POLAROGRAPHIC DETERMINATION OF STABILITY CONSTANTS IN ACETONITRILE

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POLAROGRAPHIC DETERMINATION OF STABILITY CONSTANTS IN ACETONITRILE

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GLOSSARY OF SELECTED SYMBOLS

A.S.C.E.	Acetone-saturated calomel electrode
C_x	Concentration of solute
D	Diffusion coefficient
D.M.E.	Dropping-mercury electrode
DMSO	Dimethyl sulfoxide
$E_{1/2}$	Half-wave potential
$\underline{F}$	Faraday's constant
F_j	DeFord and Hume's F functions
$\underline{i}$	Current
$\underline{i}_d$	Diffusion current
$\underline{I}$	Current density
$\underline{I}_d$	Diffusion-current constant
m	Mass
$\bar{n}$	Average number of bound ligands
N	Number of electrons
R	Resistance
$\underline{R}$	Gas-law constant
s	Surface area
S.C.E.	Saturated calomel electrode
t	Time
µa	Microamps
α_j	Degree of formation of the jth complex

GLOSSARY OF SELECTED SYMBOLS (Continued)

β_j	Stability constant of the jth complex
δ	Diffusion layer thickness

CHAPTER I

INTRODUCTION

Few techniques in chemistry have the same versatility as electrochemical methods. Measurements of resistance, current, and time as a function of potential have all been used as bases for methods of electrochemical analysis (1).

The study of current-voltage relationships comes under the general heading of voltammetry. Voltammetric studies have been of great importance in extending our knowledge of what occurs during electrolysis. When a dropping mercury electrode (D.M.E.) serves as the polarizable electrode, the technique is known as polarography.

Polarography has often been used to determine stability constants in aqueous solutions (2,3,4,5). The purpose of this study was to extend the polarographic method of stability constant determination to nonaqueous solutions. The method of DeFord and Hume (2) offers a straightforward way of calculating stability constants from polarographic data for mononuclear complexes with a single ligand. It is applicable to complexes in which the metal ion is rapidly and reversibly reduced at the D.M.E. and the method requires a knowledge of the shift in half-wave potential and the change in the magnitude of the diffusion current as the ligand concentration increases.

Acetonitrile was chosen as the nonaqueous solvent for various reasons. Acetonitrile is a good aprotic solvent which is readily available and is easy to dry and purify. Its dielectric constant, 36.2 at 25°C, is large enough that many inorganic salts are soluble. The reduction of nickel(II) is known to be reversible in acetonitrile (6), and this reaction was chosen to develop the method. In particular, nickel perchlorate was used since the perchlorate anion has a smaller tendency to associate with nickel ion than other common anions. Dimethyl sulfoxide (DMSO) was used as the ligand; it is readily available and its coordination chemistry is being investigated in a related program in this laboratory.

As the DMSO concentration was increased the half-wave potential was observed to shift to more negative values, while the magnitude of the diffusion current decreased. From the observed half-wave potentials and calculated diffusion current constants, the beta values for the nickel-DMSO system were calculated. The results are somewhat inconclusive, but seem to indicate that the polarographic method for stability constant determination can be used in nonaqueous solutions.

CHAPTER II

FUNDAMENTAL PRINCIPLES OF POLAROGRAPHY

Introduction

Polarography involves the electrolysis of solutions of reducible materials between a D.M.E. and a nonpolarizable reference electrode (1). As the potential between the electrodes is varied, changes in current flow are measured. The D.M.E. consists of a fine glass capillary tube attached to a reservoir containing mercury, and is usually the cathode. In polarography an inert electrolyte is added to carry the current, and the reducible species arrives at the D.M.E. by diffusion alone.

The essential circuit required to obtain current-voltage curves is shown in Figure 1. The potential is varied by means of a potential divider circuit, A. A saturated calomel electrode, B, is the reference electrode in this case. G is a microammeter. R_1 and R_2 provide the shunt resistance for the microammeter. Dissolved oxygen is reduced at -0.1 and -0.9 v. vs. S.C.E. and interferes in almost all polarographic determinations. It must be removed by purging the solution with nitrogen or an inert gas.

As the applied potential is increased, negligible current will flow until the decomposition potential of the reducible species is reached. At this point, the reduction process begins:

$$M^{z+} + Z\ e^{-} = M(Hg) \qquad (1)$$

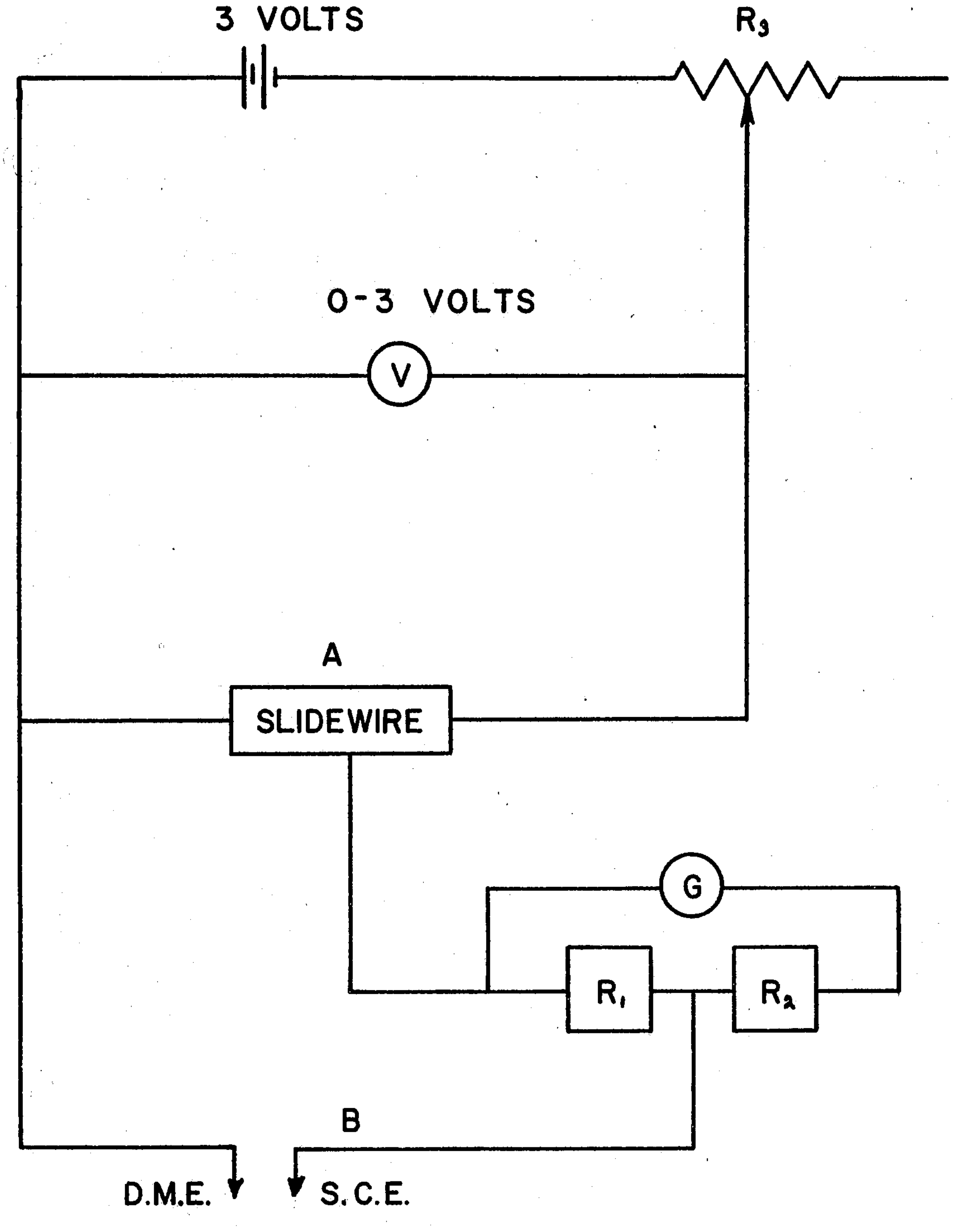

Figure 1. Basic Circuit for Obtaining Current-Voltage Curves

As the potential is increased the rate of reduction increases and the current continues to rise. Finally a plateau current is reached at which the reducible species is reduced as soon as it reaches the electrode surface. This plateau current minus the residual current is the diffusion current, $\underline{i}_d$.

An electrical double layer, with some characteristics resembling an electrical condenser, forms at the surface of each new mercury drop. As this "condenser" is charged a small residual current flows, even though no electrolysis is occurring. This current is called the residual current.

The current-voltage curve has the form shown in Figure 2. The diffusion current and the potential at the midpoint of the wave, called $E_{\frac{1}{2}}$, are of interest. So long as the reaction is reversible, there is a linear dependence between the magnitude of the diffusion current and concentration. $E_{\frac{1}{2}}$ is a constant for each different reducible species, and the current at $E_{\frac{1}{2}}$ is exactly half the diffusion current.

