EQUILIBRIUM CONSTANTS FOR THE FORMATION OF SILVER AMMINES IN ETHANOL-WATER MIXTURES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

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*****

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ACKNOWLEDGMENT

I wish to express my deep appreciation to my preceptor, Professor Frank Verhoek, for suggesting this problem, and for his advice and encouragement during the course of the work.

I also wish to thank the Cincinnati Chemical Works for providing a fellowship under which much of this work was done.
This dissertation is a report of experimental studies on the equilibrium constants of a number of silver ammine complexes in ethanol-water solution, with the purpose of examining the relationship between the stabilities of these complexes and the basic strengths and structures of the amines. Formation constants of the complex silver ions and dissociation constants of the amines were obtained at 25°C in 50 mole % ethanol-water mixtures from pH measurements of solutions containing known amounts of silver ion, acid, amine and neutral salt. The glass electrode used was calibrated on solutions for which the pH had been determined by potentiometric measurements with hydrogen electrodes and by spectrophotometric measurements using an indicator.
# TABLE OF CONTENTS

ACKNOWLEDGMENT ....................................... ii
PREFACE ............................................... iii
LIST OF TABLES ......................................... vi
LIST OF ILLUSTRATIONS ................................... ix
LIST OF AMINES (ALPHABETICAL) .......................... x
LIST OF AMINES (BY NUMBER SYMBOL) .................... xi

I. INTRODUCTION ........................................ 1
   A. The Electronic Theory of Acids and Bases .... 3
   B. Silver Ion as a Reference Acid ................. 7
   C. The Bjerrum Method for Studying Complex Formation 11
   D. Calculation of the Consecutive Formation Constants 15
   E. Use of the Glass Electrode in 50 mole % Ethanol-Water. 19
   F. Scope of the Work ................................ 23

II. EXPERIMENTAL .......................................... 25
   A. Glass Electrode Measurements .................. 25
   B. Hydrogen Electrode Measurements .............. 31
   C. Spectrophotometric Measurements .............. 32
   D. Materials ...................................... 33

III. RESULTS ................................................ 36
   A. Acid Dissociation Constants of the Amines .... 36
   B. Formation Constants of the Silver Ammines .... 39
<table>
<thead>
<tr>
<th>TABLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>10</td>
</tr>
<tr>
<td>II</td>
<td>38</td>
</tr>
<tr>
<td>III</td>
<td>42</td>
</tr>
<tr>
<td>IV</td>
<td>45</td>
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<td>V</td>
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<td>VI</td>
<td>62</td>
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<td>VII</td>
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<td>65</td>
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<td>80</td>
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<tr>
<td>XV</td>
<td>80</td>
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<tr>
<td>XVI</td>
<td>81</td>
</tr>
<tr>
<td>TABLE</td>
<td>PAGE</td>
</tr>
<tr>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>XVII</td>
<td>Acid Dissociation Constant of p-Anisidine</td>
</tr>
<tr>
<td>XVIII</td>
<td>Acid Dissociation Constant of Morpholine</td>
</tr>
<tr>
<td>XX</td>
<td>Acid Dissociation Constant of Di-sec-butylamine</td>
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<tr>
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<td>Acid Dissociation Constant of Di-n-butylamine</td>
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<tr>
<td>XXI</td>
<td>Acid Dissociation Constant of Decahydroquinoline</td>
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<tr>
<td>XXII</td>
<td>Acid Dissociation Constant of Diethylamine</td>
</tr>
<tr>
<td>XXIII</td>
<td>Acid Dissociation Constant of Dibenzyamine</td>
</tr>
<tr>
<td>XXIV</td>
<td>Acid Dissociation Constant of Diethanolamine</td>
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<tr>
<td>XXV</td>
<td>Acid Dissociation Constant of Quinoline</td>
</tr>
<tr>
<td>XXVI</td>
<td>Acid Dissociation Constant of Pyridine</td>
</tr>
<tr>
<td>XXVII</td>
<td>Acid Dissociation Constant of N-ethylmorpholine</td>
</tr>
<tr>
<td>XXVIII</td>
<td>Acid Dissociation Constant of Tri-n-butylamine</td>
</tr>
<tr>
<td>XXIX</td>
<td>Acid Dissociation Constant of Triethylamine</td>
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</tr>
<tr>
<td>XXXIII</td>
<td>Acid Dissociation Constant of Diethyl-o-toluidine</td>
</tr>
<tr>
<td>XXXIV</td>
<td>Acid Dissociation Constant of Diethyl-p-toluidine</td>
</tr>
<tr>
<td>XXXV</td>
<td>Acid Dissociation Constant of N-ethylpiperidine</td>
</tr>
<tr>
<td>XXXVI</td>
<td>2,6-Xyldine - Silver Ion System</td>
</tr>
<tr>
<td>XXXVII</td>
<td>Aniline - Silver Ion System</td>
</tr>
<tr>
<td>XXXVIII</td>
<td>Ethanolamine - Silver Ion System</td>
</tr>
<tr>
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<td>t-Octylamine - Silver Ion System</td>
</tr>
<tr>
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<td>PAGE</td>
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<td>-------</td>
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<td>96</td>
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I. INTRODUCTION

The silver ammines belong to a class of compounds known as Werner complexes\(^1\), coordination compounds in which the coordinated complex ion is capable of independent existence in solution. These complexes have been classified by Biltz\(^2\) as "normal complexes" or "penetration complexes". In the normal complexes the bonding is sufficiently weak to result in a reversible dissociation in solution, while the penetration complexes show no evidence of such dissociation, the bond being approximately as strong as the normal covalent bond.

Kossel\(^3\) attempted to explain the formation of Werner complexes on the basis of electrostatic attraction between the metal ion and the negative charge or dipole (permanent or induced) of the ligand. The relative stabilities of the complexes were presumed to be determined by the size, charge, and polarizability of the central ion and the ligand. However, the spatial requirements of complexes and the development of the electronic theory of the covalent bond by Lewis\(^4\) and Sidgwick\(^5\) have led to the modern concept of the typical complex as consisting of polarized electron-pair bonds formed through occupation of orbitals in the

electron system of the metal ion by electron-pairs from the ligands, and subsequent hybridization to form coordinated covalences directed at definite angles in space. According to this latter view, which has been extensively developed by Pauling\(^6\), the bonding in complexes may range from the ionic extreme to the covalent extreme with no sharp dividing lines between. Some complexes, such as FeF\(_6^2-\) or CoF\(_6^2-\), are described as having bonds which are "essentially ionic", whereas the bonds in complexes such as Co(NH\(_3\))\(_6^{3+}\) are considered to be "essentially covalent". Measurements of the magnetic moments of the complexes are often used to make this distinction, but this does not rule out a small amount of covalent character in the former group or an amount of ionic character in the latter.

Even the classification into normal and penetration complexes is a purely empirical one. The asymmetric complex \([\text{Co en}_3]^{3+}\) can be resolved and the optically active forms can be kept in solution for extended periods of time without change in the rotation, and it is therefore considered a penetration complex. Between such unreactive complexes and normal complexes, which are in labile equilibrium with their constituent parts in solution as shown by exchange studies, are complexes such as that between ferric ion and dipyridyl which can be resolved and kept in solution for shorter periods but which racemize slowly.

Complexes are also classified as "outer orbital" or "inner orbital" complexes, depending on whether d orbitals below the valence

shell are involved in the bonding. Where inner orbitals are available, magnetic moment data are useful for determining in which classification a given complex belongs.

The bicovalent complexes of univalent silver, such as the silver ammines, are normal, outer orbital, linear complexes.

The formation of a complex bond between a metal ion such as Ag⁺ and a ligand such as an amine may be represented in the following equation:

\[
\text{Ag}^+ + \text{H}_2\text{N}:\text{R} \rightleftharpoons \left[\text{Ag}:\text{H}_2\text{N}:\text{R}\right]^+ 
\]

(1)

A. Electronic Theory of Acids and Bases

A reaction of the above type is considered a neutralization of a base with an acid according to the electronic theory of acids and bases, first proposed by Lewis in 1923. This theory correlates a large number of acid-base phenomena. An excellent presentation of the Lewis theory has been made by Luder and Zuffanti, in which they point out that it includes as special cases the water or Arrhenius theory, the proton theory of Brönsted, and the theory of solvent systems begun by Franklin and extended by Germann and Cady and Elsey.

7. L. Pauling, op. cit. p. 89.
According to Lewis, the fundamental difference between acids and bases is to be found in their electronic structures. An acid is a substance which can accept a pair of electrons from a base to form a coordinate bond. A base is a substance which can donate a pair of electrons to form a coordinate bond. Neutralization is, therefore, the formation of a coordinate bond between an acid and a base. Such a reaction may be carried out without a solvent, in a neutral solvent, or in a solvent which reacts with the acid or base or both. When an acid dissolves in a solvent, the reaction between the acid and solvent depends both on the strength of the acid (its tendency to accept an electron-pair) and the basic strength of the solvent (its tendency to donate an electron-pair). Thus the reaction of an acid with a basic solvent, or a base with an acidic solvent, is a neutralization according to the Lewis theory. The addition of a stronger base than water to a water solution of an acid is merely the replacement of the weak base, water, by a stronger base. The reaction of an amine A with a water solution of a strong acid may be represented by

$$A + H_3O^+ \rightleftharpoons AH^+ + H_2O$$

(2)

where $AH^+$ is the "onium" ion of the amine. The relative basic strengths of a series of amines may be determined from the values of the equilibrium constant of the above reaction:

$$K = \frac{[AH^+][H_2O]}{[A][H_3O^+]}$$

(3)

It would seem possible to arrange all bases and acids in order of strength by measurements of equilibrium constants of the above type,
but for any one solvent this is limited by the strength of the solvent as an acid or base. This is known as the leveling effect\textsuperscript{14}, and is one reason suggested by Luder as a complicating factor in any attempt to arrange a monotonic series of acids and bases. Within this limitation, however, it is possible, for a given solvent, to compare basic strengths towards the proton quantitatively by determination of constants of the type given in equation (3). If another acid is substituted for the proton as a reference acid, one might expect, again within the limits of the leveling effect, to obtain the same order of basic strengths. In general, however, this is not true. Lewis\textsuperscript{15} and Lingafelter\textsuperscript{16} cite several specific instances in which there is a reversal of basic strength with respect to different reference acids. Of particular interest in this connection is the work of Brown and coworkers\textsuperscript{17} on the effects of steric strain on the stabilities of the acid-base compounds formed between amines and boron alkyls or boron trifluoride. They found that trimethylamine is a stronger base than pyridine using boron trifluoride or hydrogen chloride as reference acids, in agreement with the behavior of these two amines in water solution. With boron trimethyl as a reference acid, however, pyridine is a stronger base than trimethylamine. This reversal was satisfactorily explained by the use of molecular

\textsuperscript{15}G. N. Lewis, J. Franklin Institute, 226, 293 (1938); G. N. Lewis and G. I. Seaborg, J. Am. Chem. Soc., 61, 1886 (1939); G. N. Lewis and J. Bigeleisen, ibid., 65, 1144 (1943).
models, by which it was shown that there is considerable steric strain in the trimethylamine-boron trimethyl compound. The triethylamine-boron trimethyl compound was found to be even less stable, and no compound formation at all was found between 2,6-lutidine and boron trimethyl.

In water the basic strength of the series—ammonia, methylamine, dimethylamine, trimethylamine—increases with the substitution of one methyl group and two methyl groups in the ammonia molecule (inductive effect), but drops sharply on addition of the third methyl group. Brown found that the same relative order of basic strengths was obtained using trimethyl-boron as the reference acid. To explain the failure of the substitution of the third methyl group in the ammonia molecule to increase the basic strength by the inductive effect he introduced the concept of "B-strain". In the free base, trimethylamine, the three methyl groups can satisfy steric requirements by a slight spreading of the C-N-C bond angles to a value greater than the tetrahedral bond angle. Addition of a fourth group by reaction with an acid forces the bonds toward the tetrahedral angles. The methyl groups are, therefore, crowded toward each other, setting up a strain which increases the tendency toward dissociation of the addition compound, and thereby reduces the measured strength of the base. Since the effect is independent of the steric requirements of the reference acid, B-strain results in a permanent decrease in the strengths of trimethylamine and other tertiary amines.

By using reference acids with greater steric requirements, Brown was able to observe even greater reversal of the basic strength
order. With the highly hindered acid, tri-t-butylboron, the basic strengths of both dimethylamine and trimethylamine were lower than that of ammonia, and the ethylamine series showed complete reversal of the order expected if only inductive effects were operating.

Brown's explanation was given in terms of "F-strain", which is caused by steric interference of the groups which are attached to different atoms resulting in a force which tends to separate the two atoms.

B. Silver Ion as a Reference Acid

Silver ion is an acid in the Lewis sense, because it can accept electron-pairs from bases to form complexes. In these compounds the characteristic coordination number has been shown to be two. It has been definitely established that the silver ion coordinates two ammonia molecules in solution¹⁸,¹⁹ and will form diammine complexes with amines in general²⁰, ²¹, ²², ²³. The silver ion may be presumed to react with the basic solvent water to form the hydrated ion:

\[ \text{Ag}^+ + 2\text{H}_2\text{O} \rightleftharpoons \text{Ag(H}_2\text{O})_2^+ \]  

If a stronger base than water, such as an amine A, is added to the solution of the silver ion, then the water will be replaced, to a

---

certain extent, by a base. We may, therefore, write an equation analogous to equation (2):

$$2A + Ag(H_2O)_2^+ \rightleftharpoons AgA_2^+ + 2H_2O$$  \hspace{1cm} (5)

The relative basic strengths of amines may then be determined from the values of the equilibrium constant

$$K = \frac{[AgA_2^+][H_2O]^2}{[A]^2[Ag(H_2O)_2^+]}$$  \hspace{1cm} (6)

which is analogous to equation (3). Since neither silver ion nor hydrogen ion is a hindered acid, we should obtain the same order of basic strength of the amines with both reference acids.

A number of investigators have made comparisons of the basic strength of various amines and their complex affinity for silver ion. Larsson\textsuperscript{24} determined only the overall complexity constant

$$K_N = \frac{[AgA_2^+]}{[Ag^+][A]^2}$$  \hspace{1cm} (7)

for several silver ammines in 50 mole \% ethanol-water mixtures at 25°C., using a silver electrode. Britton and Williams\textsuperscript{25} measured the overall complexity constants of the silver ion complexes of primary, secondary, and tertiary methyl- and ethylamines by a combination of solubility measurements of silver oxide in aqueous solutions of the amines and silver electrode measurements at 16°C. Their data show that the stabilities of the complexes decrease in the order: primary, secondary, tertiary, rather than being strictly dependent on the basic

\textsuperscript{24} E. Larsson, Z. physik. Chem., A 169, 207 (1934).
strengths of the amines toward hydrogen ion. However, if the primary, secondary, and tertiary amine complexes are considered separately, there is a dependence of stability on the conventional basic strengths. These two conclusions are also evident from a study of Larsson's data.

The formation of silver ammines obviously does not occur in one step, but rather in two steps:

\[
\begin{align*}
Ag^+ + A &\rightleftharpoons AgA^+ \quad (8) \\
AgA^+ + A &\rightleftharpoons AgA_2^+ \quad (9)
\end{align*}
\]

The equilibrium constants for these steps are called the consecutive constants and are given respectively by:

\[
\begin{align*}
k_1 &= \frac{[AgA^+]}{[Ag^+][A]} \quad (10) \\
k_2 &= \frac{[AgA_2^+]}{[AgA^+][A]} \quad (11)
\end{align*}
\]

Carlson, McReynolds and Verhoek\textsuperscript{26}, Bruehlman and Verhoek\textsuperscript{27}, and Bjerrum and coworkers\textsuperscript{28} have determined the consecutive constants using the glass electrode according to the method introduced by Bjerrum\textsuperscript{29}.

Table I is a compilation of the results of all of these investigators. The amines are listed in column one in the order of increasing basic strength toward hydrogen ion, which is given in column two as $pK_{AH}$, defined as $\log \frac{1}{K_{AH}}$, where $K_{AH}$ is the acid dissociation constant.

\textsuperscript{29} J. Bjerrum, "Metal Ammine Formation in Aqueous Solution", P. Haase and Son, Copenhagen (1941).
Table I

The Stabilities of Complex Silver Ammones

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of the substituted ammonium ion in water. In the table log $K_2$
refers to the logarithm of the overall complexity constant (equation
7) and log $k_1$ is the logarithm of the formation constant for the
addition of the first amine molecule to the silver ion (equation 10).
All values are for 25°C, except those of Britton and Williams (15°C)
and Carlson, McReynolds, and Verhoek (30°C), and only monoamines are
included.

C. The Bjerrum Method for Studying Complex Formation

We will now consider the method of Bjerrum$^{30}$ for the treatment
of complex formation with metal ions. Bjerrum's work is important
because he considers the formation of metal complexes as a succession
of stepwise reactions and shows how the intermediate constants, as
well as the overall constant, for a system may be obtained.

If the solvated central ion is represented by $M$ and the coordinat­
ing ligand by $A$, the stepwise equilibria for the formation of the
complex ion, $MA_N$, are given by equations:

\[
\begin{align*}
M + A & \rightleftharpoons MA \\
MA + A & \rightleftharpoons MA_2 \\
MA_{N-1} + A & \rightleftharpoons MA_N
\end{align*}
\]

The corresponding concentration mass action constants for the
system Bjerrum calls formation constants:

$^{30}$ J. Bjerrum, "Metal Ammine Formation in Aqueous Solution",
P. Haase and Son, Copenhagen (1941).
The term complexity constant refers to the concentration mass action constant for the overall reaction and is represented by:

\[ k_N = \frac{[MA_N]}{[M][A]^N} = \prod_{n=1}^{n=N} k_n \]  

(14)

The term \( \overline{n} \) is defined as the average number of ligands attached to the central ion \( M \). It is equal to the ratio of the total concentration of bound amine to the total concentration of metal ion:

\[ \overline{n} = \frac{[MA] + 2[MA_2] + \cdots + N[MA_N]}{[M] + [MA] + [MA_2] + \cdots + [MA_N]} \]  

(15)

If the equations (13) are solved for the concentrations of the intermediate ions, \( MA_n \), and the results substituted in equation (15), then elimination of \( [M] \) from numerator and denominator gives the following expression:

\[ \overline{n} = \frac{k_1[A] + 2k_1k_2[A]^2 + \cdots + Nk_1k_2\cdots k_N[A]^N}{1 + k_1[A] + k_1k_2[A]^2 + \cdots + k_1k_2\cdots k_N[A]^N} \]  

(16)

This equation expresses the quantity \( \overline{n} \) in terms of the free ligand concentration \([A]\). Instead of the concentration \([A]\), Bjerrum uses the quantity
and the curve obtained when $n$ is plotted against $p[A]$ is called the formation curve of the system.

