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A study of the chelation of 1,3-bis-(tris-(hydroxymethyl)-methylamino)-2-propanol dihydrochloride with copper (II), nickel (II), cobalt (II)

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A STUDY OF THE CHELATION OF 1,3-BIS-(TRIS-(HYDROXYMETHYL)-METHYLAMINO)-2-PROPANOL DIHYDROCHLORIDE WITH COPPER (II), NICKEL (II), COBALT (II)

BY

VELTA ERDMANIS

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MASTER OF SCIENCE IN CHEMISTRY

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TABLE OF CONTENTS

ABSTRACT

In this study 1,3-bis-(tris-(hydroxymethyl)-methylamino)-2-propanol dihydrochloride chelates with calcium, manganous, cobaltous, nickelous, cupric and zinc ions were investigated.

Potentiometric titrations were performed to obtain information about the stability of the chelates formed. Calcium and manganous ions showed little chelating ability. Cobaltous, nickelous, cupric and zinc ions formed stable chelates when the ratio of the chelating agent concentration to the metal ion concentration was 1:1 or larger.

Job's method of continuous variations was used for determining the composition of the cupric, nickelous and cobaltous chelates and it was found that these metal ions form a 1:1 chelate with 1,3-bis-(tris-(hydroxymethyl)-methylamino)-2-propanol dihydrochloride.

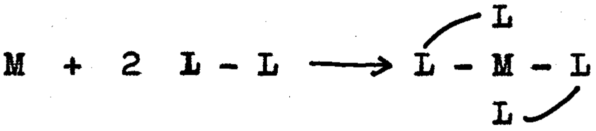
Stability constants of cupric, nickelous and cobaltous ion chelates were determined spectrophotometrically. The logarithms of the stability constants for the metal chelates are: Cu(II) - 6.45, Ni(II) - 4.86, and Co(II) - 3.66. This order of stability of the chelates is in agreement with the Irving-Williams stability series based on the central metal ion.

I INTRODUCTION

A General Discussion

The chemistry of metal chelate compounds dates back to 1891, when Alfred Werner[1] started a new phase of the inorganic chemistry with his coordination theory. He explained the formation of molecular complexes by introducing the coordination number depending on the nature of the central metal ion.

A coordination compound is formed on combination of a metal ion with an electron donor. If the combining molecule has more than one donor group, and the spatial arrangement permits formation of one or more rings, the resulting compound is called a chelate compound and the electron donating molecule the chelating agent.



$$M + 2\ L - L \longrightarrow L - \overset{L}{\underset{L}{M}} - L$$

where M = metal ion having a coordination number of four;

L - L = chelating agent.

Since the beginning of this century there has been an increasing number of investigations performed attempting to ascertain the nature of chelates and the factors

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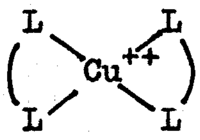
(1) Alfred Werner, "Beitrag zur Konstitution Anorganischer Verbindungen", Akademische Verlagsgesellschaft M. B. H., Leipzig, 1924.

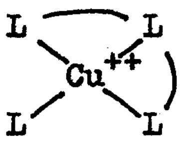
influencing the formation and the stability of these complexes.

Morgan and Drew[2] were the first to use the term "chelation" for coordination compounds with ring systems. They also proposed the terms unidentate, bidentate, tridentate, etc. for complexing agents having one, two, three, etc. donor groups, respectively. A unidentate substance would not permit ring formation; thus chelation is restricted to bidentate, tridentate and higher donor groups.

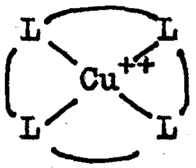
The number of chelating groups combining with a metal ion is determined by the coordination number of the metal. For example, cupric ion has the coordination number of four, and thus can combine with two bidentate groups, but only one tridentate or quadridentate group:



I



II



III

The bonding between the central metal ion and the donor atom in a chelate compound is usually considered to be ionic or covalent or of some intermediate character.

The structure and properties of chelate compounds

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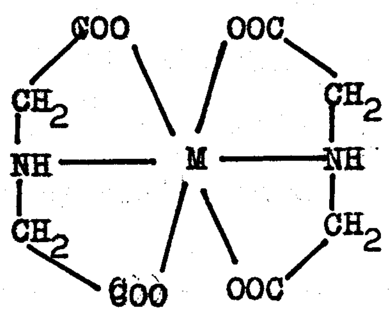
(2) Morgan and Drew, J. Chem. Soc., 117, 1456,(1920).

are determined to a great extent by the nature of the chelating agent. The size and the number of rings formed, as well as basicity, steric factors and possible resonance will influence the stability of the chelate. Also, the nature of the donor atom and the nature of the central metal ion has to be considered.

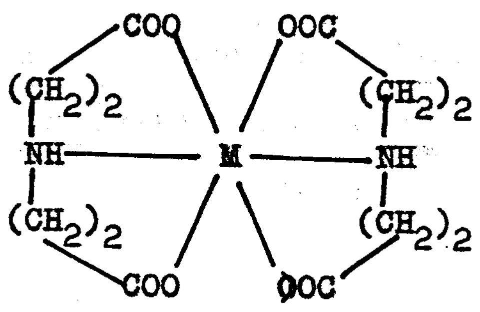
Size of the Ring.

Investigations have shown that five and six-membered chelates are the most stable and common chelates. Boeseken[3] studied chelates formed between boric acid and glycols and found that the most stable chelates were formed with α-β-dihydroxy compounds, thus forming five-membered rings.

Chaberek and Martell[4] have investigated stabilities of some transition metal chelates with iminodiacetic (IV) and iminodipropionic (V) acids:



IV



V

It was found that an increase in the size of the rings

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(3) Boeseken, Ber., 46, 2612 (1913).
(4) S. Chabarek, Jr. and A. E. Martell, J. Am. Chem. Soc., 74, 5052,(1952).

from five to six members resulted in a rather marked decrease in the stability constants of the chelates.

An interesting study on the ring size was also conducted by Irving and Williams[5]. They investigated cupric and nickelous ion chelates with ethylenediamine, propylenediamine and 1,3-diaminopropane. Although the basic strength of 1,3-diaminopropane is greater, the six-membered ring chelates formed had lower stability than the five-membered ring chelates with ethylene- and propylene-diamines:

Table I

	Cu^{++}	Ni^{++}
Ethylenediamine[6] Log K (k_1k_2)	19.60	13.80
Propylenediamine Log K (k_1k_2)	19.66	13.71
1,3-diaminopropane[5]	16.94	-

Slightly different values were reported by Laitinen et al.[7] for ethylenediamine, propylenediamine and diethylenetriamine chelates with cupric ion:

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(5) H. Irving and R. J. P. Williams, J. Chem. Soc., 1953, 3192.

(6) G. A. Carlson, J. P. McReynolds and F. H. Verhoek, J. Am. Chem. Soc., 67, 1334 (1945).

(7) H. A. Laitinen, E. I Onstott, J. C. Bailar, Jr., S. Swann, Jr., J. Am.Chem. Soc., 71, 1551 (1949).

Table II

	Log K
Ethylenediamine	19.72
Propylenediamine	20.12
Diethylenetriamine	20.85

They suggested that the relative stability of diethylenetriamine chelate indicate a coordination number of six for cupric ion. However, it is questioned by other workers[8], because no tendency has been observed for hexacovalency of cupric ion.

Jonassen and Dexter[9] investigated cupric ion and ethylenediamine complexes and proposed two different complex ions formed:

$$(Cu(en)_2)^{+} \quad \text{and} \quad (Cu(en))^{++},$$

where en = ethylenediamine.

They used spectrophotometric methods and observed a shift in the absorption maximum toward shorter wave length when the ratio of ethylenediamine to cupric ion was increased two to one. Their observations agreed with the results obtained by Carlson and McReynolds[10], who studied these complexes by potentiometric titration methods.

Number of Rings.

Besides the size of the rings formed the number of rings

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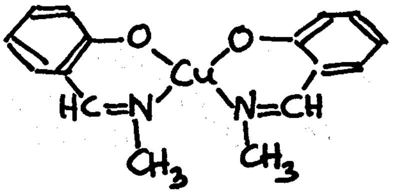
(8) J. Bjerrum, Chem. Revs., 46, 381 (1950).

(9) H. B. Jonassen and T. H. Dexter, J. Am. Chem. Soc., 71, 1553 (1949)/

(10) G. A. Carlson, J. P. McReynolds, F. H. Verhoek, J. Am. Chem. Soc., 67, 1334 (1945).

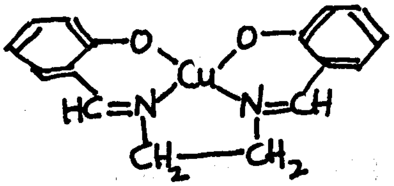
is an important factor in determining the stability of the chelate. Investigations have shown that an increase in the number of rings in a particular chelate results in an increase in the stability of the chelate.

Calvin and Bailes[11] performed polarographic studies of cupric chelates with substituted salicylaldimines:



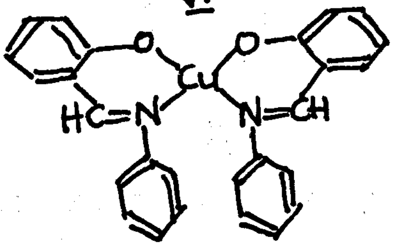
$E_{1/2} = 0.02$

VI



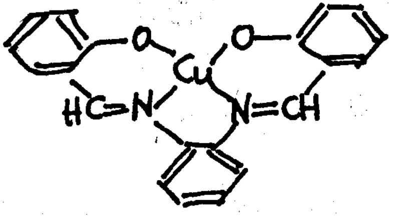
$E_{1/2} = -0.75$

VII



$E_{1/2} = -0.12$

VIII



$E_{1/2} = -0.76$

IX

The difference between these chelates is in the number of rings formed. The reported half-wave potentials (more negative values indicate a more stable chelate) show that an increase in the number of rings results in a greater stability of the chelate.

