A POLAROGRAPHIC STUDY OF AQUO-COMPLEXING OF COP-

PER(II) AND LITHIUM PERCHLORATES IN 1-BUTANOL

By

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ii

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TABLE OF CONTENTS

LIST OF FIGURES

CHAPTER I

INTRODUCTION

As research in solution chemistry has evolved from the study of
simple aqueous solutions to the study of complicated organic solvents or
mixtures of solvents, so has polarography evolved to complicated systems.
Three-electrode, resistance-compensating polarographic potentiostats
have been developed[4], and thus the limitations removed on the use of
solvents with low dielectric constants.

As the literature becomes filled with studies in non-aqueous sol-
vents, it seems that in many, if not in most of the studies, no special
precautions have been taken to eliminate residual water. Also in many
of the studies the amount of residual water is not measured and may not
be constant throughout the study. The effect of residual water is many
times neglected in the intrepretation of results. The fact that the
actual effect of residual water on the behavior of ions has received
little systematic consideration makes it imperative that this problem be
examined carefully. It is seldom appreciated that even solvents of
99.98% purity, i.e., 0.02% in water, are still 0.01M in water--a value
of the same order of magnitude as the limited solubility of inorganic
substances.

A knowledge of the formation constants for aquo complexes in or-
ganic solvents is required in order to adequately describe and under-
stand salt-water interactions at low water-salt ratios. Also it is im-

1

portant to know to what degree hydration is involved in solvent extraction processes, i.e., how much of the co-extracted water is hydrate or "bound" water and how much is second sphere or "free" water.

Quite a variety of opinion exists as to the detailed nature of transition metal aquo complexes in nonaqueous solvents[14,22,28,33]. Since these opinions were formed from studies in which different methods and different solvents were employed, it would seem that much more needs to be done if one is to be able to correlate and correctly interpret the results.

Formation constants have been studied for a very limited number of transition metal aquo complexes in only a few solvents and solvent mixtures[14,22,28,33,35,16]. The method of Bjerrum[7] has been most widely used for calculating the formation constants. The three techniques which have been applied to these studies are the spectroscopic, polarographic, and calorimetric.

It is the objective of this study to obtain additional information about ion-solvent interactions in hydrous alcohols and to examine the possibility of using the dropping mercury electrode (DME) in studying aquo-metal ion complexes. The solvent, 1-butanol, was chosen for study since it is the lowest molecular weight alcohol that can be used in solvent extractions because of miscibility. Recently, 1-butanol has been used in fundamental studies of solvent extraction processes in our laboratories. Cheung[8] studied enthalpies of transfer of copper, nickel, and cobalt perchlorate salts from aqueous phases to the equilibrium 1-butanol phases.

The solvent 1-butanol has been examined by Lewis[29] and has been shown to have suitable properties. Because of its low dielectric con-

stant (ϵ = 17.1 at 25°C) it provides a test of the suitability of work-
ing in lower dielectric constant solvents for polarographic investiga-
tions of complexing. A literature search revealed no previous studies
of aquo-metal ion complexes with the dropping mercury electrode.

Two metal ions were selected for study, Cu(II) and Li. Larson and
Iwamoto[28] and Nelson and Iwamoto[34] have determined formation constants
for aquo-copper(II) complexes in the solvents nitromethane and acetone.
Larson and Iwamoto[26] used both the polarographic method with the ro-
tating platinum electrode and the IR spectrophotometric method in the
solvent nitromethane. Nelson and Iwamoto[34] used the polarographic meth-
od with the rotating platinum electrode in the solvent acetone. One of
the difficulties in using polarography for studying aquo-complexing, as
noted by Nelson and Iwamoto[34], is that a high concentration of a second
or supporting electrolyte is necessary. Whereas, such an electrolyte
might not strictly affect the polarographic measurements as such, it is
difficult to imagine that the chemical hydration process of the salt
being investigated would be totally unaffected. Nelson and Iwamoto[34]
have recognized that lithium perchlorate might compete with copper(II)
perchlorate for free water in the solution, but stated that no quantita-
tive evidence was available to show that it did; they therefore ignored
the possible interaction of water with the carrier lithium perchlorate
in the interpretation of their polarographic results.

Spectroscopy is the method most often chosen for aquo complexing
studies. However, spectroscopic information is inherently linked to
molar extinction coefficients which nearly always are small in the vis-
ible region for aquo complexes of transition metals. It is generally
difficult also to find a metal-water solvent system which has an infra-

red absorption band for water dependent only on the water-metal interactions and not complicated by other vibrational modes. At best the data have considerable scatter which leads to uncertainty in the formation constants[14,22,28].

The third method, calorimetry, provides a more complete thermodynamic description. This method is capable of yielding information about the stepwise enthalpies and entropies of formation, which make possible deeper insight into the nature of the salt-solvent interactions. This method also lends itself quite well to Bjerrum's method of calculating successive formation constants, since the system passes through a series of successive equilibrium states as repetitive additions are made to the same solution in the thermometric titration. The method is described by Fielder[11] and by Harris[16]. One of the disadvantages to the thermometric titration with liquid water is the necessity of making a correction for the heat of mixing of the solvent with the titrant. However, Harris[16] has shown in the study of aquo complexing of cobalt(II) and nickel(II) perchlorates in 1-butanol that the heat of mixing of water with 1-butanol is a linear function of the water concentration.

One of the objectives of this study is to obtain additional information about ion-solvent interactions in hydrous 1-butanol and to gain information which could later be correlated with a similar study performed calorimetrically.

CHAPTER II

THEORY OF THE POLAROGRAPHIC METHOD FOR

THE STUDY OF COMPLEXES

Voltammetry, which is now a well-established technique in electro-
analytical chemistry[9,21], is based on current-voltage curves obtained
when an electroreducible or electrooxidizable substrate is electrolyzed
in a cell containing two electrodes: a large nonpolarizable reference
electrode, and an indicating electrode which is small and polarizable.
The most commonly employed reference electrode is a saturated calomel
electrode (SCE) while the dropping mercury electrode (DME) is the most
versatile indicator electrode. This system defines what is today rec-
ognized as polarography. The DME has many desirable characteristics
such as a continuously renewed surface, a large usable voltage range,
and the ability to dissolve many of the reduction products (i.e., metals
which form amalgams).

For some years polarography has proved to be a useful technique for
determination of stability constants of metal complexes in solution.
Studies have been made with different metal ions in aqueous and nonaque-
ous solvents with different types of ligands[30,40,7,26,34,20,39,17,38].

The most widely used methods are based on the determination of the
half-wave potential of a metal ion and the shift of the half-wave po-
tential, usually to more negative values, with the addition of increas-
ing proportions of ligand. By measuring this shift as a function of the

5

concentration of the complex forming substance, both the formula and stability constant of the complex can be determined. The reaction taking place at the polarizable electrode may involve the reduction of either the free metal ion (solvated) or the complex ion or both.

The reduction to the metallic states (amalgam) of a complex ion of a metal that is soluble in mercury may be represented by

$$ML_p^{(n-pb)+} + ne^- + Hg \rightarrow M(Hg) + pL^{b-} \tag{1}$$
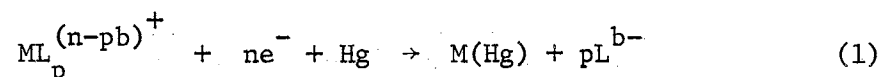
where M(Hg) represents the amalgam formed on the surface of the dropping electrode, and L^{b-} is the complex forming substance. It is convenient, although not strictly necessary, to regard this net reaction as the sum of the partial reactions:

$$ML_p^{(n-pb)+} \rightarrow M^{n+} + pL^{b-} \tag{2}$$

and

$$M^{n+} + ne^- + Hg \rightarrow M(Hg), \tag{3}$$
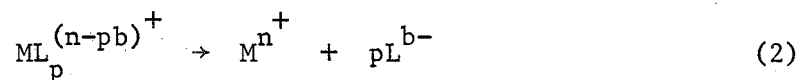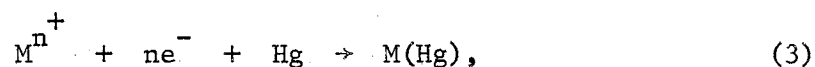
where M^{n+} symbolizes the simple or solvated ions of the metal.

If the foregoing reactions are rapid and reversible at the DME, then the potential of the latter at any point on the wave should be given by

$$E_{de} = E_a^o - \frac{RT}{nF_y} \ln \frac{C_a^o f_a}{a_{Hg} C_M^o f_M} \tag{4}$$

where C_a^o is the concentration of the amalgam formed on the surface of the dropping electrode, C_M^o is the concentration of the simple metal ions

at the electrode surface, f_a and f_M are the corresponding activity co-
efficients, and a_{Hg} is the activity of the mercury on the surface of the
dropping electrode.

When the dissociation of the complex ion is sufficiently rapid so
that equilibrium with respect to reaction (2) is practically maintained
at the electrode surface, an expression for the half-wave potential ($E\frac{1}{2}$)
may be derived by following through a series of rearrangements and sub-
stituting for the equilibrium constant[24], at 25°C:

$$E\frac{1}{2} = \varepsilon + \frac{0.059}{n} \log \frac{K_c f_{ML} K_a}{f_a k_c} - p \frac{0.059}{n} \log C_L f_L \qquad (5)$$

where K_c is the dissociation constant of the metal ion complex, k_a and
k_c are proportional to the square roots of the diffusion coefficients of
the complex metal ions and the metal in the amalgam, respectively, and
ε is equal to $E_a^o + (RT/nF_y) \ln a_{Hg}$.

From Equation (5) the half-wave potential of a complex metal ion
should shift with changing activity of the complex forming substance
according to

$$\frac{E\frac{1}{2}}{\log C_L f_L} = - p \frac{0.0591}{n} \qquad (6)$$

This relation is important because it enables us to determine the aver-
age ligand number p of the complex metal ion and thus its formula. For
this purpose it is usually sufficiently accurate to employ the concen-
tration of L^{b-} in place of its activity.

From Equation (5) we see that the half-wave potential depends on
the logarithm of the dissociation constant of the complex metal ion, and

it is more negative the smaller the value of K_c, i.e., the more stable

the complex ion. The polarographic wave of the solvated metal ion which

forms a complex ion whose dissociation, according to Equation (2), is

sufficiently rapid so that equilibrium is maintained at the surface of

the electrode is shown in Figure 1.
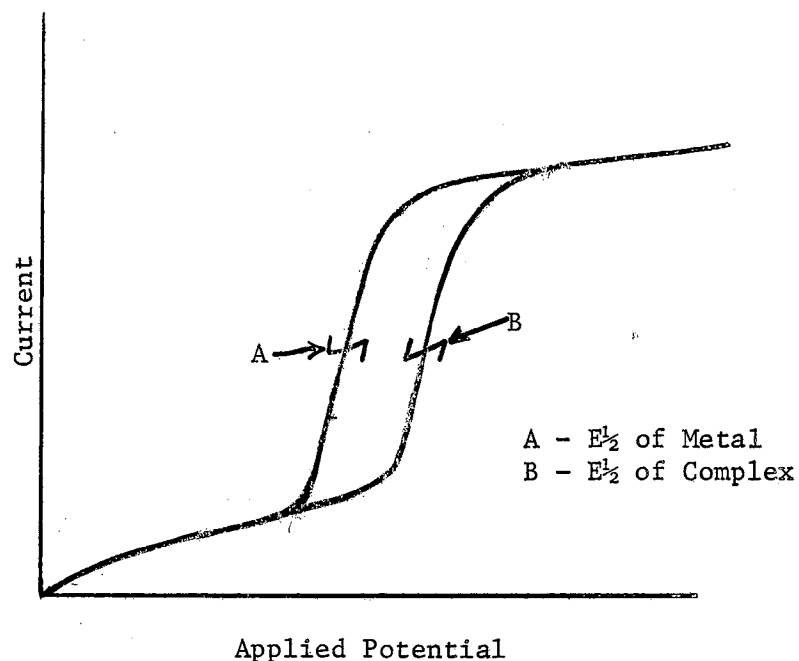
Figure 1. Polarogram of Complex With One Wave

When the free energies of the various possible oxidation states of

a complex ion are sufficiently different, reduction from a higher to a

lower oxidation state can proceed in stages at the DME to produce a

polarogram consisting of two or more separate waves. This situation is

illustrated in Figure 2.

