7) From the data of Table 27, the second 1,10-phenanthroline is added to copper 200 times less readily than the first, while the third 1,10-phenanthroline is added only 40 times less readily than the second. This to be compared to the ethylenediamine complexes, in which the second ligand adds 20 times less readily than the first, and the third ligand essentially does not add.

The following interpretation is proposed to explain the preceding observations: The octahedral configuration of copper(II) is not symmetrical[1]. The bonding orbitals are probably the $3d4s4p^2$ hybrid (square planar), and the $4p_z$

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[1] Rundle, R. E., Ames, Iowa. The electronic structure of planar complexes of copper(II). Private communication. 1957.

orbital which is elongated (weaker bonding) above and below the plane of the dsp^2 orbitals. Thus the 2:1 ethylenediamine complex could easily exist in the <u>trans</u> form, while the third ligand addition requires not only bonding with the weak p_z orbital, but the breaking of one of the dsp^2 ligand- metal bonds to accomodate the second nitrogen donor atom on the bidentate ligand. The 3:1 complex is understandably weak. The first two ligands attach themselves to the copper ion nearly equally readily. 1,10-Phenanthroline, however, does not appear to favor the <u>trans</u> position, since the second 1,10-phenanthroline adds much less readily than the first. There may be a steric reason for this, as the copper ion is the smallest of the series, and in a model, the 2,9-position hydrogens on the 1,10-phenanthroline tend to interfere with each other. It may be, then, that the second 1,10-phenanthroline adds in a <u>cis</u> configuration, in spite of the weaker bonds formed. The remaining positions, being <u>cis</u> to each other, are then well suited to accept the third 1,10-phenanthroline. All this is consistent with the observations on copper in points (5), (6), and (7). It is also evident that part of the reason for the unusual order of stabilities of the 3:1 complexes of the 1,10-phenanthrolines is that the copper complex is less stable, overall, than it should be on the basis of the assumption of a symmetrical octahedral configuration. The nickel(II) and cobalt(II) complexes with

1,10-phenanthroline, as the solids, have been observed to be diamagnetic (no unpaired electrons), and paramagnetic (three unpaired electrons), respectively (56). In solution, however, the nickel(II) complex becomes paramagnetic (57). The indication is that $4s4p^34d^2$ hybrid orbitals may be involved in the bonding. While this is difficult to reconcile with the observed kinetic slowness of the nickel(II) complex formation (36), the relative overall stabilities of the nickel and cobalt complexes are consistent with the use of the same set of hybrid bonding orbitals for both metals. The 3:1 iron(II) complex involves, without a doubt, $3d^24s4p^3$ hybrid bonding orbitals, as the complex is diamagnetic (56). The use of these more electronegative hybrid orbitals, as opposed to those of nickel and cobalt, with the concomitant increase in the covalent character of the metal-ligand bonds, is sufficient to account for the position of the iron complex as on a par with that of copper in the order of stabilities of the 3:1 transition-metal-1,10-phenanthroline complexes. The 1:1 complex of iron(II) with 1,10-phenanthroline, if it could be isolated, should prove to be paramagnetic, since its stability is in line with the Irving-Williams series. The ease with which 1,10-phenanthroline adds, in succession, to zinc(II) is worthy of comment. The "inner" 3d orbitals in zinc are completely filled with non-bonding electrons. The preferred steric configuration of zinc is tetrahedral, using the $4s4p^3$ hybrid bonding orbitals. Because both ethylenediamine and 1,10-phenanthroline form 3:1 complexes with zinc, it is assumed that the octahedral $4s4p^34d^2$ hybrid bonding orbitals are used. It is not known whether the 1:1 and 2:1 complexes are tetrahedral, followed by a change in configuration to form the 3:1 complex, or whether the octahedral configuration is favored by all the complexes. No problem involving the steric considerations proposed for the copper complexes arises with either the tetrahedral or a _cis_ octahedral configuration for the 2:1 complex of zinc.

It is not necessary to resort to the concept of pi-bonding in any of the transition-metal-1,10-phenanthroline complexes to explain qualitatively the order of stabilities and the relative substituent effects. In the 3:1 iron(II) complex, the evidence for pi-bonding seems fairly convincing, and yet, if it does exist, it does not seem to change the substituent effect from that expected on the assumption of sigma bonding alone.

SUMMARY

A comparison of the stability constants of various transition-metal complexes of 5-substituted-1,10-phenanthrolines, measured by several methods of approach, indicate the following:

1. The stability of the 1:1 complexes can be correlated with the second ionization potentials of the metals.

2. Configurational differences exist in the 3:1 complexes which result in an apparent change in the order of stabilities compared to that of the 1:1 complexes. The copper(II) complexes are considerably weaker in stability than expected, while the iron(II) complexes are much more stable than expected, on the basis of the electronegativities of the metals and comparisons to related complexes. The reduced stability of the 2:1 and 3:1 copper(II) complexes is assigned to an unsymmetrical octahedral configuration, while the additional strength of the 3:1 iron(II) complex results from the utilization of a lower energy hybrid orbital system, d^2sp^3, than the other metal complexes use. The possibility of pi-bonding also exists in the latter case.

3. A correlation is observed between the substituent effects and the relative stabilities of the various complexes. This is considered to be due to the effect of changes in nuclear repulsion terms with changes in the electronegativity of the metal and ligand hybrid orbitals.