If, as is the case in this study, the ligand $A$ is a monoamine, the total amine concentration in a solution of the amine, acid, and metal salt is given by:

$$C_A = [A] + [AH^+] + nC_M$$

(17)

where $C_A$ is the total amine concentration, $[A]$ is the concentration of free amine, $[AH^+]$ is the concentration of amine bound to hydrogen ion, and $C_M$ is the total concentration of metal ion. The total concentration of amine not complex-bound to metal ion may be represented by

$$C'_A = [A] + [AH^+]$$

(18)

Substitution of (18) into (17) and rearranging gives

$$n = \frac{C_A - C'_A}{C_M}$$

(19)

Carlson, McReynolds, and Verhoek\textsuperscript{31} have defined $\alpha_A$ as the fraction of the un-complexed amine which exists as free amine, and $\bar{n}_A$ as the fraction of un-complexed amine which is bound to hydrogen ion, according to the expressions:

$$\alpha_A = \frac{[A]}{C_A} = \frac{[A]}{[A] + [AH^+]}$$

(20)

$$\bar{n}_A = \frac{[AH^+]}{C'_A} = \frac{[AH^+]}{[A] + [AH^+]}$$

(21)

The equilibrium concentration of amine bound to hydrogen ion may be obtained from the equation for the acid dissociation constant of the amine:

$$K_{AH} = \frac{[A][H^+]}{[AH^+]} \quad (22)$$

from which we obtain:

$$[AH^+] = \frac{[A][H^+]}{K_{AH}} \quad (23)$$

If (23) is substituted into equations (20) and (21) they become, respectively:

$$K_{att} = \frac{K_{AH}}{[H^+]^n} \quad (24)$$

$$\frac{n}{A} = \frac{[H^+]}{K_{AH} + [H^+]^n} \quad (25)$$

By solving equation (21) for $C_A'$ and substituting into equation (19) we obtain:

$$\bar{n} = \frac{C_A - \frac{[AH^+]}{n_A}}{C_M} \quad (26)$$

Elimination of $C_A'$ from equations (20) and (21) yields:

$$[A] = \bar{n} \frac{[AH^+]}{n_A} \quad (27)$$

or

$$p[A] = \log \frac{n}{A} - (\log \bar{n} + \log [AH^+]). \quad (28)$$

The quantity $[AH^+]$ is equal to the total acid concentration of the solution, $C_H$, less the concentration of free hydrogen ion, $[H^+]$:

$$[AH^+] = C_H - [H^+] \quad (29)$$
Therefore, assuming \(-\log [H^+] = \text{pH}\), if we measure the pH of a solution of known metal ion, acid, and amine concentration \((C_M, C_H,\) and \(C_A)\) for an amine whose ionization constant, \(K_{AH}\), is known, we can calculate \(e_A\) and \(E_A\) from (24) and (25) and \(n\) and \(p[A]\) from (26) and (28). From the values of \(n\) and \(p[A]\) for a series of solutions of varying \(C_A\) the formation curve of the system may be obtained. From the formation curve, in turn, the formation constants can be calculated as shown below. This procedure, determination of formation constants of complex ions from measurements of the hydrogen ion concentrations in solutions of amine, metal ion, and acid is frequently called the "method of Bjerrum". In most cases in this study the complex formation began at such a high pH that \([AH^+]\) could be taken equal to \(C_H\). Only in the systems containing aniline, 2,6-xylidine, pyridine, and quinoline was it deemed necessary to correct for the free acid remaining.

D. Calculation of the Consecutive Formation Constants

According to Adams, Wegscheider, and Bjerrum the first approximation to the ratio of two consecutive constants of a complex system is that they are determined statistically, and Bjerrum uses this fact as an aid in determining the values of the constants.

If it is assumed that the tendency of a complex ion \(MA_n\) to split off a ligand is proportional to \(n\), and its tendency to take up

33. R. Wegscheider, Monatshefte, 16, 153 (1895).
a ligand is proportional to $N-n$, then the $N$ consecutive constants are proportional to the quantities

$$\frac{N}{1}, \frac{N-1}{2}, \ldots, \frac{N-n+1}{n}, \frac{N-n}{n+1}, \ldots, \frac{2}{N-1}, \frac{1}{N}.$$ 

Therefore, if only statistical considerations apply, and other influences may be ignored, the ratio of two consecutive constants is given by:

$$\frac{k_n}{k_{n+1}} = \frac{(N-n+1)(n+1)}{n(N-n)} \quad (30)$$

and

$$\log \frac{k_n}{k_{n+1}} = \log \frac{(N-n+1)(n+1)}{n(N-n)} \quad (31)$$

In the case of silver ion, for which $N=2$, equations (30) and (31) become

$$\frac{k_1}{k_2} = 4 \quad (32)$$

$$\log \frac{k_1}{k_2} = \log 4 \quad (33)$$

BJERRUM here introduces the spreading factor $x$, to take care of deviations from the statistical approximation, so that equation (32) is now written:

$$\frac{k_1}{k_2} = 4x^2 \quad (34)$$

Then if the constants $k_1$ and $k_2$ are expressed by an average constant $k$, we obtain:

$$k_1 = 2xk$$

$$k_2 = \frac{k}{2x} \quad (35)$$
Comparison of equations (32) and (34) shows that when \( x = 1 \) the ratio of the constants is statistically determined; when \( x > \frac{1}{2} \), then \( k_1 > k_2 \) and when \( x < \frac{1}{2} \), \( k_1 < k_2 \).

For \( N = 2 \), the formation equation (16) becomes

\[
\bar{n} = \frac{k_1 [A] + 2k_1k_2 [A]^2}{1 + k_1 [A] + k_1k_2 [A]^2} \tag{36}
\]

Substituting equations (35) into (36) we find:

\[
\bar{n} = \frac{2xk [A] + 2k^2 [A]^2}{1 + 2xk [A] + k^2 [A]^2} \tag{37}
\]

At the midpoint of the curve, where \( \bar{n} = 1 \), this equation leads to

\[
k = \frac{1}{[A]_{n=1}} \tag{38}
\]

Since \( K_2 = k_1k_2 = k^2 \) we may also state this as

\[
\log K_2 = 2 p [A]_{n=1} \tag{39}
\]

The connection between the spreading factor \( x \) and the slope of the formation curve is found by differentiating equation (37) with respect to \( \ln [A] \). Then the slope \( \Delta \), defined by the expression

\[
\Delta = \frac{\Delta n}{\Delta \ln [A]} = - 0.4343 \frac{\Delta n}{\Delta p [A]} \tag{40}
\]

will be given by the equation

\[
\Delta = \frac{2xk [A] + 4k^2 [A]^2 + 2xk^3 [A]^3}{(1 + 2xk [A] + k^2 [A]^2)^2} \tag{41}
\]

At the midpoint of the curve, where \( k [A] = 1 \), the slope will be given by
Thus from the value of $p[A]$ and the slope of the formation curve at $\bar{n}=1$, the average constant $k$ and the spreading factor $x$ may be calculated from equations (38), (40), and (42) and the consecutive constants $k_1$ and $k_2$ calculated from equations (35).

Although he prefers to use the slope method, Bjerrum notes that the solution of $N$ simultaneous equations, each derived by substituting a point on the formation curve into the formation function, will serve to determine the $N$ formation constants for any system. When $N$ is large this method is tedious, but its use is recommended by several investigators, among them Hindman and Sullivan and Schwarzenbach and Ackermann. Hindman and Sullivan recommend using half-integral values of $\bar{n}$ for the points which determine the $N$ simultaneous equations.

For the case of $N=2$, we have, substituting $K_2 = k_1 k_2$ into equation (36):

$$\bar{n} = \frac{k_1[A] + 2K_2[A]^2}{1 + k_1[A] + K_2[A]^2}$$

or

$$\bar{n} + (\bar{n}-1) [A] k_1 + (\bar{n}-2) [A]^2 K_2 = 0 \quad (43)$$

For $\bar{n}=0.5$, equation (43) becomes:

$$0.5[A]_{\bar{n}=0.5} k_1 + 1.5[A]^2_{\bar{n}=0.5} K_2 = 0.5 \quad (44)$$

For $\bar{n}=1.5$ equation (43) becomes:

$$0.5[A]_{\bar{n}=1.5} k_1 - 0.5[A]^2_{\bar{n}=1.5} K_2 = -1.5 \quad (45)$$

The solution of equations (44) and (45), using Cramer's rule is:

Both of these methods of calculating the consecutive constants of the silver ammines from the experimentally determined formation curve will be employed in this study.

E. Use of the Glass Electrode in 50 mole % Ethanol-Water

If the method of Bjerrum is to be applied to the study of complex formation in solvents other than water, the significance of the potential of the cell, containing the glass electrode and a reference electrode and possessing a liquid junction, must be determined. A knowledge of the difference between the observed potential of such a cell and that necessary to yield the true hydrogen ion activity of the solution at each point over the pH range being used, would make possible the conversion of pH meter readings into true pH values.

Dole\textsuperscript{37} has reported that the glass electrode yields erroneous pH values when used in organic solvent-water mixtures, and Goodhue and Hixon\textsuperscript{38} found that they could not obtain correct values for dissociation constants of acids and amines from pH measurements with

\[ k_1 = \begin{pmatrix} 0.5 & 1.5[A]_{n=0.5}^2 \\ -1.5 & -0.5[A]_{n=1.5}^2 \\ 0.5[A]_{n=0.5} & 1.5[A]_{n=0.5}^2 \\ 0.5[A]_{n=1.5} & -0.5[A]_{n=1.5}^2 \end{pmatrix} \]

\[ k_2 = \begin{pmatrix} 0.5[A]_{n=0.5} & 0.5 \\ 0.5[A]_{n=1.5} & -1.5 \\ 0.5[A]_{n=0.5} & 1.5[A]_{n=0.5}^2 \\ 0.5[A]_{n=1.5} & -0.5[A]_{n=1.5}^2 \end{pmatrix} \]

a glass electrode in ethanol. Yui measured pH values of 0.01N HCl solutions at 25°C in alcohol-water mixtures up to 50% alcohol by weight with both a hydrogen electrode and a glass electrode using a calomel reference electrode. He reported that the reproducibility of the potentials obtained by the glass electrode in the alcoholic solutions was not entirely satisfactory. Deviations of the potential measured by the glass electrode from those by the hydrogen electrode were positive and were found to increase linearly up to about 30% alcohol, above which an abrupt increase was observed. The maximum deviation observed was 2.5 mv. which corresponds to a pH difference of about 0.04 logarithmic unit. Yui suggested that the abrupt increase in pH might be due to association of H⁺ and Cl⁻. However, this explanation is not in agreement with the work of Bezman and Verhoek, who show from conductivity measurements that hydrochloric acid is completely dissociated in ethanol-water solutions containing more than 2.39 moles of water per liter (approximately 3% water by weight).

However, a number of other investigators have found that with proper allowances the glass electrode can give satisfactory results over a wide range of solvent composition. Izmailov and coworkers state that the glass electrode is perfectly usable for pH measurements in ethanol-water, methanol-water, and acetone-water mixtures, although the range of its applicability becomes somewhat narrower with decreasing water content. For ethanol and ethanol-water mixtures their plots of the potential of the cell: glass electrode | test solution | reference electrode

against the pH of the test solution show that the straight line portions of the curves for 20, 71.9, 83.5 and 93.7% ethanol are parallel to the curve for water solutions and displaced from it only slightly. The usable pH range for 71.9% ethanol (50 mole %) is approximately 2-10 and the deviations are positive by approximately 10 mv. Only in absolute ethanol was the straight-line portion of the curve displaced markedly from that for water and the water-ethanol mixtures. Calvin and Wilson\textsuperscript{42} measured chelation constants in 50 volume % dioxane-water mixtures using a glass electrode. They reported that the glass electrode gave very nearly correct values of pH in this solvent. In the first of a series of papers on coordination compounds involving principally measurements of formation constants of metal chelate complexes, Van Uitert and Haas\textsuperscript{43} introduce a method for determining thermodynamic equilibrium constants in mixed solvents using the glass electrode for pH measurements. To avoid confusion they use the term "pH" in reference to aqueous solutions only, and designate the meter reading obtained for nonaqueous solutions by the symbol $B$. They observe a straight line relationship with the correct Nernst slope for a plot of the E.M.F. of the cell:

$$
\begin{align*}
H_2 & \mid H^+ , Cl^- (75\% \text{ dioxane}) \mid AgCl \mid Ag
\end{align*}
$$

against the $B$ reading of the glass electrode in the same solutions over a range of $B$ values from 1.6 to 11.6. The $B$ values are converted into hydrogen ion concentrations by use of a conversion factor $U_H$, which is defined by the equation

The correction factor, \( \log U_H \), was determined for each solvent composition and ionic strength by observing the \( B \) value for a 0.00116 N HCl solution for which the \( [H^+] \) was assumed to be known, sodium chloride being used to adjust the ionic strength. Thermodynamic constants were calculated by introducing activity coefficients, assuming that the activity coefficient of a neutral molecule is unity and that the activity coefficients of the ionic species are equal to the mean activity coefficient, \( \gamma \), of hydrochloric acid for the solvent composition and ionic strength under consideration. For this purpose they define

\[
U_H^\circ = U_H \cdot \frac{1}{\gamma}
\]

From this it is evident that \( \log U_H^\circ \) is a correction term for converting meter readings, \( B \), into hydrogen ion activities, whereas \( \log U_H \) converts them into hydrogen ion concentrations. This technique was also applied to chelation studies in absolute ethanol.

A method similar to that of Van Uitert was employed in calibrating the glass electrode for the solvent and ionic strength used in this study. Three amine buffers, of the type used in determining the acid dissociation constants, were made up and their \( B \) values (ranging from 4.40 to 6.81) determined with the same glass electrode-calomel electrode cell used for the rest of the work. The pH of each of these buffers was then determined from the E.M.F. of the cell

\[
\text{Pt} \hspace{1cm} \text{H}_2 \parallel \text{HCl}(.001M), \text{LiNO}_3(.525M) \parallel \text{buffer} \parallel \text{H}_2 \parallel \text{Pt}
\]

assuming that the pH of the hydrochloric acid solution is known from its stoichiometric concentration and activity coefficients taken from the literature. A comparison of these pH values with the corresponding B values was made to check the linearity of the glass electrode response and to determine the value of the correction term to be applied to the B readings.

A value for this correction term was also obtained by comparing the B value for amine buffers with the pH as determined by spectrophotometric measurements using an indicator.

F. Scope of the Work

The object of this study was to select a series of primary, secondary, and tertiary monoamines, representing a reasonably wide range of basic strength, and to determine the formation constants for the addition of one and two amine molecules to a silver ion in ethanol-water mixtures. It was hoped that consideration of these data would (1) give further evidence of the applicability of Bjerrum's method, particularly in the use of the glass electrode, in non-aqueous solvents, (2) extend the measurements of basic strength constants and silver complex formation constants to amines and complexes too insoluble to be studied in water by this method, (3) reveal any effects of the nature of the solvent on the stabilities of these complexes, and (4) suggest some explanation for discrepancies between the order of basic strengths as measured by hydrogen ion and by silver ion.

This dissertation reports the results of a study of the formation constants at 25°C in 50 mole % ethanol-water of the silver complexes
of aniline, 2,6-xylidine (primary aromatic); t-butylamine, t-octylamine, ethanolamine (primary aliphatic); diethylamine, dibenzylamine, diethanolamine, di-n-butylamine, di-sec-butylamine (secondary aliphatic); morpholine, decahydroquinoline (secondary heterocyclic); triethylamine, tri-n-butylamine, triethanolamine, diethyl-ethanolamine, methyl-diethanolamine (tertiary aliphatic); and quinoline, pyridine, and N-ethylmorpholine (tertiary heterocyclic). The acid dissociation constants at 25°C in 50 mole % ethanol-water for these amines and for diethyl-o-toluidine, diethyl-p-toluidine, p-anisidine, and N-ethylpiperidine are also reported.
II. EXPERIMENTAL

It was shown in the preceding section that the formation curve and successive formation constants of a metal ammine complex ion may be calculated from the pH values of a series of solutions containing known amounts of metal ion, acid, and amine, provided the acid dissociation constant of the amine is known. If a high concentration of neutral salt is employed, the ionic strength of the solutions will vary little, and the activities of the reactants may be assumed to be proportional to their concentrations. However, the concentration of neutral salt may not be too high or "salting out" effects will occur at high amine concentrations. In order that more meaningful comparisons might be made with their work, the experimental methods used in this study were as nearly as possible like those of Carlson, McReynolds, and Verhoek\textsuperscript{45}, and Bruehlman and Verhoek\textsuperscript{46}. However, because the solubility of the potassium nitrate used in the earlier work is limited in 50 mole % ethanol-water, lithium nitrate was substituted for it as the neutral salt in making up the solutions.

A. Glass Electrode Measurements

The pH measurements were made with a Beckman Model G pH Meter using a Beckman General Purpose glass electrode having a 30 inch shielded lead, and a saturated calomel reference electrode. The two pieces of glass apparatus shown in Figures 1 and 2 were mounted back

Figure I. Glass electrode apparatus
Figure 2. Calomel electrode apparatus
to back at the lower end of a vertical brass rod in clamps made of brass bands bent to fit the contours of the pieces. The upper end of the brass rod was clamped to a horizontal bar extending over the bath, so that the whole apparatus could easily be raised from, or lowered into the bath.