In the first wave, reduction to a lower valency occurs and in the

second wave, reduction of the reduced form of the complex to metal takes

place. In this case, provided both waves are reversible, the number of
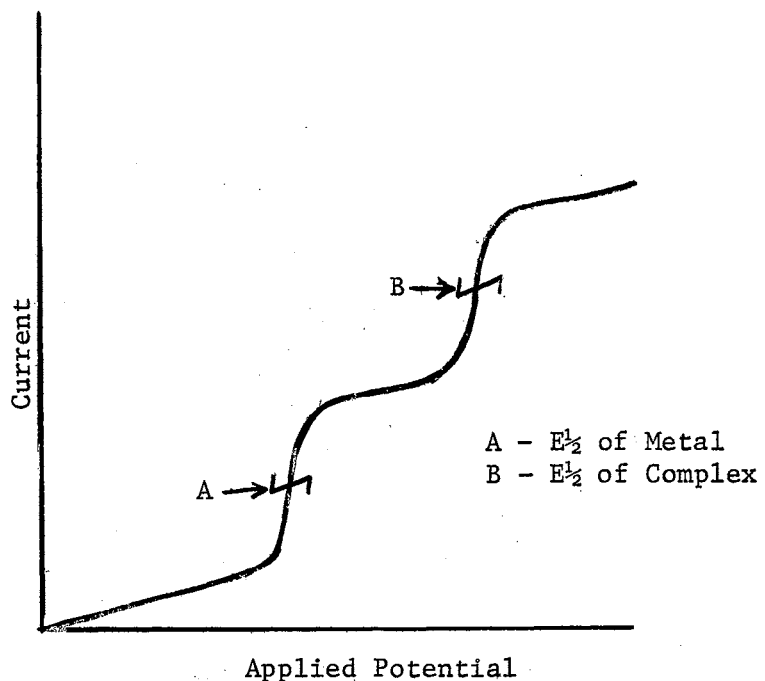
Figure 2. Polarogram of a Complex Showing
Two Separate Waves

ligands and the stability constant of the complex form can be determined from the shift in the half-wave potential of the second wave.

Stability constants of metal complexes can be calculated from the dependence of the linear shift of the polarographic half-wave potential with the change of logarithm concentration of the free ligand[15]. This method can be applied in investigations of very stable metal complexes where predominantly one complex ionic species exists over a wide concentration range of the complexing agent. However, in the investigation of less stable metal complexes, the stability constants can be calculated by the method of DeFord and Hume[10]. Both of the previously mentioned methods of calculation require that the reductions be reversible. For irreversible reductions an indicator metal ion must often be employed,

as described by Ringbom and Eriksson[36]. The indicator ion is used to indicate the free ligand concentration in solutions consisting of different proportions of a required metal ion and the ligand under study.

The simplest case of a single complex formation should provide ample illustration of the usefulness of polarography for obtaining the average ligand number of a complex. The polarographic half-wave potential ($E\frac{1}{2}$) then varies with the concentration of the species present in a manner given by the Nernst equation. Thus for the reduction:

$$\text{Oxidized form} + ne^- = \text{Reduced form} \tag{7}$$

in which the oxidized form is reduced reversibly to a metal which forms an amalgam with the dropping mercury electrode, one may write the Nernst equation as:

$$\text{at } 25^{\circ}C \quad E_{de} = E^{o} + \frac{0.059}{n} \log \frac{[M^{n+}]}{[M(Hg)]} \tag{8}$$

When a complexing ligand is present, the reduction equation (7) is not the only reaction taking place. The additional complexation reaction occurring is the reverse of Equation (2). For this complexation equilibrium, the stability constant, K, is given by:

$$K = 1/K_c = \frac{[ML_p^{(n-pb)+}]}{[M^{n+}][L^{b-}]^p} \tag{9}$$

From this equation,

$$[M^{n+}] = \frac{[ML_p^{(n-pb)+}]}{K[L^{b-}]^p} \tag{10}$$

For the simple calculation it is usually sufficiently accurate to employ

the concentrations of the ligand and metal in place of their activities. If this assumption is made and if the activity of the mercury is considered unity, Equation (4) becomes equal to Equation (8). Substituting Equation (10) into Equation (8) gives an expression for E_{de} in terms of K.

$$E_{de} = E^O + \frac{0.059}{n} \log \frac{\left[ML_p^{(n-pb)^+}\right]}{K [L^{b-}]^P [M(Hg)]} \tag{11}$$

The half-wave potential $E_{\frac{1}{2}}$ is defined as the potential at which half of the oxidized form which reaches the DME is reduced. If the complex is fairly stable and the ligand concentration, L, is sufficiently large, then at $E_{de} = E_{\frac{1}{2}}$ and $M(Hg) = ML_p^{(n-pb)+}$, Equation (11) becomes

$$E_{\frac{1}{2}} = E^O + \frac{0.059}{n} \log \frac{1}{K [L^{b-}]^P} \tag{12}$$

or

$$E_{\frac{1}{2}} = E^O + \frac{0.059}{n} \log K - p \frac{0.059}{n} \log [L^{b-}] \tag{13}$$

The average ligand number p may be obtained from a plot of $E_{\frac{1}{2}}$ versus log [L] which should be a straight line of slope $-0.059p/n$ where n is known from the charge on the ion. K may also be determined from a polarogram of a solution for which [L] = 1.

One application of the study of metal complexes is furnished by a polarographic study of aquo-metal ion formation constants in nonaqueous solvents. As water is added to the system containing the metal ion, values of $E_{\frac{1}{2}}$ shift usually to more negative voltages. Larson and Iwamoto[28], attribute this shift to the increase in solvation energy of

the metal ion as a result of selective solvation by water molecules.

Larson and Iwamoto[28] have reported successive aquo-Cu(II) ion for-
mation constants in the solvent nitromethane with the rotating platinum
electrode. Although they do not state a reference for their method of
calculation, it seems to follow the method outlined by DeFord and Hume[10].
They report nine constants in this solvent. A later study by Nelson
and Iwamoto[34] parallels the above study, but in the solvent acetone.
Four constants are reported in this study.

CHAPTER III

EXPERIMENTAL

Materials

Acetone (Fisher Scientific). Reagent grade was used after a single distillation under nitrogen; b.p. $56.0-56.5^{\circ}C$.

1-butanol (Fisher Scientific). Reagent grade was used after a single distillation under nitrogen; b.p. $117.5^{\circ}C$. The solvent was then dried by a method which will be explained in detail later (page 16).

Copper(II) perchlorate (Hydrated) (G. Fredrick Smith Co.). Reagent grade was placed directly in the solvent and the solution was dried by a procedure to be explained later (page 16).

Di sodium Ethylenediaminetetraacetate (J. T. Baker). Analyzed reagent grade was used without further purification.

95% Ethanol (U.S. Industrial Chemical). U.S.P. grade was used without further purification.

Karl Fischer Reagent (Baker and Adamson). Stabilized solution was used after dilution with methanol.

Lithium Chloride (J. T. Baker). Reagent grade was used without further purification.

Nitrogen (Linde). Lamp grade was used for purging equipment and drying and distilling solutions after being passed through a molecular sieve trap. For the polarographic analysis the gas was used after being passed in succession through two towers of chromous sulfate-sulfuric

acid and amalgamated zinc as described by Arthur[3]. It was then passed through a column of glass wool, two scrubbing towers containing concentrated sulfuric acid, another column of glass wool, a large tube containing Molecular Sieve 4A, two recirculating presaturator towers filled with 1-butanol and dry molecular sieve, and a final sieve trap.

Silicon Lubricant (Dow Corning). Used for all glassware connections.

Silver Nitrate (J. T. Baker). Reagent grade was used without further purification.

Lithium Perchlorate (G. Fredrick Smith Chemical Co.). Anhydrous reagent grade was used with further purification.

Magnesium (Mallinckrodt). Reagent grade powder was used without further purification.

Mercurous Chloride (Baker and Adamson). Reagent grade was used without further purification.

Mercury (Bethlehem Instrument). Triple-distilled was used. After using, the mercury was repurified by a thorough washing with distilled water and filtering the dross through a pin hole in filter paper. A thorough washing with 1M nitric acid followed and then a drying with acetone. The final steps in the treatment were an oxifying treatment, another filtering, and finally two vacuum distillations.

Methanol, Absolute (Baker analyzed). Reagent grade was used without further purification.

Molecular Sieve (Union Carbide Corporation). Type 4A was used after being reactivated at $450^{\circ}C$ in a drying oven for 48 hours.

Sodium Perchlorate (G. Fredrick Smith Chemical Co.). Anhydrous reagent grade was used without further purification.

Sulfuric Acid (Fisher Scientific). Reagent grade was used without further purification.

Tetra-n-Butylammonium Bromide (Eastman Organic Chemicals). White label grade was used without further purification.

Tetra-n-Butylammonium Perchlorate (G. Fredrick Smith Chemical Co.). Reagent grade was used after drying under vacuum at 70°C in a drying pistol for 48 hours.

Tetraphenyl-Arsonium Chloride Hydrochloride (Eastman Organic Chemicals). White label grade was used without further purification.

Zinc Metal (J. T. Baker). Reagent grade sticks were used.

Procedures

Preparation of Tetra-n-Butylammonium Perchlorate

This was prepared according to the method originally suggested by Kolthoff and Coetzee[23] with a slight alteration. Stoichiometric amounts of tetra-n-butylammonium bromide and sodium perchlorate were used in order to increase the yield.

The method used is outlined as follows: forty grams of tetra-n-butylammonium bromide was dissolved in 250 ml of distilled water by heating to 100°C and then added with constant stirring to 16 grams of sodium perchlorate dissolved in 500 ml of water. After the mixture was cooled overnight in an ice bath, the solution was filtered and the tetra-n-butylammonium perchlorate (TNBAP) was washed free of bromides with ice water. The TNBAP was then dried in a drying pistol at 70°C for 72 hours.

Preparation of Standard Perchlorate Solutions

The standard perchlorate solutions were prepared by weighing out approximately the required amount of the hydrated salts into a flask and diluting with 1-butanol. The lithium perchlorate solutions were dried by the method of Arthur[5] with molecular sieves and a modified Soxhlet extractor. The copper(II) perchlorate solutions were dried by the method of Harris[16], which is essentially the same as that described by Arthur except for the addition of apparatus for refluxing under vacuum conditions.

The copper(II) concentration was determined by EDTA titration as described by Flaschka[13] using PAN as an end-point indicator. The concentrations were determined first on a weight basis as molalities and then converted to molarities by density measurements. The linear relationship between density and molality determined by Wallace[42] for copper(II) perchlorate solutions in 1-butanol was used.