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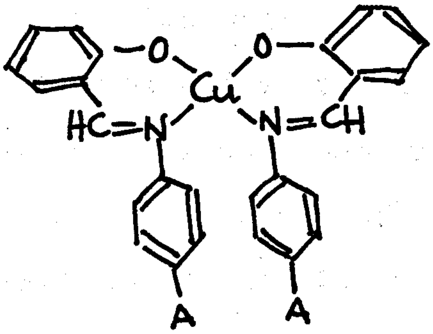
(11) M. Calvin and J. Bailes, J. Am. Chem. Soc., 68, 949 (1946).

Basicity of the Coordinating Group.

Another important factor determining the stability of the chelate is the basic strength of the chelating agent. Calvin and Bailes[12] investigated the stabilities of copper chelates with substituted anils of salicylaldehyde:



X

A	$E_{1/2}$
$-NO_2$	0.03
$-SO_3Na$	-0.09
	- 0.10
-H	-0.12
$-CH_3$	-0.15
-OH	-0.17
$-OCH_3$	-0.21

The reported half-wave potentials indicate an increase in the stability with the increasing base strength of the corresponding substituted anilines, except for the hydroxyl and methoxyl groups. The authors assume that the inversion of these two groups may be due to the uncertainties in the measurements. This is in agreement with the conclusions of Calvin and Wilson[13], that the more available the coordinating electron pair, the stronger the bonds formed with the metal ion. In this case an electron releasing group such as hydroxyl group

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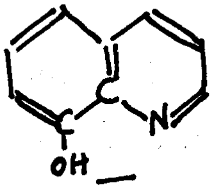
(12) M. Calvin and J. Bailes, J. Am. Chem. Soc., 68, 949, (1946).

(13) M. Calvin and K. W. Wilson, J. Am. Chem. Soc., 67, 2003, (1945).

will cause a shift of the electrons towards the nitrogen, thus making it more negative and increasing the availability of electrons for the nitrogen-cupric ion bond. An electron attracting group, such as nitro group will have the opposite effect: electrons will be drawn away from the nitrogen, and the strength of the bond between nitrogen and metal ion will be weakened.

Irving and Rossotti[14] have reported the stabilities of some metal chelates with 8-hydroxyquinoline and related substances. The aim of their study was to determine the changes in the stability of metal chelates with changes in the environment of the functional chelating group:



XI

They modified the chelating power of this group by changing the inductive effects on the hydroxyl group and the nitrogen atom by introducing substituents in the oxine skeleton and by replacing one -CH= in the heterocyclic ring by -N=.

The dissociation constants for the chelating agents were determined and it was found that pK_{OH} was increased

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(14) H. Irving and H. S. Rossotti, J. Chem. Soc., 1954, 2910.

by alkyl substitution in the 2-, 5-, and 7-positions of the oxine system, while substitution in the 6-position produced no change. This is in agreement with the expected inductive effect. Aza-substitution resulted in lowering of pK_{OH}, which may be attributed to the electron attracting power of the nitrogen atom.

Inductive effect causes an increase in pK_{NH} on alkyl substitution in the 2-, 5-, and 2:3-positions in oxine, while the lowering by substitution in the 7-position was explained as due to a displacement of the hydroxyl group by the methyl group towards the basic nitrogen atom resulting in hindering the approach of protons.

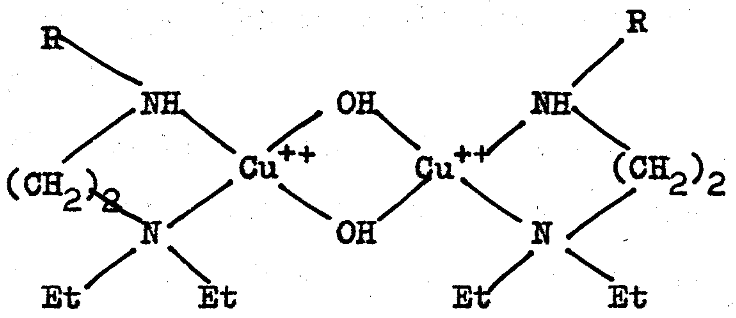
The strengths of the -OH and $>N^+-H$ bonds in the acids conjugate to oxine and its alkyl derivatives in the absence of steric factors were expected to show a quantitative relationship between the stabilities of the metal and proton complexes.

The authors state that for a given metal and a series of reagents of similiar type it can be shown that the free energy of formation of the metal complexes should be a linear function of the free energy of formation of the corresponding proton complexes. Deviations from the theoretically predicted behaviour were caused by steric hindrance when the reagent had substituents adjacent to the chelating nitrogen atom, and also by differences in the coordinating powers of the nitrogen atoms in the various reagents. With magnesium ion, which forms only weak links to nitrogen, the deviations were largely caused by steric hindrance, but zinc and nickel chelates in addition also displayed deviations caused by the inductive effect. Zinc and nickel form fairly strong metal-nitrogen bonds which may appreciably modify the inductive effects on the other chelating atom. This effect would be most noticeable with copper chelates because of its great affinity for nitrogen atoms. Thus, in cases where the metal ion is very strongly bonded to one of the chelating atoms it may cause changes in the inductive effects of the other atom, and theoretical predictions about the stability based upon the dissociation constants of the chelating agent may not be justified.

Steric Factors.

Steric factors are very important in chelate formation. A large bulky molecule will not form as stable a chelate as would be expected considering only the groups involved in chelation. Chelation can also be completely prevented by steric hindrance.

Irving, Butler, and Ring[15] have discussed the steric factors involved in chelate formation between cupric ion and substituted ethylenediamines. Cupric ion has the coordination number of four, and forms a one to two chelate with ethylene diamine, N-methyl ethylenediamine and NN'-diethyl ethylenediamine, while a binuclear complex is formed with N-methyl (or ethyl)-N'-diethyl ethylenediamine:



XI

where R = methyl or ethyl group,

Et = ethyl group.

Irving and Griffiths[16] performed a study of nickel, copper and zinc chelates with NN'-dimethyl ethylenediamine and NN-diethyl-NN-dimethyl ethylenediamine. They found that increasing substitution reduces stabilities of the chelates. This observation can be interpreted in terms

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(15) H. Irving, E. J. Butler and M. F. Ring, J. Chem. Soc., 1949, 1489.

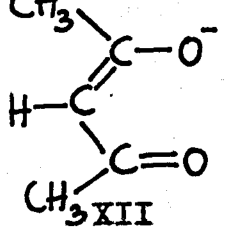
(16) H. Irving and J. M. M. Griffiths, J. Chem. Soc., 1954, 213.

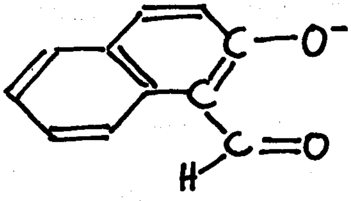
of steric hindrance. Also, when a metal reacts with more highly substituted chelating agents, the steric factors account for the preferential formation of basic or polynuclear chelates.

Resonance Effect.

Substitution of a group on the chelating agent not only may change the basicity of the donor groups and decrease the stability of the chelate by steric hindrance, but it also affect the possible resonance of the organic chelating molecule.

Calvin and Wilson[17] studied the influence of some structural factors upon the stability of the chelates of cupric ion with chelating agents such as β-diketones or o-hydroxy aromatic aldehydes. These organic compounds form chelates in which the four atoms bound to the metal are oxygen. The four groups of compounds studied may be represented by the following ions:


XII
Enolate ion of acetyl acetone


XIII
Naphtholate ion of 2-hydroxynaphthaldehyde-1

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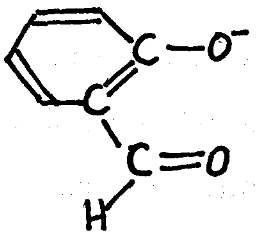
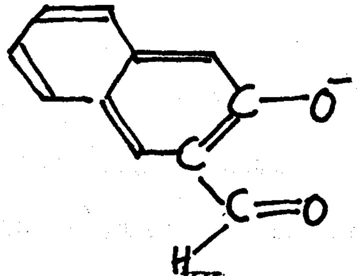
(17) M. Calvin and K. W. Wilson, J. Am. Chem. Soc., 67, 2003, (1945).



XIV

Phenolate ion of
salicylaldehyde



XV

Naphtholate ion of
2-hydroxynaphthaldehyde-3

In these compounds there is a modification of the nature of the double bond between the two carbon atoms of the three carbon system forming the conjugated chain between the oxygen atoms. In acetylacetone the two methyl groups do not enter into the resonating system, while in the other ions (XIII, XIV, XV) the double bond also takes part in the resonance of the aromatic ring. According to Pauling[18], numerical values can be assigned to double bonds in a resonating system. If a value of two is assigned to the double bond in the enolate ion of acetylacetone (XII), then the value of the double bond will decrease for the other ions because of additional resonance forms. Thus, the following values are obtained: for the double bonds:

XII = 2.00 XIV = 1.50

XIII = 1.67 XV = 1.33

The authors observed that this was also the order

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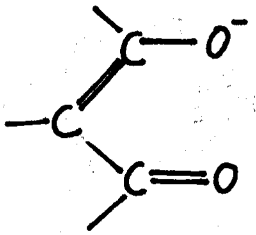
(18) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1941

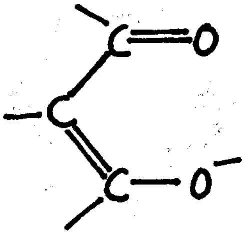
of decreasing stability of the copper chelates at a constant acidity of the chelating agent.