There are three potential factors involved in bringing the reducible species to the electrode surface. These factors are migration, diffusion, and convection. Migration is an electric field effect and depends on the charge of the species. Its effect is governed by the transport number of the ion. Diffusion is not an electrical effect, but depends upon temperature and concentration. Convection may arise from thermal or concentration gradients or mechanical agitation. Its effect is difficult to treat mathematically, and it is easier to work under conditions where convection effects are small. By adding a supporting electrolyte 50 to 100 times more concentrated than the species of interest the migration of the latter is reduced to a negligible value, hence,

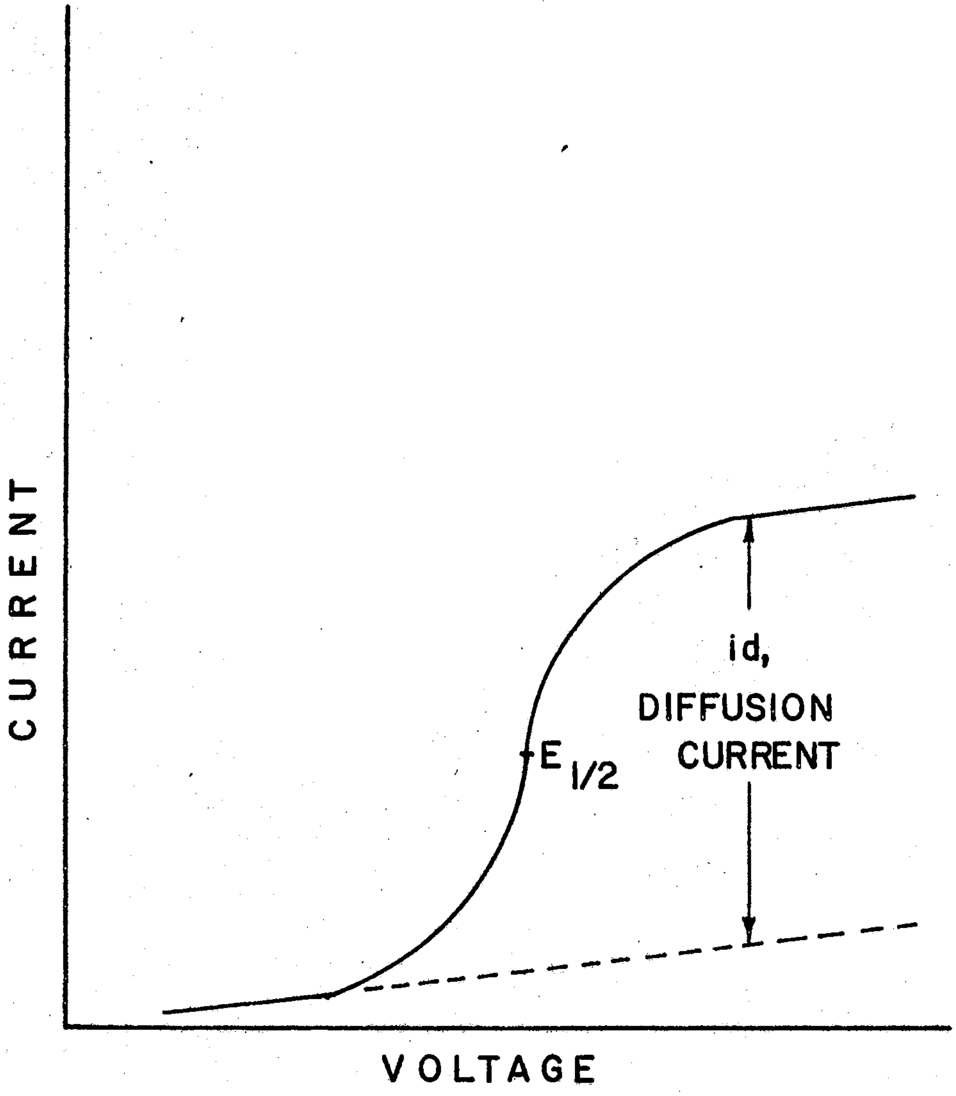

Figure 2. Current-Voltage Curve

the only mass transfer process of importance is diffusion.

Current and Diffusion

The current density $\underline{I}$ is given by

$$\underline{I} = \underline{i}/s \tag{2}$$

where $\underline{i}$ is the current that passes through an electrode of area s. From Fick's first law of diffusion

$$\partial r/\partial t \propto (\partial c/\partial x)_{x=0} \tag{3}$$

the rate of diffusion is proportional to the concentration gradient (1). The following equation can be written

$$\underline{I}/N\underline{F} = D(\partial c/\partial x)_{x=0} \tag{4}$$

where N is the number of electrons involved, $\underline{F}$ is the Faraday constant, D is the diffusion coefficient, and $(\partial c/\partial x)_{x=0}$ is the concentration gradient. Solving Equation (2) for $\underline{I}$ and substituting in Equation (4) gives the following equation involving the measured current:

$$\underline{i} = N\underline{F}sD(\partial c/\partial x)_{x=0} . \tag{5}$$

The concentration gradient can be pictured using the model shown in Figure 3. C_o is the bulk concentration, C_e is the concentration at the electrode surface, and δ is the diffusion-layer thickness. As a first approximation, the diffusion-layer thickness remains constant and the concentration gradient is confined to this layer (7). Such conditions are hypothetical and the dotted curve in Figure 3 more nearly represents

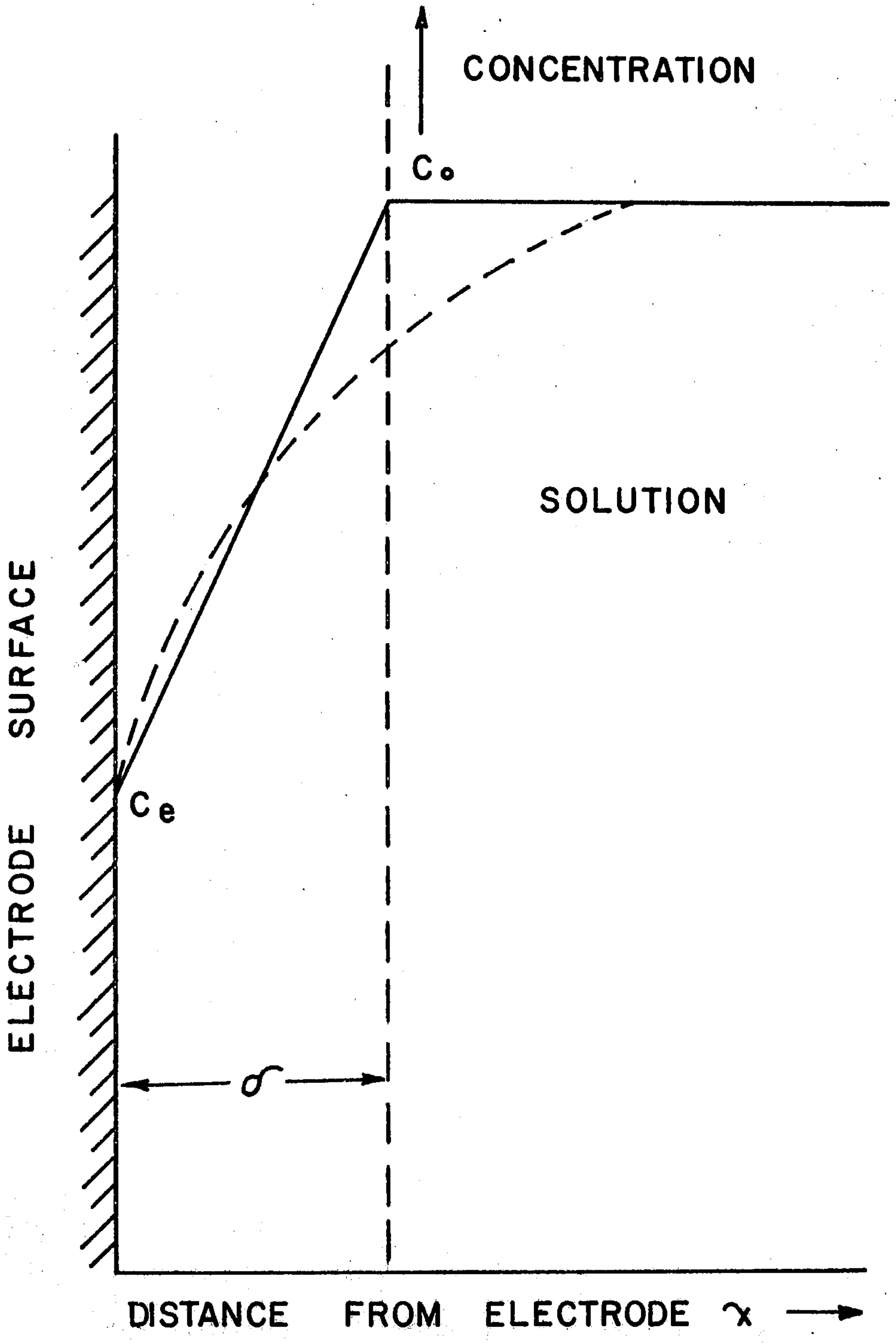

Figure 3. Model of Diffusion Layer

the real condition. Using the dotted line as a second approximation:

$$(\partial c/\partial x)_{x=0} = (C_o - C_e)/\delta \qquad (6)$$

As $\underline{i}$ increases, C_e becomes much smaller than C_o, and the current reaches a maximum value termed the diffusion current, $\underline{i}_d$, given by:

$$\underline{i}_d = (N\underline{F}sDC_o)/\delta \qquad (7)$$

The diffusion current exhibits a linear dependence on the concentration of the reducible species in the solution.

