A STUDY OF CHELATING AGENTS AND METAL CHELATES IN NONAQUEOUS SOLVENTS

By

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A STUDY OF CHELATING AGENTS AND METAL CHELATES

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CHAPTER I

INTRODUCTION

Various substances of organic composition such as paints, petroleum, and petroleum products contain trace or larger amounts of metallic components. Reliable analytical methods of analysis are essential since the quality of the finished products depends upon the nature and concentration of the metals present. Although many methods are available for determining cations in water solutions, the water-insolubility of the organic compounds in paints and petroleum products makes it impossible to apply the common methods of analysis directly to the metals in these mixtures.

In the paint industry driers, which are usually heavy metal soaps of organic acids, are sometimes added to paints to accelerate the conversion of the liquid coating to the dry film (43). The concentration of the metals in the paint is rather critical and must be known to a certain degree of accuracy in order to determine the quality and the speed of drying of the paint.

A similar problem exists in the petroleum industry. Various metals that produce destructive effects in the catalytic cracking process by poisoning the catalysts may be introduced into petroleum during the refining and processing procedures. Trace quantities of metals such as copper in gasoline catalyze the oxidative deterioration of the fuel (36). The corrosive effects of some metal compounds on machinery, pipelines, etc. are quite costly, and engine wear is sometimes attributed to the

presence of metals in oils. Not all effects are bad, however. Metallic compounds are sometimes purposely introduced into products such as lubricating oils and gasolines to give them more desirable characteristics. Prime examples of these additives include metal sulfonates which act as detergents and antiknock additives such as tetraethyllead.

For obvious reasons paint and petroleum industries are interested in simple, rapid, and accurate methods for determining the metal concentrations in these products. Since the metals are present in a nonaqueous phase and the addition of water leads to the formation of a heterogeneous system, it is usually necessary to initially get rid of the organic portion in some manner. This usually involves burning off the organic part with subsequent ignition of sample until only an inorganic ash remains. The residue obtained by ashing is then dissolved in acid solution, and the metal concentrations are determined by any one of a number of common analytical methods. Another common separation method is the aqueous acid extraction of the metals from the organic phase. Even though these methods are commonly used, both are laborious and time-consuming due to the fact that they require separation of the metals from the organic phase before the samples can be analyzed for the various cations present.

In order to get around this pre-separation of the metals from the organic phase several direct methods of analysis have been developed. Among these is a polarographic method in which the concentration of metals in driers is calculated from their diffusion currents by reference to calibration data obtained from a standard solution of the drier of known metal concentration under the same conditions (29). A blank correction for a supporting electrolyte must also be made under the same conditions.

Several emission spectrographic methods have been developed which

differ mainly in the method of introduction of sample into the arc, spark, or flame. These methods are advantageous in that the sample does not have to be previously ashed, but they do require the use of calibration standards and rather expensive equipment. Inter-element interference also presents some problems.

The use of atomic absorption spectrometry in the direct analysis of lubricating oils is one of the more recently developed instrumental methods. Burrows and co-workers (10) analyzed such substances by spraying a solution of the oil in 2-methyl-4-pentanone directly into the flame. The use of calibration standards was required, and it was found that the oil concentration affected the absorbance obtained with the various metal solutions. For this reason it was necessary to incorporate metal-free oil in the standard solutions. It was reported that inter-element interference was negligible.

With the increasing popularity and use of chelating agents such as (ethylenedinitrilo)tetraacetic acid (EDTA) came the development of titrimetric methods for analyzing the above mentioned products. The first of these methods was applied to the ash residues or extraction concentrates. Later developments in the use of EDTA titrations bypass the prior ashing of the sample and use procedures in which the metal driers or oil samples are dissolved in a suitable organic solvent or in an aqueous-organic mixed solvent. An aqueous buffer solution and an excess of an aqueous EDTA solution are added to the samples. Metal concentrations are determined by backtitration of excess EDTA with standard metal solution using Eriochrome Black T as indicator. The main difficulty encountered in these mixed solvent systems is turbidity (due probably to separation of the oil phase when water is added) which makes detection of the end-

points difficult in some cases.

A literature search revealed no investigations in which chelating agents such as EDTA and related chelating agents were prepared in organic solvents for use as titrants. This is probably due to the extremely low solubility of this type of compound in nonaqueous solvents. It is quite possible that easier methods for determining metal ions in water-insoluble organic products could be developed if more were known about the nature of these reagents in nonaqueous solvents.

CHAPTER II

HISTORICAL

Chelating Agents in Aqueous Solutions

Ligands in general can be classified according to the number of points of attachment their molecules possess for metals as monodentate, bidentate, etc. Monodentate ligands such as NH_3 normally are not very satisfactory as quantitative analytical reagents due to the stepwise formation of numerous complexes and the tendency of these complexes, particularly the higher ones, to dissociate with dilution (35). The greatest success has been obtained with chelating agents, which are polydentate ligands in which the points of attachment are such that they form very stable five- or six-member rings with the complexed metal. Thus certain polyamines tend to form complexes in which the coordination requirements of metals are more nearly satisfied in 1:1 or 2:1 ligand-to-metal ratios. For example, diethylenetriamine, a tridentate ligand, reacts with copper(II), zinc(II), cadmium(II), and nickel(II) to form two such complexes (13, 26, 35). Higher homologs, such as triethylenetetramine or tetraethylenepentamine, form only 1:1 complexes, and therefore, have been used as titrants in metal analysis. The use of polyamines has been restricted to the determination of those cations which show a strong tendency to coordinate through basic nitrogen, e.g., copper(I and II), cobalt(II and III), zinc(II), cadmium(II), and mercury(II) (50).

The incorporation of carboxylic acids into the polyamine structure led to the development of chelating agents such as (ethylenedinitrilo)-

tetraacetic acid (EDTA). This hexadentate ligand can form, with many metals, chelates of the type shown in Figure 1. The presence of a number of chelate rings tends to make these complexes very stable. Since the introduction of such chelating agents the applicability of EDTA titrations has been extended to the determination of some fifty elements either directly or indirectly (49). Books, which give detailed procedures for metal analysis, have been written on the uses of EDTA (15, 50, 56).

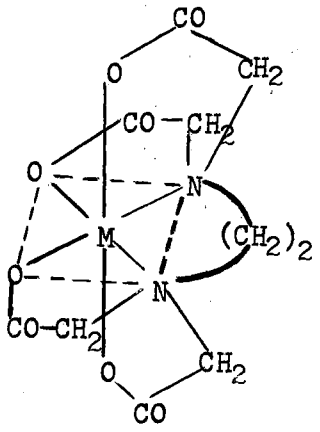


Figure 1. A Typical Metal-EDTA Chelate

An interesting analogue of EDTA, trans-(1,2-cyclohexylenedinitrilo)-tetraacetic acid (CDTA), was synthesized by Schwarzenbach and Ackerman (51) in 1949. Investigations have shown that the metal chelates of CDTA are usually more stable than the EDTA complexes, but the reaction rate of CDTA is usually slower. Since CDTA has been found to have very few advantages over EDTA as a titrant, it has not been investigated as extensively. It, however, has been used in analysis of a few metals (18, 21, 24, 28, 30) and in a few polarographic investigations (23, 48).

A number of chelating agents are now available, and the stability constants of a number of metal chelates in aqueous solution have been

tabulated (52). Holloway and Reilley (22) determined the metal chelate stability constants for a number of polydentate ligands potentiometrically using a mercury indicator electrode. Books have been written on the aqueous chemistry of chelating agents and metal chelates (14, 34).

Analytical Determinations with Chelating Agents in Mixed Solvent Systems

The use of chelating agents in aqueous-organic solvents has not been extensively investigated. Most investigators chose such media to increase the solubility of the metal chelates, to increase the sensitivity of the Eriochrome Black T endpoint, or to make direct analysis of metal ions in organic solutions possible.

Pflaum and co-workers (44) used the chelating agent 2,2'-biquinoline in the analysis of copper samples. The solvent, 50% water-50% dimethylformamide, served as the reductant in the reduction of copper(II) to copper(I). Copper concentrations were determined spectrophotometrically from absorbance values of the copper(I)-2,2'-biquinoline complex and calibration curves. This method eliminated the extraction of the complex from the aqueous phase which was necessary in the determination of copper with 2,2'-biquinoline in n-amyl alcohol (19).

It has been reported that the indicator, Eriochrome Black T, forms very strong complexes with some metal ions in aqueous solutions (50). Due to this fact, the direct titration of such solutions with EDTA results in very poor endpoints since the replacement of the indicator by EDTA may be very slow. Kiss (27) reported that Eriochrome Black T could be used satisfactorily in the determination of such metal ions in mixtures of water and organic solvents. In his investigations an excess of aqueous EDTA solution was added to the aqueous solutions of copper(II), cobalt

(II), aluminum(III), nickel(II), and iron(III). The solution was then buffered to a pH of 10, with an aqueous buffer and an organic solvent, such as methanol, ethanol, or acetone, was added so that the solution contained about 50%-70% organic solvent. After the addition of a small amount of Eriochrome Black T, the excess EDTA was titrated with a standard aqueous metal solution. The investigator reported that the color change at the endpoint became sharper with increasing concentration of organic solvent, but he did not infinitely increase the concentration of the organic solvent owing to the trouble caused by the lower solubility of the metal-EDTA complexes in the organic liquids employed.

Effects of the organic solvents on the Eriochrome Black T endpoint were not completely elucidated by Kiss (27). It seemed that effects other than that of the dielectric constant of the organic solvents were influencing the color change of the indicator employed. In a discussion on the determination of iron, the investigators stated that the functional groups of the organic solvents employed were theoretically capable of coordinating with the metal ion, and that the solvent molecules may actually enter the coordination sphere to produce a complex that is more stable kinetically toward the indicator (32).

The determination of zinc(II) with diphenylthiocarbazone (dithizone) usually involves the extraction of the metal complex from an aqueous phase into an organic phase, but Vallee (55) determined zinc(II) directly in a 1:1 water-methyl cellosolve solution by a spectrophotometric method. It was necessary to measure the absorbance of the metal chelate samples within fifteen minutes after addition of dithizone because the color of the solutions slowly faded after longer periods of time.

Gerhardt and Hartmann (16) developed a method for the direct determination of calcium and zinc additives in lubricating oils and

concentrates. Samples were dissolved in acetone to which was added aqueous buffer solution and an excess of a standard aqueous EDTA solution. The resulting solutions, which contained greater than 70% organic solvent, were back-titrated with standard magnesium chloride. A slight cloudiness of solutions sometimes resulted, but quantitative results were reported.

Analysis for metals such as calcium, cobalt, zinc, lead, and manganese in paint driers has been reported (31). The drier samples were dissolved in a small amount of benzene, diluted with alcohol, then determined by the back-titration method in solutions which were approximately 50% water. Total iron(II) and iron(III) concentration of paint driers was determined by the same procedure in alcohol-water solutions (32). pH adjustment of the solution was necessary in order to chelate quantitatively both oxidation states of iron. With iron and cobalt samples it was necessary that the solutions contain at least 50% alcohol and the back-titrations be completed within approximately two to three minutes to prevent indicator blocking.