Experimental data showed that the enolate resonance of the type



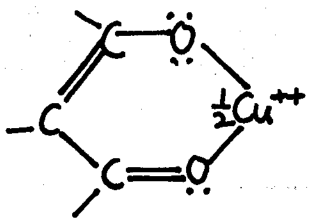
XVI

and



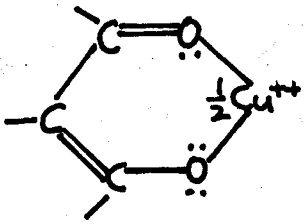
XVII

does not have an equal effect on the bonding of hydrogen and cupric ion, which leads to the assumption that the enolate resonance plays a different and greater part in the bonding of cupric ion that in the bonding of hydrogen. Calvin[17] suggested two possible explanations for this phenomenon. Transition elements are the most easily chelated metals, because their ions have low-lying vacant orbitals capable of accepting electron pairs to form covalent bonds. For cupric ion these bond orbitals may be either $3d^1 4s^1 4p^2$ or $4s^1 4p^3$. If a covalent bond is formed between oxygen and cupric ion, then the following structures are conceivable:



XVIII

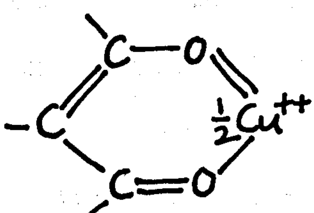
and



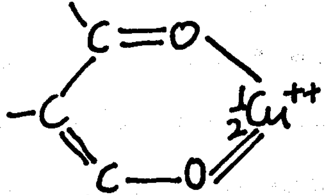
XIX

These charge distributions would account for the increased energy contribution of the enolate resonance.

As a second possibility the authors suggested a completely conjugated six-membered ring system:

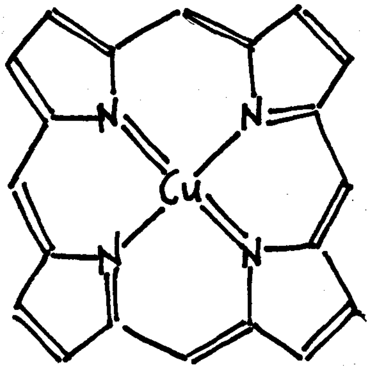

XX

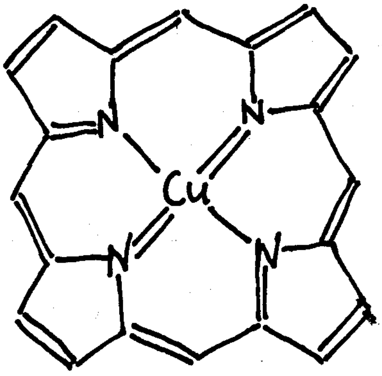
and


XXI

The possibility of such a structure would be governed by the availability and geometry of the orbitals of the metal ions involved in the chelate formation.

The importance of resonance is fully shown in natural pigments[19] such as chlorophyll, in which a porphyrin derivative is bound to a divalent metal ion. There are very stable chelates with resonating structures of the following type:


XXII


XXIII

A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, 1952.

Nature of the Donor Atom.

Discussion of the nature of the donor atom in a quantitative sense is difficult because the changes in the nature of the donor atom are usually accompanied by changes in basic strength, resonance, steric factors, size and number of rings, etc. Nevertheless, some qualitative trends can be observed. The most important factor affecting chelation with different donor atoms is the change in their basic strength. An interesting discussion about the tendencies of various donor atoms to complex with the metal ion was published by Sidgwick[20]. Chelation and studies of chelation have been mostly restricted to organic chelating agents in which the donor atoms are oxygen, nitrogen, and sulfur. Sidgwick pointed out that oxygen and nitrogen are quite similiar in their affinities for metal ions, because they both form very stable chelates with many metal ions. He also pointed out that increased substitution results in a decrease in the tendency for coordination with the metal ion:

$$H_2O > ROH > ROR$$
$$H_3N > RNH_2 > R_2NH > R_3N$$

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(20) Sidgwick, J. Chem. Soc., 1941, 433.

He divided metals into categories depending on the relative tendencies to coordinate with nitrogen and oxygen atoms. Ferric and cobaltous ions show a greater affinity for oxygen than for nitrogen, while cupric and nickelous ions prefer nitrogen. Of course, such factors as influence of substituents on the acidity, ring size and steric factors have to be considered for each specific chelating agent.

Irving and Williams[21] attempted to correlate the increments in stability constants for different metal ions with the nature of the donor atom. They found that the stability increment from metal to metal was greatest for nitrogen type chelating agents (ethylenediamine), less for N - O type (glycine), and still less for O - O type (oxalic acid). The differences between the slopes of the stability graphs led to the following order of stability:

ethylenediamine > amino acids > salicylaldehyde.

This shows that the more electropositive the coordinating atom of the chelating agent, the greater the stability increment from metal to metal.

Van Uitert and Fernelius[22] plotted electronegativity versus log K of the corresponding chelate and found an

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(21) H. Irving and R. J. P. Williams, J. Chem. Soc., 1953, 3192.

(22) L. G. Van Uitert and W. C. Fernelius, J. Am. Chem. Soc., 76, 375, (1954).

a variation in the slopes of chelating agents with different donor groups, which was least for O - O chelating agents and greatest for N - N chelating agents, This observation is in agreement with the previously discussed results obtained by Irving and Williams[21].

Nature of the Metal Ion.

Another factor influencing the stability of a chelate is the nature of the metal ion. Recently several studies have been made on the order of stability of various metals with a single chelating agent.

Mellor and Maley[23] examined the results reported by several investigators[24, 25, 26] about the stabilities of ethylenediamine and salicylaldehyde chelates with several metal ions and found that the stability of the bivalent metal chelates follows the order

$$Pd > Cu > Ni > Pb > Co > Zn > Cd > Fe > Mn > Mg$$

irrespective of the nature of the chelating agents involved. They pointed out that the stability of the chelate seemed to decrease with increasing basicity of the metal ion. This would indicate that the strength of the bonds in these chelates depends on the ability of

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(23) Mellor and Maley, Nature, 159, 370 (1947).
(24) J. Bjerrum, Chem. Abstracts, 35, 6527 - 6534 (1941).
(25) G. A. Carson, J. P. McReynolds, F. H. Verhoek, J. Am. Chem. Soc., 67, 1334 (1945).
(26)

of the metal ion to form covalent bonds. Thus, the metals which form the strongest covalent bonds form the most stable chelates.

Irving and Williams[26] investigated the stability of ferric, cobaltous, nickelous, cupric and zinc chelates. They proposed the following stability series: Fe

$$Fe < Co < Ni < Cu > Zn$$

This series was found to hold for nearly all chelates irrespective of the nature of the chelating agent or the number of molecules involved. Theoretical justification of this order can be found by considering the reciprocals of ionic radii and the second ionization potentials of the metals concerned.

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(26) H. Irving and R. J. P. Williams, J. Chem. Soc., 1953, 3192.

Metals of the first transition series have an incomplete 3d shell of electrons, which makes it available for bond formation with donor atoms. The fact that electrons can be rather easily removed from the metal accounts for the large number of chelates formed by these metals.

R. S. Nyholm(27) in his review on nickel complexes states that nickelous ion complexes can be divided into two classes on the basis of magnetic moments. Paramagnetic complexes have a tetrahedral structure formed by $4s4p^3$ bonds, which would give two unpaired 4p electrons, or octahedral structure formed by $4s4p^3 4d^2$ bonds, leaving two unpaired electrons in 3d orbital. There is a significant color difference between paramagnetic and diamagnetic complexes of nickelous ion. Paramagnetic complexes are usually green or blue, while diamagnetic are red, brown or yellow.

Dwyer and Mellor[28] found that differences between electronegativity of nickelous ion and the atoms linked to it in chelate compounds play an imporatant role. A large difference tends to make bonds predominantly ionic

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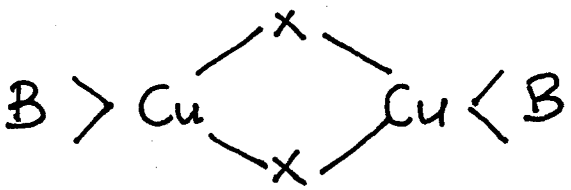
(27) R. S. Nyholm, Chem. Revs., <u>53</u>, 263 (1953).
(28) F. P. Dwyer and D. P. Mellor, J. Am. Chem. Soc., <u>63</u>, 81, (1941).

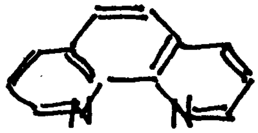
in character. They also found that nickelous complexes with four oxygens are paramagnetic, and readily take up two additional groups to assume octahedral configuration.

Copper has a great affinity for donor groups and readily forms stable chelate compounds. It has a coordination number of four, and no stable chelates copper chelates with a higher coordination number have been reported.

