A STUDY OF CUPRIC AMINE COMPLEX IONS

FORMED IN 2-PROPANOL

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PREFACE

Complex ions can be studied in a number of ways. One of the least used of these is by using the results obtained by amperometric titrations. Many problems are posed by a study of this nature, one of the largest problems being brought about by the high resistance of the non-aqueous solutions used. This problem has been largely solved through use of the iR-compensator developed by Dr. Paul Arthur. Another difficulty encountered is obtaining sufficiently anhydrous solvents. This problem is partially solved by proper purification methods and the care taken in handling the solvents.

The purpose of this research was to examine the behavior of copper (II) ions in 2-propanol in the presence of various supporting electrolytes and different amines. It was hoped that by performing amperometric titrations on these solutions the nature of the complex ions formed could be discovered.

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CHAPTER I

INTRODUCTION

In 1903, Kucera (38) employed a dropping mercury electrode for the purpose of studying the electrocapillary curve of mercury in various solutions. During the course of his investigations, he observed certain peculiar inflections in the curve when an electroreducible substance was present. This led Heyrovsky (21, 22, 23, 25) to perform investigations which led to the development of an instrument, the polarograph, which would record current-voltage curves obtained with cells employing dropping mercury electrodes.

Polarography is now a well-established branch of electroanalytical chemistry. The technique is based on data from current-voltage curves obtained when solutions of electrooxidizable or electroreducible substances are electrolyzed in a cell containing two electrodes: a reference electrode which is large and non-polarizable and an indicating electrode which is very small and easily polarized. The saturated calomel electrode (SCE) is most often used as the reference electrode while the dropping mercury electrode (DME) is the most common indicating electrode. The DME has the marked advantages of having a reproducible surface area, of having an unusually large usable voltage range, and of being self-cleaning, the formation of each new drop yielding a fresh electrode surface.

The apparatus necessary for the basic polarographic circuit consists

of four units: (1) a source of electromotive force; (2) a means of vary-
ing the potential applied across the cell; (3) the cell in which the elec-
trolysis takes place; and (4) the current-measuring circuit, commonly
a potentiometric recorder. When the chart of the recorder and the applied
potential are both increased as a function of time we get a curve which
is a plot of current versus potential. Such a curve is called a polaro-
gram and is of the type shown in Figure 1.

Ilkovic (27) derived an equation, on a purely theoretical basis,
for the diffusion current in terms of concentration of the reducible
substance, its characteristic diffusion current, the amount of mercury
flowing from the DME per second, and the drop time. This equation was
later re-derived by, and supported by MacGillavry and Rideal (45). The
following is the original Ilkovic equation.

$$i_d = 0.627 nFD^{1/2}Cm^{2/3}t^{1/6}$$

In this equation the diffusion current, i_d, is expressed in amperes,
n is the number of faradays of electricity required for the reduction
of one mole of the substance in question, F is the faraday (96,500 cou-
lombs), D is the diffusion coefficient of the reducible substance in
cm.^{2} sec.$^{-1}$, C is the concentration of the reducible substance in milli-
moles per liter, m is the weight of mercury in grams flowing from the
DME per second, and t is the time in seconds for the formation of each
drop.

This theoretical derivation received experimental verification
and was shown to be essentially correct by Lingane and Kolthoff (39)
and by Maas (43).

Lingane and Loveridge (40) pointed out that although the derivation
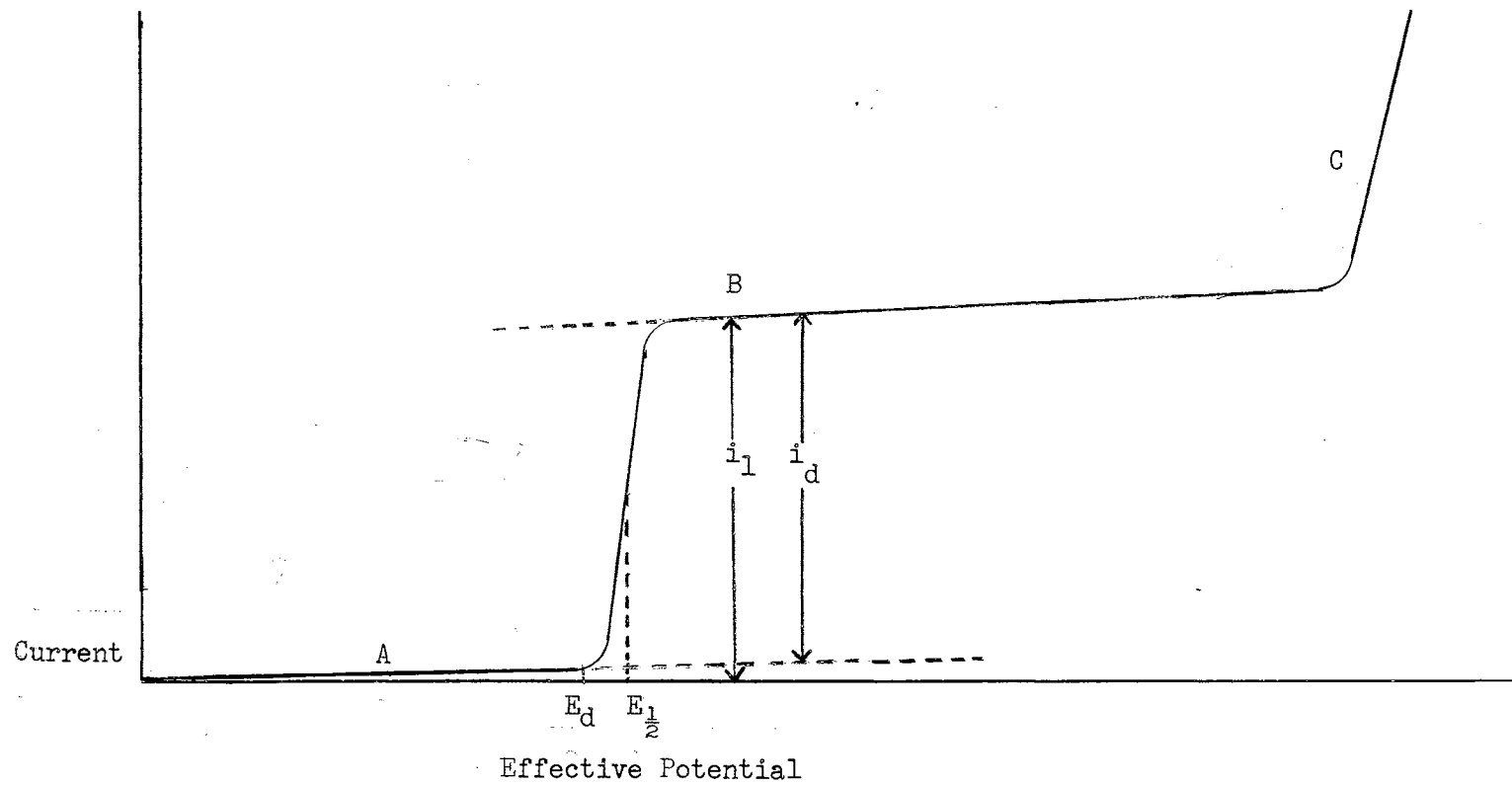
A = Residual current line E_d = Decomposition potential
B = Limiting current line $E_{\frac{1}{2}}$ = Half-wave potential
C = Carrier wave i_l = Limiting current
     i_d = Diffusion current

Figure 1. A Typical Polarogram

of the Ilkovic equation begins with the postulate of symmetrical diffusion, the simplifications introduced in the intermediate mathematical operations are equivalent to neglect of the curvature of the electrode surface (36). When these simplifications were not introduced the equation was derived to be as follows:

$$i_d = 0.627 nFD^{1/2} C_m^{2/3} t^{1/6} \left[1 + 39 D^{1/2} t^{1/6} m^{-1/3} \right]$$

At about the same time, an equation identical to this except with the constant 17 in the place of 39 was derived by Strehlow and von Stackelbert (65).

The Ilkovic equation has been rearranged and simplified to give an expression for the diffusion current constant, I, as follows:

$$I = \frac{i_d}{C_m^{2/3} t^{1/6}}$$

It is evident from the Ilkovic equation and its modifications that, with all other factors constant, the diffusion current of a given reducible substance should be directly proportional to its concentration. This simpler linear relationship, $i_d = KC$, is the basis for quantitative polarographic analysis.

Nejedly (48) studied the diffusion currents of several metal ions at the DME. He found that the average temperature coefficients from 20° to 50° C range from 1.3 to 2.3 percent for each degree of temperature rise. This was in good agreement with values obtained from a theoretical equation.

Heyrovsky and Ilkovic (24) have shown that the potential at any point on the rising portion of the polarographic wave is given by the equation

$$E_{d.e.} = E_{\frac{1}{2}} - \frac{0.0591}{n} \log \frac{i}{i_d - i}$$

where $E_{d.e.}$ is the potential of the DME at any point on the wave, $E_{\frac{1}{2}}$ is the half wave potential, n is the number of electrons taking part in the electrode reaction, i is the current measured at potential $E_{d.e.}$, and i_d is the diffusion current.

It is evident from the above equation that a plot of $E_{d.e.}$ versus $\log \frac{i}{i_d - i}$ should produce a straight line with a slope equal to $\frac{0.0591}{n}$, and the potential at which the log term becomes zero should be the half wave potential. The validity of the above equation has been experimentally verified by Kolthoff and Lingane (35) who found a slope of 0.061 for univalent metal ions. One of the most valuable theoretical aspects of this curve is the slope, since it is possible to calculate from it the value of "n". This is important since it often explains the nature of the electrode reaction taking place. It should be pointed out, however, that if the electrode process is irreversible or if the current is controlled by factors other than diffusion, the "n" values calculated are not correct.

Nonaqueous Polarography

Although water has been the most commonly used solvent in polarography, a large volume of work has been done using mixtures of organic solvents and water, examples of which are included here. Kolthoff and Pan (37) suggested an alcohol-water mixture for the amperometric titration of sulfate ion with lead ion, the purpose of the alcohol in this mixture being to suppress the solubility of lead sulfate formed during the titration. Kolthoff and Harris (34) developed a method for the

titration of mercaptans in 95 percent ethanol with an equeous solution of silver nitrate. Kolthoff and Bovey (33) reported the titration of styrene in a 75 percent methanol solution with potassium bromate.

In spite of the large amount of work which has been performed with mixtures of water and organic solvents, that done in anhydrous organic solvents has been relatively small. Glacial acetic acid was one of the earliest anhydrous solvents used. MacGillavry (44) reported its use as a polarographic solvent in 1936, although the results he obtained were very unsatisfactory. Bachman and Astle (8, 9) later obtained very good polarographic waves for a number of inorganic metal ions in anhydrous acetic acid. They reported that the degassing of the solution was a very critical step with determinations in this solvent, long periods of degassing with nitrogen being required to prevent interference from dissolved oxygen. Bergman and James (11) also used this solvent to determine a large number of nitro compounds while Arthur and Lyons (6) used it for the determination of lead and cadmium.

The satisfactory amperometric titrations of olefins in methanol with bromine in carbon tetrachloride was reported by Braae (12).

