REACTIONS OF 1,10-PHENANTHROLINE WITH HYDROGEN, LITHIUM, SODIUM AND POTASSIUM IONS

by

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INTRODUCTION AND LITERATURE SURVEY

Coordination or chelate compounds of alkali metals are relatively rare. This is to be expected from their large ionic radii, small electronegativities and high degree of association with water molecules.

The effect of these factors on stability and other properties of chelates have been reviewed by Martell and Calvin (18, chapter 5). Certain trends were established in studies of the correlation of stability constants with ionization potential, charge and radius of metal ion, and aquation. The majority of these correlations were made with rare earths and transition elements. The stability of chelates decreased with increasing ionic radius, lower ionization potential, and increasing hydration.

The study of the chelates of alkali metal ions has been primarily through isolation of solid compounds and salts. Some of the neutral compounds are listed in Table 1 taken from a paper by Brewer (5). The usual attachment of the metal ion is to oxygen or to oxygen and nitrogen of the organic ligand. Attachment to nitrogen atoms alone has been shown in a small number of compounds.

From the composition of these chelates it appears that a coordination number of 4 may be assigned to lithium, sodium, and potassium and a coordination number of 6 to rubidium and caesium. The tris chelates of 1,4 dihydroxy anthroquinone

Table 1. Neutral complexes of alkali metals

Abbreviations for enolate ions: acetylacetone, A; benzoylacetone, B; 1/2(quinazarine), Q; saliacylaldehyde, S; O-nitrophenol, N.

Metal	4 covalent	6 covalent
Lithium	$LiB \cdot 2H_2O$	
	$LiHS_2$	
Sodium	$NaB \cdot 2H_2O$	$NaB \cdot 4H_2O$
	NaHNS	NaH_2QS_2
Potassium	$KA \cdot 2H_2O$	KH_2QS_2
	$KS \cdot 2H_2O$	KH_2S_3
Rubidium	$RbHS_2$	RbH_2S_3
Caesium	$CsHS_2$	CsH_2S_3

hereinafter referred to as quinizarine with all the alkali metals except lithium (24) indicate that a coordination number of 6 may apply to sodium and potassium as well. Martell and Calvin (18, p. 241) state that Pfeiffer assigned a coordination number of 12 to the alkaline earths and alkali metals. This assignment was based upon studies of hydrates and other crystalline compounds. It should be noted that some of the ligand molecules present in crystals merely serve to fill empty spaces in the crystal. They do not act as true ligands in the sense of forming bonds with the metal ion. Compounds of this type are of no value in determining the coordination numbers which apply to equilibria between ligand molecules and metal ions in solution.

The covalent nature of the neutral alkali metal chelates is indicated by their solubility in organic solvents, low aqueous solubility and low melting points. Sodium benzoylacetone isolated from an aqueous solution behaves like an ionic compound. It chars without melting and is insoluble in hydrocarbon solvents. However, if this salt is recrystallized from 96% ethanol solution it takes up two molecules of water. The resulting covalent chelated compound is soluble in dry toluene, and melts at 115°C (24). Some of the alkali metal complexes which are insoluble in organic solvents can be dissolved if some of the ligand is added to the solvents.

Salts of the charged complexes have been isolated from solution. Pfeiffer and Christeleit (20) prepared the perchlorates of mono(1,10-phenanthroline)lithium(I) and bis(1,10-phenanthroline)sodium(I) from 50% methanol. These white crystalline solids were reported to be soluble in hot water, nitrobenzene, and dioxane. Mono(1,10-phenanthroline) potassium(I) iodide and bis(1,10-phenanthroline)ammonium(I) perchlorate have been prepared by Herzog (11) from absolute alcohol.

Reaction of lithium chloride with 2,2'-pyridine is indicated in a paper by Krumholtz (13). He observed that an absorption maximum in solutions of monoprotonated 2,2'-bipyridine appears at higher wave lengths when lithium chloride is added.

Figure 1 shows the spectral evidence of Grimes (10a) for the reaction of alkali metals with 1,10-phenanthroline. The absorption spectrum of free-base 1,10-phenanthroline is nearly the same as that of the solution containing potassium ions. An acidified solution of 1,10-phenanthroline has the same spectra as that shown for solutions containing lithium ions.

Solutions containing tris(1,10-phenanthroline)iron(II) or tris(2,2'bipyridine)iron(II) complexes are decolorized by lithium and sodium salts. The concentration of the alkali metal salts must be relatively large compared to the original concentration of the complexes. Fortune and Mellon (8) studied the interferences in the determination of iron with 1,10-phenanthroline. Their data indicates that the log of the stability constants of mono(1,10-phenanthroline) lithium(I) and mono(1,10-phenanthroline)sodium(I) cannot be any greater than 3.6 and 4.0 respectively.

The stability constants for some of the alkali metal chelates are given in Table 2 (2). These were all determined by means of pH measurements with a hydrogen or glass electrode. The stabilities are relatively low compared to

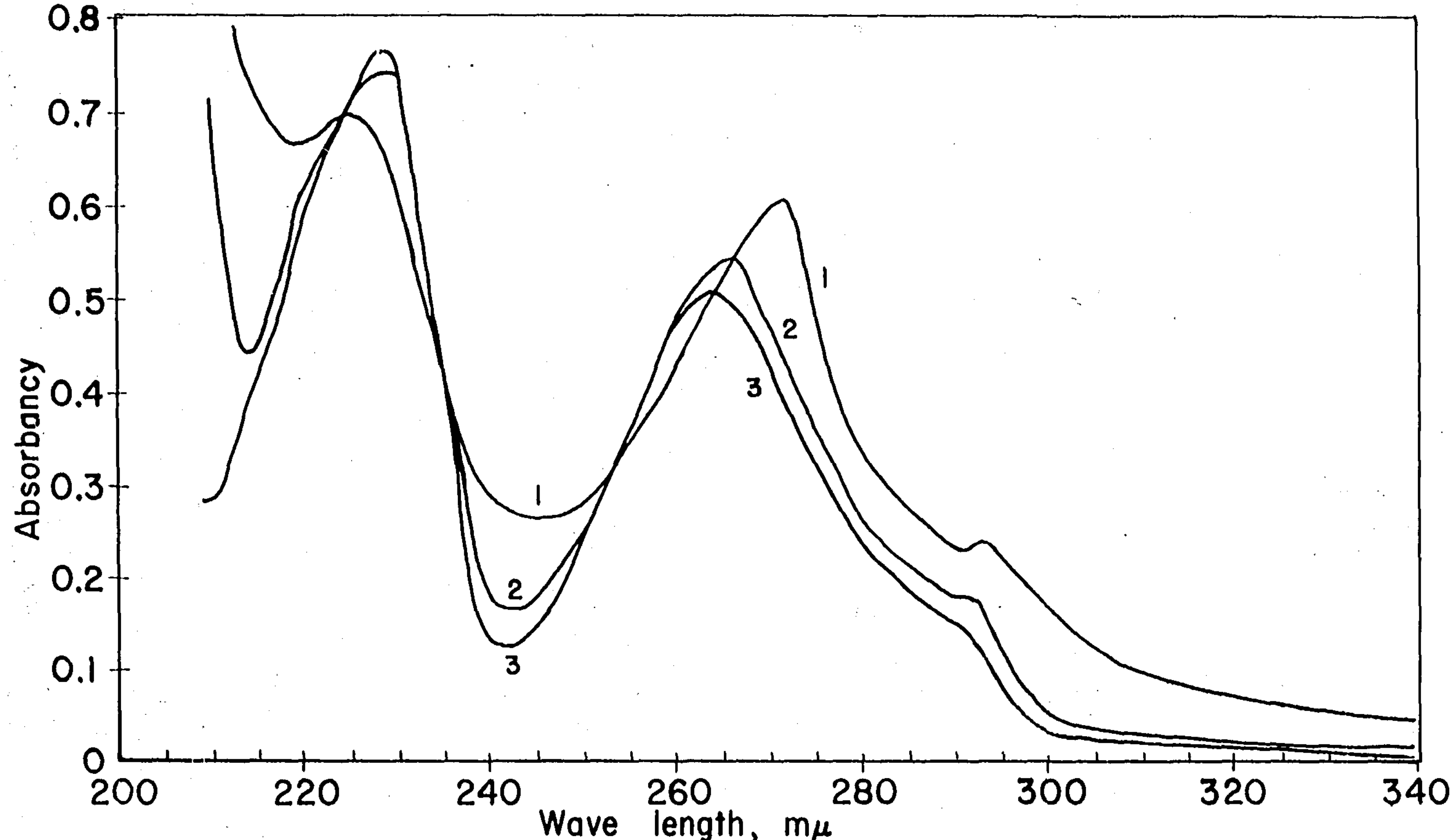


Figure 1. Spectrophotometric evidence of alkali metal complexes of 1,10-phenanthroline at pH 6.8

All curves were 1.7×10^{-5} M in 1,10-phenanthroline. Solutions 1, 2, and 3 contained 3.3 M L. Cl, 3.0 M NaCl, and 3.3 M KCl, respectively. Curve 3 is also the spectrum of 1,10-phenanthroline.

Table 2. Stability constants of alkali metal complexes

Metal	Compound	Temp.	log K_1	Conditions	Ref.[1]
K	Dibenzoylmethane	30	3.60	75% dioxane	(1)
Li	o-Carboxyphenylimino-diacetic acid	20	2.18	0.1M KCl	(2)
Li	Dibenzoylmethane	30	5.95	75% dioxane	(1)
Li	Ethylenediaminetetra-acetic acid	20	2.79	0.1M KCl	(3)
Li	Glycollic acid	25	-0.12	0[a]	(4)
Li	Lactic acid	25	0.20	0	(4)
Li	Nitrilotriacetic acid	20	3.28	0	(5)
Li	Sulphophenylimino-diacetic acid	20	2.26	0.1M KCl	(6)
Li	Uramildiacetic acid	20	5.40	0	(7)

[1]The data in the table is taken from Stability Constants Part 1: Organic Ligands by Bjerrum *et al.* (2). They cited the following references:

1. Fernelium, W. C. and Van Uitert, L. G., Acta Chem. Scand., 8, 1726, (1954).
2. Willi, A., Diss., Zurich, (1950).
3. Ackerman, H., and Schwarzenbach, G., Helv. Chim. Acta, 30, 1798, (1947).
4. Davis, P. B., and Monk, C. B., Trans. Faraday Soc., 50, 128, (1954).
5. Schwarzenbach, G., Helv. Chim. Acta, 38, 1147, (1955).
6. Bach, R. O., Schwarzenbach, G., and Willi, A., Helv. Chim. Acta, 30, 1303, (1947).
7. Kampitsch, E., Schwarzenbach, G., and Steiner, R., Helv. Chim. Acta, 29, 364, (1946).
8. Kampitsch, E., Schwarzenbach, G., and Steiner, R., Helv. Chim. Acta, 28, 828, (1945).

[a]Corrected to zero ionic strength.

Table 2. (Continued)

Metal	Compound	Temp.	log K_1	Conditions	Ref.
Na	o-Carboxyphenylimino-diacetic acid	20	0.98	0.1M KCl	(2)
Na	Dibenzoylmethane	30	4.18	75% dioxane	(1)
Na	Ethylenediaminetetra-acetic acid	20	1.66	0.1M KCl	(3)
Na	Nitrilotriacetic acid	20	2.1	0	(8)
Na	Sulphophenylimino-diacetic acid	20	0.98	0.1M KCl	(6)
Na	Uramildiacetic acid	20	3.32	0	(7)

the stabilities of transition elements with the same organic ligand. The high stability of the complexes in 75% dioxane is of some interest. Under these conditions the competing effect of aquation is minimized.

The number of papers in the literature on the reactions of 1,10-phenanthroline and related 2,2'-bipyridine is increasing. Studies have been made on the complexes of these reagents in regard to their stability, extractability, use as analytical reagents, and rate of formation and racemization. In nearly all of these studies alkali metal salts are either accidently present or are used to maintain constant ionic strength.

In interpreting these data and future studies a knowledge of the stability and chemistry of alkali metal chelates with 1,10-phenanthroline would be most advantageous and useful.

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. Beckman Model G and GS pH meters were used for potentiometric and pH measurements. Conductometric measurements were made with a Leeds and Northrup No. 4866 conductivity bridge.

The anhydrous 1,10-phenanthroline obtained from the Aldrich Chemical Company melted at 117°C and was used without purification. The 1,10-phenanthroline monohydrate from G. F. Smith Chemical Company was not pure. It was recrystallized once from benzene-petroleum ether mixture and then several times from water. A portion of the resultant monohydrate was converted to the anhydrous compound by drying over magnesium perchlorate in a desiccator. The melting points agreed with the values reported in the literature.

The lithium hydroxide used was C. P. All other chemicals used were reagent grade. Glassware of class A specifications was used for all critical measurements.

THE DETERMINATION OF THE STABILITY CONSTANTS OF 1,10-PHENANTHROLINE COMPLEXES BY CONVENTIONAL MEANS

Introduction

The determination of the stability constants is a matter of widespread concern in the literature. Martell and Calvin (18, p. 76), Sullivan and Hindman (26) have reviewed and summarized the approaches to measuring stability constants. The success with which any of these methods may be applied to a particular metal complex system is greatly a function of that particular system.

Several classical methods were applied in this study of the stability of 1,10-phenanthroline-alkali metal chelates. A new method using a silver/bis(1,10-phenanthroline) silver(I) nitrate electrode was developed and applied.

For the present, let us consider only the generalizations concerning these particular methods.

In a solution containing a metal salt, MX, a ligand, L, and an acid, HA, the following reactions may take place:

a) $MX \rightleftharpoons M^+ + X^-$ Eq. (1)

b) $HA \rightleftharpoons H^+ + A^-$ Eq. (2)

c) $H^+ + L \rightleftharpoons HL^+$ Eq. (3)

d) $H^+ + HL^+ \rightleftharpoons H_2L^{++}$ Eq. (4)

e) $HL^+ + L \rightleftharpoons HL_2^+$ Eq. (5)

f) $HL^{+}_{(i-1)} + L \rightleftharpoons HL_i^{+}$ Eq. (6)

g) $M^{+} + L \rightleftharpoons ML^{+}$ Eq. (7)

h) $ML^{+} + L \rightleftharpoons ML_2^{+}$ Eq. (8)

i) $ML^{+}_{(i-1)} + L \rightleftharpoons ML_i^{+}$ Eq. (9)

The stability constants for these reactions may be defined as follows:

$$K_i = k_1k_2k_3 \text{----} k_i = (M^{+}) \quad (L)^i/(ML_i^{+}) = \frac{1}{\alpha_i} \qquad \text{Eq. (10)}$$

$$k_i = (ML_{i-1}^{+}) \quad (L)/(ML_i^{+}) \qquad \text{Eq. (11)}$$

$$K_{ai} = k_{a1}k_{a2}k_{a3} = (H^{+}) \quad (L)^i/(HL_i^{+}) = \frac{1}{\alpha_{ai}} \qquad \text{Eq. (12)}$$

$$k_{ai} = (HL_{i-1}^{+}) \quad (L)/(HL_i^{+}) \qquad \text{Eq. (13)}$$

The various constants may be named as follows: K_i is the overall dissociation constant for the i-th complex, α_i is the overall formation constant of the i-th complex, k_i is the step-wise dissociation constant of the i-th complex. The subscript a refers to the special case of the acid dissociation constants.