The glass electrode was mounted in bulb D by using a rubber stopper. The cell B was filled with a saturated solution of lithium nitrate in 50 mole % ethanol-water, and was connected to cell H by an aqueous salt bridge of agar-potassium nitrate. Both cell H and cell J were filled with aqueous saturated potassium chloride solution, and the calomel electrode was mounted in cell J. After flushing out junction C, the solution to be measured was introduced into the glass electrode chamber through stopcock F, a tube of Ascarite being placed at E to prevent carbon dioxide absorption. Saturated lithium nitrate solution was then added through stopcock A to bring the level in B even with that of the test solution in D.

The whole apparatus was lowered into the water bath, which was thermostatically controlled at 25.00±0.02°C using a mercury-capillary thermoregulator and a thyratron circuit. About fifteen minutes in the bath was sufficient for the sample to come to equilibrium, since room temperature was usually close to 25°C. The stopcock G was then opened to connect chambers B and D, and the meter reading recorded. The stopcock was closed and a second reading taken five minutes later. No appreciable change in readings was noted. The apparatus was then raised from the bath and the test solution drained out through stopcock G. The wall of the glass electrode chamber was covered with Desicote
to eliminate the need for rinsing with the solution to be measured.

The meter was adjusted for asymmetry and temperature by the use of two water buffers of known pH value. One of these was 0.05 M potassium acid phthalate which has a pH of 4.00 at 25°C. The other was Beckman Concentrated pH7 buffer diluted to produce a pH of 7.00 at 25°C. At the beginning of a day both were used for proper adjustment and later during the course of the day's measurements a check was made using one or the other of these buffers, but seldom was readjustment necessary. In fact little or no difference was observed from one day to the next. When not in use the glass electrode was stored in a tube of 50 mole % ethanol-water and the calomel electrode in a tube of aqueous saturated potassium chloride, both of which were immersed in the constant-temperature bath. A fresh salt bridge was made up for each amine and was stored over night with the ends dipping into aqueous saturated potassium nitrate.

All the volumetric equipment was recalibrated to 25°C and solutions were brought to this temperature during mixing by immersion in the bath.

For the determination of the formation curves of the silver complexes, solutions approximately 0.025 M with respect to silver nitrate, 0.1 M with respect to nitric acid and 0.500 M with respect to lithium nitrate in 50 mole % ethanol-water were made up in one-liter volumetric flasks. Fifty-milliliter samples of these solutions were pipetted into 125-ml. glass-stoppered Erlenmeyer flasks and weighed portions of amine or amine solution were added from a weight
burette. The volume of amine or amine solution was calculated from its density and the weight added. The final volume of the solution, obtained by assuming additivity of volumes, was used to calculate the final concentrations of acid, amine, and silver ion.

Solutions for the determination of the acid dissociation constants of the amines were made up in a manner similar to that described above, except that the silver nitrate was replaced by an equal concentration of lithium nitrate in order to maintain the solutions at the same ionic strength as those containing the silver ion. Each value of the acid dissociation constants and each point on the formation curves represents a measurement on a separate fifty-milliliter sample. Since no solution was used for more than one pH measurement, each formation curve is free from additive concentration errors which might have occurred if a titration procedure had been used.

The most volatile amines were weighed out as solutions in 50 mole % ethanol-water. The weight percent of amine in these solutions was determined by adding an excess of standard 1 M nitric acid to a weighed portion of the solution and back-titrating with standard 0.1 N sodium hydroxide using methyl red as an indicator. The amines which were solids at room temperature were weighed out first in the 125 ml. glass-stoppered Erlenmeyer flasks, and the 50 ml. portion of acid-silver-neutral salt solution was added next.

Special precautions to avoid absorption of carbon dioxide from the air were taken only in weighing out the amines which are strong bases, and in handling the solutions for determination of their acid dissociation constants. In these instances the air in the glass-
stopped Erlenmeyer flasks was replaced by dry, CO₂-free nitrogen before addition of the amine, and a slow flow of the gas was maintained during the addition. For the transfer of the solution, the glass electrode chamber was flushed out with dry CO₂-free nitrogen and the solution forced into it with nitrogen pressure.

B. Hydrogen Electrode Measurements

The potentiometric measurements for calibration of the glass electrode were made using two hydrogen electrodes each immersed in a different solution, one of which was a reference solution, the other a solution whose pH was being determined. These solutions were contained in two electrolytic beakers suspended in the constant temperature bath at 25°C. Electrical contact between the solutions was made through an aqueous agar-potassium nitrate salt bridge.

The platinum electrodes were cleaned with aqua regia and coated with platinum black by immersing them in a solution of 3 grams of chloroplatinic acid and 0.025 grams of lead acetate in 100 ml. of water, connecting them to a battery, and reversing the direction of the current every 30 seconds. They were then rinsed with distilled water and a direct current passed between them in a 10% sulfuric acid solution for 30 minutes, reversing the direction every minute. They were then rinsed and stored in 50 mole % ethanol-water. The electrodes were freshly prepared for each measurement. Before mounting each electrode in its chamber it was rinsed twice with portions of the same solution as in the cell.
The hydrogen gas for each electrode was supplied from a separate cylinder of compressed, electrolytic hydrogen purified by passing through a liquid nitrogen trap and then through a long coil of Tygon tubing in the bath. The hydrogen for the electrode in the unbuffered solution was passed through two towers containing portions of the same solution as in the cell in order to minimize changes in concentration caused by bubbling the gas through the solution in the cell. The buffered solutions did not show any appreciable change in the time required for a measurement. The E.M.F. of each cell was measured with a conventional slide wire potentiometer.

The primary reference solution was 0.00100M with respect to hydrochloric acid and 0.525 M with respect to lithium nitrate in 50 mole % ethanol-water. Three amine buffers were made up in the same manner as for the acid dissociation constant measurements by adding amine from a weight burette to 200 ml. of a solution approximately 0.1 M in nitric acid and 0.525 M in lithium nitrate.

C. Spectrophotometric Measurements

The spectrophotometric measurements for calibration of the glass electrode were made with a Beckman Model DU Quartz Spectrophotometer, using a pair of matched 5 cm. cells each having a capacity of approximately 17 ml.

A solution 0.0100 M with respect to hydrochloric acid and 0.525 M with respect to lithium nitrate in 50 mole % ethanol-water was made up in a 500 ml. volumetric flask. Portions of this solution were
diluted with 0.525 M lithium nitrate in 50 mole % ethanol-water to make a series of solutions in which the hydrochloric acid concentrations were 0.00667 M, 0.00500 M, 0.00333 M, 0.00250 M and 0.00100 M. To 100 ml. portions of each of these hydrochloric acid solutions was added 10 ml. of a solution 0.525 M with respect to lithium nitrate and approximately 0.0001 M with respect to thymol blue in 50 mole % ethanol-water. The absorption of each of these solutions was measured at 10 mμ intervals between 530 and 590 mμ, the blank cell being filled with 50 mole % ethanol-water. Several quinoline buffers were made up in the same way as for the acid dissociation constant measurements and diluted with one-tenth their volume of the indicator solution. The absorption of each of these buffer solutions was measured at the same wave lengths as the hydrochloric acid solutions, the blank cell being filled with the buffer diluted with one-tenth its volume of 0.525 M lithium nitrate in 50 mole % ethanol-water. In all, two sets of measurements on the hydrochloric acid solutions and buffer solutions were made, using two different thymol blue concentrations.

The B values of the quinoline buffers and some of the hydrochloric acid solutions were measured in the glass electrode-calomel cell used for the equilibrium constant determinations.

D. Materials

Amides. The amines used for the most part in this study were research grade materials obtained from Eastman Kodak Company. Exceptions were Baker's Analyzed Reagent aniline and pyridine, Rohm
and Haas tert-octylamine and tert-butylamine, and Delta Chemical Company methyl-diethanolamine. Each amine was distilled under vacuum, and a middle fraction, comprising about 70% of the total, was collected. The vacuum in the distillation apparatus was broken by admitting dry, CO₂-free nitrogen, and the amine was transferred to the weight burette by nitrogen pressure. Tert-butylamine and diethylamine were distilled under approximately one atmosphere of dry, O₂- and CO₂-free nitrogen, and dissolved in 50 mole % ethanol-water before being stored in the weight burette. Diethanolamine and decahydroquinoline, which were obtained as white crystalline solids, were used without further purification.

Solutions. Standard aqueous solutions of 1.0 M nitric acid, 0.5 M silver nitrate, 0.1 M sodium hydroxide, and 0.1 M hydrochloric acid prepared by the Control and Reagent Laboratory of The Ohio State University Laboratory Supply Stores were used in making up and analyzing the solutions. These stock solutions were checked from time to time and very slight variations in their concentrations were noted. Oven-dried (105-110°C), analytical reagent grade lithium and potassium nitrates were used. All solutions were prepared with double distilled water. For some of the experiments this was obtained from the Laboratory Supply Stores and for the remainder it was prepared by distilling the regular distilled water from alkaline permanganate in an all-glass apparatus.

The ethanol used in making up all solutions was grain alcohol obtained from the Laboratory Supply Stores. This was used without
purification and was analyzed by density measurements, assuming water to be the only impurity. The density measurements were made with a pycnometer of approximately 27 ml. capacity. Sufficient additional water was added to bring the composition to 50 mole % (71.88% ethanol by weight), and the resulting mixture checked by density measurements. In preparing solutions, the amount of water present in the aqueous stock solutions used was calculated from density tables, and enough of the undiluted grain alcohol was added to bring the composition of the solvent to 50 mole %. Final dilution was then made with the 50 mole % stock.
III. RESULTS

A. Acid Dissociation Constants of the Amines.

The calculation of the formation curves of the silver ammine complex ions has been shown to require that the acid dissociation constant of the amine used be known. The acid dissociation of an amine A is given by the equation

$$\text{AH}^+ \rightleftharpoons A + H^+ \quad (49)$$

for which the equilibrium constant is given by the following expression:

$$K_{\text{AH}} = \frac{[H^+][A]}{[\text{AH}^+]} \quad (50)$$

where \([H^+]\) is the hydrogen ion concentration, \([A]\) is the concentration of free amine, and \([\text{AH}^+]\) is the concentration of amine salt. In the terminology used in the calculation of the formation curves we may rewrite equation (50) in the following form:

$$K_{\text{AH}} = \frac{[H^+]}{C_H} (C_A - C_H) \quad (51)$$

where \(C_A\) is the total concentration of amine, and \(C_H\) is the total acid concentration. If we substitute \(n = \frac{C_H}{C_A}\) into equation (51) we obtain the expression:

$$pK_{\text{AH}} = -\log [H^+] + \log \frac{n}{1-n} \quad (52)$$

This expression is least accurate at \(n\) values near unity. In this study the validity of equation (52) was checked by making four determinations of \(pK_{\text{AH}}\) for each amine, spread over a reasonably wide range...
of amine concentrations. The highest value of \( n \) reported is 0.944 and only three values are over 0.9. No consistent deviations were noted in the systems studied.

In Tables XII - XXXV in the Appendix, which report the results of the determinations of the acid dissociation constants of the amines in 50 mole % ethanol-water, \( C_i \) represents the initial concentration of acid and neutral salt before addition of the amine, and is given at the top of the table together with the weight percent of amine in the added amine solution and the density of the solution where this was necessary. In the columns, \( W_A \) represents the weight in grams of pure amine added to 50 ml. of acid-neutral salt solution, \( V_A \) represents the volume in milliliters of the amine added, \( C_H \) represents the final total concentration of nitric acid in moles per liter, \( C_A \) represents the final total amine concentration in moles per liter, and \( pH \) is the observed meter reading. The \( pK_{AH} \) values in the last column were calculated using equation (52), assuming that the meter reading is equal to \(-\log [H^+]\). The validity of this assumption will be examined later. In cases where an amine solution was used, a column headed \( W_S \) is included which gives the weight in grams of solution added, and \( V_S \) gives the volume in milliliters of this added solution. The total volume of the solution is given by \( V_A + 50.00 \text{ ml.} \) (or by \( V_S + 50.00 \text{ ml.} \)) and is used to calculate \( C_H \) and \( C_A \).

A summary of the acid dissociation constants obtained in this study is presented in Table II together with values obtained for these amines in water solution by other investigators. The number preceding each amine in Table II corresponds to that given in the lists of
Table II
The Acid Dissociation Constants of Amines at 25°C in 50 mole % Ethanol-Water

<table>
<thead>
<tr>
<th>No.</th>
<th>Amine</th>
<th>pK$_{AH}$ (this study)</th>
<th>pK$_{AH}$ (water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2,6-xylidine</td>
<td>3.62</td>
<td>4.39$^a$</td>
</tr>
<tr>
<td>2</td>
<td>aniline</td>
<td>4.42</td>
<td>4.62$^b$</td>
</tr>
<tr>
<td>3</td>
<td>ethanolamine</td>
<td>9.34</td>
<td>9.74$^c$</td>
</tr>
<tr>
<td>4</td>
<td>t-octylamine</td>
<td>9.92</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>t-butylamine</td>
<td>10.24</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>p-anisidine</td>
<td>5.39</td>
<td>5.29$^b$</td>
</tr>
<tr>
<td>7</td>
<td>morpholine</td>
<td>8.36</td>
<td>8.70$^o$</td>
</tr>
<tr>
<td>8</td>
<td>di-sec-butylamine</td>
<td>10.00</td>
<td>11.31$^b$</td>
</tr>
<tr>
<td>9</td>
<td>di-n-butylamine</td>
<td>10.08</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>decahydroquinoline</td>
<td>10.20</td>
<td>11.16$^d$</td>
</tr>
<tr>
<td>11</td>
<td>diethylamine</td>
<td>10.36</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>dibenzylamine</td>
<td>8.09</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>diethanolamine</td>
<td>8.73</td>
<td>8.88$^b$</td>
</tr>
<tr>
<td>14</td>
<td>quinoline</td>
<td>3.78</td>
<td>4.92$^c$</td>
</tr>
<tr>
<td>15</td>
<td>pyridine</td>
<td>4.34</td>
<td>5.45$^c$</td>
</tr>
<tr>
<td>16</td>
<td>N-ethylmorpholine</td>
<td>7.35</td>
<td>7.35$^c$</td>
</tr>
<tr>
<td>17</td>
<td>tri-n-butylamine</td>
<td>9.16</td>
<td>9.33$^b$</td>
</tr>
<tr>
<td>18</td>
<td>triethylamine</td>
<td>9.73</td>
<td>10.75$^e$</td>
</tr>
<tr>
<td>19</td>
<td>triethanolamine</td>
<td>7.40</td>
<td>7.77$^b$</td>
</tr>
<tr>
<td>20</td>
<td>methyl-diethanolamine</td>
<td>8.28</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>diethyl-ethanolamine</td>
<td>9.18</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>diethyl-o-toluidine</td>
<td>6.06</td>
<td>7.18$^b$</td>
</tr>
<tr>
<td>23</td>
<td>diethyl-p-toluidine</td>
<td>5.14</td>
<td>7.09$^b$</td>
</tr>
<tr>
<td>24</td>
<td>N-ethylpiperidine</td>
<td>9.48</td>
<td>10.41$^b$</td>
</tr>
</tbody>
</table>

amines on pages x and xi and will be used to identify the amine and its silver complex in all subsequent figures and tables.

B. Formation Constants of the Silver Ammines

The formation curves of the silver ammine complexes were determined from glass electrode measurements on 50 ml. samples of solutions of nitric acid, silver nitrate, lithium nitrate, and amine in 50 mole % ethanol-water. The results of these measurements are presented in Tables XXXVI - LVI in the Appendix. The initial concentrations, $C_i$, of acid, silver salt, and neutral salt are given at the top of each table. The columns headed $W_A$, $W_S$, $V_A$, $V_S$, $C_H$, $C_A$ and $pH$ have the same significance as in the tables for the acid dissociation constants. The column headed $C_{Ag}$ represents the final concentration in moles per liter of the silver ion. The values of $\alpha_A$ and $\bar{n}_A$ were calculated from the $pH$ values and $pK_{AH}$ of the amine, and in the last two columns are the values of $\bar{n}$ and $p[A]$ calculated from $\alpha_A$, $\bar{n}_A$, $C_H$, $C_A$ and $C_{Ag}$ according to the method outlined in the introductory section. The formation curves in Figures 7 - 14 in the Appendix were plotted from these values of $\bar{n}$ and $p[A]$. The figure which contains the formation curve of each amine is indicated at the bottom of the table.

Table LVI contains the data and calculations for diethyl-o-toluidine. In place of the column for $\bar{n}$ is one headed $C_H/\bar{n}_A$. Examination of equations (26) and (29) shows that this quantity must be subtracted from the value of $C_A$ in calculating $\bar{n}$. From inspection of the corresponding values of these two quantities in the table, it
is evident that \( \bar{n} \) will have a small negative value at all amine concentrations used. If there were no complex formation with silver ion, the values of \( \bar{n} \) should be zero at all amine concentrations. While a negative value of \( \bar{n} \) has no physical meaning, it would appear at least, that no complexing has occurred in this case, although the amine concentrations covered nearly the entire range used for the other amines, several of which have much lower basic strengths.

Diethyl-p-toluidine reduced silver ion rapidly in solution, as did p-anisidine. N-ethylpiperidine precipitated silver oxide even at low amine and silver ion concentrations. Therefore, no measurements of silver complex formation could be made for these three amines.

The consecutive formation constants of each silver ammine complex were calculated by both of the methods outlined in Section I, part D: (1) from the values of \( p[A] \) and the slope of the formation curve at \( \bar{n}=1 \), and (2) from the values of \( p[A] \) at \( \bar{n}=0.5 \) and \( \bar{n}=1.5 \) substituted into equation (46).