Although in recent years a fair number of polar nonaqueous solvents have been employed in polarography, those of most interest from the standpoint of problems encountered in the research reported here are limited in number. Thus Allison (2) was able to obtain polarographic waves for lead in methanol. He found that dissolved oxygen could be removed by degassing with nitrogen which had been bubbled through one or more scrubbers containing alkaline pyrogallate to remove the oxygen present in the nitrogen tank. Lyons (42) studied the polarographic waves of cadmium in methanol, and pyridine. Jones (30) performed amperometric titrations

of acids and bases in a 2-propanol-2,2,4-trimethylpentane mixture, while

Vleck (67) was able to make determinations of several strong acids in

ethanol. Other workers were able to determine p-nitrosodiethylaniline

and carbon disulfide in ethanol (32, 68). Hans and von Strum (19, 20)

obtained polarographic waves for copper in methanol, ethanol, 1-butanol,

and 1-pentanol, although in the higher alcohols it was necessary to plot

the curves manually to correct for the iR-drop.

Accompanying this increase in the study of nonaqueous polarography

was an increase in the study of instruments for rapid, accurate, and

convenient use with nonaqueous solvents. In ordinary polarography, the

current is plotted against the potential applied to the cell. Actually

what should be plotted is the effective potential, but since the cell

resistance in aqueous work is of such value that the iR-drop does not

normally introduce an appreciable error it is usually ignored. In

nonaqueous solvents the cell resistance is of such high value the iR-

drop can no longer be ignored. If the cell resistance is known, the

curve may be corrected for the iR-drop and the effective potential may

be determined by the following equation:

$$E_{eff} = E_{app} - iR$$

where $\underline{i}$ is the current at the applied potential, $\underline{R}$ is the resistance of

the cell and circuit, and $\underline{E}_{eff}$ and $\underline{E}_{app}$ are the effective and applied

potentials. If either the cell resistance or the current becomes ex-

tremely large, the curve may become so distorted that the polarographic

waves are not recognizable.

Several methods have been devised to compensate for iR-drop auto-

matically. Nicholson (50) reported a method of compensation in which

an auxiliary bridge, operated by the pen chart circuit, was connected in series with the cell. This device applied to the cell a corrective voltage which was equal and opposite to the iR-drop. Arthur et al (4, 5, 41) first approached the problem by devising a polarograph which plots the current against the actual effective potential. Sawyer, Pecsok and Jenson (61) reported the development of an iR-compensating polarograph which is similar in principle to the instrument developed by Arthur et al. Jackson and Elving (28) described a compensator in which a standard resistor is placed in series with the polarographic cell and the iR-drop across the resistor is made equal to the iR-drop across the cell by amplification. The amplifier output is placed in series with the applied potential from the bridge and thereby compensates for the iR-drop within the cell. Kelley, Jones and Fisher (31) and Oka (51) have also reported instruments which compensate for the iR-drop.

In 1961 Arthur (7) reported the development of a compensator which can be used with almost any conventional polarograph. This compensator requires the use of a polarographic cell containing two calomel electrodes and the usual DME.

Amperometric Titrations

The diffusion current is dependent on the concentration of the oxidizable or reducible ion present. If one reduced the concentration of that ion present, one would also reduce the diffusion current. Titrations based on measurement at a selected potential, of the diffusion current of the substance being titrated, or that of the reagent, or of both, during the titration are called amperometric titrations (37, 46). The current is measured after each addition of reagent. When these

current measurements are plotted against the volume of reagent added, the points should describe two straight lines, the intersection of these lines being the end point of the titration.

There are four main types of amperometric titrations based on the shape of the titration curves they give. The different shapes are dependent upon whether the substance being titrated, the reagent, or both, are oxidizable or reducible at the applied e. m. f. used. Consider the titration of a substance A with a reagent B which removes A from the solution by precipitation, complex formation, oxidation, or reduction. The following shapes of curves would result.

(a) Substance A yields a diffusion current while reagent B does not. As B is added, the diffusion current decreases continuously (see Figure 2) until just before the equivalence point is reached. Very near the equivalence point the current has a value dependent upon the equilibrium concentration of A and upon the residual current. After the equivalence point is passed, the current very rapidly approaches the residual current. The current should be corrected for the volume change during the titration, according to the equation:

$$I_{corr} = I_{obs} \frac{V + x}{V}$$

where I_{corr} and I_{obs} are the corrected and observed currents, V is the original volume, and x is the volume of reagent added. A graph of the corrected current plotted against the volume of reagent added consists of two straight lines with the exception of a curved portion near the equivalence point owing to the equilibrium concentration of A. If the two straight lines are extrapolated, their intersection is the end point of the titration. Typical graphs are shown in Figure 3.
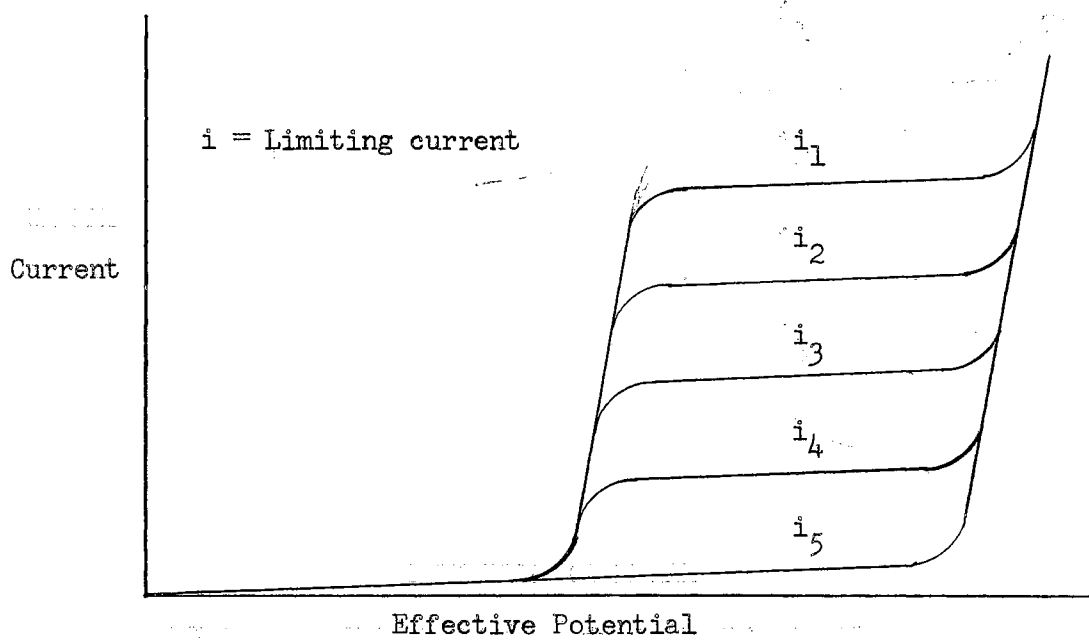
Figure 2. Change in Polarogram during an Amperometric Titration
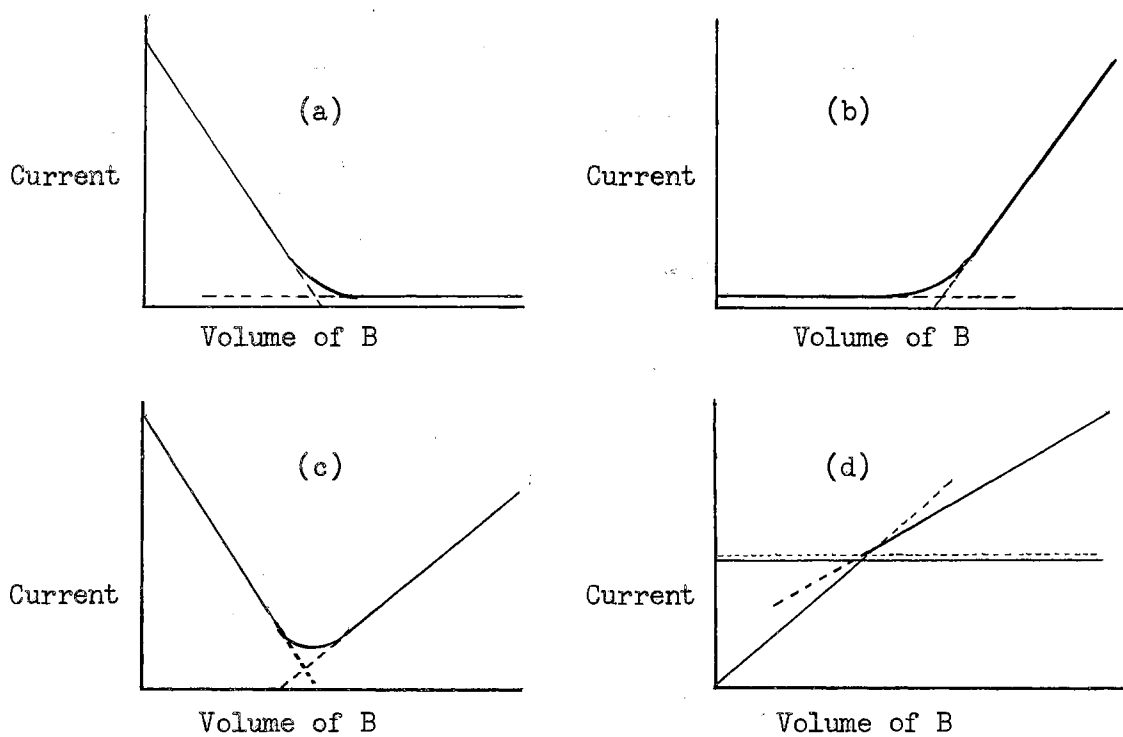
Figure 3. Common Amperometric Titration Curves

(b) Substance A is not oxidized or reduced at the DME, but reagent B yields a diffusion current at the applied voltage. The explanation of this curve is very similar to that in (a).

(c) Both substances A and B give diffusion currents at the applied e. m. f. The explanation again is similar to that in (a).

(d) Substance A gives an anodic diffusion current at the same voltage as that at which B gives a cathodic diffusion current. Prior to the end point the anodic diffusion current of A is decreasing and after the end point the cathodic diffusion current of B is increasing. At the end point the current is equal to the residual current. There is usually a small inflection at this point owing to the difference in diffusion coefficients of A and B.

Nonaqueous Metal-amine Complexes

The study of the formation, stability, properties, and decomposition of complex ions in aqueous solutions is a well established field. Several books have been written covering the subject (10, 18, 59). There are a few investigators working in this field who are using nonaqueous solvents; however, the number of investigators who are working with the amine complexes is quite small. Almost all of the investigators working in the area of nonaqueous metal-amine complexes are preparing the solid crystals and studying the composition, structures, and properties of these.

Presad, Chatterjee and Rao (55) prepared compounds of stannic iodide with various amines in a benzene medium and studied their properties. They found a ratio of four moles of primary amine or two moles of secondary amine to each mole of stannic iodide. These iodide salts of the stannic amine complex ions were stable in a dry atmosphere,

insoluble in benzene, ether, chloroform, and acetone, soluble in dilute hydrochloric acid, and decomposed by sodium hydroxide.

The complex salts of zinc acetate with pyridine and zinc acetate with n-butylamine were prepared by Senenenko and Kurdyumov (63) by the direct addition of the anhydrous zinc acetate to the amine. These complex salts were found to be very unstable in contact with the atmosphere and soluble in water. Thiele (66) prepared the dimethylzinc complexes of several tertiary amines by direct addition and studied their properties. Sharma and Sinka (64) studied the complex of zinc and methylamine by means of the distribution between chloroform and water and found a $Zn:CH_3NH_2$ mole ratio of 1:2.8. This mole ratio was independent of the methylamine concentration.