Analytical Determinations with Chelating Agents in Nonaqueous Solvents

Several spectrophotometric determinations in nonaqueous solvents have been reported which involved either the precipitation of the metal chelate followed by dissolution in an organic solvent or the extraction of the metal chelate from the aqueous phase into the organic phase prior to analysis of the samples. Examples of such investigations are given below. Chelometric titrations performed directly on the cations in organic solutions are relatively few in number. Most of the chelating agents studied under such conditions are those which are more soluble in nonaqueous solution than in aqueous media.

Chromium(III) has been determined spectrophotometrically in a 1:1 benzene-chloroform solution following a chromatographic separation (6). It was first precipitated as its 8-hydroxyquinolate or 8-hydroxyquinaldate, dissolved in chloroform, diluted with benzene, and passed through an activated alumina column to separate it from other metals. The concentration was determined from the optical density of the eluate. Copper(II) was determined in a similar manner (7). The method differed somewhat in that the copper-8-hydroxyquinaldate complex was extracted from aqueous solution into chloroform prior to the chromatographic separation.

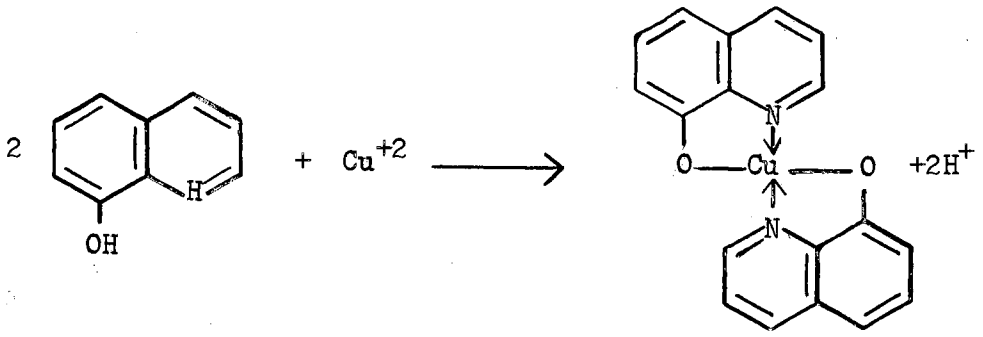
Marple and co-workers (33) reported a photometric method for the determination of zinc(II) in lubricating oils. The oil samples were diluted with benzene containing 8% methanol, and aliquots of this solution were titrated with dithizone. A small amount of ammonium acetate was added to the solutions to prevent fading of the excess dithizone color, the effect being attributed to the action of ammonium acetate as a buffer in the stabilization of the excess dithizone. These workers stated that in the titration curves there was some indication of competition between the additive and the dithizone for the zinc. However, results that agreed with polarographic assays were reported.

Spectrophotometric titrations of copper(II), zinc(II), cadmium(II), nickel(II), lead(II), and uranyl ion with 8-quinolinol were investigated in dioxane-n-propyl alcohol mixtures and in dimethylformamide (8). It was reported that the presence of an organic base enhanced the completeness of the reaction considerably. Copper, zinc, and cadmium could be determined quantitatively, but it was reported that cadmium, nickel, lead, and uranyl ion showed evidence of reaction with more than two moles of 8-quinolinol. These metal chelates were soluble in the organic solvents.

Copper(II) ions in 0.0015M acetic acid solution in dimethylformamide and nickel(II) ions in a dimethylformamide solution made basic with n-butylamine were titrated spectrophotometrically with 1-nitroso-2-naphthol in dimethylformamide (53). Zinc(II), lead(II), and uranyl ions showed evidence of chelation with the titrant in dimethylformamide, but the absorbance of these chelates overlapped that of the chelating agent. It was found necessary that solutions of the titrant be freshly prepared before the titrations because the titrant gradually decomposed in dimethylformamide.

Behm and Robinson (5) used a 1:1 chloroform-isopropyl alcohol solvent system in the spectrophotometric titrations of several divalent metals with dimethylglyoxime. It was reported that nickel(II) could be titrated in solutions made basic with n-butylamine with an average error of 2%. An average error of 3% was obtained in the titrations performed on cobalt (II) solutions made basic with cyclohexylamine.

The nonaqueous indirect potentiometric titrations of nickel(II), cobalt(II), and copper(II) with dimethylglyoxime, dithizone, 8-quinolinol and 1-nitroso-2-naphthol have been reported (9). The aqueous metal samples were evaporated on a steam bath and then dissolved in 20% methanol-80% benzene solution. An excess of chelating agent was added. A typical equation for the reaction of a chelating agent with a metal ion is that of 8-quinolinol with copper(II):



The hydrogen ions liberated in the reaction were titrated with standard sodium hydroxide in benzene-methanol solution, and the endpoints were determined graphically from plots of millivolts vs. milliliters of titrant.

Complex Formation in Nonaqueous Solutions

The influence of the solvent on the composition and stability of complexes in solution has not been investigated thoroughly though several different systems have been studied and stability constants for certain complexes have been determined in nonaqueous solutions. Curtis and Burns (11) passed gaseous ammonia through isoamyl alcohol solutions of various metals and isolated precipitates of the following composition: $CoCl_2 \cdot 3NH_3$, $ZnCl_2 \cdot 2NH_3$, $CuCl_2 \cdot 2NH_3$, and $CdI_2 \cdot 2NH_3$. German and Jamsett (17) studied ammine formation in ethanol and methanol by conductometric titrations. They reported that silver coordinated with two molecules of ammonia in both solvents, while compounds of indefinite composition precipitated from alcoholic solutions of mercuric chloride. Their conductivity curves indicated the formation of a monoammine of nickel(II) chloride in ethanol and of a diammine in methanol. A 1:2 copper-to-ammine complex precipitated from ethanol, and there was evidence of a 1:3 complex in methanol solution. Coordination numbers of six, six, four, two, and four were found for iron(III), cobalt(II), nickel(II), antimony(III), and bismuth(III), respectively, in compounds which precipitated from ammoniacal solutions of the corresponding metal chlorides in ethanol, in amyl alcohol, and in ether (47).

Jonassen and co-workers (25) studied the effect of the dielectric constant on the stability of $Ag(C_2H_5NH_2)_2^+$ complexes and found that there was an increase in the stability of the complexes with decreasing dielectric constant in the solvents water, ethanol, and 2-propanol.

Popa and co-workers (46) found that the stability of complexes of silver with methylamine, dimethylamine, diethylamine, and piperidine increased in a non-linear fashion with increasing concentration of methanol in methanol-water solutions. This non-linearity was interpreted as being due to the unequal influence of the solvent on the activity coefficients of the ions in solution.

Complex formation of metals with monoethanolamine in ethanol was studied conductometrically by Pinkston and Briscoe (45). Their data indicate the formation of complexes with 1:1 and 1:3 ratios of copper(II) to ethanolamine. A 4:1 monoethanolamine-to-cobalt(II) complex was reported.

Cadmium, lead, and zinc complexes of monoethanolamine (MEA) in ethanol solutions were studied polarographically at a dropping mercury electrode by Migal' and Serova (39). The reference electrode for solutions in 97% and in absolute alcohol respectively, consisted of absolute ethanol saturated with ammonium chloride and mercurous chloride. As would be expected, the half-wave potentials of the complexes became increasingly more negative with increasing concentrations of monoethanolamine. The compositions of the complexes were determined and it was reported that in more concentrated solutions of ethanol the lower coordinated complexes such as $Cd(MEA)_2^{+2}$ were not present but that higher coordination complexes such as $Cd(MEA)_5^{+2}$ appeared. The stability of these complexes was reported as increasing with increasing ethanol concentration.

A similar study of the diethanolamine (DEA) complexes was conducted by Migal' and Serova (40). In absolute ethanol the higher complexes, $Cd(DEA)_4^{+2}$ and $Zn(DEA)_4^{+2}$, appeared. The stability of the complexes also increased with increasing ethanol concentration, the increase being particularly marked at 80% ethanol. This increased stability was attributed by the investigators to changes in the solvate sheath of the metal ion at the

higher alcohol concentrations.

Migal' and Tsiplyakova have studied cadmium-thiourea complexes in methanol and in ethanol solutions (41, 42). They reported that increased concentrations of the alcohols led to an increase in the stability of the complexes, the greatest increase in stability again being observed in solutions containing over 80% alcohol. In aqueous methanol and in absolute methanol solutions a complex with coordination number five was reported, while in ethanol the highest coordination number reported was four. In absolute ethanol the investigators detected only one complex, $[Cd(thio)_4]^{+2}$.

Complex formation of formamide with cadmium, lead, and zinc ions in absolute ethanol and in methanol was studied polarographically by Migal' and Grinberg (38). The degree of complex formation and the stability constants for the dominant species were greater in ethanol than in methanol.

Pyridine complexes of nickel(II) and cobalt(II) were studied spectrophotometrically in methanol, ethanol, n-propanol, n-butanol, and acetone (1). It was noted that the stability of the predominant species was greatest in acetone and increased from methanol to n-butanol in the alcohol series. A small amount of water added to the solutions decreased the stability considerably. The investigators stated that the stability of complex compounds depends not only on the dielectric constant, but also on the chemical nature of the solvent.

Ablov and Nazarova (2) studied copper(II)-pyridine complexes in organic solutions containing 0.01-0.1% water. The stability of the monopyridine-copper complex increased in the different solvents in the order methanol, ethanol, and acetone.

Mead, Maricle, and Streuli (37) determined the stability constants of silver-amine complexes in acetone. The silver ions were generated coulometrically, and potentiometric data was collected using a quinhydrone

reference electrode and a platinum wire electroplated with silver as the indicator electrode. The stability constants of silver-amine complexes in acetone were found to be two to four orders of magnitude greater than values obtained in aqueous systems. Activity coefficients were not determined or estimated so the constants are not thermodynamically significant.

Uitert and co-workers (54) studied the chelation of nickel(II) by acetylacetone, malonates, and β-keto esters in ethanol solutions. From potentiometric data, they calculated formation constants of the nickel (II) chelates of acetylacetone and some β-keto esters.

Approximate values of the stability constants of the chelates of cadmium(II), zinc(II), and nickel(II) with 2,4-pentanedione in anhydrous ethanol were reported by Day and Rouayheb (12). The constants were calculated from data obtained in the potentiometric titrations of the hydrogen ions liberated in the reactions of the chelating agent with the metal ions.

CHAPTER III

SCOPE OF INVESTIGATION

In the investigation reported here, an attempt was made to develop a simple method for the direct determination of metals in organic media. The method was to be such as to eliminate the need for any pre-separation of the metal from the organic phase in the analysis of such substances as paint driers, petroleum, petroleum products, etc.