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

$$(M)_t = (M^+) \sum_{1}^{i} (ML_i^+) \qquad \text{Eq. (14)}$$

$$(L)_t = (L) + \sum_{1}^{i} i(ML_i^+) + \sum_{1}^{i} i(HL_i^+) \qquad \text{Eq. (15)}$$

$$(H)_t = (H^+) + \sum_{1}^{i} (HL_i^+) \qquad \text{Eq. (16)}$$

where $_t$ refers to total. Upon substitution of corresponding values from the stability equations for (ML_i^+) and (HL_i^+), the following equations can be derived:

$$(M)_t = (M^+) \left[1 + \sum_{1}^{i} \alpha_i (L)^i \right] \qquad \text{Eq. (17)}$$

$$(L)_t = (L) + (M^+) \sum_{1}^{i} i\, \alpha_i (L)^i + (H^+) \sum_{1}^{i} i\, \alpha_{ai} (L)^i \qquad \text{Eq. (18)}$$

$$(H)_t = (H^+) \left[1 + \sum_{1}^{i} \alpha_{ai} (L)^i \right] \qquad \text{Eq. (19)}$$

In a system containing only ligand and hydrogen ions the concentration of hydrogen ions, (H^+), can be eliminated from Eq. (18) and Eq. (19) as follows:

$$\bar{n} = \frac{L_t - (L)}{(H)_t} = \frac{\sum_1^i i\, \alpha_{ai}\, (L)^i}{1 + \sum_1^i \alpha_{ai}\, (L)^i} \qquad \text{Eq. (20)}$$

When metal ions are also present the free metal ion (M^+) can be eliminated from Eq. (17), Eq. (18) as follows:

$$\bar{n} = \frac{(L)_t - (L) - (H^+) \sum_1^i i\, \alpha_{ai}\, (L)^i}{(M)_t} = \frac{\sum_1^i i\, \alpha_i\, (L)^i}{1 + \sum_1^i \alpha_i\, (L)^i} \qquad \text{Eq. (21)}$$

The term $\bar{n}$ represents the average number of ligands bound to the central entity per central entity.

Therefore, from a sufficient number of well chosen experimental determinations of $\bar{n}$, (L), and (H^+) under appropriate conditions, the constants α_1 through α_i and α_{a1} through α_{ai} can be determined.

Methods of Measurement

All the methods used to determine the stability constants for the alkali metals involved either a direct or an indirect measurement of the free-base 1,10-phenanthroline.

Competition

Solutions of tris(1,10-phenanthroline)iron(II) sulfate in the pH range from 2 to 9 are stable for several months. However, these solutions will fade when alkali metal salts are added to the solution. It was thought that this fact could be used to measure the stability constants of the alkali metal chelates.

Irving and Mellor (12) have recently used the ability of various metals to compete with iron for 1,10-phenanthroline, which reduces the absorbancy at the 510 mμ absorption band, to measure portions of the formation curve. The formation curve is the plot of $\bar{n}$ against the logarithm of the ligand concentration and is expressed analytically in Eq. (21). This 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 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 attained. The pH is kept constant and it is assumed that no volume change occurs in these steps.

Because the absorbancy for the initial and the final solutions is the same, it is known that the amounts of iron complexes must be the same; therefore, the concentration of free-base 1,10-phenanthroline is also the same in these solutions. The free-base 1,10-phenanthroline can then be calculated from the known stability constant for the iron complexes. The amount of 1,10-phenanthroline added in step 3 must necessarily react completely with metal added in step 2.

The ratio of these amounts is $\bar{n}$ and thus one point on the formation curve has been determined. Other points may be obtained starting with different initial absorbancies, while holding the ion concentration constant.

An attempt was made to study the lithium-1,10-phenanthroline system by this method. To obtain a measureable decrease in absorbancy, the lithium ion concentration had to be greater than 10^4 times the concentration of the iron complex. The magnitudes of the $\bar{n}$'s calculated from data obtainable under these conditions are quite small. An approximate pk_1 of 2.8 was calculated for the 1:1 lithium-1,10-phenanthroline complex. The pk is the logarithm of the constant.

Unless precision spectrophotometric techniques are used, this method is limited to the portion of the formation curve lying between free-base concentrations of $2x10^{-8}$ to $1x10^{-7}$ M. For accurate determination of stability constants the free-base concentration and the constant must be of the same order of magnitude. Therefore, this method has only limited usefulness in determining alkali metal constants.

<u>Spectrophotometry</u>

Because of the quantitative relation of absorbancy to concentration, spectrophotometry is a particularly useful means of determining stability constants. This is especially true when wave lengths can be found at which the various metal complexes absorb appreciably, but the ligand absorption is negligible.

A prime example is the 1,10-phenanthroline complexes of iron(II). The iron complexes absorb in the visible region while the ligand, 1,10-phenanthroline, absorbs only in the ultra-violet region. However, most of the complexes of 1,10-phenanthroline 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 complexes AL_1, exist in a given solution. This condition is generally, but not always, met when an excess of metal ion is used. Under these conditions only a 1:1 complex should be formed. The 1:1 formation constants for zinc and copper complexes of 1,10-phenanthroline have been determined by Bystroff (6) and McClure (19a) in this manner. The constants for higher complexes can be easily obtained only if the successive stepwise formation constants differ by a factor of a hundred or more. Under these conditions each of the various complexes form exclusively of the others. As this condition is seldom met, a tedious technique of successive approximations with rigorous data must be used.

Krumholtz (13) observed a change in the spectrum of monoprotonated 2,2'-bipyridine solutions upon the addition of lithium salts. Grimes (10a) has observed a change in the spectrum of 1,10-phenanthroline solutions upon the addition of alkali metal salts (Figure 1).

An attempt was made to use the difference in the spectra of 1,10-phenanthroline and of lithium-1,10-phenanthroline complex to determine the stability constants of the complex. Several difficulties made this approach unfeasible. The high molar absorptivity of free-base 1,10-phenanthroline at the 264 mμ absorption band limits the workable concentration of ligand to less than 3×10^{-5} molar. Appreciable changes in the absorption spectra were observed only when the concentration of lithium ion was greater than ten thousand times the ligand concentration. Under these conditions there would be great variations in ionic strength and activity coefficients of the ionic species. Although the chemicals used were reagent grade, the concentration of impurities, such as iron, were large compared to the total ligand concentration. Because the stabilities of the 1,10-phenanthroline complexes of impurities are large relative to those alkali metals, a significant but unknown amount of ligand could be complexed. Under these conditions only a small portion of the formation curve could be calculated, and the constants determined in this manner would probably be inaccurate.

pH Measurements

The use of titrimetric pH measurements for the determination of the formation curves of metal complexes was first extensively employed by Bjerrum (1). This method consists 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 $\bar{n}$ can then be calculated. The free-base ligand concentration is derivable from the known concentration of uncomplexed ligand and pH of the solution. Experimentally an acid solution of the ligand of known concentration is titrated with a base. A similar titration of the ligand with a known quantity of metal present is then performed. The difference in the number of moles of base required to reach the same pH values in the two titrations corresponds to the amount of ligand used in complexing the metal, providing the addition of the metal has not disturbed the degree of association of protons with the ligand.

There are certain limitations in applying this method to determine the stability constants. The primary limitation is the accuracy of the pH determinations. The measurement of weak complexes has other requirements. As a means of insuring measurable formation of a complex, the uncomplexed metal and ligand concentrations must be relatively large. This may be accomplished by a proper combination of pH ranges and total concentration of reactants.

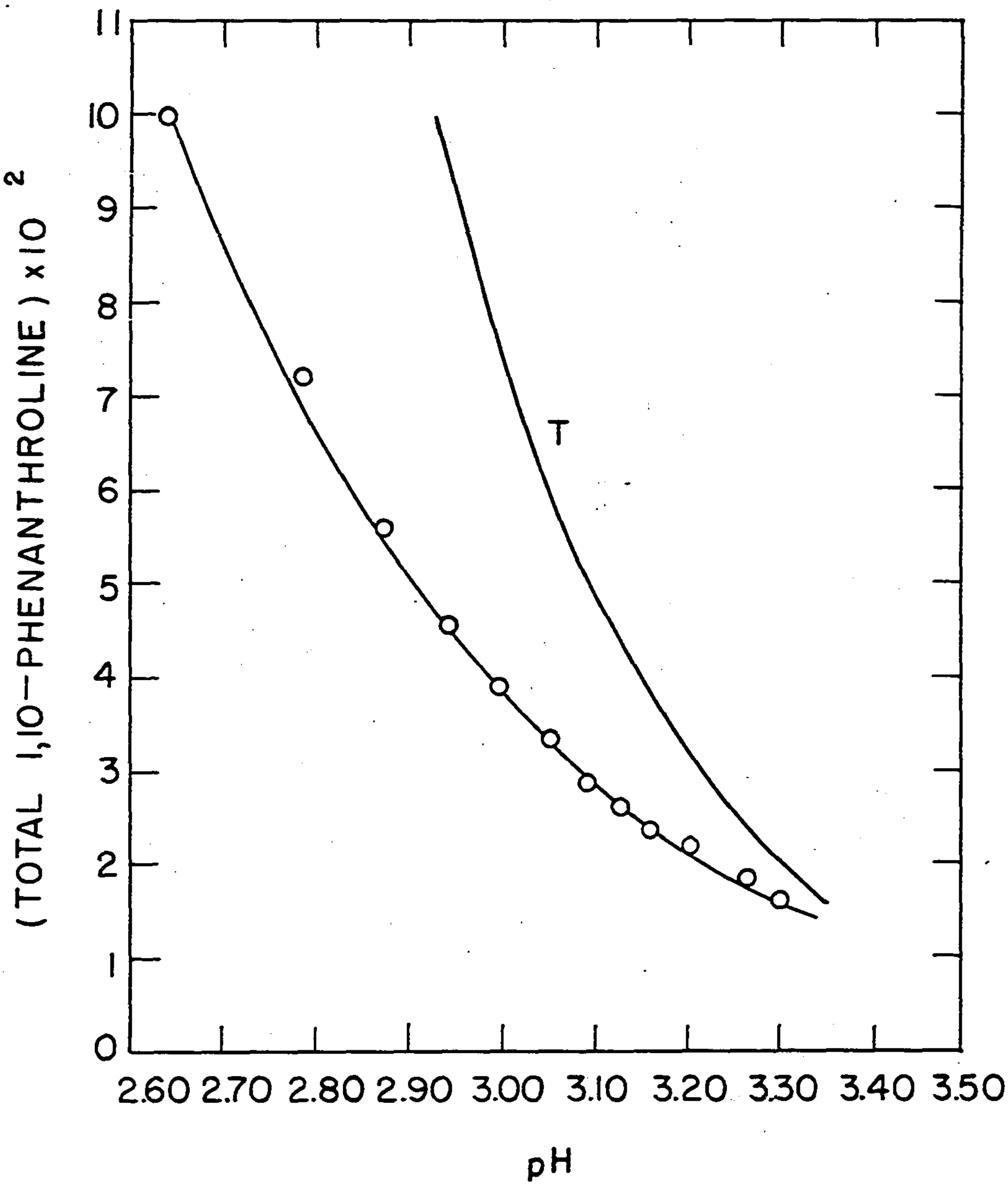
This method, as outlined above, was applied to the alkali metal-1,10-phenanthroline system. A solution 0.0050 M in 1,10-phenanthroline and 0.0166 M in hydrochloric acid was titrated with 0.111 M potassium hydroxide. A similar solution which was also 0.10 M in lithium chloride was titrated with the base. The course of the titrations was followed with a glass-saturated calomel electrode system using a Beckman Model GS pH meter. The results are shown in Figure 2a.

These curves show a reaction of the lithium ions with 1,10-phenanthroline. However, there is a considerable difference in ionic strength at corresponding pH values of the two curves. Because the ionic strength affects the magnitude of the ligand acid dissociation constants, the $\bar{n}$'s calculated from these curves would be in error.

A variation of the commonly employed procedure outlined above was used to overcome the effect of differences in the ionic strengths. An acidified solution of 1,10-phenanthroline was titrated with the metal. Provided the ionic strength of the two solutions is the same, the ionic strength will be constant during the titration. The low stability constants

Figure 2a. Titration of 10 ml. of a solution 0.10 M in 1,10-phenanthroline and 0.10N in hydrochloric acid with 0.10 M potassium chloride

The titration was followed with a glass-saturated calomel electrode pair. The curve labeled T is the theoretical curve.



(TOTAL 1,10-PHENANTHROLINE) x10 2
0
1
2
3
4
5
6
7
8
9
10
11
2.60
2.70
2.80
2.90
3.00
3.10
3.20
3.30
3.40
3.50
pH
T

of the alkali metal chelates dictate ionic strengths in the order of 0.1.

1,10-Phenanthroline(0.1 mole) was dissolved in 0.1N hydrochloric acid and titrated with 0.1N potassium chloride. A second solution was titrated with 0.1 lithium chloride. The course of the titrations was followed with a glass-saturated calomel electrode system and a Beckman Model GS pH meter. Changes in pH as small as 0.003 units may be detected with this meter. The data are plotted in Figure 2b. The curve for lithium is nearly superimposable on the potassium curve.

The initially observed pH of the acidified 1,10-phenanthroline solutions differs greatly from that calculated from the reported acid dissociation constants of 1,10-phenanthroline. However, lower total concentrations of 1,10-phenanthroline were used in determining the values stated in the literature. Lee _et al_. (15) found a constant 1.25×10^{-5} at an ionic strength of 0.10. They considered that 1,10-phenanthroline was a mono acidic base. Curve T was calculated using the concentrations in the above experiment and an acid dissociation constant of 1.25×10^{-5}. It was assumed in this computation that only dilution effects occurred.