Using various lithium aluminum hydride derivatives as the solute, M, and ether-P as cosolvents where P was tetrahydrofuran, methanol, or ethanol, Hollingsworth, Smalley and Podder (26) formed complexes of the general formula M·mP. Values for $\underline{m}$ when methanol or ethanol was the solvent varied from 1.0 to 1.2.

Several investigators have conducted studies of nickel (II) complex ions. Ahmed and Wilkins (1) studied the ethylenediamine complex in acid solutions. Prasad and Krishnan (56) determined the formula, color, and melting points of several heavy primary amines in ether, while Sacconi and Lombarde (60) conducted their investigations on interactions of several amines and diacetyl bisbenzoylhydrozinonickel(II) in benzene. The spectral and magnetic properties of several tris complexes of nickel(II) perchlorate with several substituted ethylene diamines isolated from different nonaqueous solutions were reported by Pavkovic and Meek (52).

Cockerell and Walton (15) studied the stability of complexes of 2-aminoethanol with Ag(I), Ni(II), and Cu(II), and of ethylenediamine with Cu(II) and Zn(II) with a cation exchange resin. The stabilities of the ethylenediamine complex were found to be greater than those found in aqueous solutions.

Schaap, Messner and Schmidt (62) determined the half wave potential of various metal ions in anhydrous ethylenediamine. They found that metal ions that form the more stable ethylenediamine complexes become relatively more difficult to reduce when the solvent is changed from water to ethylenediamine.

The complexes formed between several semicarbazones and cupric chloride in ethanol were reported by El Khadem, Iskander, and Zayan (17). They found some ratios of 1:1 and some of 1:2 between the central copper ion and the semicarbazone and proposed possible structures based on their study of the infrared spectra.

Callahan, Fernelius and Block (14) determined the thermodynamic formation constants of several divalent metal ions with various ligands in a 50 and 75 volume percent dioxane-water mixture. James and Williams (29) used a 50 volume percent dioxane-water mixture as the solvent and determined the oxidation-reduction potentials for Cu(I) and Cu(II) complexes with ammonia, ethylenediamine, aniline, and several other ligands.

Pflaum and Brandt(53) studied the stability constants and formulas of the Cu(II) complexes with 1,10-phenanthroline, 2,2'-bipyridine, and 2,2', 2''-terpyridine. These complexes were prepared in a 50 volume percent nonaqueous solvent-water mixture and extracted with benzene, chloroform, carbon tetrachloride, isoamyl alcohol and toluene.

Caglioti, Furlani, Dessey and Ibarra (13) prepared numerous complexes in alcohol, using cupric chloride and aliphatic diamines with two to ten carbon atoms. The complexes, which generally precipitated immediately, had compositions and appearances which varied with the ratio of the reagents. With an excess of cupric chloride, the composition was $CuCl_2 \cdot \frac{1}{2}Am$ (Am = diamine); in solutions containing approximately equal molar concentrations, the composition was $CuCl_2 \cdot Am$; and in solutions with a large excess of diamine, the composition was $CuCl_2 \cdot 2Am$. These complexes were insoluble in most organic solvents and decomposed in water and in aqueous sodium hydroxide. These investigations were all conducted at a concentration of 0.1 molar for the amines and for the cupric chloride.

Using a mixture of high molecular weight primary monamines (with an average molecular weight of 207) in a 1:1 mixture of 2-propanol and 2,2,4-trimethylpentane, Moran (47) performed amperometric titrations with cupric chloride with 0.05 M lithium nitrate as a supporting electrolyte. He found an amine-to-Cu(II) ion mole ratio of 1.70 to 1.73 when the concentration of the amine was 2×10^{-3} M. When the concentration of the amine was reduced to 5×10^{-4} M the ratio was 1.99 and with a concentration of 1×10^{-4} M the ratio was 2.06.

Crowe (16) performed amperometric titrations in 2-propanol using a rotating platinum microelectrode. Using 0.1 M lithium nitrate as the supporting electrolyte, he found apparent coordination numbers in 10^{-4} M amines as follows: ammonia, 2.21; methylamine, 1.64; ethylamine, 1.64; and n-butylamine, 1.54. Crowe also reported an increase in apparent coordination number with a decrease in concentration but found this was

corrected when he ran a blank on the solution and made the calculations on a corrected volume of titrant.

Nelson and Iwamoto (49) found aquo-copper (II) complexes formed in acetone and reported appreciable values for their formation constants. In their investigations they found that unless extreme precautions are taken to exclude the water from the solvents, the water molecules will compete with other ligands in the formation of complexes.

CHAPTER II

SCOPE OF INVESTIGATION

The purpose of this investigation was to examine the behavior of copper (II) ions in 2-propanol in the presence of different supporting electrolytes and with different amines. It was hoped that by performing amperometric titrations on these solutions the nature of the complex ions formed could be discovered. Another purpose of this investigation was to develop a technique that could be followed in investigations involving different metal ions, solvents, supporting electrolytes, and amines from those used in this work.

CHAPTER III

APPARATUS

The polarograph used in this investigation was a Sargent Model
XV Pen Recording Polarograph. All polarographic work was performed
using the Sargent Polarographic iR Compensator designed by Arthur (7).

The polarographic cell used in this work was the Arthur 3-electrode
polarographic electrolysis vessel which was purchased from E. H. Sargent
& Co. This cell was designed by Dr. Paul Arthur (7) and is shown in
Figure 4. The electrolysis reference electrode and the stable refer-
ence electrode were both aqueous saturated calomel electrodes. The
salt bridges contained in the cell consisted of small asbestos fibers
sealed in the glass between the calomel cells and the electrolysis
cell. The resistance of these salt bridges was found to be about 30,000
ohms each. It was found that as long as the liquid level in the elec-
trolysis cell was kept above that in the reference electrode cells, no
diffusion was observed to take place into the electrolysis cell.

Since the calomel electrodes are separate units from the cell it-
self, it was possible to completely degas the solution before any liquid
was added to the calomel cell holders. To connect the calomel cells it
was necessary to add only a small amount of saturated KCl to the calo-
mel cell holders and insert the cells. The purpose of the saturated
KCl was to make electrical contact with the salt bridges. The calomel

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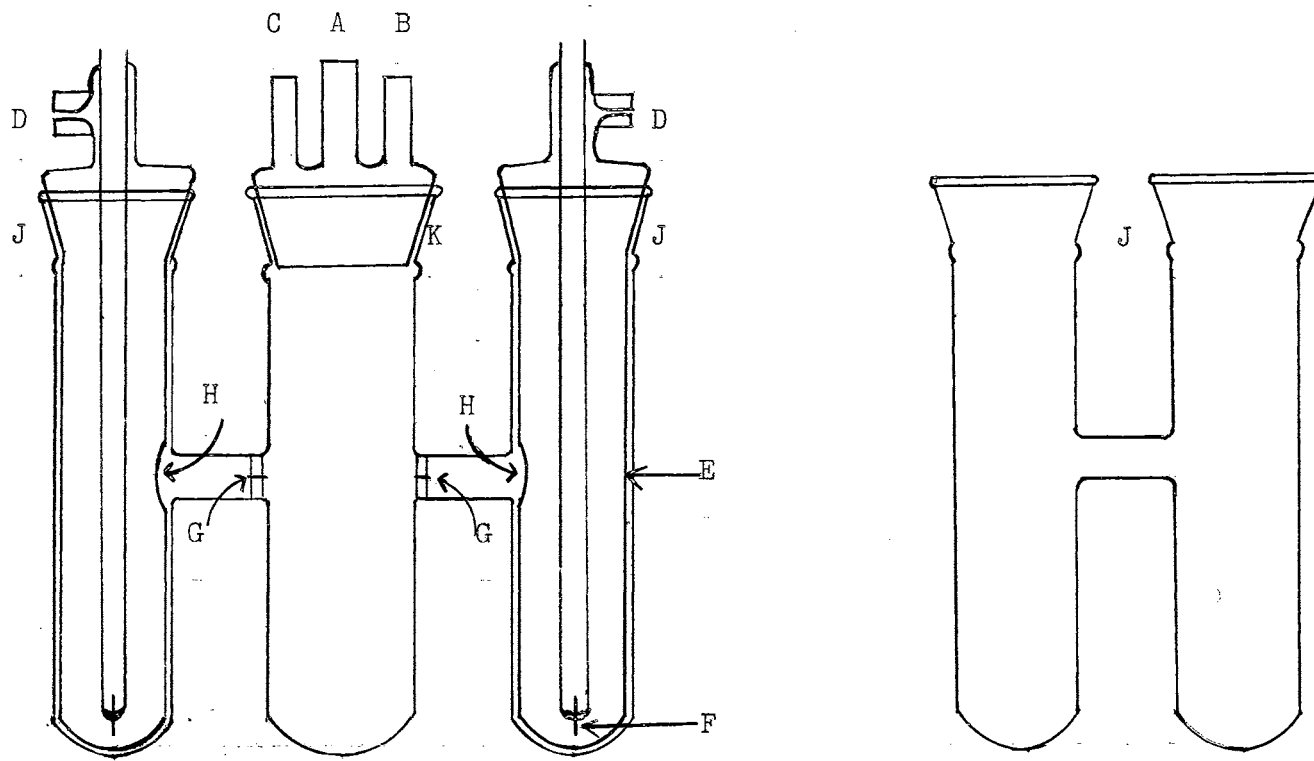
a. Electrolysis Vessel   b. Storage compartment

A. DME inlet   D. Air Vent   G. Asbestos fiber salt bridge
B. Gas dispersion tube inlet   E. Calomel electrode   H. Inlet to electrode
C. Burette delivery tip inlet   F. Platinum wire   J. Standard taper 24/40 joint
                                                                          K. Standard taper 34/28 joint

Figure 4.   Three Electrode Polarographic Electrolysis Vessel and Calomel Cell
                                    storage compartment.

cells were never inserted until just before the polarograms were made in order to keep any diffusion that might have occurred to a minimum. The cells were stored in a separate compartment designed for just such purpose. This compartment (Figure 4) always had a small amount of saturated KCl in it to eliminate the possibility of the calomel cells becoming dry.

The work performed at extreme limits of sensitivity was performed with the Sargent Micro Range Extender for the Model XV Polarograph.

A Beckman Zeromatic pH meter was used in the standardization of the amine solutions. The pH meter was connected to a Sargent Model SR Potentiometric Recorder for plotting the titration curves. Standard HCl was added by means of a 10 ml. syringe whose plunger was driven at a constant rate by a motor arrangement designed by Dr. Paul Arthur.

In the amperometric titrations, a microburette with a capacity of 10 ml. and graduations every 0.02 ml. was used.

The dropping mercury electrode consisted of a length of marine-barometer tubing cut to adjust the drop time to the desired period. This was attached to a constant-head mercury reservoir by means of a stopcock and standard taper joint arrangement which permitted easy changing of the DME for use in different solvents. Surgical rubber tubing was used and held to the glass tubing with tightly twisted wire. Each DME was always left standing in the solvent in which it was used and was never used in any other solvents.

CHAPTER IV

REAGENTS

Acetic Acid. Baker glacial reagent grade was used without further purification.

Ammonium Hydroxide. Baker reagent grade was used without further purification.