In the beginning there was no special interest in any particular chelating agent. The main objective was to find a reagent or reagents that could be used in analytical determinations in nonaqueous media. To serve its purpose, the chelating agent needed to meet the following requirements:

1. It should be soluble in an organic solvent such as 2-propanol which is miscible with petroleum products.

2. It should react stoichiometrically with the metal ions so that a basis for calculation exists.

3. It should react sufficiently rapidly so that a titration can be performed in a reasonable length of time.

4. It should form complexes of sufficient stability that poor endpoints caused by dissociation would be avoided.

5. It should be of such nature that a simple method for locating the endpoint could be devised.

The proposed method consists mainly of dissolving the sample in a suitable organic solvent, adding a complexing agent to keep the metals in

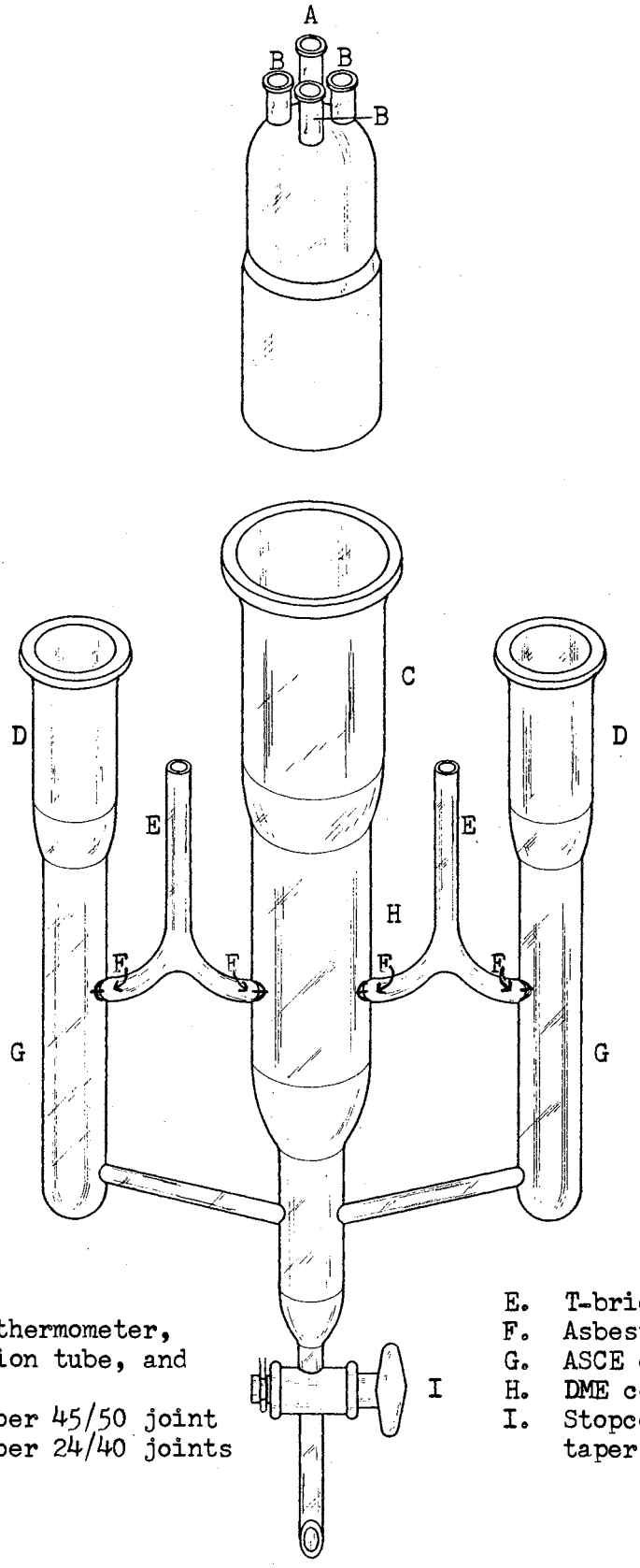
solution, and titrating with a suitable chelating agent prepared in an organic solvent. Amperometric methods were chosen for endpoint detection.

CHAPTER IV

APPARATUS

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

The polarographic cell used in the earlier exploratory studies was a three compartment polarographic cell for use in nonaqueous polarography (Sargent Catalog No. S-29322). To meet the demands of later experiments some changes were made in the design of the standard polarographic cell. Inverted T-tubes separating the main solution compartment from the reference electrode compartments were added to slow the diffusion of ions from the side compartments to the main compartment. The T-tubes were filled with fresh supporting electrolyte solution during each polarographic run. The lower part of the center compartment was constricted in diameter so that smaller volumes of solution could be used. A diagram of this polarographic cell is shown in Figure 2.



A. DME inlet
B. Inlets for thermometer, gas dispersion tube, and burette tip
C. Standard taper 45/50 joint
D. Standard taper 24/40 joints
E. T-bridging tubes
F. Asbestos fibers
G. ASCE compartments
H. DME compartment
I. Stopcock - standard taper #2

Figure 2. Polarographic cell

CHAPTER V

REAGENTS

2-Aminoethanol. Eastman Organic Chemicals white label grade was distilled under nitrogen and stored in dark bottles.

Ammonia. Matheson, Coleman and Bell tank nitrogen was used without further purification.

Ammonium Nitrate. Allied Chemical purified grade was used without further purification.

n-Butylamine. Matheson, Coleman and Bell white label grade was distilled under nitrogen and stored in brown bottles.

Cadmium Nitrate Tetrahydrate. Fisher Scientific reagent grade was used without further purification.

Calcium Chloride. Mallinckrodt anhydrous reagent grade was used without further purification.

Calcium Nitrate Tetrahydrate. J. T. Baker reagent grade was used without further purification.

Cupric Chloride. Allied Chemical anhydrous reagent grade was used without further purification.

Cyclohexylamine. Eastman Organic Chemicals white label grade was used without further purification.

(1,2-Cyclohexylenedinitrilo)tetraacetic Acid. Matheson, Coleman and Bell practical grade was used without further purification.

Diethylenetriamine. Eastman Organic Chemicals technical grade was vacuum distilled at a low constant pressure. The fraction distilling at

83-88°C was used in experimental work.

Diethylenetriaminepentaacetic Acid. K and K Laboratories, Inc. reagent was used without further purification.

Disodium Dihydrogen 1,2-Cyclohexanediaminetetraacetate. Hach Chemical Company reagent was used without further purification.

Disodium Ethylenediaminetetraacetate. Fisher Scientific reagent grade was used without further purification.

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

(Ethylenedinitrilo)tetraacetic Acid. J. T. Baker reagent grade was used without further purification.

Lead Chloride. J. T. Baker reagent grade was used without further purification.

Lead Nitrate. J. T. Baker reagent grade was used without further purification.

Lithium Chloride. J. T. Baker reagent grade was used without further purification.

Lithium Hydroxide. City Chemical Corporation purified grade was used without further purification.

Lithium Nitrate. J. T. Baker reagent grade was dried overnight in the oven at 120°C before use.

Magnesium Nitrate Hexahydrate. J. T. Baker reagent grade was used without further purification.

Mercuric Nitrate Monohydrate. J. T. Baker reagent grade was used without further purification.

Mercury. Bethlehem Instrument triple-distilled mercury was used without further purification. After use, the mercury was thoroughly washed, dried with acetone, filtered, oxified, and vacuum distilled.

Methanol. Fisher Scientific reagent grade was distilled once before use.

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

Nitrogen. Linde laboratory grade nitrogen was used after purification by the method described by Arthur (4).

2-Propanol. Fisher Scientific reagent grade was distilled before use.

Silver Nitrate. J. T. Baker reagent grade was used without further purification.

2,2,4-Trimethylpentane. Matheson, Coleman and Bell white label grade was used without purification.

Zinc Nitrate Hexahydrate. J. T. Baker reagent grade was used without further purification.

CHAPTER VI

EXPERIMENTS AND DISCUSSION

Exploratory Studies

Metal chelate formation was studied polarographically at a dropping mercury electrode (DME), information about the reaction between selected metal ions and selected chelating agents being obtained from the polarograms. Since the half-wave potential ($E_{\frac{1}{2}}$) is characteristic of the species being reduced at the dropping mercury electrode, it can be used to identify the species present in the solution. Thus when metal ions undergo complex formation, the half-wave potential of the complex normally is found to be more negative than is true for the solvated cation (see Figure 3). The extent to which the half-wave potential is shifted depends upon both the nature and the stability of the complex and upon the concentration of free ligand. Since the diffusion current or wave height is proportional to the concentration of the species that is being reduced, this, too, aids in determining whether or not the chelating agent reacts with metal ions quantitatively.

During the course of this study, several different cations were titrated amperometrically with the selected chelating agents. The polarographic cell which was used has been described in Chapter IV. The basic steps in the experimental procedure employed in performing the amperometric titrations are listed below.

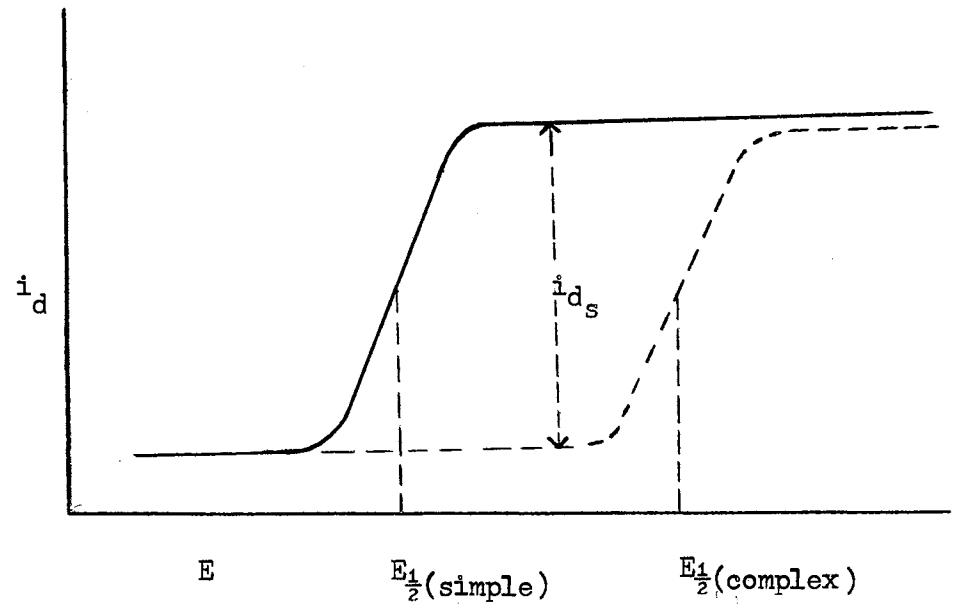


Figure 3. A Typical Polarogram

1. Transfer a measured volume of the metal ion solution containing carrier electrolyte to the polarographic cell.

2. Degas the solution approximately 30 minutes.

3. After degassing, put supporting electrolyte solution in the inverted T-bridging tubes and stopper with small septums. Release the pressure in the T-tubes by using a hypodermic needle inserted through the septum.

4. Pour saturated acetone-calomel solution into the electrode compartments and insert the electrodes.

5. Start mercury flow in the dropping mercury electrode. Rinse the electrode with solvent and wipe dry with Kimwipe. Lower the dropping mercury electrode into the polarographic cell.

6. Obtain a polarogram of the simple metal ion in the solution.

7. Titrate with the chelating agent, adding the reagent in small portions and obtaining polarograms after each addition of titrant.

8. After the titration is completed, remove the dropping mercury electrode from the solution, rinse well with 2-propanol, immerse the tip of the dropping mercury electrode in 2-propanol in a test tube and stop the mercury flow.

In performing these amperometric titrations, complete polarograms were obtained after each addition of titrant so that appropriate voltages for current measurements could be selected. The diffusion current of the simple ion at the chosen potential was plotted versus milliliters of titrant added, corrections for dilution being made in the current.