As a check on the calculations, the formation constants, calculated by the second method, and several experimental values of \( p[A] \) were used to calculate corresponding values of \( \bar{n} \) using equation (36). These calculated points are given at the bottom of each table for comparison with the experimentally determined values. In nearly all cases in which the calculated values of \( \bar{n} \) differ by more than .01-.02 from the experimental values, the calculated points are observed to lie nearer to the formation curve.
Table III summarizes the results of the calculations of the consecutive formation constants and complexity constants obtained in this study. In this table, gives the midpoint slope of the formation curve multiplied by $-0.4343$; $\log k = p [A]_{n=1}$ is the logarithm of the average constant of the system; $\log k_1$ is the logarithm of the formation constant for the addition of the first amine molecule; $\log k_2$ is the logarithm of the formation constant for the addition of the second amine molecule; $\log K_2 = \log k_1 + \log k_2$ is the logarithm of the overall complexity constant; and $pK_{AH}$ is the exponent of the acid dissociation constant repeated from Table II. The first value for each amine under the headings $\log k_1$, $\log k_2$, and $\log K_2$ is that calculated by method (1) above; the value beneath it is that calculated by method (2).
Table III

The Consecutive Formation Constants and Complexity Constants of Silver Ammonia at 25°C

<table>
<thead>
<tr>
<th>No.</th>
<th>Amine</th>
<th>$\Delta$</th>
<th>$x$</th>
<th>log $k$</th>
<th>log $k_1$</th>
<th>log $k_2$</th>
<th>log $k_1/k_2$</th>
<th>$pK_{AH}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2,6-xylidine</td>
<td>0.630</td>
<td>0.588</td>
<td>1.40</td>
<td>1.47</td>
<td>1.33</td>
<td>2.80</td>
<td>+.16</td>
</tr>
<tr>
<td>2</td>
<td>aniline</td>
<td>0.695</td>
<td>0.439</td>
<td>1.44</td>
<td>1.38</td>
<td>1.50</td>
<td>2.88</td>
<td>-0.07</td>
</tr>
<tr>
<td>3</td>
<td>ethanolamine</td>
<td>0.797</td>
<td>0.255</td>
<td>3.70</td>
<td>3.41</td>
<td>3.99</td>
<td>7.40</td>
<td>-0.31</td>
</tr>
<tr>
<td>4</td>
<td>t-octylamine</td>
<td>0.695</td>
<td>0.439</td>
<td>4.08</td>
<td>4.02</td>
<td>4.14</td>
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<td>5</td>
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<td>2.94</td>
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<td>0.736</td>
<td>0.359</td>
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<td>3.42</td>
<td>6.56</td>
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<tr>
<td>No.</td>
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<td>$\Delta$</td>
<td>$x$</td>
<td>log $k$</td>
<td>log $k_1$</td>
<td>log $k_2$</td>
<td>log $k_1/k_2$</td>
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<tr>
<td>12</td>
<td>dibenzylamine</td>
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<td>.220</td>
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<td>1.97</td>
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<td></td>
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<td></td>
<td>-.23</td>
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<td>pyridine</td>
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<td>.404</td>
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<td>1.87</td>
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<td></td>
<td>-.21</td>
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<tr>
<td>16</td>
<td>N-ethylmorpholine</td>
<td>.356</td>
<td>1.809</td>
<td>1.51</td>
<td>2.07</td>
<td>.95</td>
<td>3.02</td>
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<td>2.11</td>
<td>.86</td>
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<td></td>
<td></td>
<td>+1.25</td>
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</tr>
<tr>
<td>17</td>
<td>tri-n-buty1amine</td>
<td>.496</td>
<td>1.020</td>
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<td>1.60</td>
<td>3.82</td>
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<td>2.25*</td>
<td>1.53*</td>
<td>3.78*</td>
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<td>18</td>
<td>triethylamine</td>
<td>.517</td>
<td>.934</td>
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<td>2.31</td>
<td>1.79</td>
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<td>2.33*</td>
<td>1.76*</td>
<td>4.09*</td>
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<td>triethanolamine</td>
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<td>1.72</td>
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<td>2.74</td>
<td>1.78</td>
<td>4.52</td>
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<td></td>
<td>+.96</td>
<td></td>
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<tr>
<td>20</td>
<td>methyl-diethanolamine</td>
<td>.565</td>
<td>.761</td>
<td>2.59</td>
<td>2.77</td>
<td>2.41</td>
<td>5.18</td>
<td>8.28</td>
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<td>2.80</td>
<td>2.43</td>
<td>5.23</td>
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</tr>
<tr>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td>+.37</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>diethyl-ethanolamine</td>
<td>.625</td>
<td>.600</td>
<td>2.50</td>
<td>2.58</td>
<td>2.42</td>
<td>5.00</td>
<td>9.18</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>2.57</td>
<td>2.42</td>
<td>4.99</td>
<td></td>
</tr>
</tbody>
</table>

* Calculated from values of $p[A]$ at $\bar{M} = 0.4$ and $\bar{M} = 0.8$. 
A. Acid Dissociation Constants of the Amines

Examination of Table II shows that with one exception the $pK_{AH}$ values of the amines in 50 mole % ethanol-water found in this study are smaller than the corresponding values obtained in water solution by other investigators. These data are plotted in Figure 3. The broken line represents equal values of $K_{AH}$ in both solvents. The solid line is drawn with unit slope and is displaced downward from the broken line by 0.7 of a logarithmic unit. This is in agreement with the results of Michaelis and Mizutani for ammonia and various amines in ethanol-water mixtures. They measured the dissociation constants of the cations of ammonia and several amines in 20, 40, 60, and 80 volume % ethanol-water mixtures and report values of the difference between the $pK_{AH}$ in the alcoholic solutions and in water solution. All these differences are negative, i.e., the $pK_{AH}$ values are lower in the alcoholic solutions, and they increase as the percentage of alcohol increases. In Table IV below are given their results for 80 volume % ethanol-water (approximately 50 mole %) together with a similar treatment of the data of this study taken from Table II. The lower values of $pK_{AH}$ mean that these amines are weaker bases in ethanol-water than they are in pure water. In both investigations the decrease in $pK_{AH}$ in going from water to 50 mole % ethanol-water is least for the primary amines and greatest.

Table IV

Comparison of the Relative Acid Strengths of Substituted Ammonium Ions in Water and in 50 mole % Ethanol-Water

<table>
<thead>
<tr>
<th>Amine</th>
<th>ΔpK_{AH}*</th>
<th>Amine</th>
<th>ΔpK_{AH}*</th>
</tr>
</thead>
<tbody>
<tr>
<td>ammonia</td>
<td>-0.48</td>
<td>(1) 2.6-xylidine</td>
<td>-0.77</td>
</tr>
<tr>
<td>methylamine</td>
<td>-0.85</td>
<td>(2) aniline</td>
<td>-0.20</td>
</tr>
<tr>
<td>ethylamine</td>
<td>-0.70</td>
<td>(3) ethanolamine</td>
<td>-0.40</td>
</tr>
<tr>
<td>aniline</td>
<td>-0.52</td>
<td>(6) p-anisidine</td>
<td>+0.10</td>
</tr>
<tr>
<td>o-toluidine</td>
<td>-0.53</td>
<td>(7) morpholine</td>
<td>-0.34</td>
</tr>
<tr>
<td>m-toluidine</td>
<td>-0.55</td>
<td>(9) di-n-butylamine</td>
<td>-1.23</td>
</tr>
<tr>
<td>dimethylamine</td>
<td>-1.00</td>
<td>(11) diethylamine</td>
<td>-0.80</td>
</tr>
<tr>
<td>methylaniline</td>
<td>-1.09</td>
<td>(13) diethanolamine</td>
<td>-0.15</td>
</tr>
<tr>
<td>trimethylamine</td>
<td>-1.25</td>
<td>(14) quinoline</td>
<td>-1.14</td>
</tr>
<tr>
<td>dimethylaniline</td>
<td>-1.39</td>
<td>(15) pyridine</td>
<td>-1.21</td>
</tr>
<tr>
<td>pyridine</td>
<td>-1.27</td>
<td>(17) tri-n-butylamine</td>
<td>-0.77</td>
</tr>
<tr>
<td></td>
<td>Ave. = -0.9</td>
<td>(18) triethylamine</td>
<td>-1.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(19) triethanolamine</td>
<td>-0.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(22) diethyl-o-toluidine</td>
<td>-1.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(23) diethyl-p-toluidine</td>
<td>-0.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(24) N-ethylpiperidine</td>
<td>-0.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ave. = -0.7</td>
<td></td>
</tr>
</tbody>
</table>

*ΔpK_{AH} = pK_{AH}(alcohol) - pK_{AH}(water)
Figure 3. $pK_{AH}$ in 50 mole % ethanol-water vs. $pK_{AH}$ in water. Primary amines O, secondary amines q, tertiary amines @.
for the tertiary amines. It is interesting to note that those compounds for which the decrease is less than the average for the class, each contain one or more alcohol or ether groups. These compounds include p-anisidine (6) in the primary amines, morpholine (7) and diethanolamine (13) in the secondary amines, and triethanolamine (19) in the tertiary amines. Since their $pK_{AH}$ values are lowered less than those of the other amines, these oxygen-containing amines are relatively stronger bases in 50 mole % ethanol-water. No oxygen-containing amines were included in the work of Michaelis and Mizutani. This may account for the higher average difference they obtained (0.9 as compared with 0.7).

If the Born equation for an activity coefficient

$$\ln f = \frac{Z^2 \varepsilon^2}{2DkT \epsilon}$$  \hspace{1cm} (53)

is applied to the acid dissociation constant of a monovalent cation acid,

$$K_{AH} = \frac{[H^+] [A]}{[AH^+]}$$  \hspace{1cm} (54)

it is evident that, if all ionic radii are assumed to be equal, a change to a medium of different dielectric constant should produce no change in the value of $K_{AH}$. The fact that a change is observed in going from water to 50 mole % ethanol-water shows that the Born equation is not entirely adequate to explain the effect of a change in the medium on ionic equilibria.
Schaefgen, Newman, and Verhoek\(^48\) have determined the thermodynamic basic ionization constants, \(K_B\), for butylamine, piperidine, and triethylamine in absolute methanol by an indicator method. They find \(pK_B\) values of these amines to be higher in methanol than in water, \(\Delta pK_B\) being 1.68 for butylamine, 2.20 for piperidine, and 2.87 for triethylamine. Thus, as in the present study, the amines are observed to be weaker bases in alcoholic solutions than in water, and the decrease in basic strength is least for the primary amine and greatest for the tertiary amine. The basic ionization constants measured by Schaefgen are for the equilibrium

\[
B + CH_3CH \rightleftharpoons BH^+ + CH_3O^- \tag{55}
\]

which is of a different ionic type from that for the acid dissociation constants reported in this work. Therefore, it is probably not valid to compare these studies except for the relative differences between primary, secondary, and tertiary amines.

B. Silver Ammine Complexes

The formation curves for the silver ion complexes show that, under the experimental conditions used here, each silver ion coordinates a maximum of two amine molecules. This is evident from the leveling off of the curves at values of \(\bar{n}=2\), in all cases in which the data were obtained at sufficiently high amine concentrations. There is no reason to suppose that the remaining amines would behave differently.

A comparison of the values of the overall complexity constants and the ratios of the consecutive formation constants obtained in this study with those reported by other investigators is presented in Table V. Only the data of Larsson are for 50 mole % ethanol-water, and the agreement in \( \log K_2 \) is seen to be fair for the three amines common to both studies. Considerable variation is noted, however, in the comparison with values of \( \log K_2 \) and \( \log k_1/k_2 \) obtained in water solution. The largest differences in \( \log K_2 \) are for morpholine(7) and the ethanol-amines, and in \( \log k_1/k_2 \) for morpholine(7) and diethylamine(11).

There are differences in the ionic strengths used by the various investigators. Larsson's work was done in solutions having ionic strengths of 0.02 and 0.008. Verhoek and coworkers and Bjerrum and coworkers maintained ionic strengths of about 0.5 through the use of neutral salt. The measurements of Vosburgh and Cogswell were made on solutions in which the ionic strength varied from approximately 0.001 to 0.02. Britton and Williams obtained values of complexity constants from solutions in which the ionic strength ranged from 0.002 to 0.79. However, ionic strength has been shown to have only slight effect on the values of these constants. For the complex between ammonia and silver ion, Bjerrum\(^{49}\) found the value of \( \log K_2 \) to be 7.05 in 0.5N \( \text{NH}_4\text{NO}_3 \), 7.03 in 2N \( \text{NH}_4\text{NO}_3 \), and 6.96 in 5.0N \( \text{NH}_4\text{NO}_3 \) at 30°C. Vosburgh and Cogswell observed a decrease of 0.06 unit of \( \log K_2 \) for pyridine in going from 0.001

### Table V

Comparison of Complexity Constants and Successive Formation Constants Obtained in this Study with those of Other Investigators

<table>
<thead>
<tr>
<th>Amine</th>
<th>(This study)</th>
<th>(Other Investigators)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>log $K_2$</td>
<td>log $k_1/k_2$</td>
</tr>
<tr>
<td>(2) aniline</td>
<td>2.91</td>
<td></td>
</tr>
<tr>
<td>(3) ethanolamine</td>
<td>7.41</td>
<td>-0.31</td>
</tr>
<tr>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(7) morpholine</td>
<td>5.47</td>
<td>+0.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(11) diethylamine</td>
<td>6.44</td>
<td>+0.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
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</tr>
<tr>
<td>(13) diethanolamine</td>
<td>6.51</td>
<td>-0.12</td>
</tr>
<tr>
<td>(14) quinoline</td>
<td>3.71</td>
<td></td>
</tr>
<tr>
<td>(15) pyridine</td>
<td>3.93</td>
<td>-0.21</td>
</tr>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(18) triethylamine</td>
<td>4.09</td>
<td>+0.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(19) triethanolamine</td>
<td>4.52</td>
<td>+0.96</td>
</tr>
<tr>
<td></td>
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</tr>
</tbody>
</table>

\textsuperscript{a} E. Larsson, Z. physik. Chem., A 169, 207 (1934).
\textsuperscript{f} W. C. Vosburgh and S. A. Cogswell, J. Am. Chem. Soc., 65, 2412 (1943).
to 0.02 ionic strength, which they attribute, however, to the in-crease in the free pyridine concentration in the solutions.

It has been pointed out in the Introduction that silver ion may be considered a Lewis acid since it is an electron-pair acceptor. Since hydrogen ion is also a Lewis acid, the equilibrium constants for the formation of silver complexes with amines and for the formation of substituted ammonium ions could be considered measures of the relative basicities of the amines. Barring any special effects such as steric hindrance due to the acid or amine, or steric strain in the amine molecules, the relative basicities of the amines with hydrogen ion as a reference acid should be in the same order as the relative basicities with respect to silver ion as a reference acid. For a comparison of the order of relative basic strengths of the amines used in this study, the values of log $K_2$ and log $K_1$ for silver amines in 50 mole % ethanol-water at 25°C have been plotted against the values of $pK_{AH}$ for the amines in 50 mole % ethanol-water at 25°C.

The plot of the logarithm of the complexity constant ($\log K_2$) against $pK_{AH}$ appears in Figure 4. Larger values of $\log K_2$ and $pK_{AH}$ mean greater basic strength for the amine. It can be seen that the primary amines give a fairly good straight line relationship. The slope of this line is 0.89. Thus the relationship between the acid dissociation constants of these amines and the complexity constants of the corresponding silver amines may be represented by $K_2 = c_1 K_{AH}^{-0.89}$, where $c_1$ is a constant. The unsaturated heterocyclic
Figure 4. Silver ammines in 50 mole % ethanol-water: log $K_2$ vs. $pK_{AH}$ at 25°C.
Primary amines $O$, secondary amines $\bullet$, tertiary amines $\Phi$. 
tertiary amines, quinoline(14) and pyridine(15), also seem to fall near this line, a fact which was observed in aqueous solution by Bruehlman and Verhoek\textsuperscript{50}.

The secondary aliphatic and heterocyclic amines fall roughly on a straight line displaced downward from that of the primary amines. The displacement is equivalent to about 1 to 1.5 units of log K\textsubscript{2}, indicating that the secondary amine complexes are about 10-30 times less stable than the complexes of primary amines of the same basic strengths toward hydrogen ion. Exceptions are dibenzylamine(12) and diethanolamine(13), which form complexes that are about as stable as primary amines. Bruehlman and Verhoek noted that the benzylamine-silver complex was appreciably more stable than that for other primary amines of comparable basic strength in water. Apparently benzylamines form stronger silver complexes than other amines in their respective classes. This suggested the use of tribenzylamine to see whether this amine would show a similar increase in complex-forming power over the other tertiary amines. However, tribenzylamine was too insoluble in 50 mole % ethanol-water to make measurements possible.

The slope of the line drawn for secondary amines is 0.65, which gives the relationship between the acid dissociation constants and the complexity constants of the silver ammines as K\textsubscript{2} = c\textsubscript{2}K\textsubscript{AH}^{0.65}, where c\textsubscript{2} is a constant.

The saturated tertiary amines, except for the ethanol-amines, fall on a third straight line displaced downward from that of the secondary amines by about 2 units of log K\textsubscript{2}. This indicates that

\textsuperscript{50} R. J. Bruehlman and F. H. Verhoek, J. Am. Chem. Soc., 70, 1401 (1948).
these tertiary amine complexes are about 100 times less stable than
the complexes of secondary amines of the same basic strength toward
hydrogen ion. The slope of the line is 0.45, giving the relation­
ship \( K_2 = c_3 k_{\text{AH}}^{0.45} \), where \( c_3 \) is a constant.