Most cupric ion chelates are hydrated and are either blue or violet-blue in color. It has been observed that cupric chelates have some tendency to form a bridged dimer, as first proposed by Mann, Purdie, and Wells[29] for cupric iodine and 2,2'-bipyridine. The following structural formula was used by Brandt, Dwyer and Gyarfas[30] to represent copper chelates with 2,2'-bipyridine and 1, 10-phenanthroline:



XXIV

where B =  or 

2,2'-bipyridine

1,10-phenanthroline

X = I^- or SCN^-.

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(29) F. G. Mann, D. Purdie, A. F. Wells, J. Chem. Soc., 1936, 1503.

(30) W. W. Brandt, F. P. Dwyer, E. C. Gyarfas, Chem. Revs., 54, 959 (1954).

Copper chelates have a square-planar structure arrangement, requiring dsp^2 orbitals. Mellor[31] postulated a rule stating that a covalent transition metal complex tends to assume that configuration which involves the least possible number of unpaired electrons. This would mean that the square-planar structure would be most common with elements like Ni^{++}, Co^{++} and Cu^{++}, which have zero or one unpaired electron, while it is very rare among ions with two or more unpaired electrons, like Fe^{++} and Mn^{++}.

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(31) D. Mellor, Chem. Revs., 33, 137 (1943).

B. Nature of This Investigation.

The present study is a continuation of the studies on chelation of a highly polar polyhydroxyamine 1,3-bis-(tris-(hydroxymethyl)-methylamino)-2-propanol dihydrochloride, which was synthesized by Pierce and Wotiz[32]. This study was initiated by Dr. Wm. E. Trout, Jr. At the present time the chelating tendencies of this substance with ferric ion are being investigated by Mrs. J. B. Gladding.

The object of this work was to determine the structure and stability of the chelates of cupric, nickelous, cobaltous, zinc, manganous and calcium ions with bis-(tris-(hydroxymethyl)-methylamino)-2-propanol dihydrochloride.

The aqueous solutions of the above mentioned substances were investigated by potentiometric titration method. Calcium, manganous and zinc ions showed very slight chelation, and the formed chelates were rather unstable. Cupric, nickelous and cobaltous ions formed relatively stable chelates with the chelating substance. Stability constants were determined by spectrophotometric studies for cupric, nickelous and cobaltous chelates. Also, the structures of the chelate compounds formed were postulated by correlating the experimental data obtained.

The dissociation constants of the chelating agent were determined by pH measurements.

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(32) J. S. Pierce and J. Wotiz, J. Am. Chem. Soc., <u>66</u>, 879 (1944).

II DISCUSSION OF METHODS USED

A. Potentiometric Titrations.

All chelating agents are either acids or bases, and the formation of a chelate results in a change of the hydrogen ion concentration of the solution. The greater the tendency of the metal ion to combine with the chelating agent, the greater will be the change in the hydrogen ion concentration of the solution as compared to the normal pH titration curve of the chelating agent alone. Thus, the pH effect can be used as an indication of the extent of chelation of a given metal ion with the chelating agent.

Hydrogen ion concentration measurements supply an accurate method for the determination of the stability constants of the chelates. A generalized method for determination of stability constants was developed by Bjerrum[33]. Martell and Calvin[34] in their book on chelate compounds have discussed this method rather thoroughly.

The formation of the complexes in an aqueous solution can be considered as occuring stepwise. The stability of the different complexes formed is characterized by the corresponding constants k_1, k_2,...

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(33) Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.
(34) Martell and Calvin, "Chemistry of the Chelate Compounds," Prentice-Hall, Inc., New York, 1953, p. 78 - 84.

k_n. If N molecules are bound with approximately the same affinity to the central ion, then the mean complexity constant $K = \sqrt[n]{k_1 k_2 \ldots k_n}$ is a measure of the complexing tendency of a system in comparison to other systems, if measurements were made under the same conditions.

The following general equilibrium occurs between the central ion and the donor molecules:

$$M + nL \rightleftarrows ML_n \qquad (1)$$

where M = central metal ion,

L = donor molecule,

n = 1, 2, 3...,

( ) represents activities.

Then the mean complexity constant is represented by

$$K_n = \frac{(ML_n)}{(M)\ (L)^n} \qquad (2)$$

The consecutive steps in the chelate formation are represented as follows:

$$M + L \rightleftarrows ML \qquad (3)$$

$$ML + L \rightleftarrows ML_2 \qquad (4)$$

....

$$ML_{n-1} + L \rightleftarrows ML_n \qquad (6)$$

and the consecutive constants are expressed as follows:

$$k_1 = \frac{(ML)}{(M)\ (L)} \qquad (7)$$

$$k_2 = \frac{(ML_2)}{(ML)\ (L)} \qquad (8)$$

$$\cdots\cdots\cdots\cdots\cdots$$

$$k_n = \frac{(ML_n)}{(ML_{n-1})\ (L)} \qquad (9)$$

The average number of donor groups bound per central metal ion is represented by

$$\bar{n} = \frac{(ML) + 2\,(ML_2) + \cdots\cdots\cdots + n\,(ML_n)}{(M) + (ML) + (ML_2) + \cdots + (ML_n)} \qquad (10)$$

On substitution of values for (ML), (ML_2), ... (ML_n) from equations (7), (8), and (9), the Bjerrum formation function is obtained:

$$\bar{n} = \frac{k_1(L) + 2\,k_1k_2(L)^2 + \cdots\cdots\cdots + n\,k_1k_2\ldots k_n(L)^n}{1 + k_1(L) + k_1k_2(L)^2 + \cdots\cdots + k_1k_2\ldots\ldots k_n(L)^n} \qquad (11)$$

Experimentally, the concentration of the uncomplexed donor molecule is determined and $\bar{n}$ is calculated from the equation

$$\bar{n} = \frac{C_L - (L)}{C_M} \qquad (12)$$

where C_L = total concentration of donor substance,

C_M = total concentration of metal ion,

(L) = concentration of uncomplexed donor substance.

If no other interfering factors are present, the ratio of two succesive constants will be inversely proportional to the number of groups attached and directly proportional to the number of unfilled positions:

$$\frac{k_n}{k_{n+1}} = \frac{n+1}{n} \quad \frac{N-n+1}{N-n} \qquad (13)$$

where n = number of groups attached,

N = total number of positions available (coordination number).

Bjerrum modified this purely statistical prediction by introducing a spreading factor x:

$$\frac{k_n}{k_{n+1}} = \frac{n+1}{n} \quad \frac{N-n+1}{N-n} \quad (x)^2 \qquad (14)$$

If the spreading factor has a value greater than one, the difference between the two successive formation constants will be greater than statistically predicted.

Bjerrum has shown that the Nth root of the over-all stability constant is equal to the reciprocal of the concentration of the uncomplexed donor molecule when the degree of formation n/N = 0.5. Also, in cases, where the spreading factor is very large, the same applies to the succesive stability constants. Thus, in a case like this a plot of $\bar{n}$ versus 1/L or pL will allow graphical determination of the stability constants.

Also, constants can be calculated by solving N simultaneous formation functions containing N unknown terms.

B. Absorption Spectra.

One of the most distinctive characteristics of chelates is their absorption spectra. Thus, spectrophotometric measurements are a valuable source for obtaining information about the chelate formed.

The composition of the chelate compound can be determined by the method of continuous variations, called Job's[35] method. When the metal ion and the chelating agent are brought together in the same ratio as they exist in the chelate, the concentration of the chelate is greatest for a constant total concentration of the reacting substances. For example, let M be the metal ion and L the chelating agent; then

$$M + nL \rightleftarrows ML_n \qquad (15)$$

$$K = \frac{(ML_n)}{(M)\ (L)^n} \qquad (16)$$

where ( ) = activities $\approx$ molar concentrations.

If (M) + (L) = c, where c is a constant, then the concentration of ML_n is the greatest, when (L)/(M) = n. The optical density of the solution is proportional to the chelate concentration in regions where the chelate compound is the only absorbing species. If the optical

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(35) Job, Ann. Chim. (10) 9, 113,9 (1928) as discussed by Martell and Calvin, op. cit., p. 28 - 30.

density if plotted versus the ratio of concentrations:

$$R = \frac{(M)}{(M) + (L)} \qquad (17)$$

the resulting curve will have a maximum at the composition corresponding to the formula of the chelate.

Spectrophotometric measurements can also be used to determine the stability constants of chelates, in which case the absorbing species must obey Beer's law and the formula of the chelate must be known.

Martell and Calvin[36] have discussed a method for determining stability constants by using the optical density of the chelate solution to determine one of the components involved in equilibrium. This implies that only one substance absorbs at the wave length used or that interference from other substances present may be overcome by applying a correction.

For the following equilibrium

$$M + L \rightleftharpoons ML,$$

the stability constant is represented by

$$K = \frac{(ML)}{(M)\ (L)} \qquad (18)$$

If the chelate ML is the only absorbing substance

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(36) Martell and Calvin, op. cit. p. 98.

present and the solution obeys Beer's law, then

$$(ML) = kX \qquad (19)$$

where k = proportionality constant,

X = optical density of the solution.

If a second solution with different concentrations for the metal and chelating agent has the same optical density, then, since

$$X_1 = X_2,$$

$$(ML)_1 = (ML)_2 \cong (ML).$$

Thus, the equation for the stability constant can be rewritten as follows:

$$K = \frac{(ML)}{(C_{M1} - (ML))\,(C_{L1} - (ML))} \cong \frac{(ML)}{(C_{M2} - (ML))\,(C_{L2} - (ML))} \qquad (20)$$

where C_{M1} and C_{M2} = total concentrations of the metal species in solution one and two,

C_{L1} and C_{L2} = total concentrations of chelating agent in solutions (1) and (2).