Lithium perchlorate concentrations were determined by evaluating the perchlorate content by a gravimetric technique[27] with tetra-phenyl-arsonium chloride hydrochloride as the precipitating agent.

Drying of 1-Butanol

Solvent 1-butanol was dried at the boiling point $117.5^{\circ}C$ in a Soxhlet extractor containing 4A Molecular Sieve for 24 to 36 hours. During the last six hours of the drying process the solution was flushed with dry nitrogen and then allowed to cool down under an atmosphere of dry nitrogen. This process was necessary to eliminate the dissolved oxygen. The solution was allowed to set for about three days before being used. This allowed sieve dust to settle out. Solutions were stored in specially adapted storage flasks with septum fittings to ex-

clude atmospheric moisture. The solutions were kept under nitrogen

pressure at all times, and storage flasks were kept in dessicators to

further eliminate moisture. This method proved quite effective for

drying 1-butanol for use as a solvent for polarographic studies. No

interference from sieve dust was noted in polarograms when the solvent

was treated in the manner described. Water content as measured by the

Karl Fischer titration was less than 0.001%.

The Determination of Water

The detection and accurate determination of water in solvents and

solutions was a necessary part of this research. Truly anhydrous solu-

tion conditions were desired in order to study the effect of water as a

ligand.

The method employed to determine the water was the Karl Fischer

technique[12]. In this technique, water is determined through its reac-

tion with a solution containing iodine, sulfur dioxide, pyridine, and

a solvent such as methanol. The essential reactions are believed to be:

$$I_2 + H_2O + SO_2 + 3C_5H_5N \rightarrow 2C_5H_5N \cdot HI + C_5H_5N \cdot SO_3$$

$$C_5H_5N \cdot SO_3 + CH_3OH \rightarrow C_5H_5N \cdot HOSO_2 \cdot OCH_3$$
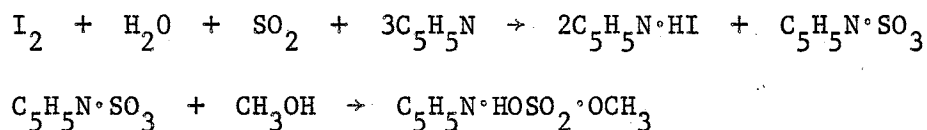
The end point of such a reaction can be determined visually; however,

electrochemical methods are more widely employed because they possess

high sensitivity.

The arrangement of the titration cell and burette is the same as

that described by Haynes[32]. The end-point of the titration was detected

by electrochemical means as described by Rulison[33].

Apparatus

A Sargent Model XXI Polarograph and a Sargent Model A IR Compensator were used in collecting all polarographic data.

The polarographic cell used in this study is a three compartment cell similar to the one described by Hunt[19] with variations to fit anhydrous solutions and a titration port. Connections between the three compartments were asbestos fibers. The resistance across each fiber as measured with a conductance bridge using 0.1M aqueous potassium chloride was 40,000 ohms. Solutions of 0.1M lithium perchlorate and 0.07 M tetra-n-butylammonium perchlorate were used in the inverted T-tubes (Figure 3).

Figure 3 is a diagram of the cell. The reference electrodes for this cell are the acetone-saturated calomel electrodes (ASCE) originally reported by Arthur and Lyons[6]. The potential of the ASCE is -.18 volts with respect to the aqueous saturated calomel electrode.

A – DME inlet
B – Inlet for gas dispersion
    tube
C – Standard taper 45/50 joint
D – Standard tube 24/40 joint
E – T-bridging tubes
F – ASCE compartments

G – Titration part
H – Asbestos fibers
I – DME compartment
J – Opening to allow
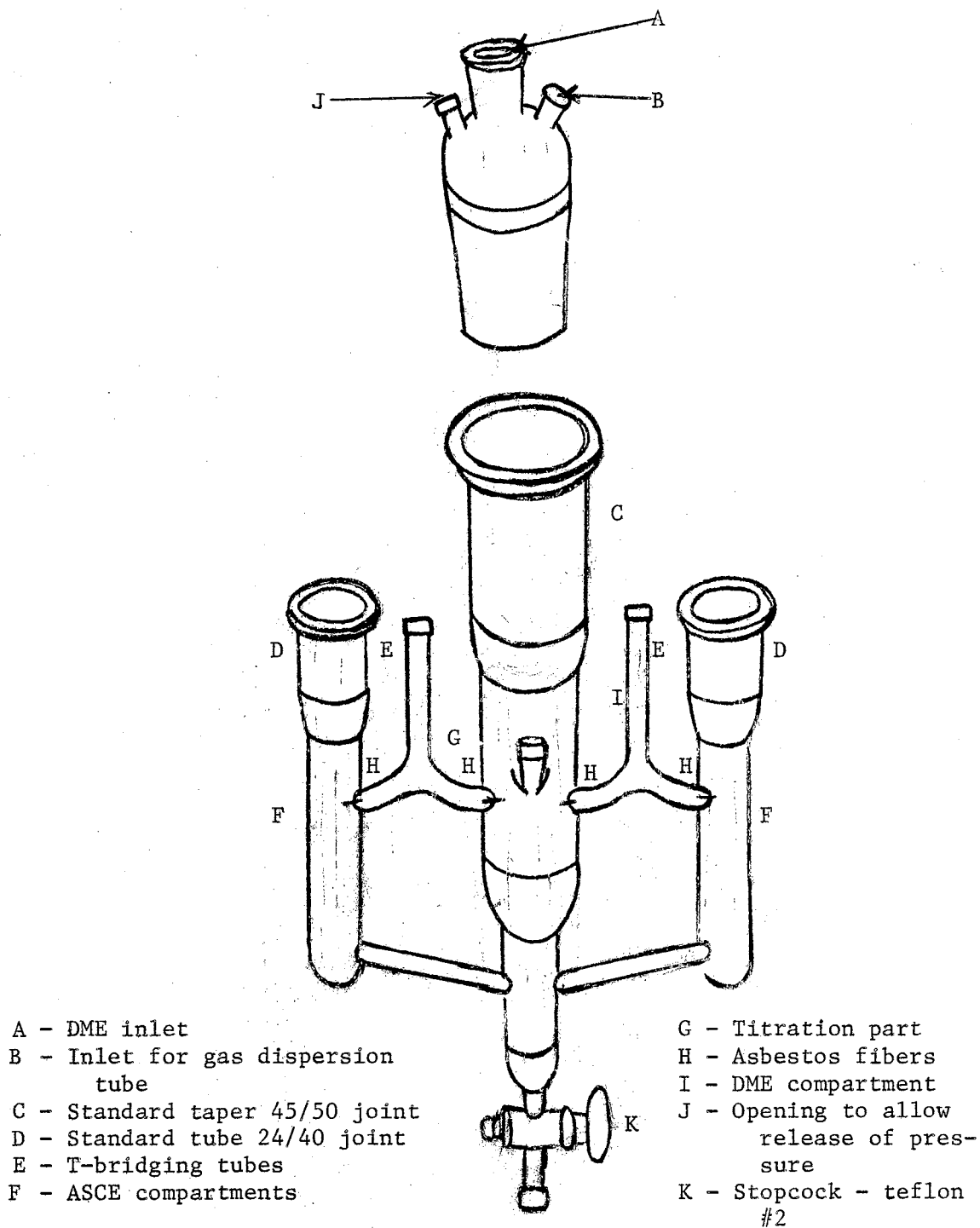   release of pres-
    sure
K – Stopcock – teflon
    #2

Figure 3. Polarographic Cell

CHAPTER IV

PROCEDURES AND DISCUSSION

Selection of a Carrier Electrolyte

The first problem encountered was the selection of a suitable carrier electrolyte for the system. Since perchlorate salts were being studied and the interaction of the cations with water was to be studied, it was undesirable to introduce any additional anion in the system which might interact with the cations or which would be in competition with the water molecule for occupation of a ligand site. This seemed to limit the carrier to a perchlorate salt. Lithium perchlorate is very soluble in 1-butanol and has a useful carrier range in this solvent of +0.7v. to -1.7v; however, since it is a hygroscopic salt and has been suspected of preferentially being solvated by water in other solvents[34], the decision was made to use this salt as one carrier electrolyte, and to parallel the study with another carrier electrolyte, which would be less readily hydrated. A comparison might then be possible of the results obtained with the two carriers.

The tetra-alkylammonium salts which are considered to have a low affinity for water were selected as a possible second choice. Various tetra-alkylammonium salts were tested in 1-butanol; tetra-methyl and tetra-ethyl-ammonium perchlorate were found insoluble. Tetra-n-hexyl-ammonium perchlorate was partially soluble but not to the extent required of a suitable carrier electrolyte in 1-butanol. Tetra-n-butyl-

ammonium perchlorate was found to be soluble to the extent of approximately 3g/100g of 1-butanol corresponding to a concentration of approximately 0.07M. Tetra-n-butylammonium perchlorate (TNBAP) also gave a useful carrier range in 1-butanol of +0.8v. to -2.3v. This salt, TNBAP, was selected as the second carrier electrolyte. Since it was not commercially available at first, but could be easily prepared using a method described in the literature[23], the first material was synthetically prepared.

Elimination of the Oxygen Maxima

The next problem was the elimination of the maximum in the polarographic wave which occurs with the copper(II) ion in 1-butanol. A maximum has been observed in aqueous solutions of copper(II), but it is easily eliminated by the addition of a surface active agent or maximum suppressor such as Triton-X-100. It was not desirable in this study to add any foreign substrate to the system which might increase the water content or might affect the interaction of the metal ion with the water. For this reason the decision was made not to add a maximum suppressor to the solutions, although Methyl Red appears to be a useful maximum suppressor for this system.

In order to eliminate the maximum it was desirable to find the reason for its existence. Although maxima have been reported in other studies with the Cu(II) ion, reasons for their existence have not been definitely identified. Different DMEs and different drop times for these, were used as a check on the electrode system, for it is well known, that incorrect positioning of the DME or incorrect drop times can contribute to polarographic maxima. Changing either of these did

not seem to affect the maximum to any extent. Several other three elec-
trode cells and different sets of ASCEs were tested, but the maximum per-
sisted in all cases. Polarograms of the Cu(II) ion with different
anions in the solvents isopropanol and ethanol revealed the same type of
maxima, but which were less pronounced at the same concentration of
Cu(II) than in 1-butanol. Solutions used in all these tests were 10^{-3}M
in Cu(II) ion or less.

Although tetra-alkylammonium salts are surface active agents and
are known to suppress polarographic maxima[23], there was no detectable
difference in the maxima with the two carrier electrolytes, lithium per-
chlorate and TNBAP.

A direct relationship between the height of the maximum and the
concentration of the Cu(II) ion was noted. Finally by decreasing the
concentration of the Cu(II) ion to 10^{-4} or less and by purging the solu-
tion with nitrogen for long periods of time to eliminate oxygen, the
maximum was finally eliminated. In this exploratory work the only pre-
caution taken to purify the 1-butanol was a single fractional distilla-
tion with the first and last fractions being discarded. In the latter
part of this study when much drier solutions were studied, the maxima
were observed to be more pronounced and could only be eliminated by
very long periods of deoxygenation (6 to 14 hours), depending on the
concentration of the Cu(II) ion in solution. Careful examination of
the observations led to the conclusion that this maximum was a result
of residual dissolved oxygen in the 1-butanol.