Thus, additional evidence has been obtained in support of the
conclusion reached by Britton and Williams and by Bruehlman and Verhoek,
that for amines of the same basic strength, the stabilities of the
silver complexes decrease in the order: primary > secondary > tertiary.
However, important exceptions to this rule are evident: the unsaturated
heterocyclic tertiary amines form silver complexes of comparable
stability to those of primary amines of the same basic strength; and
the secondary and tertiary ethanol-amine complexes are considerably
more stable than those of other amines in their respective classes—
diethanolamine-silver(13) having nearly the stability expected for a
primary amine complex and the silver complexes of triethanolamine(19),
methyl-diethanolamine(20), and diethyl-ethanolamine(21) having
stabilities approximating those of secondary amine complexes.
Bruehlman made enough preliminary measurements to lead him to
suggest that the silver complex with triethanolamine was more stable
than that of other tertiary amines. The value reported for this com­
plex in water solution by Bjerrum (see Table V) is indeed higher than
would be expected for a tertiary amine of its relatively low basic
strength. The value obtained in this work in 50 mole % ethanol-
water is even higher. Evidently, the presence of OH groups in the
molecule gives triethanolamine (and the other tertiary and secondary

51 R. J. Bruehlman, Ph.D. Dissertation, The Ohio State University
(1946).
ethanol-amines) additional complexing power with silver ions in both solvents, possibly by acting as weak Lewis base centers and donating electron pairs to the silver ions. A part, however, of the extra stability exhibited by these ethanol-amine complexes in 50 mole % ethanol-water seems to be attributable to the solvent, since these amines are also the ones whose $pK_{AH}$ values were lowered to a smaller extent in changing from water to 50 mole % ethanol-water. In other words, the secondary and tertiary ethanol-amines are relatively stronger bases toward both silver ion and hydrogen ion in 50 mole % ethanol-water.

In this connection, it should be mentioned that morpholine(7) was one of the amines showing a smaller-than-average decrease in $pK_{AH}$ in going from water to 50 mole % ethanol-water. If this relatively greater basic strength were also exhibited toward silver ion, it would mean that the line for secondary amines in Figure 4 should be drawn below this point. Unfortunately, the morpholine value was used to determine the position of the line, because no other suitable amine in this region could be found and because it had been similarly used by Bruehlman and Verhoek.

The explanation offered above for the added stability of the silver complexes of secondary and tertiary ethanol-amines over alkyl amine complexes is not very satisfactory since it would apply to hydrogen ion as well as silver ion, and does not explain why the value for $\log K_2$ of the silver complex of the primary member of the group, ethanolamine(3), does not lie above the line for primary amines.
Carlson, McReynolds, and Verhoek\textsuperscript{52}, on the basis of meager data, suggested that possibly a better relationship might be obtained between the constant for the addition of the first amine molecule ($k_1$) and the acid dissociation constant of the amine. Bruehlman and Verhoek, however, found that, because the two consecutive constants for any amine are so nearly equal ($\log k_1 \approx \log k_2 = \frac{1}{2} \log k_2$), a plot of $\log k_1$ or $\log k_2$ against $pK_{AH}$ for their data in water solution revealed essentially the same relationships among the amines as did the plot of $\log K_2$ against $pK_{AH}$. That this is also true for the present study may be seen by referring to Figure 5, which is a plot of $\log k_1$ against $pK_{AH}$, using data obtained in 50 mole % ethanol-water. The values of $\log k_1$ for secondary amines lie below those for primary amines, and the values for tertiary amines below those for secondary amines, with the tertiary ethanol-amines again showing higher stabilities. Several differences may be noted in the two plots, however. The secondary amines all lie closer to a single straight line than was the case for the plot using $\log K_2$. Also, the line for the tertiary amines can be extended (perhaps fortuitously) to include the unsaturated tertiary heterocyclic amines. The point for diethyl-ethanolamine(21) is observed to lie noticeably nearer the line drawn for tertiary amines than do the points for methyl-diethanolamine(20) and triethanolamine(19). Evidently, as the number of ethanol groups in a tertiary amine is increased, the stability of the silver complex is increased, even though the basic strength toward hydrogen ion decreases.

Figure 5. Silver ammines in 50 mole % ethanol-water: log $k_1$ vs. $pK_{AH}$ at 25°C.
Primary amines $O$, secondary amines $\bullet$, tertiary amines $\Theta$. 
Perhaps the greatest difference between the results of this study and the work of Bruehlman and Verhoek is to be found in the relative magnitudes of the two consecutive formation constants for each amine. Reference to Table I will show that for all the amines studied by Bruehlman and Verhoek in water solution the constant for the addition of the first amine molecule to silver ion \( k_1 \) is smaller than the constant for the addition of the second amine molecule \( k_2 \). On the other hand, more than half of the complexes studied in the present work have \( k_1 \gg k_2 \). This is shown graphically in Figure 6, in which values of \( \log k_1 \) are plotted against the corresponding values of \( \log k_2 \). The straight line represents equal values of \( k_1 \) and \( k_2 \). All points above this line are for complexes having \( k_1 \gg k_2 \), while for those points below the line \( k_1 < k_2 \).

Of the tertiary amines, only pyridine(15) and quinoline(14) lie below the line. Since pyridine and its homologs were the only tertiary amines whose complex formation constants with silver ion were measured by Bruehlman and Verhoek, this accounts in part for the absence of any cases in their work in which \( k_1 \gg k_2 \).

In addition to the tertiary amines, one primary amine, 2,6-xylidine(1), and four secondary amines, morpholine(7), di-sec-butylamine(8), decahydroquinoline(10), and diethylamine(11), were found to have \( k_1 \gg k_2 \). As was pointed out in the introductory section, if statistical effects only are considered, the consecutive constants of any complex should become successively smaller.

Bjerrum, in his review paper\(^{53}\), shows that this is true for the

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Figure 6. Silver ammines in 50 mole % ethanol-water: log $k_1$ vs. log $k_2$ at 25°C.

Primary amines $\bigcirc$, secondary amines $\bullet$, tertiary amines $\oplus$
complexes of most metal ions with a variety of ligands, but that for the complexes of silver ion with ammonia and most of the simpler amines, the value of \( k_1/k_2 \) is less than unity. It must, therefore, be considered "normal" for the silver ammines to have \( k_1 < k_2 \). No satisfactory explanation has ever been given for this anomaly. It appears that in the case of silver ion after the first amine molecule has been coordinated, presumably by displacing a solvent molecule, the second amine molecule coordinates more readily. Possibly this is due to instability of a complex consisting of one solvent molecule and one amine molecule, relative to one containing two amine molecules. Whatever the reason, it has been suggested\(^{54,55}\) that an unusually high ratio of \( k_1/k_2 \) for a metal complex might be interpreted in terms of the steric requirements of the ligand.

In comparing 2,6-xylidine(1) with aniline(2), we find that although the basic strength and complexity constant for 2,6-xylidine are smaller than those for aniline, the second amine molecule is added with relatively greater difficulty in the case of the xylidine. A possible explanation might lie in interference between the ortho methyl groups on the two amine molecules.

The interference of relatively large groups might lessen the probability of a tertiary aliphatic amine approaching close enough to the solvated silver ion to replace one of the solvent molecules, thus lowering the value of \( k_1 \) for the tertiary amine relative to amines of smaller size. After the first such amine molecule had

been added, its bulk would increase the size of the coordinated silver ion, thus lowering still further the probability that a second amine molecule would coordinate. Such a picture is consistent with the large values of $k_1/k_2$ found for the tertiary aliphatic amines. The presence of the less space-requiring ring structures of pyridine and quinoline could then account for their more "normal" behavior.

This picture is much less satisfying when applied to the secondary amines. The branching on the carbon adjacent to the nitrogen atom in di-sec-butylamine(8) might account for the larger value of $k_1/k_2$ for this amine complex than for that of di-$n$-butylamine(9), but it is difficult to explain on the basis of steric interference why diethylamine-silver(11) should have a higher $k_1/k_2$ ratio than di-$n$-butylamine-silver(9).

C. The pH Scale in 50 Mole % Ethanol-Water

The values of $[H^+]$ necessary for the calculations of the acid dissociation constants and the silver ammine formation constants have been obtained on the assumption that the meter reading $B$, recorded in Tables XII - LVI as pH, is equal to $-\log [H^+]$. In other words, we have assumed that $B = \text{pH} = -\log [H^+]$. To examine the validity of these assumptions we will now consider the results of the potentiometric and spectrophotometric measurements made to calibrate the glass electrode.

1. Results of Potentiometric Measurements

A summary of the results obtained from the hydrogen electrode measurements is given in Table VII. Solution 1 was the reference
0.00100M HCl solution, solution 2 was an aniline buffer, solution 3 was a diethyl-o-toluidine buffer, and solution 4 was a triethanolamine buffer.

**Table VI**

Potentiometric Measurements for Calibration of the Glass Electrode

<table>
<thead>
<tr>
<th>Solution</th>
<th>WA</th>
<th>B</th>
<th>Cell</th>
<th>E.M.F. (mv.)</th>
<th>pH</th>
<th>log (U^0_H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.37</td>
</tr>
<tr>
<td>2</td>
<td>3.664</td>
<td>4.40</td>
<td>1-2</td>
<td>60.9</td>
<td>4.40</td>
<td>0.00</td>
</tr>
<tr>
<td>3</td>
<td>4.300</td>
<td>5.56</td>
<td>2-3</td>
<td>72.1</td>
<td>5.62</td>
<td>+0.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1-3</td>
<td>129.0</td>
<td>5.55</td>
<td>-0.01</td>
</tr>
<tr>
<td>4</td>
<td>3.782</td>
<td>6.81</td>
<td>3-4</td>
<td>77.0</td>
<td>6.85</td>
<td>+0.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1-4</td>
<td>204.5</td>
<td>6.83</td>
<td>+0.02</td>
</tr>
</tbody>
</table>

In the table \(W_A\) represents the weight of amine added to 200 ml. of acid-neutral salt solution, \(B\) represents the observed meter reading of the glass electrode-calomel electrode cell, and \(\log U^0_H\) is the correction to be applied to the meter reading (added if positive, subtracted if negative). The pair of solutions comprising the cell is given in column four, and the observed potential of the cell is given in column five. The pH values in column six were calculated from the Nernst equation

\[
E = \frac{RT}{nF} \ln \frac{a_1}{a_2}
\]  

(56)
which may be written

\[(\text{pH})_2 = (\text{pH})_1 + \frac{E}{0.0591}\]  \quad (57)

The value of \((\text{pH})_1\) in this equation is the pH of the hydrochloric acid solution for cells in which solution 1 was in one of the electrode compartments, or, in the other cases, that of the buffer whose pH had already been determined from a cell containing the hydrochloric acid solution.

The value of 3.37 for the pH of the 0.00100M HCl solution, upon which all the other pH values depend, was arrived at by using a value of 0.43 for the activity coefficient of hydrogen ion. This was obtained by graphical interpolation of the data of Harned and Owen \(^56\) for the mean activity coefficient of hydrochloric acid as a function of concentration in 50 mole \% ethanol-water, assuming that the activity coefficient of hydrochloric acid in a mixture of hydrochloric acid and lithium nitrate is the same as that for a solution containing hydrochloric acid alone at the same total concentration of electrolyte. The value 0.43 is valid for hydrochloric acid over the range from 0.35 M to 0.75 M.

If only the data for cells 1-2, 1-3, and 1-4, in which each buffer pH is determined directly in reference to the hydrochloric acid solution, are considered, the glass electrode appears to behave as a hydrogen electrode in these solutions, and the average correction term is 0.00. Greater deviations are noted for the pH values as determined from the cells having a buffer solution in both compartments. No satisfactory explanation of this discrepancy has been found.

2. Results of Spectrophotometric Measurements

The pH values of the five reference hydrochloric acid solutions used in the spectrophotometric experiments for calibration of the glass electrode, were obtained by making the same assumptions regarding the activity coefficients in the mixtures as were made in the potentiometric measurements. Table VII gives the pH values of these five solutions, using the value 0.43 for the activity coefficient of hydrogen ion, together with the pH meter reading, B, of the glass electrode-calomel electrode cell, in those cases in which this measurement was made. The concentration of hydrochloric acid is that calculated for the dilution produced by addition of the indicator solution.

Table VII

<table>
<thead>
<tr>
<th>[HCl]</th>
<th>pH</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00909</td>
<td>2.41</td>
<td>2.44</td>
</tr>
<tr>
<td>.00606</td>
<td>2.59</td>
<td></td>
</tr>
<tr>
<td>.00455</td>
<td>2.71</td>
<td>2.74</td>
</tr>
<tr>
<td>.00303</td>
<td>2.89</td>
<td>2.89</td>
</tr>
<tr>
<td>.00227</td>
<td>3.01</td>
<td>3.02</td>
</tr>
</tbody>
</table>

The hydrogen ion concentrations of these solutions were compared with those of quinoline-quinolinium buffers by spectrophotometric measurements using thymol blue as indicator. Table X in the Appendix gives the optical densities of four of these hydrochloric acid
solutions and quinoline buffer 1. Figure 15 in the Appendix is a plot of the optical density against the pH for the hydrochloric acid solutions at each wavelength, from which values of the pH of buffer 1 were read. Similar data and plots are given in Table XI and Figure 16 in the Appendix for all five hydrochloric acid solutions and buffers 2 and 3, using an indicator solution of slightly different concentration.

The results for the buffers used are presented in Table VIII. The pH values for each buffer as read from the plots of optical density against pH are given in columns two-six. Comparison of the average pH read from the curve, in column seven, with the glass electrode meter reading in column eight, yields the correction term, \( \log U_H^0 \), in column nine.

<table>
<thead>
<tr>
<th>Buffer</th>
<th>( \lambda (\text{nm}) )</th>
<th>550</th>
<th>560</th>
<th>570</th>
<th>580</th>
<th>590</th>
<th>Ave.</th>
<th>( B )</th>
<th>( \log U_H^0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-0.02</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-0.02</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-0.02</td>
</tr>
</tbody>
</table>

The value of \( \log U_H^0 \) by this method is, therefore, -0.02.

3. **Final Value of pH Meter Correction**

The average of the six values of the correction term \( \log U_H^0 \), three potentiometric and three spectrophotometric, is -0.01. Since
this is within the experimental error of the glass electrode measurements, no correction is necessary to convert pH meter readings into pH values, i.e. pH = B.

If we take the logarithm of both sides of equation (48), page 22, and rearrange, we have:

\[ \log U_H = \log U^0_H + \log \gamma \]

Therefore, \( \log U_H = \log 0.43 = -0.37 \) for the solvent composition and ionic strength used in this study. Hence from equation (47):

\[ -\log [H^+] = B - 0.37 \]

Thus, while it is true that the meter reading, B, is equal to pH, the assumption that \( B = -\log [H^+] \) is not correct.

It is obvious that the magnitude and sign of the correction term, \( \log U^0_H \), are determined, for the particular solvent composition and electrolyte concentration used, by the value of the activity coefficient of the hydrogen ion. The choice of the value 0.43 for this coefficient is supported by the work of Van Uitert and Haas in dioxane-water mixtures. They assume that to a first approximation there are no differences among the activity coefficients of the various ions of similar electrolytes in the same solvent and, therefore, one may use for the activity coefficient "any experimental activity coefficient, provided the coefficient for the appropriate solvent composition and total ionic concentration is selected". Treatment of their data on this basis led them to agreement with the data of other investigators from thermodynamic cell measurements. They conclude that "the agreement indicates support of the basic assumption, since the

activity coefficients used in the calculations were for HCl, whereas they are being applied to a mixed HCl-NaCl solute."

Table IX presents values of the correction term, log $U_H$, taken from their data for three total electrolyte concentrations.

Table IX

Log $U_H$ as a Function of Mixture Composition and Electrolyte Concentration (Data of Van Uitert and Haas).

<table>
<thead>
<tr>
<th>Mole Fraction</th>
<th>Total 1-1 Electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dioxane</td>
<td>.00586</td>
</tr>
<tr>
<td></td>
<td>.0172</td>
</tr>
<tr>
<td></td>
<td>.0312</td>
</tr>
<tr>
<td>.041</td>
<td>-0.01</td>
</tr>
<tr>
<td></td>
<td>-0.06</td>
</tr>
<tr>
<td></td>
<td>-0.08</td>
</tr>
<tr>
<td>.077</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>-0.06</td>
</tr>
<tr>
<td></td>
<td>-0.08</td>
</tr>
<tr>
<td>.174</td>
<td>+0.09</td>
</tr>
<tr>
<td></td>
<td>+0.02</td>
</tr>
<tr>
<td></td>
<td>-0.04</td>
</tr>
<tr>
<td>.199</td>
<td>+0.13</td>
</tr>
<tr>
<td></td>
<td>+0.04</td>
</tr>
<tr>
<td></td>
<td>0.00</td>
</tr>
<tr>
<td>.230</td>
<td>+0.19</td>
</tr>
<tr>
<td></td>
<td>+0.10</td>
</tr>
<tr>
<td></td>
<td>+0.04</td>
</tr>
<tr>
<td>.310</td>
<td>+0.38</td>
</tr>
<tr>
<td></td>
<td>+0.27</td>
</tr>
<tr>
<td></td>
<td>+0.19</td>
</tr>
<tr>
<td>.418</td>
<td>+0.70</td>
</tr>
<tr>
<td></td>
<td>+0.52</td>
</tr>
<tr>
<td></td>
<td>+0.42</td>
</tr>
</tbody>
</table>

At each ionic strength the value of log $U_H$ increases, passing from negative to positive, as the dioxane content of the solvent increases. For a given solvent composition the value of log $U_H$ becomes less positive as the ionic strength increases. In the solvents of lower dioxane content the value of the correction term is seen to pass through zero and become negative even within the relatively narrow range of ionic strengths used in their work. If the trend toward less positive values continues, log $U_H$ should
also become negative in the higher dioxane solvents at sufficiently high ionic strengths.

The work of Åkerlöf, Teare, and Turok\textsuperscript{58} shows that the validity of the above assumption about activity coefficients of hydrochloric acid depends upon the particular salt which is used. For 20, 30, 40, 50, and 60 weight \% methanol-water solutions of hydrochloric acid and sodium chloride in which the hydrochloric acid concentration was varied from 1 m to 0.1 m at a constant total electrolyte concentration of 1 m, they found that the activity coefficient of hydrochloric acid decreased linearly as the salt fraction of the electrolyte increased. This effect was independent of the solvent composition. The activity coefficients of sodium chloride are known to be lower than those of hydrochloric acid. With lithium chloride, whose activity coefficients are nearly the same as those of hydrochloric acid, they could detect no difference between the activity coefficient of pure hydrochloric acid solutions and the hydrochloric acid-lithium chloride mixtures, within the experimental error.