For fast and reversible systems the familiar Heyrovsky-Ilkovic Equation (8) holds:

$$E = E_{\frac{1}{2}} + (\underline{R}\underline{T}/N\underline{F}) \ln (\underline{i}_d - \underline{i})/\underline{i} \qquad (8)$$

It describes the current-voltage relationship for reversible polarographic waves.

High Resistance Polarography

In aqueous polarography, polarographic cells and circuits are designed to keep resistance as low as possible, so that the effective potential is equal to the applied potential; hence, in aqueous polarography the current is plotted as a function of the voltage applied to the cell. Correction for $\underline{i}R$ loss is usually not required. Some modern polarographs are not suitable for use with solutions of high resistance because in solutions of high resistance only a portion of the applied voltage is being used in the electrolysis. The remainder, the $\underline{i}R$ loss, is used to overcome the high resistance in the cell and circuit. The problem of high resistance can be overcome by automatically introducing enough voltage into the circuit to compensate for the iR loss.

Arthur (9) designed a cell containing two reference electrodes and showed that when a voltage is applied between the D.M.E. and the electrolysis reference electrode, the potential difference between the D.M.E. and the stable reference electrode will be the effective voltage. The applied voltage equals the sum of the effective voltage and the iR loss:

$$E_a = E_e + iR \qquad (9)$$

If the two reference electrodes are the same kind, the potential difference between them will be equal to the iR loss in the cell.

An iR compensator consists of a highly stable direct-current amplifier with an accurate 1:1 amplification. The input is connected across the two reference electrodes. The output is connected in series with the polarograph and the cell. When iR loss causes a difference in potential between the reference electrodes, the exact correction voltage is fed into the circuit (10).

In the circuit described by Arthur (10) the amplifier has the necessary high input impedance and the necessary low output impedance (10,000 megohms and about 400 ohms respectively). The positive and negative power supplies have a stability of ± 0.1% from 10 to 20 ma. The error in compensation voltage is less than ± 5 mV over the range ± 20 volts. The error is slightly larger than this up to the upper limit of ± 30 volts.

A polarographic cell similar to the one described by Arthur (10) was used in this research. The asbestos fiber junctions each have a resistance of 36 to 38,000 ohms with 0.1 M LiCl in the compartments. Tests have shown that diffusion through the fibers is inconsequential even after several hours (10). Little is known about the size of junction potentials that occur with this type of cell. It is assumed that the junction potential will remain constant during the run, and that it will be reproducible from run to run.

The nature of the reference electrodes is important (9). Either S.C.E. or A.S.C.E. work well (10). The reproducibility of the S.C.E. is well known. Arthur and Lyons (11) developed the A.S.C.E. and found it to be very satisfactory for polarographic work in nonaqueous solvents.

CHAPTER III

THE NATURE OF METAL COMPLEXES

Introduction

A complex is any species in solution which is formed by a combination of two or more simpler species which can also exist independently. Metal ions in solution are never in the uncomplexed state, since there are always a number of solvent molecules bound to the metal ion (12,13).

The formation of metal complexes in solution with particular ligands occurs by successive replacement of solvent molecules. The shape of the polarographic wave is dependent on both the thermodynamics and kinetics of the complexation reaction. A complex is termed labile when substitution reactions occur rapidly and inert when substitution occurs slowly. A labile complex has a one step polarographic wave while an inert complex has a two step wave. A labile complex has a one step polarographic wave since there is only one species being reduced. The two steps of an inert complex are due to 1) the complex itself being reduced and 2) the free metal being reduced. The thermodynamic stability is a measure of the extent to which a complex will be formed in a system at equilibrium.

Stability of Complexed Ions in Solution

Complexation of a metal ion, M, with a monodentate ligand, X, may be written as:

$$M(\text{solvent})_n + n\,X = MX_n + n\ \text{solvent} \tag{10}$$

Neglecting activity coefficients, the overall stability constants β_j of the species MX_n is defined as

$$\beta_j = [MX_j]/[M][X]^j \tag{11}$$

where the brackets refer to the concentration of each species (11,12).

The complexing process occurs in a series of steps, and it is possible to write an equilibrium expression for the formation of each intermediate complex, as well as overall stability constants:

$$M + X = MX \qquad \beta_1 = [MX]/[M][X] \tag{12}$$

$$M + 2\,X = MX_2 \qquad \beta_2 = [MX_2]/[M][X]^2 \tag{13}$$

$$M + 3\,X = MX_3 \qquad \beta_3 = [MX_3]/[M][X]^3 \tag{14}$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$M + n\,X = MX_n \qquad \beta_{\bar{n}} = [MX_n]/[M][X]^n \tag{15}$$

Ligand Number and Degree of Formation

The ligand number, $\bar{n}$, of a metal-ligand system is defined as (Total concentration of X bound to M)/(Total concentration of M), i.e.,

$$\bar{n} = (C_x - [X])/C_m \tag{16}$$

where C_x and C_m represent the total concentration of ligand and metal respectively and [X] is the free ligand concentration (11,12).

The degree of formation of the $j^{\underline{th}}$ complex, α_j, is given by:

$$\alpha_j = [MX_j]/C_m \qquad (17)$$

When $\bar{n}$ data is available as a function of [X], the formation curve for the system may be drawn (11,12).

If all β_j or α_j and [X] are known, the other two parameters can be calculated. Assuming that β_j is known, α_j can be calculated from the following relationship (13):

$$C_X = [M^{+n}]\ (1 + \beta_1[X] + \beta_2[X] + \ldots + \beta_n[X]^n) \qquad (18)$$

$$\alpha_0 = [M^{+n}]/C_X \qquad (19)$$

$$\alpha_1 = \beta_1[X]\alpha_o \qquad (20)$$

$$\alpha_2 = \beta_2[X]^2\alpha_o \qquad (21)$$

$$\vdots \qquad \vdots$$

$$\alpha_n = \beta_n[X]^n\alpha_o \qquad (22)$$

The relation between $\bar{n}$ and α_j is (13):

$$\bar{n} = \alpha_1 + 2\alpha_2 + 3\alpha_3 + \ldots + n\alpha_n \qquad (23)$$

In studying complexes some experimental approaches lead to β values while others lead to $\bar{n}$ values. The above relationships are necessary to interconvert these parameters.

CHAPTER IV

NONAQUEOUS SOLVENTS

Solvent coordination of solutes and its ramifications are very important in nonaqueous solvent chemistry. If an inorganic salt dissolves it is nearly always accompanied by solvent coordination. This coordination involves a Lewis acid-base type interaction. Information about electrolytes in nonaqueous solvents comes mainly from conductivity measurements; activity data is virtually nonexistent (14). This is why activity coefficient corrections were not made in this study. Much of the conductivity data falls into two groups. These two groups of solvents are differentiating and leveling solvents (14). The leveling solvents are the hydroxylic solvents in which inorganic salts are highly dissociated. The difference between the two classes of solvents can be attributed to differences in solvation energy.

Plots of equivalent conductance of electrolytes in nonaqueous solvents often exhibit a minimum. One possible explanation for these conductance minima is the formation of ion aggregates, the association of the solute to give particles of more than normal molecular weight. These ion aggregates are in equilibrium with various ionized forms. The formation of these ion aggregates is dependent on the dielectric constant of the solvent; the lower the dielectric constant the lower the conductance minima (14). During the course of this study DMSO was added to the acetonitrile in large enough quantities such that the resulting solutions were really mixed solvents. This results in a small change in the dielectric constant of the solvent; calculated on a mole fraction basis the dielectric constant ranges from 36.2 to 39.6. The extent to which this change in dielectric constant will affect the various equilibria is not known. A similar effect will be noted with water. The change when water is added is somewhat larger than with DMSO: 36.2 to 42.4.

Acetonitrile is the most common of the nitrile solvents. The conductance data for the alkali metal perchlorates follows the expected trend in association constants: Li < Na < K < Rb < Cs (15). With the large quaternary ammonium ions the picture is somewhat different. The extent of ion association is determined in part by the dielectric constant of the solvent. In acetonitrile the least associated quaternary ammonium salts are those with large anions. This is the reason why tetraethylammonium perchlorate was used as the supporting electrolyte in this study.

Experimental data relating to the degree of association of nickel (II) perchlorate and other divalent salts in acetonitrile is unavailable at this time. However, data is available on several other salts. The pK value of tetraethylammonium perchlorate, the carrier electrolyte in this study, is 1.05 (14). At the concentration at which this study was made, about 60% of the tetraethylammonium perchlorate is associated. Silver perchlorate is another salt which has been studied in acetonitrile; its pK value is 1.64. Should this data become available, it should be possible to make some of the corrections mentioned in the results and discussion section of this thesis.

CHAPTER V

DETERMINATION OF STABILITY CONSTANTS OF COMPLEXED METAL IONS IN REVERSIBLE, DIFFUSION CONTROLLED SYSTEMS

Introduction

When metal ions in solution complex with ligands other than water, the half-wave potential usually becomes more negative, and the magnitude of the diffusion current usually decreases. The determination of stability constants polarographically involves the determination of the shift in both the half-wave potential and the diffusion current in the presence of increasing amounts of ligand; the shift increases with increasing ligand concentration. One reason for this is the formation of a new species which requires more energy to undergo reduction (7). The increased bulk of the complexed ion can account for the decrease in the diffusion current (7).

