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ELECTROANALYTICAL AND SPECTROPHOTOMETRIC STUDIES OF OXIDATION-REDUCTION AND COMPLEXATION IN ACETONITRILE

by

ISMAIL MOHAMMAD AL-DAHER

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH IN
PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA
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THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled ELECTROANALYTICAL AND SPECTROPHOTOMETRIC STUDIES OF OXIDATION-REDUCTION AND COMPLEXATION IN ACETONITRILE submitted by ISMAIL MOHAMMAD AL-DAHER in partial fulfilment of the requirements for the degree of DOCTOR OF PHILOSOPHY in CHEMISTRY.

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ABSTRACT

In this work several oxidation-reduction and complexation reactions in acetonitrile or acetonitrile-water mixtures were investigated. The thesis is divided into four parts. In the first part the reduction of water-insoluble aromatic nitro compounds with coulometrically generated chromium(II) was studied. Samples were dissolved in acetonitrile or in a mixture of acetonitrile-water or ethanol-water. Constant-current potentiometry was chosen for end-point detection in the coulometric titrations because it gives excellent potential changes at the equivalence point for systems involving one reversible and one irreversible couple as were encountered in this work. Samples of the order of 0.2 to 0.5 micromole could be determined with about one precent precision and accuracy for a number of substances; others reacted too slowly to permit direct determination. Reduction was in most instances to either the corresponding hydroxylamines or amines.

The second part reports studies of oxidation of ferrocenes, thiols and other compounds with coulometrically generated copper(II) in acetonitrile. Copper(II) was generated at 100% current efficiency from solutions of copper(I) perchlorate in acetonitrile. Micromolar quantities of ferrocene and several alkyl-substituted ferrocenes were determined with high precision and accuracy. The scope for coulometric procedure for the determination of thiols, thiourea, and tetramethylbenzidene appears more limited than

does the direct titration.

In the third part a study is described of the potentiometric titration in acetonitrile of the ions of transition metals and alkaline earths in solutions of about 10^{-3} M, both individually and in mixtures, with ethylenediamine (en), diethylenetriamine (dien), and triethylenetetramine (trien). The polyamines were selected as titrants because of their stability and the solubility of the corresponding metal complexes in acetonitrile. A number of metal ions could be determined quantitatively with these amines. For these complexation titrations in acetonitrile a variety of indicating electrodes -- platinum, copper ion selective electrodes, carbon rod, silver-silver ion and mercury-en or mercury-trien -- were investigated. Platinum was found to be superior to any of the other indicating electrodes investigated; it was simple and easy to use, and gave sharper and larger potential breaks for most of the systems studied. This is the first known report of platinum as an indicating electrode for complexation titrations.

The fourth part reports the spectrophotometric determination of the stability constants of copper(II) with en and dien, the spectrophotometric determination of the stability constants of copper(I) with phenanthroline and bipyridine, and the potentiometric determination of the overall formation constants of copper(I) with en, dien, and trien, all in acetonitrile. In general the stability constants measured in acetonitrile are smaller for both copper(II) and copper(I) complexes of the amines than are the corresponding values in water. This indicates that acetonitrile interacts more strongly with the copper ions than does water.

ACKNOWLEDGEMENTS

I would like to express my thanks, appreciation, and admiration to my supervisor, Professor Byron Kratochvil, for his guidance and encouragement during the course of this research.

In addition deepest thanks to my wife, Muna for her understanding, help, and encouragement. She, along with our children, Bassom, Ayad, and Shatha, have been a source of happiness and strength that has made this experience a pleasant one.

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PART I

REDUCTION OF NITRO COMPOUNDS WITH COULOMETRICALLY GENERATED CHROMIUM(II)

I. INTRODUCTION

The usefulness of aromatic nitro compounds in a variety of commercial products and as intermediates in chemical synthesis makes the determination of this functional group of broad interest (1,2). Analytical methods for the nitro group have centered on reduction either to the corresponding amine or to one of several intermediate oxidation states, generally either polarographically (3) or by addition of excess standard reductant, usually Ti^{3+} or Cr^{2+}, and back titration of the excess with a standard oxidant (4,5). Some direct titrations have been investigated in a limited way (6). Polarographic methods tend to lack precision and require careful calibration curves, while indirect titrimetric methods necessitate storage and handling of oxygen-sensitive solutions.

Electrochemical generation of strong analytical reductants by constant-current coulometry eliminates calibration curves, and avoids the difficulties of handling and standardizing oxygen-sensitive solutions. High precision is possible, and analyses can be performed on microsamples.

The technique of coulometry is reviewed briefly in the following section. This is followed by a survey of the electroreduction of nitro compounds, and then by the application of constant-current coulometry to the determination of nitro compounds.

A. Scope of Coulometry

The term coulometry applies to those techniques which are based on measurements of the coulomb (the product of current and time). In an electrolytic cell in which a metal ion or a compound is to be determined by measurement of the product of the current and time, either constant current or controlled potential can be used. If a constant current is applied to the cell, the potential must vary as governed by concentration of the electroactive species through the Nernst equation. As electrolysis proceeds, the potential difference between the generating cathode and anode increases as the concentration of the generated species increases. Thus if in the reduction of an electroactive species a second reducible component such as a metal ion or other substance is present, it too will eventually enter into the reaction and current will be used for its reduction as well as for the sample species. On the other hand, if a constant potential is used, the current decreases as a function of time due to the decrease in the concentration of the current carrying species in solution. This slows the reaction, but eliminates interference from competing reactions that might occur at higher potential.

Both techniques are commonly used in analysis. Constant-current coulometry is used primarily for coulometric titrations where high precision and accuracy are sought, whereas constant-potential coulometry provides the selectivity of potential control, but with somewhat less precision and accuracy. It is important to note that quantitative coulometric measurements do not need standard solutions for calibration, since the coulometer is internally calibrated by measuring the current-time product.

The purity of a substance can be calculated from the following equation

$$\% \text{ purity} = 100 \times itM/nFW \qquad (1)$$

where i is the value of the current in amperes used in a coulometric titration; t is the time of current flow in seconds; M is the atomic, molecular, or formula weight of the substance being determined; n is the number of equivalents per mole of substance; F is the faraday; and W is the mass of the sample being titrated. The values of i and t can be determined accurately, often to within a few parts in a million. F and, in most cases, M also are known with high accuracy. If a large enough sample is taken, W can also be determined to within any desired level of accuracy. Therefore it would seem that constant-current coulometry provides a way of assaying a substance relatively conveniently to an accuracy of as much as a few parts in a million. The greatest variability in highly precise work usually arises from the uncertainty in atomic weights.

For quantitative analysis by constant-current coulometry, four criteria must be satisfied. First, an appropriate solvent-solute system must be found which can provide a medium that will allow electrochemical generation of the desired titrant species. Second, a current level must be chosen such that the current density i/A, where A is the surface area of the generating electrode, is sufficiently low to ensure 100% current efficiency. Third, appropriate instrumentation for generation of constant, reproducible currents and for accurate measurement of times of current generation must be available. Finally, a method for end-point detection must be selected. In practice coulometric titrations are closely parallel to classical volumetric titrations except that the buret is replaced by a current generator and a working electrode -- it is in effect a titration with electrons.

Constant-current coulometry is capable of higher levels of accuracy and precision than most volumetric or gravimetric methods (7). This is especially true for the determination of very small samples (μg range and lower). In 1959, Taylor and Smith (8), working at the National Bureau of Standards, proposed that constant-current coulometry could be a suitable technique for the essay of primary standard materials, and outlined several advantages that recommend its application. Titrant can be added at any rate desired by methods that are more convenient than those required to dispense a standard solution. Since standard solutions are not required, the uncertainties associated with determining their composition are eliminated. Applications of constant-current coulometry to the assay of several standard substances has shown this technique to be one that is capable of high precision. It has been employed to provide a chemically measured value for the Faraday that is widely accepted, 96,487.0 ± 1.6 coulombs (9).

B. Electrochemistry of Aromatic Nitro Groups

The reduction of aromatic nitro compounds on cathodes with a high hydrogen overvoltage occurs by stepwise addition of protons and electrons to the nitro group (10-13). The electrochemical reduction in an acid medium can be represented as follows:

$$RNO_2 + 2H^+ + 2e \longrightarrow RNO + H_2O \qquad (2)$$

$$RNO + 2H^+ + 2e \longrightarrow RNHOH \qquad (3)$$

$$RNHOH + 2H^+ + 2e \longrightarrow RNH_2 + H_2O \qquad (4)$$

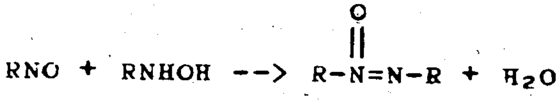
As a rule, it is not possible to isolate the nitroso compound produced in equation (2) because it is more readily reduced to the hydroxylamine at the cathode than is the initial compound. Therefore equations (2) and (3) are often combined in one equation as:

$$RNO_2 + 4e + 4H^+ \longrightarrow RNHOH + H_2O \qquad (5)$$

Thus, the electrochemical reduction of aromatic nitro compounds in acid media is as a rule treated as a two-step electrochemical reduction in which four protons and four electrons are added to form hydroxylamines which are subsequently reduced under appropriate conditions to the corresponding amines. Each of these stages takes place in a definite cathode potential range, and each is extremely sensitive to a number of variables (14). Several of these are discussed in the following sections.

Effect of pH of the Medium

The pH of the electrolysis solution plays an important role in determining the nature of the reduction product of nitro groups. Under acidic conditions the products are generally hydroxylamines, amines, and substances derived from their rearrangements (e.g., p-aminophenol from hydroxylamine) (15,16). Under basic or neutral conditions (using a high overvoltage cathode) the products are generally formed from bimolecular reaction of reduction intermediates (17,18), as in equation (6).



$$RNO + RNHOH \dashrightarrow R-\overset{\overset{O}{\|}}{N}=N-R + H_2O \qquad (6)$$

Nature of the Electrode Material

Reduction is more advanced on cathodes with a high hydrogen overvoltage. Under certain conditions the electrochemical reduction of aromatic nitro compounds on mercury, lead, zinc, tin and certain alloys of these materials yields the corresponding amines in almost quantitative yields, whereas arylhydroxylamines are obtained if the cathodes are made of nickel, graphite, carbon, or platinum (14).

Current Densities and Electrode Potentials

It is difficult to lay down consistent rules concerning the effect of current density on the yield of arylamines formed during the electrochemical reduction of aromatic nitro compounds. Khomutov *et al.*, reported that the yield of metanilic acid obtained by electrochemical reduction of nitrobenzene-*m*-sulfonic acid in a sulfuric acid medium on nickel, iron, steel (19), platinum and copper (20,21) decreases with an increase in the current density, while with zinc cathode the current yield of metanilic acid remains constant and quantitative (19) over a fairly wide range of current densities (0.002 - 0.04 A/cm^2).

Nature of Medium

Electrolytes used in the electrochemical reduction of aromatic nitro compounds in an acid medium include sulfuric acid, hydrochloric acid, a mixture of one of these acids with its salt, acetic acid and acetates (22-24). The concentration of mineral acid should not exceed the values at which these acids can participate in the substitution reactions in the benzene ring. For example the reduction of nitrobenzene in concentrated hydrochloric acid can afford the *o*- and *p*-chloroanilines (22). When ethanol is used under acidic conditions (H_2SO_4) the *p*-aminophenol is esterified to afford *p*-phenetidine (25,26). If the reaction is carried out in fuming sulfuric acid, the *p*-aminophenol can be sulphonated to give 2-hydroxy-5-aminobenzenesulfonic acid (27).

Temperature of Electrolyte

Systematic studies of the effect of the electrolyte temperature on the course of electrolytic reduction of nitro compounds, and on the yield of products, are scanty. According to Izaryshev and Floshin (28), who studied the electrochemical reduction of nitrobenzoic acid on cathodes with a high hydrogen overvoltage (lead, tin and lead amalgams), the yield of aminobenzoic acid increases when the temperature is raised from 20 to 40°C. At higher temperatures the yield of aminobenzoic acid no longer depends on the temperature.

C. Chromium(II) Generation by Constant-Current Coulometry in the Determination of Nitro Compounds

As mentioned previously constant-current coulometry has several advantages over other electroanalytical methods. It was therefore decided to investigate the use of coulometrically generated chromium(II) for the determination of water-insoluble aromatic nitro compounds because this reagent is one of the strongest known reducing agents for nitro compounds, and because it can be generated quantitatively from solutions under controlled conditions, as described in the experimental part. The slow rate of generation of chromium(II) from the trivalent ion has precluded its use. This problem was solved by use of $CrBr(H_2O)_5^{++}$ as reagent, for from this species chromium(II) can be generated rapidly and quantitatively at a mercury cathode in strongly acidic solutions (29). Nitro compounds coulometrically titrated to amperometric end points with about 1% accuracy by this reagent include *p*-nitrophenol, *p*-nitroaniline, and *o*-, *m*-, and *p*-nitrobenzoic acid (29,30).

We became interested in determining whether this method could be extended to the direct determination of other nitro compounds, especially if water-insoluble. The following three chapters report on the scope of the method.

II. EXPERIMENTAL

A. Chemicals

Chromium(III) bromide (K & K Laboratories) was washed twice with ethyl ether, the excess ether removed by suction and the solid dried under vacuum. This material yields $CrBr(H_2O)_5^{++}$ on dissolution in water (29). A solution 0.1 M in $CrBr(H_2O)_5^{++}$ and 1.5 M in HCl was prepared for use as the catholyte in the coulometric cell. o- and m-Nitrotoluene (Eastman Organic Chemicals), and nitroethane (J. T. Baker Chemical Co.) were distilled under vacuum and the middle portions of the distillates used. The following compounds were recyrstallized from ethanol until melting points within ± 1°C of reported values were obtained: p-aminoazobenzene and 4-nitrophthalic acid (British Drug House); p-nitrotoluene, 1-nitronaphthalene, p-nitrobiphenyl, o-nitrophenol and 2,4-dinitroanisole (Matheson, Coleman and Bell, MCB). m-Nitrophenol (BDH) was recrystallized from 1 M HCl, p-nitrobenzoic acid (Eastman) from water, azobenzene (Eastman) from 12:1 $MeOH:H_2O$, and p-nitrophenol (Eastman) from benzene. o- and m-Nitrobenzoic acids (Aldrich Chemical Co.) were analyzed by potentiometric titration with standard NaOH and found to be 99.6 and 99.0% pure. Sodium nitrite (J. T. Baker), 5-nitro-1-napthylamine (Eastman) and o-nitroanisole (Eastman) were used as received. Acetonitrile (MCB) was purified by distillation from calcium hydride. Only the middle fraction was retained.

B. Apparatus and Procedure

A constant-current coulometer designed and built in the electronics shop of the Department of Chemistry, University of Alberta, was used. The design incorporates several features that provide excellent current stability. The output from a Kepco Model OPS-500 power supply was passed through a sensing resistor (General Radio precision resistor, Type 1440), the voltage drop across the resistor being monitored and maintained constant by means of a feedback circuit as outlined in Figure 1. The resistors labeled Ri, Rf, and Rs in the figure were placed in a polystyrene-insulated plug-in module on the front of the instrument. This arrangement minimized short term temperature changes in these three resistances; also, since Ri and Rf were located near each other the ratio of their values, which must be kept constant for precise current regulation, was little affected by temperature changes. Three plug-in modules provided a choice of 20, 5, or 0.5 mA current. The control unit was designed to allow manual starting and stopping of the current in conjunction with a digital clock which indicated elapsed time to the nearest 0.1 sec, and also had provision for automatic shut-off of the current when the potential between the indicating electrodes reached a preset value.

The stability of the current provided by this instrument is excellent. For example, current variation with the 20 mA module was less than 0.01% over three hours, and

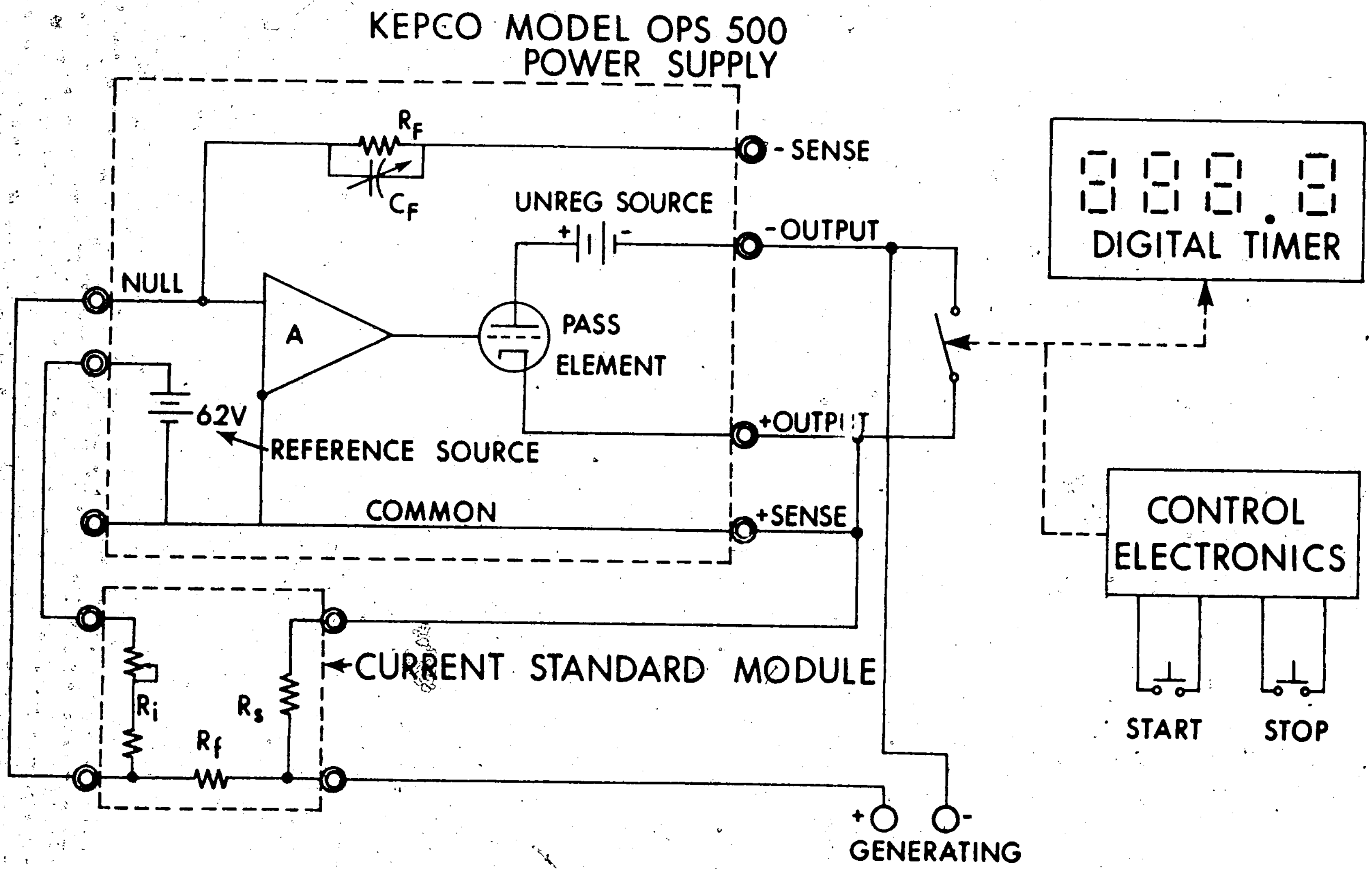


Figure 1. Diagram of Major Components of Constant Current Coulometer.

less than .05% over 24 hours. These tests were run with output loads varying between 0 and 1000 ohms both upon completion of the instrument and again after several months of use.