Since no actual experimental values of the coefficients of hydrochloric acid-lithium nitrate mixtures in 50 mole \% ethanol-water were available, it was decided that the use of the hydrochloric acid value was the best approximation that could be made.

We must now consider the effect on the values of equilibrium constants calculated in this study of the use of the incorrect assumption that \( B = -\log [H^+] \). The acid dissociation constants were calculated from the equation:

\[
pK_{AH} = -\log [H^+] + \log \frac{n}{1-n}
\]  

(60)

Since the last term in this equation is determined only by the stoichiometric composition of the solution, an error in \( -\log [H^+] \) will produce an exactly equal error in \( pK_{AH} \). If we represent the true \( pK_{AH} \) value by \( pK_{AH}' \) and the value reported in the tables in this study by \( pK_{AH}'' \), then we have

\[
pK_{AH}' = B - 0.37 + \log \frac{n}{1-n}
\]  

(61)

and

\[
pK_{AH}'' = B + \log \frac{n}{1-n}
\]  

(62)

Therefore, subtracting equation (62) from equation (61):

\[
pK_{AH}' = pK_{AH}'' - 0.37
\]  

(63)

Thus, the \( pK_{AH} \) values reported should all be reduced by 0.37, but this does not change the relative values of the basic strengths of the amines, since the experiments reported in this section as well as those of Van Uitert and Haas show that the correction is constant over the entire pH range.

The values of the formation constants of the silver complexes are determined by the values of \( n \) and \( p[A] \), which in turn are determined by the values of \( \alpha_A \) and \( n_A \) and the stoichiometric composition of the solutions. The expression for \( \alpha_A \) is:
Substituting the expression for $K_{AH}$ in equation (22) into (64), we have:

\[
\alpha_A = \frac{K_{AH}}{K_{AH} + [H^+]}
\]

(64)

If we represent the correct values of $[H^+]$ by $[H^+]'$, we may rewrite equation (59) as:

\[
[H^+]' = 10^{-(B-0.37)}
\]

(66)

Since we assumed that $B = -\log[H^+]$, the incorrect values of $[H^+]$, may be represented by:

\[
[H^+]'' = 10^{-B}
\]

(67)

Substitution of (66) and (67) into (65) gives the expressions for the correct and incorrect values of $\alpha_A$:

\[
\alpha'_A = \frac{10^{-(B-0.37)} \frac{[A]}{[AH^+]} + 10^{-(B-0.37)}}{10^{-(B-0.37)} \frac{[A]}{[AH^+]} + 10^{-(B-0.37)}}
\]

(68)

\[
\alpha''_A = \frac{10^{-B} \frac{[A]}{[AH^+]} + 10^{-B}}{10^{-B} \frac{[A]}{[AH^+]} + 10^{-B}}
\]

(69)

Equation (68) may be simplified:

\[
\alpha'_A = \frac{10^{0.37} \cdot 10^{-B} \frac{[A]}{[AH^+]} + 10^{-B} \frac{[A]}{[AH^+]} + 10^{-B}}{10^{0.37} \left(10^{-B} \frac{[A]}{[AH^+]} + 10^{-B} \right)}
\]

(70)
Comparison of equations (69) and (70) shows that $\alpha_A' = \alpha_A''$. A similar treatment can be used to show that $\overline{m}_A' = \overline{m}_A''$. In other words, there will be no difference in $\alpha_A'$ and $\overline{m}_A'$, and hence in $\overline{m}$ and $p[A]$ and the formation constants, whether a correction is applied to the meter reading or not, providing that the correction is a constant independent of the pH of the solution. Only if the correction is very large and is not applied or if the applied correction is greatly in error, will the formation curve be changed significantly, and then only in those cases where $[H^+]$ must be subtracted from $C_H$ to obtain $[AH^+]$ for calculation of $\overline{m}$ and $p[A]$ by equations (26) and (28). A check of the calculations for the four cases in this study in which this correction was necessary, shows that the difference of 0.37 in $-\log [H^+]$ makes no significant change in the formation curves.

Therefore, without applying the calibration correction, we have obtained the true values of the silver ammine formation constants and the correct relative values of the acid dissociation constants. The plots in Figures 3, 4, and 5 are correct if the scale for $pK_{AH}$ in 50 mole % ethanol-water is shifted by 0.37 logarithmic unit. Since Michaelis and Mizutani used hydrogen electrodes and calculated their constants using pH instead of $-\log [H^+]$, their acid dissociation constants are comparable to the uncorrected values reported in this study, and the comparisons previously made with their work are valid.
V. SUMMARY

(1) The response of the glass electrode to hydrogen ions in 50 mole % ethanol-water and at 0.525 M lithium nitrate concentration has been determined by potentiometric measurements with hydrogen electrodes and by spectrophotometric measurements using thymol blue as an indicator.

(2) The acid dissociation constants of 2,6-xylidine, aniline, ethanolamine, t-octylamine, t-butylamine, morpholine, di-sec-butylamine, di-n-butylamine, decahydroquinoline, diethylamine, dibenzylamine, diethanolamine, quinoline, pyridine, N-ethylmorpholine, tri-n-butylamine, triethylamine, triethanolamine, methyl-diethanolamine, diethyl-ethanolamine, diethyl-o-toluidine, diethyl-p-toluidine, p-anisidine, and N-ethylpiperidinedine were determined at 25°C in 50 mole % ethanol-water.

(3) The formation of complex silver ions with 2,6-xylidine, aniline, ethanolamine, t-octylamine, t-butylamine, morpholine, di-sec-butylamine, di-n-butylamine, decahydroquinoline, diethylamine, dibenzylamine, diethanolamine, quinoline, pyridine, N-ethylmorpholine, tri-n-butylamine, triethylamine, triethanolamine, methyl-diethanolamine, diethyl-ethanolamine, diethyl-o-toluidine was investigated at 25°C by glass electrode measurements on solutions containing known amounts of amine, silver ion, acid, and neutral salt in 50 mole % ethanol-water.

(4) The basic strengths of the amines toward hydrogen ion, as measured by $pK_{AH}$ values, were found to be lower in 50 mole % ethanol-water than in water solution. The average decrease was
least for the primary amines and greatest for the tertiary amines. Amines containing oxygen (as ether linkages or OH groups) were observed to have smaller decreases than other amines in their respective classes.

(5) The stabilities of the silver complexes of primary, secondary, and tertiary aliphatic amines of the same basic strength decrease in 50 mole % ethanol-water in the order primary > secondary > tertiary in agreement with the data of Britton and Williams,60 and Bruehlman and Verhoek61 for aqueous solutions. The primary aromatic amines, secondary heterocyclic amines, and N-substituted tertiary heterocyclic amines form complexes with silver ion which are, relative to their basic strengths, as stable as those of the primary, secondary, and tertiary aliphatic amines, respectively.

(6) The tertiary heterocyclic amines containing unsaturated nitrogen form complexes with silver in 50 mole % ethanol-water of relatively the same stability as those of primary amines of the same basic strength. This is in agreement with results obtained by Bruehlman and Verhoek in aqueous solution.

(7) Within the groups primary, secondary, and tertiary amines, relationships between the stabilities of the complexes and the acid dissociation constants of the amines were observed. Exceptions were dibenzylamine and diethanolamine for the secondary amines, and triethanolamine, methyl-diethanolamine,

and diethyl-ethanolamine for the tertiary amines, all of which formed relatively more stable complexes than other amines in their classes.*

(8) The ratio of the two consecutive formation constants, \( k_1/k_2 \), has been found to be greater than unity for 2,6-xylidine, morpholine, decahydroquinoline, di-sec-butylamine, diethylamine, and all the tertiary amines except pyridine and quinoline.
VI. SUGGESTIONS FOR FUTURE WORK

Before any further studies of this type are conducted, a more thorough effort should be made to clarify the behavior of the glass electrode in nonaqueous solvents containing high concentrations of salt. It would be necessary to approximate more closely the activity coefficients of strong acids in such solutions, and to determine the effect of variation in both solvent composition and ionic strength upon any correction to be applied to the meter readings.

The only tertiary aromatic amine whose solutions were satisfactory for investigation by the method used in this study, diethyl-o-toluidine, gave no evidence of complex formation, possibly due to steric effects. From its $pK_{AH}$ value of 6.06 it would be expected to have a log $K_2$ value of about 2.4. Therefore, it might be interesting to study other such amines, by other methods if necessary, to discover whether all tertiary aromatic amines fail to complex or whether this is an isolated case. Secondary aromatic amines should be investigated, since no suitable compounds of this type were found in this study.

Brown$^{62}$ observed steric hindrance in the stability of the complex between 2,6-lutidine and boron trifluoride or trimethyl boron and Bruehlman$^{63}$ found the silver complex of this amine insoluble in water. The use of ethanol-water as a solvent should make possible a measurement of the silver complex formation constants of 2,6-


$^{63}$ R. J. Bruehlman, Ph. D. Dissertation, The Ohio State University (1946).
lutidine and possibly throw additional light on steric effects in silver ammines.

The possibility that morpholine and N-ethylmorpholine, which were important in determining the positions and slopes of the lines for the plots of log $k_2$ and log $k_1$ vs. $pK_{AH}$ for secondary and tertiary amines respectively, may not be typical of their classes suggests the desirability of trying to find secondary and tertiary aliphatic amines in the $pK_{AH}$ range 7-8, and determining the constants for these amines in 50 mole % ethanol-water as a check on the correctness of the relationships represented by the lines as drawn.

The question as to whether the straight line relationship found in the plot of log $k_1$ vs $pK_{AH}$ for the unsaturated tertiary heterocyclic amines and the aliphatic tertiary amines is real or accidental might be decided by measuring log $k_1$ and $pK_{AH}$ for the picolines, lutidines, and other homologs of pyridine and quinoline in 50 mole % ethanol-water.

All the measurements of acid dissociation constants and silver complex formation constants of amines reported in this study were made at 25°C. Measurements of these constants at one or more different temperatures would allow calculation of changes in heat content and entropy, as well as the free energy changes for these reactions.
VII APPENDIX
Table X

Optical Densities of Hydrochloric Acid Solutions and Quinoline Buffer 1 Using First Thymol Blue Solution

<table>
<thead>
<tr>
<th>λ(μm)</th>
<th>[HCl] .00909</th>
<th>.00455</th>
<th>.00303</th>
<th>.00227</th>
<th>Buffer</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>.446</td>
<td>.262</td>
<td>.194</td>
<td>.146</td>
<td>0.260</td>
</tr>
<tr>
<td>560</td>
<td>.439</td>
<td>.248</td>
<td>.178</td>
<td>.134</td>
<td>.248</td>
</tr>
<tr>
<td>570</td>
<td>.343</td>
<td>.201</td>
<td>.142</td>
<td>.103</td>
<td>.200</td>
</tr>
<tr>
<td>580</td>
<td>.240</td>
<td>.139</td>
<td>.100</td>
<td>.073</td>
<td>.137</td>
</tr>
<tr>
<td>590</td>
<td>.142</td>
<td>.084</td>
<td>.063</td>
<td>.043</td>
<td>.082</td>
</tr>
</tbody>
</table>

Table XI

Optical Densities of Hydrochloric Acid Solutions and Quinoline Buffers 2 and 3 Using Second Thymol Blue Solution

<table>
<thead>
<tr>
<th>λ(μm)</th>
<th>[HCl] .00909</th>
<th>.00606</th>
<th>.00455</th>
<th>.00303</th>
<th>.00227</th>
<th>Buffer</th>
<th>Buffer</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>.450</td>
<td>.332</td>
<td>.272</td>
<td>.206</td>
<td>.166</td>
<td>.187</td>
<td>.387</td>
</tr>
<tr>
<td>560</td>
<td>.435</td>
<td>.320</td>
<td>.259</td>
<td>.193</td>
<td>.151</td>
<td>.177</td>
<td>.372</td>
</tr>
<tr>
<td>570</td>
<td>.355</td>
<td>.262</td>
<td>.212</td>
<td>.164</td>
<td>.125</td>
<td>.141</td>
<td>.304</td>
</tr>
<tr>
<td>580</td>
<td>.249</td>
<td>.184</td>
<td>.152</td>
<td>.111</td>
<td>.087</td>
<td>.098</td>
<td>.208</td>
</tr>
<tr>
<td>590</td>
<td>.154</td>
<td>.114</td>
<td>.095</td>
<td>.074</td>
<td>.055</td>
<td>.061</td>
<td>.126</td>
</tr>
</tbody>
</table>
Table XII

Acid Dissociation Constant of 2,6-Xylydine at 25°C.

\[
\begin{array}{cccccccc}
\text{Sol'n} & W_A & V_A & C_H & C_A & n & \log \frac{n}{1-n} & \text{pH} & \text{pK}_{AH} \\
1 & 1.126 & 1.149 & .0976 & .1817 & .557 & .06 & 3.56 & 3.62 \\
3 & .929 & .948 & .0979 & .1505 & .651 & .27 & 3.35 & 3.62 \\
4 & .780 & .796 & .0982 & .1267 & .775 & .54 & 3.08 & 3.62 \\
\text{Ave.} & & & & & & 3.62 & \\
\end{array}
\]

Table XIII

Acid Dissociation Constant of Aniline at 25°C.

\[
\begin{array}{cccccccc}
\text{Sol'n} & W_A & V_A & C_H & C_A & n & \log \frac{n}{1-n} & \text{pH} & \text{pK}_{AH} \\
2 & .915 & .895 & .0984 & .1931 & .510 & .02 & 4.40 & 4.42 \\
3 & .787 & .770 & .0987 & .1665 & .593 & .16 & 4.25 & 4.41 \\
4 & .622 & .609 & .0990 & .1320 & .750 & .48 & 3.94 & 4.42 \\
\text{Ave.} & & & & & & 4.42 & \\
\end{array}
\]
Table XIV

Acid Dissociation Constant of Ethanolamine at 25°C.

\[ \text{C}_1\text{HNO}_3 = .1002\text{M} \quad \text{C}_1\text{LiNO}_3 = .525\text{M} \]

<table>
<thead>
<tr>
<th>Sol'n</th>
<th>( W_A )</th>
<th>( V_A )</th>
<th>( C_H )</th>
<th>( C_A )</th>
<th>( \log \frac{n}{1-n} )</th>
<th>pH</th>
<th>( pK_{AH} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.466</td>
<td>.456</td>
<td>.0993</td>
<td>.1512</td>
<td>.657</td>
<td>9.04</td>
<td>9.32</td>
</tr>
<tr>
<td>2</td>
<td>.524</td>
<td>.513</td>
<td>.0992</td>
<td>.1698</td>
<td>.584</td>
<td>9.20</td>
<td>9.35</td>
</tr>
<tr>
<td>3</td>
<td>.401</td>
<td>.392</td>
<td>.0994</td>
<td>.1303</td>
<td>.763</td>
<td>8.82</td>
<td>9.35</td>
</tr>
<tr>
<td>4</td>
<td>.574</td>
<td>.562</td>
<td>.0991</td>
<td>.1859</td>
<td>.533</td>
<td>9.29</td>
<td>9.35</td>
</tr>
<tr>
<td>Ave.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9.34</td>
</tr>
</tbody>
</table>

Table XV

Acid Dissociation Constant of t-Octylamine at 25°C.

\[ \text{C}_1\text{HNO}_3 = .0995\text{M} \quad \text{C}_1\text{LiNO}_3 = .525\text{M} \]

<table>
<thead>
<tr>
<th>Sol'n</th>
<th>( W_A )</th>
<th>( V_A )</th>
<th>( C_H )</th>
<th>( C_A )</th>
<th>( \log \frac{n}{1-n} )</th>
<th>pH</th>
<th>( pK_{AH} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.908</td>
<td>1.149</td>
<td>.0976</td>
<td>.1374</td>
<td>.710</td>
<td>9.63</td>
<td>9.92</td>
</tr>
<tr>
<td>2</td>
<td>.684</td>
<td>.866</td>
<td>.0981</td>
<td>.1041</td>
<td>.943</td>
<td>8.68</td>
<td>9.89</td>
</tr>
<tr>
<td>3</td>
<td>.891</td>
<td>1.128</td>
<td>.0976</td>
<td>.1548</td>
<td>.724</td>
<td>9.51</td>
<td>9.93</td>
</tr>
<tr>
<td>4</td>
<td>.741</td>
<td>.938</td>
<td>.0980</td>
<td>.1126</td>
<td>.870</td>
<td>9.09</td>
<td>9.92</td>
</tr>
<tr>
<td>Ave.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9.92</td>
</tr>
</tbody>
</table>
Table XVI

Acid Dissociation Constant of t-Butylamine at 25°C.

\( C_1HNO_3 = .1002M \)
\( C_1LiNO_3 = .525M \)

Weight % amine in solution = 42.28
d\( d_{sol'n} = .801 \ g/ml \)

<table>
<thead>
<tr>
<th>Sol'n</th>
<th>( W_S )</th>
<th>( W_A )</th>
<th>( V_S )</th>
<th>( C_H )</th>
<th>( C_A )</th>
<th>( n \log \frac{n}{1-n} )</th>
<th>pH</th>
<th>( pK_{AH} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.028</td>
<td>.435</td>
<td>1.283</td>
<td>.0977</td>
<td>.1159</td>
<td>.843</td>
<td>.73</td>
<td>9.51</td>
</tr>
<tr>
<td>2</td>
<td>1.281</td>
<td>.542</td>
<td>1.599</td>
<td>.0971</td>
<td>.1435</td>
<td>.677</td>
<td>.32</td>
<td>9.92</td>
</tr>
<tr>
<td>3</td>
<td>.997</td>
<td>.442</td>
<td>1.245</td>
<td>.0977</td>
<td>.1125</td>
<td>.869</td>
<td>.82</td>
<td>9.41</td>
</tr>
</tbody>
</table>

Ave. 10.24

Table XVII

Acid Dissociation Constant of p-Anisidine at 25°C.