The Method of DeFord and Hume

The method of DeFord and Hume (2) for treating polarographic data to determine stability constants is based on the equations described by Leden (16). The reduction process can be written as:

$$n\ e^- + MX_j^{n+} = M(Hg) + j\ X \qquad (24)$$

where j is between zero and the coordination number of the ion. It is impossible to determine which species is being reduced (17). The method is based on the following equations defining successive F functions:

$$F_o = \exp(N\underline{F}/\underline{R}T(E_{\frac{1}{2}})) + \ln(\underline{i}_{d\underline{s}}/\underline{i}_{d\underline{c}}) = 1 + [X]\beta_1 + [X]^2\beta_2 + \ldots [X]^n\beta_n \quad (25)$$

$$F_1 = (F_o - 1)/[X] = \beta_1 + [X]\beta_2 + [X]^2\beta_3 + \ldots [X]^{n-1}\beta_n \quad (26)$$

$$F_2 = (F_1 - \beta_1)/[X] = \beta_2 + [X]\beta_3 + [X]^2\beta_4 + \ldots [X]^{n-2}\beta_n \quad (27)$$

$$\vdots \qquad\qquad\qquad \vdots$$

$$F_n = (F_{n-1} - \beta_{n-1})/[X] = \beta_n \quad (28)$$

where β_j is the overall successive formation constant, [X] is the ligand concentration, and subscripts $\underline{s}$ and $\underline{c}$ correspond to the free metal and complexed metal, respectively. The above equations are valid only for mononuclear complexes with a single ligand, and for systems where the observed shift in half-wave potential is due only to complex formation. The equations can be extended to systems in which there is more than one ligand present (7,17). A study carried out by Laitinen and co-workers (18) showed that clustering of anions, by ion-dipole and electrostatic attractions about the central complex, shifted the half-wave potential in a more negative direction and caused a corresponding decrease in the magnitude of the diffusion current. The dielectric constant was found to have a pronounced effect on the stability of the complexes; the stability constants vary inversely with the dielectric constant (17,19). The effects of ion-pairing and ion-aggregation are unknown. Hence, the formation constants determined in this way are "concentration-constants" and not true thermodynamic constants (17).

The successive values are found by plotting F_j against [X] and extrapolation to [X] = 0. The intercepts are β_1, β_2, ... β_n successively. Such a graphical approach offers a useful method and has been widely accepted. Some points of F_j do not fit a smooth curve, especially in the low [X] region (where the assumption that C_x = [X] is no longer valid). This region is most important for extrapolation.

The Method of Momoki, Sato, and Ogawa

From experimental data and Equation 24, a set of *n* equations in *n* unknowns can be set up (3). Taking the natural logarithm of both sides of Equation 24 we have:

$$\ln(1 + \Sigma\, [X]^j \beta_j) \quad = \quad \ln F_o \qquad (29)$$

The value of $\ln F_o$ can be calculated from experimental data:

$$\ln F_o \quad = \quad N\underline{F}/RT\Delta E_{\frac{1}{2}} + \ln(\underline{i}_{d\underline{s}}/\underline{i}_{d\underline{c}}) \qquad (30)$$

If we let G_i equal the $i^{\underline{th}}$ calculated value of $\ln F_o$, Equation 28 now becomes:

$$\ln(1 + \Sigma\, [X]^j \beta_j) \quad = \quad G_i \qquad (31)$$

Equation 31 must be linear before it can be solved easily. This is done by replacing each unknown beta value by its approximate value, β_{jo}, which is arbitrarily obtained by an initial guess. The deviation of β_{jo} from the true β_j is given by:

$$\beta_j \quad = \quad \beta_{jo} - \Delta\beta_j \qquad (32)$$

Equation 31 now becomes:

$$\ln(1 + \Sigma\ [X]^j\ (\beta_{jo} - \Delta\beta_j)) = G_i \qquad (33)$$

Expanding Equation 33 in a Taylor series and neglecting higher terms we have:

$$\ln[(1 + \Sigma\ [X]^j \beta_{jo}) - ([X]\Delta\beta_1 + [X]^2\Delta\beta_2 + \ldots$$

$$[X]^n\Delta\beta_n)/(1 + \Sigma\ [X]^j\beta_{jo})] = G_i \qquad (34)$$

Equation 34 is now linear in $\Delta\beta_j$.

The values obtained for $\Delta\beta_j$ by solving Equation 34 are inserted into Equation 31 where new values of β_j and β_{jo} are obtained. This process is continued until $\Delta\beta_j$ becomes negligible.

CHAPTER VI

EXPERIMENTAL

Apparatus

All measurements were made in a dry air box with a Sargent Model XXI recording polarograph, using a Sargent Model A iR compensator. The three-electrode cell shown in Figure 4 was used. Each chamber is jacketed for independent temperature control. The reference electrode and the anode are both acetone-saturated calomel electrodes (A.S.C.E.). These electrodes were prepared in the manner described by Arthur and Lyons (11).

Preparations of Reagents

Acetonitrile was prepared for use by passing it over a column of 4 Å molecular sieve. The acetonitrile was then fractionally distilled. Acetonitrile treated in this manner was suitable for polarographic work. The method for purification of acetonitrile described by Cokal and Wise (20) was found to be unsuitable for this work. Their method calls for extracting the acetonitrile with saturated NaOH. The NaOH seemed to cause hydrolysis of the acetonitrile. The hydrolysis reaction was suspected because of a strong odor of ammonia that was noted after the extraction. Ammonia is one of the products of the hydrolysis reaction of acetonitrile (21).

Tetraethylammonium perchlorate was used as the supporting electro-

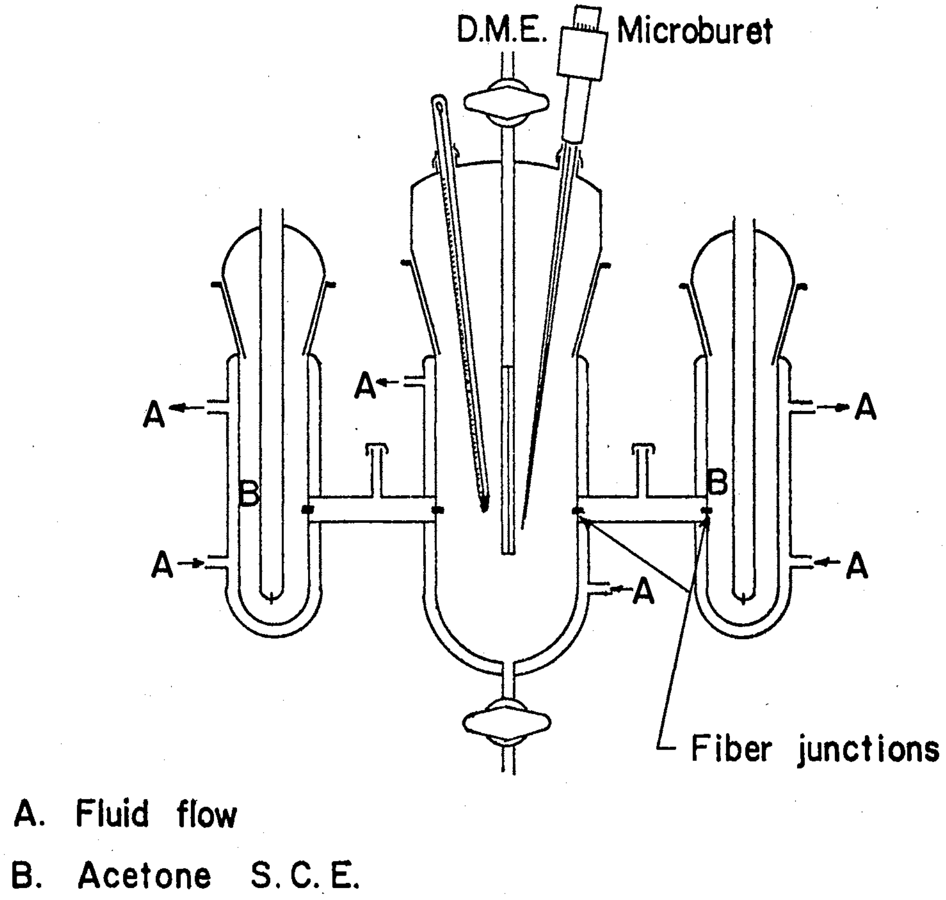

Figure 4. Polarography Cell

lyte (20). Since a maximum was not observed when tetraethylammonium perchlorate was used, but was observed if either lithium or sodium perchlorate was used, it was assumed that the tetraethylammonium perchlorate was acting as a maximum surpressor. The salt was prepared by the method described by Cokal and Wise (20).

Reagent grade DMSO was used without further purification. It was kept dry by storing it over 4 Å molecular sieve.