For successful titrations, curves of the type shown in Figure 4 were obtained. In these the diffusion current decreases linearly with increasing volume of titrant added and since none of the titrants used yields a diffusion current, the current measured past the endpoint is only the residual current.

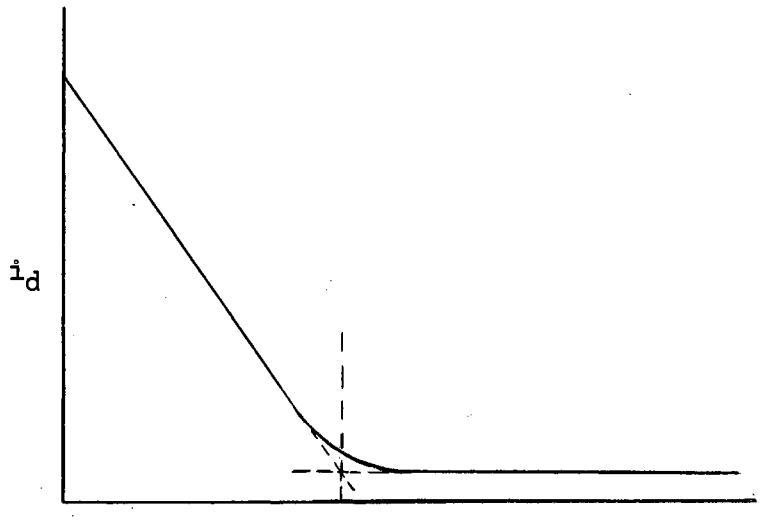


Figure 4. Amperometric Titration Curve

The chelating agents used in the early stages of the investigation

were selected from those readily available rather than because of any special interest in any particular chelating agent. The main objective was to find suitable chelating agents for analytical determinations in organic solvents. This resulted in the study of EDTA, CDTA, and the disodium salts of these compounds. Even though these reagents have been widely used in quantitative analysis in aqueous solutions, knowledge of the organic chemistry of polyaminocarboxylic acid chelating agents is limited. Aiken (3) attributes this partly to the tendency of workers to concentrate on the inorganic chemistry of these compounds due to their ability to form strong complexes with metals and partly to the reluctance of such compounds to undergo typical organic reactions.

Solubility Problems with CDTA. In the course of this study it was found that the compounds mentioned above are only very slightly soluble in organic solvents. Millimolar solutions of the disodium salt of CDTA represented the maximum concentration that could be prepared in methanol while the other reagents seemed to be even less soluble. Since lithium salts are usually more soluble than sodium salts in organic solvents, it was decided to try to prepare the lithium salt of CDTA. Solid LiOH was added to CDTA in a 2:1 ratio (LiOH to CDTA) in methanol, 2-propanol, and a mixture of methanol and 2-propanol. These lithium salts were found to be soluble only to the extent of about 10^{-3}M in methanol and in 60% methanol-40% 2-propanol, and the solubility seemed to be even lower in 2-propanol. Since such concentrations are not great enough for general analytical determinations, these compounds were not investigated further at this time.

Studies with Dien. Owing to its ready solubility in organic solvents and its well-known properties as a chelating agent, diethylenetriamine (dien) was next tried. The compound was dissolved in 2-propanol for use

as a titrant. Fifty ml of 10^{-3}M $Cd(NO_3)_2$ in 2-propanol was titrated amperometrically with approximately 10^{-2}M dien solution. Both solutions contained 0.1M $LiNO_3$ as the supporting electrolyte. Aqueous saturated calomel electrodes (SCE) were used as reference electrodes. The polarogram of the original solution showed one polarographic wave at about -0.42V vs. SCE. The polarogram made after the first addition of titrant had three waves. The first two waves overlapped to some extent, and the third wave (the one with the most negative $E_{\frac{1}{2}}$) exhibited a maximum. As more titrant was added, the first two waves seemed to overlap even more. After the addition of enough titrant to exceed a 2:1 dien-to-Cd(II) ratio, only the third wave remained. The height of this complex wave was about 0.9 that of the original simple cadmium wave. The first wave seemed to be due to uncomplexed Cd(II), and the second one was probably due to a moderately stable complex, possibly of a 1:1 type. The third wave was probable due to a much more stable 2:1 dien-to-Cd(II) complex.

Titration of a 50-ml sample of 10^{-3}M $CuCl_2$ in 2-propanol solution was performed in a similar manner, 0.1M LiCl being used as the supporting electrolyte. The polarogram of the Cu(II) solution showed a polarographic wave with a maximum, the maximum appearing around zero potential vs. SCE. After the first addition of titrant, a polarographic wave appeared at about -0.06V vs. SCE followed by a wave with a maximum. The wave with the maximum was very uneven. This may have been due to the formation of chlorocomplexes and/or to reduction products as noted by Haynes (20) in the study of copper(II)-amine complexes. The first wave became smaller with addition of more dien and disappeared after the addition of enough dien to form a 2:1 dien-to-Cu(II) complex. The solution changed in color from yellow-green to green to blue with addition of dien.

Due to difficulties encountered in trying to obtain a suitable simple

zinc wave, a reverse titration was performed. A 50-ml sample of 2.7 x 10^{-3}M dien solution in 2-propanol was titrated with 10^{-2}M $Zn(NO_3)_2$ in the same solvent. Tenth molar $LiNO_3$ was the supporting electrolyte. The dien solution did not give a polarographic wave. At about -1.4V vs. SCE a polarographic wave with a maximum appeared with the first addition of titrant. After enough Zn(II) had been added to make the dien-to-Zn(II) ratio smaller than 2:1 another polarographic wave appeared around -1.1V vs. SCE. Judging from the difference in the half-wave potentials of the two waves, the wave appearing at -1.1V was probably due to the formation of a less stable, lower coordinated Zn(II)-dien complex.

In the titrations mentioned previously, difficulties were encountered from clogging of the asbestos fibers with KCl from the aqueous SCE and obvious diffusion of materials from the SCE compartments into the DME compartment. For these reasons the cell described in Chapter IV was constructed. This cell, equipped with acetone-saturated calomel electrodes (ASCE), was used in all later studies. So that half-wave potentials could be compared, the potential of the ASCE was measured against an aqueous SCE, the acetone electrode proving to be 0.18V negative with respect to the other.

With the new cell, a study of the reaction of Ag(I) with dien was carried out, a reverse titration being employed as with zinc. It was decided that information about the Ag(I)-dien complexes could be obtained from polarograms of the dien solution, of a solution containing the Ag(I)-dien complex, and of a solution containing both the Ag(I)-dien complex and excess Ag(I). For this reason polarograms were obtained after the addition of 0, 5, 15, and 25 ml of 10^{-2}M $AgNO_3$ in 2-propanol to 100 ml of 2 x 10^{-3}M dien in 2-propanol, both solutions being 0.1M in $LiNO_3$. With the first two additions of Ag(I) solution, a slight precipitate formed and a wave

appeared. This wave had reached its height at zero potential with reference to an ASCE and was roughly proportional to the amount of Ag(I) solution added. After 25 ml of the titrant had been added there was so much precipitate present in the solution that the DME became erratic. There was also a large decrease in diffusion current upon addition of this last increment, the ratio of dien to silver at this point being approximately 1:1.2. These results would be expected if a higher coordination complex were formed at the higher dien-to-silver ratios and if this complex were more soluble in 2-propanol than was the complex formed later in the titration.

Studies of Mercury(II)-Dien Systems. The use of mercury(II)-chelate indicator electrodes in the potentiometric titration of metal ions in aqueous solutions with various chelating agents has been reported in the literature. To see if it might be possible to use similar electrodes in nonaqueous solutions, several mercury(II)-dien systems were investigated.

Some difficulties were encountered in preparing $Hg(NO_3)_2$ solutions due to the insolubility of the compound in 2-propanol. After some time, the reagent seemed to dissolve in 50% methanol-50% 2-propanol, but later it precipitated out again. Due to these difficulties, the mercury(II) concentrations quoted below are only approximate. Tenth molar $LiNO_3$ was the supporting electrolyte in these solutions.

Forty ml of 6.6×10^{-3}M dien in 2-propanol were added to 25 ml of 10^{-2}M $Hg(NO_3)_2$ in 50% methanol-50% 2-propanol (1.06 dien:1 Hg), and a white flocculent precipitate formed. This solution gave a polarographic wave which had reached its height at zero potential vs. ASCE. The very small diffusion current and the precipitate indicated the formation of a mercury chelate of rather low solubility. To see if Cd(II) would replace mercury from the complex, 10 ml of 10^{-2}M $Cd(NO_3)_2$ in 2-propanol was added

to the solution. A polarogram of the solution showed some evidence of the formation of cadmium complexes, but there was no wave present to account for a mercury-dien complex or for solvated mercury ions.

Ten ml of 10^{-2}M $Ca(NO_3)_2$ in 2-propanol was added to 50 ml of a Hg(II)-dien solution in which the Hg(II) concentration was about 2 x 10^{-3}M and the dien-to-Hg(II) ratio was 1.5:1. Polarograms of both the Hg(II)-dien solution and the solution containing Ca(II) showed polarographic waves with maxima, the maxima occurring at zero potential vs. ASCE. After addition of the Ca(II) solution the wave height was about 0.9 that of the wave height of the original solution.

A polarogram of a solution containing 10 ml of approximately 10^{-2}M $Hg(NO_3)_2$ in 50% methanol-50% 2-propanol and 40 ml of 4 x 10^{-3}M dien in 2-propanol (1.6 dien : 1 Hg) likewise yielded a polarographic wave with a maximum at about zero potential vs. ASCE. This solution was slightly cloudy. With the addition of $Pb(NO_3)_2$ in methanol, another wave appeared at a more negative $E_{\frac{1}{2}}$ and more precipitate formed. The more negative $E_{\frac{1}{2}}$ corresponded to that of the Pb(II)-dien complex found in the titration of lead with dien. The Hg(II) wave decreased to about one-fourth of its original value.

In looking for reasons for the results obtained when other metals were added to the Hg-dien mixtures, it was noted that in millimolar solutions of Hg(II)-dien in which the ratio of Hg(II) to dien approached 1:1, there was so much precipitate that the dropping mercury electrode became erratic. The addition of more dien to the solutions seemed to decrease the amount of precipitate and better polarographic waves were obtained. These observations indicated that a lower coordinated, less soluble mercury-dien complex is formed at lower dien-to-mercury ratios. From this viewpoint, it would seem that the metal ions which were added

to the mercury-dien solutions were reacting with the ligand, resulting in the formation of a lower coordinated Hg(II)-dien complex which was less soluble. This could account for the formation of more precipitate and for the decrease or disappearance of the mercury wave with the addition of metal ion solutions.

Addition of $CaCl_2$ in 2-propanol and $PbCl_2$ in methanol to separate millimolar Hg(II)-dien solutions produced very large increases in the diffusion currents at all voltages, and it was noted that there seemed to be less precipitate after the addition of Ca(II) and Pb(II). Addition of LiCl produced the same effects, so the increase in wave height and the decrease in the amount of precipitate was probably due to the formation of more soluble chloro-complexes of mercury.