The titration vessel was a borosilicate H-cell with a 150-mL cathode compartment and a 60-mL anode compartment similar to that described by Bard and Petropoulos (31). It is represented in Figure 2. Samples were introduced as approximately millimolar solutions by hypodermic syringe through a rubber serum cap. The quantity of sample taken for each titration was obtained by weighing the syringe to the nearest mg on a top-loading balance before and after sample introduction. The mercury pool cathode, 19.6 cm^2 in area, could be introduced or withdrawn through a side arm connected by Tygon tubing to a mercury reservoir. The cadmium rod anode was placed in a tube with a fine glass frit at one end to separate it from the bulk anode compartment, which in turn was separated by a second fine frit and an agar-KCl salt bridge from the cathode compartment. Both the fritted tube and the bulk anode compartment contained 0.01 M HCl in 1 M KCl as analyte. A current of 19.995 mA was used for all titrations, this approximate level having been reported previously to be optimum (29). Nitrogen, passed through two wash bottles of 0.1 M chromium(II) or vanadium(II) chloride in 0.1 M HCl over amalgamated zinc, was used to remove oxygen from the solutions in the H-cell. The same results were obtained

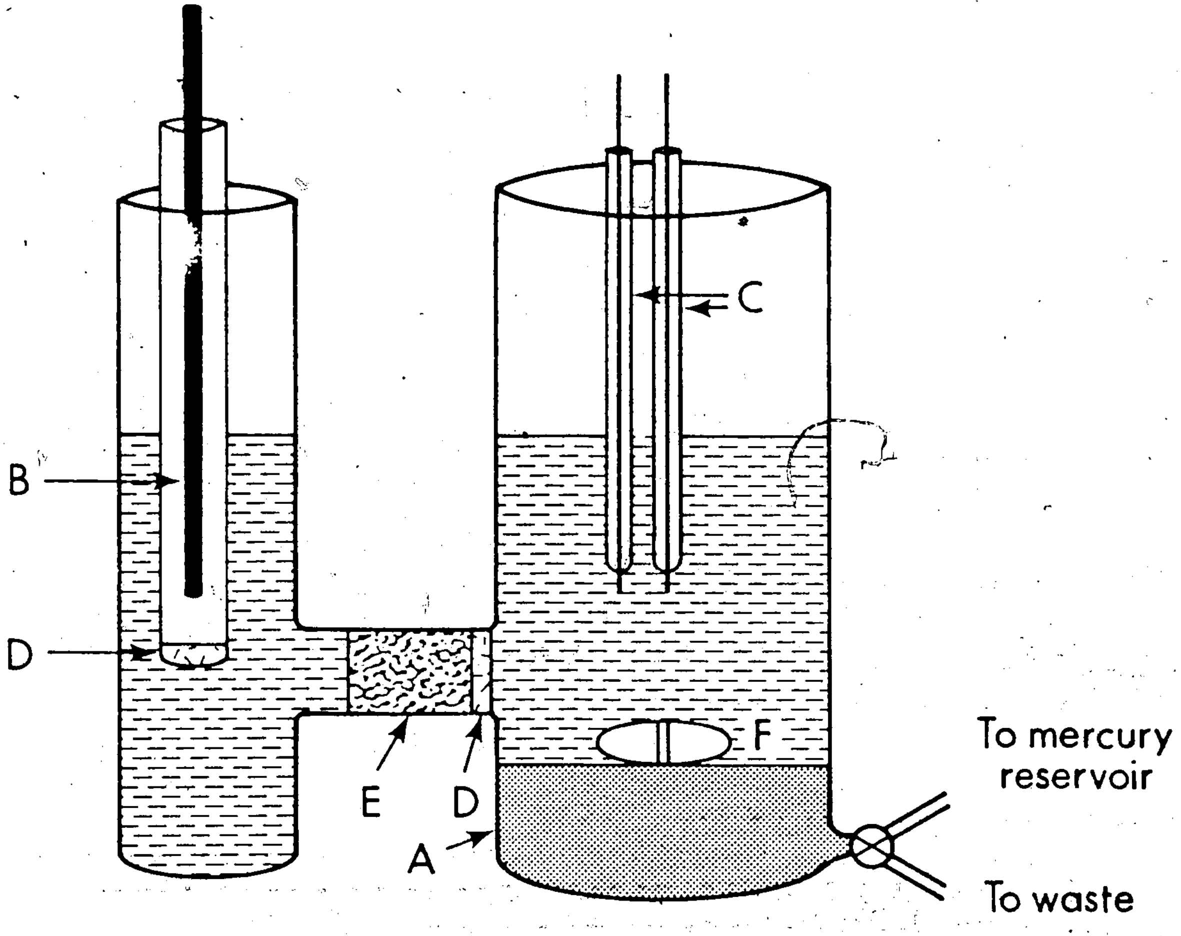


Figure 2. Coulometric cell and electrodes. A, mercury pool generating cathode; B, cadmium rod generating electrode; C, platinum wire indicating electrodes; D, fine glass frits; E, agar-potassium chloride plug; F, magnetic stirring bar.

whether chromium(II) or vanadium(II) was used.

The indicating electrodes were a pair of platinum wires approximately 2 mm in diameter and 1 cm long, spaced about 1 cm apart. A Fisher Model 520 Accumet pH meter was used to provide a 10-μA current between the indicator electrodes and to measure the potential difference.

C. Procedure

For each run approximately 60 mL of freshly prepared supporting electrolyte 0.1 M in $CrBr(H_2O)_5^{++}$ and 1.5 M in HCl were placed in the cathode compartment and the solutions in both the anode and cathode compartments of the cell were deaerated with nitrogen for 15 minutes. The inlet was then raised so that the nitrogen stream was directed over the surface of the catholyte and the mercury pool was introduced into the cell by raising the mercury reservoir. A magnetic stirring bar on the mercury pool stirred both the catholyte and the mercury surface. A blank was run by generating chromium(II), continuously at first and then in increments of 1 to 5 seconds near the end point, until a small excess was present. Potential and time readings were recorded just before and beyond the end point. A portion of sample solution then was injected and chromium(II) generated again, with time and potential readings recorded as for the blank. The readings were plotted and the end points located by linear extrapolation (Figure 3).

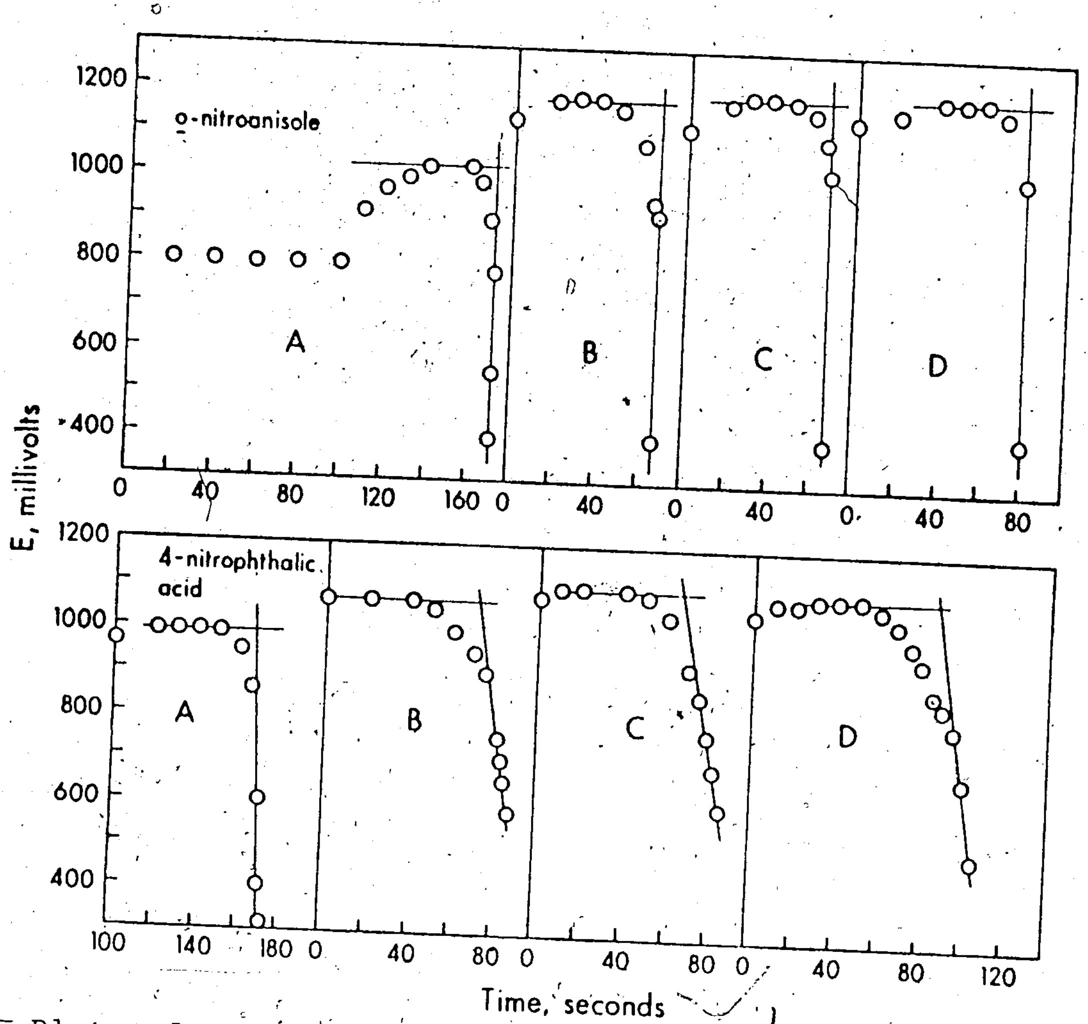


Figure 3. Plots of end-point potentials between two platinum electrodes polarized with a 10 μA constant current in the coulometric titration with electrogenerated chromium(II) of o-nitroanisole (above) and 4-nitrophthalic acid (below). A: blank; B, C, and D: successive titrations of approximately 0.5-μmol samples in the same cell solution.

The amount of chromium(II) generated past the end point depended upon the compound being determined. With sharp end points, as with *o*-nitroanisole, only about 0.2% excess was needed; for 4-nitrobenzoic acid about 30% was necessary. In each case successive runs were performed by addition of samples to the chromium(II) remaining in the cathode compartment from the preceding sample. Sample solutions were approximately millimolar, and were always used within a few hours of preparation. For water-insoluble compounds acetonitrile or a mixture of acetonitrile-water or ethanol-water was used as sample solvent.

III. RESULTS

The optimum conditions for the constant-current coulometric generation of chromium(II) from $CrBr(H_2O)_5^{2+}$ have been worked out previously. The best solution concentrations were found to be 0.1 M for $CrBr(H_2O)_5^{2+}$ and 1.5 M for HCl (29); the best current level was found to be 20 mA (32).

Mononitro, dinitro and azo-compounds were titrated; the results of the titrations are summarized in Table I. The rate of reaction varied widely, with 1-nitronaphthalene being the most rapid. On the other hand, under our conditions m-nitrophenol and 4-nitrophthalic acid react stoichiometrically but too slowly to be attractive analytically, while nitroethane, nitrite ion and azo-benzene react too slowly to be determinable. 1-Chloro-4-nitrobenzene gave scattered results indicating a reduction of between four and five electrons per mole. 1-Nitro-2-naphthol gave results several percent low for a 6-electron reduction. p-Nitrobiphenyl gave results that were 11 percent low for a 4-electron reduction.

Considerable variation was encountered in the number of samples that could be titrated successively in a single portion of analyte solution. With o-nitroanisole six or more samples could be determined in one portion, with o-nitrotoluene five samples could be determined, while with 4-nitrophthalic acid only one sample could be determined within a percent. For most compounds two or three determinations could be run on one portion of analyte. In

TABLE I.

SUMMARY OF RESULTS OF TITRATIONS OF NITRO COMPOUNDS WITH COULOMETRICALLY GENERATED CHROMIUM(II)[a]

Compound	No. e⁻'s in reduction used in calculations	Detns.	Ave. error, %	Rel. std. dev., %	Solvent for sample	Observations
o-nitrobenzoic acid	4	3	+ .3	.1	H_2O	
m-nitrobenzoic acid	4[b]	4	- .3	.3	H_2O	
p-nitrobenzoic acid	4[b]	4	- .6	.4	1:5 AN-H_2O	
o-nitrotoluene	4	10	0	.9	AN	End point sharp.
m-nitrotoluene	4	6	0	.1	AN	
p-nitrotoluene	5	4	-4.2	2.5	AN	Not analytically useful.
o-nitroanisole	4	18	0	.2	AN	End point sharp.
2,4-dinitroanisole	10	6	- .1	.2	AN	
o-nitrophenol	5	9	-5.6	2.0	1:25 EtOH-H_2O	Not analytically useful.
m-nitrophenol	6[b]	1	- .2	-	H_2O	Reaction extremely slow.
p-nitrophenol	6	7	+ .1	.4	H_2O	
4-nitrophthalic acid	4	3	- .7	.5	1:25 AN-H_2O	Reaction slow.
1-nitronaphthalene	6	9	+ .2	1.0	AN	End point sharp.
5-nitro-1-naphthylamine	5	7	+ .3	.4	AN	

[a] Samples were in the range of 0.2 to 0.5 µmole.

[b] Previously reported: $6e^-$ in H_2O (7); $4e^-$ in DMSO (10).

some cases, as with 1-nitronaphthalene, the first sample portion gave erratic results and was used as a blank.

IV. DISCUSSION

Aikens and Carlita reported that *o*-nitrobenzoic acid undergoes 4-electron reduction to the hydroxylamine, while the *m*- and *p*-acids undergo 6-electron reduction to the amines (29). It was found in this work, however, that all three undergo only a 4-electron reduction. This is in agreement with the controlled potential coulometric results at a mercury cathode in dimethylsulphoxide obtained by Lindbeck and Freund (33). Our values for the number of electrons involved in reduction also agree with the results of Lindbeck and Freund except for *m*-nitrophenol, where they report a 4 and we a 6-electron reduction. Bergman and James report either 4- or 6-electron reduction for the nitro group in a range of compounds at a mercury cathode in aqueous solution, depending on the potential applied (34). In most of the systems in which we observed 4-electron reduction a slow potential drift at and past the 4-electron equivalence point indicated that further reduction was taking place. This suggests that part of the difference in the *n*-values found may reside in the time allowed for reaction; cell conditions, especially acidity, may also be important.

Lindbeck and Freund suggest that partial reoxidation of the reduced species by a component of the cell solution such as hydrogen ion may be responsible for positive errors in subsequent analyses carried out in the same solution (33).

They propose that the process probably involves the following steps:

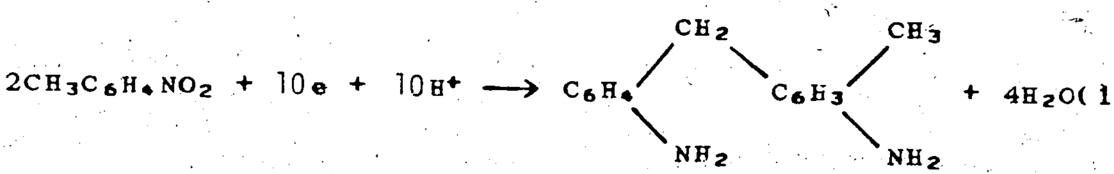
$$O + ne \longrightarrow R \qquad (7)$$

$$R + mS \longrightarrow O' + mS' \qquad (8)$$

$$O' + me \longrightarrow R \qquad (9)$$

where equation (8) is the rate determining step, O is the nitro compound, and R is the corresponding reduced compound. O' may or may not be the original oxidized state, and S may be a solvent molecule or a hydrogen ion.

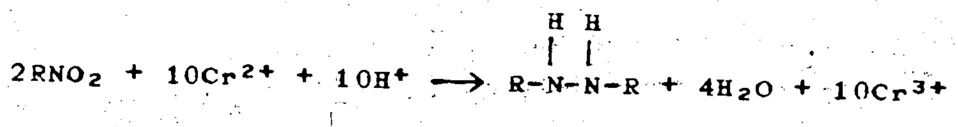
o-Nitrotoluene undergoes a 4-electron reduction with accurate and sharp end points. The method may be used to determine up to five samples in one analyte portion. *m*-Nitrotoluene undergoes a 4-electron reduction with accurate results, but only two samples can be determined in one analyte portion. In contrast, *p*-nitrotoluene undergoes a less than 5-electron reduction with poor accuracy and precision because of the formation of small amounts of a bicyclic compound (35,36):



$$2CH_3C_6H_4NO_2 + 10e + 10H^+ \longrightarrow \overset{\displaystyle CH_2}{\underset{\displaystyle NH_2}{C_6H_4}}\;\; \overset{\displaystyle CH_3}{\underset{\displaystyle NH_2}{C_6H_3}} + 4H_2O \qquad (10)$$

o-Nitroanisole undergoes a 4-electron reduction with a precise, accurate and very sharp end point. The method can be used to determine six or more samples in one portion of analyte with all samples giving the same accuracy, precision and sharpness of end points. The neighboring methoxy group may stabilize the hydroxylamine product through hydrogen bonding. 2,4-Dinitroanisole undergoes a 10-electron reduction; the ortho nitro group probably is reduced to hydroxylamine while the para nitro group is reduced to the amine. It is possible to determine two samples only in one portion of analyte. *o*-Nitrophenol undergoes less than a 5-electron reduction and so chromium(II) reduction is not analytically useful because the reaction is not stoichiometric. *m*-Nitrophenol undergoes a 6-electron reduction but the reaction is extremely slow, too slow to be attractive as an analytical method. *p*-Nitrophenol undergoes a 6-electron reduction. In this system the first sample gave consistently scattered results, but subsequent samples were satisfactory. Therefore the first sample in each fresh cell solution was considered as a blank and not used in the calculations.

4-Nitrophthalic acid is reduced stoichiometrically in a 4-electron process, though very slowly. 1-Nitronaphthalene undergoes a rapid 6-electron reduction with a sharp end point. Up to three samples can be titrated in one portion of cell solution but, as with *p*-nitrophenol, it is best to use the first sample as a blank. 5-Nitro-1-naphthylamine undergoes a stoichiometric 5-electron reduction. The reduction product was not isolated and identified; the stoichiometry corresponds to formation of a coupled hydrazo species:



$$2RNO_2 + 10Cr^{2+} + 10H^+ \longrightarrow R-\overset{H}{\overset{|}{N}}-\overset{H}{\overset{|}{N}}-R + 4H_2O + 10Cr^{3+} \qquad (11)$$

Hydrazo products of electrochemical reduction of nitro groups are well known in alkaline solutions, but not in acid (14). 1-Nitro-2-naphthol gave results several percent low for a 6-electron reduction, perhaps owing to stabilization of the intermediate 1-nitroso-2-naphthol with chromium(III).

Nitroethane reacts too slowly to be determinable. The analytical applicability of reduction of the aliphatic nitro compounds has not been studied as extensively as has that of the aromatic ones, mainly because of the instability of their reduction intermediates and also perheps because of the limited use of these compounds and their products in organic synthesis. The reaction of the nitrite ion, added as sodium nitrite, also was too slow for it to be determined by direct chromium(II) reduction under our conditions.

Neither azobenzene nor p-aminoazobenzene could be determined stoichiometrically by our method. The reduction is very slow in both cases. Reduction is reported to lead to the formation of several products such as aniline, hydrazobenzene, and benzidine (37); therefore the lack of stoichiometric reaction was not unexpected.

1-Chloro-4-nitrobenzene undergoes reduction corresponding to between 4 and 5 electrons. Interaction between this compound and its intermediate reduction products and mercury has been reported (38), and is likely responsible for the nonstoichiometric results observed.

Constant-current potentiometry was chosen for end-point detection in this study because it often gives excellent potential changes at the equivalence point for systems involving one reversible and one irreversible couple, as are encountered in this work (39). Examples of a set of successive titration end-point plots in the same analyte solution are shown in Figure 3 for *o*-nitroanisole, where reduction is clean and stoichiometric, and 4-nitrophthalic acid, where the end points are successively more drawn out and sloping. Satisfactory results are obtained, even in those cases where slopes are severe, if a straight line is drawn through the two or three steepest points past the equivalence point so as to intersect with a horizontal line drawn through the two or three points corresponding to the highest potential observed prior to the end point.

In summary, samples of the order of 0.2 to 0.5 micromole can be determined with about 1% precision and accuracy for a number of substances; others reacted too slowly to permit direct determination. Reduction was in most instances to either the corresponding hydroxylamines or amines.

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PART II

STUDIES OF OXIDATION WITH COULOMETRICALLY GENERATED COPPER(II) IN ACETONITRILE

V. INTRODUCTION

The simplicity of synthesis and ease of purification of ferrocene, the stability of its solutions and the easy and reversible oxidation of ferrocene to the blue ferricinium ion have resulted in much study of this compound as an analytical reagent. Its official chemical name is dicyclopentadienyliron, $Fe(C_5H_5)_2$. In the last five years, ferrocene has been widely investigated by several Russian workers as an analytical reagent for the potentiometric determination of iron in alloys (1), and for the reduction of silver(I) (2), both by titration in organic-aqueous media. Other applications of ferrocene and its derivatives have been suggested. For example, ferrocene has been proposed as an antianemic agent (3), and addition of 1,1'-diethylferrocene by 0.05 to 5 weight percent to diesel fuel is reported to decrease soot formation by 50 to 60 percent (4). Also, to obtain uniform discoloration and to decrease the color of polyethylene, ferrocene can be added at a level of 0.05 to 0.35 wt % to the compound (5).

Copper(II) in acetonitrile is a useful reagent for the determination of oxidizable compounds that are insoluble or react with water (6-16). Acetonitrile solutions of copper(II) are fairly stable, but require periodic standardization. Ferrocene has been proposed as a primary standard for this purpose because it is soluble in acetonitrile, can be purified readily, is stable on storage, and is oxidized quantitatively to the ferricinium ion by copper(II) (9).

As discussed in Part I, constant-current coulometry has several advantages over direct titrations. Chief among them are the elimination of the need for preparation, storage, and standardization of titrant solutions, and the ability to generate electrochemically exceedingly small quantities of chemically reactive species with accuracy and precision. Quirk and Kratochvil (9,10) found the reaction between copper(II) and ferrocene, along with some ferrocene derivatives, to be quantitative. The equation is

$$\mathrm{Fc} + \mathrm{Cu}^{2+} \rightleftharpoons \mathrm{Fc}^{+} + \mathrm{Cu}^{+} \qquad (12)$$

where Fc is ferrocene and Fc^{+} is the ferricinium ion. We became interested in finding whether the generation of copper(II) from copper(I) in acetonitrile is quantitative. Therefore the ferrocene system was chosen as a chemical system for this investigation. The method was then tested with sulfur-containing compounds and hydroquinone.

VI. EXPERIMENTAL

A. Chemicals

Commercial acetonitrile (Matheson Coleman and Bell) was either used as received [illegible]urified by the method of O'Donnell, Ayers, and Mann (17), except that the decantation following addition of sulfuric acid was replaced by a vacuum distillation below 55°C (9).

Tetrakis(acetonitrile) copper(I) perchlorate was prepared by adding excess copper powder (Allied Chemical) to a solution of hydrated copper(II) perchlorate in acetonitrile, allowing the reduction of copper(II) to go to completion, as indicated by the disappearance of the blue color, filtering off the excess powder, evaporating the solution to concentrate the copper(I) salt, cooling, then collecting and drying the salt under vacuum at room temperature overnight (18). The salt was analyzed by oxidation of portions to copper(II) with nitric acid, followed by titration of the copper(II) with EDTA. The salt was found to be 99.8% pure; the impurity is probably acetonitrile (19). *n*-Butyl-, amyl-, *t*-butyl-, and di-n-butyl derivatives of ferrocene were obtained from Arapahoe Chemicals, and used as received. Ferrocene (Arapahoe Chemicals) was recrystallized twice from heptane and sublimed once. Thiourea (Baker and Adamson) and dodecanethiol (Matheson Coleman and Bell) were used as received. Tetramethylbenzidine (Eastman Organic Chemicals) was recrystallized from acetonitrile. Thiophenol (Terochem Laboratories Ltd.) was distilled under vacuum. Hydroquinone had been previously purified by P. Quirk of this laboratory. He recrystallized commercial material (Fisher Scientific purified grade) once from 95% ethanol and dried the product 8 hours under vacuum to room temperature. Hexamethylenetetramine (HMT) (J. T. Baker) was purified by sublimation.