Reagent grade nickel perchlorate was dried in a vacuum at 50°C. for 24 hours to remove surface moisture and then stored in vacuum. The polarographic solutions were made by weighing out approximate amounts of salts. Nickel was determined after drying by precipitation with dimethylglyoxime (22). Knowing the final nickel concentration and the initial weight of nickel taken, the final volume of the solution can be calculated. Knowing the final volume of the solution and the initial weight of tetraethylammonium perchlorate, its concentration can be calculated. The nickel concentration was about 0.001 M while the tetraethylammonium perchlorate concentration was about 0.1 M. The above solutions were dried in a modified molecular sieve reflux extractor, shown in Figure 5 (23). The water content of the solutions was checked by taking a 50 cc sample and titrating with Karl Fischer reagent. The drying process was continued until the 50 cc sample showed no water content. This corresponds to a water content of less than 10 ppm (24). This drying process took about a week.

General Methods

Water was introduced using a Gilmont 250 microliter syringe until a total volume of 2.00 ml had been added. The syringe was refilled after

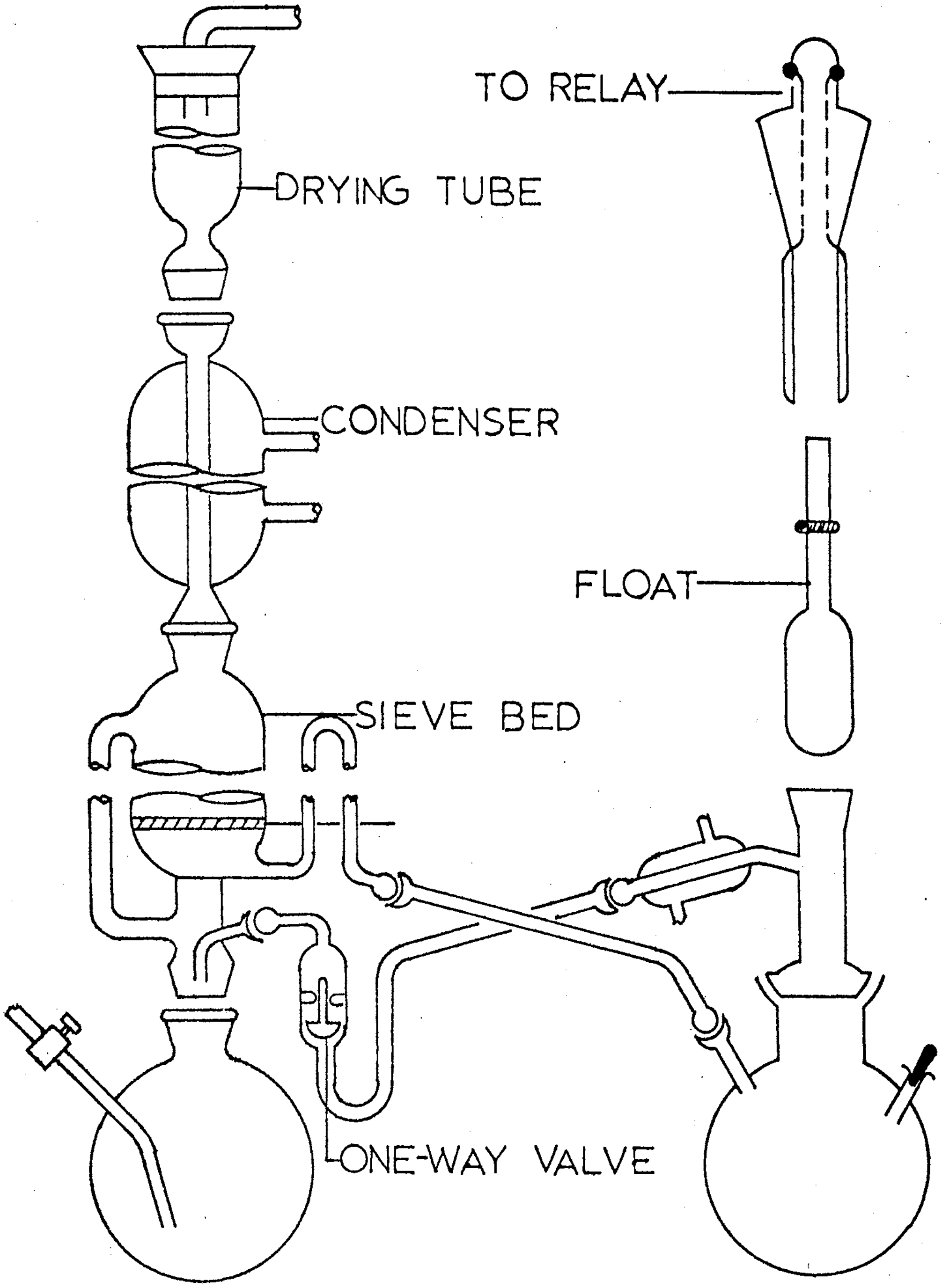

Figure 5. Modified Molecular Sieve Reflux Extractor

each addition. The water concentration in the polarographic cell was varied between 0.122 and 1.791 M.

DMSO was added in the same way, corresponding to a concentration range of 0.077 to 0.600 M. Both the water and DMSO concentration were found by multiplying the volume added by the known density of the liquid in question. It is not known if this is a sound analytical method for determining concentration. Since the metal-ion concentration was approximately 0.001 moles per liter it should be noted that the ligand concentration was always in excess. Polarograms were made after each addition of ligand. All measurements were made at 25 ± 0.2°C.

The half-wave potentials and diffusion currents were found using the method described by Willard, Mertitt, and Dean (25). For the water data the polarograph was set with an initial voltage of 0.00 volts and a span voltage of 0.60 volts. The sensitivity used was 0.30 ua/mm. For the DMSO data the polarograph was set with an initial voltage of -0.10 volts and a span voltage of 0.600 volts. The initial and final potentials were measured to within 0.1 mv. The use of a small span voltage resulted in an expansion of the curve. All current measurements used in the calculations were taken as the average pen excursions.

CHAPTER VII

RESULTS AND DISCUSSION

The values for $E_{\frac{1}{2}}$ and $\underline{I}_d$, the diffusion current constant given by

$$\underline{I}_d = \underline{i}_d / Cm^{2/3} t^{1/6} \qquad (35)$$

where C is the concentration of metal, m the mass of the drop, and t is the drop time, for the DMSO complexes are given in Table I. The calculated logarithm values of F_j are also given and plotted in Figures 6 and 7. The values at zero ligand concentration were found by extrapolation of a plot of $\underline{i}_d$ vs. concentration (26,27,28). The F_j values were calculated at each of the eight ligand concentrations. Only the first four F_j functions were plotted. The other F_j functions did not fit a smooth curve in the low region of ligand concentration.

Since only the first three beta values could be found by the graphical approach, the solution of simultaneous equations was used to obtain the six beta values for the nickel-DMSO complexes. These values are given in Table II along with standard deviations and T-values for each beta value. Since only six of the sixteen data points taken are needed to solve the six equations, a random number process was used to pick any six points with which to make the calculation. This process was repeated five times for each of the two zero points, for a total of ten calculations. The standard deviations and T-values were found using these ten values.

TABLE I

POLAROGRAPHIC DATA FOR NICKEL-DMSO COMPLEXES IN ACETONITRILE

DMSO, M	$-E_{\frac{1}{2}}$, v	$\underline{I}_d$,	Tabulated as Logarithms of the Values						
			F_o	F_1	F_2	F_3	F_4	F_5	F_6
0.000	0.317	3.42	0.00	---	---	---	---	---	---
	0.314	3.37	0.00	---	---	---	---	---	---
0.077	0.352	3.27	0.873	1.924	2.992	3.413	4.053	4.785	5.881
	0.339	3.27	1.207	2.292	3.387	4.332	5.288	6.387	7.497
0.154	0.383	2.95	2.193	3.004	3.817	4.574	5.366	6.144	6.977
	0.377	2.95	2.318	3.127	3.940	4.717	5.470	6.274	7.083
0.231	0.413	2.80	3.308	3.944	4.580	5.207	5.841	6.473	7.107
	0.409	2.71	3.322	3.981	4.617	5.246	5.867	6.504	7.138
0.306	0.435	2.35	3.997	4.512	5.025	5.539	6.053	6.567	7.079
	0.429	2.50	4.155	4.669	5.185	5.699	6.207	6.721	7.233
0.381	0.467	2.41	4.977	5.396	5.816	6.236	6.654	7.072	7.490
	0.457	2.45	5.225	5.644	6.064	6.483	6.902	7.320	7.739
0.454	0.499	1.97	5.832	6.176	6.518	6.862	7.204	7.546	7.890
	0.480	1.92	6.386	6.728	7.107	7.415	7.758	8.100	8.444
0.527	0.505	1.70	6.111	6.389	6.668	6.946	7.223	7.500	7.777
	0.486	1.70	6.674	6.952	7.230	7.508	7.786	8.064	8.342
0.600	0.530	1.65	6.611	6.832	7.057	7.274	7.496	7.718	7.940
	0.530	1.65	7.535	7.757	7.979	8.201	8.423	8.645	8.680