Further Study of the Cd(II)-Dien System. From the titrimetric studies of Cd(II), Zn(II), and Cu(II) with dien, it was evident that at least two complexes were forming in solutions of each metal. The concentrations of the complexes were dependent upon the ligand concentration. In trying to find a medium in which only one complex was formed quantitatively, Cd(II) was selected as a representative metal ion to study.

It was decided to study Cd(II) in a solution made basic with NH_3, since in more basic solutions the nitrogen atoms of the ligand would be less likely to be protonated, and therefore the coordinating atoms would be more available to chelate the metal ions and satisfy the coordination requirements of the metal ions. It was thought, too, that perhaps a Cd (II)-NH_3 complex would be formed that would prevent the formation of what appeared to be the less stable of the two Cd(II)-dien complexes, thereby resulting in the formation of only the more stable dien complex of Cd(II).

Solutions were prepared in 2-propanol in which the dien-to-Cd(II) ratios were 3.7:1 and 1.4:1. The solutions were in the 10^{-5}M concentration

range in order to avoid polarographic maxima. In the solution with the higher dien ratio, one polarographic wave appeared around -0.6V vs. ASCE. In the other solution, polarographic waves appeared at -0.39V and -0.6V vs. ASCE. Both solutions were then saturated with dry gaseous NH_3, and polarograms of these solutions showed only one wave at -0.6V vs. ASCE. This may have been due to the formation of slightly soluble ammonia complexes or to mixed ligand complexes of Cd(II) which shifted the half-wave potential to a more negative value so that the polarographic wave merged with that of the Cd(II)-dien complex.

The "pH" of the solutions was measured with a Heath pH Recording Electrometer. In the solution with the dien-to-Cd(II) ratio of 3.7:1 the "pH" was 7.5. After NH_3 was bubbled through the solution the "pH" was 9.1. In the other original solution the "pH" was 5.5, and the ammoniacal solution had a "pH" of 9.2.

When NH_3 gas was bubbled through a millimolar solution of Cd(II) in 2-propanol, a precipitate formed. This restricted the further use of NH_3. Tests made in search of a substitute for ammonia, however, showed that the organic base, ethanolamine, formed metal complexes that are soluble in 2-propanol.

The shift in half-wave potential of the Cd(II) wave with addition of ethanolamine to 4.9×10^{-4}M $(Cd(NO_3)_2$ in 2-propanol was studied with ethanolamine concentrations varying from 0 to 3M, 0.1M NH_4NO_3 being used as the supporting electrolyte. The half-wave potential shifted from about -0.18V to -0.66 V vs. ASCE.

Since future plans included the possible use of a Hg(II) indicator electrode, the shift in half-wave potential of Hg(II) with increasing ethanolamine concentration (0 to 2.75M) was also studied, a titrimetric approach being used. When the first portion of titrant was added, the

solution turned cloudy and the diffusion current decreased. At ethanolamine concentrations of 1.5M and above, however, the diffusion current increased and, at the end of the titration, the solution was practically clear. Formation of insoluble basic salts which later dissolved with further complexing would account for this. There were only slight shifts in the half-wave potentials with increasing ethanolamine concentrations.

Leaving further studies of mercury for future research, attention was again focussed on cadmium. From the half-wave potentials exhibited by the polarograms of the Cd(II)-ethanolamine system, it appeared that a 0.05M ethanolamine solution was the best to be used in the determination of cadmium with dien. More concentrated solutions shifted the half-wave potential of the Cd(II)-ethanolamine complex over to the point where it coincided with the more stable Cd(II)-dien complex wave, while at lower concentrations of ethanolamine the Cd(II)-ethanolamine complex is not formed strongly enough to prevent the formation of the less stable Cd(II)-dien complex.

A Cd(II) solution which was 0.05M in ethanolamine, therefore, was titrated with dien. Two waves appeared, the second having a pronounced maximum. The first wave never leveled off to any usable degree, but it did disappear after addition of enough dien for a 2:1 dien to Cd(II) complex to form. There was some question as to whether the first polarographic wave was due to a less stable Cd(II)-dien complex, a Cd(II)-ethanolamine complex, or to a combination of the two. Regardless of its origin, however, the wave could not be used very successfully in an amperometric titration due to the fact that it did not level off.

An amperometric titration was performed on a Cd(II) solution in 2-propanol which contained 0.1M HNO_3-n-butylamine buffer, an excess of n-butylamine being added to complex the Cd(II) and hold it in solution.

Two polarographic waves again preceded the wave with the maximum. When more n-butylamine was added, there was only one wave before the maximum. This wave never leveled off, and there was again the question of what was being reduced at this potential.

Since the main interest was not in the study of the dien complexes in particular, but in finding chelating agents that could successfully be used in the determination of metals in organic solvents, studies of this reagent were abandoned.

Triethylenetetraamine (trien), the next higher analog of dien, has four nitrogen atoms available for coordination. With the added coordination position, this ligand should more nearly satisfy the coordination requirements of the metal ions and prevent the formation of the multiplicity of complexes that presented problems with dien. There being none of this reagent available at the time, it was not investigated.

Solubility of EDTA-Type Chelating Agents in Solutions Containing Ethanolamine or n-Butylamine. Diethylenetriaminepentaacetic acid (DTPA) and its lithium salts were found to be relatively insoluble in methanol and in 2-propanol. However, it was found that when ethanolamine was added to DTPA solutions, the solid acid did dissolve. Further tests showed that 0.1M solutions of DTPA, EDTA, and CDTA could be easily prepared in methanol which was 1M in ethanolamine. This discovery led to the hope that the sodium salt of EDTA would be soluble enough in the presence of ethanolamine for use as a titrant. Such solutions could well be very useful for the salt is commercially available as a primary standard and standard solutions could be easily prepared from it. However, the salt dissolved only to the extent of about 10^{-2}M in methanol, and that only when the mixture was shaken overnight on a mechanical shaker. Its solubility in 2-propanol was somewhat lower. In 2-propanol, a 0.05M CDTA

solution could be prepared by making the mixture 1M with ethanolamine and shaking for some time; but a solid precipitated out after the solution stood for a few hours. A 10^{-2}M DTPA solution in 2-propanol could be prepared with ethanolamine by shaking the solution overnight on a mechanical shaker, but the acid form of EDTA was not that soluble. CDTA seems to go into solution somewhat more rapidly than the other reagents, the cyclohexane ring apparently increasing the solubility of its salts in organic solvents. Consequently, it was decided to investigate further the use of CDTA as a chelating agent for use in nonaqueous solutions.

Since the results with ethanolamine showed that organic bases helped to get the reagent into solution, primary n-butylamine was selected as an alternate base to see how it would compare with ethanolamine. The following solutions were prepared in 2-propanol:

10^{-2}M CDTA, 1M n-butylamine

10^{-2}M CDTA, 1M ethanolamine

0.05M CDTA, 1M n-butylamine

0.05M CDTA, 1M ethanolamine

CDTA seemed to go into solution a little easier with n-butylamine than with ethanolamine. After the solution had stood for 6 to 8 hours, a precipitate formed in those containing ethanolamine, appearing as if the ethanolamine precipitate formed almost quantitatively. The solutions containing n-butylamine, however, remained clear. The fact that the CDTA with ethanolamine first dissolved, then later precipitated pointed to the possibility that perhaps a slow reaction was taking place in which one or more additional molecules of ethanolamine reacted with the CDTA to form a compound of lower solubility. If this were the case one would think that a lower ethanolamine concentration might prevent this reaction. However, after about 12 hours precipitation still occurred even in 0.16M

ethanolamine solutions--the lowest concentration that seemed able to dissolve the reagent adequately.

When attempts were made to use these reagents in amperometric titrations, it was soon found that the lithium nitrate carrier gave a precipitate with the reagent. This is not too surprising since the lithium salts of CDTA were found to be only very slightly soluble in 2-propanol. A 10^{-2}M CDTA solution containing 1M ethanolamine was made 0.01M in $LiNO_3$ without immediate precipitation, but precipitation quickly occurred in 0.02M $LiNO_3$ solution. In n-butylamine solutions a 0.02M $LiNO_3$ solution remained clear, but 0.03M $LiNO_3$ caused precipitation.

Preliminary Studies with CDTA. Since the lithium interference did not seem to appear until the concentration of ligand became relatively high, the metal ion solutions to be analyzed were made 0.16M with ethanolamine and 0.1M with $LiNO_3$ unless otherwise stated. 2-Propanol was used as solvent. The ethanolamine was to stabilize the basicity of the solution, to keep both chelating agent and metal ions (as complexes) in solution, and to provide a basic condition which would favor chelation; for in acid media, protons compete with the metal ions for the coordination sites on the molecules of the chelating agent.

An interest in the possible use of mercury or silver indicator electrodes led to a study of the reactions of these metal ions with CDTA. Solutions of 2×10^{-4}M $Hg(NO_3)_2$ and 1.1×10^{-3}M $AgNO_3$ were titrated amperometrically with 0.05M CDTA in 2-propanol containing 0.16M ethanolamine. Although addition of titrant produced precipitates in both solutions, there were only slight decreases in diffusion currents and no noticeable shifts in half-wave potentials. The titrant used was freshly prepared since, as was mentioned earlier, it began to precipitate out of solution after standing approximately four hours.

A 50-ml sample of 10^{-3}M $Cd(NO_3)_2$ in 2-propanol was titrated amperometrically with 10^{-2}M CDTA in 50% methanol-50% 2-propanol. Both solutions contained 0.05M ethanolamine. The titrated solution became noticeably cloudy after the addition of 3 ml of titrant, and the cloudiness increased throughout the titration. The endpoint should have been at about 5 ml, but the cadmium wave did not disappear until after the addition of 8 ml.

Due to the instability of the solutions of CDTA with ethanolamine in 2-propanol, it was decided to prepare the titrant in 95% ethanol which was 0.16M with ethanolamine. In this solvent, solutions of concentrations of 0.01M, 0.05M, and 0.1M were prepared without precipitation.

A 50-ml sample of 10^{-3}M $Zn(NO_3)_2$ in 2-propanol 0.1M with $LiNO_3$ was titrated with CDTA in 95% ethanol. There were significant decreases in the diffusion current and increasing cloudiness with each addition of titrant, but the endpoint occurred later than calculated. The wave of the complex, however, either did not appear at all or was masked by the supporting electrolyte wave. This probably indicated that the complex had a half-wave potential that at least approached that of the supporting electrolyte and may have been even more negative. Such a large shift of half-wave potential would indicate a highly stable complex; consequently, the lack of agreement of the actual and the theoretical endpoints was not at all to be expected.

Next, a 1.4×10^{-3}M $Pb(NO_3)_2$ solution was prepared in 95% ethanol. When a sample of this solution was titrated, the solution remained clear, and the endpoint was approximately the same as that calculated.