4. Several reports of stability constants in the literature are shown to be erroneous or questionable. These reports generally have not adequately taken into consideration the limitations of the particular method of measuring the stability constants.

5. An empirical rule which relates the stabilities of the transition-metal-5-substituted-1,10-phenanthroline complexes to each other in a simple manner is proposed, and may be found to hold for other ligand complexes as well.

SUGGESTIONS FOR FUTURE WORK

Considerable work needs to be done to further understand both the nature of the substituent effect and the nature of the 1,10-phenanthroline complexes in aqueous solutions. The following is suggested:

1. The formation curves of the nickel(II), zinc(II), and manganese(II)-5-nitro-1,10-phenanthroline systems should be obtained in detail by partition methods. The chloroform-water system should prove satisfactory for these systems of complexes if the aqueous solutions are somewhat acidic. The partition coefficient for 5-nitro-1,10-phenanthroline should be measured more accurately, and the pK_a value should be determined by an independent method, such as conductivity. To overcome the solubility limitations in determining the upper portions of the formation curves, the possibility of using dioxan-water mixtures should be considered in the application of pH measurements to stability determinations.

2. The temperature dependence of the stability constants should be obtained to test the validity of the assumption that the substituent effect on the entropy terms is negligible compared to the enthalpy terms.

3. The manganese(II)-1,10-phenanthroline system should be studied to determine the stoichiometry of the formation of the various complexes, and the stability of each species. It would be valuable to have data on the magnetic suscepti-

bility of these complexes in solution and in the crystalline state to determine the configuration. The rates of formation and dissociation would be useful in classifying these complexes as labile or inert. There is a possibility that the formation reaction may be slow enough to measure spectrophotometrically.

4. The adsorption phenomenon of 1,10-phenanthrolines on glass should be studied to determine its extent under various solution conditions. The validity of pH measurements in 1,10-phenanthroline solutions will remain in question until this is done.

5. The magnetic susceptibilities of the nickel(II) complexes of 1,10-phenanthroline should be measured in both the solid and the water. There are now conflicting reports in the literature. It is important to find a configuration for the various complexes consistent both with the stability picture and kinetic inertness of the reactions.

6. The general approach of measuring substituent effects should be systematically extended to the many varieties of ligands now used analytically. Not only will such data be of theoretical importance in the understanding of the bonding in coordination compounds, but they will make possible the prediction of the stabilities of many highly insoluble complexes. Such knowledge will aid the analytical chemist in

his choice of selective reagents, and in the design of new reagents for specific purposes.

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APPENDIX: LIST OF ABBREVIATIONS

M	any divalent transition metal, as, Mn^{++}, Fe^{++}, Co^{++}, Ni^{++}, Cu^{++}, and Zn^{++}
L	in general, a monobasic ligand. in particular, any 1,10-phenanthroline, as the free base.
H	the proton. also, enthalpy.
$\bar{F}^o, \bar{H}^o, \bar{S}^o$	the partial molar standard free energy, enthalpy, and entropy.
L_s	a ligand with a substituent s.
ML	a 1:1 metal-ligand complex.
HL	the mono-protonated ligand. in particular, the 1,10-phenanthrolium ion.
Δ_s	the difference with respect to the substituent s.
M_1, M_2	subscripts indicate two different metal ions.
E	the energy level of the hypothetical hybrid bonding orbitals.
K_i	i = 1, 2, 3. the overall dissociation constant of the i-th complex.
k_i	the stepwise dissociation constant of the i-th complex.
β_i	$1/K_i$. the overall formation constant of the i-th complex.
K_a	the acid dissociation constant for a monobasic ligand, in particular, the 1,10-phenanthroline under discussion.
T	temperature in °K, or, as a subscript, the analytical total concentration of the species in question.
$\bar{n}$	the average number of ligands complexed with the metal per metal species in solution.
Ph	in general, any 5-substituted 1,10-phenanthroline as the free base, in particular that 1,10-phenanthroline under discussion.

A	the absorbancy of a solution at a particular wavelength.
a	the molar absorptivity of the species in question in l./mole-cm.
b	the cell length in cm.
	wavelength, in mμ.
p	the operator, $-\log_{10}$.
α	1. the degree of association of a particular complex, as $(CuPh_2)/(Cu)_T$ (p. 45), $(CuPh)/(Ph)_T$ (p. 47), $(HPh)/(Ph)_T$ (p. 79) or $(MPh)/(Ph)_T$ (p. 81). 2. defined as $(H)_M/(H)_1$, pp. 49-50. used in reference to the titrimetric pH method only.
γ_H	the activity coefficient of the proton.
Ph_iH	a species in which more than one 1,10-phenanthroline is associated with the proton.
Q	$K_DV_o + V_w(1 + (H)/K_a$, defined on p. 34.
K_D	the partition coefficient of the 1,10-phenanthroline under discussion between chloroform or 2-ethyl-1-hexanol and water. defined as $(Ph)_o/(Ph)_w$.
o, w	as subscripts, these refer to the organic and water phases, respectively.
A_{max}	the maximum attainable absorbancy of a 1,10-phenanthroline containing solution with a given concentration of iron(II).
1, 2	1. as subscripts, in reference to the titrimetric method only, refer to the ligand solution at the start, and during the titration, respectively. 2. as subscripts, in reference to the competition method only, refer to solutions which contain different amounts of the metal whose formation curve is to be measured. see pp. 67-69.
A, AgA, HA	the amine, silver-ammine, and ammonium ion, respectively.