B. Apparatus and Procedure

Solutions approximately 0.02 *M* in copper(I) perchlorate were prepared in either commercial or purified acetonitrile. About 5 to 10 drops (0.15 to 0.30 mL) of distilled water were added in each run because the presence of water in the solutions had been found previously to give sharp potential breaks and stable potentials by stabilizing the ferricinium ion produced from the oxidation of ferrocene (10).

The constant current coulometer described in Part I was used as the current source and timer. An Orion Model 801 digital pH meter was used to locate the end points.

The titration vessel, shown in Figure 4, was a borosilicate H-cell with a 150-mL anode compartment and a 60-mL cathode compartment. Samples were introduced as approximately 0.9 to 1.1 grams of solutions containing ferrocenes in the range of 10^{-2} to 10^{-3} *M* (i.e., one to ten micromoles) by hypodermic syringe through a rubber serum cap. The quantity of sample taken for each titration was determined by weighing the syringe to the nearest milligram on a top-loading balance before and after sample introduction. The end-point detection electrodes in the anode compartment consisted of a platinum wire as the indicating electrode and a silver wire immersed in 0.01 M $AgNO_3$ in acetonitrile in a glass tube as the reference electrode, with a cracked glass junction separating the $AgNO_3$ solution from the bridge solution of 0.1 M lithium perchlorate and a fine frit separating the bridge solution from the titration compartment. The glass junctions were prepared after the design of Nils S. Moe (20) in tubes of different diameters. Resistances of the junctions to 1000 Hz in 0.1 M aqueous KCl were typically on the order of 20,000 to 100,000 ohm. The anode and cathode compartments were separated by an anion exchange membrane (AMF A104-EC, American Machine and Foundry Co.). The anion membrane was converted from the chloride form to the perchlorate form by soaking in 0.5 M aqueous lithium perchlorate solution overnight. After that it was dried in air for two hours, then immersed in pure acetonitrile for a further two hours before use. The membrane was stored in acetonitrile between runs. The cathode compartment contained 50 mL of 0.14 M acetic acid in 0.04 M $LiClO_4$ as catholyte, while the anode compartment contained 70 mL of 0.02 M $CuClO_4$ and 5 to 10 drops of distilled water. The generating electrodes in both the cathode and anode compartments were platinum gauze with large surface areas.

Air oxidation of copper(I) in acetonitrile is not a serious problem; however, to avoid possible slight oxidation, the cell contents were deaerated with nitrogen that had been passed through a wash bottle of acetonitrile; the stream of nitrogen was directed over the surface of the solution during the titrations. Magnetic stirring was used in the anode compartment.

The experimental procedure was as follows. A weighed portion of sample solution was injected, and copper(II) titrant coulometrically generated from copper(I) at 5 mA constant current at a platinum gauze electrode (measured value, 5.000 mA). The end point was determined potentiometrically by following the rapid change in potential indicated by the digital pH meter until a predetermined value was reached. The first sample was considered as a blank, and successive portions were titrated by injection of weighed samples into the same analyte solution. The current was stopped either automatically or manually at a preset potential (end-point potential) for all samples. Seven to nine samples could be titrated successively in a single portion of analyte solution before the potential change at the end-point became too drawn out to be useful.

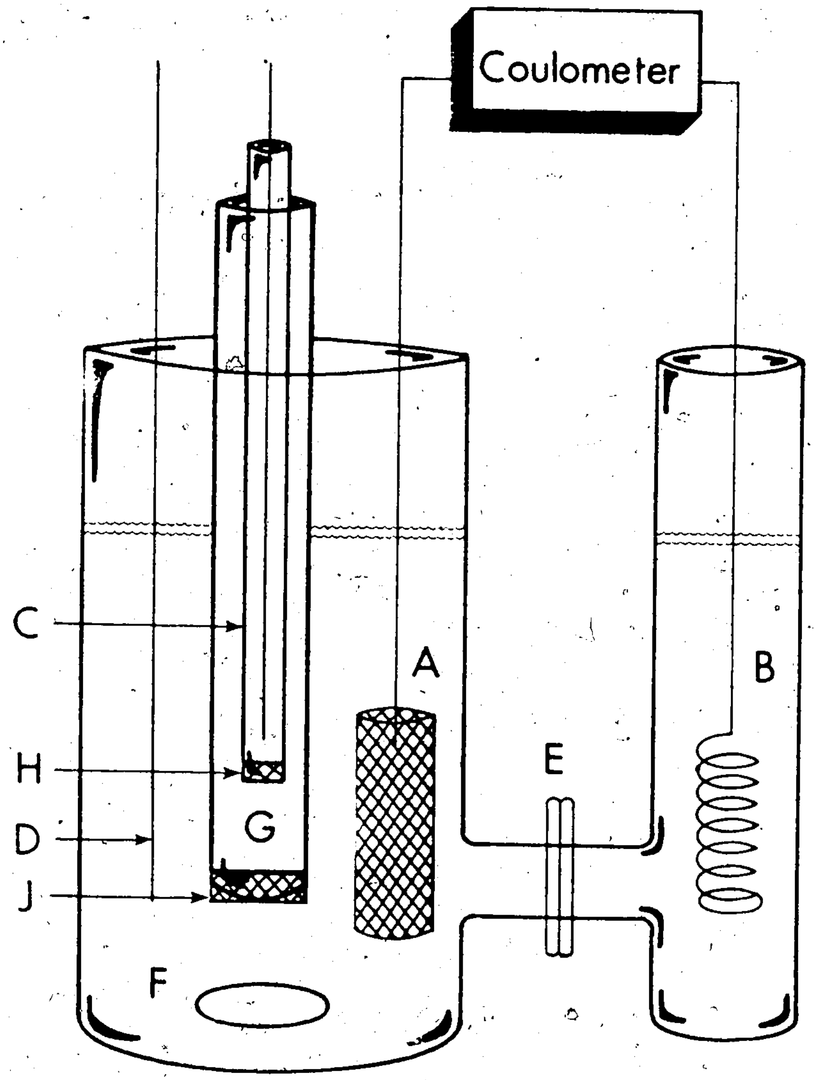

Figure 4. Coulometric cell and electrodes. A, platinum gauze anode; B, platinum wire cathode; C, Ag, 0.01 $\underline{M}$ $AgNO_3$ in acetonitrile reference electrode; D, platinum indicating electrode; E, anion exchange membrane; F, magnetic stirring bar; G, 0.1 $\underline{M}$ lithium perchlorate in acetonitrile; H, glass junction; J, fine frit.

VII. RESULTS AND DISCUSSION

A. Ferrocene and Ferrocene Derivatives

Results of a series of titrations of ferrocene and four derivatives with coulometrically generated copper(II) are given in Table 2. Relative standard deviations ranged from 1 to 4 parts per thousand. Considering the purity of purified ferrocene to be 100%, the relative error found for the determination of ferrocene in the present work ranged from 0.06 to 0.14%. For the ferrocene derivatives, which were used as received, the results indicated that the purity of the derivatives ranges from 97.3 to 99.9%. These values were in the same general range as obtained earlier by conventional potentiometric titrations with a standard solution of copper(II).

n-Butyl- and t-butylferrocene appeared to be the most pure of the derivatives analyzed. Acetylferrocene and benzoylferrocene gave too small a change in potential to be determinable, confirming the earlier work (9).

Titrations of ferrocene in pure and in commercial acetonitrile gave results that agreed within 0.4 part per thousand. Therefore commercial acetonitrile was used in the remainder of this work.

Upon doubling the amounts of ferrocene, and maintaining the current at 5 mA, the same percentage compositions were obtained. Therefore the sample quantity does not affect the precision or accuracy of the results.

TABLE 2.

TITRATION OF FERROCENE COMPOUNDS WITH COULOMETRICALLY GENERATED COPPER(II) IN ACETONITRILE[a]

Compound	Potential at End Point, mV	Detns.	Purity of Compound, %	Rel. Std. Dev., %
Ferrocene	317	7	99.86	.29
"	319	9	100.06	.23
"	320	10	100.09	.21
"	320	9	100.10	.40
"	320	9	100.11	.11
"	320	8	100.06	.29
Ferrocene[b]	246	7	100.08	.30
"	246	8	100.02	.35
"	246	8	100.02	.18
n-Butylferrocene	239	9	99.66	.48
Amylferrocene	234	8	99.17	.31
t-Butylferrocene	245	8	99.90	.31
Di-n-butylferrocene	244	9	97.30	.36

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[a] Samples were in the range of 10^{-5} to 10^{-6} mole.

[b] Solvent was commercial acetonitrile.

Acetylferrocene and benzoylferrocene did not give satisfactory end points when titrated by this method. Most of the ferrocene derivatives possessing a carbonyl function adjacent to one or both of the cyclopentadienyl rings, besides being more difficult to oxidize, were oxidized slowly past 1:1 stoichiometry (10). It was concluded that these compounds could not be determined satisfactorily by the oxidation procedure described here.

B. Sulfur-containing Compounds and Tetramethylbenzidine

The same coulometric procedure used for the determination of ferrocene derivatives except for the addition of small amounts of water necessary to stabilize the ferricinium oxidation product was also investigated as a possible analytical method for the determination of thiophenol, tetramethylbenzidine, thiourea, and 1-dodecanethiol. The thiols undergo oxidation under appropriate conditions to the disulfides,

$$2RSH + 2Cu^{+2} \rightleftharpoons R{-}S{-}S{-}R + 2Cu^{+} + 2H^{+}, \qquad (13)$$

but the reduction potentials of some of these compounds were too high to give satisfactory titration curves; that is, the potential breaks were too small to be useful. Also, the lack of a proton acceptor in the system may have contributed to the poor results by this coulometric method.

Acetonitrile is a very weak Bronsted base, and in pure acetonitrile oxidation of compounds such as hydroquinone and thiophenol is inhibited by the absence of a sufficiently strong base to accept the hydrogen ions produced (7). Most Bronsted bases are also Lewis bases of some strength in their reaction with copper(II), however, and the addition of compounds such as ammonia or pyridine results in undesirable complexation of copper(II). Of a number of proton scavenging species considered for accepting the proton in the oxidation of proton generating compounds, it was found that hexamethylenetetramine (HMT) appeared promising for this purpose. Addition of excess HMT to solutions of thiophenol prior to generation of copper(II) resulted in sharp potential changes of several hundred millivolts at the end point, but the location of the end point varied with the amount of HMT present, and tended to be on the order of 2% early. Also, a precipitate, apparently copper(I) thiophenolate, appeared after addition of thiophenol to the cell solution, and only slowly redissolved near the end point. The presence of some undissociated copper(I) thiophenolate at the end point may account in part for the low results in the analysis.

Potentiometric Titration

To investigate the reasons for the early end poin' for 1 to 1 stoichiometry, potentiometric titrations th copper(II) of thiophenol, 1-dodecanethiol, and hydroquinone (H_2Q) in the presence of varying amounts of HMT were performed using the titration cell and procedure described in Part III of this thesis, but with argon gas in place of nitrogen. The results are represented in Tables 3 and 4.

Titrations of 2 to 1 mixtures of thiophenol and HMT in 0.1 M $LiClO_4$ with copper(II) showed two potential breaks. The first break had an inflection of about 80 mV, was smaller than the second break, and appeared at a copper(II) to thiophenol mole ratio of less than 0.5. The second break had a height of about 180 mV and appeared at a copper(II) to thiophenol mole ratio of about 1 (0.998 and 0.996). A precipitate appeared prior to the first break and dissolved before the second break started. The precipitate is thought to be the copper(I) salt of the thiol anion. The two breaks, then, are probably caused by formation of the thiol precipitate, followed by dissolution and oxidation of the precipitate according to the following equations:

$$4RSH + 2Cu^{2+} + 4HMT \longrightarrow RSSR + 2CuSR(s) + 4H_2MT^+ \quad (14)$$

$$2CuSR + 2Cu^{+2} \longrightarrow RSSR + 4Cu^+ \quad (15)$$

When the amount of HMT was increased to a level equivalent to that of thiophenol, the end point came at a copper(II) to thiophenol mole ratio of 1.15. When HMT was added to the copper(II) titrant solution in a 1 to 1 mole ratio, and the titration was done two hours after mixing, a large sharp break, on the order of 640 mV, was obtained at a copper(II) to thiophenol mole ratio of 0.942. No precipitate appeared in this titration. This is as expected on the basis of the above explanation, since excess HMT is not available to react with RSH to form CuSR and H_2MT^+. The reaction then is

$$2CuHMT^{2+} + 2RSH \longrightarrow 2Cu^{+} + RSSR + 2H_2MT^{+} \qquad (16)$$

Repeating the last titration 24 hours after mixing of the HMT with copper(II) gave a ratio of copper(II) to thiophenol of 1.16, and the sharpness of the break decreased. This indicates a slow reaction between copper(II) and HMT that results in copper(II) not being available for oxidation of thiophenol. Solutions of copper(II) in acetonitrile are blue, but turn dark green on addition of HMT. The reaction possibly is formation of a stable copper(II) complex with HMT or, more likely, a decomposition product of HMT. If a complex is formed with HMT the stability constant must be small, because potentiometric titrations of HMT with copper(II) show a steady change in potential with no visible inflection at 1 to 1 or 2 to 1 stoichiometries. No evidence for a reaction between copper(II) and HMT has been reported in the literature except for an observation by Mel'nichenko and Gyunner (21) that copper(II) chloride and HMT do not react in water, but do form a dark brown precipitate in methanol at an equivalence point corresponding to a ratio of copper to HMT of 5 to 3. The precipitate composition was given as $5CuCl_2 \cdot 3HMT$. The only other metal-HMT complex reported is that of silver; P. Job (22) and F. Pawelka (23) report the stability constant of silver ion with HMT in aqueous solutions as 3.1×10^3 and 3.75×10^3 respectively.

Overall, the addition of HMT to either the copper(II) titrant or to the solution being titrated does not appear useful from an analytical point of view.

When 1-dodecanethiol in 0.1 M $LiClO_4$ was titrated with a 1 to 1 mixture of copper(II) and HMT, the titration curve showed a potential break of 280 mV at a copper(II)/1-dodecanethiol mole ratio of 1.41. Again the large amount of copper(II) required is likely caused by reaction of a portion of the copper(II) with HMT.

C. Hydroquinone

Titrations of mixtures of hydroquinone and HMT in a ratio of 1 to 1.96 in 0.1 M $LiClO_4$ with copper(II) showed a potential break of 400 mV at a copper(II) to hydroquinone mole ratio of 1.997. When the amount of HMT was increased to a level equivalent to exactly double the amount of H_2Q the stoichiometry and size of break do not change. When the H_2Q to HMT ratio was changed to 1 to 1.06 and 1 to 1.60 the end points came at copper to H_2Q ratios of 1.15 and 1.68 respectively, while the potential breaks became larger and sharper. Increasing the amount of HMT to a ratio of 1 to 2.04, or even to 1 to 4.1 H_2Q to HMT resulted in a positive error at the end point of about 7% relative. The quality of the end point was excellent and gave good precision (see Table 4).

In summary, it has been shown that copper(II) can be produced with 100% current efficiency from solutions of copper(I) in acetonitrile, and that micromolar quantities of ferrocene and some alkyl-substituted ferrocenes can be determined with high precision and accuracy by constant current coulometric generation of copper(II). The scope of the coulometric procedure for the determination of other substances appears more limited than does direct titration. Potentiometric investigations of the effect of proton acceptors such as HMT on the analytical utility of copper(II) oxidations of thiols and hydroquinone indicate that these systems do not appear to be practical.

TABLE 3.

EFFECT OF HEXAMETHYLENETETRAMINE ON POTENTIOMETRIC TITRATIONS OF THIOPHENOL AND 1-DODECANETHIOL WITH COPPER(II) IN ACETONITRILE

Titrand*	Titrant	Ratio of Cu^{2+}/thiol at End point	Size of Break, mV
Thiophenol + HMT in 2:1 mole ratio	$Cu(ClO_4)_2$	.998 .996	180, poor
Thiophenol + HMT in 1:1.07 mole ratio	$Cu(ClO_4)_2$	1.14_6 1.15_8 1.18_6	drawn out, poor
Thiophenol	$Cu(ClO_4)_2$ + HMT in 1:1 mole ratio, used 2 hours after preparation.	.928 .956	640, sharp
Thiophenol	$Cu(ClO_4)_2$ + HMT in 1:1 mole ratio, used 24 hours after preparation.	1.16_8 1.16_3 1.16_0	620, not sharp
1-Dodecanethiol	$Cu(ClO_4)_2$ + HMT in 1:1 mole ratio used 24 hours after preparation	1.41_3 1.41_7	280, fair

*0.1 M $LiClO_4$ in dry acetonitrile used as solvent.

TABLE 4.

EFFECT OF HEXAMETHYLENETETRAMINE ON POTENTIOMETRIC TITRATIONS OF HYDROQUINONE WITH COPPER(II) IN ACETONITRILE

Ratio of H_2Q to HMT	Titrant	Ratio of Cu^{2+}/H_2Q at End Point	Size of Break, mV
1:1.96	$Cu(ClO_4)_2$	1.99_7 1.99_7	440
1:2.00		1.99_7	400
1:2.02		2.00_6	400
1:1.06		1.15_6	560, very sharp
1:1.60		1.68_0	520, very sharp
1:2.04		2.13_6 2.13_7 2.13_7 2.13_4 2.13_9	440
1:4.08		2.13_9	440
H_2Q only		---	No break
H_2Q only	$Cu(ClO_4)_2$ + HMT in 1:2 mole ratio (used within 24 hours of preparation)	2.35_7 2.37_6	120, poor 120, poor

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PART III

POTENTIOMETRIC STUDIES OF METAL COMPLEXATION WITH POLYAMINES IN ACETONITRILE

VIII. INTRODUCTION

Acetonitrile has been used as a medium for fundamental solvation studies and has found wide use as a practical solvent for many synthetic and analytical applications. For this study acetonitrile was selected as solvent since it is a poor hydrogen donor or acceptor, is readily available, has a moderately high dielectric constant ( ) of 36 which allows dissolution of ionic as well as nonionic solutes, is relatively nontoxic, and has a convenient liquid range and low viscosity. Since acetonitrile is a polar Lewis base, it stabilizes cations moderately well, although solubilities of ionic salts are not always large because it does not solvate anions to any appreciable extent. Salts which have large or polarizable univalent anions, such as perchlorate or iodide, have reasonable solubilities (1). It was reported that acetonitrile is a useful solvent for oxidation-reduction reactions because it has a wide potential range which extends from +2.3 V to -2.7 V versus the aqueous calomel electrode (2).

Determinations of a number of metal cations by complexation titration with a large number of mono and multidentate ligands have been carried out in aqueous media by either direct or back titration (3). Aqueous titrations often involve addition of masking agents or adjustment of solution pH to provide the required specificity and keep unwanted species from reacting with the titrant. Buffering of the solution also is often necessary to allow proper indicator functioning, to prevent metal hydroxide formation, or to decrease protonation of the ligand.

If chemical reactions resulting in the formation of complex species in solutions are to be applicable to automatic titrations, they should fulfil the following four basic requirements: (a) The complex which is formed during the titration reaction must be sufficiently stable; (b) The reaction must be stoichiometric, leading to the formation of a well-defined species in one reaction step; (c) The reaction must proceed at a suitable rate, preferably instantaneously; and (d) a suitable method of end point detection must be available. If potentiometry is used, an indicator electrode must exist, the potential of which changes uniformly and rapidly with the concentration of one of the species (reactant, titrant or product) involved in the titration.

The practical application of reactants leading to the formation of complexes became widespread with the introduction of polydentate ligands as titrants. Such reagents generally form either one to one or two to one complexes with metal ions, although ethylenediamine forms three to one complexes with several metals. The polyamines are one class of ligands that tend to form complexes of appreciable stability with a number of metals, especially copper(II) (4).

In this section a study is described of the titration in acetonitrile of the ions of transition metals and alkaline earths, both individually and in mixtures, with ethylenediamine (en), diethylenetriamine (dien), and triethylenetetramine (trien). These polyamines were selected as titrants because of their solubility and the solubility of the corresponding metal complexes in acetonitrile, and because of the stability of some of the ligand-metal complexes (4).

IX. EXPERIMENTAL

A. Chemicals

Ethylenediamine, diethylenetriamine and triethylenetetramine (all J. T. Baker Chemical Co.) were purified by redistillation under reduced pressure (5). Ten grams of potassium hydroxide were added to 300 mL of amine, shaken occasionally for two hours and left overnight to allow the hydroxide to react with the amine oxides. The amine was decanted into a distillation flask and the flask and contents placed in a heating mantle and stirred by a magnetic stirrer under vacuum for five hours to remove dissolved gases. Next the temperature of the mantle was increased gradually from room temperature until distillation started. The first 50 mL of distillate and the last 50 mL remaining in the flask were rejected, and only the middle fractions were retained. En, dien, and trien were distilled at constant temperatures of 30, 76 and 105°C respectively. Dimethylsulfoxide (DMSO) (Caledon Laboratories Ltd.) was purified under the same conditions used for purification of amines, except that the addition of potassium hydroxide was omitted; it was distilled at 50°C. Acetonitrile (Matheson Coleman and Bell) was dried overnight over calcium hydride and distilled. The first 100 mL of distillate and the last 100 mL remaining in the three liter distillation flask were rejected.