Previous studies have shown certain of the transition metals to be
sensitive catalysts for the polarographic reduction O_2--H_2O to give a
single wave[41]. It is also interesting to note that, according to

Klothoff and Miller[26], in unbuffered, neutral solution, the OH^- liberated in the interphase from the first step in the O_2 reduction process, interferes with the polarographic reduction of Pb(II) by precipitation it in the form of its hydroxide. Polarograms of Pb(II) and Ni(II) ions in 1-butanol indicate maxima similar to the one observed for the Cu(II) ion. Copper(II) hydroxide is insoluble in 1-butanol and this could explain why there is a sudden drop in potential following the maximum.

A complete study of the catalytic reduction of O_2 by Pb(II) has been carried out in aqueous solutions by Arévalo and Bazo[2]. They observed that the presence of Pb(II) in an air-saturated polarographic solution alters the morphology of the double reduction wave of O_2. The change, as illustrated in Figure 4, consists of an increase in the first wave followed by a sudden decrease in the current when the potentials are between -0.5 and 0.6v. If the concentration of Pb(II) is inadequate, i_d of the process $O_2 + 4e^- = H_2O$ and the beginning of the reduction wave of Pb(II) can be observed just before the sudden decrease of the current. The exaltation of the first wave by reduction of the H_2O_2 ceases when the Pb(II) is deposited at the DME.

A description similar to the above can be given for the polarogram of copper(II) perchlorate in 1-butanol as illustrated in Figure 5. This polarogram shows the characteristic maximum associated with the Cu(II) wave in 1-butanol.

An estimation of the solubility of oxygen in 1-butanol was made by plotting the solubility parameters[18] of solvents with properties similar to 1-butanol vs. the mole fraction of oxygen. A value of the solubility of oxygen in 1-butanol was extrapolated from this polt. The mole frac-
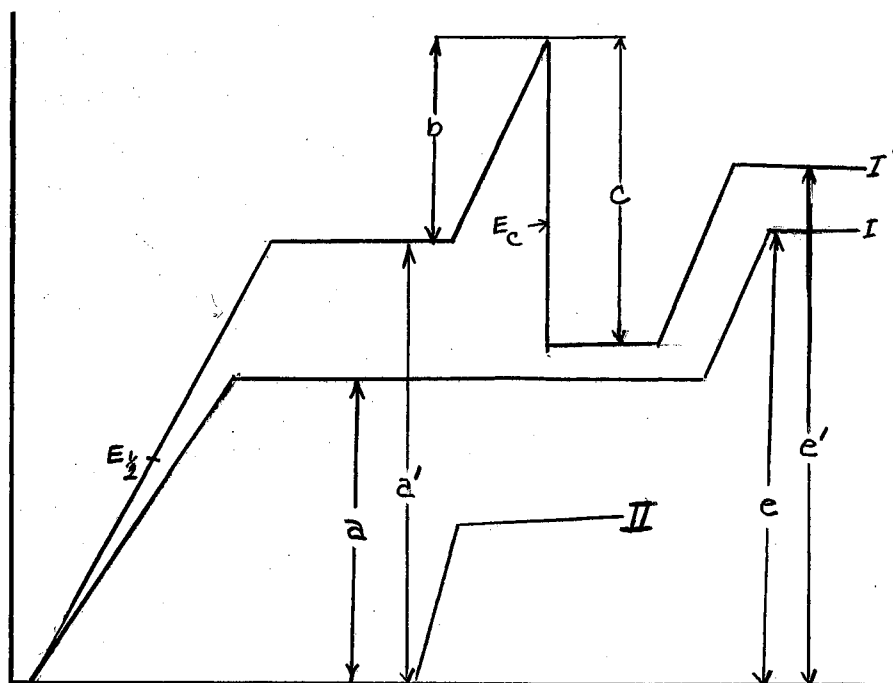
Figure 4. Schematic Polarograms. I, O_2; I', $O_2 + Pb(II)$;
II, Pb(II);(a and a') i_d First Wave;(b) Start-
ing Reduction Current Pb(II); (c) Current
Fall; (e and e') i_d Total; $E^{\frac{1}{2}}$ and E_c: Half-
Wave and Fall-Wave Potentials Respectively.

tion of the solubility of the solubility of oxygen in 1-butanol was
found to be approximately 6×10^{-4}, the same value in water is 2.3×10^{-5}. Thus giving a value of the solubility of oxygen in 1-butanol a-
bout 30 times that of water. This appears to be consistent with the
observations.

Considering the high solubility of oxygen in 1-butanol and the
difficulties encountered with its presence polarographically, an effi-
cient removal of oxygen from the solutions was certainly deemed neces-
sary. A careful examination of the method employed to dry the solvent
revealed that the solvent was refluxed in dry air, which meant a high

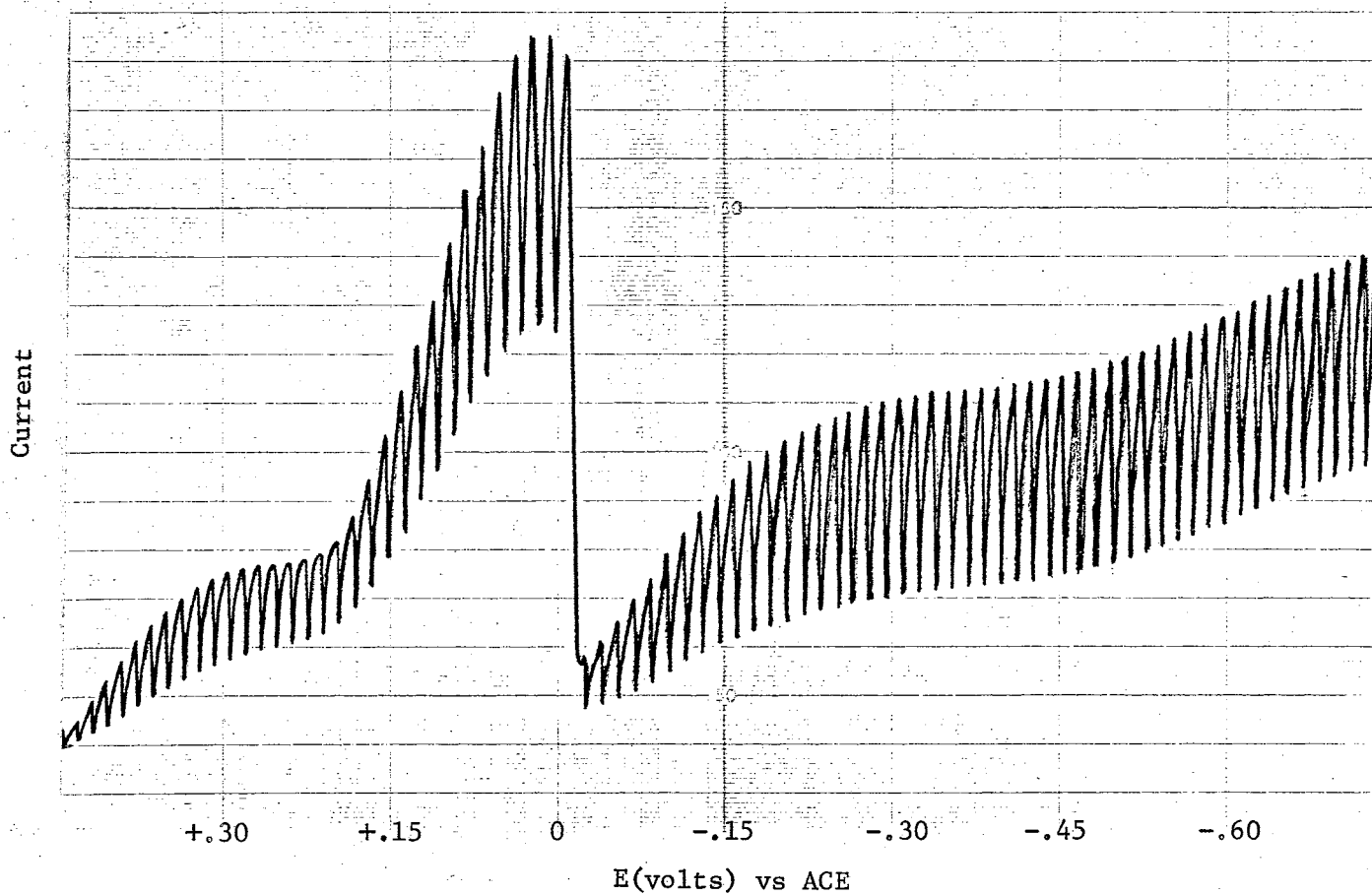Figure 5. Polarogram for the Reduction of Cu(II) Perchlorate in 1-Butanol, Showing a Typical Maximum. Concentration of Cu(II) = 5 x 10^{-4} Carrier Electrolyte = .1M $LiClO_4$ Current Sensitivity is 0.3 μa/mm.

concentration of oxygen inside the Soxhlet, and as the solvent refluxed it probably increased its oxygen content. The original method of drying was subsequently modified by simply flushing the solution and Soxhlet with dry nitrogen during the last 5 to 6 hours of the drying process, then allowing the solution to cool under an atmosphere of dry nitrogen. This drying method eliminated much of the dissolved oxygen and decreased the time of a deoxygenating the solutions for study to from 10 minutes to 1 hour for the complete elimination of the maxima with solutions in the concentration range 4×10^{-4} to $1 \times 10^{-5}M$ in Cu(II) or less.

Studies at High Water Content

Exploratory studies of Cu(II) ion in 1-butanol at high water concentrations (0.55M to 6.7M) were performed with solutions of both carrier electrolytes to determine the effect of high water concentrations on the half-wave potential for the reduction wave. All solutions in these studies were 10^{-4} in Cu(II) and either 0.07M TNBAP or 0.1M lithium perchlorate. In these studies only one wave was observed for the Cu(II) reduction. This wave was not diffusion controlled and appeared to be irreversible. A plot of E_{de}' vs log $i/i_d - i$ showed a slope of approximately 0.041, but this slope changes with increasing water concentration with lithium perchlorate as the carrier, whereas with the carrier TNBAP the slope remains essentially constant over this high range of water concentration.