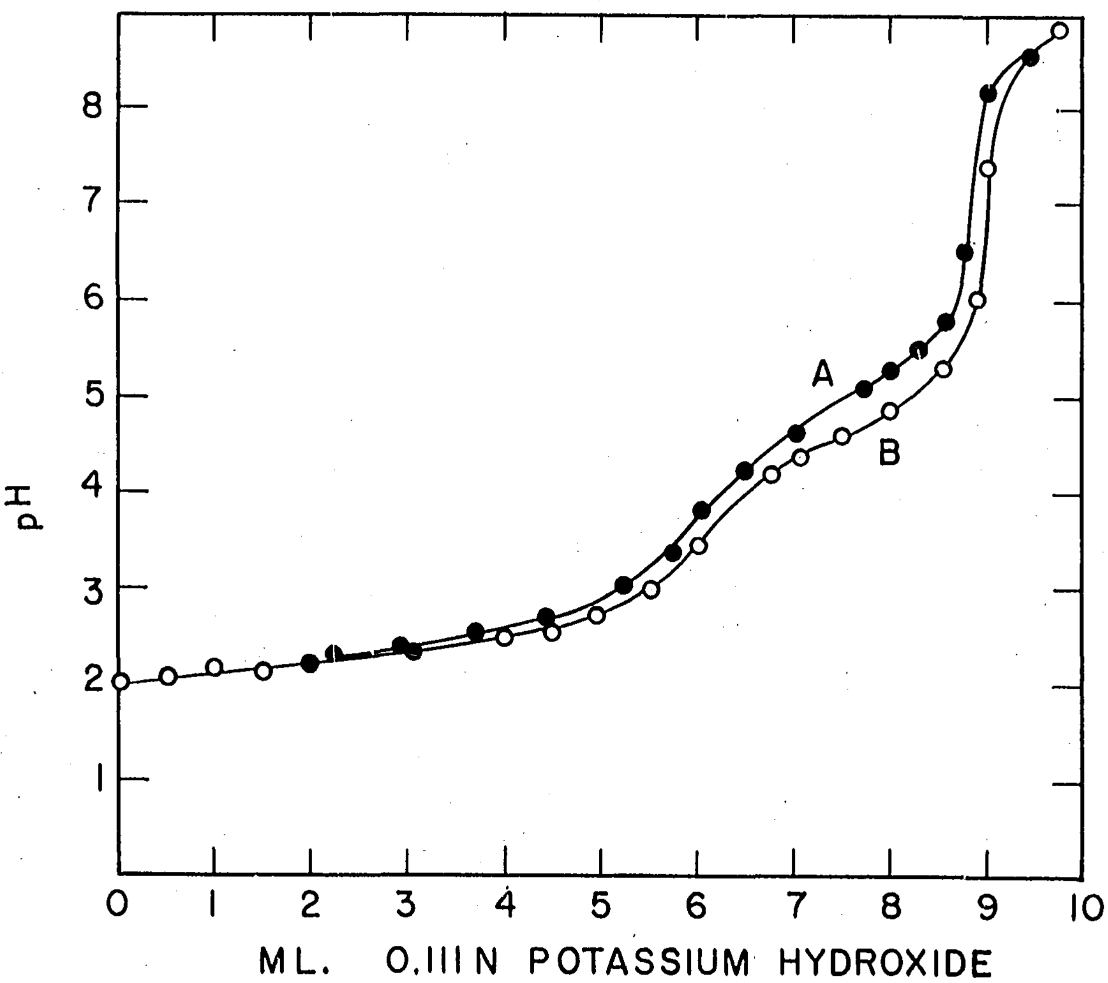
The difference between the observed and calculated pH could be explained by considering the existance of appreciable amounts of poly-1,10-phenanthroline hydrogen ion species (P_iH). A knowledge of the dissociation constants of these

Figure 2b. Titration of acidified solutions of 1,10-phenanthroline with base

A Titration of 60 ml. of a solution 5.0×10^{-3} M on 1,10-phenanthroline and 1.66×10^{-2}N in hydrochloric acid with 1.11×10^{-1}N potassium hydroxide.

B Titration of 60 ml. of solution 5.0×10^{-3} M in 1,10-phenanthroline 1.666×10^{-2}N in hydrochloric acid and 1.0×10^{-1} M in lithium hydroxide with 1.11×10^{-1}N potassium hydroxide.

Titrations were followed with glass-saturated calomel electrode pair.


pH
ML. 0.111 N POTASSIUM HYDROXIDE
A
B
0
1
2
3
4
5
6
7
8
9
10

species is necessary to compute the free-base 1,10-phenanthroline concentration in the above experiments.

Obviously, the use of pH measurements to determine the stability constants of the alkali metal chelates depends upon a further knowledge of the chemistry of the reaction of 1,10-phenanthroline and hydrogen ions. This will be discussed in a later section.

DETERMINATION OF STABILITY CONSTANTS OF 1,10-PHENANTHROLINE CONSTANTS WITH SILVER/BIS(1,10-PHENANTHROLINE)SILVER(I) NITRATE

Introduction

It was evident from the failure of the methods previously tried that a new technique of measuring the stability constants of alkali metal chelates of 1,10-phenanthroline would have to be devised. The weakness of these complexes dictates that the concentrations of total metal, total 1,10-phenanthroline, and uncomplexed 1,10-phenanthroline be relatively high to insure measurable complex formation. Concentrations of free-base 1,10-phenanthroline should be of the same order of magnitude as the stepwise dissociation constants for optimum accuracy in the measurement of these constants. A method which would directly measure free-base 1,10-phenanthroline over a wide concentration range would be ideal for determining the stability of 1,10-phenanthroline complexes. An electrode system which responds to free-base 1,10-phenanthroline concentration would meet this condition.

Methods in the literature using a mercury metal electrode gave a clue to designing the desired electrode system. Schwartzenbach and Anderegg (23) and Schmid and Reilley (22b) have used a mercury electrode in the determination of stability constants of complexes of ethylenedinitrilotetraacetic acid, hereinafter referred to as EDTA. The determination of the stability constant of calcium EDTA complex by Schwartzenbach and Anderegg (23) will be used to illustrate this method. Solutions containing known quantities of mercury(II) and calcium-EDTA complexes and calcium nitrate were allowed to equilibriate. The equilibrium concentration of mercury(II) ions was determined from the potential of the mercury electrode and saturated calomel electrode pair. The uncomplexed EDTA was then computed from the previously determined stability constant of mercury(II)-EDTA complex and the known or measured quantities. The $\bar{n}$ could also be computed from the known quantities (Eq. 21). The stability of the calcium-EDTA was then calculated in the usual manner. The same procedure, with some slight modifications, was used to determine the complex stability constants for other metals. Schmid and Reilley (22b) used a graphical method to determine the stability constants.

In theory, the mercury electrode could be used to determine the stabilities of complexes with other ligands, provided that the mercury(II) ligand complex constants are known. In practice, only those complexes that are four pK units weaker than mercury(II) complexes can be conveniently determined by this method.

Unfortunately, the chemistry of mercury(II)-1,10-phenanthroline complexes had not been studied. The only report in the literature discussed the preparation of a solid salt having the composition of tris(1,10-phenanthroline) mercury(II) perchlorate (20). Some semiquantitative experiments indicated that the reaction of mercury(II) ions and 1,10-phenanthroline is very complex. The application of a mercury electrode method to determine stability constants of 1,10-phenanthroline complexes would be difficult.

In theory, metals other than mercury could be used as electrodes with suitable modifications in the method discussed above. Practical considerations would limit the choice of metals to those which normally give reproducible potential and do not dissolve appreciably in solutions having pH greater than 3. The noble metals would be suitable. Silver was chosen for this work.

Reaction of Silver(I) with 1,10-Phenanthroline

The reaction of silver(I) with 1,10-phenanthroline was studied by means of potentiometric titrations. The only report found in the literature of this reaction was the preparation of bis(1,10-phenanthroline)silver(I) nitrate (20). An indication of this reaction is given by Fortune and Mellon (8). They state that silver interferes in the determination of iron(II) with 1,10-phenanthroline.

Forty ml. of a 2.49×10^{-3}N silver nitrate solution was titrated with 1.146×10^{-2} M 1,10-phenanthroline. A light yellow colored precipitate formed after the addition of the first few drops of 1,10-phenanthroline. A silver-saturated calomel electrode pair was used to follow the titration. A 0.1N potassium nitrate agar-agar bridge was used to separate the calomel electrode from the silver nitrate solution. The titration curve is plotted in Figure 3.

A silver sulfate solution was titrated in an analogous manner. In this case a precipitate did not form during the titration. These data are plotted in Figure 4.

Seventy five ml. of a solution 6.94×10^{-4}N in silver sulfate and 2.66×10^{-3} M in 1,10-phenanthroline was titrated with 1.042×10^{-3}N silver sulfate. The course of the titration was followed with the previously described electrode system and the data are plotted in Figure 5.

A quantity of the precipitate was dissolved in a liter of 0.1 M sulfuric acid, and the absorbancy due to the monoprotonated-1,10-phenanthroline was determined at 272 mμ. This determination of 1,10-phenanthroline indicated that the precipitate was bis(1,10-phenanthroline)silver(I) nitrate.

The bis(1,10-phenanthroline)silver(II) nitrate is not decomposed by light. Richard (21b) investigated the possibility of using the precipitation of bis(1,10-phenanthroline) silver(I) nitrate as a gravimetric method for silver and nitrate. This method was quantitative, but many anions and cations interferred.

Inspection of the titration curves indicated that a tris(1,10-phenanthroline)silver(I) species does not form under the conditions studied. The stability of the bis(1,10-

Figure 3. Titration of 40 ml. of 2.49×10^{-3}N silver nitrate with 1.146×10^{-2} M 1,10-phenanthroline

The course of the titration was followed with a silver-saturated calomel electrode pair, separated by a 0.1N potassium nitrate agar-agar salt bridge.

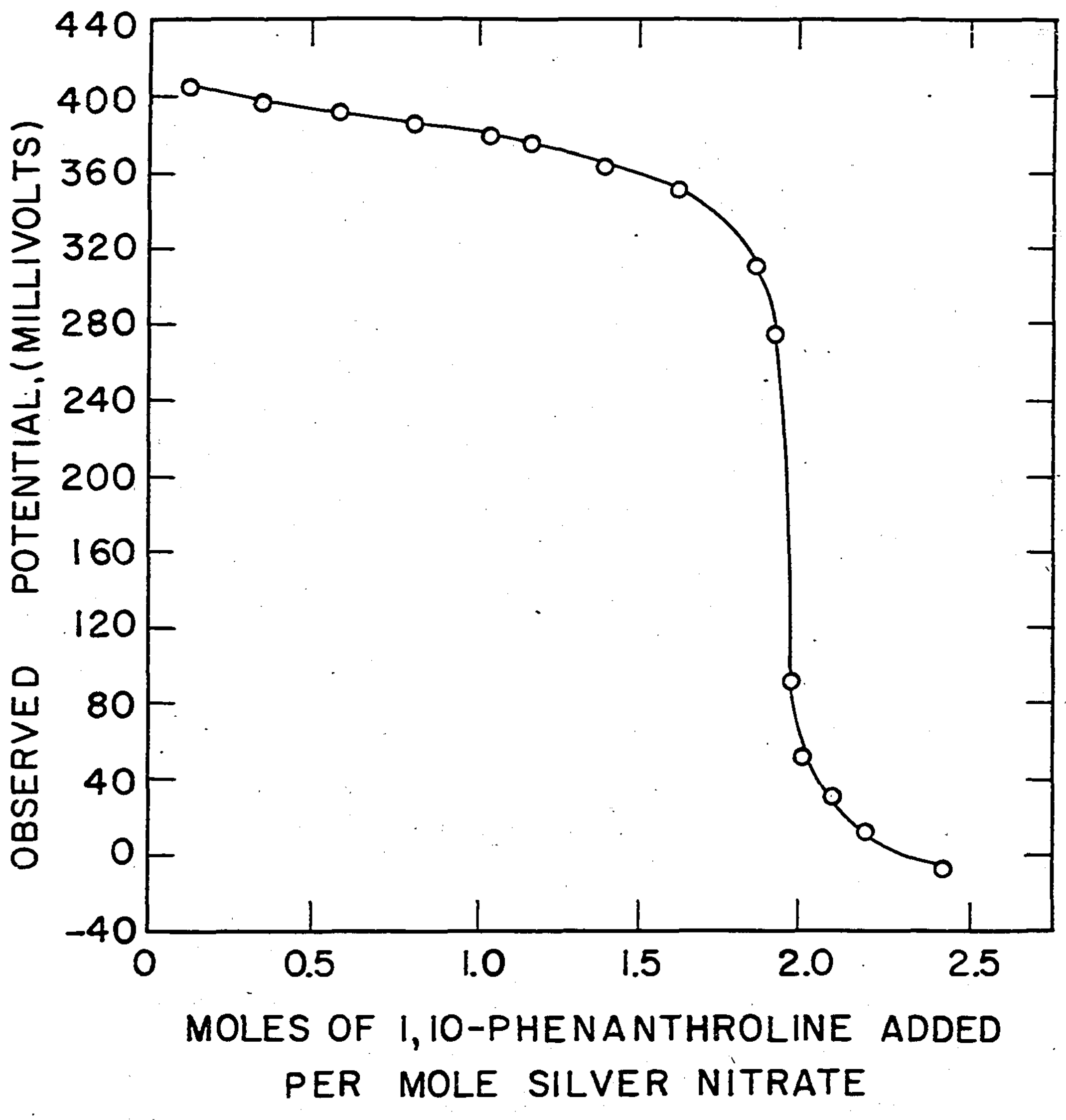
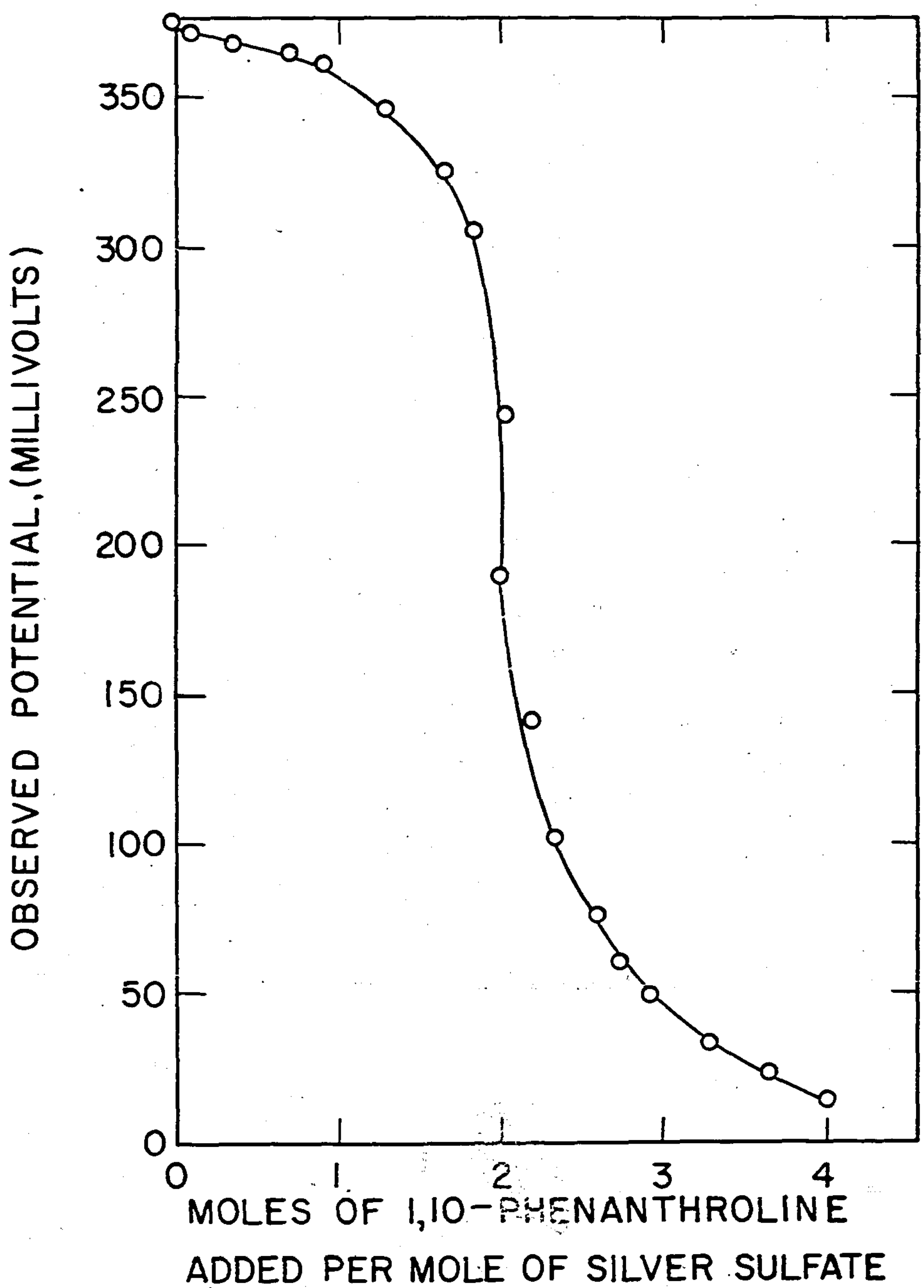