The hydrated perchlorate salts of copper(II), zinc(II), manganese(II), nickel(II), iron(III), cobalt(II) and chromium(III) were converted to the corresponding dimethylsulfoxide solvates by either the method of Selbin, Bull and Holmes (6) or of Cotton and Francis (7). The copper(II) salt prepared following the outlined method (7) analyzed as the pentasolvate rather than the reported tetrasolvate (Table 5). The dimethylsulfoxide solvates of the perchlorates of magnesium, calcium, and strontium have not been previously reported, so were prepared as follows.

$Mg(ClO_4)_2 \cdot 6(CH_3)_2SO$

To a saturated solution of anhydrous $Mg(ClO_4)_2$ in dry acetone was added an equal volume of dimethyl sulfoxide. Upon addition of ethanol a white precipitate formed. The precipitate was filtered, washed twice with ethanol, and dried overnight under vacuum at room temperature.

$Ca(ClO_4)_2 \cdot 6(CH_3)SO$

A slurry of 20 g of $CaCO_3$ in 50 mL of water was treated with 70% $HClO_4$ in 1-mL portions until evolution of CO_2 ceased and a pH of 1 was obtained. The solution was placed under vacuum until solid $Ca(ClO_4)_2$ appeared, and the majority of water was removed. The residue was dissolved in a minimum amount of acetone, filtered, an equal volume of DMSO added, and the mixture shaken. Upon addition of ethyl ether a heavy white precipitate formed. After cooling in ice, the precipitate was filtered, washed twice with portions of ether, and dried overnight under vacuum at room temperature.

$Sr(ClO_4)_2.6(CH_3)_2.SO$

This material was prepared in the same way as the calcium salt except that the precipitate obtained was dissolved in acetone and reprecipitated with ether before drying overnight under vacuum. Results of the analyses are given in Table 5.

B. Procedure For Titration

Approximately 40 mg portions of each of the $M(ClO_4)_n.XDMSO$ salts were dissolved in 40 mL dry acetonitrile and titrated with 0.06 M amine in dry acetonitrile. An 80-mL cylindrical cell with a Teflon lid was used as a titration vessel (Figure 5). A platinum flag indicating electrode and a silver, 0.01 M silver nitrate in acetonitrile reference electrode were used. The reference electrode was separated from the cell solution by the same bridge as described in Chapter VI for the coulometer cell. A double junction is important here to prevent silver from entering the cell solution, since silver would otherwise complex with the amine titrants and cause error. A Metrohm potentiograph E 436 automatic recording titrator delivered titrant by means of a syringe buret without exposure to air, and recorded the titration curves on a built-in chart

TABLE 5.

ANALYTICAL DATA FOR DIMETHYLSULPHOXIDE (DMSO) SOLVATES OF METAL PERCHLORATES

		Analytical Data, %					
		Carbon		Hydrogen		Metal	
Compound	Color	Theory	Found	Theory	Found	Theory	Found
$Cu(ClO_4)_2 \cdot 5DMSO$	pale blue	18.39	18.46	4.63	4.62	9.73	9.74[a]
$Ca(ClO_4)_2 \cdot 6DMSO$	white	20.36	19.75	5.12	4.94	5.66	5.64[b]
$Sr(ClO_4)_2 \cdot 6DMSO$	white	19.08	18.51	4.80	4.59		
$Mg(ClO_4)_2 \cdot 6DMSO$	white	20.83	20.68	5.20	5.19	3.52	3.50[b]

[a] By iodometric titration.

[b] By EDTA titration.

recorder. Titrant was delivered from a 5 mL buret at a rate of 0.25 mL per minute. Air oxidation was minimized by starting each titration immediately upon dissolution of the sample, and by passing nitrogen through the solution during the titration. Magnetic stirring was used.

The reproducibility of delivery of the titrant by the Metrohm automatic titrator was determined by delivery of several samples and comparison of the amounts delivered with the recorded volumes. As an example of the precision of the titration system, a set of five weighings of the water delivered by the 5-mL buret gave an average of 5.043 g with standard deviation of 0.002. The weight of water was divided by the density to obtain the volume. The distance traveled by the pen on the chart paper during delivery of the buret contents was measured in centimeters, and a factor for the number of milliliters per centimeter was used in determining the volume of the titrant at the equivalence points in the titrations.

The shapes of the titration curves for the metal ions with the amines ranged from symmetric to highly asymmetric. Also some of the metal-ligand complex reactions, such as copper(II) and cobalt(II) with ethylenediamine, have large potential changes at the inflection point while others, such as magnesium(II) and cobalt(II) with dien, gave small potential changes. Therefore to provide consistency the end point was taken in all cases as that point of the curve equidistant from parallel lines drawn tangent to the curve in the potential break region (Figure 6).

To compare the platinum indicating electrode with the mercury and silver electrodes, which have been suggested previously as indicating electrodes for potentiometric complexation titrations in aqueous media, we used the same titration system with the same conditions described above except that the platinum electrode was replaced by a mercury or silver indicating electrode. For the mercury electrode, one of the arrangements of Reilley and Schmid was employed (8). It consisted of a small circular glass cup sealed to the end of a piece of glass tubing. The tube and the annular cup were both partially filled with mercury. Contact between the two was made by a short length of platinum wire sealed through the tubing near the end containing the cup; contact with the potential measurement device was made by a copper wire immersed in the mercury in the tube. One drop of a 10^{-3} M solution of mercury-en or mercury-trien was added to the solution to be titrated to provide a mercury(II)-mercury metal couple. For the silver-silver ion electrode a silver wire 0.7 mm in diameter was used in place of the platinum, and one drop of 0.008 M silver nitrate in acetonitrile was added to the solution to provide a finite amount of silver(I) for the silver couple, as described by Fritz and Garralda for complexation titrations in aqueous media (9).

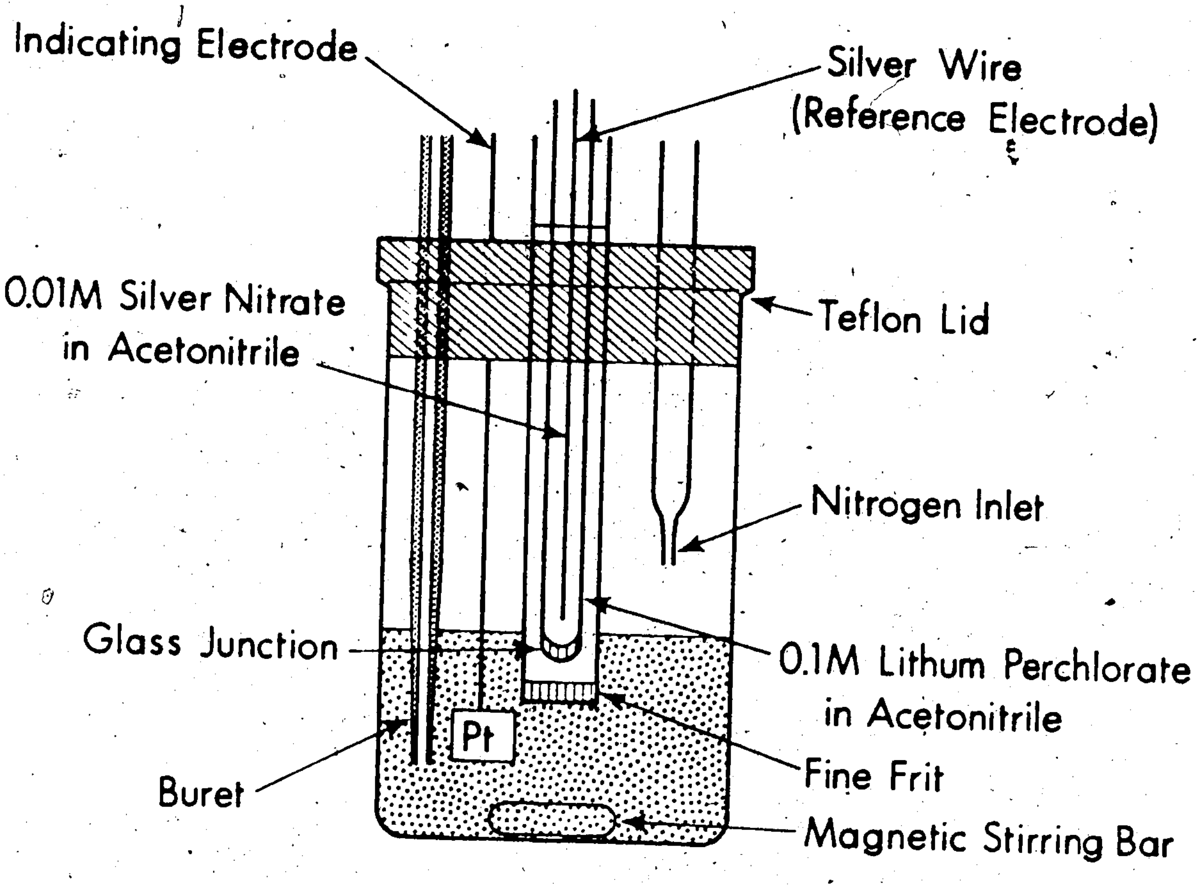

Figure 5 Cell for Potentiometric Titrations in Acetonitrile

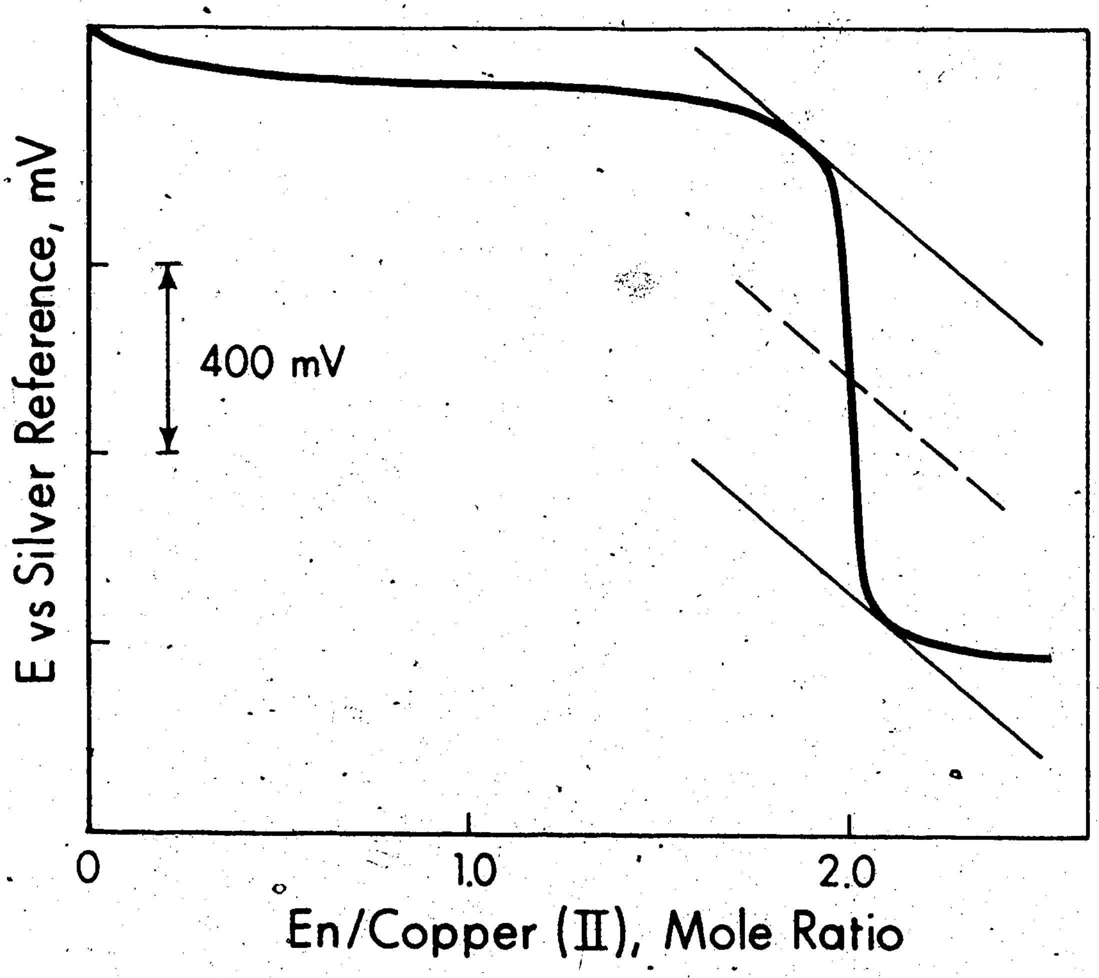

Figure 6. Potentiometric Titration of Copper(II) with en in Acetonitrile

X. RESULTS

Platinum has not been reported before as an indicator electrode in complexation titrations of metal ions. As part of this study the metal ions copper, cobalt, nickel, zinc, manganese, iron, magnesium, calcium, strontium, and chromium in the form of the DMSO solvates of the perchlorate salts, $M(ClO_4)_n \cdot XDMSO$, were titrated potentiometrically with en using a platinum indicating electrode.

The key features are that cobalt(II) and copper(II) show sharp inflection points at 2 to 1 ratios of en to metal, while manganese(II) and magnesium(II) show smaller inflections at 3 to 1 ratios. For copper(II) a set of titrations in which $Cu(ClO_4)_2 \cdot 4CH_3CN$ was used as the sample in place of the DMSO solvate gave identical titration curves to those in which DMSO was present. Calcium(II), strontium(II), chromium(III), and silver(I) do not yield titration breaks, but zinc gives two, a small sharp break at a ratio of en to zinc of about 1.85 to 1, and a more drawn out break at a ratio of somewhat over 3 to 1. The behavior of iron(III) is similar to that of zinc(II), but the break at the 3 to 1 ratio is sharper and cleaner. Nickel(II) gave a small sharp break at a 3 to 1 ratio, with a slight inflection just preceding it at a ratio of about 2.5 to 1. Figure 7 represents the titration curves of copper(II), cobalt(II), magnesium(II), manganese(II) and nickel(II) with en.

The largest potential change is observed with copper(II). Mixtures of equal amounts of copper with calcium, copper with strontium, copper with chromium, copper with a mixture of calcium, strontium and chromium and iron(III) with chromium, were titrated under the same conditions as for the individual ions. The results showed that calcium, strontium, and chromium have no effect on stoichiometry or end point detection, that is, they do not complex strongly enough, or in the case of chromium, rapidly enough, to interfere in the titrations.

To judge the relative basicity of the two nitrogens in en a sample of the ligand was titrated with perchloric acid in acetonitrile. As can be seen from Table 6 and Figure 8, quantitative results were obtained with two sharp breaks at 1 to 1 and 1 to 2 ratios of en to hydrogen ion, corresponding to the reactions:

$$H_2NCH_2CH_2NH_2 + H^+ \longrightarrow H_2NCH_2CH_2NH_3^+ \qquad (17)$$

$$H_2NCH_2CH_2NH_3^+ + H^+ \longrightarrow (H_3NCH_2CH_2NH_3)^{2+} \qquad (18)$$

Titration of a mixture of copper and zinc gave a good break of about 600 mV, but the end point was 3 to 7 percent early for total copper(II) and zinc(II), so analytical application of the method to this mixture is not possible. Titration of a mixture of copper, zinc and silver gave a very poor, drawn out break that could not be used to calculate an end point. A mixture of manganese and chromium was also titrated but again the method was not analytically useful because it gave a drawn out break about 2 percent late for a 3 to 1 en to manganese ratio. A mixture of nickel with chromium gave a fair break but scattered results.

Copper, aluminum, cobalt, nickel, manganese, iron(II), iron(III), and magnesium were also titrated in the form of the hydrated perchlorate salts, $M(ClO_4) \cdot 6H_2O$. The results, calculated on the basis that all the salts were the hexahydrates, were within 1 or 2 percent, except for aluminum. Table 6 lists the ion titrated, the size of the breaks in millivolts, the sharpness of the breaks, and the ratios of en to metal ions or protons at the inflection points for a large number of titrations with en.

Table 7 summarizes the results of titrations of a series of metal ions with dien. Copper(II) shows breaks at ratios of both 1 to 1 and 2 to 1. In both cases the curves are sharp and stoichiometric. The only other ions studied that reacted in a clean stoichiometric ratio with dien were magnesium(II), cobalt(II), and manganese(II), all of which produced small but sharp inflections at 2 to 1 ratios (Figure 9).

Table 8 represents the results obtained when trien was used as a titrant. Quantitative reaction was obtained only with copper(II). Very poor breaks and undeterminable end points occurred in the titration of magnesium and calcium.

Results of titrations of a series of metal ions with

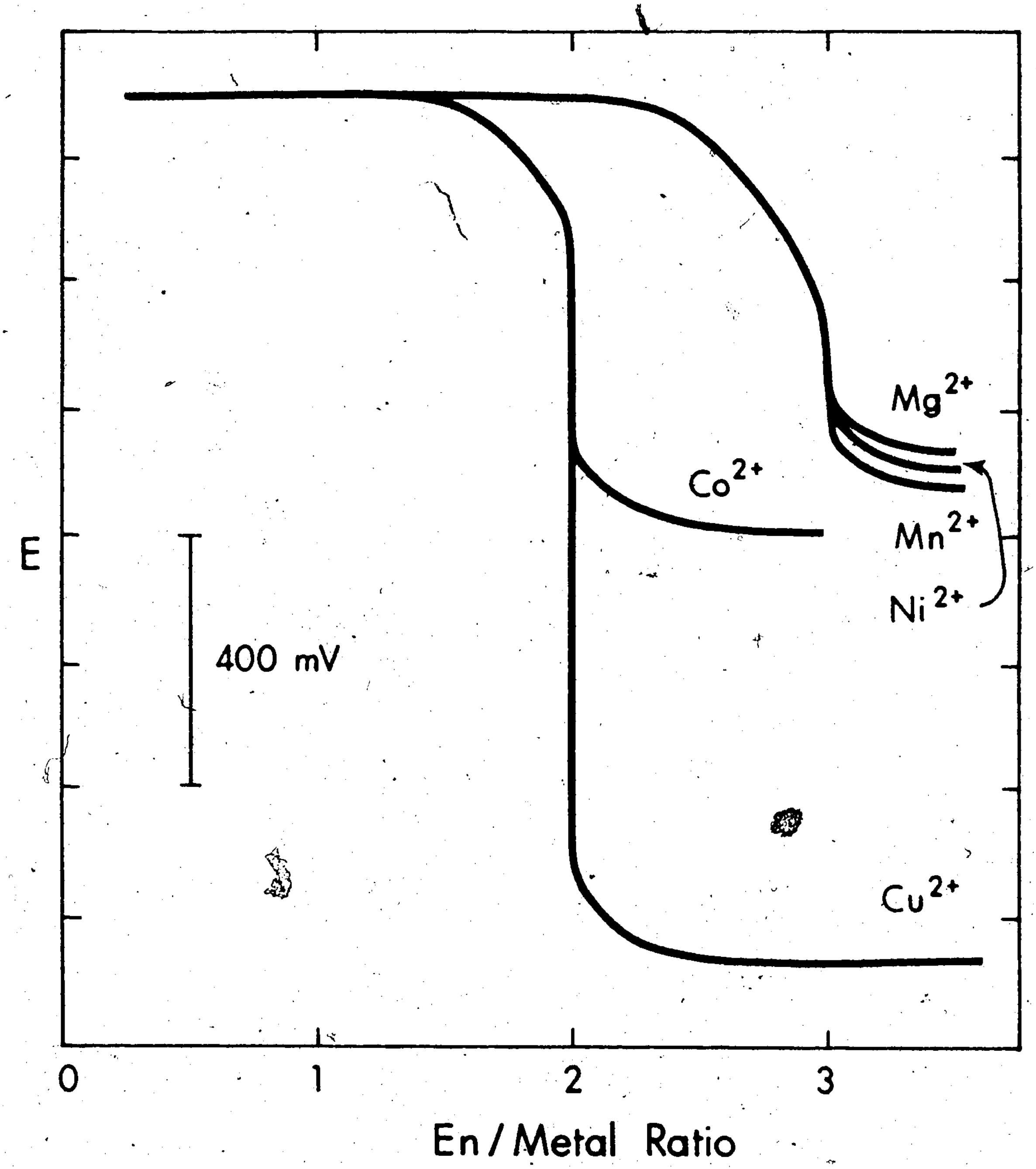

Figure 7. Relative Magnitude of Breaks at the Inflection Point for the Potentiometric Titration of Metal Ions with en in Acetonitrile