A definite shift in the $E\frac{1}{2}$ value of the single wave in these solutions with increasing water concentration was also observed; however, the trend of the shift varies with the carrier electrolyte. A plot of $E\frac{1}{2}$ vs $\%H_2O$ is shown in Figure 6 and Figure 7 with the two carrier elec-
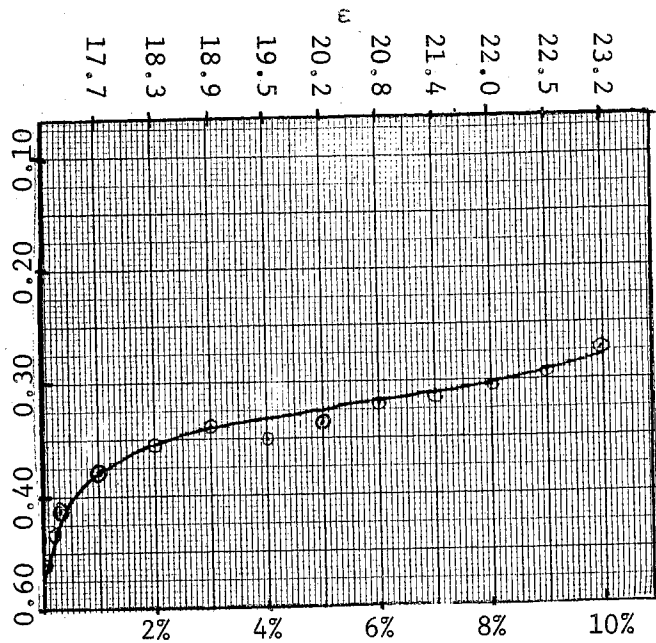
Figure 6. Plot of $E\frac{1}{2}$ vs $\%H_2O$, Carrier, 0.07M TNBAP
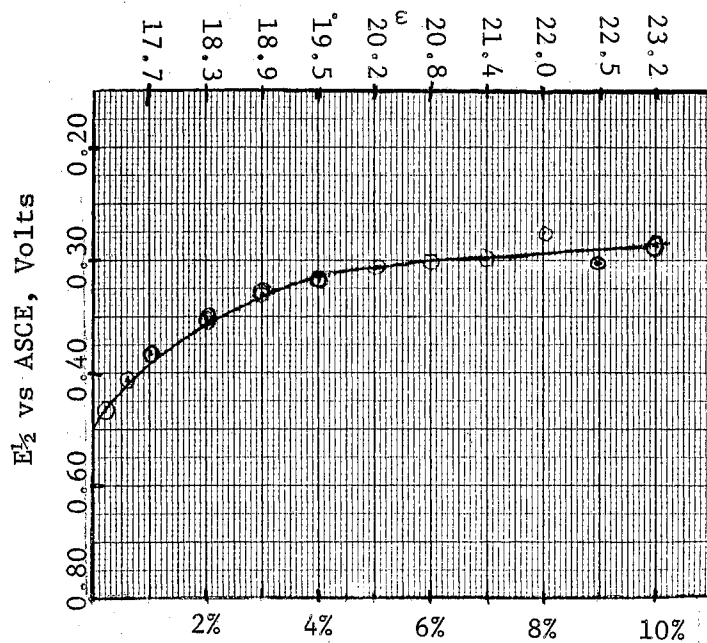

Figure 7. Plot of $E\frac{1}{2}$ vs $\%H_2O$, Carrier, 0.1M $LiClO_4$

Figure 6 and 7. ε has been calculated at each vol. $\%H_2O$ and is plotted along upper horizontal axis.

trolytes. Dielectric constants for the 1-butanol-water mixtures are plotted along the upper horizontal axis. These dielectric constants were calculated by the equation

$$\varepsilon = \varepsilon_{H_2O} X_{H_2O} + \varepsilon_{BuOH} X_{BuOH} \quad \begin{array}{l} \text{where } X = \text{volume fraction} \\ \text{and } \varepsilon = \text{dielectric constant.} \end{array}$$

This shows a trend of $E\frac{1}{2}$ to shift toward more negative potentials with the increasing dielectric constant of the solution mixture. The half-wave potential of a metal ion, which is reversibly electroreduced, depends on the activity of the metal in the amalgam (which is normally taken as unity since the concentration of the metal in the amalgam is so low) and upon the activity coefficient of the metal ion in solution as discussed in Chapter II. The effect of dielectric constant upon the activity coefficient of an ion is very great. The Debye-Hückel equation (14) relates the ion dielectric constant ε to the ion activity coefficient in a given solvent and the ionic strength.

$$\log f_i = \frac{(1.82 \ 10^6) \ z_i^2 \ (I)^{\frac{1}{2}}}{\varepsilon \ T^{3/2} \ [1 + 50(\varepsilon T)^{-\frac{1}{2}} \ a^o (I)^{\frac{1}{2}}]} \tag{14}$$

where I is ionic strength and a^o is ion size parameter. The smaller the dielectric constant, the smaller the ionic strength at which deviation from the limiting Debye-Hückel expression starts to occur. Lowering the value of ε causes the activity coefficient to decrease more rapidly with increasing ionic strength than it does at higher values of dielectric constant. The deviation from unity of the activity coefficient for ions with a charge greater than unity is also greater than for univalent ions[25]. A difference in the solubilities alone of the

two carrier electrolytes would indicate a difference in the ionic strength of their solutions. Lithium perchlorate is approximately seventy times more soluble in 1-butanol than TNBAP. This effect combined in Equation (14) could give a partial explanation for the differences in the trends with the two carriers.

Studies at Low Water Content

The next part of this study was directed toward lower water concentrations. It was necessary to exercise great care in this part of the study and to develop techniques for handling anhydrous solutions. Syringe techniques were used throughout. The syringes were fitted with stainless steel Leur-Lok stopcocks. All transfers of solutions were made by nitrogen pressure and a one way suction bulb.

In preparing the anhydrous solutions for analysis, these steps were followed in each case with the carrier TNBAP: a weight of solid TNBAP necessary to achieve a 0.07M solution at the desired dilution was weighed quickly and transferred to a hot volumetric flask which had been taken directly from a 130°C oven. All glassware, syringes, and needles used in this section were predried in a 130°C oven and stored there until used. The volumetric flask was then quickly stoppered with a rubber septum cap.

A 2cc syringe fitted with a Leur-Lok stainless stopcock was filled with an approximate amount of copper(II) perchlorate standard stock solution. The syringe was then weighed and the solution was injected through the septum cap into the volumetric flask with the aid of a one-way suction bulb used to create a partial vacuum inside the flask. The volumetric flask was next filled to about one inch below the mark with

dry butanol. The solution was then heated to 50°C in an oil bath. This heating was necessary to completely dissolve the carrier electrolyte TNBAP, which dissolved very slowly at 25°C. After the TNBAP was completely dissolved, the solution was placed in a 25°C oil bath, allowed to equilibrate to 25°C and then filled to the mark with anhydrous butanol as previously described.

The preparation of copper(II) perchlorate solutions containing lithium perchlorate as carrier electrolyte was somewhat simpler. A heated volumetric flask was taken directly from the oven and stoppered with a septum cap. An amount of lithium perchlorate stock solution necessary to give a 0.1M solution was weighed in a 50cc syringe and added to the flask through the septum cap by the previously described method. A weighed amount of copper(II) perchlorate stock solution was added and then the flask was filled to within one inch of the mark, allowed to equilibrate to 25°C in the oil bath, and filled to the mark with dry butanol. The concentration of the solutions was calculated by converting the weight of the stock solution to volume through the density then using the method of dilution to calculate the molarity of the solution. Possible changes in the volume of the volumetric flasks were corrected for in all cases by density measurements.

The water content of each solution was measured before the titration or during the titration process itself. Initial water contents of the solutions of copper(II) perchlorate in TNBAP carrier solution were from 0.03% to 0.01% as measured by the Karl Fischer titration. Water content of the copper(II) perchlorate in lithium perchlorate carrier solutions ranged from 0.05% to 0.01%. Solutions of lithium perchlorate with TNBAP as carrier were all 0.009% H_2O.

Procedure for a Typical Titration

The polarographic cell was taken from the oven and assembled while
hot. Septum caps were wired in place over all openings, and the fritted
gas dispersion tube was wired in place and sealed at the opening in the
cell top by a polystyrene collar to eliminate air. Liberal amounts of
silicon lubricant were used on all glass fittings. A 19-guage needle
was inserted into the septum cap at the top of the cell to allow re-
lease of pressure as the cell was purged with dry nitrogen. After the
cell had cooled to room temperature, the mercury flow was started at the
DME, and the DME was extended into the cell which was clamped in place
on a mobile rack mounted over a constant temperature bath. The bath
contained paraffin oil maintained at $25^\circ \pm 0.1^\circ C$.

A 50cc syringe was purged with dry nitrogen and used to weigh out
approximately 30cc of the solution to be studied. The solution was
then injected into the cell through the titration port. The syringe
was finally reweighed to determine the weight of solution in the cell.
The T-tubes were filled with 1.5 ml of the same carrier solution as in
the main body of the cell. The electrode compartments were filled
approximately half-full of a solution of acetone saturated with lithium
chloride and mercurous chloride, and then the ASCEs were inserted into
the compartments. During this time the solution in the cell was being
purged with dry nitrogen to eliminate dissolved oxygen.

Next the cell was lowered into the constant temperature bath and
at least 15 minutes was allowed for thermal equilibriumation. The elec-
trodes were then connected to the polarograph, and an initial polarogram
of the solution was taken. If the polarogram showed no evidence of a
maximum the titration was begun. If a maximum was observed, the deoxy-

genation process was continued until the polarogram showed no evidence of a maximum.

The titration was carried out using a 0.2 ml Gilmont micrometer syringe fitted with a Luer-Lok stainless steel stopcock and a 2 in. 22-guage needle. While the actual polarograms of the solutions were being recorded, the gas dispersion tube was raised inside the cell to a level above the solutions so that the gas flow was diverted over the solution. Before each addition of water the gas dispersion tube was lowered into the solution and the water added while nitrogen bubbled vigorously through the solution. This proved to be a very efficient method of stirring the solution. This process was continued for about two or three minutes after each addition of water. Additions of water were 0.01 ml with the accuracy of the Gilmont syringe being 0.5%. From 10 to 14 additions of H_2O were made in each titration.

Polarographic Interpretation of the Copper(II) Wave(s)

Polarograms of copper(II) perchlorate in 1-butanol show what appears to be one wave. The $E^{\frac{1}{2}}$ for this wave in the driest solution tested, as measured by a plot of E_{de} vs log i/i_d-i, is $E^{\frac{1}{2}} = +0.560$ v vs ASCE. This solution was 0.011% H_2O; therefore, the $E^{\frac{1}{2}}$ for a completely anhydrous solution probably occurs at some value greater than +0.560 v. The $E^{\frac{1}{2}}$ of this wave shifts toward more negative potentials with the addition of water in agreement with the expected behavior if the solvation energy of the Cu(II) ion increases as a result of selective solvation by water molecules[28]. The shifts were well defined in the carrier TNBAP. A 50 mv shift is observed over a concentration range

of water from 5 x 10^{-3}M to 0.26M. Consecutive titrations performed 24 hours apart were reproducible with TNBAP as carrier. A plot of the shift of the values of $E\frac{1}{2}$ vs log $1/i_d$ - i with TNBAP is shown in Figure 8. It is interesting to note here that the shift of $E\frac{1}{2}$ over the concentration range of water is much less than that observed by Larson and Iwamoto[28] and Nelson and Iwamoto[34] in the solvents nitromethane and acetone, respectively.

Consecutive titrations with copper(II) perchlorate solutions and lithium perchlorate as carrier, when performed 24 hours apart, show very little reproducibility, in fact, almost none. Three titrations on the same solution performed 24 hours apart are plotted in Figure 9. The $E\frac{1}{2}$ for each titration is plotted vs - log H_2O. The initial concentration of each of the three solutions was the same (0.03%); however, the first titration appears to follow the trend observed with TNBAP and the shift of the $E\frac{1}{2}$ is much less than would be expected over the concentration range based on results from studies with TNBAP. The plot of the second titration is shifted further down, as if it had a water concentration higher than the first; the third plot shows still a further shift downward, and the slope of this curve best fits the slope of curves observed with the carrier TNBAP over the same concentration range of water. These trends were observed in all consecutive titrations on the same solutions of copper(II) perchlorate with lithium perchlorate as the carrier electrolyte.