440
400
360
320
280
240
200
160
120
80
40
0
-40
OBSERVED POTENTIAL, (MILLIVOLTS)
0
0.5
1.0
1.5
2.0
2.5
MOLES OF 1,10-PHENANTHROLINE ADDED
PER MOLE SILVER NITRATE

Figure 4. Titration of 50 ml. of 1.082×10^{-3}N silver sulfate with 9.88×10^{-3} M 1,10-phenanthroline

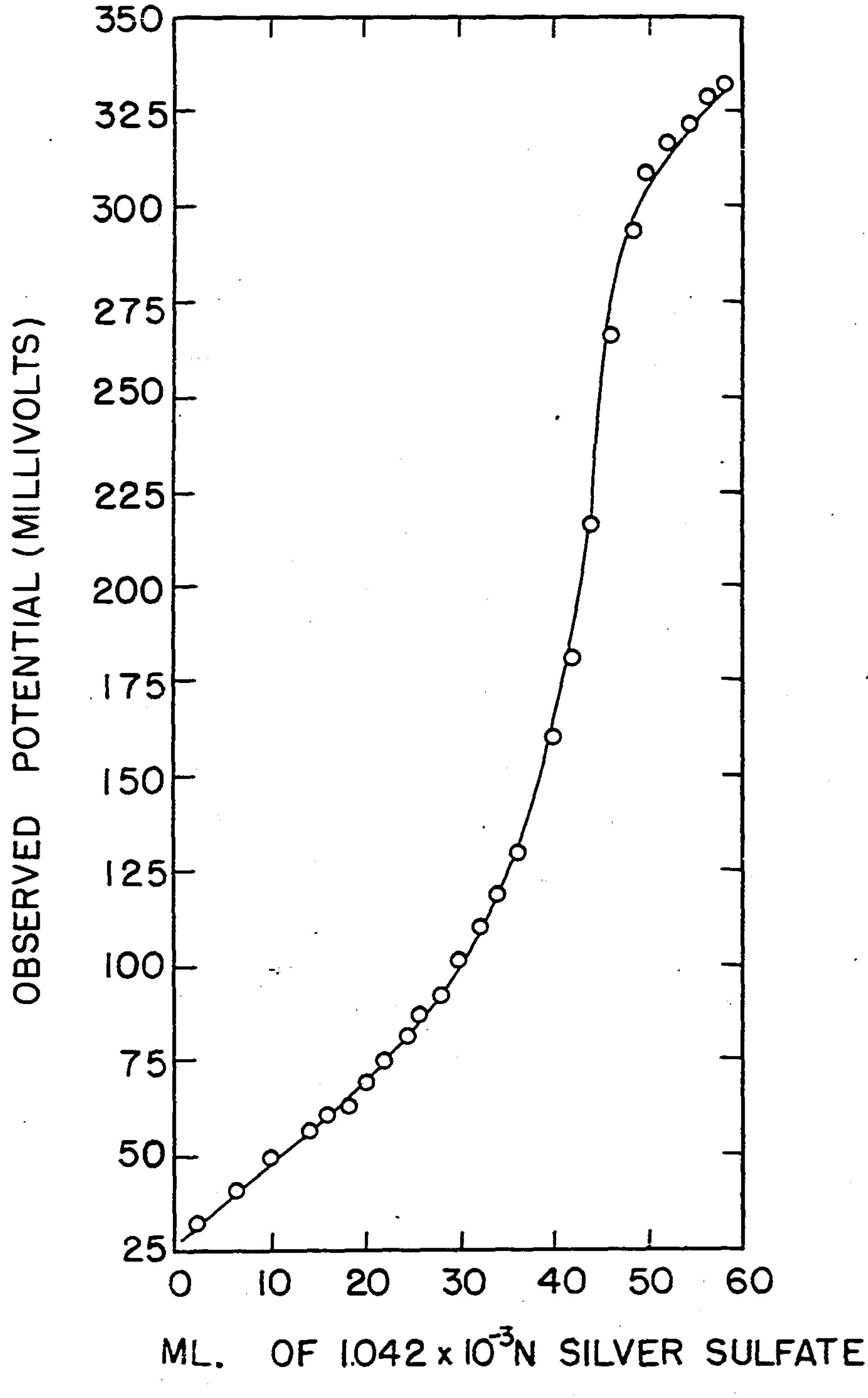
The course of the titration was followed with a silver-saturated calomel electrode pair, separated by a 0.1N potassium nitrate agar-agar salt bridge.



350
300
250
200
150
100
50
0
OBSERVED POTENTIAL, (MILLIVOLTS)
0
1
2
3
4
MOLES OF 1,10-PHENANTHROLINE
ADDED PER MOLE OF SILVER SULFATE

Figure 5. Titration of 75 ml. of a solution 6.94×10^{-4}N in silver sulfate and 2.66×10^{-3}M in 1,10-phenanthroline with 1.042×10^{-3}N silver sulfate

The course of the titration was followed with a silver-saturated calomel electrode pair, separated by a 0.1N potassium nitrate agar-agar salt bridge.



OBSERVED POTENTIAL (MILLIVOLTS)
350
325
300
275
250
225
200
175
150
125
100
75
50
25
0
10
20
30
40
50
60
ML. OF 1.042 x 10^{-3}N SILVER SULFATE

phenanthroline)silver(I) is greater than that of the mono (1,10-phenanthroline)silver(I). The uncomplexed silver ion concentration, which had been determined from the observed potentials, and the known concentrations of silver nitrate and 1,10-phenanthroline were used to estimate the stability constants. Because the calculations of the stability constant of mono(1,10-phenanthroline)silver(I) are dependent upon a term involving the difference of two large numbers, the constant is correct only to an order of magnitude. The values found were $10^{11.6}$ for the bis-chelate and 10^{4} for the mono-chelate. A solubility product constant of $10^{-8.8}$ for bis(1,10-phenanthroline)silver(I) nitrate was also estimated from the data.

Silver/Bis(1,10-phenanthroline)silver(I) Nitrate Electrode

The competition of silver nitrate and a metal nitrate for 1,10-phenanthroline can be used to determine the strength of metal-1,10-phenanthroline complexes. The insolubility of the bis(1,10-phenanthroline)silver(I) nitrate simplifies the use of the competition method. Such a system may be described by the following equations:

$$(M^{+})_{t} = (M^{+}) + \sum_{1}^{i} (MP_{i}^{+}) \qquad \text{Eq. (22)}$$

$$(Ag^+)_t = (Ag^+) + \sum_1^2 (AgP_i^{\ +}) \qquad \text{Eq. (23)}$$

$$(H^+)_t = (H^+) + \sum_1^i (HP_i^{\ +}) \qquad \text{Eq. (24)}$$

$$(P)_t = (P) + \sum_1^i i(MP_i^{\ +}) + \sum_1^2 i(AgP_i^{\ +}) + \sum_1^i i(HP_i) \qquad \text{Eq. (25)}$$

$$(NO_3^{\ -})_t = (NO_3^{\ -}) + (M^+)_t + (Ag^+)_t + (H^+)_t \qquad \text{Eq. (26)}$$

$$K_{sp} = (AgP_2^{\ +})\ (NO_3^{\ -}) \qquad \text{Eq. (27)}$$

$$k_{1M} = (M^+)\ \ (P)/(MP^+) = \frac{1}{\alpha_{1M}} \qquad \text{Eq. (28)}$$

$$k_{2M} = (MP^+)\ \ (P)/(MP_2^{\ +}) = \frac{1}{\alpha_{2M}} \qquad \text{Eq. (29)}$$

$$k_{iM} = (MP^+_{\ i-1})\ \ (P)/(MP_i^{\ +}) = \frac{1}{\alpha_{iM}} \qquad \text{Eq. (30)}$$

$$k_{1S} = (Ag^+)\ \ (P)/(AgP^+) = \frac{1}{\alpha_{1S}} \qquad \text{Eq. (31)}$$

$$k_{2S} = (AgP^{+}) \quad (P)/(AgP_2^{+}) = \frac{1}{\alpha_{2S}}$$ Eq. (32)

$$k_{1a} = (H^{+}) \quad (P)/(HP^{+}) = \frac{1}{\alpha_{1a}}$$ Eq. (33)

$$k_{2a} = (HP^{+}) \quad (P)/(HP_2^{+}) = \frac{1}{\alpha_{2a}}$$ Eq. (34)

$$k_{3a} = (HP_2^{+}) \quad (P)/(HP_3^{+}) = \frac{1}{\alpha_{3a}}$$ Eq. (35)

The subscript t refers to total. Eq. (24) considers the poly-(1,10-phenanthroline) hydrogen ion species. These are discussed in a later section.

Combining Eq. (27), Eq. (31), and Eq. (32), the following equation may be obtained.

$$(Ag^{+}) = k_{1S}\, k_{2S}\, K_{sp}/(P)^2\ (NO_3)$$ Eq. (36)

If activities are considered this equation becomes:

$$a_{Ag^+} = K_{sp}\, K_{12S}/a_{p^2}\, a_{NO_3^-} = K_{sp}\, K_{12S}/(P)^2\, a_{NO_3} .$$

Eq. (37)

At low concentrations the activity coefficient of a neutral molecule may be considered to be unity.

A combination of the Nernst equation for a silver electrode,

$$E = E^{o}_{Ag^+/Ag} + 0.059 \quad \log a_{Ag^+}$$

with Eq. (37) gives

$$E = E^{o}_{Ag^+/Ag} + 0.059 \log K_{sp} \; K_{12S}/(P)^2 \; a_{NO_3}. \quad \text{Eq. (38)}$$

The concentration of free-base 1,10-phenanthroline may be calculated by means of Eq. (38) from the potential of a silver-reference electrode pair, provided the activity of the nitrate ion and the dissociation and solubility product constants are known. The stability constants of the metal-1,10-phenanthroline complexes may be determined from the concentration of the free-base 1,10-phenanthroline the total metal ion concentration and the total 1,10-phenanthroline concentration which is available for complexing with the metal. The available 1,10-phenanthroline is a function of the concentration of the poly-1,10-phenanthroline hydrogen ion species as determined by the pH, and the concentration of silver-1,10-phenanthroline complexes. The insolubility of the bis(1,10-phenanthroline)silver(I) nitrate would make the concentration of the mono(1,10-phenanthroline)silver(I) and bis(1,10-phenanthroline)silver(I) ions negligible in most cases and these species can be ignored.

The Eq. (38) indicates that when solid bis(1,10-phenanthroline)silver(I) nitrate is present in the system under investigation, the potential of a silver-reference electrode pair is a function of the free-base 1,10-phenanthroline concentration and the activity of the nitrate ion.

In practice this condition can be satisfied by adding solid, bis(1,10-phenanthroline)silver(I) nitrate or by adding silver nitrate to a solution containing 1,10-phenanthroline.

An alternate method is to form a coating of bis(1,10-phenanthroline)silver(I) nitrate on a silver electrode.

This can be done in a manner analogous to that used in making silver/silver halide electrodes. In this case silver/bis(1,10-phenanthroline)silver(I) nitrate electrode is formed. If the reaction

$$AgP_2NO_3 + e \rightleftharpoons Ag^o + 2P + NO_3^- \qquad \text{Eq. (39)}$$

is considered for this electrode, an electrode equation

$$E = E^o_{AgP_2NO_3/Ag} + 0.0591 \log 1/_{(P)^2 a_{NO_3^-}} \qquad \text{Eq. (40)}$$

may be written. This equation could be obtained by combining the constant terms in Eq. (38). When this electrode is combined with a reference electrode, the potential of the system is a function of the concentration of 1,10-phenanthroline and activity of nitrate ions in the solution being measured.

The following procedure was used to prepare the bis (1,10-phenanthroline)silver(I) nitrate electrode. A Beckman billet type silver electrode was etched in 6N nitric acid for a few seconds. The silver metal was then polished with scouring powder and washed with a mild detergent. A platinum flag electrode was cleaned with 6N nitric acid and washed with a detergent. This silver electrode was attached to the positive terminal and the platinum electrode to the negative terminal of a 1.5 volt battery. Both electrodes were then dipped into a solution of 0.015 M 1,10-phenanthroline and 0.001 M potassium nitrate. The electrolysis was continued for thirty minutes. During the electrolysis the electrode was coated with a firmly adhering layer of yellow bis(1,10-phenanthroline)silver(I) nitrate.

The concentrations of the potassium nitrate and 1,10-phenanthroline are important. If the concentration of 1,10-phenanthroline is less than 0.01 M the electrolysis is slow. However, if the potassium nitrate concentration is much greater than 0.001 M, a gelatinous, white, loosely adherent coating forms on the electrode. This material may be mono (1,10-phenanthroline)silver(I) nitrate.

The response of the electrode to the concentration of free-base 1,10-phenanthroline and the activity of the nitrate ions was tested in the following experiment. A saturated aqueous solution of bis(1,10-phenanthroline)silver(I) nitrate was titrated with 0.01N 1,10-phenanthroline. The course of the titration was followed with the silver/bis(1,10-phenanthroline)silver(I) nitrate-saturated calomel electrode pair. A 0.1N potassium nitrate agar-agar salt bridge was used to separate the saturated calomel electrode from the solution being titrated.