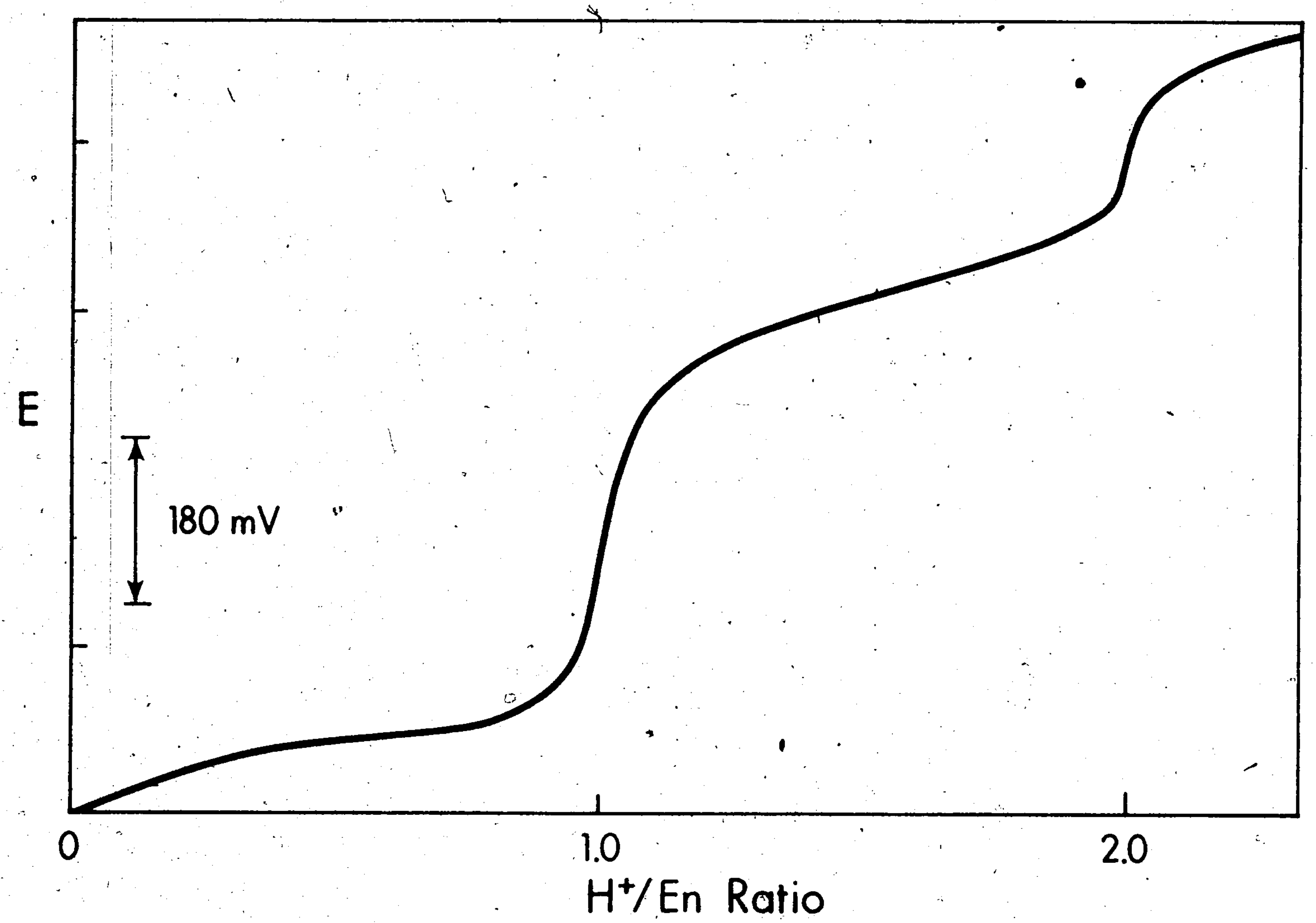

Figure 8. Potentiometric Titration of en with Perchloric Acid in Acetonitrile

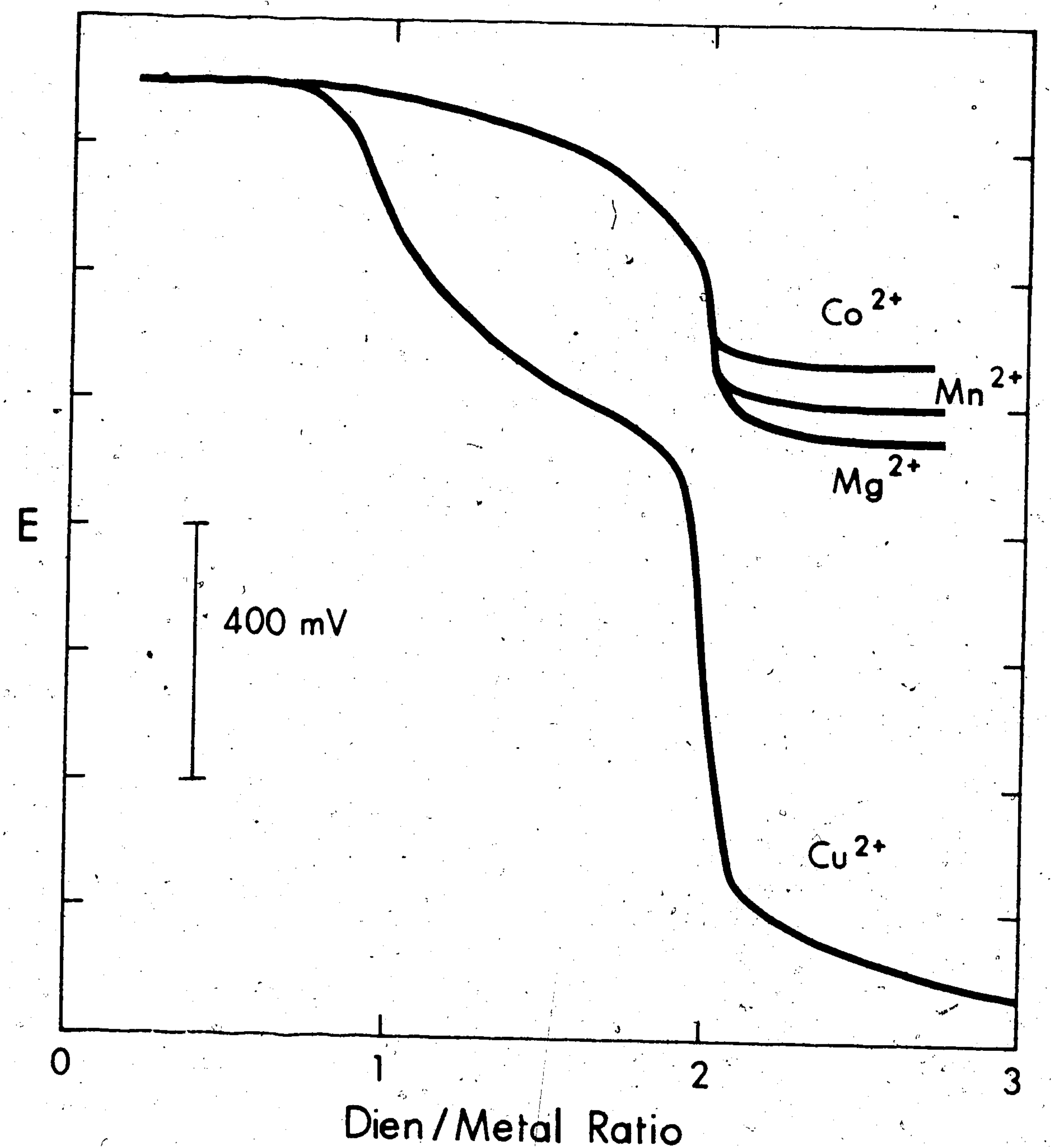

Figure 9. Relative Magnitude of Breaks at the Inflection Point for the Potentiometric Titration of Metal Ions with dien in Acetonitrile

en, using either the mercury-en or silver-silver ion systems as indicating electrodes and a silver-silver ion reference electrode, are summarized in Tables 9 and 10. As with the platinum indicating electrode, copper(II) shows the sharpest and largest potential breaks. Cobalt(II) titrations also show sharp inflection points at 2 to 1 ratios of en to cobalt(II) in the case of the mercury electrode, but at less than 2 to 1 for the silver indicating electrode. Similar sharp potential breaks, but at a 3 to 1 ratio of ligand to metal, are seen with both electrodes for the titration of nickel(II). With both electrodes manganese(II) shows drawn out potential breaks at about 3 to 1 ratios that are not analytically useful. Calcium(II) does not yield titration breaks with either electrode, while magnesium(II) shows a poor, drawn out break at about 3 to 1 ratio with the silver indicating electrode, but no inflection with the mercury electrode.

Tables 11 and 12 summarize the results of titrations of a series of ions with trien, using mercury-trien or silver-silver ion indicating electrodes and a silver-silver ion reference electrode. The only metal studied that reacted in a clean stoichiometric 1 to 1 ratio was magnesium(II) with the mercury-trien indicating electrode. All the other metals showed nonstoichiometric ratios of more than 1 to 1, even though some of them gave good inflections.

Using the silver-silver ion indicating electrode, no metal gave stoichiometric breaks. Instead all showed drawn out, poor breaks at ratios of more than 1 to 1; the exception is magnesium(II), which showed fair though nonstoichiometric breaks.

TABLE 6

RESULTS OF TITRATION OF $M(ClO_4)_n \cdot XDMSO$ SALTS WITH EN IN ACETONITRILE, USING PLATINUM AS INDICATING ELECTRODE

Ion titrated	en:metal ratio at inflection point	Potential change in mV and sharpness of break at inflection point
Cu^{2+}	2.00_2, 2.00_7 2.00_6, 2.00_0	960 very sharp (smooth break)
Cu^{2+}*	2.00_0, 2.00_0, 1.99_9	950, very sharp
Cu^{2+}**	1.99_9, 1.99_7	960, very sharp
Cu^{2+}***	2.00_0, 1.99_9, 2.00_0	960, very sharp
Co^{2+}	1.99_9, 2.00_1 1.99_9, 2.00_1	240, sharp
Zn^{2+}	1.83, 1.8, 1.86 3.00, 3.28, 3.15	80, (1st) sharp; 120, (2nd) drawn out, difficult to locate 2nd end point
Mn^{2+}	2.99_9, 3.00_1 3.00_0	120, good
Fe^{3+}	2.99_7, 3.00_1 3.00_1, 3.00_3	120, fair, with small wiggle just before major break
Ni^{2+}	3.00_9 3.00_4 3.00_0	90, sharp, with small wiggle at 2.5 to 1 ratio
Mg^{2+}	2.99_8, 3.00_1 3.00_2	80, fair to poor
Ca^{2+}	No inflection	
Sr^{2+}	No inflection	
Cr^{3+}	No inflection	
Cu^{2+} + Ca^{2+}	1.99_7, 2.00_0, 2.00_0	740, very sharp, only Cu^{2+} titrated
Cu^{2+} + Sr^{2+}	2.00_4, 1.99_9, 2.00_2	840, very sharp, only Cu^{2+} titrated

$Cu^{2+} + Cr^{3+}$	$2.00_0, 1.99_6, 2.00_4$	1040, extremely sharp, only Cu^{2+} titrated
$Fe^{3+} + Cr^{3+}$	$3.00_2, 3.00_3$ $2.99_8, 2.99_7, 2.99_8$	100-150, fair; only Fe^{3+} titrated
$Mn^{2+} + Cr^{3+}$	$3.06_1, 3.06_5, 3.05_7$	140, drawn out, only Mn^{2+} titrated
$Mg^{2+} + Ca^{2+} + Sr^{2+}$	No inflection	
$Ni^{2+} + Cr^{3+}$	$3.08_6, 2.83_3$	180, fair to good, only Ni^{2+} titrated
$Mn^{2+} + Ca^{2+}$	No inflection	
$Cu^{2+} + Zn^{2+}$		600, very good, end point 3 to 7% early for total Cu^{2+} and Zn^{2+}
$Cu^{2+} + Zn^{2+} + Ag^{+}$		one very poor and drawn out break, not stoichiometric with total of $Cu^{2+} + Zn^{2+}$
$Cu^{2+} + Zn^{2+} + Ag^{+}$ (Ag^{+} added as $AgNO_3$)		ppt formed, very poor and drawn out break about 3% early for total of $Cu^{2+} + Zn^{2+}$
Cu^{2+} + $AgNO_3$	2.01_4	120, ppt formed, fair break, only Cu^{2+} titrated

Titration of Hydrated Salts $M(ClO_4)_n.6H_2O$

Cu^{2+}	2.00_0, 1.96_3	810, sharp
Al^{3+}	$1.42, 1.43, 1.38, 1.38, 1.33$	200, (1st), very sharp
	$3.09_2, 3.11_8, 3.04_4, 2.99, 2.94_7$	200, (2nd), very sharp
Co^{2+}	$1.96_7, 2.02_5$	200-300, sharp
Ni^{2+}	2.98	100, fair to good, asymmetric

Mn^{2+}	3.09_5, 3.08_3, 3.02_8, 3.10_8	100-160, fair to good preceded with a very drawn out break at more than 2 to 1 ratio
Fe^{2+}	1.97_7, 1.95_0 2.72, 2.68	120 (1st), fair to good 80 (2nd), fair to good
Fe^{3+}	1	(1st) very poor break, difficult to locate end point
	2.05, 2.07_8	240, (2nd) fair to good break
H^+****	1.00_2, 1.00_0, 1.00_3 1.99_4, 1.99_8, 1.99_5	300 (1st), sharp 140 (2nd), sharp
Mg^{2+} (from anhydrous $Mg(ClO_4)_2$	2.46, 2.65	140, drawn out

<u>$Cu(ClO_4)_2.5DMSO$ Titrated with en using copper ion selective electrode instead of platinum indicating electrode</u>

Cu^{2+}	2.135, 2.143 2.148, 2.145	450, inflection point is preceded by a large wiggle; difficult to locate end point

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*Copper(II) added as $Cu(ClO_4)_2.4CH_3CN$.

**Platinum pretreated with concentrated nitric acid.

***Platinum pretreated with 0.1 M ferrous sulphate.

**** H^+ from $HClO_4.2H_2O$ (70% aqueous acid) used as titrant for en; therefore ratios shown are for H^+ to en.

TABLE 7.

TITRATION OF $M(ClO_4)_n \cdot XDMSO$ SALTS WITH DIEN IN ACETONITRILE USING PLATINUM AS INDICATING ELECTRODE

Ion titrated	dien:metal ratio at inflection point	Potential change in mV and sharpness of break at inflection point
Cu^{2+}	$1.00_0, 1.00_3, 1.00_6$ $2.00_0, 1.98_8, 2.00_6$	330 (1st), very sharp 630 (2nd), very sharp
Mg^{2+}	$2.00_3, 2.00_1$ $2.00_0, 1.99_8$	200, good
Zn^{2+}	$2.00_1, 2.03_9,$ $2.01_7, 2.12_1$	360, very sharp
Fe^{3+}	1.69, 1.68, 1.68	300, very sharp
Ni^{2+}	2.02, 2.03, 2.04	220, very sharp
Co^{2+}	1.99_7, 2.04, 1.98	100, sharp
Mn^{2+}	1.99, 2.00, 2.01	140, very sharp
Ni^{2+} + Zn^{2+}	2.04	180, one good break equivalent to total Ni^{2+} and Zn^{2+}
Ca^{2+}	2.16, 2.13, 2.14	60, very drawn out, poor
Mg^{2+} + Ca^{2+}	2.01_2	180, one fair to good break corresponding to total Mg^{2+} and Ca^{2+}

<u>Titration of $Mg(ClO_4)_2 \cdot 6DMSO$ and $Cu(ClO_4)_2 \cdot 5DMSO$ using Carbon Electrode Instead of Platinum Indicating Electrode</u>

Mg^{2+}	No inflection	
Cu^{2+}	1.00_2; 1.99_7	120, 300, (1st) fair, (2nd) sharp

TABLE 8.

TITRATION OF $M(ClO_4)_n \cdot XDMSO$ WITH TRIEN IN ACETONITRILE USING PLATINUM AS INDICATING ELECTRODE

Ion titrated	Trien:metal ratio at inflection point	Potential change in mV and sharpness of break at inflection point
Cu^{2+}	1.00_8, 1.00_1 1.00_0	840, very sharp
Zn^{2+}	1.07,1.13,1.08	400, fair
Co^{2+}	1.08,1.07	140, fair
Ni^{2+}	1.09,1.09,1.09	120, poor to fair; drawn out
Fe^{3+}	1.23,1.44,1.39 1.66,1.88,1.84	120 (1st), poor 100 (2nd), poor
Mn^{2+}	1.05,1.07,1.07	70, fair to good
Mg^{2+}	undeterminable end point	~90 very poor break
Ca^{2+}	not usable	~100 very poor, drawn out

TABLE 9.

SUMMARY OF TITRATIONS OF $M(ClO_4)_n \cdot XDMSO$ SALTS WITH EN IN ACETONITRILE, USING Hg/EN INDICATING ELECTRODE

Ion titrated	en: metal ratio at inflection point	Potential change in mV and sharpness of break at inflection point
Cu^{2+}	$1.99_8, 1.99_8, 1.99_9, 2.00_0$	360-560, very sharp
Co^{2+}	$2.00_3, 1.99_9, 2.00_1$	280, very sharp
Mn^{2+}	~3	drawn out, not useful
Ni^{2+}	$3.00_2, 3.00_3$	130, good
Mg^{2+}	no inflection	drawn out
Ca^{2+}	no inflection	

TABLE 10.

SUMMARY OF TITRATIONS OF $M(ClO_4)_n \cdot XDMSO$ SALTS WITH EN IN ACETONITRILE USING Ag/Ag^+ INDICATING ELECTRODE

Ion titrated	en:metal ratio at inflection point	Potential change in mV and sharpness of break at inflection point
Cu^{2+}	$1.99_8, 2.00_0, 2.00_0$	180, sharp
Cu^{2+}	$1.99_8, 2.00_0$ (only silver wire, no Ag^+ added)	200, sharp
Co^{2+}	1.99_2, 1.91_6	240, sharp
Co^{2+}	1.99_8 (only silver wire, no Ag^+ added)	220, very sharp
Mn^{2+}	~3	120 poor, hard to locate the end point
Ni^{2+}	$3.00_1, 2.99_8, 3.00_3$	150, sharp
Mg^{2+}	~3	poor, drawn out
Ca^{2+}	no inflection	gradual potential change throughout titration of about 60 mV

TABLE 11.

SUMMARY OF TITRATIONS OF $M(ClO_4)_n$·XDMSO SALTS WITH TRIEN IN ACETONITRILE USING Hg/TRIEN INDICATING ELECTRODE

Ion titrated	trien:metal ratio at inflection point	Potential change in mV and sharpness of break at inflection point
Cu^{2+}	~1.1, 1.1, 1.1	360 (1st), asymmetric
	~1.4, 1.3, 1.4	180 (2nd), asymmetric
Co^{2+}	1.09_3, 1.08_9, 1.09_5, 1.09_0	240, sharp
Mn^{2+}	1.06_5, 1.05_4 1.29, 1.29_5	120 (1st), good 80 (2nd), fair
Ni^{2+}	1.10_6, 1.09_6, 1.11_3 with a second break drawn out at less than 2:1 ratio	90, good
Mg^{2+}	1.00_0, 1.00_2, 1.00_0, 1.00_6, 1.00_2	150, good
Ca^{2+}	~1.2	drawn out, not calculatable

TABLE 12.

SUMMARY OF TITRATIONS OF $M(ClO_4)_n \cdot XDMSO$ SALTS WITH TRIEN IN ACETONITRILE USING Ag/Ag^+ INDICATING ELECTRODE

Ion titrated	trien:metal ratio at inflection point	Potential change in mV and sharpness of break at inflection point
Cu^{2+}	~ 1 ~ 1.4	200 (1st) poor 120 (2nd), drawn out
Co^{2+}	1.12_1	120, poor
Mn^{2+}	~ 1.1	100, poor
Ni^{2+}	~ 1.1, 1.1, 1.1	800, poor
Mg^{2+}	1.10_3, 1.08_7, 1.25_0, 1.05_4	180, fair
Ca^{2+}	~ 1	drawn out

XI. DISCUSSION OF POTENTIOMETRIC TITRATIONS

In the present work, several previously unreported salts have been prepared -- $Mg(ClO_4)_2 \cdot 6DMSO$, $Ca(ClO_4)_2 \cdot 6DMSO$, and $Sr(ClO_4)_2 \cdot 6DMSO$.

Titrations of samples of $Mg(ClO_4)_2 \cdot 6DMSO$ and $Ca(ClO_4)_2 \cdot 6DMSO$ with EDTA yielded formula weights of 691.19 and 705.1 g/mole whereas the theoretical values are 691.23 and 707.7 g/mole respectively. These results in conjunction with microanalysis for hydrogen and carbon in the compounds show that each formula weight contains six molecules of DMSO. The results of the carbon analyses for the calcium and strontium salts do not agree very closely with the theoretical value for six molecules of DMSO, but the hydrogen results are somewhat better. Further study of the strontium compound was not carried out because it did not react with any of the amines in an analytically useful way. Their preparation is straight forward, and will not be discussed further. They are easy to handle and provide a convenient form for these metal ions when water-free salts soluble in solvents of moderate to low dielectric constant are needed.

As mentioned earlier, the copper(II) perchlorate salt was isolated as the pentasolvate rather than the tetrasolvate. The theoretical formula weight of $Cu(ClO_4)_2 \cdot 5DMSO$ is 653.07 g/mole. Titration of a sample of this compound with standard $Na_2S_2O_3$ gave a formula weight of 653.9 ~~g~~/mole.

Analysis of this compound for hydrogen and carbon was done in the microanalytical laboratory at the Department of Chemistry of the University of Alberta. The values found were in satisfactory agreement with the theoretical values. Therefore we have two pieces of evidence that the compound prepared in this work is $Cu(ClO_4)_2 \cdot 5DMSO$ and not $Cu(ClO_4)_2 \cdot 4DMSO$ as previously reported. In chloroform Greddon (10) has shown that five-coordination appears to be quite common in copper(II) complexes, and he found no evidence of six-coordination. Llewellyn and Waters also found five-coordination of copper(II) with 2-hydroxy-1-naphthylaldehyde when crystallized from water. The ligands were arranged in a pyramidal configuration with four "normal" planar bonds and a fifth copper-water bond (11). The difference in the number of DMSO molecules found here as compared to previous work could be related to differences in the conditions of drying for the salt.

A. Titrations with Ethylenediamine

Table 6 shows the results of titrations of selected transition and alkaline earth metal ions with en. No complexation occurred with calcium, strontium, and chromium. Stability constants for the alkaline earths with the polyamines studied here have not been reported in water except for the magnesium(II)-en system, where a value of

0.37 for log K_1 was found. This suggests that stability constants of these systems in acetonitrile are also likely to be small, and so the absence of an inflection point in the titration curves is not surprising. Chromium(III) is nonlabile so it reacts only very slowly with ligands. Therefore it would not be expected to be directly titratable in water or a nonaqueous solvent.