The above equation (20) is first solved for the concentration of the chelate compound (ML) and then for the stability constant K, as the concentrations of the metal ion and chelating agent are known.

III EXPERIMENTAL

A. Materials and Apparatus Used.

The chelating agent used in this investigation was 1,3-bis-(tris-hydroxymethyl-(methylamino)-2- propanol dihydrochloride will be referred to as "Disec" in the following discussion. "Disec", prepared by Mrs. J. B. Gladding[39] according to the method of Pierce and Wotiz[37], was purified by recrystallization from a water and ethyl alcohol solution. "Disec" was dissolved in a water solution until the solution was saturated and hot alcohol was added. It was found that a purer substance was obtained by adding approximately eight parts of alcohol to each part of the saturated water solution[38]. The recrystallized substance was dried in an oven at 110°C for two hours, and the melting point was determined. The pure product melted between 184° - 187°C , which is in agreement with the value of 184° - 186°C reported by Pierce and Wotiz[37].

The following nitrates were used as sources of cations: cupric, nickelous, cobaltous, zinc, manganous and calcium. All salts were Baker & Adamson Analytical reagent grade. Water, redistilled from a dilute potassium permanganate solution, was used to prepare .10 M salt solutions.

Cupric nitrate solution was standardized by the

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(37) J. S. Pierce and J. Wotiz, J. Cm. Chem. Soc., 73, 2594 (1951)
(38) J. S. Pierce, private communications.
(39) J. B. Gladding, Thesis, University of Richmond, 1955.

iodometric method[40]. Nickelous and cobaltous nitrate solutions were standardized by the potassium cyanide-silver nitrate method[41].

Sodium hydroxide solution was prepared CO_2 free and was standardized against potassium acid phthalate[42], primary standard analytical reagent, Mallinckrodt.

Sodium nitrate solution was prepared from dried sodium nitrate, analytical reagent, Mallinckrodt.

Titrations were performed using a Beckman Model G glass electrode pH meter. It was frequently calibrated with a Beckman buffer solution of pH 7.00 ± .01 @ 25°C, based on U. S. National Bureau of Standards certified buffers.

A constant temperature bath was used to keep sample solutions at constant temperature.

Spectrophotometric measurements were made with a Beckman DU spectrophotometer. One centimeter calibrated silica cells were used in measurements. These cells were calibrated against each other using redistilled water. over the spectral range used.

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(40) W. C. Pierce and E. L. Haenisch, "Quantitative Analysis," John Wiley & Sons, Inc., New York, 1948, p. 247.

(41) Scott's Standard Methods of Chemical Analysis, N. H. Furman, Editor, D. Van Nostrand Co., Inc., New York, 1946, Vol. 1, p.319,622.

(42) Pierce and Haenisch, op. cit., p.127.

B. Potentiometric Titrations.

A preliminary pH titration study was performed to determine the chelating tendencies of cupric, nickelous, cobaltous, zinc, manganous, and calcium ions with "Disec". When this compound was titrated in the presence of a metal ion, in the reaction in which chelate formation occurs, more moles of sodium hydroxide were required to reach a given pH value than in the absence of the metal ion.

A typical acid-base titration of the hydrochloride of the polyamino alcohol was carried out with sodium hydroxide and the changes in pH were determined by using a Beckman Model G pH meter calibrated with a Beckman buffer solution of pH 7. The concentration of "Disec" was 5×10^{-3} molar. The ionic strength was kept constant at 0.2 molar by adding 1.0 molar sodium nitrate solution. The sample solution was kept in a constant temperature bath at $28^{\circ} \pm .2^{\circ}C$ until the titration, during which frequent checks were made of the temperature of the solution. Titrations were performed in a nitrogen atmosphere. The nitrogen gas was passed through a drying tube containing soda lime and then through a pre-saturator containing sodium nitrate solution. During the titration the solution was kept stirred by a magnetic stirrer.

The pH titration curve for "Disec" obtained by the above described procedure was used as a reference curve in determining the chelating tendencies of the metal ions. Specified conditions were kept constant for all pH titrations.

Copper.

Solutions of cupric nitrate and "Disec" were prepared of the following ratios of cupric ion to "Disec" of 1:1, 1:2, 1:3 and 1:6. The concentration of "Disec" was kept constant at 5×10^{-3} molar, while the cupric ion concentration was varied. Figure II shows that no changes are produced in the shapes of the curves with different ratios. This indicates that only one complex is formed between cupric ion and "Disec".

The titration curves also show that a relatively stable chelate is formed with cupric ion. Chelation starts at about pH 2.5 and is completed at pH 4.

A titration was attempted in which the ratio of "Disec" to cupric ion was 1:2, but cupric hydroxide formation was observed at about pH 6. This indicates that the chelate formed is of a ratio of cupric ion concentration either equal or less than "Disec" concentration.

Solutions were left standing for two weeks at pH 11, and at the end of this period no precipitation was observed. This was accepted as a further demonstration

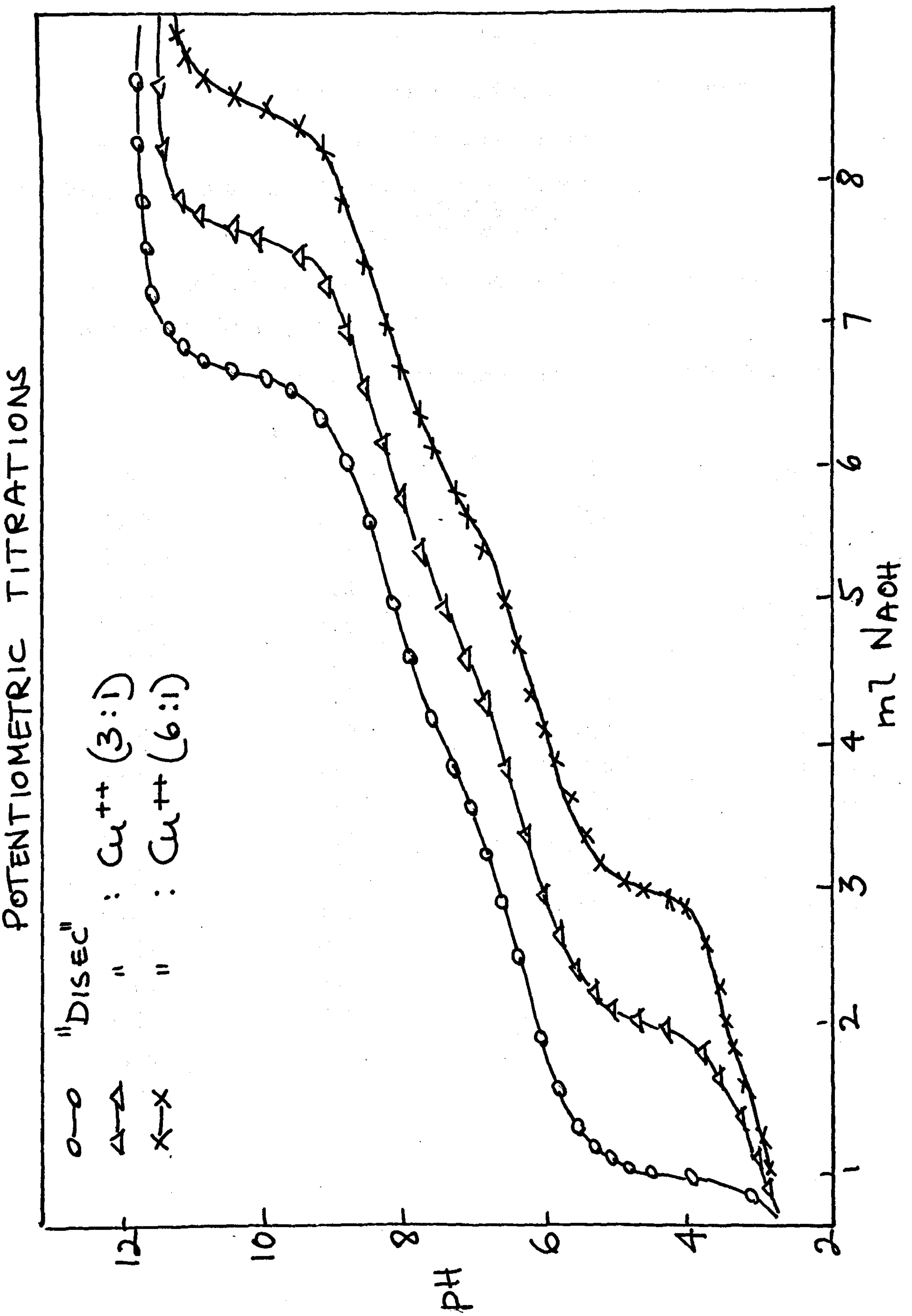

POTENTIOMETRIC TITRATIONS
o—o "DISEC"
△—△ " : Cu++ (3:1)
×—× " : Cu++ (6:1)
pH
2
4
6
8
10
12
1
2
3
4
5
6
7
8
ml NaOH

FIGURE II

TABLE III

(1) Potentiometric Titration of "Disec".

(Data for Figure II)

Sample solution: 50 ml .100 M "Disec"
20 ml 1.0 M $NaNO_3$
10 ml .101 M HNO_3

Solution was diluted to 100 ml; temperature was kept at 28°C ± .2°.