Boric Acid. Baker Analyzed reagent grade was used without further purification.

n-Butylamine. Matheson reagent grade was used without further purification.

Cadmium Chloride. Baker and Adamson reagent grade was used without further purification.

Chromic Sulfate. Mallinckrodt Analytical reagent grade $Cr_2(SO_4)_3 \cdot XH_2O$ was used without further purification.

Copper Metal. Baker and Adamson reagent grade was used without further purification.

Cupric Chloride. Baker and Adamson reagent grade was used without further purification.

Cupric Nitrate. Fisher Scientific reagent grade was used without further purification.

n-Decylamine. Columbia Organic Chemicals Company purified grade was used after being redistilled.

Ethanol. U. S. Industrial Chemicals Company reagent grade was used without further purification.

Hydrochloric Acid. Baker Analyzed reagent grade was used without further purification.

Lithium Chloride. Baker Analyzed reagent grade was used after being dried in an oven at 115°C.

Lithium Nitrate. Fisher Scientific reagent grade was used after being dried in an oven at 115°C.

Mercuric Nitrate. Baker Analyzed reagent grade was used without further purification.

Mercurous Chloride. Fisher Scientific reagent grade was used without further purification.

Mercury. Baker reagent grade was used without further purification. The used mercury was reclaimed by pre-oxidation, filtration through a gold-adhesion filter, and vacuum distillation.

Nitric Acid. Baker Analyzed reagent grade was used without further purification.

Nitrogen. Linde laboratory grade nitrogen was used after being purified by the method described by Arthur (3).

Phenolphthalein. Baker reagent grade powder was used after being dissolved in a 1:1 ethanol-water solution.

Potassium Acid Phthalate. Mallinckrodt Analytical reagent grade was used without further purification.

Potassium Carbonate. Fisher Scientific reagent grade was used without further purification.

Potassium Chloride. Fisher Scientific reagent grade was used without further purification.

Potassium Hydroxide. Fisher Scientific Reagent grade was used without further purification.

Potasium Iodide. Baker and Adamson reagent grade was used without further purification.

Potassium Thiocyanate. Fisher Scientific reagent grade was used without further purification.

2-Propanol. Baker Analyzed reagent grade was used after being redistilled in the presence of KOH and again after treatment with K_2CO_3.

n-Propylamine. Matheson, Coleman & Bell reagent grade was used without further purification.

Sodium Borate. Baker reagent grade was used without further purification.

Sodium Hydroxide. Fisher Scientific reagent grade was used without further purification.

Sodium Thiosulfate. Fisher Scientific reagent grade was used without further purification.

Starch. Baker Analyzed reagent grade was used without further purification.

Sulfuric Acid. Fisher Scientific reagent grade was used without further purification.

Urea. Merck reagent grade was used without further purification.

Zinc Chloride. Mallinckrodt Analytical reagent grade was used without further purification.

Zinc Metal. Fisher Scientific rods were used without further purification.

CHAPTER V

EXPERIMENTATION AND DISCUSSION

Although a few investigators are working in the area of nonaqueous copper(II)-amine complexes, their work consists mainly of preparing the solid crystals, studying their properties and structures, and from this postulating what has happened in the solution. One purpose of this investigation was to study the formation of the copper(II)-amine complexes in nonaquaeous solutions through the use of amperometric titrations. That this approach might be feasible was shown by the exploratory work of Moran (47). Crowe (16) performed experiments of this type using a rotating platinum electrode, and in the research reported in this thesis, the solvent chosen was 2-propanol as it had been shown to be a reliable solvent by both Moran and Crowe.

The first step in this investigation was to develop methods to rapidly and accurately prepare and standardize the solutions used. The solutions were found to give erratic results after standing for long periods of time; therefore, it was necessary to make them fresh quite often.

The 2-propanol was prepared in anhydrous form by dissolving a small amount of potassium hydroxide in it and allowing this to stand at least 24 hours. The solution was then distilled in a nitrogen atmosphere. The distillation was stopped with 100 to 150 ml. of the 2-propanol solution left in the distillation flask, the volume left depending on

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the color of the solution and the temperature. The distillate was then allowed to stand, with occasional stirring, for at least 24 hours over anhydrous potassium carbonate. Distillation of this solution was accomplished in the same manner as described above. The anhydrous 2-propanol was prepared fresh as needed and was kept in a tightly closed container.

The amine solutions were first prepared at a concentration of 1×10^{-3} M in 2-propanol. Twenty-five ml. of this amine solution was then diluted to 50 ml. with distilled water which had been boiled. This solution was titrated with a standard aqueous solution of hydrochloric acid. The acid was added at a constant rate and the titration curve was plotted with a potentiometric recorder. When successive samples of these amines were titrated with a copper(II) solution the volume of titrant required decreased (see Table I). This was probably the result of adsorption of the amine on the glass walls of the container. Since the amount of adsorption would be small, it would not make an appreciable error in the concentration of a more concentrated solution; consequently, the amines were then made at a concentration of 0.1 M and allowed to stand overnight before standardization. To obtain the desired concentration of amine in the electrolysis cell, a 1.00 ml. sample of the 0.1 M solution of amine was taken and added to 99 ml. of 2-propanol with supporting electrolyte. Standardization of this more concentrated amine was accomplished as before except with a more concentrated standard acid. Concentration of these amine solutions were found not to change significantly in the four-week period in which the 2-propanol remained anhydrous.

The hydrochloric acid solutions were standardized using a sodium

hydroxide solution which had been standardized with potassium acid phthalate employing the phenolphthalein endpoint.

The 2-propanol soultions with supporting electrolyte were prepared fresh each week. The concentration of the supporting electrolyte was 0.1 M in all cases. These solutions were stored in tightly closed containers.

Cupric chloride and cupric nitrate were prepared at a concentration of approximately 0.1 M in 2-propanol. After standing overnight, the solutions were filtered. Samples of these solutions were diluted to five times their volume with water and standardized with sodium thiosulfate using the iodometric method described in Pierce, Haenisch and Sawyer (54). The sodium thiosulfate had been previously standardized with reagent grade copper wire using the same method. These solutions were considered the stock solutions and it was found that they could be stored for longer periods of time as they were seldom exposed to the atmosphere. The stock solutions were quantitatively diluted with 2-propanol to a concentration of approximately 0.02 M. These solutions contained the supporting electrolyte in 0.1 M concentration, were prepared fresh each week, and were used in all titrations reported in Tables I through VIV.

The second step in this investigation was the development of a technique which gave reproducible data. It was necessary to keep all solutions as nearly as possible closed against the atmosphere to keep them in the anhydrous form. To perform an amperometric titration, 99 ml. of 2-propanol with supporting electrolyte was placed in the cell. To this was added 1.00 ml. of the amine solution; then the entire solution was degassed for 30 minutes. There was no difference in the end

point of the amperometric titration with the amine added before or after degassing. From this it was concluded that no amine was lost during the degassing procedure. All nitrogen passing through the cell was pre-saturated with 2-propanol to avoid loss of alcohol from the cell and thus avoid a change in concentration of the amine.

When degassing was near completion, a small volume of saturated potassium chloride solution was added to each calomel cell holder and the calomel electrodes were fitted into place care being taken that no air bubbles were trapped to prevent contact. The cell was then brought into contact with the dropping mercury electrode. The dropping mercury electrode used had a drop time of six seconds per drop.

The 10 ml. microburette used for the titrations was fitted with an angled extension tip to allow more convenient manipulation of the stopcock. The angled extension tip was then inserted into the cell. Each piece of apparatus entering the cell was fitted with a short piece of rubber tubing which was stretched over the cell outlet. The arrangement used allowed for escape of the nitrogen under a small pressure, but prevented air from diffusing back into the cell.

The titrant was added in 0.5 ml. increments with the solution being degassed for a period of three minutes after each addition. This degassing time was found to be sufficient as a polarogram run after three minutes was not different from a polarogram run after thirty minutes degassing time. Three minutes was felt to be necessary to allow for complete mixing of the solution and titrant. Before lowering the nitrogen dispersion tube into the solution after each addition of titrant, it was touched to the end of the delivery tip of the burette to make certain all titrant measured was in solution.

The polarograph was set so that the applied potential at the dropping mercury electrode was 0.50 volts negative. This potential value was not critical as long as it remained constant during each single titration, the polarogram for copper(II) showing that any potential between 0.5 and 1.0 volt negative was acceptable unless a large excess of copper(II) was to be added. When a large excess of copper(II) was used, the potential chosen was 0.9 volts negative. This point is well past the maximum shown on the polarogram with solutions of relatively high copper(II) concentration.

The first amperometric titrations were performed using 100 ml. of 9.92×10^{-4} M n-butylamine, with 0.1 M lithium nitrate as the supporting electrolyte. This was titrated with 0.0200 M cupric chloride. The titration curves obtained were similar to the one shown in (b) of Figure 4. All points except those very near the end point fell on a straight line except those in sample 4. This curve is shown in Figure 5. The results of a series of five amperometric titrations are summarized in Table I.

TABLE I

TITRATION OF 100 ML. OF 9.92×10^{-4} M n-BUTYLAMINE AND 0.1 M LITHIUM
NITRATE IN 2-PROPANOL WITH 0.0200 M CUPRIC CHOLORDE

Sample	End Point (ml.)	N*	Deviation	Deviation^2
1	3.45	1.44	0.07	0.0049
2	3.33	1.49	0.02	0.0004
3	3.37	1.47	0.04	0.0016
4	3.16	1.57	0.06	0.0036
5	3.16	1.57	0.06	0.0036
Mean	3.30	1.51	0.05	0.0028

Standard Deviation = (Mean of Deviation^2)$^{\frac{1}{2}}$ = 0.053

Relative Standard Deviation = $\dfrac{\text{Standard Deviation}}{\text{Mean of N}}$ = 0.0351 = 3.51%