This trend may be attributed to a possible kinetic effect. A possible mechanism for this could be:

$$yH_2O + Li(BuOH)_xClO_4 \xrightleftharpoons{Fast} Li(H_2O)_y(BuOH)_{x-y}ClO_4 + yBuOH \qquad (15)$$
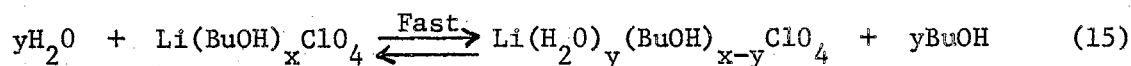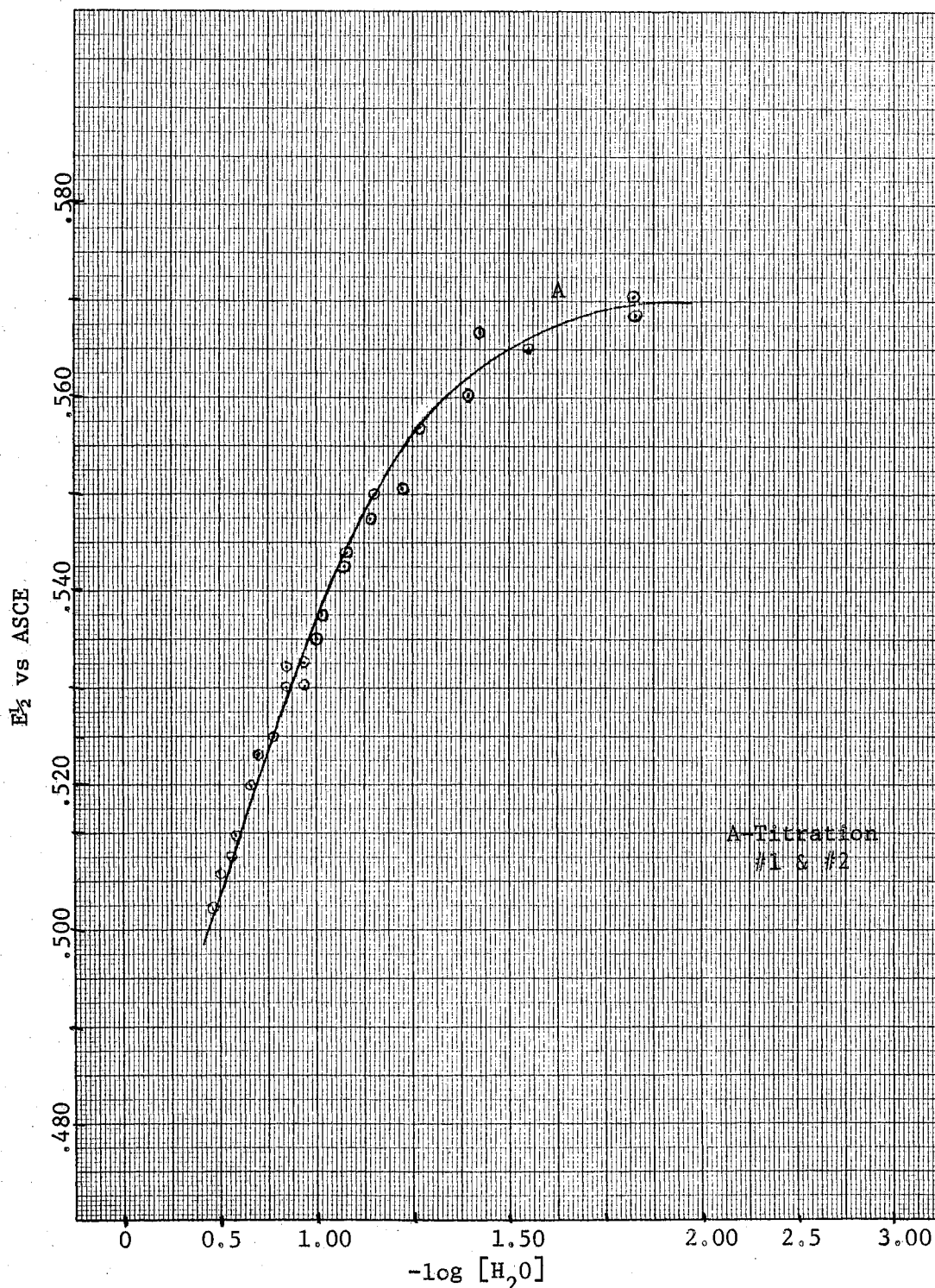
Figure 8. Plot of Shift of $E\frac{1}{2}$ vs -log $[H_2O]$ for Cu(II) in 1-Butanol. Carrier Electrolyte is TNBAP. Two Titrations Performed on the Same Solution 24 Hours Apart. $[Cu^{++}] = 3.24 \times 10^{-4}M$ $[TNBAP] = .07M$.

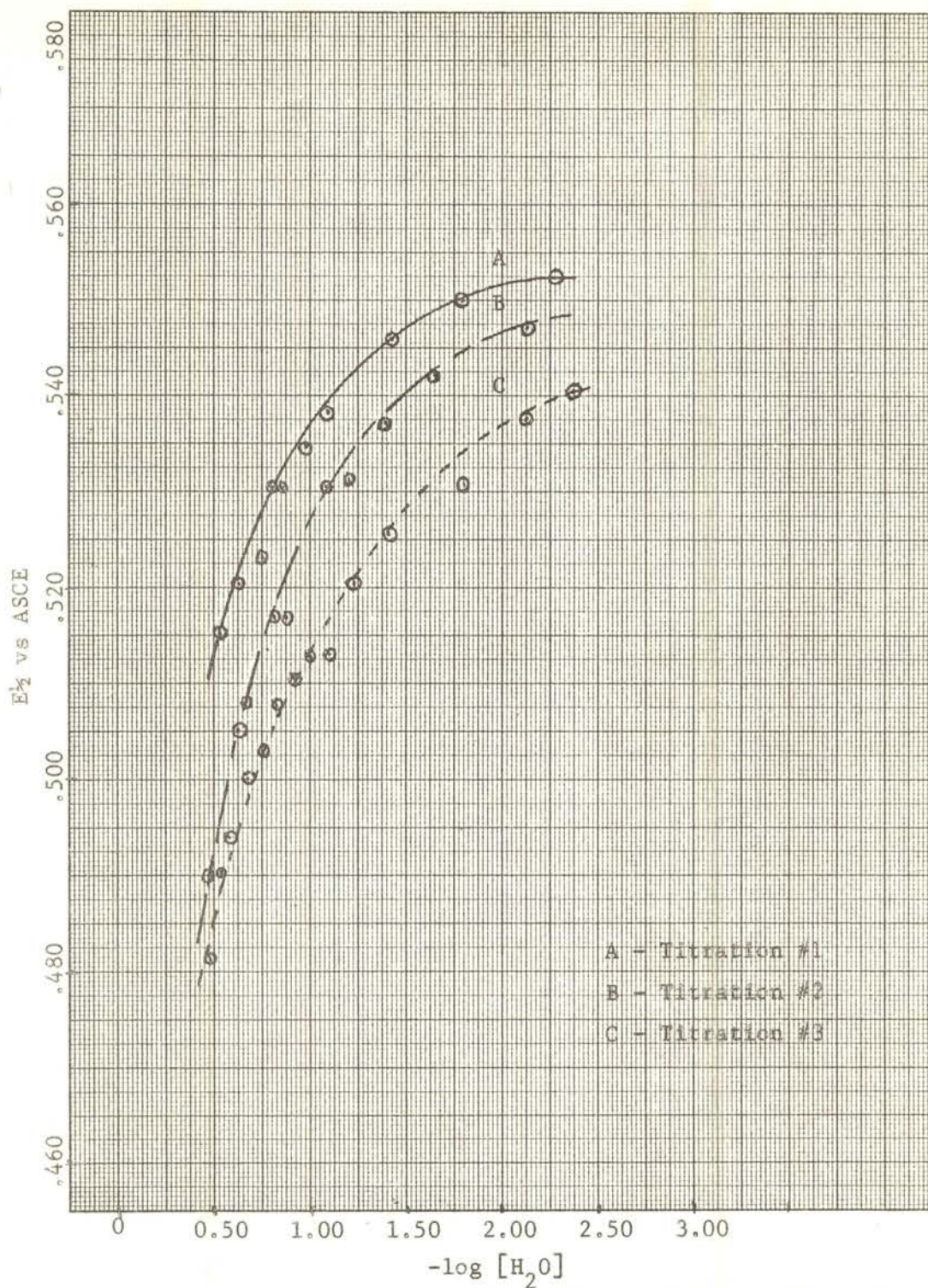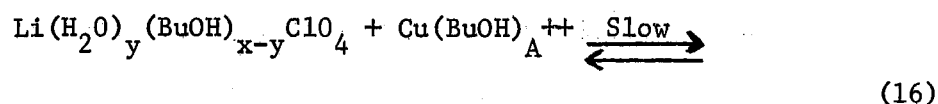Figure 9. Plot of $E^{\frac{1}{2}}$ vs $-\log[H_2O]$ for Cu(II) in 1-Butanol.

Carrier Electrolyte is $LiClO_4$. Three Titrations
Performed 24 Hours Apart on the Same Solution.
$[Cu^{++}] = 3.35 \times 10^{-4}$ $[LiClO_4] = 0.1M$.

$$Li(H_2O)_y(BuOH)_{x-y}ClO_4 + Cu(BuOH)_A^{++} \underset{\longleftarrow}{\overset{Slow}{\longrightarrow}}$$

<div align="right">(16)</div>

$$Li(H_2O)_{y-z}(BuOH)_{x-y} + {}_zClO_4 + Cu(BuOH)_{A-z}(H_2O)_z^{++}$$

According to Equation (15) in the first titration the lithium per-chlorate reaction with the water is a fast reaction, so that Cu(II) ions appear to be much drier, but if a slow reaction takes place between the Cu(II) ion and the water associated with the lithium ion over the 24 hour period separating the two titrations, this could explain why the Cu(II) ion appears to be hydrated to a greater extent in the second titration than in the first, and hydrated even more in the third titration which was performed 48 hours after the first. The concentration of lithium perchlorate (0.1M) is of the order of 1000 times greater than the concentration of the Cu(II) ions. This high concentration of lithium by a mass effect would be expected to interact with the water appreciably, even though the direct reaction between $Cu(BuOH)_A^{++}$ and H_2O may be fast, the fact that the reaction changes with time appears to indicate such a kinetic effect.

As stated previously, in all polarograms of copper(II) perchlorate in 1-butanol with both of the carrier electrolytes tested, only one wave was observed. This wave appeared to be similar to the wave observed in aqueous solutions, the $Cu(II) \rightarrow Cu^o(Hg)$ wave. However, plots of E_{de} vs log $i/i_d - i$ over a range of twenty concentrations of water, in solutions of copper(II) with lithium perchlorate as carrier, show a decrease in the slopes of these plots as the water concentration increases. Slopes of these plots of E_{de} vs log $i/i_d - i$ over a range of twenty con-

centrations of water in solutions of copper(II) with lithium perchlorate
as carrier, show a decrease in the slopes of these plots. Slopes of
these plots for the first ten solutions having water concentrations of
from 5×10^{-3} to 0.5M are about the same and have an average value of
0.068 which corresponds to an n-value of 0.86 e^-. The slopes of the
plots in the range of higher concentrations of water, 1M to 6.7M, de-
crease gradually to a value of 0.03 corresponding to an n-value of
1.85 e^-. Similar behavior is observed in plots of E_{de} vs log $i/i_d - i$
for the Cu(II) wave with TNBAP. Plots of the first ten solutions with
essentially the same water concentrations as quoted for lithium per-
chlorate carrier solutions, have an average slope of 0.07 in the low
water concentration range. Plots for the high water concentration with
TNBAP as carrier give an essentially constant slope of 0.041. A change
in the slope of these plots occurs at concentrations of about 0.1M
water. This seems to indicate a change in the course of the electrode
reaction or a change in the solution itself. A calorimetric study of
the interaction of water with copper(II) perchlorate in 1-butanol has
shown a similar "break" in the trend of changes of the heat or reaction
per mole of metal with the addition of water. The "break" occurs also
at approximately the same concentration of water[42].