Titration was performed with 1.050 N NaOH.

pH	ml NaOH	pH	ml NaOH
2.18	0.00	7.64	4.24
2.37	0.40	7.93	4.65
2.61	0.62	8.16	5.08
2.97	0.83	8.49	5.60
3.87	0.95	8.83	6.04
4.50	1.00	9.11	6.31
4.75	1.03	9.62	6.55
4.97	1.09	9.95	6.62
5.24	1.18	10.35	6.68
5.50	1.33	10.84	6.75
5.74	1.55	11.04	6.82
6.04	1.96	11.27	6.93
6.37	2.52	11.53	7.21
6.62	2.91	11.77	7.88
6.84	3.25	12.00	9.36
7.08	3.58	12.04	10.02
7.36	3.90		

TABLE IV

Potentiometric Titration of "Disec" and Copper.

(Data for Figure II)

Solutions:

(1)	(2)
30 ml ,100 M "Disec"	30 ml .100 M "Disec"
10 ml .103 M $Cu(NO_3)_2$	5 ml .103 M $Cu(NO_3)_2$
20 ml 1.0 M $NaNO_3$	20 ml 1.0 M $NaNO_3$
10 ml .101 M HNO_3	10 ml .101 M HNO_3

Solutions were diluted to 100 ml; temperature was kept st 28°C ± .2°.

Titration was performed with 1.050 N NaOH.

(1)

pH	ml NaOH
2.16	0.00
2.26	0.20
2.37	0.40
2.52	0.61
2.65	0.80
2.78	0.99
2.91	1.18
3.04	1.40
3.13	1.60
3.23	1.81
3.32	2.00
3.46	2.32
3.68	2.64
3.99	2.85
4.27	2.92
4.52	2.96
4.72	3.00
4.97	3.10
5.16	3.20
5.38	3.37
5.59	3.58
5.79	3.85
5.95	4.06
6.16	4.38
6.34	4.66
6.56	4.98
6.84	5.31
7.04	5.53
7.27	5.76
7.59	6.05
7.83	6.32
8.05	6.63
8.28	7.00
8.56	7.42
8.84	7.80
9.22	8.17
9,53	8.36
9.95	8.51
10.40	8.60
10.65	8.65
10.90	8.70
11.16	8.81
11,37	9.00
11.62	9.37
11.76	10.00

(2)

pH	ml NaOH
2.20	0.00
2.40	0.45
2.64	0.76
2.96	1.10
3.22	1.40
3.44	1.66
3.72	1.84
4.35	2.00
4.66	2.03
5.00	2.13
5.24	2.24
5.47	2.40
5.67	2.61
5.97	2.98
6.24	3.40
6.52	3.86
6.81	4.28
7.14	4.67
7.44	4.97
7.76	5.37
8.03	5.75
8.25	6.12
8.54	6.57
8.82	6.94
9.12	7.24
9.48	7.47
10.14	7.63
10.46	7.70
10.86	7.75
11.06	7.81
11.27	7.94
11.55	8.28
11.80	9.00
11.97	10.08

of the cupric ion-"Disec" chelate stability.

The copper-"Disec" chelate water solution was violet blue as compared to a light blue cupric nitrate solution.

Nickel.

The same procedure as for cupric ion-"Disec" system was employed with nickelous ion-"Disec" solutions. The concentration of "Disec" was kept constant at 5×10^{-3} molar and the concentration of nickelous ion was varied at the following ratios of nickel to "Disec": 1:1, 1:2.5, 1:3. The shapes of the titration curves remained the same for all these titrations, and this was interpreted as an indication that only one complex is formed between nickelous ion and "Disec".

Precipitation took place at pH 7.5, when the ratio of nickelous ion to Disec was 2:1, showing that the complex formed contains either equimolar amounts of nickelous ion and "Disec" or more than one mole of "Disec" per each mole of nickel (II).

Nickelous nitrate solution showed precipitation starting with pH 7.5, caused by nickel hydroxide formation.

Chelation between nickelous ion and "Disec" starts at about pH 4 as indicated by Figure III. The chelate

POTENTIOMETRIC TITRATIONS

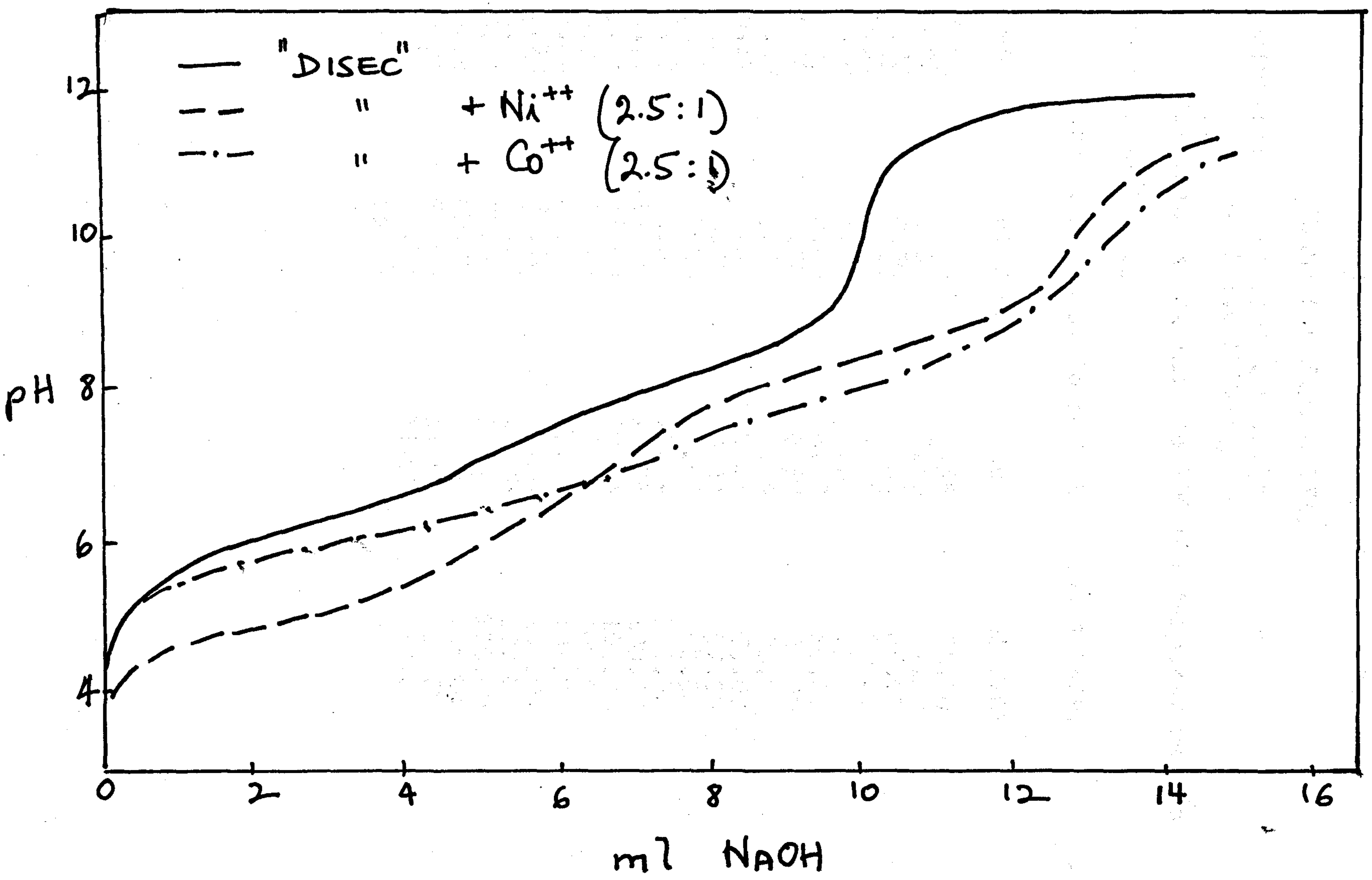


FIGURE III

TABLE V

Potentiometric Titration of "Disec".

(Data for Figure III)

Solution: 50 ml .100 M "Disec"
20 ml 1.0 M $NaNO_3$

Solution was diluted to 100 ml; temperature was kept at 28°C ± .2°.

Titration was performed with .100 N NaOH.

pH	ml NaOH	pH	ml NaOH
3.66	0.00	7.54	58.00
4.00	.30	7.68	61.00
4.32	0.60	7.81	65.00
4.53	1.00	7.98	70.00
4.70	1.50	8.14	75.00
4.83	2.00	8.32	80.00
4.94	2.50	8.50	85.00
5.02	3.00	8.73	90.00
5.17	4.00	9.07	95.00
5.26	5.00	9.27	97.00
5.43	7.00	9.53	98.50
5.55	9.00	10.04	100.00
5.71	12.00	10.33	100.50
5.83	15.00	10.53	101.00
5.95	18.00	10.78	102.00
6.04	21.00	10.95	103.00
6.18	25.00	11.16	105.00
6.34	30.00	11.28	107.00
6.53	35.00	11.40	110.00
6.73	40.00	11.54	115.00
6.95	45.00	11.63	120.00
7.18	50.00	11.75	130.00
7.42	55.00		

TABLE VI

Potentiometric Titration of $Ni(NO_3)_2$ and "Disec".

(Data for Figure III)

Solution: 50 ml .100M"Disec"
20 ml .101 M $Ni(NO_3)_2$
20 ml 1.0 M $NaNO_3$

Solution was diluted to 100 ml; temperature was kept at 28°C ± .2°.