A comparison of the results with zinc in 2-propanol and lead in 95% ethanol suggested that a possible explanation of the results with

zinc might be that some of the chelating agent was precipitating out as the lithium salt when it was added to the 2-propanol solution and was therefore not reacting with the metal ions. Such behavior would account for the precipitates and for the fact that there was no decrease in diffusion currents in some of the previous titrations; for all the precipitates seem to be more soluble in ethanol solutions. With this in mind, zinc and cadmium were both titrated in 95% ethanol solutions. In both cases, the solutions remained clear and the endpoints were approximately as calculated. No complex waves were visible. When $Hg(NO_3)_2$ was titrated likewise, the solution remained clear. There was a decrease in the diffusion current and a complex wave appeared at about -0.51V vs. ASCE. It was quite evident that the CDTA was complexing the mercury and this led to the hope that a Hg(II)-CDTA electrode might function as an indicator electrode in potentiometric titrations with CDTA.

Applications of CDTA to the Determination of Metals in Nonaqueous Solvents

Hg(II)-CDTA Indicator Electrode Studies. Having thus gained some idea of the complexing characteristics of CDTA with various metals in 95% ethanol, it was decided to test the feasibility of using the Hg(II)-CDTA indicator electrode for potentiometric titrations. Such an electrode has been used in aqueous solutions. The theory behind this is as follows:

The potential exhibited by a mercury electrode in contact with a solution containing metal ions to be titrated and containing some Hg(II)-CDTA complex may be found by combining the Nernst equation for a mercury electrode with the stability constant expressions for the Hg(II)-CDTA complex and the metal-CDTA complex, as follows, where Y^{-4} represents the expected form for CDTA (by analogy with its behavior in aqueous solutions),

MY^{-2} represents the expected complex, and the various K-values represent formation constants.

$$E = E^{o}_{Hg} + \frac{0.059}{2} \log[\bar{Hg}^{+2}]$$

$$Hg^{+2} + Y^{-4} \rightleftharpoons HgY^{-2} \qquad K_{HgY} = \frac{[\bar{HgY}^{-2}]}{[\bar{Hg}^{+2}][\bar{Y}^{-4}]}$$

$$M^{+2} + Y^{-4} \rightleftharpoons MY^{-2} \qquad K_{MY} = \frac{[\bar{MY}^{-2}]}{[\bar{M}^{+2}][\bar{Y}^{-4}]}$$

$$E = E^{o}_{Hg} + 0.03 \log \frac{[\bar{HgY}^{-2}][\bar{M}^{+2}]K_{MY}}{K_{HgY}[\bar{MY}^{-2}]} = E^{o}_{Hg} + 0.03 \log \frac{K_{MY}}{K_{HgY}} \times \frac{[\bar{HgY}^{-2}]}{[\bar{MY}^{-2}]}$$

$$+ 0.03 \log[\bar{M}^{+2}]$$

Thus near the equivalence point, HgY^{-2} and MY^{-2} approach a maximum constant value and the electrode potential is proportional to $-\log[\bar{M}^{+2}]$ or pM. Therefore, if the electrode is reversible and attains equilibrium sufficiently rapidly, one should be able to titrate metal ions with CDTA using a mercury electrode just as acids are titrated using a glass electrode.

To test this idea, a mercury indicator electrode, patterned after the one used by Holloway and Reilley (22), was made from a piece of 6-mm glass tubing, and a saturated calomel electrode was used as the reference electrode. A polarographic cell served as the titration vessel and a Beckman Zeromatic pH meter was used as a potentiometer.

Millimolar solutions of $Cd(NO_3)_2$ in 95% ethanol to which was added different amounts of varying concentrations of Hg(II)-CDTA (10^{-3} to 10^{-1} mole per liter) were titrated with CDTA. Both solutions were 0.16M with ethanolamine. There were no significant breaks in the titration curves, and the total change in potential was usually around 70 mv which is not enough for an accurate titration. Larger quantities of Hg(II)-CDTA did not seem to improve the titration, nor did a larger electrode (10 mm

diameter).

Titration of a millimolar Hg(II) solution with CDTA using a mercury indicator electrode produced only a 75 mv change in the potential. Since this was the basic reaction involved, the method did not look very promising, and it was not studied further.

Holloway and Reilley (22) reported that the Hg(II)-CDTA indicator electrode functioned smoothly in aqueous solutions, but equilibrium potentials were reached very slowly. As mentioned earlier, CDTA usually forms more stable complexes than does EDTA but does so at a slower rate. The increased stability has been attributed to the fact that the nitrogen atoms of CDTA are preoriented in a favorable position for chelation to take place while the carbon atoms of EDTA have to be rotated to bring the nitrogen atoms into suitable positions for chelation (14).

Amperometric Titrations with CDTA. Earlier polarographic data indicated that amperometric titrations could be performed successfully; consequently, the other approaches were dropped and the amperometric method was used in the remaining studies.

Since one of the practical uses of the titrimetric method is concerned with the analysis of petroleum, lubricating oils, paints, etc., in which the metals or their compounds are present in an organic phase which is not water-soluble, it was decided to use a solvent medium somewhat similar to solutions in which it was hoped analyses could be done directly. The solvent chosen was 50% 2-propanol-50% isooctane. One-tenth molar $LiNO_3$ was used as the supporting electrolyte in the metal ion solutions; for even though it was known that the lithium salts of CDTA were of low solubility, it was thought that as long as there were other metal ions in the solution the titrant would react with these in preference to the lithium ions.

A 50-ml sample of 10^{-3}M $Pb(NO_3)_2$ solution containing ethanolamine was titrated with 0.1M CDTA--0.33M ethanolamine in 95% ethanol. With lead solutions, the ethanolamine concentration had to be increased to 2M in order to keep the lead in solution. On titration, it was found that a precipitate formed with the first addition of titrant, the amount increasing throughout the titration and even after the expected endpoint. The Pb(II) wave, which occurred at about -0.45V vs. ASCE, never completely disappeared but gradually decreased past the endpoint. This was at first interpreted as indicating the formation of a slightly soluble Pb(II)-CDTA chelate. When the data was plotted (ml vs i_d) the titration curve was very rounded near the endpoint.

Another Pb(II) solution was titrated under the same conditions to check the preceding one. Precipitation again occurred, but the decrease in diffusion current was not nearly quantitative and the results did not even approximate those from the first titration. Even after the addition of twice the amount of titrant required to reach the endpoint, there was still a very significant Pb(II) wave present. On the suspicion that the precipitate might be lithium-CDTA, the solution was allowed to stand for a few minutes, then it was degassed for approximately five minutes after which a new polarogram was made. Although no more titrant had been added, the new curve showed a pronounced decrease in diffusion current. Apparently the lead was slowly replacing the lithium from the solid lithium-CDTA. On testing, it was found that the precipitate in the polarographic cell was soluble in 95% ethanol.

In view of these results, changes were made in solution conditions and experimental procedure. First, the $LiNO_3$ concentration was decreased to 0.01M, this concentration being still sufficient for measurement of a diffusion current only. Secondly, 2-propanol alone was used as solvent

for the metal salts because the isooctane was found to decrease the solubility of the lithium salt of the chelating agent. Third, the solution was stirred with nitrogen during the additions of titrant to prevent local concentration of the titrant into a small volume of solution and to decrease the opportunity for the precipitation of the chelating agent before it reacted with lead ions. Results with this procedure were much better. The $Pb(NO_3)_2$ solution titrated in this way remained clear during the titration until after an excess of titrant had been added, and graphing the data gave a much sharper titration curve with an endpoint approximately as calculated.

A 50-ml sample of 1.2×10^{-3}M $Cd(NO_3)_2$ in 2-propanol which was 0.01M with $LiNO_3$ was titrated with 0.1M CDTA. The solution became cloudy after the second addition of titrant, and the cloudiness increased during the titration. Evidently the Cd(II)-CDTA complex is insoluble in 2-propanol. A graphical plot of the data showed an endpoint a little earlier than that calculated.

A $Zn(NO_3)_2$ solution was titrated in the same manner. The solution remained clear until just before the endpoint was reached, but the data obtained did not give a very good titration curve when plotted.

Indicator Ion Studies. Among the metals of interest which might be present in petroleum, petroleum products, and paints are calcium and magnesium. These metals are not sufficiently easily reduced to readily be determined directly in an amperometric titration. It was decided, therefore, to seek an indicator ion for these determinations. Such an indicator ion would need to yield a limiting current at a suitable potential and react with the titrant but form a complex that is less stable than that of calcium or magnesium. The titration curve should look something like the one in Figure 5.

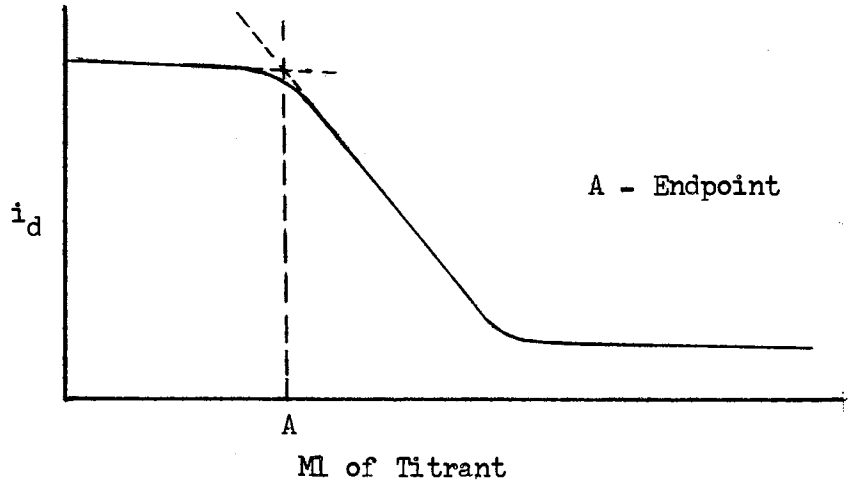


Figure 5. Amperometric Titration Using an Indicator Ion

If titrant is added to a solution containing Ca(II) or Mg(II) and the indicator metal ion, the diffusion current of the indicator ion should remain constant (except for dilution) until all the Ca(II) or Mg(II) is chelated. The titrant should then react with the indicator ion and cause a decrease in the diffusion current until all of it is complexed. At this point the diffusion current should remain essentially constant.

To millimolar solutions of zinc, cadmium, and lead chelates were added calcium and magnesium nitrate solutions. With the lead solution a Pb(II) wave reappeared, but the wave height indicated that not all the Pb(II) was replaced by Ca(II) or Mg(II). In the zinc and cadmium solutions, no polarographic waves reappeared with the addition of Ca(II) or Mg(II). None of these metals appear to be suitable for use as an indicator ion with CDTA under the conditions employed.

Titrations of Mixtures of Metal Ions with CDTA. Interest in being able to titrate some metal ions in preference to others led to the study of a three-component system. A solution which contained Pb(II), Cd(II), and Zn(II) was prepared in 2-propanol. The approximate composition of the solution is given below.

3.04×10^{-4}M $Cd(NO_3)_2$

2.83×10^{-4}M $Pb(NO_3)_2$

2.5×10^{-4}M $Zn(NO_3)_2$

2M ethanolamine

0.01M $LiNO_3$

A polarogram of this solution showed three polarographic waves which were separated fairly well under these conditions. The approximate half-wave potentials with reference to an acetone-saturated calomel electrode are listed below.