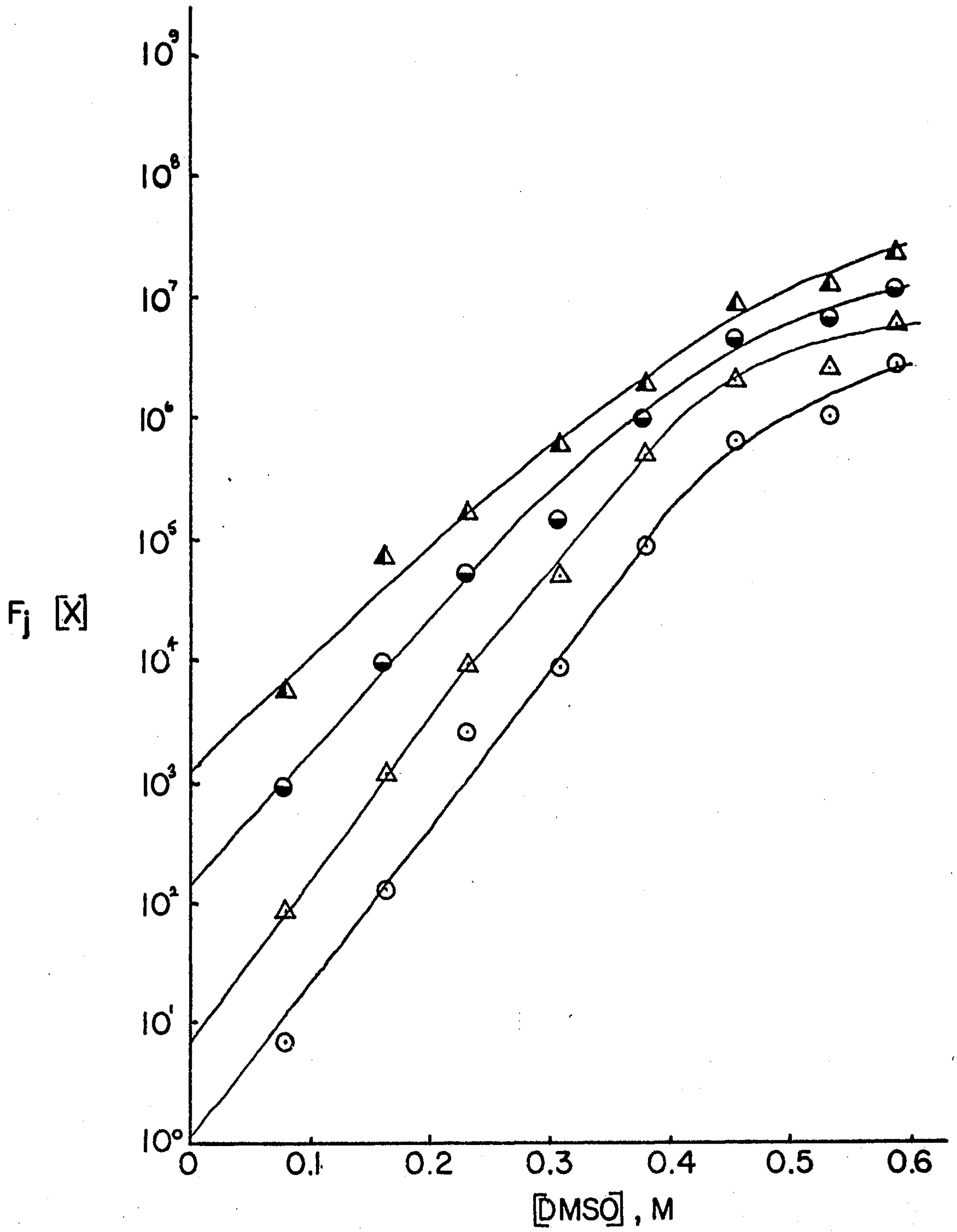

Figure 6. Values of F_j as a Function of Free Ligand Concentration, First Trial

⊙ $F_o[X]$ ● $F_2[X]$
△ $F_1[X]$ ▲ $F_3[X]$

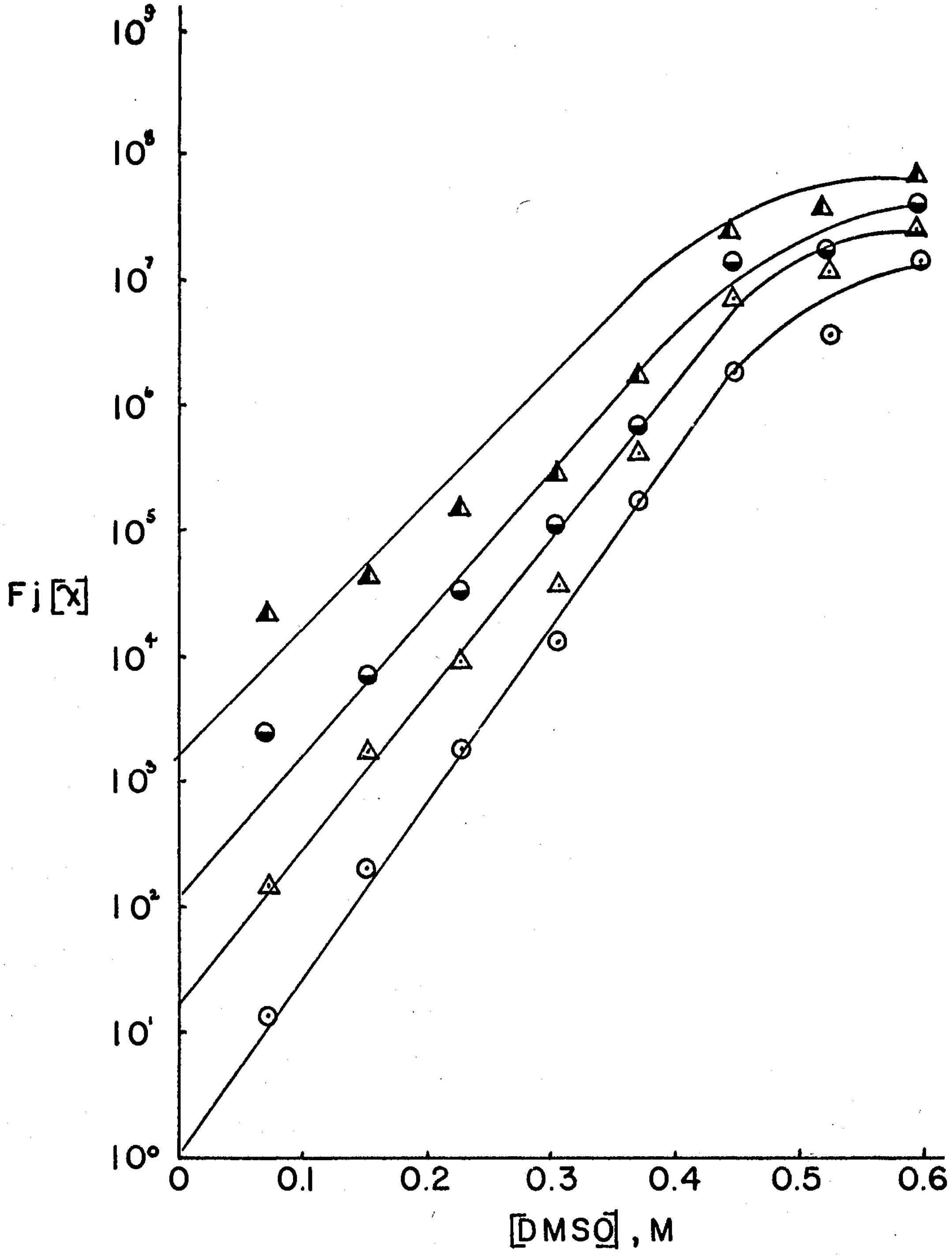

Figure 7. Values of F_j as a Function of Free Ligand Concentration, Second Trial

⊙ F_o ◒ F_2

△ F_1 ▲ F_3

TABLE II

STABILITY CONSTANTS OF NICKEL-DMSO COMPLEXES

Beta Values		T-Values
β_1	8.73 ± 3.77	2.31
β_2	$(7.8 \pm 1.6) \times 10^2$	4.93
β_3	$(1.7 \pm 0.4) \times 10^3$	4.38
β_4	$(6.9 \pm 1.2) \times 10^3$	5.92
β_5	$(2.0 \pm 1.6) \times 10^3$	1.29
β_6	$(7.4 \pm 1.6) \times 10^4$	4.51

The values of α_j and $\bar{n}$ for the DMSO complexes are given in Table III at a series of free ligand concentrations. The α_j values are plotted as a function of the DMSO concentration in Figure 8. This plot shows that at the last ligand concentration taken the sixth complex was the predominate species.

The values of $E_{\frac{1}{2}}$ and $\underline{I}_d$ for the water complexes are given in Table IV. The F_j values were not plotted for the water data. The six β values for the nickel-water complexes are given in Table V along with standard deviations and T-values for each β value. The values were calculated in the same way as the DMSO complexes, however, there were four zero points, which were obtained by extrapolation in the same manner as the zero point for DMSO, giving a total of twenty calculations. The α_j and $\bar{n}$ values for the water complexes are given in Table VI.

The value of $m^{2/3}t^{1/6}$ is 1.51. For all practical purposes this value is insensitive to the drop time since t is taken to the one-sixth power. The drop time does vary with the applied potential, but up to potentials of -1.0 volts this variation is insignificant (25). The drop time was measured for each run.