\( C_1HNO_3 = .1002M \)
\( C_1LiNO_3 = .525M \)

<table>
<thead>
<tr>
<th>Sol'n</th>
<th>( W_A )</th>
<th>( V_A )</th>
<th>( C_H )</th>
<th>( C_A )</th>
<th>( n \log \frac{n}{1-n} )</th>
<th>pH</th>
<th>( pK_{AH} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.926</td>
<td>.849</td>
<td>.0985</td>
<td>.1479</td>
<td>.666</td>
<td>.30</td>
<td>5.09</td>
</tr>
<tr>
<td>2</td>
<td>.722</td>
<td>.662</td>
<td>.0989</td>
<td>.1157</td>
<td>.854</td>
<td>.77</td>
<td>4.61</td>
</tr>
<tr>
<td>3</td>
<td>.978</td>
<td>.897</td>
<td>.0984</td>
<td>.1560</td>
<td>.631</td>
<td>.23</td>
<td>5.15</td>
</tr>
<tr>
<td>4</td>
<td>.801</td>
<td>.735</td>
<td>.0987</td>
<td>.1282</td>
<td>.770</td>
<td>.53</td>
<td>4.86</td>
</tr>
</tbody>
</table>

Ave. 5.39
Table XVIII

Acid Dissociation Constant of Morpholine at 25°C.

\[ C_1\text{HNO}_3 = .1002M \quad C_1\text{LiNO}_3 = .525M \]

<table>
<thead>
<tr>
<th>Sol'n</th>
<th>( W_A )</th>
<th>( V_A )</th>
<th>( C_H )</th>
<th>( C_A )</th>
<th>( n )</th>
<th>( \log \frac{n}{1-n} )</th>
<th>pH</th>
<th>( \text{pK}_{AH} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.764</td>
<td>.762</td>
<td>.0987</td>
<td>.1728</td>
<td>.571</td>
<td>.13</td>
<td>8.24</td>
<td>8.37</td>
</tr>
<tr>
<td>2</td>
<td>.806</td>
<td>.804</td>
<td>.0986</td>
<td>.1821</td>
<td>.541</td>
<td>.07</td>
<td>8.29</td>
<td>8.36</td>
</tr>
<tr>
<td>3</td>
<td>.635</td>
<td>.634</td>
<td>.0989</td>
<td>.1440</td>
<td>.687</td>
<td>.34</td>
<td>8.02</td>
<td>8.36</td>
</tr>
<tr>
<td>4</td>
<td>.711</td>
<td>.710</td>
<td>.0988</td>
<td>.1609</td>
<td>.614</td>
<td>.20</td>
<td>8.15</td>
<td>8.35</td>
</tr>
</tbody>
</table>

Ave. 8.36

Table XIX

Acid Dissociation Constant of Di-sec-butylamine at 25°C.

\[ C_1\text{HNO}_3 = .1002M \quad C_1\text{LiNO}_3 = .525M \]

<table>
<thead>
<tr>
<th>Sol'n</th>
<th>( W_A )</th>
<th>( V_A )</th>
<th>( C_H )</th>
<th>( C_A )</th>
<th>( n )</th>
<th>( \log \frac{n}{1-n} )</th>
<th>pH</th>
<th>( \text{pK}_{AH} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.724</td>
<td>.924</td>
<td>.0980</td>
<td>.1100</td>
<td>.891</td>
<td>.91</td>
<td>9.10</td>
<td>10.01</td>
</tr>
<tr>
<td>2</td>
<td>.882</td>
<td>1.126</td>
<td>.0976</td>
<td>.1355</td>
<td>.731</td>
<td>.45</td>
<td>9.57</td>
<td>10.00</td>
</tr>
</tbody>
</table>

Ave. 10.00
Table XX
Acid Dissociation Constant of Di-n-butylamine at 25°C.

C\textsubscript{1}HNO\textsubscript{3} = .1002M
C\textsubscript{1}LiNO\textsubscript{3} = .525M

<table>
<thead>
<tr>
<th>Sol'n</th>
<th>V\textsubscript{A}</th>
<th>V\textsubscript{A}</th>
<th>C\textsubscript{H}</th>
<th>C\textsubscript{A}</th>
<th>n</th>
<th>log ( \frac{n}{1-n} )</th>
<th>pH</th>
<th>pK\textsubscript{AH}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.125</td>
<td>1.465</td>
<td>.0970</td>
<td>.1691</td>
<td>.573</td>
<td>.13</td>
<td>9.94</td>
<td>10.07</td>
</tr>
<tr>
<td>2</td>
<td>.900</td>
<td>1.172</td>
<td>.0975</td>
<td>.1361</td>
<td>.717</td>
<td>.41</td>
<td>9.67</td>
<td>10.08</td>
</tr>
<tr>
<td>3</td>
<td>.713</td>
<td>.928</td>
<td>.0980</td>
<td>.1083</td>
<td>.904</td>
<td>.98</td>
<td>9.12</td>
<td>10.10</td>
</tr>
<tr>
<td>4</td>
<td>.982</td>
<td>1.279</td>
<td>.0975</td>
<td>.1482</td>
<td>.657</td>
<td>.28</td>
<td>9.79</td>
<td>10.07</td>
</tr>
<tr>
<td>Ave.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.</td>
<td></td>
<td></td>
<td>10.08</td>
</tr>
</tbody>
</table>

Table XXI
Acid Dissociation Constant of Dehydroquinoline at 25°C.

C\textsubscript{1}HNO\textsubscript{3} = .1002M
C\textsubscript{1}LiNO\textsubscript{3} = .525M

<table>
<thead>
<tr>
<th>Sol'n</th>
<th>V\textsubscript{A}</th>
<th>V\textsubscript{A}</th>
<th>C\textsubscript{H}</th>
<th>C\textsubscript{A}</th>
<th>n</th>
<th>log ( \frac{n}{1-n} )</th>
<th>pH</th>
<th>pK\textsubscript{AH}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.854</td>
<td>.813</td>
<td>.0986</td>
<td>.1207</td>
<td>.612</td>
<td>.64</td>
<td>9.55</td>
<td>10.19</td>
</tr>
<tr>
<td>2</td>
<td>.826</td>
<td>.787</td>
<td>.0986</td>
<td>.1168</td>
<td>.844</td>
<td>.74</td>
<td>9.46</td>
<td>10.20</td>
</tr>
<tr>
<td>3</td>
<td>1.281</td>
<td>1.220</td>
<td>.0978</td>
<td>.1796</td>
<td>.544</td>
<td>.08</td>
<td>10.12</td>
<td>10.20</td>
</tr>
<tr>
<td>4</td>
<td>1.007</td>
<td>.959</td>
<td>.0983</td>
<td>.1419</td>
<td>.693</td>
<td>.35</td>
<td>9.85</td>
<td>10.20</td>
</tr>
<tr>
<td>Ave.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.</td>
<td></td>
<td></td>
<td>10.20</td>
</tr>
</tbody>
</table>


### Table XXII

Acid Dissociation Constant of Diethylamine at 25°C.

\[ \text{C}_1\text{HNO}_3 = 0.1002 \text{M} \quad \text{C}_1\text{LiNO}_3 = 0.525 \text{M} \]

Weight % amine in solution = 41.58

<table>
<thead>
<tr>
<th>Sol'n</th>
<th>( W_S )</th>
<th>( W_A )</th>
<th>( V_S )</th>
<th>( C_H )</th>
<th>( C_A )</th>
<th>( n \log \frac{n}{1-n} )</th>
<th>pH</th>
<th>( \text{pK}_{AH} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.067</td>
<td>.444</td>
<td>1.325</td>
<td>.0976</td>
<td>.1182</td>
<td>.826</td>
<td>.68</td>
<td>9.69</td>
</tr>
<tr>
<td>2</td>
<td>1.252</td>
<td>.521</td>
<td>1.555</td>
<td>.0972</td>
<td>.1381</td>
<td>.704</td>
<td>.38</td>
<td>9.98</td>
</tr>
<tr>
<td>3</td>
<td>.956</td>
<td>.398</td>
<td>1.188</td>
<td>.0979</td>
<td>.1062</td>
<td>.922</td>
<td>1.07</td>
<td>9.30</td>
</tr>
<tr>
<td>4</td>
<td>1.407</td>
<td>.585</td>
<td>1.748</td>
<td>.0968</td>
<td>.1546</td>
<td>.626</td>
<td>.23</td>
<td>10.12</td>
</tr>
</tbody>
</table>

Ave. 10.36

### Table XXIII

Acid Dissociation Constant of Dibenzylamine at 25°C.

\[ \text{C}_1\text{HNO}_3 = 0.0995 \text{M} \quad \text{C}_1\text{LiNO}_3 = 0.525 \text{M} \]

<table>
<thead>
<tr>
<th>Sol'n</th>
<th>( W_A )</th>
<th>( V_A )</th>
<th>( C_H )</th>
<th>( C_A )</th>
<th>( n \log \frac{n}{1-n} )</th>
<th>pH</th>
<th>( \text{pK}_{AH} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.191</td>
<td>1.159</td>
<td>.0975</td>
<td>.1180</td>
<td>.827</td>
<td>.68</td>
<td>7.42</td>
</tr>
<tr>
<td>2</td>
<td>1.392</td>
<td>1.325</td>
<td>.0972</td>
<td>.1375</td>
<td>.707</td>
<td>.38</td>
<td>7.72</td>
</tr>
<tr>
<td>3</td>
<td>1.737</td>
<td>1.729</td>
<td>.0965</td>
<td>.1742</td>
<td>.554</td>
<td>.09</td>
<td>7.99</td>
</tr>
<tr>
<td>4</td>
<td>1.093</td>
<td>1.063</td>
<td>.0977</td>
<td>.1085</td>
<td>.901</td>
<td>.95</td>
<td>7.14</td>
</tr>
</tbody>
</table>

Ave. 8.09
### Table XXIV

**Acid Dissociation Constant of Diethanolamine at 25°C.**

\[ C_1\text{H}_2\text{NO}_3 = 0.1002 \text{M} \quad C_1\text{LiNO}_3 = 0.525 \text{M} \]

<table>
<thead>
<tr>
<th>Sol'n</th>
<th>( W_A )</th>
<th>( V_A )</th>
<th>( C_H )</th>
<th>( C_A )</th>
<th>( n )</th>
<th>( \log \frac{n}{1-n} )</th>
<th>pH</th>
<th>( pK_{AH} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.772</td>
<td>0.704</td>
<td>0.0988</td>
<td>0.1448</td>
<td>0.682</td>
<td>0.35</td>
<td>8.41</td>
<td>8.74</td>
</tr>
<tr>
<td>2</td>
<td>0.838</td>
<td>0.764</td>
<td>0.0987</td>
<td>0.1570</td>
<td>0.628</td>
<td>0.23</td>
<td>8.50</td>
<td>8.73</td>
</tr>
<tr>
<td>3</td>
<td>0.922</td>
<td>0.840</td>
<td>0.0985</td>
<td>0.1725</td>
<td>0.571</td>
<td>0.13</td>
<td>8.60</td>
<td>8.73</td>
</tr>
<tr>
<td>4</td>
<td>0.646</td>
<td>0.589</td>
<td>0.0990</td>
<td>0.1215</td>
<td>0.615</td>
<td>0.64</td>
<td>8.09</td>
<td>8.73</td>
</tr>
</tbody>
</table>

**Ave.** 8.73

### Table XXV

**Acid Dissociation Constant of Quinoline at 25°C.**

\[ C_1\text{H}_2\text{NO}_3 = 0.0995 \text{M} \quad C_1\text{LiNO}_3 = 0.525 \text{M} \]

<table>
<thead>
<tr>
<th>Sol'n</th>
<th>( W_A )</th>
<th>( V_A )</th>
<th>( C_H )</th>
<th>( C_A )</th>
<th>( n )</th>
<th>( \log \frac{n}{1-n} )</th>
<th>pH</th>
<th>( pK_{AH} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.946</td>
<td>0.864</td>
<td>0.0981</td>
<td>0.1440</td>
<td>0.681</td>
<td>0.33</td>
<td>3.45</td>
<td>3.78</td>
</tr>
<tr>
<td>2</td>
<td>0.828</td>
<td>0.756</td>
<td>0.0983</td>
<td>0.1263</td>
<td>0.778</td>
<td>0.54</td>
<td>3.24</td>
<td>3.78</td>
</tr>
<tr>
<td>3</td>
<td>1.160</td>
<td>1.059</td>
<td>0.0977</td>
<td>0.1759</td>
<td>0.556</td>
<td>0.11</td>
<td>3.67</td>
<td>3.78</td>
</tr>
<tr>
<td>4</td>
<td>0.779</td>
<td>0.711</td>
<td>0.0984</td>
<td>0.1189</td>
<td>0.827</td>
<td>0.68</td>
<td>3.09</td>
<td>3.77</td>
</tr>
</tbody>
</table>

**Ave.** 3.78
Table XXVI

Acid Dissociation Constant of Pyridine at 25°C.

\[ \text{C}_1\text{HNO}_3 = .1002\text{M} \quad \text{C}_1\text{LiNO}_3 = .525\text{M} \]

<table>
<thead>
<tr>
<th>Sol'n</th>
<th>( W_A )</th>
<th>( V_A )</th>
<th>( C_H )</th>
<th>( C_A )</th>
<th>( n \log \frac{n}{1-n} )</th>
<th>pH</th>
<th>( \text{pK}_{AH} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.748</td>
<td>.762</td>
<td>.0987</td>
<td>.1863</td>
<td>.580 .05</td>
<td>4.18</td>
<td>4.25</td>
</tr>
<tr>
<td>2</td>
<td>.574</td>
<td>.585</td>
<td>.0990</td>
<td>.1435</td>
<td>.690 .35</td>
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<td>4.24</td>
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<td>.1464</td>
<td>.676 .32</td>
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<td>4.23</td>
</tr>
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<td>.0992</td>
<td>.1259</td>
<td>.788 .57</td>
<td>3.68</td>
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</table>

Ave. 4.24

Table XXVII

Acid Dissociation Constant of N-ethylmorpholine at 25°C.

\[ \text{C}_1\text{HNO}_3 = .1002\text{M} \quad \text{C}_1\text{LiNO}_3 = .525\text{M} \]

<table>
<thead>
<tr>
<th>Sol'n</th>
<th>( W_A )</th>
<th>( V_A )</th>
<th>( C_H )</th>
<th>( C_A )</th>
<th>( n \log \frac{n}{1-n} )</th>
<th>pH</th>
<th>( \text{pK}_{AH} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.796</td>
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<td>.0987</td>
<td>.1362</td>
<td>.725 .42</td>
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<td>7.34</td>
</tr>
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<td>1.098</td>
<td>1.046</td>
<td>.0981</td>
<td>.1868</td>
<td>.525 .04</td>
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<td>7.35</td>
</tr>
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<td>.677</td>
<td>.0988</td>
<td>.1217</td>
<td>.811 .65</td>
<td>6.72</td>
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<td>.1523</td>
<td>.647 .26</td>
<td>7.10</td>
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</tr>
</tbody>
</table>

Ave. 7.35
Table XXVIII

Acid Dissociation Constant of Tri-n-butylamine at 25°C.

\[ C_1\text{HNO}_3 = .1002M \quad C_1\text{LiNO}_3 = .525M \]

<table>
<thead>
<tr>
<th>Sol'n</th>
<th>( W_A )</th>
<th>( V_A )</th>
<th>( C_H )</th>
<th>( C_A )</th>
<th>( n )</th>
<th>( \log \frac{n}{1-n} )</th>
<th>pH</th>
<th>( pK_{AH} )</th>
</tr>
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<tbody>
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<td>.1182</td>
<td>.824</td>
<td>.67</td>
<td>8.50</td>
<td>9.17</td>
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<td>1.370</td>
<td>1.761</td>
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<td>1.684</td>
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<td>.1561</td>
<td>.712</td>
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<td>1.200</td>
<td>1.542</td>
<td>.0972</td>
<td>.1256</td>
<td>.774</td>
<td>.54</td>
<td>8.63</td>
<td>9.17</td>
</tr>
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</tr>
</tbody>
</table>

Table XXIX

Acid Dissociation Constant of Triethylamine at 25°C.

\[ C_1\text{HNO}_3 = .1002M \quad C_1\text{LiNO}_3 = .525M \]

<table>
<thead>
<tr>
<th>Sol'n</th>
<th>( W_A )</th>
<th>( V_A )</th>
<th>( C_H )</th>
<th>( C_A )</th>
<th>( n )</th>
<th>( \log \frac{n}{1-n} )</th>
<th>pH</th>
<th>( pK_{AH} )</th>
</tr>
</thead>
<tbody>
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<td>.0980</td>
<td>.1551</td>
<td>.632</td>
<td>.23</td>
<td>9.49</td>
<td>9.72</td>
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<tr>
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<td>.851</td>
<td>.0985</td>
<td>.1207</td>
<td>.616</td>
<td>.64</td>
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<td>.681</td>
<td>.33</td>
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<td>9.72</td>
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<td>.927</td>
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<td>.0977</td>
<td>.1757</td>
<td>.547</td>
<td>.08</td>
<td>9.66</td>
<td>9.74</td>
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</tr>
</tbody>
</table>
Table XXX

Acid Dissociation Constant of Triethanolamine at 25°C.

\[
\begin{array}{cccccccc}
\text{Sol'n} & W_A & V_A & C_H & C_A & n & \log \frac{n}{1-n} & \text{pH} & \text{pK}_{AH} \\
1 & 1.099 & .976 & .0979 & .1445 & .677 & .32 & 7.06 & 7.38 \\
2 & 1.017 & .903 & .0980 & .1339 & .732 & .43 & 6.98 & 7.41 \\
3 & .919 & .816 & .0982 & .1212 & .810 & .63 & 6.77 & 7.40 \\
4 & 1.213 & 1.077 & .0977 & .1592 & .514 & .20 & 7.20 & 7.40 \\
\text{Ave.} & 7.40 & & & & & & & \\
\end{array}
\]