* N is the Apparent Coordination Number = $\dfrac{\text{Moles of Amine}}{\text{Moles of Cu(II)}}$
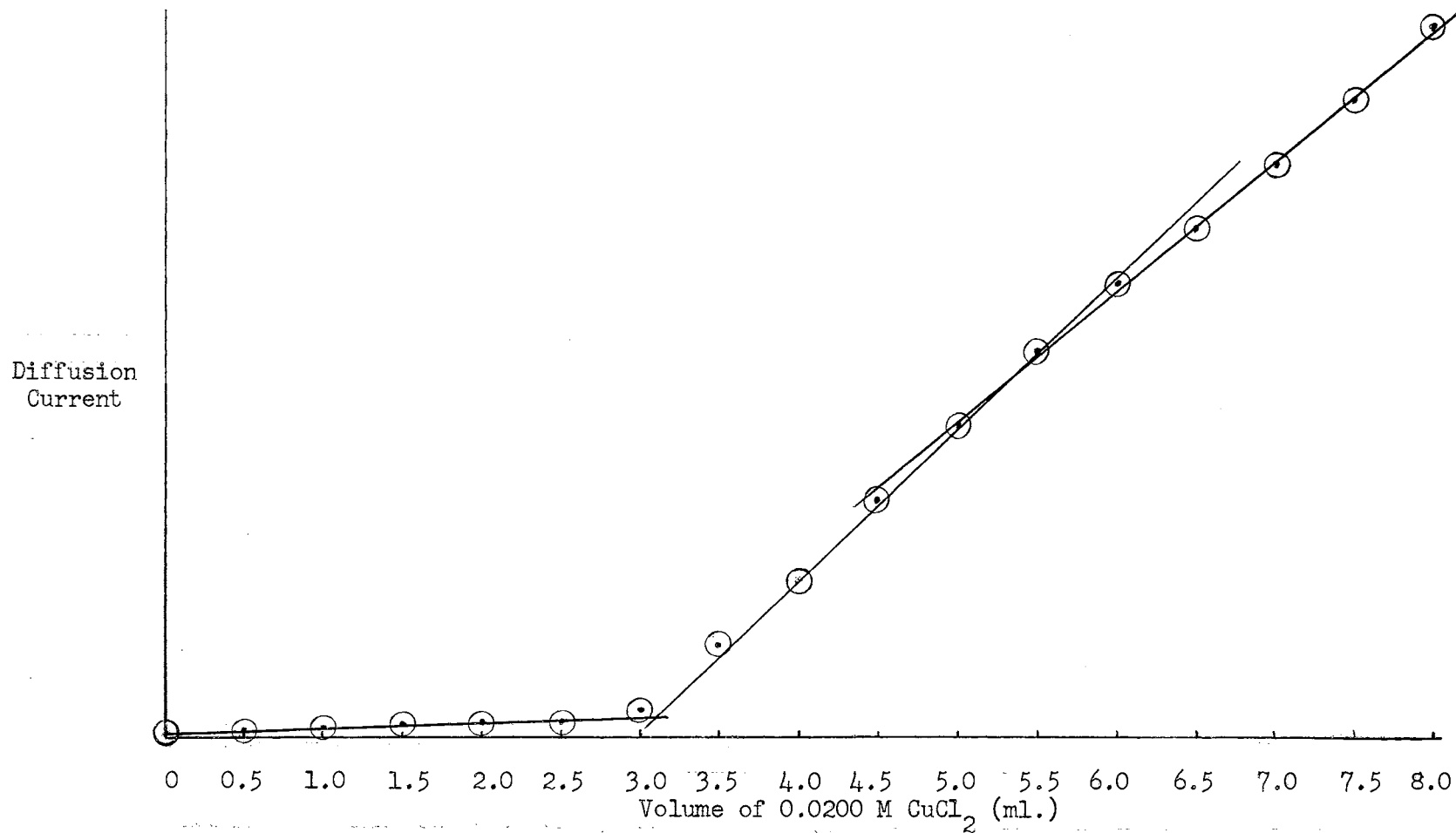
Figure 5. Titration Curve of 100 ml. of 0.000992 M n-Butylamine with 0.02 M Cupric Chloride in 0.1 M Lithium Chloride in 2-Propanol

Sample number 1, Table I, was performed on one afternoon, samples number 2 and 3 were performed on the next afternoon and samples number 4 and 5 were performed on the third afternoon. We see good agreement between numbers 2 and 3 and between numbers 4 and 5 but not among all of the samples. The probable reason for this was adsorption of amine on the walls of the container, as explained earlier. Efforts with amines of this concentration were abandoned in favor of the more concentrated amines which were diluted just prior to titration.

It is interesting at this point to note that if a third straight line is plotted, as is done in Figure 5 using the points from 6.5 to 8.0 ml., we get a line which intersects our second straight line. This intersection occurs at a value of $\underline{N}$ of 0.972. This is very close to a 1:1 ratio of moles amine:moles copper(II). This line was not plotted at this point in the research since it appeared in only one titration and was considered to be a random error; therefore, its possible significance was not grasped.

The next amperometric titrations were performed using 1.00 ml. of approximately 0.1 M n-butylamine added to 99 ml. of 2-propanol with supporting electrolyte. This was titrated with 0.0200 M cupric chloride using 0.1 M lithium nitrate as the supporting electrolyte. The amperometric titrations were performed in the same way as those whose results are shown in Table I. Seven titrations were run over a period of seven days to note whether or not the same effect with time was noted as before. There was no decrease in volume of titrant necessary so it was concluded that this was a reliable technique. The results of this series of titrations are shown in Table II.

TABLE II

TITRATION OF n-BUTYLAMINE IN A LITHIUM NITRATE-2-PROPANOL
SOLUTION WITH CUPRIC CHLORIDE

Sample	End Point*(ml.)	N	Deviation	Deviation^2
1	3.41	1.32	0.03	0.0009
2	3.36	1.34	0.01	0.0001
3	3.24	1.39	0.04	0.0016
4	3.30	1.36	0.01	0.0001
5	3.38	1.33	0.02	0.0004
6	3.33	1.35	0.00	0.0001
7	3.36	1.34	0.01	0.0001
Mean	3.34	1.35	0.02	0.0005

Standard Deviation = 0.022

Relative Standard Deviation = 0.0163 = 1.63%

* For 100 ml. of 9.01 X 10^{-4} M amine titrated with 0.0200 M cupric chloride

As can be seen, the reproducibility of the results for the concentrated n-butylamine which was diluted just prior to titration is much better than for the dilute amine solution. The plots for the titration curves were also all regular with all points except those very near the end point falling on two straight lines.

In the solutions titrated so far, there were several ligands which could be involved in the complex; n-butylamine molecules, nitrate ions, chloride ions, the solvent molecules, and water molecules in very small concentrations (from the $CuCl_2 \cdot 2H_2O$). In an effort to limit the number of different ligands in solution, the next amperometric titrations performed used the same solution as was used before but the titrations were with cupric nitrate instead of cupric chloride as before. This eliminated

the possibility of chloride ions in the solution to become involved in the complex ion. Seven titrations were again performed over a period of seven days. The results of this series of amperometric titrations are shown in Table III.

TABLE III

TITRATION OF n-BUTYLAMINE IN A LITHIUM NITRATE-2-PROPANOL
SOLUTION WITH CUPRIC NITRATE

Sample	End Point*(ml.)	N	Deviation	Deviation^2
1	3.10	1.60	0.03	0.0009
2	3.15	1.58	0.01	0.0001
3	3.22	1.54	0.03	0.0009
4	3.16	1.57	0.00	0.0000
5	3.16	1.57	0.00	0.0000
6	3.15	1.58	0.01	0.0001
7	3.20	1.55	0.02	0.0004
Mean	3.16	1.57	0.01	0.0003

Standard Deviation = 0.018

Relative Standard Deviation = 0.115 = 1.15%

*For 100 ml. of 9.01 X 10^{-4} M amine titrated with 0.0182 M cupric nitrate

From these results it was assumed that the chloride ion was a fairly good ligand in 2-propanol and was complexing in competition with the n-butylamine, for a lower apparent coordination number was obtained with the cupric chloride than was obtained with cupric nitrate. This was a false assumption as will be shown later in this report.

It was desirable at this point to observe the behavior of a different amine and note what effects the nature of the amine would have on the complex formed. The second amine chosen was n-propylamine as there

had been no previous work reported using this amine. The same conditions existed in these titrations as existed with the n-butylamine titrations. The same solvent and the same supporting electrolyte were used. New solutions of cupric chloride and cupric nitrate were made; so the concentrations of these solutions were different.

The results of a series of six amperometric titrations each of n-propylamine with cupric chloride and with cupric nitrate are seen in Table IV and Table V respectively.

TABLE IV

TITRATION OF n-PROPYLAMINE IN A LITHIUM NITRATE-2-PROPANOL
SOLUTION WITH CUPRIC CHLORIDE

Sample	End Point*(ml.)	N	Deviation	Deviation^2
1	2.99	1.40	0.00	0.0000
2	3.00	1.39	0.01	0.0001
3	2.99	1.40	0.00	0.0000
4	2.96	1.41	0.01	0.0001
5	2.95	1.41	0.01	0.0001
6	3.00	1.39	0.01	0.0001
Mean	2.98	1.40	0.01	0.0001

Standard Deviation = 0.01

Relative Standard Deviation = 0.0071 = 0.71%

* For 100 ml. of 8.26 X 10^{-4} M amine titrated with 0.0198 M cupric chloride

By comparing Tables II and III with Tables IV and V it can be seen that the amine makes only a little difference. The values obtained with n-butylamine are different from those obtained with n-propylamine by only 3.5%. This indicates that there probably is only a small steric

hindrance effect with a change in amines.

TABLE V

TITRATION OF n-PROPYLAMINE IN A LITHIUM NITRATE-2-PROPANOL SOLUTION WITH CUPRIC NITRATE

Sample	End Point*(ml.)	N	Deviation	Deviation^2
1	2.73	1.62	0.02	0.0004
2	2.82	1.57	0.03	0.0009
3	2.78	1.60	0.00	0.0000
4	2.80	1.58	0.02	0.0004
5	2.74	1.62	0.02	0.0004
6	2.76	1.61	0.01	0.0001
Mean	2.77	1.60	0.02	0.0003

Standard Deviation = 0.017

Relative Standard Deviation = 0.0106 = 1.06%

* For 100 ml. of 8.26 X 10^{-4} M amine titrated with 0.0198 M cupric nitrate

An effort to determine the extent of the affect caused by the chloride ion was made by using lithium chloride as the supporting electrolyte. If the chloride ion was competing with the amine molecule in coordinate bonding, there should be a decrease in the value of N, when lithium chloride is employed. Amperometric titrations were performed under the same conditions that existed using lithium nitrate as the supporting electrolyte except with lithium chloride in this case. The results of these amperometric titrations are shown in Tables VI through IX.

TABLE VI

TITRATION OF n-PROPYLAMINE IN A LITHIUM CHLORIDE-2-PROPANOL
SOLUTION WITH CUPRIC CHLORIDE

Sample	End Point*(ml.)	N	Deviation	Deviation^2
1	2.36	1.75	0.04	0.0016
2	2.41	1.72	0.01	0.0001
3	2.46	1.68	0.03	0.0009
4	2.42	1.71	0.00	0.0000
5	2.45	1.69	0.02	0.0004
Mean	2.42	1.71	0.02	0.0006

Standard Deviation = 0.025

Relative Standard Deviation = 0.0144 = 1.44%

* For 100 ml. of 8.20 X 10^{-4} M amine titrated with 0.0198 M cupric chloride

TABLE VII

TITRATION OF n-PROPYLAMINE IN A LITHIUM CHLORIDE-2-PROPANOL
SOLUTION WITH CUPRIC NITRATE

Sample	End Point*(ml.)	N	Deviation	Deviation^2
1	2.58	1.67	0.06	0.0036
2	2.64	1.64	0.03	0.0009
3	2.73	1.58	0.03	0.0009
4	2.74	1.58	0.03	0.0009
5	2.70	1.60	0.01	0.0001
Mean	2.70	1.61	0.03	0.0013

Standard Deviation = 0.036

Relative Standard Deviation = 0.0224 = 2.24%

* For 100 ml. of 8.04 X 10^{-4} M amine titrated with 0.0186 M cupric nitrate

TABLE VIII

TITRATION OF n-BUTYLAMINE IN A LITHIUM CHLORIDE-2-PROPANOL
SOLUTION WITH CUPRIC CHLORIDE

Sample	End Point*(ml.)	N	Deviation	Deviation^2
1	3.01	1.64	0.06	0.0036
2	3.02	1.64	0.06	0.0036
3	3.28	1.51	0.07	0.0049
4	3.24	1.53	0.05	0.0025
Mean	3.14	1.58	0.06	0.0036

Standard Deviation = 0.060

Relative Standard Deviation = 0.0380 = 3.80%

* For 100 ml. of 9.80 X 10^{-4} M amine titrated with 0.0198 M cupric chloride

TABLE IX

TITRATION OF n-BUTYLAMINE IN A LITHIUM CHLORIDE-2-PROPANOL
SOLUTION WITH CUPRIC NITRATE

| Sample	End Point*(ml.)	N	Deviation	Deviation^2
1	3.11	1.62	0.04	0.0016
2	3.07	1.64	0.02	0.0004
3	2.95	1.71	0.05	0.0025
4	3.02	1.67	0.01	0.0001
Mean	3.04	1.66	0.03	0.0012

Standard Deviation = 0.034

Relative Standard Deviation = 0.0204 = 2.04%

* For 100 ml. of 1.08 X 10^{-3} M amine titrated with 0.0214 M cupric nitrate

The amperometric titration curves obtained with the lithium chloride as the supporting electrolyte were not the same as the curves obtained using lithium nitrate. The current increased continuously until just before the end point was reached with the lithium chloride. Very near the end point the current showed its usual curved portion. After the end point was passed the current increased at a faster rate. Typical amperometric titration curves are shown in Figure 6 for titrations using lithium nitrate and lithium chloride as the supporting electrolyte.