Reactions were stoichiometric, with single breaks at 2 to 1 or 3 to 1 en to metal ratios, for all the transition metal ions that formed complexes (Figure 7) except for zinc, where two breaks were observed, the first at a less than 2 to 1 ratio and the second at a more than 3 to 1 ratio. Difficulty was found in weighing the zinc DMSO perchlorate salt because it tended to pick up moisture from the atmosphere readily. This could explain the less than two to one ratio observed for the first end point. The second inflection was so broad and drawn out that location of the end point could only be roughly estimated; it probably comes at a ratio of three to one. In water both two to one and three to one complexes have been found to exist in equilibrium with each other (12).

The sharpest and largest potential break was obtained with copper at a 2 to 1 ratio. A previous study of $Cuen_2(ClO_4)_2$ in methanol, dimethylformamide and nitroethane (13) showed that the structure of the complex is square planar.

Titration of copper in the form of $Cu(ClO_4)_2 \cdot 4CH_3CN$ in place of DMSO solvate gave identical titration curves to those in which DMSO was present. Therefore DMSO does not affect the shape of the curves. Perchloric acid was used as a titrant for en. Quantitative results were obtained with two breaks at 1 to 1 and 1 to 2 en to H^+ ratios. These agree with results previously reported by Zgoda and Petri (14).

En proved to be a selective titrant for copper in the presence of calcium, strontium, and chromium(III), for iron(III) in the presence of chromium(III) and for manganese(II) in the presence of chromium(III). None of the results indicate an advantage in selectivity over aqueous systems using pH adjustment and masking.

Titrations of metal ions in the form of the hydrated salts $M(ClO_4)\cdot 6H_2O$ were not stoichiometric. The reason may be related to the contribution of protons present in the solution to the ligands, and to the formation of metal hydroxides.

B. Titrations with Diethylenetriamine

Copper(II) showed a stoichiometric reaction with dien with very sharp potential breaks at 1 to 1 and 2 to 1 ratios. Magnesium(II), cobalt(II), and manganese(II) produced small but sharp inflections at 2 to 1 ratio.

Titrations of Zn(II), Fe(III), Ni(II), Co(II), Mn(II), and Ca(II) were not stoichiometric. Figure 9 represents the relation between the potential and dien to metal ratio for several titrations.

C. Titrations with Triethylenetetramine

Copper(II) is the only metal ion that yields a stoichiometric reaction with trien. This may be due to the strong affinity of copper(II) for ligands containing nitrogen donating atoms. The solid $Cu(ClO_4)_2$•trien complex has been previously isolated and studied. This complex has high stability and a square planar structure (15,16).

The observed nonstoichiometry of trien with manganese(II) might be the result in part, at least, of formation of mixtures of trien complexes of 1 to 1, 2 to 1, and 3 to 2 ratios which have been reported in ethanol and in water-methanol mixtures by Chiswell (17). This point is discussed later. It may be that other metals such as nickel(II), iron(III), cobalt(II), and zinc(II) form with trien a series of complexes of more than 1 to 1 ratio in a similar way. Part of the uncertainty also can be attributed to difficulty in selecting reproducible end points from the drawn out, asymmetric titration plots. As mentioned earlier, the platinum electrode has not been used as an indicator electrode in complexation titrations of metal ions. Instead, usually the silver electrode or the mercury electrode has been employed as an indicator electrode in potentiometric titrations of metal ions with complexing agents (18,19). However the application of the platinum indicator electrode to titrations with aliphatic amines in acetonitrile offers several advantages compared to the other indicating electrodes. Platinum is simple and easy to use in that preparation and addition of other solutions such as mercury(II) complexes or silver nitrate is unnecessary. Also, platinum sometimes gives sharp and larger potential changes at end points.

How platinum functions as an indicating electrode in these titrations is not clear. Measurements of the potentials of a series of solutions of varying copper(II) concentrations in acetonitrile with platinum indicating and silver-silver nitrate reference electrodes did not yield linear or even reproducible response. Pretreatment of the platinum with nitric acid or acidic iron(II) sulfate had no effect. These results indicate that the breaks are not likely to be due to a platinum-platinum ion redox couple. A possibility is a potential-shifting effect caused by adsorption or other interaction of the excess amines on the surface of the platinum after the metal is complexed. This explanation is supported by the fact that the titration curves are not Nernstian in shape, but instead flat, prior to and after the inflection. Figure 10 shows the response of platinum and copper ion selective electrodes to 10^{-5} to 10^{-1} M trien in solution of 0.05 M $LiClO_4$ in acetonitrile, using a silver-silver ion reference electrode.

$Ni(ClO_4)_2 \cdot 6H_2O$ was titrated with en using an SCE as the reference electrode instead of the silver-silver ion electrode, and the platinum electrode was used as indicator electrode. Potential breaks were obtained. This is an indication that the breaks are not due to diffusion of trace amounts of silver ion from the silver reference compartment into the cell solution.

Other indicating electrodes were investigated in addition to platinum. These included carbon and a copper ion selective electrode. $Cu(ClO_4)_2 \cdot 5DMSO$ was titrated with dien using a carbon rod (Spex Spectroscopic grade), treated with hot wax to decrease porosity (20), in place of the platinum electrode. The remainder of the titration system was as previously described. The complexation reaction was stoichiometric with fairly sharp breaks of 120 and 300 millivolts at ligand to metal ratios of 1 to 1 and 2 to 1.

$Cu(ClO_4)_2 \cdot 5DMSO$ was also titrated with en using a copper ion selective electrode (Orion Research, Model 94-29A) instead of a platinum indicator electrode. The results were not satisfactory. In four titrations inflection points were obtained at 2.135 to 1, 2.143 to 1, 2.148 to 1, and 2.145 to 1 ratios of en to Cu^{2+}. The magnitude of the inflection was large enough to be useful for the estimation of copper, being on the order of 450 mV, but the inflection contained a significant wiggle which made end point location difficult. We conclude that platinum is the best choice as a material for the preparation of indicating electrodes for complexation titrations in acetonitrile because it gives better results and is more convenient than the copper ion selective electrode or the carbon rod electrode.

Mercury-en, mercury-trien and silver-silver ion were investigated as indicating electrodes instead of platinum for titration of several metal ions with en and trien. Figure 11 shows the relative magnitude of breaks at inflection points for potentiometric titration of copper(II) ion with en in acetonitrile using three types of indicating electrodes: platinum, mercury-en, and silver-silver ion. The largest break was obtained with the platinum electrode.

Figure 12 shows the relative magnitude and shape of the inflections for potentiometric titrations of magnesium(II) ion with trien in acetonitrile using platinum, mercury-trien, and silver-silver ion indicating electrodes. The mercury-trien electrode was the only one that was found useful for this system of titration; with this electrode magnesium(II) reacted in a clean stoichiometric 1 to 1 ratio.

All the titrations of metal salts with trien using the silver-silver ion indicating electrode gave stoichiometries that were greater than unity. Two reasons were considered for this, the first being titration of the silver ion added, and the second being uncertainty in selection of the end point in the poorly defined inflections of the titration curves as is illustrated by curve C in Figure 12. Calculation of the amount of silver nitrate added shows that the end-point error owing to titration of the silver ion would be on the order of one percent. This is considerably smaller than the errors observed in the titrations, which ranged typically from 4 to 15 percent. An end point that is close to one to one stoichiometry must appear at the start of the potential change. This would occur if all the metal ion were complexed at that point and the silver ion formed so weak a complex with trien in acetonitrile that the silver ion concentration, and thus the potential, changed only gradually as excess trien was added.

Similar arguments are not easily applied to the mercury indicating electrode system because no free mercury(II) ions have been added to the solution, and the stability of the mercury(II)-trien complex could be expected to be large. Furthermore, some of the titration breaks are quite sharp, so that end point location is not subject to significant error. An explanation for these results cannot be posulated.

Titration of aqueous solutions of manganese(II) perchlorate or tetraphenylborate with an ethanolic solution of trien has been reported by Chiswell (17) to yield a precipitate of $[Mn_2trien_3]X_4 \cdot nH_2O$ at a titration ratio of two manganese(II) to three trien. A one to one salt could be obtained by mixing $Mn(ClO_4)_2$ and trien in equimolar amounts in ethanol and allowing the solution to crystallize over a period of weeks. These results indicate that end points at ratios of both one to one and greater than one to one might be expected for the manganese(II) and perhaps other metal titrations with trien. This is seen in the manganese(II)-trien titration using a mercury-mercury(II) trien indicating electrode; two small breaks are observed (Table 11), the first at trien to manganese ratios of about

1.05 to 1, and the second at ratios of about 1.29 to 1. Only single breaks, however, were seen with the platinum and silver-silver ion indicating electrodes, at about 1.05 and 1.14 to 1 ratios.

In conclusion, from the results of titrations of a variety of metal ions with en and trien, as detailed in Tables 6 to 12 using various indicating electrodes, platinum is considered to be superior to any of the other indicating electrodes investigated, including the mercury, silver, carbon, and copper ion selective electrodes.

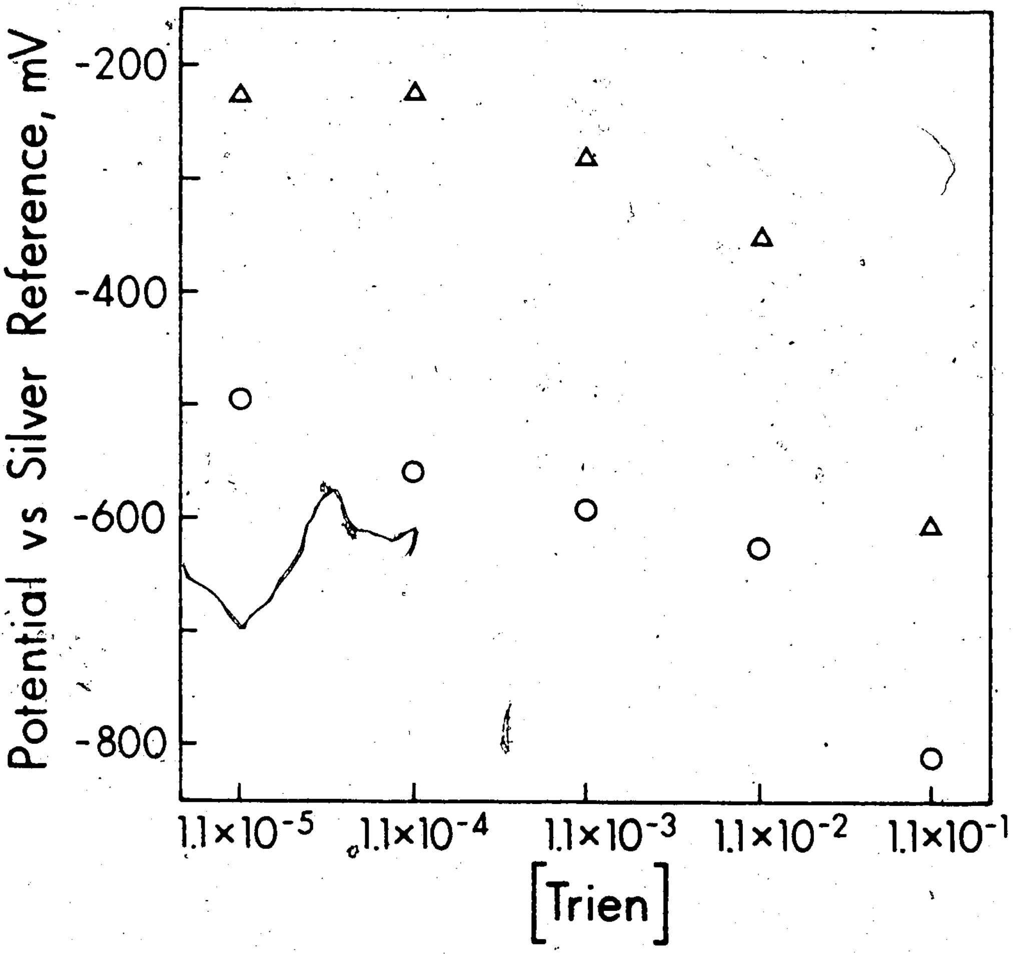

Figure 10. Response of Copper Ion Selective Electrode ○ , and Platinum Electrode △ , to trien Concentration in 0.05 M $LiClO_4$ in Acetonitrile.

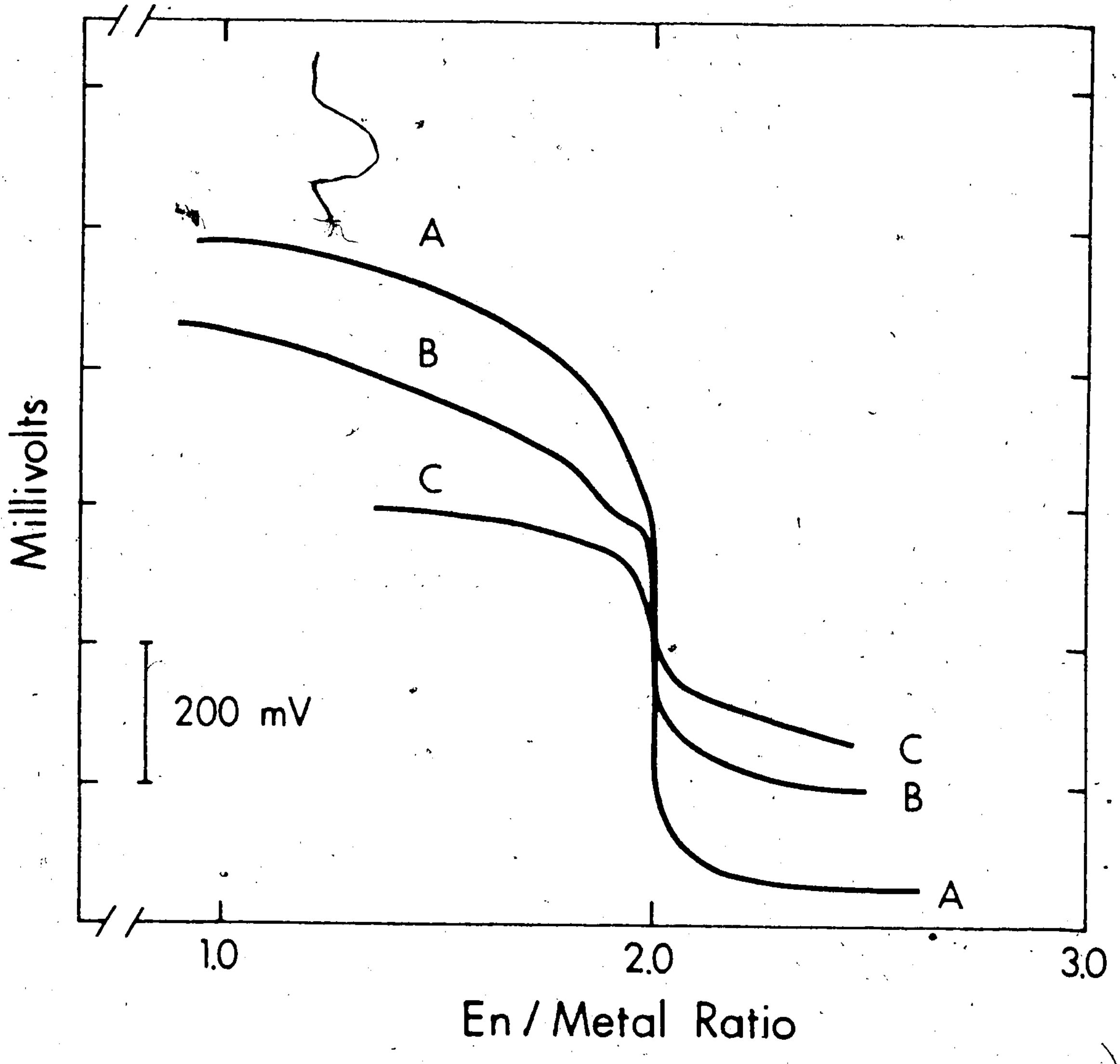

Figure 11 Relative Magnitude of Breaks at Inflection Points for Potentiometric Titration of Copper(II) Ion with en in Acetonitrile Using Indicating Electrodes; A, platinum; B, Hg,Hg(II)en; C, Ag,Ag(I).

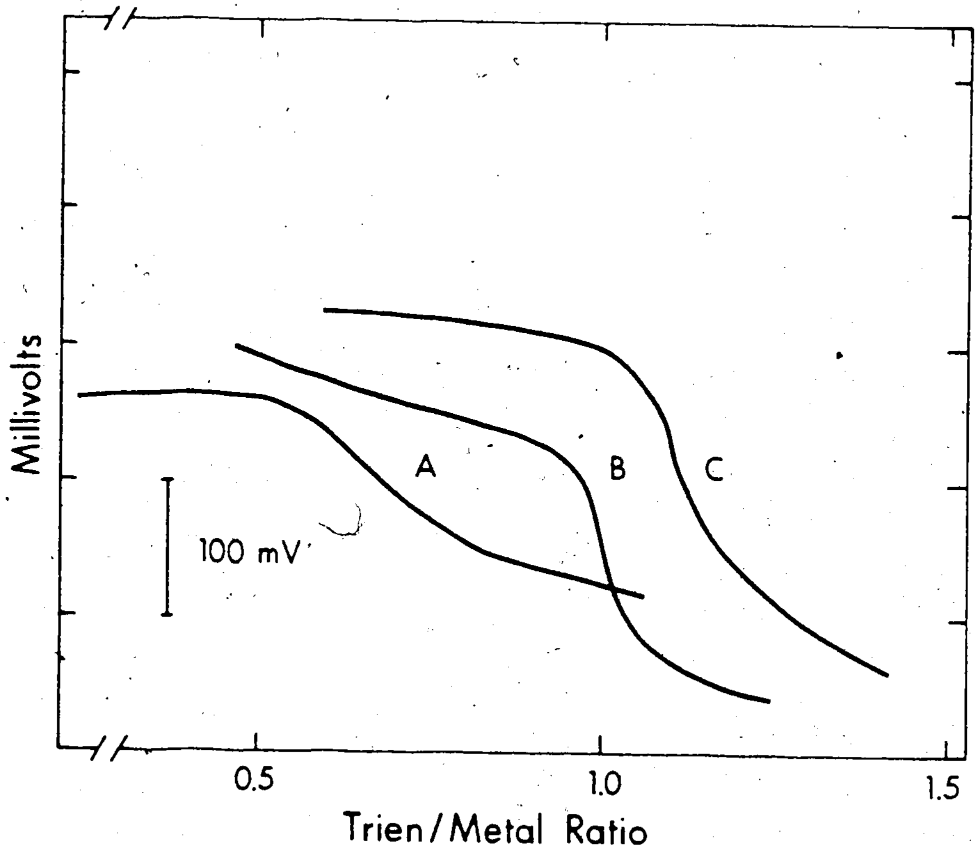

Figure 12. Relative Magnitude of Breaks at Inflection Points for Potentiometric Titration of Magnesium(II) Ion with trien in Acetonitrile Using Indicating Electrodes; A, platinum; B, Hg,Hg(II)trien; C, Ag,Ag(I).

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PART IV

SPECTROPHOTOMETRIC AND POTENTIOMETRIC DETERMINATION OF STABILITY CONSTANTS OF POLYAMINES WITH COPPER(II) AND (I) IONS IN ACETONITRILE

XII. INTRODUCTION

Extensive studies of complexation equilibria between copper(II) and the amine ligands en, dien, and trien in aqueous solutions under a variety of conditions of pH and ionic strength have been made over the years. Stability constants determined for many of these systems have been tabulated by Martell and Smith (1). Some work has also been done on these and related systems in nonaqueous solvent systems. For example, in 1961 Williams (2) determined the stability constants of copper(II) and copper(I) with en, 1,10-phenanthroline (phen), and 2,2'-bipyridyl (bipy) in 50% dioxane-water mixtures. The stepwise formation constants of the chloro complexes of copper(II) and of copper(I) in acetonitrile were evaluated in 1965 by Manahan and Iwamoto through a combination of spectrophotometric and electrochemical methods (3). In 1969, Kratochvil and Yeager studied the ion-pair stability constants of the anions perchlorate, tetrafluoroborate and hexafluorophosphate with copper(I) in acetonitrile by conductance measurements (4). In addition the stepwise formation constants of several other univalent anions with the chloride, bromide, iodide, nitrate, and thiocyanate salts of copper(I) in acetonitrile have been determined by potentiometric titration (5).

In Part III of this thesis it was shown that copper(II) can be titrated quantitatively with en, dien, and trien in acetonitrile. Although the formation of complexes between copper(II) and amines is well known and has been exhaustively studied in aqueous solutions, comparatively little information other than the data mentioned above is available in nonaqueous systems. The present work reports the spectrophotometric determination of the stability constants of copper(II) with en, and dien, the spectrophotometric determination of the stability constants of copper(I) with phen and bipy, and the potentiometric determination of the overall formation constants of copper(I) with en, dien, and trien, all in acetonitrile. With this information the analytical applicability of complexation reactions involving these species in acetonitrile can be more readily assessed.

XIII. EXPERIMENTAL

A. Chemicals

The purification of acetonitrile, en, dien and trien was as reported in Part III. Also $CuClO_4 \cdot 4CH_3CN$ and $Cu(ClO_4)_2 \cdot 5DMSO$ were the same materials reported in Chapter IX. 1,10-Phenanthroline (Fisher) and 2,2'-bipyridine (G. F. Smith) were used as received. Anhydrous $LiClO_4$ (G. F. Smith) was dried overnight under vacuum at 60°C.