Titration was performed with .100 N NaOH.

pH	ml NaOH	pH	ml NaOH	pH	ml NaOH
3.60	0.00	5.78	46.00	8.37	98.00
3.87	.50	5.90	48.00	8/43	100.00
4.03	1100	6.02	50.00	8.53	103.00
4.13	1.50	6.12	52.00	8.63	106.00
4.17	2.00	6.23	54.00	8.75	110.00
4.23	2.50	6.33	56.00	8.86	113.00
4.26	3.00	6.44	58.00	8.88	116.00
4.33	4.00	6.56	60.00	9.20	120.00
4.40	5.00	6.69	62.00	9.34	122.00
4.44	6.00	6.84	64.00	9.52	124.00
4.52	8.00	6.90	65.00	9.75	126.00
4.57	10.00	6.96	66.00	10.02	128.00
4.64	12.00	7.03	67.00	10.31	130.00
4.69	14000	7.10	68.00	10.53	132.00
4.73	16.00	7.17	69.00	10.72	134.00
4.78	18.00	7.25	70.00	10.85	136.00
4.83	20.00	7.38	72.00	10.97	138.00
4.87	22.00	7.49	74.00	11.09	140.00
4.96	25.00	7.62	76.00	11.17	142.00
5.02	27.00	7.72	78.00	11.25	144.00
5.08	30.00	7.78	80.00	11.33	146.00
5.16	32.00	7.86	82.00	11.37	148.00
5.23	34.00	7.98	85.00	11.43	150.00
5.28	36.00	8.04	87.00		
5.37	38.00	8.14	90.00		
5.46	40.00	8.20	92.00		
5.56	42.00	8.26	94.00		
5.67	44.00	8.32	96.00		

TABLE VII

Potentiometric Titration of $Co(NO_3)_2$ and "Disec".

(Data for Figure III)

Solution: 20 ml .102 M $Co(NO_3)_2$
50 ml .100 M "Disec"
20 ml 1.0 M $NaNO_3$

Solution was diluted to 100 ml; temperature was kept at 28°C ± .2°.

Titration was performed with .100 N NaOH.

pH	ml NaOH	pH	ml NaOH
3.65	0.00	7.26	76.00
4.45	1.00	7.38	78.00
4.74	2.00	7.44	80.00
4.92	3.00	7.55	83.00
5.03	4.00	7.65	86.00
5.12	5.00	7.77	90.00
5.26	7.00	7.95	95.00
5.40	10.00	8.12	100.00
5.48	12.00	8.28	105.00
5.57	15.00	8.48	110.00
5.66	18.00	8.71	115.00
5.72	20.00	9.00	120.00
5.78	23.00	9.13	122.00
5.85	26.00	9.27	124.00
5.90	28.00	9.43	126.00
5.94	30.00	9.61	128.00
6.00	33.00	9.77	130.00
6.06	36.00	9.95	132.00
6.16	40.00	10.15	134.00
6.26	45.00	10.33	136.00
6.38	50.00	10.52	138.00
6.53	55.00	10.69	140.00
6.67	60.00	10.85	142.00
6.85	65.00	10.97	144.00
6.93	67.00	11.15	146.00
7.03	70.00	11.23	148.00
7.12	72.00		
7.18	74.00		

seems to be most stable above pH 9.5.

The solutions were left standing for two weeks, and no precipitation was observed at the end of this period. This indicates that nickel-"Disec" chelate is rather stable in water solution at a high pH.

The color of the chelate solution was lavender, while nickel nitrate in water solution is light blue.

Cobalt (II).

In pH titrations of cobaltous ion-"Disec" solutions the concentration of "Disec" was constant at 5×10^{-3} molar, and the concentration of cobaltous ion was varied to give the ratios of 1:2, 1:2.5 and 1:3 of the metal ion to "Disec". No change in the shape of the curve was observed with the change in the concentration ratios. This suggests that only one complex is formed between cobaltous ion and "Disec".

When the ratio of cobalt to "Disec" was 2;1, precipitation occured at about pH 8, which shows that not all cobaltous ions have formed complexes with "Disec" and thus are free to form cobaltous hydroxide.

Cobaltous nitrate solution showed precipitation around pH 8.

Slight chelation between cobaltous ion and "Disec" starts at pH 5.5 (Figure III), showing an increase with increasing pH values.

Precipitation was observed on the next day with a cobalt-"Disec" solution at pH 11. This indicates that the cobalt-"Disec" chelate is rather unstable in water solution.

The color of the cobalt-"Disec" chelate water solution was deep red as compared with cobaltous nitrate solution, which is pink.

Zinc, Manganous and Calcium Ions.

With the concentration of "Disec" kept constant at 5×10^{-3} molar, solutions of the ratio 1:2 of zinc, manganous and calcium ions to "Disec" were prepared.

Chelation between zinc ion and "Disec" started at about pH 6 as shown in Figure IV. The chelate compound is most stable above pH 9.

Zinc chelate with "Disec" is a colorless substance in water solution. It showed some hydroxide formation on standing.

Manganous ion shows to have very small tendency to chelate "with "Disec")(Figure IV). Only at pH 8.5 and above some chelation was observed. On potentiometric titration the color of the manganousion -"Disec" solution

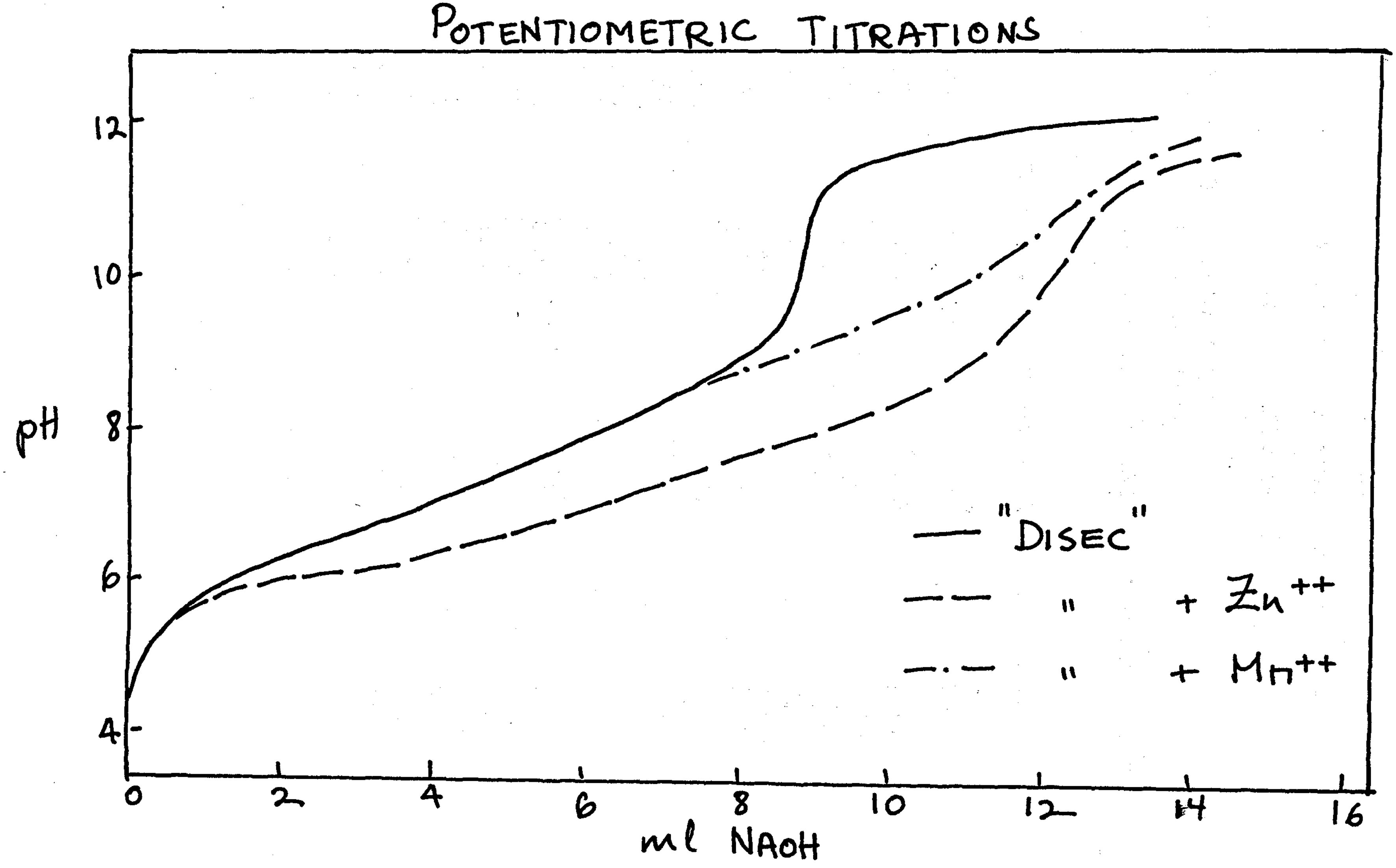

POTENTIOMETRIC TITRATIONS
pH
12
10
8
6
4
0
2
4
6
8
10
12
14
16
ml NaOH
"DISEC"
" + Zn++
" + Mn++

FIGURE 4

TABLE VIII

Potentiometric Titration of "Disec".

(Data for Figure IVI)

Solution: 50 ml ,100 M "Disec"
20 ml 1.0 M $NaNO_3$

Solution was dilited to 100 ml; temperature was kept at 28°C ± :2°.