As can be seen from the tables, the precision for these titrations was not what would be desirable. This is caused in part by the shape of the curves, since it was more difficult to determine the end point, and in part by a behavior encountered here which was not seen earlier. Near what was expected to be the end point, a faint blue-green precipitate appeared as a very slight cloudiness. The amount of this precipitate seemed to increase as the volume of copper(II) solution added increased until the titration was halted. To follow the formation of the precipitate, the room was darkened after each addition of titrant and a narrow beam of bright light was passed through the solution in the titration cell. No Tyndall effect was present at first, but one appeared before the end point was reached, increased during the remainder of the titration, and appeared strongest at the end of the titration. In ordinary light, the solution appeared only a little cloudy.

During tests for the Tyndall effect, the solution would stand for longer periods of time than the normal three minutes required for degassing and for measurement of the current. It was during this time a decrease in current with time was noticed. If the solution was allowed to stand after each addition of titrant, the current would decrease slowly

Current

Volume of copper(II) solution
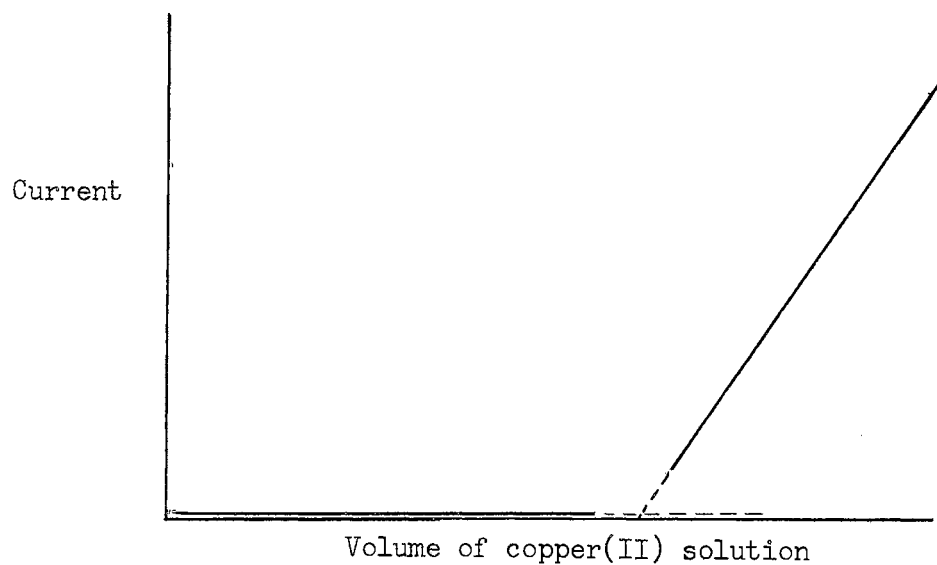
(a) Lithium Nitrate Used as Supporting Electrolyte

Current

Volume of copper(II) solution
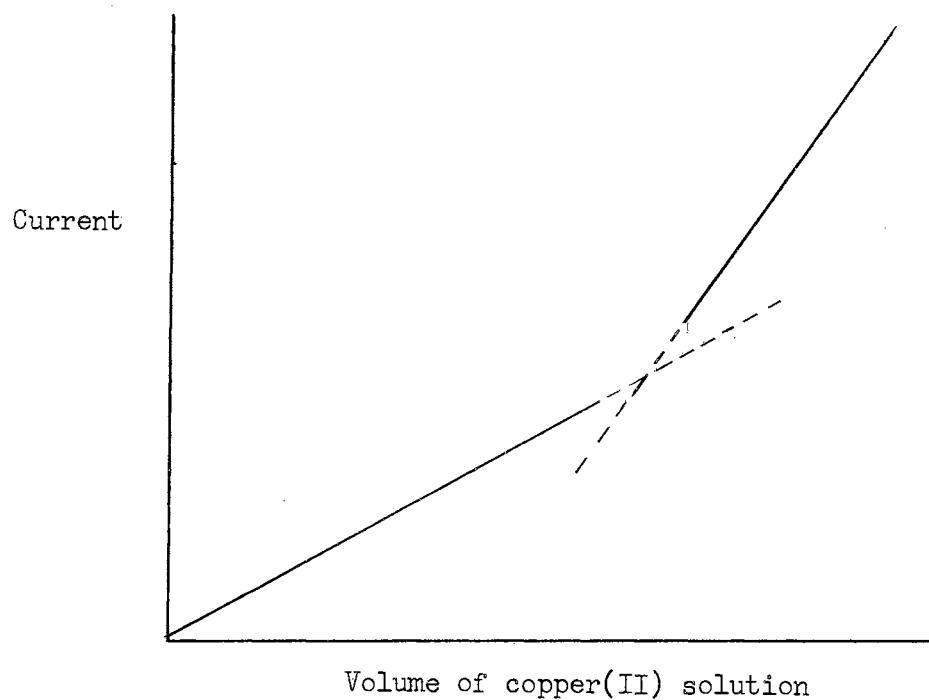
(b) Lithium Chloride Used as Supporting Electrolyte

Figure 6. Amperometric Titrations of an Amine with a Copper(II)
Solution Using Lithium Nitrate and Lithium
Chloride as Supporting Electrolytes

over a long period of time. This decrease occurred both with or without stirring of the solution by passing nitrogen through it. It was necessary to allow the solution to stand overnight for no further decrease in current to be obtained, and the Tyndall effect increased as the solution stood.

This same behavior was encountered by another worker, Jean Lentz, in the same laboratory who was performing amperometric titrations by titrating an amine into a copper(II) solution. In this case, the behavior was much more pronounced, a more definite precipitate was formed. This work was temporarily halted to allow Miss Lentz time to develop a reliable technique to use in the study of the precipitate-forming amperometric titrations.

In order to study the steric hindrance effects of the amines more closely, the same type titrations were performed with n-decylamine as the ligand molecule. These titrations were performed with the same technique as was used on the other amines, and were performed using both lithium nitrate and lithium chloride as the supporting electrolytes. The results of these amperometric titrations are shown in Tables X through XIII.

TABLE X

TITRATION OF n-DECYLAMINE IN A LITHIUM CHLORIDE-2-PROPANOL
SOLUTION WITH CUPRIC CHLORIDE

Sample	End Point*(ml.)	N	Deviation	Deviation^2
1	3.76	1.35	0.01	0.0001
2	3.74	1.36	0.02	0.0004
3	3.94	1.30	0.04	0.0016
Mean	3.81	1.34	0.02	0.0007

Standard Deviation = 0.026
Relative Standard Deviation = 0.0197 = 1.97%
* For 100 ml. of 7.90 X 10^{-4} M amine titrated with 0.0156 M cupric chloride

TABLE XI

TITRATION OF n-DECYLAMINE IN A LITHIUM CHLORIDE-2-PROPANOL
SOLUTION WITH CUPRIC NITRATE

Sample	End Point*(ml.)	N	Deviation	Deviation^2
1	3.52	1.17	0.03	0.0009
2	3.65	1.13	0.01	0.0001
3	3.65	1.13	0.01	0.0001
Mean	3.61	1.14	0.02	0.0004

Standard Deviation = 0.02

Relative Standard Deviation = 0.0142 = 1.42%

*For 100 ml. of 7.90 X 10^{-4} M amine titrated with 0.0192 M cupric
nitrate

TABLE XII

TITRATION OF n-DECYLAMINE IN A LITHIUM NITRATE-2-PROPANOL
SOLUTION WITH CUPRIC CHLORIDE

Sample	End Point*(ml.)	N	Deviation	Deviation^2
1	4.50	1.13	0.02	0.0004
2	4.42	1.15	0.00	0.0000
3	4.37	1.16	0.01	0.0001
Mean	4.43	1.15	0.01	0.0002

Standard Deviation = 0.014

Relative Standard Deviation = 0.0123 = 1.23%

*For 100 ml. of 7.90 X 10^{-4} M amine titrated with 0.0156 M cupric
chloride

TABLE XIII

TITRATION OF n-DECYLAMINE IN A LITHIUM NITRATE-2-PROPANOL
SOLUTION WITH CUPRIC NITRATE

Sample	End Point*(ml.)	N	Deviation	Deviation^2
1	3.33	1.23	9.03	0.0009
2	2.14	1.31	0.05	0.0025
3	3.35	1.23	0.03	0.0009
Mean	3.27	1.26	0.04	0.0014

Standard Deviation = 0.037

Relative Standard Deviation = 0.0296 = 2.96%

* For 100 ml. of 7.90×10^{-4} M amine titrated with 0.0192 M cupric nitrate

From the values listed on these tables, it would seem that the steric
hindrance effects of n-decylamine are much more pronounced than with
either n-propylamine of n-butylamine. This is in line with the values
reported for Santolene J by Moran (47) and with the values reported for
ammonia, methylamine, ethylamine, and n-butylamine reported by Crowe (16).

When a comparison is made of the values listed, it cannot be said
that the evidence showed the chloride ion as a stronger ligand than the
nitrate. The values shown for the apparent coordination number are
higher in every case with lithium chloride as the supporting electro-
lyte than with lithium nitrate except with n-decylamine in the titra-
tion with cupric nitrate. The values for n-propylamine and for n-butyla-
mine in the titration with cupric nitrate are very close together with
either lithium chloride or lithium nitrate as the supporting electrolyte.

In the titration of n-butylamine with cupric chloride using lithium
nitrate for the supporting electrolyte, we have several possible ligands

in solution, i.e., n-butylamine molecules, nitrate ions, chloride ions, solvent molecules, and water molecules in very small concentration. When the titrations were performed using lithium chloride for the supporting electrolyte, the number of possible ligands was reduced. The value for the apparent coordination number showed a very definite increase from 1.35 to 1.59. This was also true in the case of n-propylamine with cupric chloride, the change being from 1.40 to 1.71, and for n-decylamine, from 1.15 to 1.34. In the titration of n-decylamine with cupric nitrate the value using lithium nitrate for the supporting electrolyte instead of lithium chloride showed an increase from 1.14 to 1.26. This was not true for the titrations of n-butylamine and n-propylamine with cupric nitrate as these values showed a slight decrease in going from lithium chloride to lithium nitrate as the supporting electrolyte, the changes being from 1.66 to 1.57 and 1.61 to 1.60, respectively. These last two values are very close to each other, however, so the fact that their behavior is different from the expected may be caused by some factor as yet undetermined.