B. Apparatus and Procedure for Spectrophotometric Measurements

All spectra were recorded with a Cary 118 spectrophotometer. All solutions were prepared in a glove bag under nitrogen, by dissolving $CuClO_4 \cdot 4CH_3CN$, $Cu(ClO_4)_2 \cdot 5DMSO$, en, dien, phen, and bipy in 0.1 M $LiClO_4$ in acetonitrile. A blank solution of 0.1 M $LiClO_4$ in acetonitrile was used in the reference compartment for all spectrophotometric measurements. One-centimeter quartz cells with Teflon stoppers were used for both blank and sample solutions. The cell compartment of the spectrophotometer was thermostated at 25 ± 0.1°C and was purged with dry nitrogen during the measurements to minimize possible water absorption by the solution.

Copper(I) in acetonitrile does not absorb at the wavelengths used for the $Cu(bipy)^+$ and $Cu(phen)^+$ complexes.

Copper(II) absorption at the same concentrations and wavelengths used for complex formation calculations were measured. From these values, molar absorptivities of copper(II) were determined by using the equation $\underline{A} = \underline{a}_{Cu}\ \underline{bC}$ where $\underline{A}$ is the absorbance, $\underline{a}_{Cu}$ is the molar absorptivity of copper(II) perchlorate in acetonitrile, $\underline{b}$ is the cell path length, 1 cm, and $\underline{C}$ is the copper(II) concentration.

Molar absorptivities of 1 to 1 ligand to metal complex ratios of Cu^{2+}, such as $Cu(en)^{2+}$, and $Cu(dien)^{2+}$, were measured by preparing solutions with a 1 to 10 ligand to metal ion concentration ratio to ensure that all ligand was present as the 1 to 1 complex. The concentration of complex was calculated assuming all the ligand was in the complex form. This was verified by measurement of absorbances in the same way with ligand to metal ratios ranging from 1 to 8 to 1 to 12; the same molar absorptivities were obtained in all cases. A similar procedure was used for $Cu(phen)^{+}$ and $Cu(bipy)^{+}$, but with 1 to 300 ligand to metal ratios. The concentration of free metal ion was calculated by subtracting the concentration of the complex from the total concentration of metal ion added. The absorbance of free metal ion was then calculated and subtracted from the total absorbance to obtain the absorbance of the 1 to 1 complex.

To determine K_1 and K_2, the stability constants for the 1 to 1 and 2 to 1 complexes of copper(II) with en, sets of five to eight solutions of different concentrations were used in each experiment. The absorbance of each solution was measured at two or three wavelengths, one at the wavelength of maximum absorption and the others on shoulders of the peak. A separate calculation of each K value was carried out using measurements at each wavelength as independent sets. None of the free ligands absorbed at the wavelengths used to measure complex formation. A similar procedure was used with copper(II) and dien. Increasing the dien to copper(II) ratio up to 7 did not increase the absorbance of the $Cu(dien)_2{}^{2+}$ complex, or cause observable spectral shift.

C. Apparatus and Procedure for Potentiometric Titrations

The titration cell was a borosilicate H-cell with two compartments separated by an anion exchange membrane (American Machine and Foundry Co., AMF A104-EC) in the perchlorate form (Figure 13). The method used for the conversion of the anion membrane from the chloride form to the perchlorate form was as discussed in Part II of this thesis. Electrical contact to the amalgam electrodes was made with a platinum wire sealed into the end of soft glass tubing.

The indicating electrode was a saturated copper amalgam, prepared by electrolyzing an aqueous 0.1 M $CuSO_4$ solution, slightly acidified with H_2SO_4, at a current density of about 0.05 A/cm^2 until the mercury cathode contained about 1% copper by weight (5). The amalgam was stored under aqueous 0.1 M H_2SO_4 in a weighing bottle and exposed to air only when the bottle was opened for removal of amalgam.

The reference electrode was a saturated silver-mercury amalgam in contact with silver perchlorate in acetonitrile. The amalgam was prepared (5) by placing 25 to 35 cm^2 of silver foil into a borosilicate glass tube with about 30 mL of mercury, sealing the tube in a flame and heating the tube and contents for 8 hours at 100^0C with occasional shaking. The tube was allowed to cool to room temperature overnight before being opened. The amalgam was stored in contact with silver foil in a dropping bottle, and portions were transferred to the reference compartment of the titration cell as needed with an eye dropper. The silver amalgam half cell contains a solution of 0.1 M $LiClO_4$ and 0.01 M $AgClO_4$ It did not require deaeration. The potential of this reference electrode attained equilibrium within seconds.

Data for the calculation of formation constants were obtained by titrating copper(I) with the appropriate ligand. All solutions were prepared in purified, dry acetonitrile in a glove bag under nitrogen. The titrant contained, in addition to the ligand, the same formal concentration of copper(I) perchlorate, generally 5.0×10^{-4} M, and 0.1 M lithium perchlorate supporting electrolyte as the solution in the copper half cell, as suggested by Manahan and Iwamoto (3). By maintaining a constant concentration of copper during the titration, treatment of the data is simplified. The ligand concentration typically was varied over the range of 0.017 to 0.048 M. Titrant was added in 0.1 to 1 mL increments to the copper half cell. The solution in the cell was deaerated continuously by passing argon gas, presaturated with acetonitrile, through it. Potential measurements were made to the nearest 0.1 mV with an Orion model 801 pH meter. Approximately thirty seconds were required after each addition for the system to reach equilibrium and give stable potentials. It was necessary to wait about thirty minutes to allow the cell potential to stabilize before starting the titrations. No stirring other than argon bubbling was used.

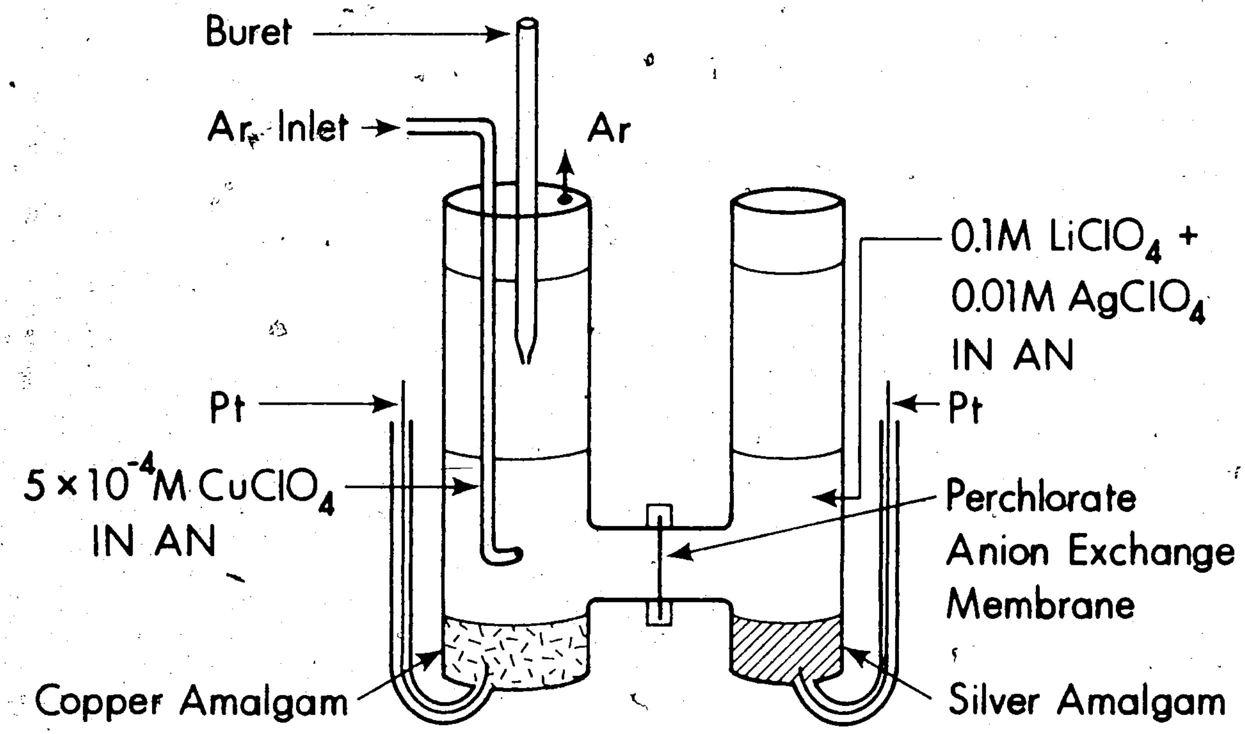


Figure 13. Cell for Potentiometric Titration of Copper(I) with en, dien and trien in Acetonitrile

XIV. RESULTS

Table 13 summarizes the concentrations of metal ions and amines taken, the wavelength of maximum absorption found for each system, and values of log stability constants calculated from the spectrophotometric measurements.

Values for the stability constants of the two to one complexes of phenanthroline and bipyridine with copper(I) in acetonitrile could not be measured because the complexes decompose too rapidly, as is indicated by the absorbance decreasing after solution preparation at a rate of about 10% per hour. Figure 14 shows the relation between absorbance and time for the $Cu(phen)_2^+$ complex. $Cu(bipy)_2^+$ behaves in a similar way. The absorbance of the solutions used to measure the constants for the $Cu(phen)^+$ and $Cu(bipy)^+$ complexes also showed a slight decrease with time, but the error was negligible if measurements were made within twenty minutes of preparation of the solutions.

It was not possible to measure the formation constants of copper(I) with en, dien and trien in acetonitrile spectrophotometrically because of turbidity and precipitate formation. Overall formation constants for these amines with copper(I) therefore were determined potentiometrically, and are represented in Table 14.

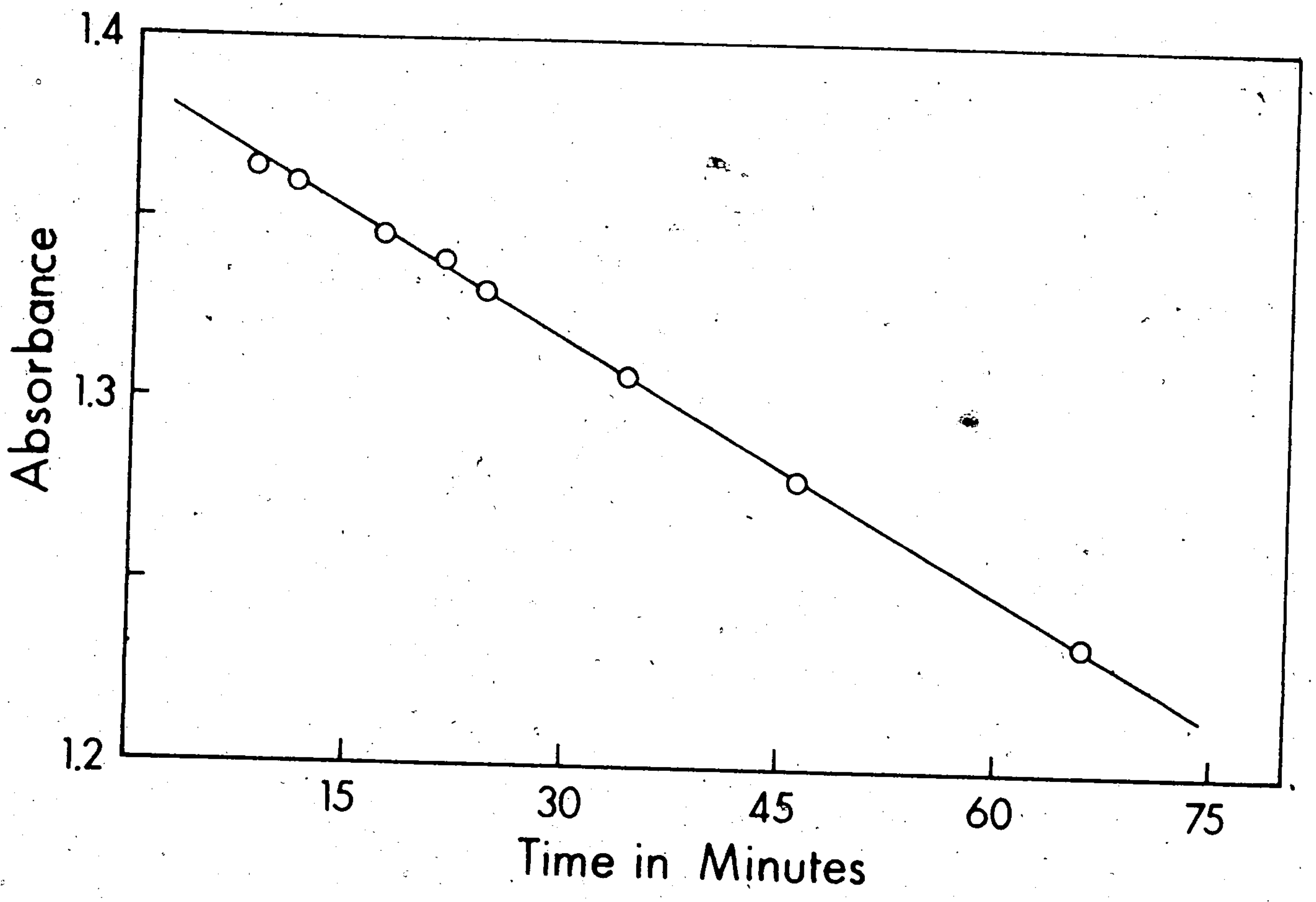


Figure 14. Variation in Absorbance of $Cu(phen)_2^+$ with Time at 440 nm.

TABLE 13.

SUMMARY OF SPECTROPHOTOMETRIC MEASUREMENTS IN ACETONITRILE OF THE STABILITY CONSTANTS OF THE 1:1 and 2:1 COMPLEXES OF COPPER(II) WITH EN AND DIEN, AND THE 1:1 COMPLEXES OF COPPER(I) WITH PHEN AND BIPY[a]

Metal Ion	Metal Ion Concentration, M	Ligand	Ratio of Ligand to Metal Ion Taken	Range of amine concentration, X	Wavelength of max. absorption, nm	Complex	Log K[b]
Cu^{2+}	2.35×10^{-3}	en	.25-1.00	$(.59 \text{ to } 2.36) \times 10^{-3}$	610	$Cu(en)^{2+}$	3.63 ± .15
Cu^{2+}	"	en	1.13-1.88	$(2.66 \text{ to } 4.43) \times 10^{-3}$	570	$Cu(en)_2^{2+}$	2.43± .18
Cu^{2+}	2.30×10^{-3}	dien	.12-0.81	$(.274 \text{ to } 1.92) \times 10^{-3}$	600	$Cu(dien)^{2+}$	3.87 ± .06
Cu^{2+}	"	dien	1.18-1.89	$(2.94 \text{ to } 4.70) \times 10^{-3}$	640	$Cu(dien)_2^{2+}$	2.33 ± .06
Cu^{+}	4.16×10^{-3}	phen	.01	4.04×10^{-5}	356	$Cu(phen)^{+}$	2.88± .04
Cu^{+}	"	bipy	.01	4.12×10^{-5}	350	$Cu(bipy)^{+}$	3.00 ± .02

[a] All measurements made in 0.1 M $LiClO_4$.

[b] Each value is the average of 3 to 15 measurements. Uncertainties shown are standard deviations of the sets. Sample sets of raw data are shown in Appendix.

TABLE 14.

SUMMARY OF OVERALL FORMATION CONSTANTS MEASURED POTENTIOMETRICALLY FOR COPPER(I) AND SEVERAL AMINES IN ACETONITRILE

Titrant	log β_2[a]
En	5.33, 5.31, 5.20 Av. 5.28 ± 0.07
Dien	9.92, 10.01, 9.88, Av. 9.94 ± 0.08
Trien	6.40, 6.34, 6.45 Av. 6.40 ± 0.05

[a] See Appendix, Tables 7, 8, and 9 for sample sets of raw data.

XV. DISCUSSION

A. Spectrophotometric Measurements

L. Newman and D. N. Hume (6) derived general equations by means of which successive formation constants of mixed and single ligand complexes could be determined from spectrophotometric data. The following section summarizes the portion of their work applicable to the systems of interest here and gives the equations used in subsequent calculations. In these equations we have retained the symbols used by Newman and Hume for consistency.

The first step in formation of a complex is expressed by the relation

$$K_q = \frac{[MX_q]}{[M][X]^q} \tag{19}$$

where [M] and [X] are the metal ion and ligand concentrations. The general expression for addition of subsequent ligands to the metal is

$$K_{q+r} = \frac{[MX_{q+r}]}{[MX_q][X]^r} \tag{20}$$

The absorbance at a single wavelength of a solution containing a series of complexes of M and X is given by

$$A = E[M] + E_q[MX_q] + E_{q+r}[MX_{q+r}] \tag{21}$$

D

E, E_q and E_{q+r} are the molar absorptivities of metal ion, first complex and second complex, respectively. When no ligand is present the absorbance is given by

$$A'_0 = EM_0 \tag{22}$$

Equation 22 is used when the absorbance is measured with only metal ion of concentration M_0 present. It is also useful to obtain the quantity A''_0

$$A''_0 = E_q X_0 \tag{23}$$

where A''_0 is the absorbance of the first complex when M is added in large excess to X, E_q is the molar absorptivity of the 1 to 1 complex, and X_0 is the total concentration of ligand under these conditions. The total concentration of M_t is given by

$$M_t = [M] + [MX_q] + [MX_{q+r}] \tag{24}$$

where MX_q and MX_{q+r} are the first and second complexes produced by stepwise formation.

Equations 25-27 were derived by Newman and Hume to calculate the stepwise stability constants for metal complexes where more than one species is present, but one or all of which absorb at the wavelengths used. These equations are useful in the systems under study here, and are applied as indicated later.

$$A = \frac{1}{K_{q+r}}\left\{\left[\frac{1}{K_q}(EM_t - A)\frac{1}{X_t} - A + E_q M_t\right]\frac{1}{X_t}\right\} + E_{q+r}M_t \qquad (25)$$

$$\log\left(\frac{A-A'_0\, M_t/M_0}{A''_0\, M_t/X_0 - A}\right) = q\left\{\log\left[X_t - q\left(\frac{A-A'_0\, M_t/M_0}{A''_0/X_0 - A'_0/M_0}\right)\right]\right\} + \log K_q \qquad (26)$$

$$\log\left(\frac{A}{A''_0 M_t}X_0\right) = q\left[\log\left(X_t - q\frac{A}{A''_0}X_0\right)\right] + \log K_q \qquad (27)$$

In determining the first stability constant K_1 for copper(II) and copper(I) with the amines used in this work, it was necessary to keep the ratio of amine to metal ion concentration at less than one to one so as to prevent the formation of appreciable amounts of higher complexes. To study K_2, the experiment was done at levels of X_t comparable to those of M_t. Equation 27 was originally derived by Newman and Hume for conditions under which M_t is greater than X_t and two species are present, but only one absorbs. In this study Equation 27 was used to calculate K_1 for $Cu(phen)^+$ and $Cu(bipy)^+$. After substitution of $q = 1$, $A''_0 = E_1X_0$, and $1/E_1 = X_0/A''_0$ the equation becomes

$$\log A/E_1M_t = 1\ \{\log\ (X_t - A/E_1)\} + \log K_1\ .$$

where A is the absorbance and E_1 the molar absorptivity of the complex, and X_t is the total concentration of the ligand.

Equation 26 was derived by Newman and Hume for systems involving two species, both of which absorb at the wavelengths used, and under conditions where M_t is comparable to X_t, therefore this equation was used to obtain a value of K_1 for the $Cu(dien)^{2+}$ complex. After substitution of $A'_0 = EM_0 = a_{Cu}\ [Cu]_t$, and $A''_0 = E_q\ X_0 = a_{Cudien}\ [dien]_t$, equation 26 becomes

$$\log\left(\frac{A - a_{Cu}[Cu]_t}{a_{Cudien}[Cu]_t - A}\right) = 1\left\{\log\left[(dien)_t - 1\left(\frac{A - a_{Cu}[Cu]_t}{a_{Cudien} - a_{Cu}}\right)\right]\right\} + \log K_1$$

where a_{Cudien} is the molar absorptivity of the $Cu(dien)^{2+}$ complex, a_{Cu} is the molar absorptivity of Cu^{2+}, and the other symbols are as before.

Equation 26 was also used to obtain a value of K_1 for the $Cu(en)^{2+}$ complex. After substitution of $A'_0 = EM_0 =$

$a_{Cu}[Cu]_t$, and $A''_0 = E_q X_0 = a_{Cuen}[en]_t$, equation 26 becomes

$$\log\left(\frac{A - a_{Cu}[Cu]_t}{a_{Cuen}[Cu]_t - A}\right) = 1\left\{\log\left[(en)_t - 1\left(\frac{A - a_{Cu}[Cu]_t}{a_{Cuen} - a_{Cu}}\right)\right]\right\} + \log K_1$$

where a_{Cuen} is the molar absorptivity of the $Cu(en)^{2+}$ complex, a_{Cu} is the molar absorptivity of Cu^{2+}, and the other symbols are as before.

Equation 25 was used to calculate K_2 for $Cu(en)_2{}^{2+}$ and $Cu(dien)_2{}^{2+}$ because three species may be present simultaneously in solution, all of which absorb. Here E and E_1 are known, and so the equation was used in the form

$$A = \frac{1}{K_2}\left\{\left[\frac{1}{K_1}(a_{Cu}[Cu]_t - A)\frac{1}{[X]_t} - A + a_{CuX}[Cu]_t\right]\frac{1}{[X]_t}\right\} + a_2[Cu]_t$$

where a_{CuX} is the molar absorptivity of $Cu(en)^{2+}$ or $Cu(dien)^{2+}$, a_2 is the molar absorptivity of $Cu(en)_2{}^{2+}$ or $Cu(dien)_2{}^{2+}$. A least squares calculation of the slope when A is plotted against the term in brackets in equation 25 gives the reciprocal of K_2.