The activity of the nitrate ion is controlled by the solubility product of the bis(1,10-phenanthroline)silver(I) nitrate and should remain nearly constant. In a saturated aqueous solution of bis(1,10-phenanthroline)silver(I) nitrate, the concentration of free-base 1,10-phenanthroline, due to dissociation of the chelate, is very small. This is evident from consideration of the solubility product and the stability constants of the bis(1,10-phenanthroline)silver(I) nitrate. The free-base 1,10-phenanthroline concentration at any point in the titration can be assumed to be equal to that of the free-base added.

The plot of observed potential vs. the logarithm of the reciprocal of the square of the total 1,10-phenanthroline concentration was linear. The range of 1,10-phenanthroline concentration was 5×10^{-4} M to 8×10^{-2} M. The slope of the line was 0.059 volts.

A thermodynamic standard reduction potential for the bis(1,10-phenanthroline)silver(I) nitrate electrode could not be conveniently determined. However, the procedure below was used to obtain a working standard reduction potential for the electrode. A solution which was 0.00010 M in potassium nitrate, 0.00010 M in potassium hydroxide and 0.00020 M in boric acid was prepared as a stock solution. 1,10-Phenanthroline ($5x10^{-4}$ mole) was dissolved in 50 ml. of the stock solution. This solution was titrated using the stock solution as a titrant. The course of the titration was followed with a bis(1,10-phenanthroline)silver(I) nitrate-saturated calomel electrode pair. The saturated calomel electrode was separated from the solution being titrated by means of a 0.1N potassium nitrate agar-agar salt bridge. Since bis(1,10-phenanthroline)silver(I) borate is soluble (21b), the observed potential should be a function of the activity of the nitrate ion and the concentration of free-base 1,10-phenanthroline.

This particular method of titration was employed to maintain the activity of the nitrate ion and the ionic strength at constant values. It was assumed that at pH 9.4 all of the 1,10-phenanthroline which did not react with the potassium ions was in the form of the free-base. Under the conditions of the experiment, the concentration of free-base 1,10-phenanthroline is very nearly equal to the total 1,10-phenanthroline.

The observed potential was plotted against the logarithm of the reciprocal of the total 1,10-phenanthroline concentration. The plot over the 1,10-phenanthroline concentration range of 10^{-2} M to 5×10^{-3} M was linear and had a slope of 117 volts.

Eq. (40) was used to calculate the standard reduction potential under the conditions of the experiment. The activity coefficients of the nitrate ion was taken as unity. A value of 0.246 volt was used for the standard reduction potential of the saturated calomel electrode. The working standard reduction potential of the bis(1,10-phenanthroline) silver(I) nitrate electrode was found to be -0.311 volt. In the computation of this value the various junction potentials were not considered.

Because the conditions used for the determination of the potential and for the determination of stability constants are similar, it seemed to be a legitimate assumption to use this value in computation of free-base 1,10-phenanthroline concentration in these experiments.

Determination of Stability Constants of the Chelates of the Alkali Metals with 1,10-Phenanthroline

1,10-Phenanthroline was dissolved in a solution containing the alkali metal nitrate and the alkali metal borate-boric acid buffer. The solution containing 1,10-phenanthroline was then titrated with the solution used to dissolve the base. The previously described electrode system was used to follow the course of the titration.

Table 3. Titration of 1,10-phenanthroline with lithium nitrate

Initial conditions

$(P)_t = 1.887 \times 10^{-2}$ M

$(Li^+)_t = 9.9 \times 10^{-3}$ M

$(NO_3^-)_t = 8.9 \times 10^{-3}$ M.

Titrant solution is

8.9×10^{-3} M $LiNO_3$

1.0×10^{-2} M LiOH

2.0×10^{-2} M Boric acid

Ml.	Observed potential (volts)	-Log(P)	$P_t \times 10^{+2}$	$\bar{n}$
0	-0.169	2.240	1.887	1.337
3	-0.168	2.248	1.763	1.222
10	-0.166	2.265	1.572	1.05
20	-0.162	2.299	1.348	0.863
30	-0.158	2.333	1.179	0.729
40	-0.152	2.384	1.048	0.648
60	-0.145	2.444	0.858	0.507
70	-0.141	2.477	0.786	0.462
80	-0.139	2.494	0.725	0.413
90	-0.137	2.511	0.674	0.373
100	-0.133	2.545	0.629	0.350
120	-0.128	2.587	0.555	0.302
140	-0.123	2.629	0.497	0.267
160	-0.118	2.672	0.445	0.241
180	-0.114	2.706	0.410	0.218

Table 4. Titration of 1,10-phenanthroline with sodium nitrate

Initial conditions

$(P)_t = 1.739x10^{-2}$ M

$(Na^+)_t = 9.9x10^{-3}$ M

$(NO_3^-)_t = 8.9x10^{-3}$ M.

Titrant solution is

$8.9x10^{-3}$ M $NaNO_3$

$1.0x10^{-3}$ M LiOH

$2.0x10^{-3}$ M Boric acid.

Ml.	Observed potential (volts)	-Log(P)	$P_t \times 10^{+2}$	$\bar{n}$
0	-0.171	2.225	1.739	1.155
5	-0.170	2.234	1.580	1.005
10	-0.167	2.259	1.448	0.907
20	-0.163	2.293	1.241	0.740
30	-0.158	2.336	1.086	0.630
40	-0.152	2.386	0.966	0.565
50	-0.148	2.420	0.869	0.494
60	-0.144	2.454	0.790	0.443
70	-0.140	2.488	0.724	0.394
90	-0.134	2.539	0.621	0.335
110	-0.128	2.589	0.543	0.289
130	-0.121	2.649	0.483	0.263
150	-0.118	2.115	0.435	0.225
195	-0.113	2.717	0.355	0.164

Table 5. Titration of 1,10-phenanthroline with potassium nitrate

Initial conditions

$(P)_t = 1.769 \times 10^{-2}$ M

$(K^+)_t = 1.00 \times 10^{-2}$ M

$(NO_3^-)_t = 9.0 \times 10^{-3}$ M.

Titrant solution is

9.01×10^{-3} M KNO_3

1.0×10^{-3} M KOH

2.0×10^{-3} M Boric acid.

Ml.	Observed potential (volts)	-Log(P)	$P_t \times 10^{+2}$	$\bar{n}$
0	-0.179	2.157	.1769	1.073
5	-0.176	2.183	1.608	0.952
10	-0.173	2.208	1.474	0.855
20	-0.169	2.242	1.263	0.691
30	-0.163	2.293	1.105	0.597
40	-0.158	2.335	0.982	0.521
50	-0.154	2.369	0.884	0.457
60	-0.150	2.403	0.804	0.409
70	-0.146	2.437	0.737	0.372
80	-0.142	2.471	0.680	0.342
100	-0.138	2.50	0.590	0.277

The concentration of uncomplexed 1,10-phenanthroline at various points in the titration was determined by means of Eq. (40). Values of the activity coefficient of the nitrate ion were taken from tables of activity coefficients of alkali metal nitrates in Latimer (14b) and Harned and Owen (10b). The assumptions used in this computation are the same as those mentioned under the determination of the working standard reduction potential of the bis(1,10-phenanthroline)silver(I) nitrate electrode.

The data from the titrations are given in Tables 3 through 5. The $\bar{n}$ equation, Eq. (21), was used to compute the stability constants. The pK_2 values for the bis(1,10-phenanthroline)alkali metal(I) chelates estimated to be as follows: lithium, 4.40; sodium 4.25; and potassium, 4.05. The mono complexes are very weak and the stabilities cannot be computed accurately. Estimated pK_1 values are as follows: lithium, 1.78; sodium, 1.58; and potassium, 1.0.

Preparation of Bis(1,10-phenanthroline)lithium(I) and Bis(1,10-phenanthroline)sodium(I) Perchlorates

Normally, the chelate containing the greatest number of 1,10-phenanthroline ligand molecules is precipitated from solution by the addition of perchlorate. This trend is evident in the excellent review of 1,10-phenanthroline chelates by Brandt *et al.* (3). The perchlorate salts of the lithium and sodium chelates were prepared in the following manner. 1,10-Phenanthroline (0.001 mole) was dissolved in 100 ml. of a solution of 0.5 M lithium hydroxide and 0.1 M lithium perchlorate at 80°C. After cooling the solution, the crystalline precipitate was removed by filtration and stored in a desiccator.

Calculated for bis(1,10-phenanthroline)lithium(I) perchlorate; 1,10-phenanthroline, 77.21%. Found: 1,10-phenanthroline, 77.2%, 76.9%.

The same procedure was used to prepare and analyze the white bis(1,10-phenanthroline)sodium(I) perchlorate.

Calculated for bis(1,10-phenanthroline)sodium(I) perchlorate; 1,10-phenanthroline, 74.64%. Found 74.5%, 74.2%.

Hydrogen Ion-1,10-Phenanthroline Reaction

The reaction of hydrogen ions with 1,10-phenanthrolines has been studied by several methods. These studies were undertaken primarily to determine the acid dissociation constant. Knowledge of this constant is necessary in stability constant measurements and in kinetic studies of 1,10-phenanthroline complexes.

A potentiometric titration by Dwyer and Nyholm (7) indicated that only one hydrogen ion reacted with each 1,10-phenanthroline molecule. Three solutions, which were 0.025 M in 1,10-phenanthroline and 0.0100 M in hydrochloric acid were also prepared. The pH of each solution, as measured by a glass electrode, was 5.35. A pK_a value of 5.2 for 1,10-phenanthroline was calculated from the pH data and the concentrations. Dwyer and Nyholm (7) also state that Albert and Goldacre found the aqueous pK_a to be a value of 4.8. This value was calculated from measurements made in 50% ethanol.

Lee _et_ _al_. (15) conducted a thorough study of the reaction of hydrogen ions with 1,10-phenanthroline. Potentiometric titration indicated that only a monoprotonated-1,10-phenanthroline forms at moderate acidity. They concluded that the two nitrogen atoms are too close together (approximately 2.5 Å) to permit the presence of two hydrogen ions. The extrapolation to infinite dilution of a plot of pH vs. the square root of the ionic strength gave a value of 4.77 for pK_a at 25°C. These data are recorded in Table 6. Calculation of the degree of hydrolysis of monoprotonated-1,10-phenanthroline from conductometric data indicated a pK_a of 4.96. The ionic strength in these measurements was 0.001. The conductometric titration of 0.01 M 1,10-phenanthroline with 0.2N hydrochloric acid showed a break in the titration curve at 1:1 acid/base ratio.

The acid dissociation constants of forty substituted 1,10-phenanthrolines were measured by Schilt and Smith (22a). They dissolved the substituted 1,10-phenanthrolines in acid and diluted to volume with water-dioxane mixtures. The use

Table 6. Dependence of hydrogen ion activity of 0.01 M phenanthroline-0.01 M phenanthrolium chloride buffer on ionic strength

Concentration of KCl, M	Observed pH	Total ionic strength	PhH^+
0.001	4.81[a]	0.011	0.91
0.010	4.83	0.020	0.87
0.100	4.91	0.11	0.73
0.500	5.03	0.51	0.55
1.000	5.12	1.01	0.45

[a]All measurements at 25 ± 0.1°C.

of water-dioxane mixtures was dictated by the low aqueous solubility of some of the substituted 1,10-phenanthrolines. The measurements were made with a glass-saturated calomel electrode pair and a Beckman Model G pH meter. The pK_a in aqueous solution was determined by extrapolating the plot of relative pK_a vs. % dioxane to 0% dioxane concentration. A pK_a value of 4.86 at 25°C was reported for 1,10-phenanthroline. The concentration of the base was 0.005 M and that of the acid approximately 0.0025 M.

The acid dissociation constants of 1,10-phenanthroline at 0°C, 25°C, 50°C, and several ionic strengths were measured by Nasanen and Uusitalo (19b). Their technique was similar to that of Lee _et al_. (15). The measurements were made using a glass-silver/silver chloride electrode pair. They reported pK_a values of 5.070 (0°C), 4.857 (25°C), and 4.641 (50°C) at infinite dilution. The 1,10-phenanthroline and hydrochloric acid concentrations in these experiments were approximately 0.005 M and 0.0025 M, respectively. The reaction of 1,10-phenanthroline with the silver-silver chloride and glass electrode may have caused errors in these measurements.

Margerum _et al_. (17) cite spectrophotometric evidence for the existence of diprotonated-1,10-phenanthroline. The existence of this species first became evident in the presence of 1 M perchloric acid. An equilibrium concentration constant of 5 was estimated from the spectrophotometric data. Spectrophotometric evidence for diprotonated-1,10-phenanthroline has also been reported by Nasanen and Uusitalo (19b).

Other measurements of the acid dissociation constant have been made. Brandt and Gullstrom (4), using a method similar to Schilt and Smith (22a), reported a pK_a value of 4.96. Yamaski and Yasuda (27) reproduced the values of Lee _et al_. (15). Krumholtz (14a) titrated various bases with acid to determine the acid dissociation constants. In the case of the 1,10-phenanthrolines he states, "K(the acid dissociation constant) shows an increase of 30% passing from the beginning to the end of neutralization." Concentration data was not given for the experiments with phenanthrolines.

The total concentration of 1,10-phenanthroline in the above experiments, in general, was less than 0.02 M. The acid concentration was half or less than half the base concentration. A trend in the pK_a values was noted. The pK_a values increased with higher base concentrations and increasing base to acid ratios.

In the present work, unexpected pH values were observed in solutions containing concentrations of acid and 1,10-phenanthroline greater than 0.02 M (Figure 2). The differences between the observed pH and the calculated pH using the values of the acid dissociation constants given in Table 6 were marked. The observed pH was always less than the calculated pH.

The larger than expected concentration of free hydrogen ion could be explained by considering that two or more 1,10-phenanthroline molecules react with one proton. These poly-1,10-phenanthroline hydrogen ion species would probably be less stable than monoprotonated-1,10-phenanthroline. Consideration of the equations for the formation of these poly species (Eq. 12, Eq. 18, Eq. 19, Eq. 20) reveals that the concentrations of these species increase with an increase in the base/acid ratio in the total base concentration. Under the conditions used for the measurements in the literature, the concentrations of the poly-1,10-phenanthroline hydrogen ion species would be small.