At this time it was decided to see if a copper polarographic wave could be detected in front of the copper complex polarographic wave, the theory being that if a equilibrium is established between copper and the copper complex, the copper polarographic wave should be detectable if the instrument could be increased in sensitivity. A solution containing only enough cupric nitrate to reach the apparent end point with n-butylamine in 0.1 M lithium nitrate was used. A Sargent Micro Range Extender was used with a sensitivity of 0.0001 microamperes per millimeter. At this sensitivity the polarographic wave

for the copper complex was so great as to be off scale. There was no detectable simple copper polarographic wave at this sensitivity or at any lower sensitivity, nor was there a copper polarographic wave found with solutions containing more, and solutions containing less cupric nitrate. There also was no copper wave detected using cupric chloride as the titrant with either supporting electrolyte. If a copper wave existed, its half wave potential is so close to the half wave potential value of the copper complex that they are impossible to separate with the instruments used here. Since no work of this nature gave usable information, further attempts were abandoned.

Five amperometric titrations were performed by adding 1.00 ml. of 0.0934 M cupric nitrate to 99 ml. of 0.1 M lithium nitrate in 2-propanol and titrating with 0.0195 M n-butylamine. Thirty minutes of degassing time was allowed the cupric nitrate solution before the current was measured. The n-butylamine was then added in 0.5 ml. increments, with nitrogen passing through the solution for only one minute (exactly) before the current was measured. The potential was applied only for the time necessary to obtain a current value and there was no attempt to allow the current to stabilize. When the current values were plotted, the points were somewhat erratic, but in most cases did describe four straight lines for three end points. The results of five amperometric titrations of this type are shown in Table XIV.

The first end point was the easiest to see, but it was in a region of very erratic behavior. In sample number five the intersection of straight line number one with straight line number two occurred prior to one of the points on line number one, so this was considered to be no intersection. The two lines did not intersect at all in sample number four.

TABLE XIV

TITRATION OF CUPRIC NITRATE IN A LITHIUM NITRATE-2-PROPANOL
SOLUTION WITH n-BUTYLAMINE

	First end point			
Sample	End Point*(ml.)	N	Deviation	Deviation^2
1	1.08	0.225	0.010	0.000100
2	0.97	0.202	0.013	0.000169
3	1.04	0.217	0.002	0.000004
4	No Intersection	----	-----	--------
5	No Intersection	----	-----	--------
Mean	1.03	0.215	0.008	0.000091

Standard Deviation = 0.0095

Relative Standard Deviation = 0.0443 = 4.43%

* For 100 ml. of 9.36 X 10^{-4} M cupric nitrate titrated with 0.0195 M amine

	Second end point			
Sample	End Point (ml.)	N	Deviation	Deviation^2
1	4.84	1.01	0.01	0.0001
2	4.85	1.01	0.01	0.0001
3	No Intersection	-----	----	-------
4	No Intersection	----	----	-------
5	4.70	0.98	0.02	0.0004
Mean	4.80	1.00	0.01	0.0002

Standard Deviation = 0.0141

Relative Standard Deviation = 0.0141 = 1.41%

Table XIV continued

Sample	End Point (ml.)	Third end point N	Deviation	Deviation^2
1	7.56	1.59	0.01	0.0001
2	7.48	1.57	0.01	0.0001
3	7.55	1.58	0.00	0.0000
4	7.55	1.58	0.00	0.0000
5	7.49	1.57	0.01	0.0001
Mean	7.53	1.58	0.01	0.0001

Standard Deviation = 0.01

Relative Standard Deviation = 0.0063 = 0.63%

In samples number three and four, lines number two and three did not intersect each other; but both did intersect line number four at the same value, 7.55 ml.

A sixth amperometric titration was performed as above except with a time period of two hours allowed for the solution to reach current equilibrium. If the current showed a decrease after this time it was allowed another two hours. If a continued decrease in current was still present another two hours were allowed and so on until constant current was obtained. Current values obtained after the first three 0.5 ml. increments were added were erratic and did not fall on a straight line when the current was plotted versus the volume of n-butylamine added; however, all other points, within experimental error, described only two straight lines with an intersection at 7.54 ml. This gives a value for the apparent coordination number of 1.58 which agrees with the value shown in Table III. This indicates the formation of a stable

complex at this amine:copper(II) ratio. Owing to the amount of time required for this titration, no further titrations of this nature were performed.

A new technique was developed in which the amperometric titrations were performed after allowing time for all solutions to reach a steady current value. A series of seventeen solutions were prepared, each with a total volume of 100 ml. of 0.1 M lithium chloride in 2-propanol. Each solution contained 1.00 ml. of 0.108 M n-butylamine and from 0.00 to 8.00 ml. of 0.0214 M cupric nitrate in 0.5 ml. increments. These solutions were allowed to stand for a period of four days. Each solution in turn was then degassed for thirty minutes after which a polarogram was made. In those solutions which contained a precipitate, there was no difference in the polarogram, with or without the precipitate being present in the electrolysis cell. The temperature was held constant to within $\pm$ 0.3°C. The current reading at 0.90 volts negative were plotted versus the volume of cupric nitrate in the solutions. A graph of these points is shown in Figure 7.

The solution containing no cupric nitrate was clear, while the solution containing 0.5 ml. of the cupric nitrate solution was a light green. Each successive solution became a darker green color until a blue-green precipitate first appeared in the solution containing 2.00 ml. of cupric nitrate. This precipitate increased in amount in each solution to the solution containing 3.5 ml. of cupric nitrate. All other solutions after this appeared to have the same amount of precipitate present. A faint yellow color first appeared in the solution containing 4.00 ml. of cupric nitrate. A very faint maximum also appeared in the polarogram of this solution. This color, and the size of the
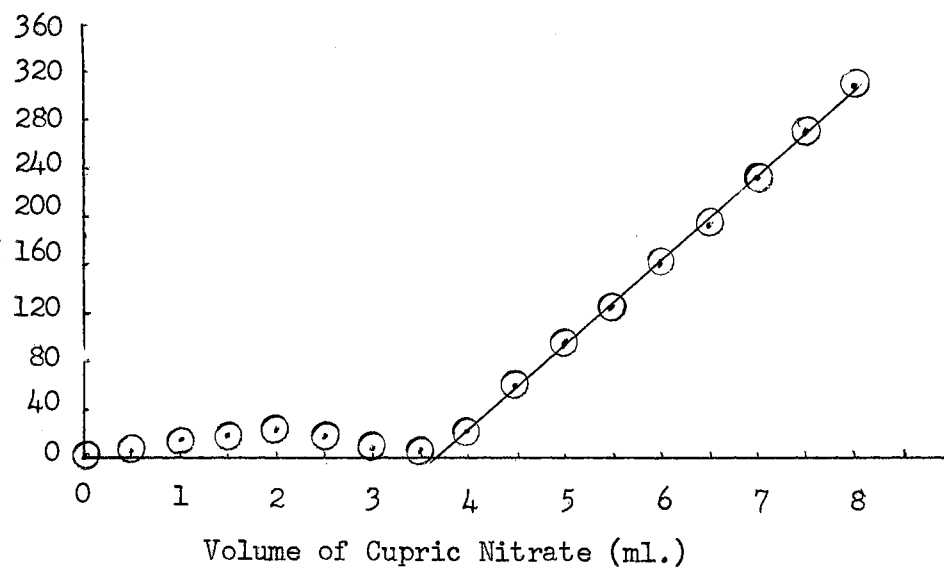
Figure 7. Amperometric Titration Curve of n-Butylamine
          with Cupric Nitrate in 0.1 M Lithium Chloride
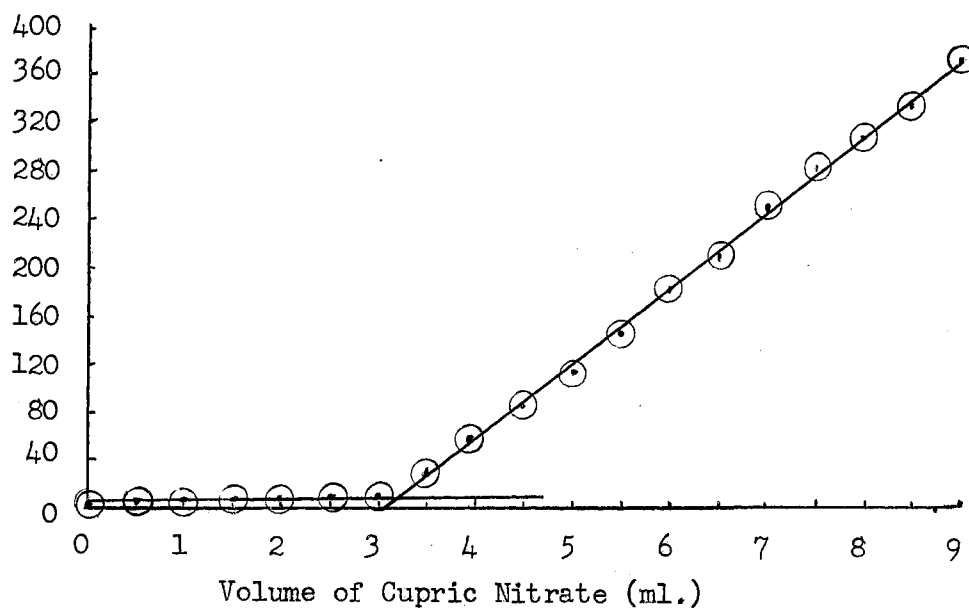   in 2-Propanol

Figure 8. Amperometric Titration Curve of n-Butylamine with
          Cupric Nitrate in 0.1 M Lithium Nitrate in
          2-Propanol

maximum increased through the remainder of the solutions. When this titration curve is compared with the one shown in Figure 6 it is noted that the points prior to the end point do not show the continued increase in value as was shown previously. This can be accounted for by considering the slow formation of a very stable complex with an apparent coordination number of approximately 1.35. This value does not agree with the value of 1.66 which is listed in Table IX.

A second series of twenty one solutions, each containing 100 ml. total volume on 0.1 M lithium nitrate in 2-propanol were prepared. Included in this total volume was 1.00 ml. of 0.100 M n-butylamine and from 0.00 to 10.00 ml of 0.214 M cupric nitrate in 0.5 ml. increments. A polarogram was made of each solution after it had stood for four ddys, each being degassed for thirty minutes after which a graph of the current was drawn as was done with the first series of solutions. The resulting graph (Figure 8) is nearly identical to the graph shown in Figure 5 (a) and the value of 1.53 obtained for the apparent coordination number agrees very well with the value of 1.57 reported in Table III. In the solutions with the lithium nitrate as the supporting electrolyte, a stable complex is apparently formed quite rapidly.

A greenish-brown precipitate first appeared in the solution containing 0.5 ml. of cupric nitrate and increased in amount until the solution contained 2.5 ml. of cupric nitrate. At this point a blue-green precipitate appeared to be mixed with the greenish-brown precipitate. In the solution containing 3.5 ml. of cupric nitrate a faint blue color was observed. This color increased in intensity throughout the remainder of the solutions in this series. A small maximum also first appeared on the polarogram of the solution containing 3.5 ml. of cupric

nitrate. The size of the maximum also increased throughout the remainder of the solutions. The presence of the maximum would tend to indicate the presence of free, uncomplexed copper(II) in the solution. The color also indicates its presence.