The T-values show that in the case of the nickel-DMSO complexes all the β values except β_1 and β_5 are statistically significant. However, since the β values for the nickel-DMSO system were calculated using the data taken at one nickel concentration (0.0005 M), and one concentration of tetraethylammonium perchlorate (0.05 M), the effect of changes in the concentration of either species is not known. Activity coefficient corrections were not made since the activity of neither of the above species in acetonitrile was known. The β values for the nickel-water system were calculated at two nickel ion concentrations, 0.0008 M and 0.0005 M,

TABLE III

ALPHA AND $\bar{n}$ VALUES

DMSO, M	α_0	α_1	α_2	α_3	α_4	α_5	α_6	$\bar{n}$
0.077	0.13	0.08	0.63	0.10	0.03	0.00	0.00	1.83
0.154	0.03	0.03	0.57	0.19	0.11	0.00	0.03	2.47
0.231	0.01	0.01	0.43	0.21	0.19	0.01	0.11	3.08
0.306	0.00	0.01	0.27	0.20	0.23	0.02	0.24	3.73
0.381	0.00	0.00	0.18	0.15	0.23	0.03	0.37	4.22
0.454	0.00	0.00	0.12	0.12	0.21	0.03	0.49	4.63
0.527	0.00	0.00	0.08	0.09	0.18	0.03	0.59	4.96
0.600	0.00	0.00	0.05	0.07	0.16	0.03	0.66	5.19

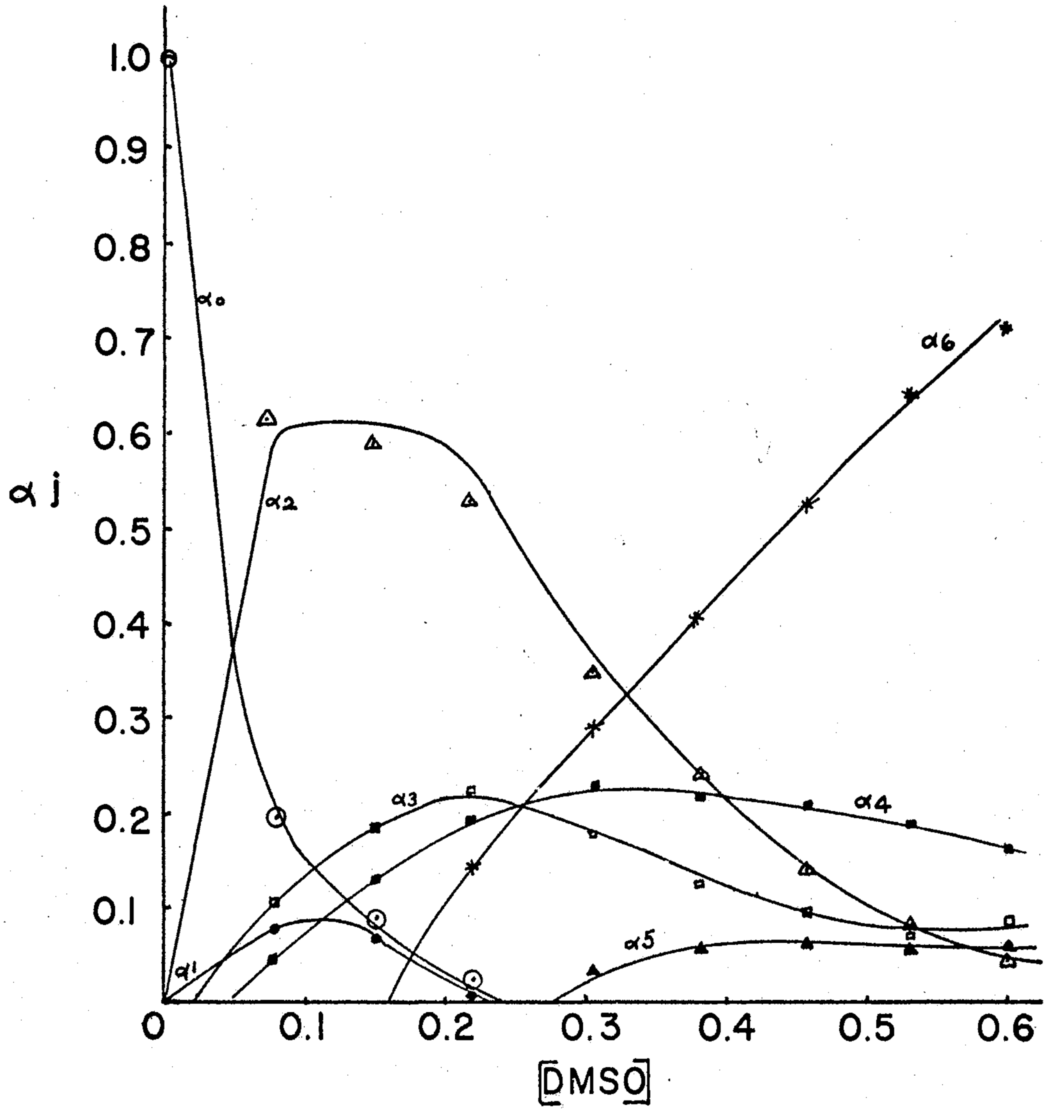

Figure 8. Alpha Values as a Function of the Free Ligand Concentration

TABLE IV

POLAROGRAPHIC DATA FOR NICKEL-WATER COMPLEXES IN ACETONITRILE

H_2O M	$-E_{1/2}$, v	$\underline{I}_d$,
0.000	0.316	3.27
	0.319	3.52
	0.313	3.14
	0.315	3.41
0.122	0.320	3.09
	0.322	3.26
0.184	0.323	2.98
	0.323	3.23
0.245	0.325	2.92
	0.324	3.04
0.366	0.325	2.86
	0.326	2.89
	0.328	2.92
	0.324	3.01
0.489	0.340	2.95
	0.343	2.98
0.609	0.354	2.69
	0.357	2.69
	0.358	2.91
	0.359	2.87
0.730	0.368	2.77
	0.362	2.82
0.849	0.370	2.34
	0.380	2.39
	0.374	2.35
	0.378	2.58
1.206	0.383	2.22
	0.387	2.28
1.791	0.396	1.81

TABLE V

STABILITY CONSTANTS OF NICKEL-WATER COMPLEXES

Beta Values	T-Value
β_1 6.42 ± 5.75	1.12
β_2 $(4.17 \pm 3.0) \times 10^2$	1.38
β_3 $(4.6 \pm 1.7) \times 10^3$	2.73
β_4 $(5.3 \pm 1.8) \times 10^3$	3.05
β_5 $(4.0 \pm 2.7) \times 10^3$	1.51
β_6 $(6.7 \pm 3.2) \times 10^4$	2.11

TABLE VI

ALPHA AND $\bar{n}$ VALUES

H_2O, M	α_0	α_1	α_2	α_3	α_4	α_5	α_6	$\bar{n}$
0.122	0.05	0.04	0.35	0.46	0.07	0.00	0.01	2.49
0.184	0.02	0.02	0.26	0.52	0.11	0.02	0.25	2.91
0.245	0.00	0.01	0.18	0.49	0.14	0.03	0.11	3.18
0.366	0.00	0.00	0.10	0.39	0.17	0.04	0.28	3.96
0.489	0.00	0.00	0.05	0.27	0.16	0.06	0.46	4.32
0.609	0.00	0.00	0.03	0.18	0.13	0.06	0.60	5.00
0.730	0.00	0.00	0.02	0.12	0.10	0.06	0.70	5.29
0.849	0.00	0.00	0.00	0.08	0.08	0.06	0.76	5.47
1.206	0.00	0.00	0.00	0.03	0.04	0.04	0.88	5.76
1.791	0.00	0.00	0.00	0.01	0.02	0.03	0.94	5.90

The corresponding tetraethylammonium perchlorate concentrations were 0.07 M and 0.05 M. The standard deviations for the β values for the nickel-water system are quite large. This could be due to the two different concentrations used or to changes in the dielectric constant as water was added. There is a similar change in dielectric constant as DMSO is added but the affect will be much smaller since the dielectric constants of acetonitrile and DMSO are similar (36.2 and 46 respectively).

The results of this research project are somewhat inconclusive for the following reasons. As was mentioned before the dielectric constant of the solution was changing as the ligand was added. It is not known how this dielectric constant was changing or how this change would affect the various equilibria. There is also the question as to the validity of the method used to determine the ligand concentration. Activity coefficient corrections were not made since the activity of the various species was unknown. Also the extent of formation of ion aggregates or polynuclear complexes is unknown. The results were also calculated using a limited amount of data. Additional data may shed some light on the above problems.

If the above problems can be solved, the polarographic method can be used in any solvent that is not reducible at potentials less negative than the reduction potential of the complex ion. The main disadvantage in working with nonaqueous solvents is the limited solubility of ionic compounds since the carrier electrolyte must be approximately 100 times more concentrated than the reducible ion. The suppression of maxima is another problem area. The choice of maximum suppressor is limited by two factors. The maximum suppressor must not complex with the metal ion of interest and it must be soluble in the solvent of interest. Another potential problem is impurities in the solvent which may give rise to polarographic waves.