Table XXXI

Acid Dissociation Constant of Methyl-diethanolamine at 25°C.

\[
\begin{array}{cccccccc}
\text{Sol'n} & W_A & V_A & C_H & C_A & n & \log \frac{n}{1-n} & \text{pH} & \text{pK}_{AH} \\
1 & .756 & .730 & .0987 & .1251 & .790 & .58 & 7.69 & 8.27 \\
2 & .882 & .892 & .0985 & .1455 & .693 & .34 & 7.95 & 8.29 \\
3 & .702 & .678 & .0988 & .1162 & .850 & .75 & 7.54 & 8.29 \\
4 & .955 & .923 & .0984 & .1574 & .625 & .23 & 8.04 & 8.27 \\
\text{Ave.} & 8.28 & & & & & & & \\
\end{array}
\]
Table XXXII

Acid Dissociation Constant of Diethyl-ethanolamine at 26°C.

\[
\begin{align*}
\text{C}_1\text{HNO}_3 &= .1002\text{M} \\
\text{C}_1\text{LiNO}_3 &= .525\text{M}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Sol'n</th>
<th>(W_A)</th>
<th>(V_A)</th>
<th>(C_H)</th>
<th>(C_A)</th>
<th>(n)</th>
<th>(\log \frac{n}{1-n})</th>
<th>(pH)</th>
<th>(pK_{AH})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.815</td>
<td>.921</td>
<td>.0984</td>
<td>.1366</td>
<td>.720</td>
<td>.41</td>
<td>8.76</td>
<td>9.17</td>
</tr>
<tr>
<td>2</td>
<td>.622</td>
<td>.703</td>
<td>.0988</td>
<td>.1047</td>
<td>.944</td>
<td>.22</td>
<td>7.96</td>
<td>9.18</td>
</tr>
<tr>
<td>3</td>
<td>.733</td>
<td>.828</td>
<td>.0985</td>
<td>.1231</td>
<td>.801</td>
<td>.60</td>
<td>8.58</td>
<td>9.18</td>
</tr>
<tr>
<td>4</td>
<td>1.024</td>
<td>1.157</td>
<td>.0979</td>
<td>.1708</td>
<td>.573</td>
<td>.13</td>
<td>9.05</td>
<td>9.18</td>
</tr>
</tbody>
</table>

Ave. 9.18

Table XXXIII

Acid Dissociation Constant of Diethyl-o-toluidine at 25°C.

\[
\begin{align*}
\text{C}_1\text{HNO}_3 &= .0998\text{M} \\
\text{C}_1\text{LiNO}_3 &= .525\text{M}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Sol'n</th>
<th>(W_A)</th>
<th>(V_A)</th>
<th>(C_H)</th>
<th>(C_A)</th>
<th>(n)</th>
<th>(\log \frac{n}{1-n})</th>
<th>(pH)</th>
<th>(pK_{AH})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.945</td>
<td>1.005</td>
<td>.0978</td>
<td>.1135</td>
<td>.862</td>
<td>.80</td>
<td>5.26</td>
<td>6.06</td>
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<tr>
<td>2</td>
<td>1.075</td>
<td>1.144</td>
<td>.0976</td>
<td>.1288</td>
<td>.758</td>
<td>.50</td>
<td>5.56</td>
<td>6.06</td>
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<tr>
<td>3</td>
<td>1.125</td>
<td>1.195</td>
<td>.0975</td>
<td>.1344</td>
<td>.725</td>
<td>.42</td>
<td>5.63</td>
<td>6.05</td>
</tr>
<tr>
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<td>1.388</td>
<td>.0977</td>
<td>.1556</td>
<td>.624</td>
<td>.22</td>
<td>5.84</td>
<td>6.06</td>
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</table>

Ave. 6.06
Table XXXIV

Acid Dissociation Constant of Diethyl-p-toluidine at 25°C.

\[ \text{C}_1\text{HNO}_3 = .0998\text{M} \quad \text{C}_1\text{LiNO}_3 = .525\text{M} \]

<table>
<thead>
<tr>
<th>Sol'n</th>
<th>( W_A )</th>
<th>( V_A )</th>
<th>( C_H )</th>
<th>( C_A )</th>
<th>( n \log \frac{n}{1-n} )</th>
<th>pH</th>
<th>( \text{pK}_{\text{AH}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.034</td>
<td>1.119</td>
<td>0.0976</td>
<td>0.1239</td>
<td>0.788</td>
<td>5.57</td>
<td>6.14</td>
</tr>
<tr>
<td>2</td>
<td>1.249</td>
<td>1.352</td>
<td>0.0972</td>
<td>0.1490</td>
<td>0.652</td>
<td>5.87</td>
<td>6.14</td>
</tr>
<tr>
<td>3</td>
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<td>1.619</td>
<td>0.0967</td>
<td>0.1775</td>
<td>0.545</td>
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<td>6.13</td>
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<td>1.151</td>
<td>1.246</td>
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<td>0.1376</td>
<td>0.708</td>
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Table XXXV

Acid Dissociation Constant of N-ethylpiperidine at 25°C.

\[ \text{C}_1\text{HNO}_3 = .1002\text{M} \quad \text{C}_1\text{LiNO}_3 = .525\text{M} \]

<table>
<thead>
<tr>
<th>Sol'n</th>
<th>( W_A )</th>
<th>( V_A )</th>
<th>( C_H )</th>
<th>( C_A )</th>
<th>( n \log \frac{n}{1-n} )</th>
<th>pH</th>
<th>( \text{pK}_{\text{AH}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.714</td>
<td>.869</td>
<td>0.0985</td>
<td>0.1240</td>
<td>0.794</td>
<td>8.69</td>
<td>9.48</td>
</tr>
<tr>
<td>2</td>
<td>.807</td>
<td>.982</td>
<td>0.0983</td>
<td>0.1398</td>
<td>0.703</td>
<td>9.11</td>
<td>9.49</td>
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<tr>
<td>3</td>
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<td>1.135</td>
<td>0.0980</td>
<td>0.1612</td>
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<td>0.641</td>
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Table XXXVI

2,6-Xylylene - Silver Ion System at 25°C

C₁ HNO₃ = .0995M  C₁ LiNO₃ = .500M
C₁ AgNO₃ = .025M  pKₐH = 3.62

<table>
<thead>
<tr>
<th>Sol'n</th>
<th>Wₐ</th>
<th>Vₐ</th>
<th>Cₕ</th>
<th>Cₐ</th>
<th>Cₐg</th>
<th>pH</th>
<th>αₐ</th>
<th>nA</th>
<th>n</th>
<th>p[A]</th>
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<tbody>
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<td>.0977</td>
<td>.1490</td>
<td>.0245</td>
<td>3.13</td>
<td>.245</td>
<td>.755</td>
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</tr>
<tr>
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<td>.649</td>
<td>.0982</td>
<td>.1036</td>
<td>.0247</td>
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<td>.398</td>
<td>.602</td>
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<td>1.19</td>
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<tr>
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<td>1.300</td>
<td>1.327</td>
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<td>.2090</td>
<td>.0244</td>
<td>3.62</td>
<td>.447</td>
<td>.553</td>
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<td>1.11</td>
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<td>.0243</td>
<td>3.59</td>
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<td>1.51</td>
<td>1.05</td>
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</table>

Calculated Values

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</tr>
</thead>
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<tr>
<td>(7)</td>
<td>.72</td>
</tr>
<tr>
<td>(8)</td>
<td>.35</td>
</tr>
<tr>
<td>(14)</td>
<td>1.29</td>
</tr>
</tbody>
</table>

(Formation curve in Figure 10)
Table XXXVII
Aniline - Silver Ion System at 25°C.

\[ C_1 \text{HNO}_3 = 0.1002 \text{M} \quad C_1 \text{LiNO}_3 = 0.500 \text{M} \]

\[ C_1 \text{AgNO}_3 = 0.025 \text{M} \quad pK_{\text{AH}} = 4.42 \]

<table>
<thead>
<tr>
<th>Sol'n</th>
<th>( W_A )</th>
<th>( V_A )</th>
<th>( C_H )</th>
<th>( C_A )</th>
<th>( C_{Ag} )</th>
<th>( pH )</th>
<th>( \alpha_A )</th>
<th>( \bar{n}_A )</th>
<th>( \bar{n} )</th>
<th>( p[A] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.704</td>
<td>.689</td>
<td>.0988</td>
<td>.1491</td>
<td>.0247</td>
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<td>.229</td>
<td>.771</td>
<td>.86</td>
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</tr>
<tr>
<td>2</td>
<td>.931</td>
<td>.911</td>
<td>.0984</td>
<td>.1964</td>
<td>.0246</td>
<td>4.23</td>
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(Formation curve in Figure 9)
Table XXXVII

Ethanolamine - Silver Ion System at 25°C

\[
\begin{align*}
C_1 HNO_3 &= .1002M \\
C_1 LiNO_3 &= .500M \\
C_1 AgNO_3 &= .025M \quad pK_a = 9.34
\end{align*}
\]

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(Formation curve in Figure 8)
Table XXXIX

t-Octylamine - Silver Ion System at 25°C

\[ C_1 \text{HNO}_3 = .0995 \text{M} \quad C_1 \text{LiNO}_3 = .500\text{M} \]
\[ C_1 \text{AgNO}_3 = .025\text{M} \quad \text{pK}_{\text{AH}} = 9.92 \]

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Calculated Values

\(\bar{n} \quad p[A]\)

| (7)    | .25   | 4.71 |
| (10)   | 1.99  | 2.28 |
| (11)   | 1.00  | 4.09 |

(Formation curve in Figure 13)
Table XL

$t$-Butylamine - Silver Ion System at 25°C

$C_1\ HNO_3 = .1002M$
$C_1\ AgNO_3 = .025M$
$C_1\ LiNO_3 = .500M$
$pK_{AH} = 10.24$

Weight % amine in solution = 42.28
$d_{sol'n} = .801$ g/ml

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(Formation curve in Figure 7)
Table XII
Morpholine - Silver Ion System at 25°C

\( C_1 \text{HNO}_3 = .1002 \text{M} \)  \( C_1 \text{LiNO}_3 = .500 \text{M} \)

\( C_1 \text{AgNO}_3 = .025 \text{M} \)  \( \text{pK}_{AH} = 8.36 \)

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(Formation curve in Figure 11)
Table XIII
Di-sec-butylamine - Silver Ion System at 25°C

\[ C_i \text{HNO}_3 = .1002\text{M} \quad C_i \text{LiNO}_3 = .500\text{M} \]

\[ C_i \text{AgNO}_3 = .025\text{M} \quad pK_{AH} = 10.00 \]

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(Formation curve in Figure 9)
Table XLIII

Di-n-butylamine – Silver Ion System at 25°C

\[ C_1 \cdot HNO_3 = 0.1002 \text{M} \]
\[ C_1 \cdot AgNO_3 = 0.025 \text{M} \]
\[ \text{pK}_a^H = 10.08 \]

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(g) .62 3.51

(Formation curve in Figure 7)
Table XLIV
Decahydroquinoline - Silver Ion System in 25°C

\[ C_1 \text{HNO}_3 = 0.1002 \text{M} \]
\[ C_1 \text{AgNO}_3 = 0.025 \text{M} \]
\[ C_1 \text{LiNO}_3 = 0.500 \text{M} \]
\[ pK_{\text{AH}} = 10.20 \]

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(Formation curve in Figure 12)
Table XLV

Diethylamine - Silver Ion System at 25°C

\[ C_1 HNO_3 = 0.1002M \]
\[ C_1 AgNO_3 = 0.025M \]
\[ C_1 I\text{Ag}NO_3 = 0.500M \]
\[ pK_{AH} = 10.36 \]

Weight % amine in solution = 41.58

\[ d_{\text{solv}} = 0.805 \text{ g/ml} \]

\[ Ci HN\text{O}_3 = 0.1002M \]
\[ Ci I\text{Ag}\text{NO}_3 = 0.500M \]

Weight % amine in solution = 41.58

\[ d_{\text{solv}} = 0.805 \text{ g/ml} \]

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\[ p[A] \]

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(9) .21  3.99
(11) 1.32  2.99
(12) 1.83  2.38

(Formation curve in Figure 14)
Table XLVI

Dibenzylamine - Silver Ion System at 25°C

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\[ C_1 AgNO_3 = 0.025 M \]
\[ pK_{AH} = 8.09 \]

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Calculated Values

\( \bar{n} \) \( p[A] \)

(4) 1.11  3.29
(6) 1.88  2.59
(15) .15  4.04

(Formation curve in Figure 10)
Table XLVII

Diethanolamine - Silver Ion System at 25°C

\( C_i \text{HNO}_3 = .1002M \)
\( C_i \text{AgNO}_3 = .025M \)
\( C_i \text{LaNO}_3 = .500M \)
\( pK_{AH} = 8.73 \)

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(3) .09 4.24
(6) 1.34 3.04
(7) .92 3.30
(14) .60 3.51

(Formation curve in Figure 8)
Table XLVII
Quinoline - Silver Ion System at 25°C

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$\text{pK}_{\text{AH}} = 3.78$

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(Formation curve in Figure 9)
Table XLIX
Pyridine - Silver Ion System at 25°C

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(Formation curve in Figure 10)
Table L

N-ethylmorpholine - Silver Ion System at 25°C

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(Formation curve in Figure 11)
Table LI

Tri-n-butylamine - Silver Ion System at 25°C

\( C_1 \text{HNO}_3 = .1002M \quad \text{C}_1 \text{LiNO}_3 = .500M \)

\( C_1 \text{AgNO}_3 = .025M, .0125M \quad pK_{\text{AH}} = 9.16 \)

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<th>( C_A )</th>
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Calculated Values

\[ \bar{n} \quad p[A] \]

(2) .57  2.31
(3) .22  2.84
(9) .39  2.55

(Formation curve in Figure 7)
Table LI

Triethylamine - Silver Ion System at 25°C

\[ C_1 \text{HNO}_3 = 0.1002 \text{M} \]
\[ C_1 \text{LiNO}_3 = 0.500 \text{M} \]
\[ C_1 \text{AgNO}_3 = 0.025 \text{M}, 0.0125 \text{M} \]
\[ \text{pK}_\text{AH} = 9.73 \]

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Calculated Values

\[
\bar{n} \quad \text{p}[A]
\]

| (3)   | 0.09 | 3.38 |
| (4)   | 0.35 | 2.72 |
| (5)   | 0.64 | 2.36 |
| (7)   | 1.03 | 2.02 |

(Formation curve in Figure 13)
Table LIII
Triethanolamine - Silver Ion System at 25°C

\[
\begin{align*}
C_i \text{HNO}_3 &= .0998M \\
C_i \text{LiNO}_3 &= .500M \\
C_i \text{AgNO}_3 &= .025M \\
pK_{AH} &= 7.40
\end{align*}
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Calculated Values

\[
\begin{align*}
\bar{n} & = \text{formation curve in Figure 8} \\
p[A] & = (3) .96 \quad 2.30 \\
& = (4) .27 \quad 3.21 \\
& = (11) 1.71 \quad 1.36
\end{align*}
\]
Table LIV

Methyl-diethanolamine - Silver Ion System at 25°C

\[ C_1 \text{HNO}_3 = .1002 \text{M} \]
\[ C_1 \text{AgNO}_3 = .025 \text{M} \]
\[ C_1 \text{LiNO}_3 = .500 \text{M} \]
\[ pK_{AH} = 8.28 \]

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Calculated Values

\[ \overline{n} \quad p[A] \]

(4) \(1.39 \quad 2.30\)

(11) \(.63 \quad 2.91\)

(14) \(.31 \quad 3.28\)

(Formation curve in Figure 14)
Table IV

Diethyl-ethanolamine - Silver Ion System at 25°C

\[ C_1 \text{HNO}_3 = .1002M \quad C_1 \text{LiNO}_3 = .500M \]
\[ C_1 \text{AgNO}_3 = .025M \quad pK_{AH} = 9.18 \]

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Calculated Values

\( \bar{n} \quad p[A] \)

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(7) 1.14 2.40
(13) .22 3.24

(Formation curve in Figure 12)
Table LVI

Diethyl-o-toluidine - Silver Ion System at 25°C

\[ C_1 \text{HNO}_3 = 0.0998 \text{M} \]
\[ C_1 \text{LiNO}_3 = 0.500 \text{M} \]
\[ C_1 \text{AgNO}_3 = 0.025 \text{M} \]
\[ pK_{\text{AH}} = 6.06 \]

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Figure 7. Silver ammine formation curves: O t-butylamine, • di-n-butylamine, © tri-n-butylamine
Figure 8. Silver ammine formation curves: O ethanolamine, □ diethanolamine, ◇ triethanolamine
Figure 9. Silver ammine formation curves: O aniline, • di-sec-butylamine, @ quinoline
Figure 10. Silver ammine formation curves: O 2,6-xylidine, • dibenzyamine, @ pyridine
Figure II. Silver ammine formation curves: ● morpholine, ○ N-ethylmorpholine
Figure 12. Silver ammine formation curves: • decahydroquinoline, ◇ diethyl-ethanolamine
Figure 13 Silver ammine formation curves: O t-acylamine, @ triethylamine
Figure 14 Silver ammine formation curves: ● diethylamine, ○ methyl-diethanolamine
Figure 15. Spectrophotometric measurements on hydrochloric acid solutions using first thymol blue solution.
Figure 16: Spectrophotometric measurements on hydrochloric acid solutions using second thymol blue solution.
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R. Wegscheider, Monatshefte, 16, 153 (1895).


I, Charles Thomas Anderson, was born in Fairmont, West Virginia, on February 26, 1921. I received my primary and secondary education in the public schools of that city. In 1942 I received from Fairmont State Teachers College the degree Bachelor of Arts, summa cum laude. I entered the Graduate School of The Ohio State University in October 1942. I was employed by the Department of Chemistry as a graduate assistant, assistant, and special assistant until September 1946, when I accepted a position as Instructor in Chemistry at Ohio University, Athens, Ohio. I returned to Graduate School in October 1951 to complete the requirements for the degree Doctor of Philosophy.