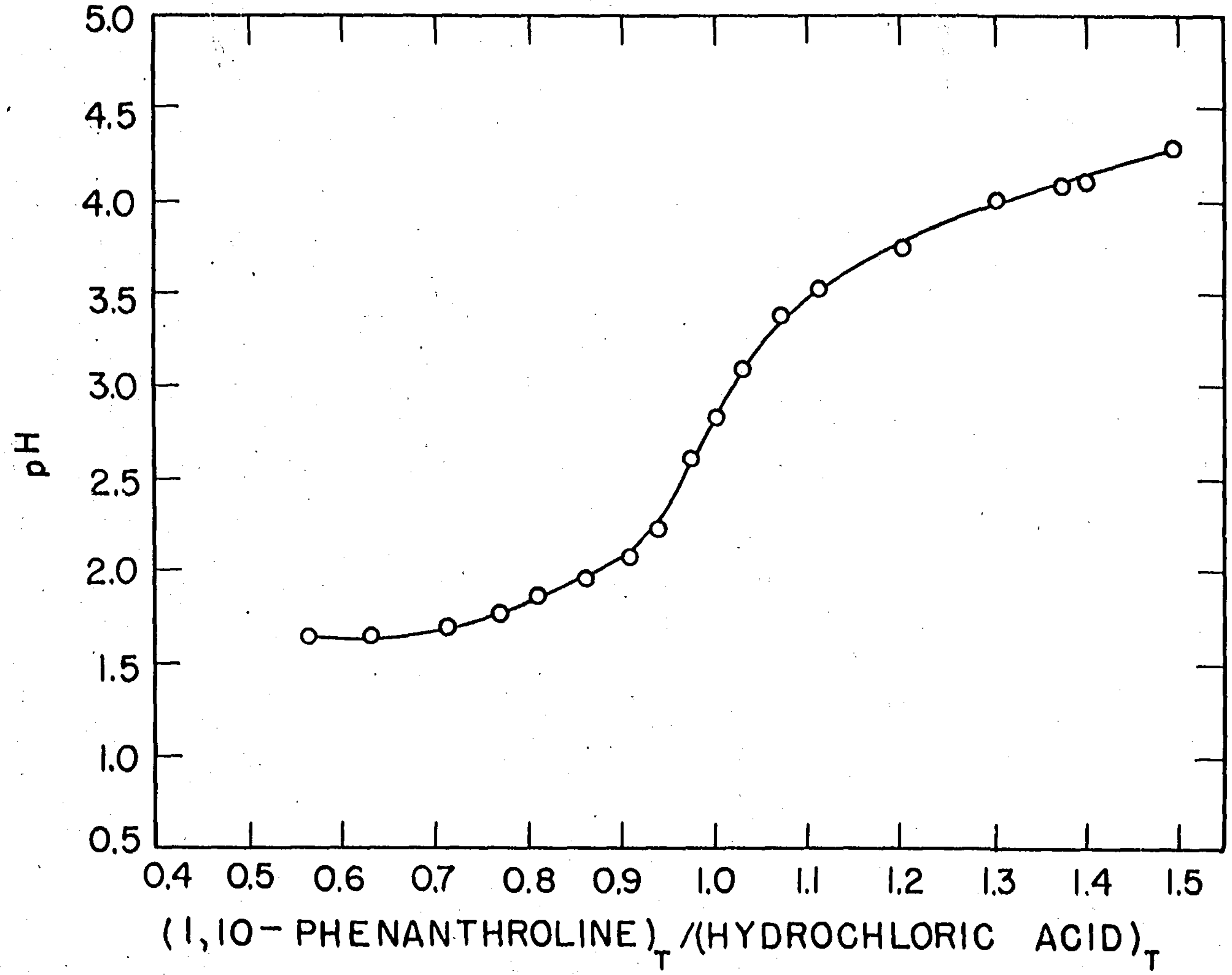
Several experiments were performed to demonstrate the poly-1,10-phenanthroline-hydrogen ion species. These will be discussed in the following sections.

pH Measurements

A solution which was 0.15 M in 1,10-phenanthroline and 0.10 M in hydrochloric acid was titrated with 0.10 M hydrochloric acid. This procedure was used to maintain a constant ionic strength during the titration. The pH was measured during the titration with a glass-calomel electrode pair. Considerable drifting of the pH readings was observed with the initial solutions, but the response was rapid and sharp during the titration. The data are plotted in Figure 6. Acid dissociation constants were calculated and are listed together with the titration data in the Table 7.

The drifting of the pH readings in solution in which the concentration of free-base 1,10-phenanthroline was large was investigated in some detail. The pH meter was standardized with a pH 9 buffer solution of large buffer capacity. A quantity of 1,10-phenanthroline was then dissolved in the buffer solution. The reading slowly changed. A stable pH reading of 8.7 was finally observed. Because the capacity of the buffer was many times greater than the quantity of 1,10-phenanthroline added, the hydrogen ion activity should

Figure 6. Titration of 20 ml. of a solution 1.502×10^{-1} M in 1,10-phenanthroline and 1.00×10^{-1}N in hydrochloric acid with 1.00×10^{-1}N hydrochloric acid



5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
pH
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
(1,10-PHENANTHROLINE)$_T$/(HYDROCHLORIC ACID)$_T$

Table 7. Titration of 1,10-phenanthroline with hydrochloric acid

Twenty ml. of solution 0.1502 M in 1,10-phenanthroline and 0.100 M in hydrochloric acid titrated with 0.100 M hydrochloric acid.

Ml. of titrant	pH	Ph_t/HCl_t	"K_a" x 10^{+5}
0	4.302	1.502	2.505
0.5	4.251	1.465	2.613
1.02	4.200	1.429	2.713
1.52	4.145	1.396	2.844
2.05	4.095	1.362	2.919
3.00	3.993	1.306	3.125
3.50	3.939	1.278	3.225
4.05	3.877	1.249	3.329
5.00	3.762	1.202	3.53
6.00	3.631	1.155	3.69
6.50	3.563	1.1336	3.739
7.00	3.492	1.1126	3.741
8.00	3.317	1.072	3.759
9.00	3.100	1.035	3.514
10.00	2.851	1.001	2.202
11.00	2.576	0.9690	-1.210
11.98	2.369	0.939	-0.68
13.00	2.208	0.910	-0.18
14.00	2.103	0.8835	
15.02	2.01	0.8578	
17.00	1.886	0.8188	
19.02	1.794	0.7698	
20.04	1.758	0.750	
22.0	1.699	0.715	
24.0	1.651	0.682	
28.02	1.600	0.625	
30.00	1.575	0.699	
32.00	1.543	0.577	
34.00	1.520	0.556	
36.00	1.487	0.536	
38.00	1.462	0.517	
41.00	1.440	0.492	

not have changed appreciably. After the electrodes were removed from this solution and placed in a fresh pH 9 buffer solution, the reading slowly returned to buffer value. Proper readings (i.e., buffer values) could be quickly obtained by dipping the electrodes in 1N hydrochloric acid and washing with water before placing them in the fresh buffer.

Similar experiments were run using pH 7 and 4 buffers. In all cases the addition of 1,10-phenanthroline caused the reading to change, indicating a pH value markedly different from that of the buffer. The change in reading was not reproducible, but depended upon the history of the electrodes. This reading change appeared to be some function of the apparent free-base 1,10-phenanthroline concentrations. The use of Desicote on the glass electrode did not change the results. Bystroff (6) observed similar phenomena with 5-chloro-1,10-phenanthroline and 1,10-phenanthroline.

It would appear that 1,10-phenanthroline is adsorbed on the surface of the glass electrode causing erroneous readings. The quantity adsorbed would be expected to be a function of the concentration of the free-base 1,10-phenanthroline. Margerum (16) performed some studies on the adsorption of 1,10-phenanthroline on glass surfaces. From the decrease in absorbancy of a 1,10-phenanthroline solution in contact with a freshly cleaned silica absorption cell walls, he estimated that approximately 5×10^{-9} moles of 1,10-phenanthroline were adsorbed per sq. cm. of surface. A monolayer would be of this order of magnitude. Adsorption is evidenced by the inability of water to wet glass surfaces which have been in contact with concentrated or neutral 1,10-phenanthroline solutions. The adsorption phenomena are not observed when there is sufficient acid present in solution to convert all of the 1,10-phenanthroline to the mono-protonated form.

Measurements of the pH of 1,10-phenanthroline solutions with a glass electrode are only approximate. The error increases with higher free-base 1,10-phenanthroline concentration. The adsorption phenomena should be thoroughly studied in order that corrections may be applied.

Experiments with buffer solutions outlined above were repeated using a quinhydrone-saturated calomel electrode system. The presence of 1,10-phenanthroline did not appear to affect the readings. This electrode system was used in later experiments whenever pH measurements of 1,10-phenanthroline solutions were required.

The titration of 1,10-phenanthroline with acid was repeated using the quinhydrone electrode system. 1,10-Phenanthroline (4.034 gm.) was dissolved in 25 ml. of 0.483N hydrochloric acid. The data are given in Table 8.

Solubility studies

The quantity of 1,10-phenanthroline which dissolved in the acid solutions is greater than expected from solubility

Table 8. Titration of 1,10-phenanthroline with hydrochloric acid

Twenty five ml. of solution 0.6396 M in 1,10-phenanthroline and 0.483 M in hydrochloric acid titrated with 0.483 M hydrochloric acid. Quinhydrone-saturated calomel electrode system used for measurement of pH.

Ml. of titrant	pH	Ph_t/HCl_t	Ml. of titrant	pH	Ph_t/HCl_t
0	4.19	1.856	20.0	2.35	1.031
0.5	4.13	1.820	21.0	2.05	1.008
0.7	4.08	1.805	22.0	1.78	0.987
1.0	4.05	1.785	23.0	1.58	0.967
2.0	3.98	1.718	24.0	1.43	0.947
3.0	3.91	1.657	25.0	1.31	0.928
4.0	3.85	1.600	26.0	1.22	0.909
5.0	3.83	1.546	27.0	1.20	0.892
6.0	3.81	1.497	28.0	1.12	0.875
7.0	3.77	1.450	29.0	1.10	0.859
8.0	3.73	1.406	30.0	1.05	0.844
9.0	3.68	1.365	32.0	1.00	0.814
10.0	3.60	1.326	34.0	0.95	0.786
11.0	3.52	1.289	36.0	0.90	0.760
13.0	3.38	1.221	40.0	0.85	0.714
14.0	3.28	1.189	45.0	0.79	0.663
15.0	3.18	1.160	50.0	0.73	0.619
16.0	3.10	1.130	55.0	0.72	0.580
17.0	2.98	1.105	65.0	0.68	0.516
18.0	2.82	1.08	70.0	0.62	0.488
19.0	2.60	1.054	80.0	0.60	0.441

data reported in the literature. One of the solutions titrated above was 0.6396 M in 1,10-phenanthroline and 0.483 M in hydrochloric acid. If all of the acid reacted with the 1,10-phenanthroline, forming a monoprotonated species, the solution would be 0.156 M in free-base 1,10-phenanthroline. Smith (25, p. 54) reports the solubility of 1,10-phenanthroline in water as 0.0160 M. The difference in ionic strength and other factors would not be sufficient to account for a ten-fold increase in solubility.

The solubility of 1,10-phenanthroline was studied as a function of total acid concentration. A series of 200-ml. volumetric flasks containing 50 ml. of hydrochloric acid of various normalities were placed in a water bath at 25 $\pm$ 0.01°C. An excess of 1,10-phenanthroline-monohydrate was added to each flask. The flasks were subjected to continuous shaking for twenty-four hours. Aliquots were analyzed for total 1,10-phenanthroline by conductometric titrations with hydrochloric acid. The normality of the titrant was the same as the normality of the acid in the aliquot. The solubilities were also measured at 40 $\pm$ 0.01°C, and the data are listed in Table 9 and plotted in Figure 7.

Conductometric titrations

A plot of the conductometric titration of a saturated aqueous solution of 1,10-phenanthroline with 0.00964N hydrochloric acid showed a break at a mole ratio of one 1,10-

Figure 7. Solubility of 1,10-phenanthroline monohydrate as a function of normality of acid

Circles: data at 40°C,

Boxes: data at 25°C.

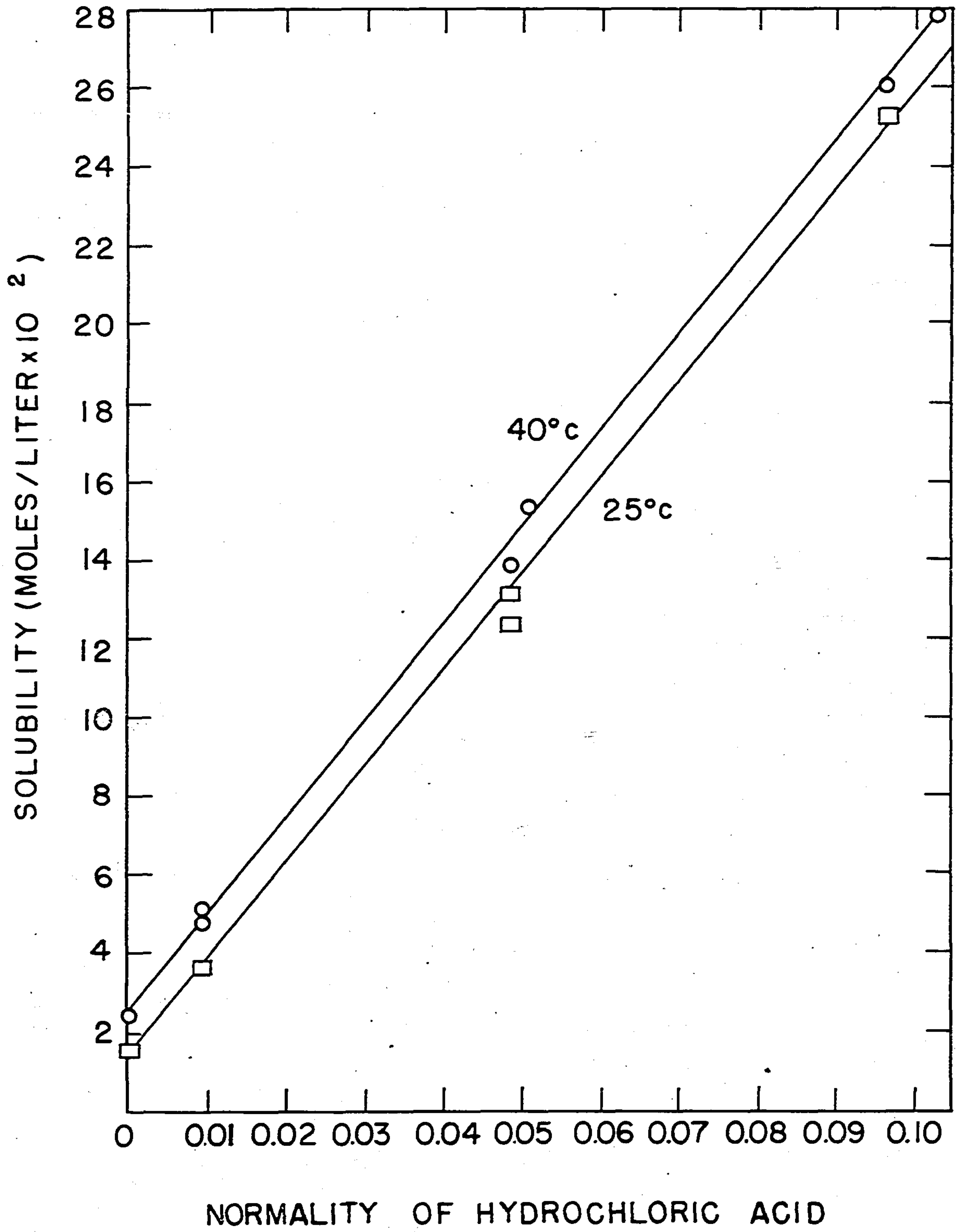

28
26
24
22
20
18
16
14
12
10
8
6
4
2
SOLUBILITY (MOLES/LITER x 10 2)
40°c
25°c
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.10
NORMALITY OF HYDROCHLORIC ACID