The accuracy with which β values can be measured polarographically depends on a number of factors. Klatt and Rouseff (29) pointed out that the important parameter of Equation 25 is $\beta_j[X]^j$. Since for a given system the β's are fixed, the magnitude of the shift in half-wave potentials is determined by the free-ligand concentration range employed. In nonaqueous solutions this is a problem area. If a non-ionic ligand is used the dielectric constant of the solution will change as the ligand is added. If an ionic species is used, the ionic strength of the solution will change due to such things as ion pairing and the formation of ion aggregates. These two conditions limit the intepretation of the polarographic data in nonaqueous solutions. The precision with which the β values can be evaluated is controlled by the [X] range, and errors associated with measuring the shift in half-wave potentials. If the error in measuring half-wave potentials is greater than 1.5 mV small formation constants may not be determined (29).

The polarographic method is usable if the above mentioned problems can be solved and if the following conditions are met. The first condition is that the salt of interest as well as a carrier electrolyte must be soluble in the solvent of interest. A large enough ligand concentration range must be used so that the shift in half-wave potentials will be large enough to be seen. A small metal ion concentration must be used since it is assumed that the total ligand concentration is equal to the free ligand concentration.

In many cases, the polarographic method is one of a very limited number of methods that can be used to study complexes in solution. Some of the other methods that can be used to obtain stability constants include spectrophotometry and potentiometry. The spectrophotometric method depends upon the metal ion having a visible-ultraviolet absorption spectrum which is sensitive to changes in the ligand field. One case where this is not generally true is with the rare earth ions. Potentiometric methods cannot be used in aprotic solvents, such as acetonitrile. It should also be kept in mind that the polarographic method has its own limitations, and before picking one method over another one should consider all the experimental difficulties that are likely to be encountered.

The polarographic method of studying metal complexes based on Equation 25 is limited when compared to the potentiometric method. This is true since the potentiometric method does not require a large ligand to metal ion ratio (29). Errors of comparable magnitude are found in the spectrophotometric and polarographic methods (29,30).

CHAPTER VIII

SUMMARY

The main objective of this research was to extend the polarographic method of stability constant determination to nonaqueous solutions. The system chosen for study was nickel-DMSO and nickel-water complexes in acetonitrile. The shift in half-wave potential for both systems was toward more negative values with increasing ligand concentration. There was also a corresponding decrease in the magnitude of the diffusion current. As was mentioned in the body of the thesis there were a large number of parameters whose affect on the system is unknown, hence, the results of this research are inconclusive. If the problems mentioned in the body of the thesis can be solved the polarographic method could be extended to nonaqueous solutions. The technique should prove useful for a wide range of complexes in nonaqueous solvents, an example of which is the study of rare earth complexes in aprotic solvents.

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APPENDIX

PROGRAM FOR DETERMINING STABILITY CONSTANTS

Line	
18	Reads in the title into a 72 space field for the identification of the output. It is read from a card and is printed out (by line 24) at the top of the output.
19	Reads in the value of the Faraday constant, FAR, the temperature at which the study was made, TEMP, the gas law constant, R, and the number of electrons involved in the reduction process, EN.
20	Reads in the number of beta values we are looking for, N, and the number of data points, M.
21	Reads in the diffusion current, DIO, and half-wave potential, EHO, for the free metal ion, and the metal ion concentration, CM.
22-23	Read in the diffusion current, DI(I), and half-wave potentials, EH(I), at the various ligand concentrations, CL(I).
24-29	Write out the input data for a validity check.
30-38	Set up the right hand side of Equation 24 (see main body of thesis) for the various ligand concentrations.

```
C   THIS PROGRAM CALCULATES STABILITY CONSTANTS FROM
C   POLAROGRAPHIC DATA.  FAR IS THE FARADAY CONSTANT.
C   TEMP, R, AND EN ARE THE TEMPERATURE, THE GAS CONSTANT
C   AND THE NUMBER OF ELECTRONS.  DIO, EHO, AND CM ARE
C   THE DIFFUSION CURRENT, HALF-WAVE POTENTIAL, AND
C   CONCENTRATION OF THE FREE METAL.  DI(I), EH(I),
C   AND CL(I) ARE THE DIFFUSION CURRENT, HALF-WAVE
C   POTENTIAL, AND LIGAND CONCENTRATION FOR EACH COMPLEX.
     1   Format (4F10.2)
     2   Format (2I2)
     3   Format (5E12.5)
     4   Format (18A4)
     6   Format (1H1, 18A4//)
     7   Format (23X, 'DIO',19X,'EHO',19X,'CM')
     8   Format (17X,2X,3(11X,E12.5))
     9   Format (17X,'I',15X,'DI(I)',18X,'EH(I)',18X,'CL(I)')
    11   Format (17X,I2,3(11X,E12.5))
    13   Format (E12.5)
    24   Format (17X,'This is Cycle',2X,I2)
    25   Format (6X,I2,3(11X,E12.5))
    26   Format (7X,1HI,15X,'Beta',17X,'Std. Dev.',12X,'T Value'//)
         Dimension G(10),D(10),DI(10),EH(10),CL(10)
         Dimension FO(10),B(10),DB(10),A(10,10),Beta(10)
         Dimension Dev(10),Var(10),Title(18),Ac(10,10)
         Dimension Std(10),T(10)
         Read(5,4) (Title(I),I=1,18)
         Read(5,1) Far,Temp,R,En
         Read(5,2) N,M
         Read(5,3) DIO,EHO,CM
         Do 5 I-1,M
     5   Read(5,3) DI(I),EH(I),CL(I)
         Write(6,6) (Title(I),I=1,18)
         Write(6,7)
         Write(6,8) DIO,EHO,CM
         Write(6,9)
         Do 10 I=1,M
    10   Write(6,11) I,DI(I),EH(I),CL(I)
C   Calculate right hand side of equation
C
         Con=(En*Far)/(R*Temp)
         Krun=1
         Do 12 I=1,M
         D(I)=DIO/DI(I)
         SDI=D(I)
         G(I)=Alog(SDI)
         G(I)=G(I)+Con*(EHO-EH(I))
         SGI=G(I)
    12   FO(I)=Exp(SGI)
C   Read in guesses
```

<u>Line(s)</u>	
39-40	Read in the trial set of beta values.
41-42	Set up the first term of the left hand side of equation 24.
44-65	Set up and solve equation 24 by Gauss elimination.
66-86	Calculate the standard deviation and T-value for the calculated values of beta.
87-90	Write out the calculated values.

```
       Do 14 I=1,N
   14  Read(5,13) B(I)
C   Setting up first term of left side of equation
C
   30  FT=1.
       Do 16 I=1,N
   16  FT=FT+(CL(I)**I*B(I))
C   Solve equation
C
       Do 17 I=1,N
       Do 17 J=1,N
   17  A(I,J)=CL(I)**J
       Nplus1=N+1
       Do 18 I=1,N
   18  A(I,Nplua1)=(Alog(FT)-G(I))/FT
       Nless1=N-1
       Do 19 K=1,Nless1
       Kplus1=K+1
       Do 19 I=K,Nless1
       Do 20 J=Kplus1,Nplus1
   20  A(I+  J)=A(I+1,JO-A(I+1,K)*A(K,J)/A(K,K)
   19  A(I+1,J)=0.
       DB(N)=A(N,N+1)/A(N,N)
       Do 21 K=2,N
       Kless1=K-1
       DB(N-K+1)=A(N-K+1,N+1)
       Do 22 J=1,Kless1
   22  DB(N-K+1)=DB(N-K+1)-A(N-K+1,N-K+1+J)*DB(N-K+1+J)
   21  DB(N-K+1)=DB(N-K+1)/A(N-K+1,N-K+1)
       Do 23 I=1,N
   23  Beta(I)=B(I)-DB(I)
       S=0.0
       Do 73 I=1,M
       Dev(I)=FO(I)-1.0
       Do 72 J=1,N
   72  Dev(I)=Dev(I)-(CL(I)**J)*B(J)
       Dev(I)=Dev(I)/FO(I)
   73  S=S+Dev(I)**2
       Do 89 K=1,N
       Do 89 J=1,N
       AC(K,J)=0.0
       Do 81 I=1,M
   81  AC(K,J)=AC(K,J)+(CL(I)**K)*(CL(I)((J)/(FO(I)**2)
       Continue
       M2=M-N-1
       Do 74 J=1,N
       I=J
       Var(J)=AC(J,I)*S/M2
       Svar+Var(J)
       Std(J)=Sqrt(Abs(Svar))
       Sbeta=Beta(J)
   74  T(J)=Abs(Sbeta/Std(J))
       Write(6,24) Krun
       Write(6,26)
```

Line(s)	
92-96	Check for convergence of the beta values.
97-99	Set up the new beta values and sends the program back to line 40.

```
         Do 400 I=1,N
   400   Write(6,25) I,Beta(I),Std(I),T(I)
         Krun=Krun+1
         Dscore=0
         Do 27 I=1,N
         If(Abs(DB(I)/B(I)) .LT. 0.0001) Dscore=Dscore+1
    27   Continue
         If(Dscore .Eq. N) Go To 28
         Do 29 I=1,N
    29   B(I)=Beta(I)
         Go To 30
    28   Continue
         Stop
         End
```

VITA

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Master of Science

Thesis: POLAROGRAPHIC DETERMINATION OF STABILITY CONSTANTS IN ACETONITRILE

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