The observed difference in the slopes of the plots of E_{de} vs log
$i/i_d - i$ and the apparent n-values for different ranges of water con-
centration led to a closer examination of the polarograms at the dif-
ferent water concentrations. The very close examination of the polaro-
grams of the drier solutions led to the conclusion that this single wave
might possibly be two waves with one directly on top of another. A

slight change in the form of the wave was noted at about $E_{3/4}$ for the total wave. This slight change in the wave was, therefore, taken as the i_d for the first wave. Plots of E_{de} vs log $i/i_d - i$ were made for the two waves and for the composite wave. An $E^{\frac{1}{2}}$ value for each wave was determined from each plot: for the first wave $E^{\frac{1}{2}} = +0.565 \pm 0.002$ volts and for the second wave $E^{\frac{1}{2}} = +0.468 \pm 0.002$ volts vs the ASCE. These waves are so close together that without a very careful examination they would not be detected and would be analyzed as a single wave. A polarogram of one of the drier solutions of copper(II) perchlorate with TNBAP as carrier is shown in Figure 10.

The slope of the plot of E_{de} vs log $i/i_d - i$ for the first wave is 0.041 corresponding to an $\underline{n}$-value of 1.5 e$^-$ and for the second wave is 0.051 corresponding to an $\underline{n}$-value of 1.15 e$^-$. The slope for the composite of the two waves when they are considered as a single wave is 0.078 comparable with the slopes previously calculated for the apparent single wave. This slight separation in the form of the single wave was only detectable at water concentrations less than 0.015%. Thus after the addition of any water to the solution the waves shifted together to appear as one wave as illustrated in Figure 11.

The nature of the reduction process for the two waves is not well defined. However, from this study and considering the nature of the solvent, the assignments of the course of the Cu(II) reduction waves in other nonaqueous solvents of rather similar properties, and the possible reductions which could occur in a Cu(II) ion system, an explanation of the nature of reduction processes can be made. Two alternative ways of assigning reduction processes to these two waves is presented for con-
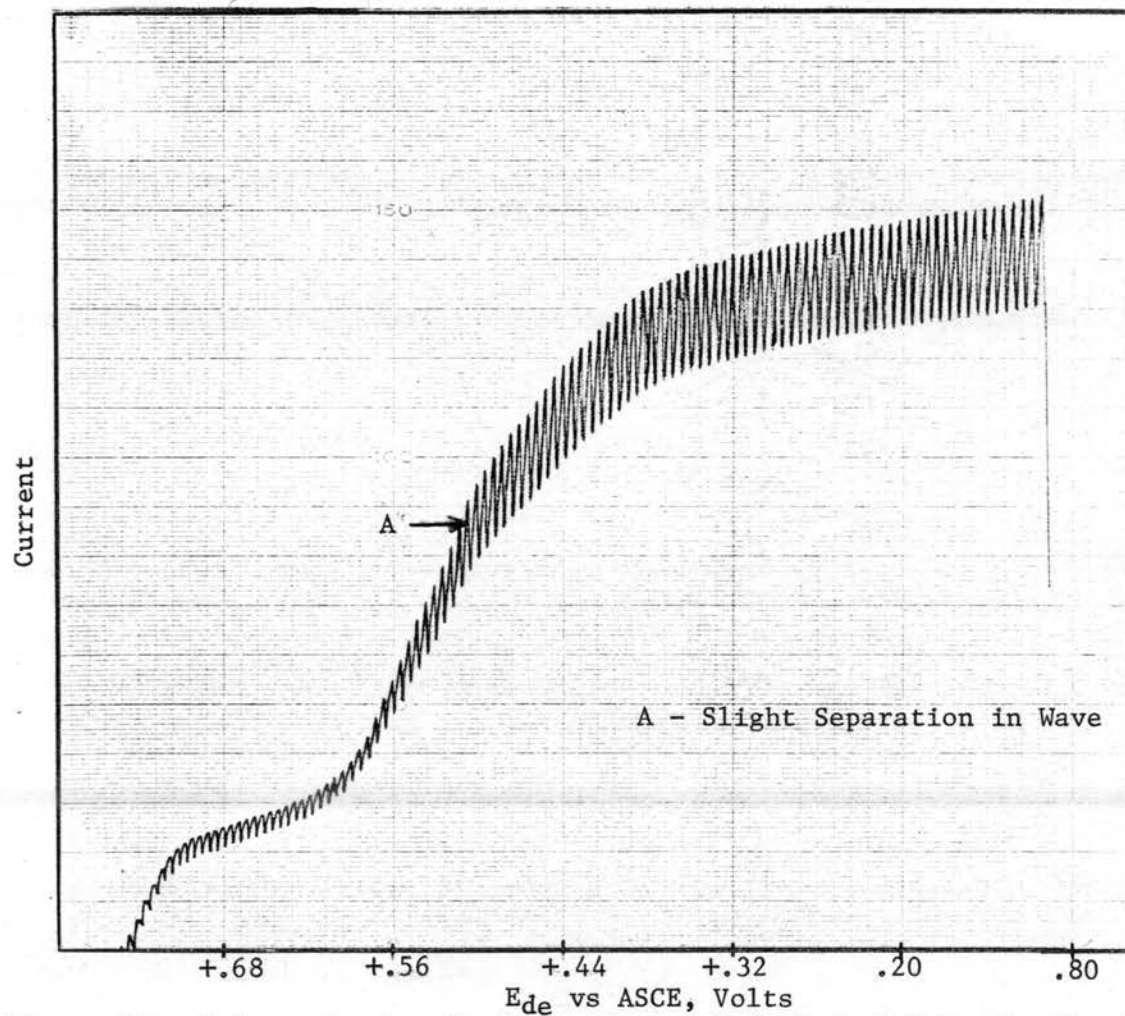
Figure 10. Polarogram for the Reduction of Cu(II) in 1-Butanol, Showing Two Waves. Carrier = 0.07M TNBAP, $[Cu^{++}]$ = 4.0 x 10^{-4}M $[H_2O]$ = 4 x 10^{-3}M, Current Sensitivity = 0.01 μa/mm, Drop Time = 4.2 sec.
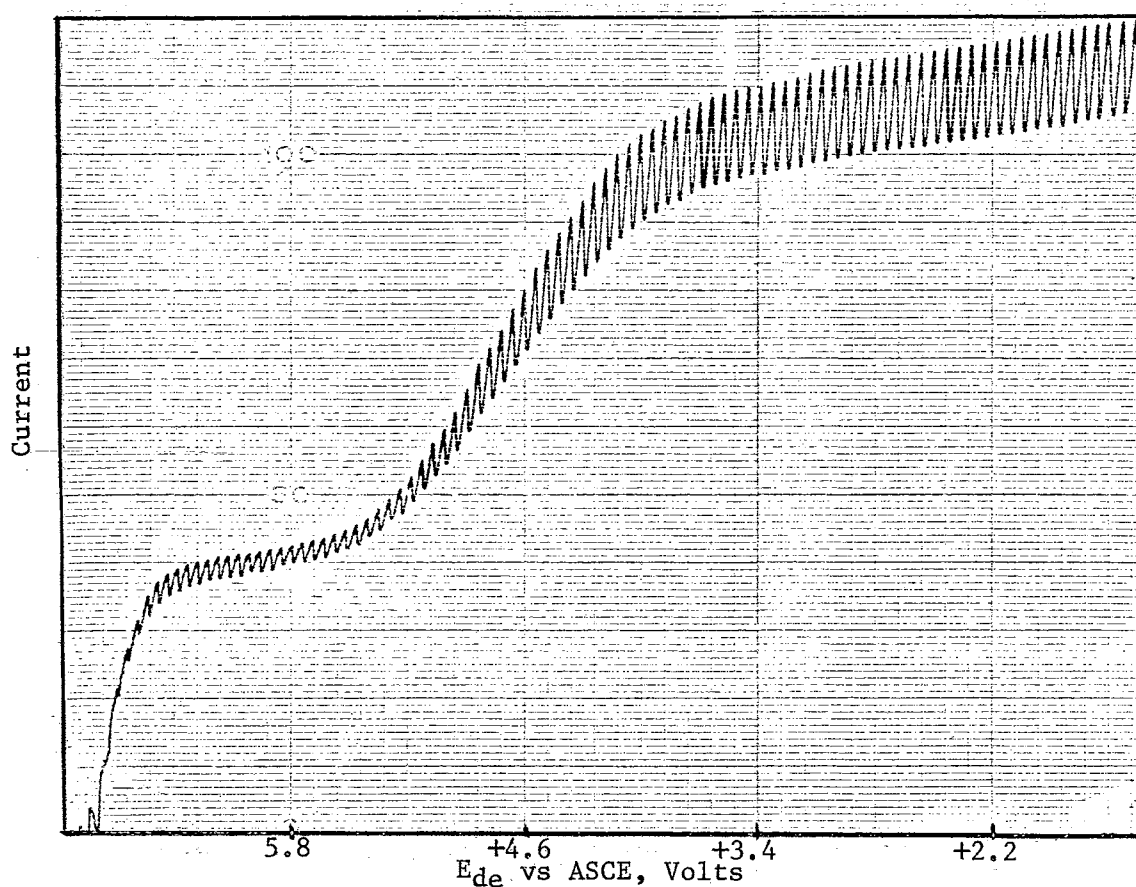
Figure 11. Polarogram for the Reduction of Cu(II) in 1-Butanol Showing One Wave. Carrier = 0.1M LiClO$_4$, [Cu^{++}] = 3.5 x 10^{-4}M. [H$_2$O] = 5 x 10^{-2}M, Current Sensitivity = 0.015 µa/mm. Drop Time = 4.2 sec.

sideration.

First, considering the electrochemical behavior of the Cu(II) ion in a noncomplexing aqueous medium, the following reductions are possible[1].

$$Cu(II) + 2e^- \longrightarrow Cu^o \qquad E^o = +0.095v \text{ vs SCE (a)}$$

$$Cu(I) + 1e^- \longrightarrow Cu^o \qquad E^o = +0.027v \text{ vs SCE (b)}$$

$$Cu(II) + 1e^- \longrightarrow Cu(I) \qquad E^o = +0.089v \text{ vs SCE (c)}$$

$$Cu(II) + 2e^- \longrightarrow Cu(Hg) \qquad E^o = +0.035v \text{ vs SCE (d)}$$

$$Cu(I) + 1e^- \longrightarrow Cu(Hg) \qquad E^o = +0.146v \text{ vs SCE (e)}$$

Since these reductions are taking place at the dropping mercury electrode, only (c), (d), and (e) are possible in this system.

In the non-aqueous solvents nitromethane, acetone, ethanol, methanol, 2-propanol, and 2-butanol two waves have been reported for the reduction of Cu(II) ions[1,28]. The first wave, occurring at the more positive potential has been assigned to the reduction process (c) and the second wave to the reduction process (e). No quantitative evidence is given for making these assignments to the two waves, however. No slopes of E_{de} vs log i/i_d - i have been quoted or values of $\underline{n}$ reported. Larson and Iwamoto[28] state that the first wave is slightly irreversible but then quote a slope of this wave of 0.108 at low water concentrations. This value of the slope is high for a one electron reduction. It would appear that more quantitative evidence is necessary in order to assign these reduction processes to the two waves they have observed.