Pb(II)	$E_{\frac{1}{2}} = -0.39$V
Cd(II)	$E_{\frac{1}{2}} = -0.63$V
Zn(II)	$E_{\frac{1}{2}} = -1.11$V

This solution was titrated with 0.1M CDTA, 0.33M with ethanolamine, in 95% ethanol. The mixture remained clear until more titrant had been added than was necessary to reach the endpoint. From the polarograms obtained it appeared that the Cd(II) and Pb(II) waves disappeared at about the same rate while the Zn(II) wave disappeared later than this. This indicates that the cadmium and lead complexes are stronger than the zinc complex which is analogous to the relative stabilities of these complexes in aqueous solution.

At this point it was not possible to tell whether or not the lead and cadmium ions were completely titrated before the zinc ions began reacting, for what seemed to be a complex wave formed at about the same half-wave potential as that of the original Zn(II). The wave formed at this potential tended to slant upward rather than remain level after the first addition of titrant, and this effect seemed to increase throughout the titration.

When, next, a 0.16M ethanolamine--2-propanol solution containing

Cd(II) and Zn(II) was titrated with CDTA, it was found that with each addition of titrant both polarographic waves decreased. It is quite evident from this that Cd(II) cannot be titrated in the presence of Zn(II) under these conditions.

Statistical Studies with CDTA. To determine the usefulness of CDTA in the determination of metal ions in nonaqueous solutions, some statistical studies were made. Amperometric titrations of lead, cadmium, and zinc were performed in about the same manner as those previously described. Attached to the burette used in these studies was a glass tube bent in such a way that it easily fit into the polarographic cell and drawn into a long (18 cm) fine capillary, the tip of which dipped into the solution to be titrated. Solutions were stirred with nitrogen during the additions of titrant.

Endpoints in the titrations were determined graphically from plots of wave height versus milliliters of titrant. No corrections were made for dilution since the concentration of the titrant was such that small volumes (0.8 ml) were needed to reach the endpoints in titrations of 50-ml samples of the metal ion solutions. As a result, corrections due to dilution were negligible.

CDTA solutions were prepared by dissolving a weighed amount of solid CDTA in 95% ethanol which was about 0.33M in ethanolamine. No $LiNO_3$ was present in these solutions.

From polarograms of $Pb(NO_3)_2$ in 2-propanol obtained previously under the same conditions, a potential of -0.9V vs. ASCE was selected as the potential at which to perform the amperometric titrations of lead. Fifty-ml samples of $Pb(NO_3)_2$ in 2-propanol which were about 2M in ethanolamine and 0.01M in $LiNO_3$ were titrated with CDTA solution. The titrant was added in 0.2 ml increments. Results of the Pb(II) titrations

are shown in Table I. A sample calculation is given below.

$$C_{Pb} = \frac{(\text{Ml of CDTA})\ (\text{Molarity of CDTA})}{(\text{Ml of Pb})}$$

$$C_{Pb} = \frac{(0.828\text{ml})\ (0.1016\text{M CDTA})}{(50\text{ ml})}$$

$$C_{Pb} = 1.68 \times 10^{-3}\text{M}$$

To check the CDTA titrations of Pb(II), 25-ml samples of the Pb(II) solution in 2-propanol were diluted with 25 ml of aqueous 0.01M $LiNO_3$ solution and titrated with aqueous Na_2EDTA solution. Readings were taken at 0.1 ml increments of titrant. Results of the titrations, which are shown in Table II, agreed fairly well with the CDTA results.

In the analysis of CD(II) in 2-propanol a 50-ml sample of the solution which was about 0.16M in ethanolamine and 0.01M in $LiNO_3$ was titrated with CDTA at a preselected potential of -0.9V vs. ASCE. The solution turned cloudy with the first addition of titrant and continued to do so throughout the titration. A plot of the data gave a titration curve which was very rounding and could not be used for reliable results. It was found, however, that with the addition of 5 ml more of ethanolamine to a 50-ml sample of the Cd(II) solution, the solution remained clear throughout the titration and the titration curves (see Figure 6) were much better. Titrant was added in 0.1 ml increments so that more points could be obtained before the endpoint. Results of the titrations are shown in Table III. CDTA titrations were again checked by titrating solutions containing 25 ml of Cd(II) in 2-propanol solution, 25 ml of aqueous 0.01M $LiNO_3$ solution, and 5 ml of ethanolamine with aqueous Na_2EDTA solution at -0.9V vs. ASCE, results of which are given in Table IV. An amperometric titration curve typical of the aqueous titrations is shown in Figure 7.

The selection of a suitable potential at which to perform an amperometric titration of a reducible metal ion with a chelating agent such as CDTA is usually not very difficult since the large stability of the complexes produces large differences in the half-wave potentials of the solvated metal ions and the metal-CDTA complexes. However, some difficulties were encountered in trying to find solution conditions such that Zn(II) solutions could be analyzed accurately. In a Zn(II) solution which was 2M with ethanolamine, a suitable potential could not be selected due to the build-up of a wave (with the addition of titrant) on top of the Zn(II) wave. A more positive potential could not be selected due to the presence of a maximum in the Zn(II) wave. The waves, both the Zn(II) wave and the wave which formed with addition of titrant, seemed to shift to more positive values as titrant was added. In an effort to avoid the overlap of the two waves, a Zn(II) solution which was 0.5M in ethanolamine was titrated. It was thought that at lower ethanolamine concentrations the Zn(II) wave would appear at a more positive potential. However, there was still a slight overlap, and the titration curve was very rounding. A suitable endpoint could not be detected under such conditions.

Before the best solution conditions and the best applied potential to use were selected, a number of Zn(II) - CDTA titrations were performed in the presence of n-butylamine or cyclohexylamine as a substitute for ethanolamine. However, solutions that were 0.5M, 0.8M, 1M or 1.5M in n-butylamine and 0.3M and 1M in cyclohexylamine did not give results that were as good as those obtained in a Zn(II) solution that was 1.5M in ethanolamine. Zn(II) solutions containing 1.5M ethanolamine and 0.01M $LiNO_3$ in 2-propanol were then titrated with CDTA at a preselected potential of -1.2V vs. ASCE. At this potential the first point on the

titration curve could not be obtained due to the maximum in the Zn(II) wave. However, this point did not seem to be of any value in the titration curves of the other metals. Results of the CDTA titrations are shown in Table V. Table VI shows the results of the aqueous Na_2EDTA titrations of 25-ml samples of the Zn(II) solution diluted with 25 ml of 0.01M $LiNO_3$.

In the titrations of lead, cadmium, and zinc in 2-propanol the solutions remained clear throughout the titrations until about the second increment past the endpoint. The precipitates which formed at this point were evidently due to the insoluble lithium salts of CDTA. Constant temperature was maintained to within 0.3°C throughout the nonaqueous titrations. In the titrations with the aqueous Na_2EDTA, solutions remained clear throughout, and there was usually less than 0.8°C change in temperature.

TABLE I

RESULTS OF Pb(II) - CDTA TITRATIONS

Sample No.	Milliliters Added (0.1016M CDTA)	Pb(II) Concentration (Calculated)	Deviations
1	0.828	1.68×10^{-3}M	-0.02×10^{-3}
2	0.842	1.71×10^{-3}M	$+0.01 \times 10^{-3}$
3	0.832	1.69×10^{-3}M	-0.01×10^{-3}
4	0.842	1.71×10^{-3}M	$+0.01 \times 10^{-3}$
	Average	1.70×10^{-3}M	$\pm 0.01 \times 10^{-3}$ (6 Pts/ 1000)

TABLE II

RESULTS OF Pb(II) - EDTA TITRATIONS

Sample No.	Milliliters Added (0.1001M EDTA)	Pb(II) Concentration (Calculated)	Deviations
1	0.410	1.64×10^{-3}M	-0.01×10^{-3}
2	0.415	1.66×10^{-3}M	$+0.01 \times 10^{-3}$
3	0.410	1.64×10^{-3}M	-0.01×10^{-3}
	Average	1.65×10^{-3}M	$\pm 0.01 \times 10^{-3}$ (6 Pts/1000)

TABLE III

RESULTS OF Cd(II) - CDTA TITRATIONS

Sample No.	Milliliters Added (9.994×10^{-2}M CDTA)	Cd(II) Concentration (Calculated)	Deviations
1	0.782	1.56×10^{-3}M	0
2	0.790	1.58×10^{-3}M	$+0.02 \times 10^{-3}$
3	0.772	1.54×10^{-3}M	-0.02×10^{-3}
4	0.770	1.54×10^{-3}M	-0.02×10^{-3}
5	0.780	1.56×10^{-3}M	0
	Average	1.56×10^{-3}M	$\pm 0.01 \times 10^{-3}$ (6 Pts/1000)

TABLE IV

RESULTS OF Cd(II) - EDTA TITRATIONS

Sample No.	Milliliters Added (9.845×10^{-2}M EDTA)	Cd(II) Concentration (Calculated)	Deviations
1	0.385	1.52×10^{-3}M	0
2	0.387	1.52×10^{-3}M	0
3	0.385	1.52×10^{-3}M	0
	Average	1.52×10^{-3}M	0

TABLE V

RESULTS OF Zn(II) - CDTA TITRATIONS

Sample No.	Milliliters Added (0.1008M CDTA)	Zn(II) Concentration (Calculated)	Deviations
1	0.740	1.49×10^{-3}M	-0.01×10^{-3}
2	0.733	1.48×10^{-3}M	-0.02×10^{-3}
3	0.750	1.51×10^{-3}M	$+0.01 \times 10^{-3}$
4	0.740	1.49×10^{-3}M	-0.01×10^{-3}
5	0.740	1.49×10^{-3}M	-0.01×10^{-3}
6	0.750	1.51×10^{-3}M	$+0.01 \times 10^{-3}$
	Average	1.50×10^{-3}M	$\pm 0.01 \times 10^{-3}$ (7 Pts/1000)

TABLE VI

RESULTS OF Zn(II) - EDTA TITRATIONS

Sample No.	Milliliters Added (0.1001M EDTA)	Zn(II) Concentration (Calculated)	Deviations
1	0.355	1.42×10^{-3}M	$+0.01 \times 10^{-3}$
2	0.355	1.42×10^{-3}M	$+0.01 \times 10^{-3}$
3	0.350	1.40×10^{-3}M	-0.01×10^{-3}
	Average	1.41×10^{-3}M	$\pm 0.01 \times 10^{-3}$ (7 Pts/1000)