It is observed in some cases that, for a given metal-ligand system, the absorption maximum of the complex shifts to longer wavelengths as the combining ratio increases (6). Figure 15 represents the spectra of the copper(II) dien complexes in acetonitrile. It can be seen that the wavelength of maximum absorption shifts to longer values in this system.

The stepwise formation constants of $Cu(en)^{2+}$, $Cu(en)_2{}^{2+}$, $Cu(dien)^{2+}$, and $Cu(dien)_2{}^{2+}$ in acetonitrile are comparatively smaller than the corresponding values obtained in aqueous solutions (Table 15). As will be noted later, this difference holds for all copper(II) and (I) complexes. Although acetonitrile is a relatively weak base compared to water (7), it may be that the interaction of copper(II) with the nitrile group is significant, since copper(II) in general tends to coordinate with compounds containing electron donor nitrogen atoms such as ammonia, amines and nitriles. Perhaps ion pairing of the divalent copper ion in a medium of lower dielectric constant also helps stabilize uncomplexed copper(II).

Since copper(I) is stabilized in acetonitrile through relatively strong Lewis acid-base interaction with this solvent, the stability constants of $Cu(phen)^+$ and $Cu(bipy)^+$ are smaller than the values in water. The stability constants of $Cu(phen)_2{}^+$ and $Cu(bipy)_2{}^+$ could not be measured in acetonitrile because the absorbance decreased after solution preparation at a rate of about ten percent per hour, indicating decomposition of the complex. The nature of decomposition products in water or acetonitrile is unknown. Figure 14 shows the relation between absorbance and time for the $Cu(phen)_2{}^+$ complex.

Moss and Mellon (10) reported that copper(I) ion reacts with phen to give an orange color in aqueous solutions,

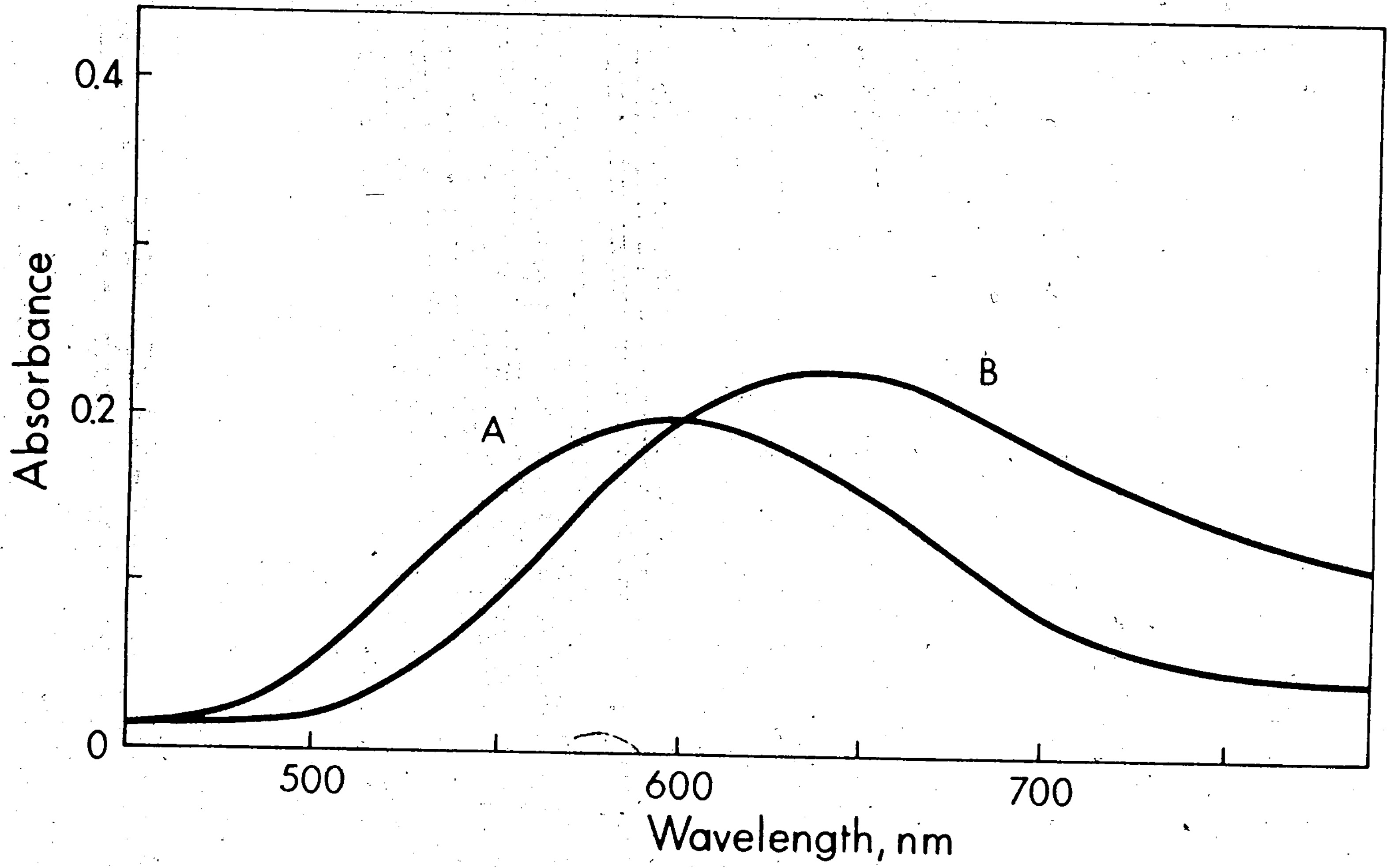


Figure 15. Spectra of Copper (II) dien Complexes. A. Cu(dien)$^{2+}$, dien to Copper (II) Ratio = 0.81; B. Cu(dien$_2^{2+}$, dien to Copper (II) Ratio = 5.5.

TABLE 15.

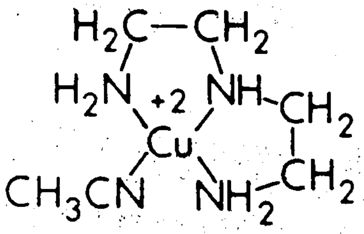
COMPARISON OF STABILITY CONSTANTS OF SEVERAL COPPER-AMINE COMPLEXES IN ACETONITRILE AND WATER

Metal Ion	Amine	Log K_1 in CH_3CN	Log K_1 in H_2O	Log K_2 in CH_3CN	Log K_2 in H_2O
Cu^{++}	en	3.63 ± .15	10.54 ± .1(1,8)	2.43 ± .18	9.1 ± .2 (1,8)
Cu^{++}	dien	3.87 ± .06	15.9 ± .1(1,8)	2.33 ± .06	5.0 ± .1 (1,8)
Cu^{+}	phen	2.88 ± .04			$\log \beta_2 = 15.82$ (2)
Cu^{+}	bipy	3.00 ± .02			$\log \beta_2 = 12.95$ (9)

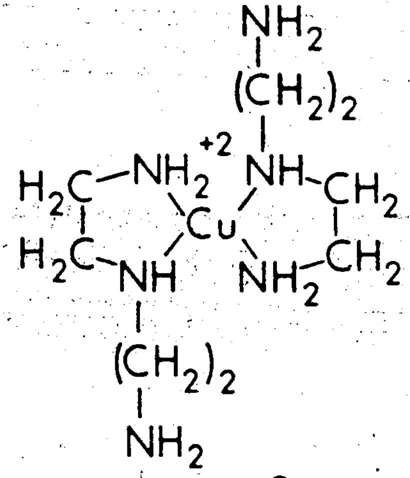
followed by slow precipitation of the complex. The time required for precipitation to occur depends on the copper(I) ion concentration. Precipitation is prevented entirely by the presence of certain alcohols or other solvents miscible with water including ethyl carbitol ($CH_3CH_2OCH_2CH_2OCH_2CH_2OH$), methyl carbitol ($CH_3OCH_2CH_2\cancel{O}CH_2CH_2OH$), dioxane, and methyl cellosolve ($CH_3OCH_2CH_2OH$), but all of these solvents cause the fading of the orange color with time except for methyl carbitol.

With en we found that the values of log β_2 for the copper(I) and copper(II) complexes in acetonitrile are of the same order. The reasons for this are not clear.

K_1 for the $Cu(dien)^{2+}$ complex was found to be larger than K_2 for $Cu(dien)_2{}^{2+}$, which is in agreement with the results obtained in water (1,8) and with the general trend for most metal-ligand systems. Potentiometric titrations of copper(II) with dien give two clean, well separated breaks corresponding to formation of 1 to 1 and 2 to 1 complexes. It seems reasonable to assume that the central metal ion is surrounded by the tridentate dien ligand, leaving only one coordination site available for the second ligand. To form the 2 to 1 complex, one of the NH_2 groups on the end of the first molecule of dien may dissociate to be replaced by an NH_2 group from the second ligand.



$Cu(dien)^{+2}$



$Cu(dien)_2^{2+}$

B. Potentiometric Titrations

Overall formation constants of copper(I) with en, dien, and trien were determined potentiometrically. Values of β_2 were calculated on a point by point basis from data taken at ratios of ligand to copper of more than two (5). Assuming the concentration of CuL^+ to be negligible,

$$Cu^+ + 2L \longrightarrow CuL_2^+ \qquad (28)$$

$$\beta_2 = \frac{[CuL_2^+]}{[Cu^+][L]^2} \qquad (29)$$

$$[L]^0 = [L] + 2[CuL_2^+] \qquad (30)$$

where $[CuL_2^+]$ = concentration of complex at any point = $[Cu]^0 - [Cu^+]$

$[L]$ = concentration of free ligand at any point = $[L]^0 - 2[CuL_2^+]$

$[Cu^+]$ = concentration of free copper(I) at any point

$[L]^0$ = total concentration of ligand

$[Cu^+]^0$ = total concentration of copper(I) in solution

The free copper concentration was calculated from the change in cell potential, using the Nernst equation

$$\Delta E = 0.0591 \log [Cu^+]^0/[Cu^+] \qquad (31)$$

where ΔE is the potential shift from the value before any ligand has been added.

Values of β_2 were calculated using the following equation

$$\beta_2[Cu^+][L]^2 + [Cu^+] - [Cu]^0 = 0 \qquad (32)$$

Results for the amines investigated are given in Table 14. Previous studies of the determination of stability constants of copper(I) with en, phen, and bipy in ecueous solutions have reported values of log β_2 only (1); no values have been reported for the stability constants of copper(I) with dien or trien. In the present work we calculated log β_2 for $Cu(en)_2^+$, $Cu(dien)_2^+$ and $Cu(trien)_2^+$ complexes. Since we observed only one potential break at a 2 to 1 ligand to copper(I) ratio for all the potentiometric titrations, it was concluded that the complexes for the 1 to 1 ligand to metal ratio are unstable and disproportionate in a way similar to that discussed by Manahan and Iwamoto (3) for the copper(I) chloride system in acetonitrile.

From the results shown in Table 14 we see that log β_2 for the $Cu(dien)_2^+$ complex is larger than log β_2 for either the $Cu(trien)_2^+$ or the $Cu(en)_2^+$ complexes. Assembly of molecular models of the complexes of en, dien, and trien with a tetrahedral configuration for copper(I) ion showed that two molecules of en can fit easily around copper(I). Dien can complex copper(I) in two ways, one with three nitrogen atoms from one dien ligand and only one from a second dien coordinating to the metal ion, and the other with two nitrogen atoms from each dien coordinating. The second of these alternatives seems more likely, because models indicate there may be some steric hindrance to attachment of the third nitrogen from a single dien; however the large β_2 value for dien over en may be the result of coordination of all three nitrogen atoms of one dien to at least some extent. In the case of trien the third and fourth nitrogen atoms may coordinate to some extent, but the fourth will be much weaker than the third for steric reasons. Therefore coordination of a second trien molecule to one of the sites may occur, although increased interference from the free $-C_2H_4NH_2$ groups appears to preclude formation of a complex in which two trien ligands each occupy two coordination sites on copper(I). For these reasons β_2 for trien is smaller than that for dien with this ion. In addition we observe from this work that the stability constants of copper(I) and copper(II) investigated in acetonitrile are smaller than the corresponding values in aqueous solutions. This is because acetonitrile has a nitrogen donating atom which stabilizes both copper(I) and copper(II) ions more than the oxygen atom in water.

In the present work we observe that log β_2 for $Cu(dien)_2^+$ is larger than log β_2 for $Cu(dien)_2^{2+}$. The reasons for this difference are unclear. James and Williams (2) have reported that copper(I) forms complexes with pyridine in aqueous solutions that are more stable than the corresponding complexes of copper(II). Also, the shift in potential of the copper(II)-(I) couple to more positive, and the copper(I)-(0) couple to more negative values on addition of acetonitrile to aqueous solutions of copper(I) (11), indicates the greater strength of copper(I)-acetonitrile complex formation compared to that of copper(II).

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APPENDIX

TABLE A1.

SAMPLE SET OF DATA FOR CALCULATION OF K_1 FOR $Cu(PHEN)^+$ IN TABLE 13.

Final Concentration of Cu^+ in 10 ml, M	Final Concentration of phen in 10 ml, M	Phen:Cu^+ ratio	Absorbance at λ max. 356 nm	Log K_1
.004162	4.036×10^{-5}	0.0096	0.0977	2.86
"	"	"	0.0954	2.82
"	"	"	0.0994	2.89
"	"	"	0.1014	2.93
"	"	"	0.0989	2.88
.01248	4.036×10^{-5}	.0032	.1300	

Molar absorptivity of $Cu(phen)^+$ at 356 nm: 3220

Value of log K_1 calculated from above data: 2.88±0.14

TABLE A2.

SAMPLE SET OF DATA FOR CALCULATION OF K_1 FOR $Cu(BIPY)^+$ IN TABLE 13.

Final Concentration of Cu^+ in 10 ml, M	Final Concentration of bipy in 10 ml, M	Bipy:Cu^+ ratio	Absorbance at λ max. 350 nm	Log K_1
0.004162	4.124×10^{-5}	0.0099	0.0866	3.00
"	"	"	0.0868	3.01
"	"	"	0.0868	3.01
"	"	"	0.0854	2.98
0.01248	4.124×10^{-5}	0.0033	0.1070	

Molar absorptivity of $Cu(bipy)^+$ at 350 nm: 2595

Value of log K_1 calculated from above data: 3.00±0.02

TABLE A3.

SAMPLE SET OF DATA FOR CALCULATION OF K_1 FOR $Cu(EN)^{2+}$ IN TABLE 13.

Final Concentration of Cu^{2+} in 10 ml, M	Final Concentration of en in 10 ml, M	En:Cu^{2+} ratio	Net absorbance at 570 nm	Log K_1
2.351×10^{-3}	5.90×10^{-4}	0.25	0.0445	3.86
"	11.8×10^{-4}	0.50	0.0703	3.86
"	16.23×10^{-4}	0.69	0.0928	3.91
"	17.71×10^{-4}	0.75	0.0953	3.75
"	23.61×10^{-4}	1.00	0.1160	3.87
2.351×10^{-3}	0	0	0.0145	

Molar absorptivities at 570 nm: $a_{Cu^{2+}} = 6.17$; $a_{Cu(en)^{2+}} = 60.8$

Value of log K_1 calculated from above data: 3.85

Average value from three sets of independent data: 3.63±0.06

TABLE A4.

SAMPLE SET OF DATA FOR CALCULATION OF K_2 FOR $Cu(EN)_2^{2+}$ IN TABLE 13.

Final Concentration of Cu^{2+} in 10 ml, M	Final Concentration of en in 10 ml, M	En:Cu^{2+} ratio	Net Absorbance at 550 nm
2.351×10^{-3}	2.656×10^{-3}	1.13	0.1094
"	2.952×10^{-3}	1.25	0.1187
"	3.30×10^{-3}	1.40	0.1253
"	3.54×10^{-3}	1.50	0.1264
"	3.72×10^{-3}	1.58	0.1318
2.351×10^{-3}	0	0	0.0078

$a_{Cu^{2+}} = 3.32$

Value of log K_2 obtained from slope of plot of above data according to Eq. 25: 2.43

Average value from three plots of independent data: 2.33 ± 0.06

TABLE A5.

SAMPLE SET OF DATA FOR CALCULATION OF K_1 FOR $Cu(DIEN)^{2+}$ IN TABLE 13.

Final Concentration of Cu^{2+} in 10 ml, M	Final Concentration of dien in 10 ml, M	Dien:Cu^{2+} ratio	Net absorbance at 580 nm	Log K_1
2.483×10^{-3}	8.23×10^{-4}	0.33	0.1009	4.00
"	10.97×10^{-4}	0.44	0.1247	3.87
"	12.34×10^{-4}	0.49	0.1378	3.89
"	13.72×10^{-4}	0.55	0.1510	3.97
"	15.09×10^{-4}	0.61	0.1626	3.87
"	16.46×10^{-4}	0.66	0.1730	3.92
"	17.83×10^{-4}	0.71	0.1875	4.00
"	19.20×10^{-4}	0.77	0.1990	3.85
2.483×10^{-3}	0	0	0.0205	

Molar absorptivities at 580 nm: $a_{Cu^{2+}} = 8.57$; $a_{Cu(dien)^{2+}} = 112$

Value of log K_1 calculated from above data: 3.92

Average value from three sets of independent data: 3.87±0.06

TABLE A6.

SAMPLE SET OF DATA FOR CALCULATION OF K_2 FOR $Cu(DIEN)_2^{2+}$ IN TABLE 13.

Final concentration of Cu^{2+} in 10 ml, M	Final concentration of dien in 10 ml, M	Dien:Cu^{2+} ratio	Net absorbance at 650 nm
2.483×10^{-3}	2.940×10^{-3}	1.18	0.1792
"	3.116×10^{-3}	1.25	0.1900
"	3.293×10^{-3}	1.32	0.1875
"	3.528×10^{-3}	1.42	0.1932
"	3.705×10^{-3}	1.49	0.1950
"	3.881×10^{-3}	1.56	0.2044
"	4.116×10^{-3}	1.65	0.2041
2.483×10^{-3}	0	0	0.0610
2.483×10^{-3}	2.744×10^{-4}	0.11	0.0739

$a_{Cu(dien)^{2+}} = 71.4$

Value of log K_2 obtained from slope of plot of above data according to Eq. 25: 2.32

Average value from three plots of independent data: 2.33±0.06

TABLE A7.

SAMPLE SET OF DATA FOR CALCULATION OF β_2 FOR $Cu(EN)_2^+$ IN TABLE 14.

ml of titrant added	ΔE in mV	$[Cu^+]$	$[Cu^+]°$	$[en]°$	$[en]$	Log β_2 (from Eq 32)
5.0	66	5.0×10^{-5}	6.43×10^{-4}	8.0×10^{-3}	6.74×10^{-3}	5.48
6.0	71	4.06×10^{-5}	"	9.25×10^{-3}	7.97×10^{-3}	5.41
7.0	76	3.38×10^{-5}	"	10.4×10^{-3}	9.12×10^{-3}	5.37
8.0	81	2.74×10^{-5}	"	11.4×10^{-3}	10.1×10^{-3}	5.37
9.0	82	2.69×10^{-5}	"	12.4×10^{-3}	11.1×10^{-3}	5.25
10.0	83	2.56×10^{-5}	"	13.3×10^{-4}	12.0×10^{-3}	5.25

15 ml of 6.43×10^{-4} M copper(I) perchlorate in acetonitrile was titrated with 4.01×10^{-2} M en containing the same concentration of Cu^+.

Value of log β_2 calculated from above data: 5.35

Average value from three sets of independent data: 5.28±.07

TABLE A8.

SAMPLE SET OF DATA FOR CALCULATION OF β_2 FOR $Cu(DIEN)_2^+$ IN TABLE 14.

ml of titrant added	ΔE in mV	$[Cu^+]$	$[Cu^+]°$	[dien]°	[dien]	Log β_2 (from Eq 32)
5	112	6.40×10^{-5}	5.027×10^{-4}	1.047×10^{-2}	9.47×10^{-3}	9.95
6	120	4.69×10^{-5}	"	1.197×10^{-2}	10.96×10^{-3}	9.96
7	123	4.18×10^{-5}	"	1.333×10^{-2}	12.29×10^{-3}	9.91
8	126	3.73×10^{-5}	"	1.457×10^{-2}	13.56×10^{-3}	9.87
9	127	3.57×10^{-5}	"	1.571×10^{-2}	14.69×10^{-3}	9.82

15 ml of 5.027×10^{-4} <u>M</u> copper(I) perchlorate in acetonitrile was titrated with 4.197×10^{-2} <u>M</u> dien containing the same concentration of Cu^+.

Value of log β_2 calculated from above data: 9.90

Average value from three sets of independent data: 9.94±0.08

TABLE A9.

SAMPLE SET OF DATA FOR CALCULATION OF β_2 FOR $Cu(TRIEN)_2^+$ IN TABLE 14.

ml of titrant added	ΔE in mV	[C[illegible]	$[Cu^+]°$	[trien]°	[trien]	Log β_2 from Eq 32)
5	93	1.332×10^{-5}	4.99×10^{-4}	4.287×10^{-3}	3.289×10^{-3}	6.55
6.05	95	1.232×10^{-5}	"	4.929×10^{-3}	3.931×10^{-3}	6.43
7.0	97	1.140×10^{-5}	"	5.457×10^{-3}	4.459×10^{-3}	6.35
8.0	98	1.096×10^{-5}	"	5.965×10^{-3}	4.967×10^{-3}	6.27

15 ml of 4.99×10^{-4} M copper(I) perchlorate in acetonitrile was titrated with 1.715×10^{-2} M trien containing the same concentration of Cu^+

Value of log β_2 calculated from above data: 6.40

Average value from three sets of independent data: 6.40±.05