However, if the same assumptions are made in the Cu(II)-1-butanol system as have been made in the other nonaqueous solvents, then the

first wave occurring at $E_{\frac{1}{2}}$ = +0.565v vs ASCE could be assigned to (c) and the second wave occurring at $E_{\frac{1}{2}}$ = +0.0468v vs ASCE could be assigned to (e). Support for this assignment is based on the assumption that, as reported for acetone and nitromethane[28,34], in 1-butanol the Cu(II), Cu(I) wave shifts with increasing concentration of H_2O, while the Cu(I), Cu(Hg) wave does not shift. This would explain why two waves are observed at the lower water concentration, but as water is added to the solution the Cu(II), Cu(I) wave shifts into the Cu(I), Cu(Hg) wave, and thus a differentiation between the two cannot be made.

An alternative assignment for the reductions corresponding to the two waves would be that the first wave, occurring at the more positive potential is reduction process (d), and the second wave is the reduction process (c), where the copper(I) remains in solution and is stabilized by 1-butanol. This assignment of reduction processes fits the calculated $\underline{n}$-values better than the first assignment. The first calculated $\underline{n}$-value of 1.5 e^- probably corresponds to a 2 e^- exchange as in (d), and the second $\underline{n}$-value of 0.855 e^- corresponds to a 1 e^- exchange as in (c). This assignment would also fit if the Cu(II), Cu(Hg) is the wave which is shifted and the Cu(II), Cu(I) shifts very little or not at all with increasing water concentrations. In the limit of a purely aqueous solution only process (d) is observed.

The Lithium Wave

In the latter part of this study, as differences in the behavior of the copper(II) ion were noted, and differences were observed in the shift of $E_{\frac{1}{2}}$ for the copper(II) wave in the two different carriers, lithium perchlorate and TNBAP, the importance of studying the lithium ion

as an ion of interest rather than a carrier electrolyte became apparent. It is possible to obtain a well defined wave for the lithium ion in 1-butanol with TNBAP as the carrier electrolyte. Figure 12 shows a typical polarogram for the lithium reduction. The $E_\frac{1}{2}$ of this wave occurs at $-1.699 \pm 0.002v$ vs the ASCE. This wave is a reversible wave with a slope of 0.071 corresponding to an n-value of $0.85\ e^-$.

Solutions of lithium perchlorate in 1-butanol with the carrier electrolyte TNBAP were titrated with water in the manner previously described, and the effect on the $E_\frac{1}{2}$ for the lithium wave was observed. No significant shift of $E_\frac{1}{2}$ for the reduction wave of the process Li^+, Li^o occurs. Water concentrations in these titrations ranged from initial concentrations of 0.003M to a final concentration of 0.3M. Lithium ion concentrations studied ranged from 3×10^{-4} to $9 \times 10^{-4}M$.
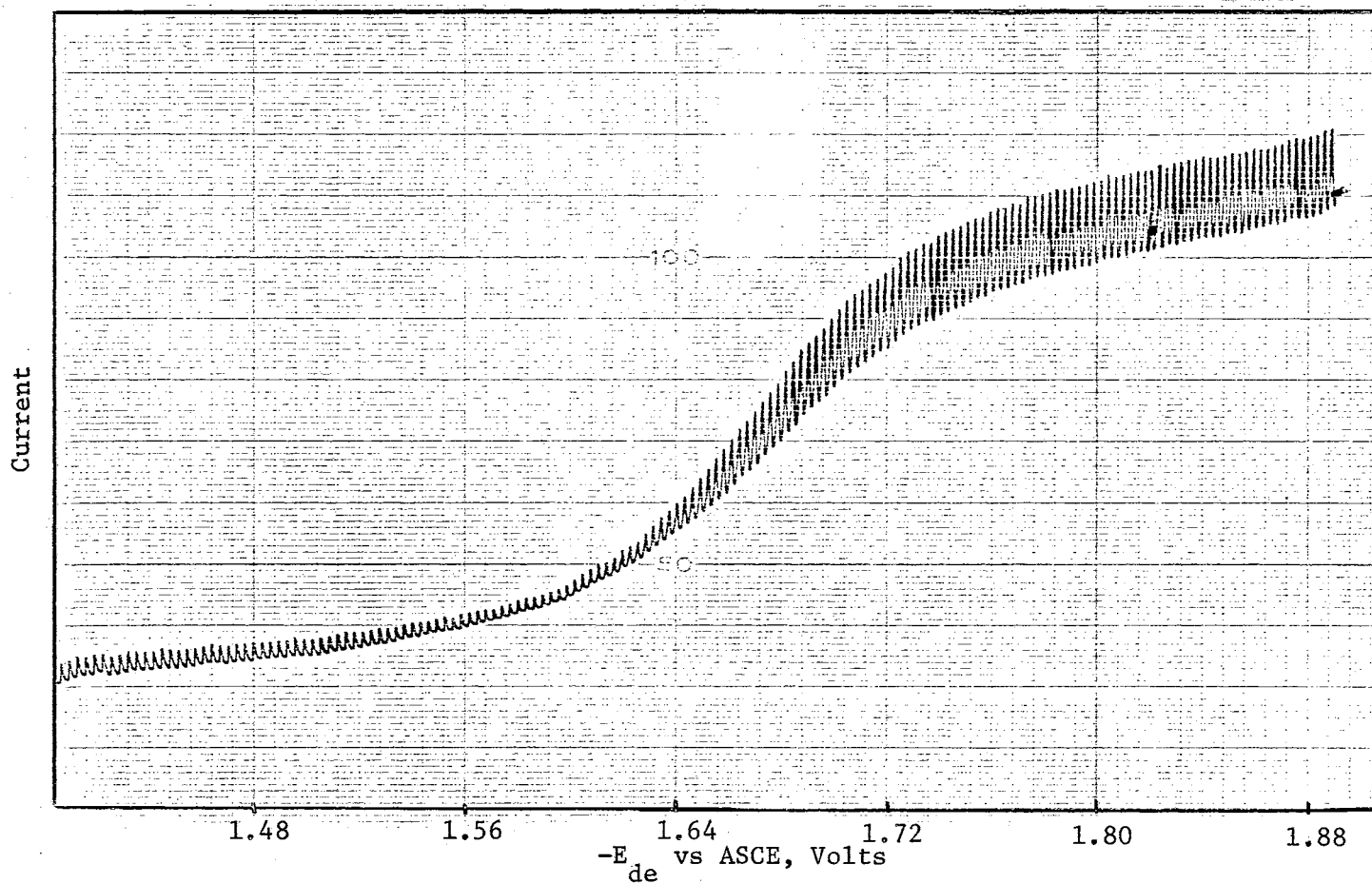
Figure 12. Polarogram for the Reduction of Lithium Perchlorate in 1-Butanol, Carrier = 0.07M TNBAP, [Li$^+$] = 9.24 x 10^{-4}M. Current Sensitivity = 0.008 µa/mm, Drop Time = 4.2 sec.

CHAPTER V

SUMMARY AND SUGGESTIONS FOR FURTHER STUDY

In this study solutions of the order of 10^{-4} in copper(II) per-
chlorate have been examined at the dropping mercury electrode. The sol-
vent for this study was 1-butanol and contained water in the molar con-
centration range of 0.003M to 6.67M. A definite trend in the shift of
the $E^{\frac{1}{2}}$ has been noted; the $E^{\frac{1}{2}}$ for the copper(II) reduction wave shifts
toward more negative values with increasing water concentration of the
solutions. However, the true nature of the electrode process has not
been defined. An understanding of the course of an electrode process is
necessary for the proper application of polarographic data to electro-
chemical problems. Qualitative deductions on the course of the elec-
trode process have been made from the shape of the polarographic curves,
slopes of the plots of E_{de} vs log i/i_d - i, and previous evidence for
copper(II) reductions in other nonaqueous solvents. Further study is
indicated to determine the true course of the electrode process.

An improvement needs to be made in the method of drying the copper
(II) perchlorate and in maintaining a dry solution. The water content
of the copper(II) solutions (0.1% in H_2O) was high compared to the con-
centration of the Cu(II) ions in solution so that these ions were almost
completely complexed with water even at the lowest water concentrations
examined. If there are actually two waves present in this reduction
process, and if the separation becomes greater at very low concentra-

45

tions of water, the course of the electrode process can be examined only at very low water concentrations.

A difference in the behavior of the system has been noted with the two carrier electrolytes. Especially at higher water concentrations as the dielectric constant begins to change. In this region the wave appears to become more reversible, approaching a slope of 0.03, approximating a 2-electron change. This effect is more pronounced in the case of lithium perchlorate as carrier. At low water concentrations a constant ionic strength is assumed since the nature of the solvent does not change appreciably. The ionic strength for the lithium perchlorate carrier solutions probably changes more than the TNBAP carrier solutions, since the lithium perchlorate is soluble in water and the smaller size of the cations in lithium perchlorate causes the solvation to be greater than it is for the TNBAP. Conductivity measurements are suggested in order to verify this assumption.

The change in the trend of the slopes of the plots of E_{de} vs log $i/i_d - i$ for the single wave for Cu(II) as water concentrations increase indicates that some change has either taken place in the nature of the electrode reaction, a change in the nature of the solution, or a combination of both has occurred. This change occurs at about 1M water. The fact that this single wave might actually be two waves combined could contribute to this change. Until the course of the reduction process is better defined, any conclusions drawn are only assumptions. Part of this effect may be due to increasing ionization of the carrier electrolyte and also to the increasing ionization of copper(II) perchlorate with increasing dielectric constant of the solvent.

The possible kinetic effect observed with the solutions containing

lithium perchlorate as carrier requires closer examination and perhaps investigation by other methods, such as thermometric studies.

A significant contribution of this study was the elimination of the characteristic maximum associated with polarographic studies of transition metals in nonaqueous solvents. A complete study of the metal ion catalysis of the $O_2 \rightarrow H_2O$ reduction in non-aqueous solutions by Cu(II) ions or by other transition metals, is needed to completely explain all factors involved.

The most significant, practical contribution from this study is the observation of a well-defined lithium ion reduction wave in 1-butanol with the carrier TNBAP. A quick efficient method of standardizing lithium perchlorate salts in 1-butanol was one problem encountered in this study. The only method presently available for determining the lithium ion in non-aqueous solutions are Fluorimetric Determinations. For a reversible wave the wave height is directly proportional to the concentration of the metal ion. Since the lithium ion wave in 1-butanol is a well-defined reversible wave this suggests a simple way of determining the lithium ion concentration in 1-butanol or in mixtures of other non-aqueous solvents with 1-butanol. A calibration curve can be made with known concentrations of the lithium ion in 1-butanol or in mixtures of 1-butanol and other solvents where 1-butanol is present in the larger concentration, by plotting i_d vs concentration of the lithium ion. Then a polarogram of the lithium ion is run under the same conditions as those of the calibration curve, the i_d is measured and the concentration of the lithium read directly from the calibration curve.

1-Butanol has been examined as a solvent for polarographic studies of aquo-copper(II) formation constants but has not been shown to be a

suitable solvent for this study. Other metal ions need to be examined before its utility can be completely ruled out, for it is a solvent which is easily dried and does appear to be a useful polarographic solvent for some types of studies.

No shift in the half-wave potential of the lithium perchlorate wave was observed over a wide range of water concentrations in agreement with the assumption made by Larson and Iwamoto[28] that the lithium ion does not interact extensively with water in the solution. An alternative explanation of this, however, might be that the aquo-lithium ion complex is reduced at the same potential as the ion itself.

This study has shown that with proper apparatus and with some attention to experimental procedure, quantitative polarographic analysis can be carried out in nonaqueous media of low dielectric constant. This technique might have many possible uses, i.e., in the analysis of the organic phase in extraction studies where a prerequisite back-extraction step is not feasible prior to analysis.

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