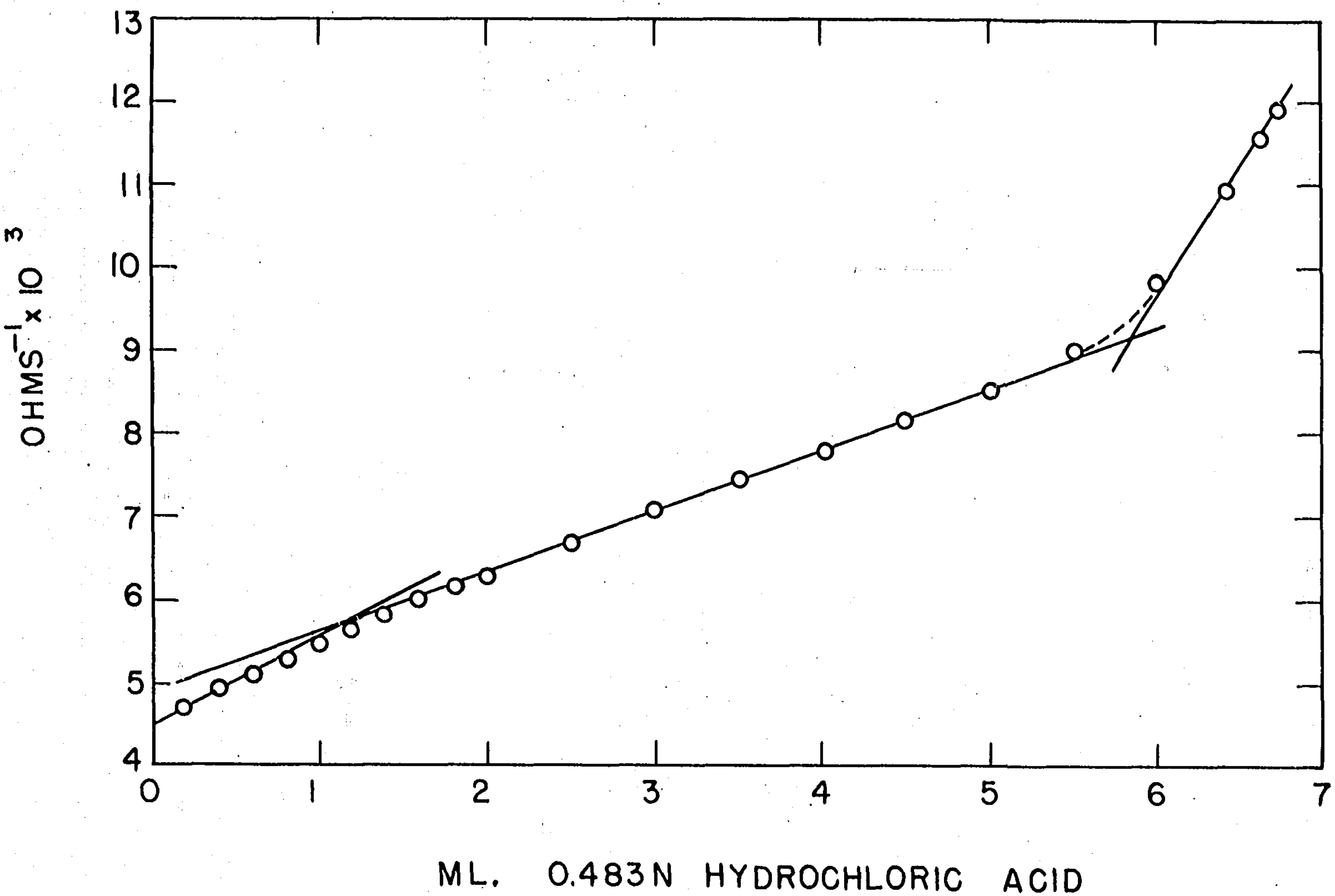
Table 9. Solubility of 1,10-phenanthroline in hydrochloric acid

Normality of acid	Molar solubility x 10^2	
	25°C	40°C
0	1.54; 1.58	2.45; 2.47
0.00964	3.64; 3.70	4.82
0.00969		5.10
0.0483	12.31; 13.08	13.81
0.0513		15.27
0.0964	23.84; 25.35	26.04
0.1025		27.88

phenanthroline to one hydrochloric acid. This plot was similar to that reported by Lee et al. (15). A second break was observed in the plots of the titration of acid solutions saturated with 1,10-phenanthroline. This second break occurred near the ratio of two moles of base to one mole of acid. This is shown in Figure 8.

The sharpness of the second break increased with higher total 1,10-phenanthroline concentration. One could increase the total concentration of 1,10-phenanthroline further by using more concentrated acid. However, the upper limit of

Figure 8. Conductometric titration of 25 ml. of 0.483N hydrochloric acid saturated with 1,10-phenanthroline with 0.483N hydrochloric acid



13
12
11
10
9
8
7
6
5
4
0
1
2
3
4
5
6
7
OHMS^{-1} x 10^{3}
ML. 0.483N HYDROCHLORIC ACID

the conductance bridge used was 0.01 $ohms^{-1}$. This limit would be exceeded if the acid concentration was greater than 0.1N.

The total concentration of 1,10-phenanthroline could be increased by using mixed solvents. Smith and Richter (25) lists the solubility of 1,10-phenanthroline in absolute alcohol as 2.78 M. 1,10-Phenanthroline (0.5567 gm.) was dissolved in 25 ml. of 80% ethanol. This solution was titrated with 0.1022N hydrochloric acid in 80% ethanol. The data are shown in Table 10 and plotted in Figure 9. A second solution of 1.7036 gm. of 1,10-phenanthroline in 25 ml. of 80% ethanol was titrated with 0.1022N hydrochloric acid in 80% ethanol. The data are given in Table 11.

Free-base-1,10-phenanthroline measurements

The stability constants of the poly-1,10-phenanthroline hydrogen ion species were estimated from the data taken from the titration of 1,10-phenanthroline with nitric acid. 1,10-Phenanthroline (6.718×10^{-3} moles) was dissolved in 50 ml. of 0.071 M nitric acid. This solution was then titrated with 0.071 M nitric acid. The course of the titration was followed with the silver/bis(1,10-phenanthroline)silver(I) nitrate-saturated calomel electrode pair. A 0.1N potassium nitrate agar-agar salt bridge was used to separate the saturated calomel electrode from the solution of nitric acid and 1,10-phenanthroline.

Table 10. Conductometric titration of 1,10-phenanthroline with hydrochloric acid (80% ethanol as solvent)

Initial $(P)_t = 1.237 \times 10^{-1}$ M

Titrant 1.022×10^{-1} M HCl

Ml. acid	Specific conductance x 10^4	P_t/HCl_t	Ml. acid	Specific conductance x 10^4	P_t/HCl_t
0	0.014	∞	23.00	10.18	1.31
1.00	1.04	30.25	24.00	10.45	1.26
2.00	1.84	15.13	25.00	10.66	1.21
3.00	2.60	10.08	26.00	10.86	1.11
4.00	3.27	7.56	27.00	11.15	1.11
5.00	3.85	6.05	28.00	11.44	1.08
6.00	4.42	5.04	29.00	11.70	1.04
7.00	4.92	4.32	30.00	11.98	1.00
8.00	5.42	3.78	32.00	12.8	0.945
9.00	5.88	3.36	34.00	13.4	0.889
10.00	6.28	3.02	36.00	14.5	0.840
11.00	6.70	2.75	38.00	15.2	0.796
12.00	7.09	2.52	40.00	15.8	0.756
13.00	7.44	2.32	42.00	16.5	0.720
14.00	7.75	2.16	44.00	17.3	0.687
15.00	8.07	2.01	48.00	18.5	0.630
16.00	8.46	1.89	52.00	19.5	0.581
17.00	8.68	1.77	56.00	20.2	0.540
18.00	9.95	1.68	60.00	20.8	0.504
19.00	9.20	1.59	64.00	21.8	0.472
20.00	9.46	1.51	68.00	22.5	0.444
21.00	9.65	1.44	72.00	22.8	0.420
22.00	9.95	1.37			

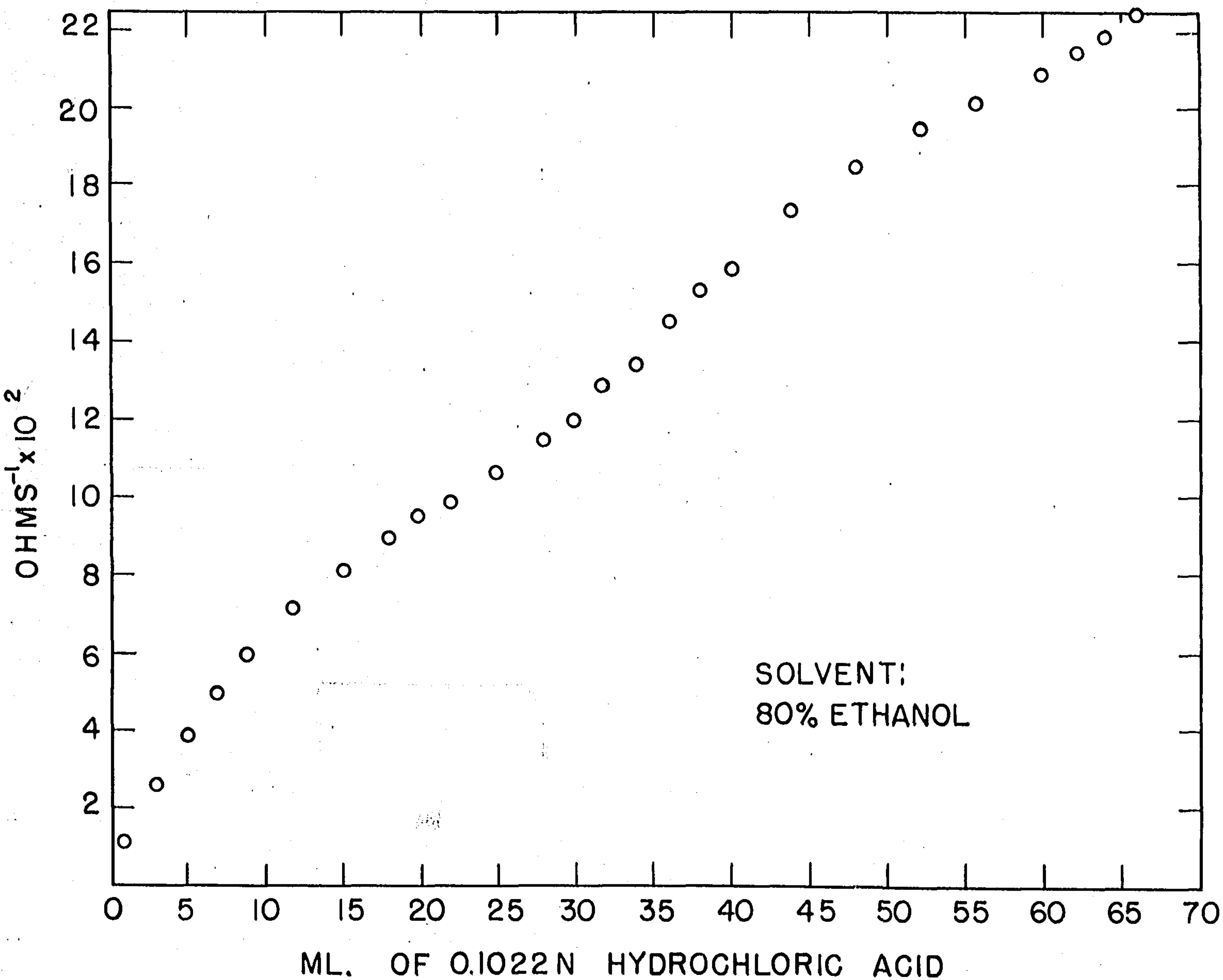
Table 11. Conductometric titration of 1,10-phenanthroline with hydrochloric acid (80% ethanol as solvent)

Initial $(P)_t = 3.786\times10^{-1}$ M

Titrant 1.022×10^{-1} M HCl

Ml. acid	Specific conductance x 10^4	P_t/HCl_t	Ml. acid	Specific conductance x 10^4	P_t/HCl_t
1.00	1.00	70.89	21.00	9.00	4.41
2.00	1.77	46.30	22.00	9.20	4.20
3.00	2.42	30.87	23.00	9.35	4.02
4.00	3.05	23.15	24.00	9.50	3.85
5.00	3.58	18.52	25.00	9.68	3.70
6.00	4.13	15.43	26.00	9.85	3.56
7.00	4.57	13.23	27.00	10.00	3.43
8.00	5.05	11.57	28.00	10.22	3.30
9.00	5.46	10.29	29.00	10.36	3.19
10.00	5.82	9.26	30.00	10.47	3.08
11.00	6.22	8.41	31.00	10.68	2.98
12.00	6.55	7.71	33.00	11.00	2.80
13.00	6.90	7.12	35.00	11.34	2.64
14.00	7.22	6.61	37.00	11.40	2.50
15.00	7.50	6.17	40.00	11.80	2.31
16.00	7.79	5.78	45.00	16.5	2.05
17.00	8.05	5.44	55.00	17.0	1.68
18.00	8.30	5.14	65.00	17.8	1.42
19.00	8.55	4.87	75.00	18.5	1.23
20.00	8.76	4.63	80.00	19.0	1.15

Figure 9. Conductometric titration of 25 ml. of 0.1237 M 1,10-phenanthroline in 80% ethanol with 0.1022N hydrochloric acid in 80% ethanol



SOLVENT:
80% ETHANOL
OHMS^{-1} x 10^{2}
ML. OF 0.1022 N HYDROCHLORIC ACID

The uncomplexed 1,10-phenanthroline was determined from the observed potential by means of Eq. (40). The previously determined working standard reduction potential of the silver/bis(1,10-phenanthroline)silver(I) nitrate electrode was used in the calculation. It was assumed that the activity of the nitrate ion and the ionic strength was constant throughout the titration. The activity coefficient of the nitrate ion was taken from a table of mean activity coefficients for nitric acid (14b). The value used in the calculations was 0.80.

The known concentrations of the uncomplexed 1,10-phenanthroline, the total nitric acid, and the total 1,10-phenanthroline were used to compute the $\bar{n}$ function. These data are given in Table 12. Eq. (20), the $\bar{n}$ equation, was used to compute the formation constants of the various species. The experimental data could best be described by the following formation constants: $\log\alpha_1$, 5.05; $\log\alpha_2$, 8.4; and $\log\alpha_3$, 10.3.