A third, fourth and fifth series of solutions were prepared as before, using 0.01 M lithium chloride in 2-propanol. In the third series 1.00 ml. of 0.108 M n-butylamine and from 0.00 to 9.00 ml. of 0.0212 M cupric chloride were added. In the fourth series, 2.00 ml. of 0.108 M n-butylamine and from 0.00 to 16.00 ml. of cupric chloride were added; in the fifth series, 1.00 ml. of 0.0108 M n-butylamine and from 0.00 to 9.00 ml. of 0.00212 M cupric chloride were added. The amperometric titration curves obtained with these solutions were nearly identical in shape with the curve shown in Figure 8. A value of 1.31 was found for the apparent coordination number in all three series. This value does not agree with the value of 1.59 which is listed in Table VIII.

In the third and fourth series the color and the precipitate were very much the same as that in the first series except the color was darker and the precipitate was heavier in the fourth, more concentrated, series. In the fifth series, there was no precipitate observed either with the unaided eye or by use of the Tyndall effect. The color of the solutions agreed very closely with the colors of the first, third and fourth series.

A sixth and final series of solutions was prepared using 1.00 ml. of 0.106 M cupric chloride and from 0.00 to 20.00 ml. of 0.0100 M n-butylamine in enough 0.1 M lithium chloride in 2-propanol to make 100 ml. total volume. Each solution was allowed to stand for a period

of nine days before a polarogram was made. When the current at 0.90 volts negative was plotted versus the volume of n-butylamine, a graph was obtained with three end points. None of these end points were very distinct as the current values were erratic. The three end points determined, however, occurred at an apparent coordination number of 0.254, 1.31, and 1.52 respectively. The latter two values agree very well with the values of 1.31 reported above and 1.59 reported in Table VIII. No previous experiments were performed from which a value comparable to 0.254 could be obtained. The value does agree as well as can be expected, considering the change in reagents, with the value of 0.215 reported in Table XIV.

CHAPTER VI

SUMMARY AND CONCLUSIONS

As was mentioned previously, the objectives of this research were
to examine the behavior of copper(II) ions in 2-propanol in the presence
of different supporting electrolytes and different amines, discover the
nature of the complex ions formed, and develop a technique that could
be used in future studies of this nature. These objectives were partly
accomplished, and in addition a number of interesting and important
facts were discovered.

Methods of rapidly and accurately preparing and standardizing the
solutions used in the study were developed. Two different techniques
were developed for the amperometric titrations of amine solutions with
copper(II) solutions and of copper (II) solutions with amine solutions.
The results obtained from these titrations indicate a need for further
work in this area.

It was found, from the amperometric titrations, that the apparent
coordination number of the stable cupric ion-amine complex was not a
small whole number. This indicated that probably a mixture of complexes
was being formed in solution and that possibly more than one copper (II)
ion was involved in the complex ion.

The complex ion formed when lithium nitrate is used as the support-
ing electrolyte is formed very rapidly with no indications of time de-
pendency; the complex ion formed with lithium chloride as the supporting

electrolyte indicates time dependency. Even when four to seven days are allowed for the solutions to reach equilibrium, the points prior to the end point, using lithium chloride as the supporting electrolyte, show erratic behavior. This would be explained by the very slow formation of a stable complex ion which shows equilibrium only in solutions of near stoichiometric ratios of copper(II) to amine.

The solutions prepared using lithium nitrate as a supporting electrolyte show very stable and predictable behavior. Using three different techniques with cupric nitrate as the titrant, n-butylamine as the ligand, and lithium nitrate as the supporting electrolyte a stable complex was formed with an apparent coordination number of 1.57, 1.58 and 1.53. These are in very close agreement.

BIBLIOGRAPHY

1. Ahmed, A. K. S. and R. G. Wilkins, J. Chem. Soc. 1960, 2895.

2. Allison, B. "Polarographic Studies of Lead in Methanol Solution,"
   M. S. thesis, Oklahoma State University, (1950).

3. Arthur, P., Anal. Chem. 36, 701 (1964).

4. Arthur, P., P. A. Lewis, and N. A. Lloyd, ibid, 26, 1853 (1954).

5. Arthur, P., P. A. Lewis, N. A. Lloyd, and R. H. VanderKam, Ibid
   33, 488 (1961).

6. Arthur, P. and H. Lyons, Ibid, 24, 1422 (1952).

7. Arthur, P. and R. H. VanderKam, Ibid, 33, 765 (1961).

8. Bachman, G. B. and M. J. Astle, J. Am. Chem. Soc., 64, 1303 (1942).

9. Bachman, G. B. and M. J. Astle, Ibid, 64, 2177 (1942).

10. Ballhausen, C. J., "Introduction to Ligand Field Theory," McGraw-
    Hill Book Company, Inc., New York (1962).

11. Bergman, I. and J. C. James, Trans. Faraday Soc., 48, 956 (1952).

12. Braae, B., Anal. Chem. 21, 1461 (1949).

13. Caglioti, V., C. Furlani, G. Dessy, and C. Ibarra, Gazz. Chim.
    Ital., 92, 1276 (1962).

14. Callahan, C. M., W. C. Fernelius, and B. P. Block, Anal. Chim.
    Acta, 16, 101 (1957).

15. Cockerell, L. and H. F. Walton, J. Phys. Chem., 66, 75 (1962).

16. Crowe, C. W., "Applicability of Solid Microelectrodes to Nonaqueous
    Amperometric Titrations," M. S. thesis, Oklahoma State Uni-
    versity (1961).

17. ElKhadem, H., M. F. Iskander, and S. E. Zayan, Z. Anorg. Allgem.
    Chem., 325, 72 (1963).

18. Graddon, D. P., "An Introduction to Co-ordination Chemistry,"
    Pergamon Press, New York (1961).

19. Hans, W. and F. von Sturm, Agew. Chem., 65, 393 (1953).

20. Hans, W. and F. von Sturm, Z Elektrochem., 57, 416 (1953).

21. Heyrovsky, J., Chem. Listy., 16, 256 (1922).

22. Heyrovsky, J., Phil. Mag., 45, 303 (1923).

23. Heyrovsky, J., Bull. Soc. Chim., 41, 1224 (1927).

24. Heyrovsky, J. and D. Ilkovic, Coll. Czech. Chem. Commun., 7, 198 (1935).

25. Heyrovsky, J. and M. Shikata, Rec. Trav. Chim., 44, 496 (1925).

26. Hollingsworth, C. A., E. W. Smalley, and S. K. Podder, Inorg. Chem. 3, 222 (1964).

27. Ilkovic, D., Coll. Czech. Chem. Commun., 6, 498 (1934).

28. Jackson, W., Jr. and P. J. Elving, Anal. Chem., 28, 387 (1956).

29. James, B. R. and R. J. P. Williams, J. Chem. Soc. 1961, 2007.

30. Jones, J. L., "Amperometric Acid-Base Titrations in a 2-Propanol-2,2,4-Trimentylpentane Mixture," M. S. thesis, Oklahoma State University (1960).

31. Kelley, M. T., H. C. Jones, and D. J. Fisher, Anal. Chem. 31, 1475 (1959).

32. Kiluchi, S., Y. Sakaguchi, and K. Honda, Bull. Chem. Soc. Japan, 25, 98 (1952).

33. Kolthoff, I. M. and F. A. Bovey, Anal. Chem., 19, 498 (1947).

34. Kolthoff, I. M. and W. E. Harris, Ind. Eng. Chem., Anal. Ed., 18, 161 (1946).

35. Kolthoff, I. M. and J. J. Lingane, Chem. Revs., 24, 1 (1939).

36. Kolthoff, I. M. and J. J. Lingane, "Polarography," 2nd Ed., p. 46, Interscience, New York (1952).

37. Kolthoff, I. M. and Y. Pan, J. Am. Chem. Soc., 61, 3402 (1939).

38. Kucera, G., Ann. Physik., 11, 529 (1903).

39. Lingane, J. J. and I. M. Kolthoff, J. Am. Chem. Soc., 61, 825 (1939).

40. Lingane, J. J. and B. A. Loveridge, J. Am. Chem. Soc., 72, 438 (1950).

41. Lloyd, N. A., "A New Polarograph for use with High Resistance Non-aqueous Solutions," Ph. D. thesis, Oklahoma State University (1950).

42. Lyons, H., "Polarography in Anhydrous Organic Solvents," M. S. thesis, Oklahoma State University (1952).

43. Maas, J., Coll. Czech. Chem. Commun., 10, 42 (1938).

44. MacGillavry, D., Trans, Faraday Soc., 32, 1447 (1936).

45. MacGillavry, D. and E. K. Rideal, Rec. Trav. Chim., 56, 1013 (1937).

46. Majer, V., Z. Electrochem. 42, 120 (1936).

47. Moran, P. E., "Amperometric Titrations of Selected Petroleum Additives and Sulfonic Acids in Nonaqueous Solutions," Ph. D. thesis, Oklahoma State University (1959).

48. Nejedly, V., Coll. Czech. Chem. Commun., 1, 319 (1929).

49. Nelson, I. V. and R. T. Iwamoto, Inorg. Chem., 3, 661 (1964).

50. Nicholson, M. M., Anal. Chem., 27, 1364 (1955).

51. Oka, S., Ibid, 30, 1635 (1959).

52. Pavkovic, S. F. and D. W. Meek, Inorg. Chem., 4, 20 (1965).

53. Pflaum, R. T. and W. W. Brandt, J. Am. Chem. Soc., 76, 6215 (1954).

54. Pierce, W. C., E. L. Haenisch, and D. T. Sawyer, "Quantitative Analysis," 4th Ed., p.p. 293-307, John Wiley & Sons, Inc., New York (1958).

55. Prasad, S., K. N. Chatterjee, and M. H. Rao, J. Indian Chem. Soc., 35, 811 (1958).

56. Prasad, S. and V. Krishnan, Ibid, 35, 352 (1958).

57. Prasad, S. and P. D. Sharma, J. Proc. Inst. Chemists (India), 30, 254 (1958).

58. Prasad, S. and P. D. Sharma, Ibid, 30, 249 (1958).

59. Rossotti, F. J. C. and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Company, Inc., New York (1961).

60. Sacconi, L. and G. Lombardo, J. Am. Chem. Soc., 82, 6266 (1960).

61. Sawyer, D. T., R. L. Pecsok and K. K. Jensen, Anal. Chem., 30, 481 (1958).

62. Schaap, W. B., A. E. Messner, and F. C. Schmidt, J. Am. Chem. Soc., 77, 2683 (1955).

63. Senenenko, K. N. and G. M. Kurdyumov, Vestnik Moskov. Univ., Ser. Mat., Melch. Astron., Fiz., Khim., 13, 207 (1958).

64. Sharma, C. S. and P. C. Sinha, J. Indian Chem. Soc., 36, 335 (1959).

65. Strehlow, H. and M. von Stackelbert, Z. Eleltrochem. 54, 51 (1950).

66. Thiele, K. H., Z. Anorg. Allgem. Chem., 325, 156 (1963).

67. Vlcek, A. A., Chem. Listy., 45, 258, 297, 377 (1951).

68. Zuman, P., R. Zumanova, and B. Soucek, Ibid, 47, 178 (1953).

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