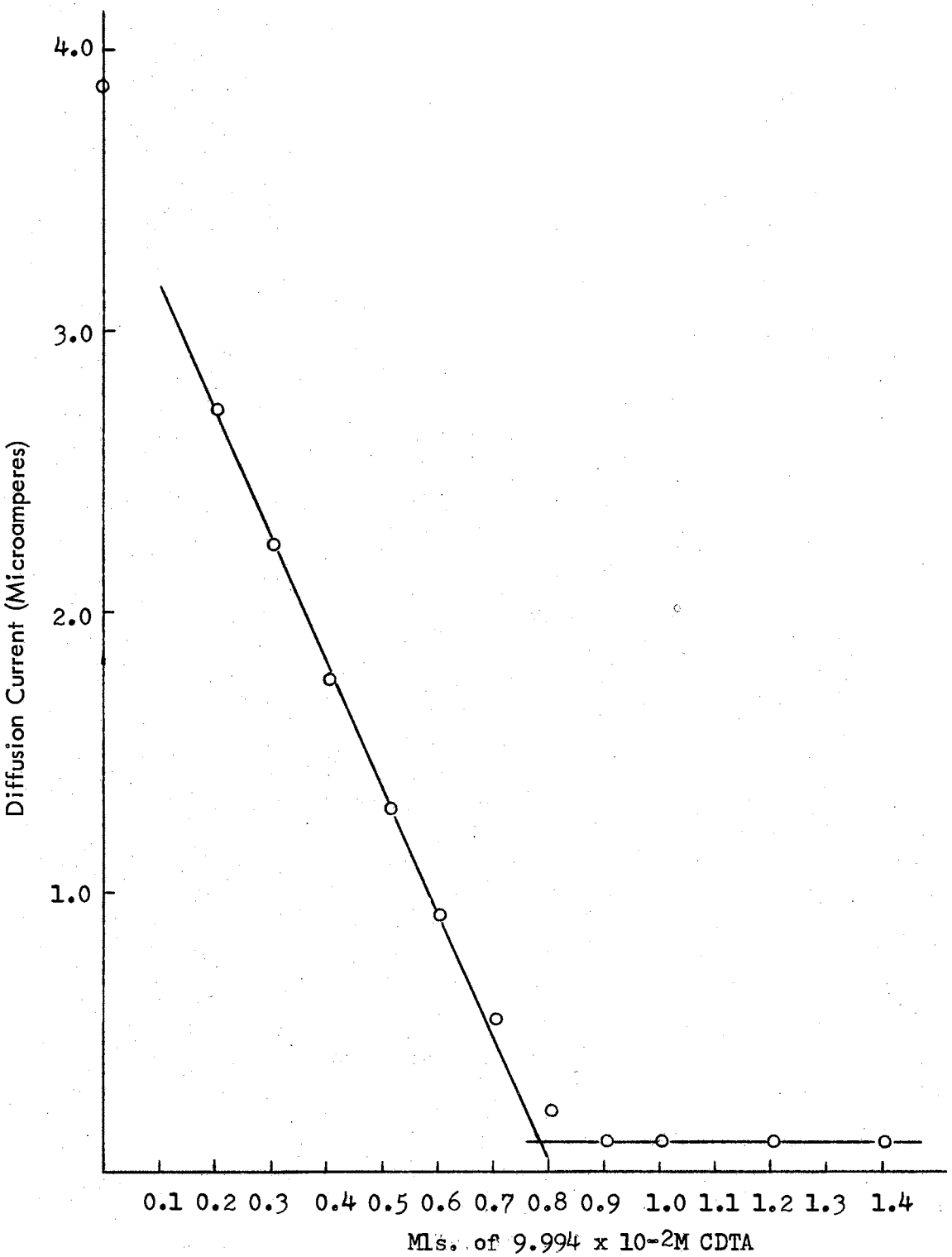


Figure 6. Amperometric Titration of Cd(II) with CDTA

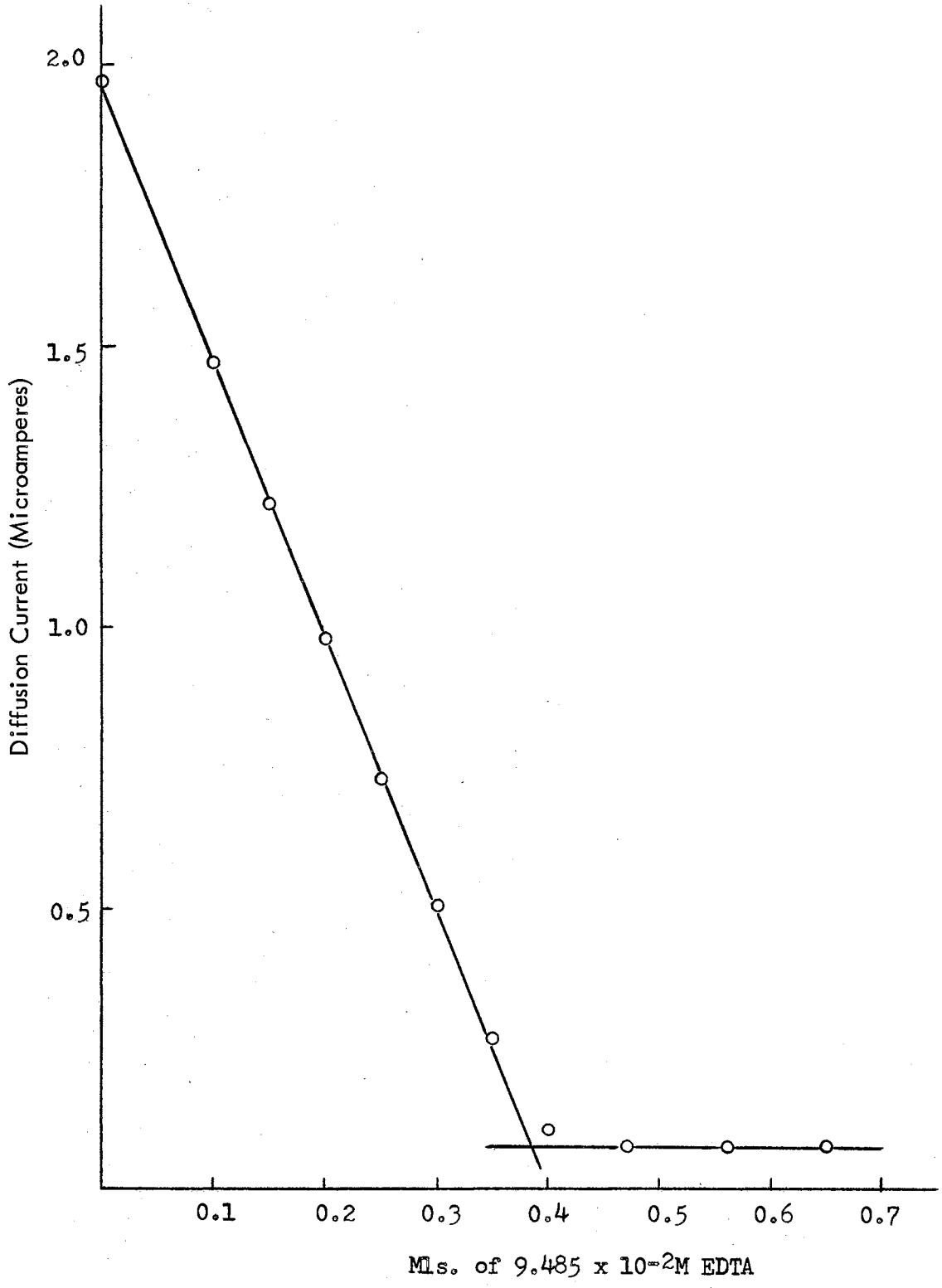


Figure 7. Amperometric Titration of Cd(II) with EDTA

CHAPTER VII

SUMMARY AND CONCLUSIONS

This research was concerned with the study of various chelating agents and metal chelates in nonaqueous solutions. The main objectives were to find chelating agents that are suitable for use in nonaqueous solutions and to develop methods for the direct determination of metals in nonaqueous solutions. A great deal of the investigation was of an exploratory nature.

Polarographic studies of the dien complexes of cadmium, copper, and zinc in 2-propanol led to the conclusion that in each case at least two complexes of the metal ion were forming in solution, the complexed metal dividing itself between the two complexes in a manner that was dependent upon the ligand concentration. No conditions were found in which only one complex was formed quantitatively so that metals could be titrated amperometrically with dien. Other chelating agents, therefore, were studied, since the main interest was in finding chelating agents that could be used in quantitative analysis for the determination of metal ions.

The discovery that EDTA-type chelating agents were soluble in alcohol solutions made basic with ethanolamine led to the study of CDTA and its metal chelates. The formation of precipitates in mixture of ethanolamine and CDTA in 2-propanol after standing for a few hours interfered with the use of 2-propanol as a solvent for CDTA. In 95% ethanol, however, a stable CDTA solution could be prepared when the mixture was about 0.33M in ethanolamine. An important discovery was made also when it was found that ethanolamine complexes of several metal ions are soluble in 2-propanol.

Thus ethanolamine could be used not only to complex the metals and keep them in solution but also to make the solutions basic--a condition which should promote the formation of complexes with all the chelating agents studied.

The use of a Hg(II)-CDTA indicator electrode in potentiometric titrations proved unsuccessful. Under the conditions employed, observed changes in potential were not large enough to produce suitable potentiometric endpoints. Further study is needed to determine the reasons for the inadequacy of the electrode which may be the result of very slow equilibrium establishment at the electrode or of the electrode's being irreversible.

Preliminary polarographic studies of the metal chelates of CDTA gave sufficient evidence that amperometric methods could be used for endpoint detection in at least certain chelometric titrations with CDTA. Thus, the shifts in half-wave potentials of the Pb(II), Cd(II), and Zn(II) chelates with CDTA indicated that sufficiently stable 1:1 metal chelates were forming in solution.

A number of samples of Cd(II), Pb(II), and Zn(II) solutions in 2-propanol made basic with ethanolamine were titrated amperometrically with CDTA in 95% ethanol. These titrations were checked by titrating the metal ions in 50% 2-propanol-50% water with aqueous Na_2EDTA solution. The titration curves showed some rounding in the vicinity of the endpoint, with the CDTA titration curves exhibiting a slightly greater degree of rounding than did the EDTA titration curves. The rounding of the curves in both the CDTA and Na_2EDTA titrations indicates some dissociation of the complexes occurred and probably additionally represented competition between the ethanolamine and the chelating agent for the metal ion.

The nonaqueous titrations agreed with the aqueous titrations to

within 2.6% for Cd(II), 3% for Pb(II), and 6% for Zn(II). Part of this error may have been due to impurities in the CDTA for which there was no available dependable independent method of standardization. Reproducible results were obtained as evidenced by the precision in the titrations. Consequently, it is apparent that if the CDTA had been standardized against metal solutions, the accuracy would have become equivalent to the precision which for all three metals would have fallen in the range of 0.6% to 0.7%.

Results indicate that CDTA can be used in the direct analysis of organic solutions containing only one of the above-mentioned metals, however it is not possible to determine the individual ions in a mixture of these metals under the conditions used. Experimental evidence indicated that the presence of small amounts of calcium or magnesium did not interfere with the titration of cadmium or zinc in 0.16M ethanolamine--2-propanol solutions. It appeared, however, that calcium and magnesium would interfere in the determination of lead. It was found that 0.1M lithium salts interfered with the CDTA titrations, but evidence showed that if such supporting electrolytes were decreased to 0.01M, the lithium interference could be minimized. It is highly probable that salts of ethanolamine or normal aliphatic amines could probably be substituted for lithium salts as supporting electrolytes. These would also serve as buffering agents.

Suggestions for further study include the investigation of other chelating agents and their metal chelates in organic solvents and the use of these reagents and masking agents in the analysis of mixtures of ions. By making use of the differences in stability of the metal complexes of different chelating agents, it should be possible to develop methods for the determination of mixtures of metal ions. The need for

auxiliary complexing agents or masking agents other than ethanolamine for use in simultaneous determinations is quite evident. It seems likely that normal primary aliphatic amines might well serve this purpose, particularly those having long hydrocarbon chains to aid in increasing the solubility of their metal complexes.

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