Determination of Stability Constants of the Zinc(II)-1,10-phenanthroline Chelates

The stability constants of zinc-1,10-phenanthroline chelates were also determined. The method employed was the same one used to determine the stability of the alkali metal and hydrogen ion complexes of 1,10-phenanthroline. A stock solution 0.0302 M in zinc nitrate, 0.5 M in acetic acid and

Table 12. Titration of 1,10-phenanthroline in nitric acid with nitric acid

Titrant solution

7.10×10^{-2} M nitric acid.

Sample solution

1.3315 g. 1,10-phenanthroline dissolved in 50 ml. of titrant solution.

Ml.	Observed potential (volts)	-Log(P)	$\bar{n}$
0	-0.115	3.122[a]	1.88
2.0	-0.109	3.173	1.81
4.0	-0.104	3.215	1.74
6.0	-0.100	3.249	1.68
10.0	-0.093	3.309	1.51
14.0	-0.082	3.402	1.47
16.0	-0.078	3.436	1.43
20.0	-0.069	3.512	1.35
24.0	-0.056	3.622	1.28
28.0	-0.040	3.758	1.21
30.0	-0.030	3.843	1.18
32.0	-0.020	3.927	1.15
34.0	-0.005	4.054	1.13
36.0	-0.012	4.198	1.10
38.0	+0.024	4.300	1.07
40.0	+0.034	4.385	1.05
42.0	+0.044	4.470	1.02
44.0	+0.050	4.520	1.00
46.0	+0.056	4.571	0.99
48.0	+0.060	4.605	0.97
50.0	+0.064	4.639	0.95
53.0	+0.065	4.656	0.92
56.0	+0.073	4.715	0.89
60.0	+0.077	4.749	0.86
62.0	+0.079	4.766	0.85
66.0	+0.082	4.792	0.82
70.0	+0.084	4.809	0.79

[a]Activity coefficient of nitrate ion taken as 0.80 nitric acid.

Table 12. (Continued)

Ml.	Observed potential (volts)	-Log(P)	$\bar{n}$
75.0	+0.087	4.834	0.76
80.0	+0.090	4.859	0.73
90.0	+0.094	4.893	0.68
100.0	+0.097	4.919	0.63
110.0	+0.100	4.944	0.59
120.0	+0.104	4.978	0.56
140.0	+0.107	5.004	0.50

0.5 M in potassium acetate was prepared. The measured pH of this solution was 4.70. 1,10-Phenanthroline (2.02×10^{-3} mole) was dissolved in 25 ml. of the stock solution. The titration of this solution, using the stock solution as titrant, was followed with the previously described electrode system. The bis(1,10-phenanthroline)silver(I) acetate is soluble, and the presence of acetate ion should not interfere with the titration. The data from the titration are given in Table 13.

The $\bar{n}$'s were computed by means of Eq. (21). The previously determined formation constants of the poly-1,10-phenanthroline hydrogen ion species were used in the computation. The values found were the following: pK_1, 6.58; pK_2,

Table 13. Titration of 1,10-phenanthroline in zinc nitrate with zinc nitrate

Titrant solution

2.974×10^{-2} M $Zn(NO_3)$

5.0×10^{-1} M acetic acid

5.0×10^{-1} M sodium acetate.

Sample solution

0.3635 g. 1,10-phenanthroline dissolved in 25 ml. of titrant solution.

Ml.	Observed potential (volts)	-Log(P)	$\bar{n}$
0	0.053	4.484[a]	2.70
0.5	0.064	4.577	2.65
1.0	0.072	4.645	2.60
1.5	0.079	4.704	2.56
3.0	0.094	4.831	2.42
5.0	0.110	4.967	2.26
7.0	0.121	5.060	2.12
9.0	0.132	5.153	1.99
12.0	0.144	5.255	1.83
15.0	0.155	5.348	1.69
18.0	0.165	5.433	1.58
21.0	0.171	5.484	1.47
25.0	0.180	5.560	1.35
30.0	0.189	5.636	1.23
35.0	0.199	5.721	1.13
40.0	0.207	5.789	1.04
45.0	0.212	5.831	0.97
50.0	0.219	5.891	0.90
55.0	0.228	5.967	0.85
60.0	0.230	5.983	0.80

[a]Activity coefficient of nitrate ion taken as 0.60.

12.4; and pK_3, 17.0. Bystroff (6) determined stability constants of the zinc-1,10-phenanthroline chelates by means of pH measurements. The values he found for the constants were as follows: pK_1, 6.36; pK_2, 12.00; and pK_3, 17.2. The reliability of the method used to determine the stability constants of the complexes of the alkali metal and hydrogen ions with 1,10-phenanthroline is shown by the agreement of the constants.

DISCUSSION AND SUMMARY

The low stability of alkali metal complexes with 1,10-phenanthroline became apparent when several conventional means of determining stability constants were applied to the systems. The optimum condition for the measurement of complexes of low stability requires that the complex be partially formed. This requirement dictates that the total concentration of ligand and metal be relatively high. The feasible methods which can be used to measure the equilibrium concentrations of the various species in such a system are limited. The high molar absorptivity of 1,10-phenanthroline eliminates convenient measurement by spectrophotometry. Partition methods are impractical because the distribution coefficient is large with most organic solvents. The existence of poly-1,10-phenanthroline on glass surfaces makes the use of pH measurements difficult. The other methods previously used to determine stability constants of 1,10-phenanthroline chelates have limitations which make their use impractical.

A new method of determining free-base 1,10-phenanthroline concentration was developed. The potential of the silver/bis(1,10-phenanthroline)silver(I) nitrate-saturated calomel electrode was found to be a function of the activity of the nitrate ion and the concentration of the free-base 1,10-phenanthroline. The developement of the electrode required some knowledge of the chemistry of the silver(I)-1,10-

phenanthroline system. The titration of silver nitrate and silver sulfate with 1,10-phenanthroline showed that the bis(1,10-phenanthroline)silver(I) complex was considerably more stable than the mono(1,10-phenanthroline)silver(I) complex.

The estimated stability constant of $pK_1 = 4$ for the mono(1,10-phenanthroline)silver(I) is of the order of magnitude of the silver(I) aromatic amine complexes. However, the stability constant of $pK_2 = 11.6$ computed for the bis(1,10-phenanthroline)silver(I) is additional evidence of the increased stabilization of 1,10-phenanthroline chelates through double bonding (3), (18, p. 162).

Statistically, the stepwise formation constant of the bis(1,10-phenanthroline)silver(I) should be less than the constant of mono(1,10-phenanthroline)silver(I) (18, p. 80). Experimentally, it is approximately 4 pK units higher than statistically predicted. This phenomena had been observed in many other 1,10-phenanthroline complexes (3), (6), (16), and (18, p. 524). A solubility product constant for bis(1,10-phenanthroline)silver(I) nitrate of $10^{-8.8}$ was also computed from the data.

The competition of silver nitrate and a metal nitrate for 1,10-phenanthroline can be observed with a silver-reference electrode pair. The observed potential is a function of the activity of the uncomplexed silver(I) ion. The free-base 1,10-phenanthroline can be computed from the activity of the silver(I) ion. The insolubility of the bis(1,10-phenanthroline)silver(I) nitrate simplifies the calculations. The presence of solid bis(1,10-phenanthroline)silver(I) nitrate in the system can be assured by plating the silver electrode with the substance. The electrode may then be viewed as a silver/bis(1,10-phenanthroline)silver(I) nitrate electrode. The electrode equation, Eq. (40), indicates that the potential of a cell involving this electrode is a function of the square of the 1,10-phenanthroline concentration and activity of the nitrate ion. This was confirmed by titrating a saturated aqueous solution of bis(1,10-phenanthroline)silver(I) nitrate with 1,10-phenanthroline.

The working standard reduction potential of -0.311 volt vs. hydrogen was determined from measurements of solutions containing known concentrations of free-base 1,10-phenanthroline and nitrate ion.

The stability constants of the zinc-1,10-phenanthroline complexes were determined. The uncomplexed 1,10-phenanthroline was calculated from the potential of silver/bis(1,10-phenanthroline)silver(I) nitrate-saturated calomel electrode pair. The constants found agreed with those stated in the literature. Spectrophotometric, partition, and pH measurement methods were employed to determine the literature values. This agreement shows the reliability of the electrode.

Evidence for the existence of poly-1,10-phenanthroline hydrogen ion species was discovered when pH measurements were used to determine stability constants of 1,10-phenanthroline complexes. The observed pH of relatively concentrated solutions of acid and 1,10-phenanthroline was loser than the pH predicted from the values of the acid dissociation constants in the literature.

The data obtained from the titration of 1,10-phenanthroline in hydrochloric acid with hydrochloric acid deviated markedly from that predicted by the constants in the literature. Species containing a ratio of 1:1, 1:2, and 1:3, 1,10-phenanthroline to hydrogen ions would be necessary to explain the deviation.

Solubility data of 1,10-phenanthroline in hydrochloric acid also indicated the existence of poly-1,10-phenanthroline hydrogen ion species. Equations (Eq. (15), Eq. (16), Eq. (33), Eq. (34), and Eq. (35)) for total 1,10-phenanthroline, total acid, and the stability constant equations for the poly-1,10-phenanthroline hydrogen ion species may be combined to obtain

$$(P)_t = (P) + \frac{\sum_{1}^{i} i\, \alpha_{ia}\, (P)^i}{1 + \sum_{1}^{i} \alpha_{ia}\, (P)^i}\, (H^+)_t \quad .$$

If the concentration of free-base 1,10-phenanthroline is considered to be relatively constant, the plot of solubility vs. concentration of acid would be linear and have a slope equivalent to the $\bar{n}$ function Eq. (20). The experimental plot was linear and had a slope of 2.5 at 25°C. and 2.64 at 40°C. A species containing a ratio of three 1,10-phenanthroline to one hydrogen ion is indicated by the $\bar{n}$ of 2.15.

The data from the conductometric titration of 1,10-phenanthroline with hydrochloric acid also indicated the poly-1,10-phenanthroline hydrogen species. Indications of breaks in the titration curve at ratios of 1:2, and 1:3 hydrogen ions to 1,10-phenanthroline were noted. This could be interpreted as showing the existence of species containing ratios of 1:2 and 1:3 hydrogen ions to 1,10-phenanthrolines.

The data from measurements in aqueous solutions indicated species containing a ratio of three 1,10-phenanthrolines to one hydrogen ion. The conductometric titrations in 80% ethanol could be interpreted as showing the existence of species containing higher base to acid ratios.

The stability constants for the hydrogen ion-1,10-phenanthroline species were computed from the titration of 1,10-phenanthroline in nitric acid with nitric acid. Values for the constants at an ionic strength of 0.07 are as follows: pK_1, 5.05; pK_2, 8.4; and pK_3, 10.3.

Riccardi and Franzosini (21a), using spectrophotometric measurements, found a value of 5.10 for pK_1 at an ionic strength of 0.064. Sodium chloride was used to adjust ionic strength. Lee et al. (15) determined the pK_1 to be 4.93 at an ionic strength of 0.1 from pH measurements. This measurement was made with fairly concentrated solutions. A pK_1 value approximately equal to the one stated in this work may be calculated from data of Lee et al. (15) by considering the poly-1,10-phenanthroline hydrogen-ion species and potassium-1,10-phenanthroline chelates.

The structure of the species formed by the reaction of 1,10-phenanthroline with hydrogen ion is of interest. It appears improbable that three 1,10-phenanthrolines could chelate with one hydrogen ion. This would imply an octahedral structure. Very high energies would be involved in the hybridization of the hydrogen ion orbitals to give an octahedral structure and would seem to preclude this possibility.

An alternate explanation would be to consider that 1,10-phenanthroline reacts with an hydronium ion, H_3O^+. A N-H-O bond could form between each 1,10-phenanthroline and hydrogen atom in $P_3H_3O^+$. Fritz et al. (9) have measured the heat of hydration of 1,10-phenanthroline. They found that the strength of N-H bond was 7.25 calories per mole. This high energy could account for the high stability of the species formed by the reaction of hydrogen ions with

1,10-phenanthroline. Ions having ratios of 1,10-phenanthroline to hydrogen ion greater than 3 could be explained by considering the reaction of 1,10-phenanthroline with $H(H_2O)_x^+$ ions.

The stability constants of the alkali metal complexes were determined by the method described for the zinc-1,10-phenanthroline complexes. The values of pK_1 found for the alkali metals were as follows: lithium, 1.78; sodium 1.58; and potassium, 1.0.

The order of stabilities of the mono complexes is that expected from consideration of ionic radii, high electronegativities, and high degree of hydration. The pK_2 values were much larger than anticipated from statistical consideration. If the hydration shpere of the metal ion is removed during the addition of one 1,10-phenanthroline, the addition of the second ligand molecule would require less energy. The higher stability constants of alkali metal chelates in nonaqueous solvents indicated the great effect of hydration of the metal ion on the stability of the chelate. This could account for the higher pK_2 values.

The results of experiments discussed above should be considered whenever the chemistry of 1,10-phenanthroline solutions is being investigated. The manner of controlling ionic strength and of measuring pH should receive special consideration. Stability constants of the various species discussed in this work should be considered whenever quantitative measurements are made on solutions containing 1,10-phenanthroline.

SUGGESTIONS FOR FUTURE WORK

1) The silver/bis(1,10-phenanthroline)silver(I) nitrate electrode could be used to determine the stability constants of many 1,10-phenanthroline complexes. The stability constant of the bis(1,10-phenanthroline)silver(I) and the solubility product constant of its nitrate salt fix an upper limit to the magnitude of the constants measureable with the electrode. Practical considerations limit the method to determination of pk_i's less than 10.

2) Electrodes could be prepared using anions which form insoluble salts with bis(1,10-phenanthroline)silver(I) in a manner analogous to that used for the preparation of the silver/bis(1,10-phenanthroline)silver(I) nitrate electrode. These electrodes might be used to determine the activity of many anions. The large number of insoluble salts would limit the use of the electrodes to measurements in solutions of known composition.

3) Electrodes could be fashioned from metals other than silver. An iron/tris(1,10-phenanthroline)iron(II) perchlorate electrode would be an interesting possibility.

4) Electrodes could probably be prepared using substituted 1,10-phenanthrolines. These might be used to determine stability constants of substituted 1,10-phenanthroline complexes.

5) Methods developed in this work could be extended to other ligands. An electrode formed by plating a bis(_vic_-dioximato-_N,N'_)nickel(II) chelate on a nickel electrode might prove interesting. The potential of a cell involving this electrode would be a function of uncomplexed _vic_-dioxime concentration. The potential would be relatively independent of anion concentration.

6) The structure of poly-1,10-phenanthroline hydrogen ion species should be investigated. The manner of attachment of the 1,10-phenanthroline molecules to a hydrogen ion is not predictable from present theory. The intriguing possibility of species containing more than three 1,10-phenanthroline molecules could be investigated using mixed solvents to increase the solubility of the 1,10-phenanthroline.

7) Some of the data on chelates of 1,10-phenanthroline in the literature could be reinterpreted in light of the species investigated in this work.

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