Titration was performed with 1.152 N NaOH.

pH	ml NaOH	pH	ml NaOH
3.74	0.00	8.06	6.00
4.05	0.02	8.22	6.40
4.33	o.04	8.37	6.80
4.48	0.06	8.54	7.20
4.62	0.08	8.73	7.60
4.72	0.10	8.97	8.00
4.86	0.14	9.14	8.20
5.02	0.20	9.37	8.40
5.14	0.26	9.86	8.60
5.25	0.34	10.04	8.64
5.33	0.40	10.26	8.68
5.44	0.50	10.56	8.72
5.53	0.60	10.78	8.76
5.66	0.80	10.95	8.80
5.88	1.20	11.12	8.86
6.03	1.50	11.23	8.92
6.24	2.00	11.34	9.00
6.47	2.60	11.43	9.10
6.73	3.20	11.55	9.30
6.92	3.60	11.67	9.60
7.13	4.00	11.78	10.00
7.34	4.40		
7.50	4.70		
7.65	5.00		
7.77	5.30		
7.91	5.60		

TABLE IX

Potentiometric Titration of $Zn(NO_3)_2$ and "Disec".

(Data for Figure IV)

Solution: 20 ml .10 M $Zn(NO_3)_2$
50 ml .100 M "Disec"
20 ml 1.0 M $NaNO_3$

Solution was diluted to 100 ml; titration was performed with 1.152 N NaOH.

pH	ml NaOH	pH	ml NaOH
3.73	0.00	7/77	8.20
4.14	0.02	7.93	8.60
4.28	0.04	8.07	9.00
4.45	0.06	8.25	9.50
4.55	0.08	8,45	10.00
4.63	0.10	8.63	10.40
4.76	0.14	8.83	10.80
4.90	0.20	9.10	11.20
5.01	0.26	9.27	11.40
5.08	0.32	9.48	11.60
5.17	0.40	9.61	11.70
5.26	0.50	9.74	11.80
5.34	0.60	9.94	11.92
5.46	0.80	10,05	12.00
5.64	1.20	10.37	12.20
5.74	1.50	10.53	12.30
5.87	2.00	10.67	12.40
6.03	2.60	10.95	12.60
6.16	3.20	11.13	12.80
6.33	3.80	11.27	13.00
6.48	4.40	11.43	13.30
6.67	5.00	11.53	13.60
6.80	5.40	11.63	14.00
6.95	5.80	11.73	14.50
7.07	6.20	11.80	15.00
7.23	6.60		
7.36	7.00		
7.51	7.40		
7.64	7.80		

turned from colorless to red. Precipitation was observed about an hour later.

Calcium ion shows even less tendency to chelate with "Disec". Probably slight chelation takes place above pH 9, but the chelate formed is very unstable, as demonstrated by immediate precipitation.

C. Spectrophotometric Measurements.

It was decided to determine the composition and stability constants of the relatively stable colored chelates formed by cupric, nickelous and cobaltous ions with "Disec".

The composition of the above mentioned chelates was determined by the method of continuous variation. This method was discussed on p. 28. This method is based on having only one of the species present exhibit absorbance at a particular wave length.

Thus, the spectra of cupric, nickelous and cobaltous salt solutions with and without "Disec" were investigated to find a suitable region for Job's method.

Metal-"Disec" solutions were prepared having the ratio of 2:5 . The ionic strength was kept constant by adding sodium nitrate solution. The pH of the solutions was adjusted with carbonate-free sodium hydroxide solution.

Water used in these solutions was previously redistilled from a dilute potassium permanganate solution. Temperature was kept controlled at 28°C ± .5°.

One-centimeter calibrated silica cells were used for the measurements. Sodium nitrate solution of the same ionic strength as that of the sample solutions was used as the reference liquid for the spectrophotometric measurements.

The spectra of the metal-"Disec" solutions were investigated at 10 mu intervals from 320 to 650 mu.

Cupric ion-"Disec" chelate showed the maximum absorbance at 610 mu. The absorbance of the cupric nitrate solution was negligible in the region from 500 to 550 mu (Figure 5).

A very interesting absorption spectrum is exhibited by nickel-"Disec" chelate. Two maxima of absorption occurs at 360 mu and at 580 mu. The best region for Job's method was considered either from 340 to 360 mu or 560 to 580 mu (Figure 6).

Cobaltous ion and "Disec" chelate shows an absorption maximum at about 540 mu. The salt solution also showed some absorbance in the visible spectral region. Best wave lengths for Job's method were found to be from 350 to 400 mu and at 600 mu, as the absorbance of the salt solution is rather small (Figure 7).

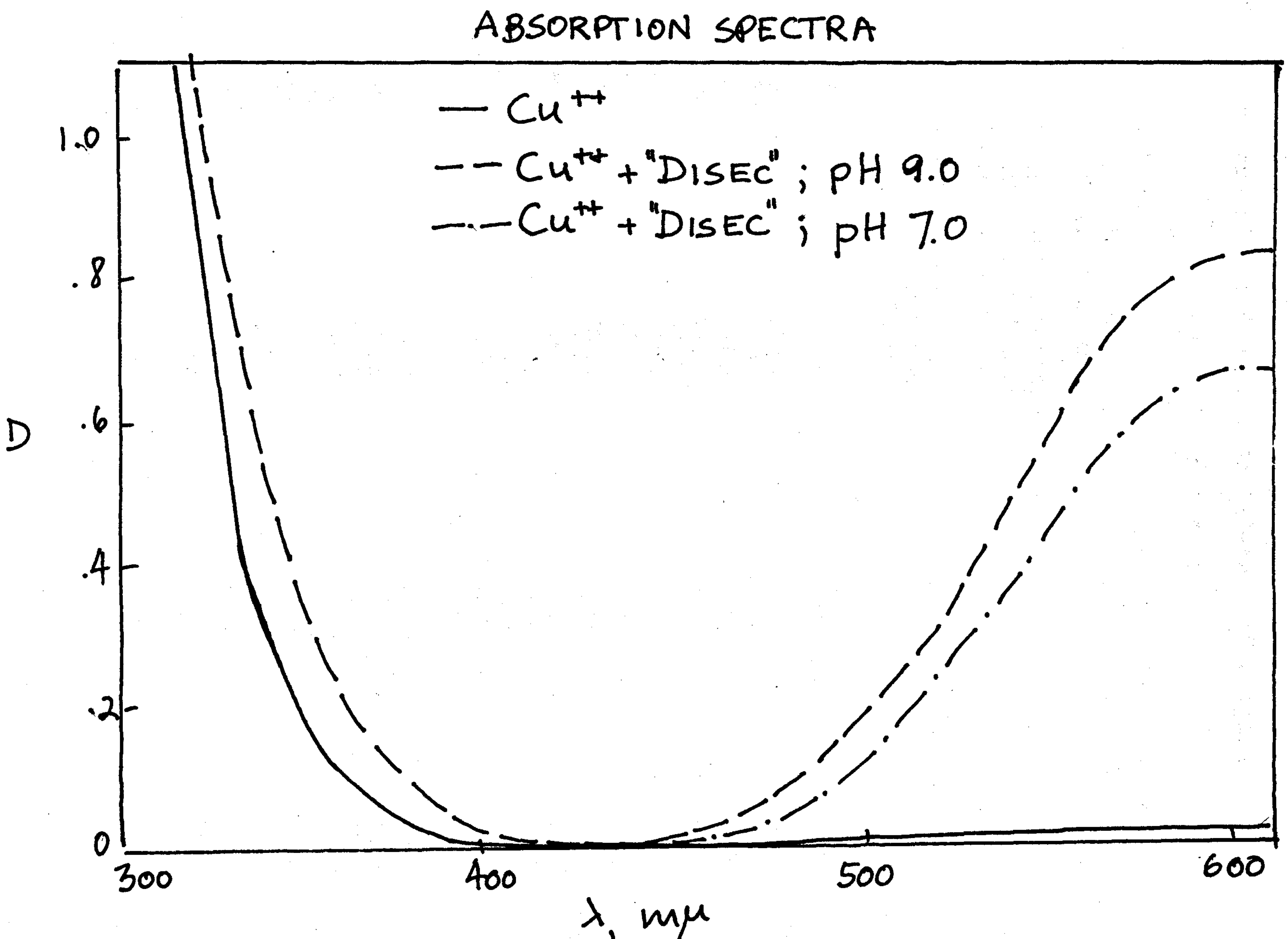

ABSORPTION SPECTRA
— Cu⁺⁺
-- Cu⁺⁺ + "DISEC" ; pH 9.0
-·- Cu⁺⁺ + "DISEC" ; pH 7.0
D
1.0
.8
.6
.4
.2
0
300
400
500
600
λ, mμ

FIGURE 5

TABLE X

Spectra of $Cu(NO_3)_2$ and Cu(II)-"Disec" complex.

(Data for Figure 5)

Solution		pH	Final Volume
1.	10 ml .103 M $Cu(NO_3)_2$ 10 ml 1.0 M $NaNO_3$	4.90	100 ml
2.	10 ml .103 M $Cu(NO_3)_2$ 25 ml .100 M "Disec" 10 ml 1.0 M $NaNO_3$	6.95	100 ml
3.	10 ml .103 M $Cu(NO_3)_2$ 25 ml .100 M "Disec" 10 ml 1.0 M $NaNO_3$	8.97	100 ml

λ	(1)	(2)	(3)
320	.950	∞	∞
330	.390	.930	∞
340	.180	.280	∞
350	.130	.120	.521
360	.100	.030	.154
380	.060	.023	.086
400	.015	.017	.007
420	.003	.012	.010
440	/002	.008	.018
460	.000	.023	.043
480	.000	.066	.100
500	.000	.128	.197
510	.000	.186	.266
520	.000	.245	.340
530	.000	.322	.441
540	.003	.385	.502
550	.006	.455	.600
560	.007	.525	.670
570	.007	.580	.735
580		.618	.780
590		.645	.810
600	.015	.654	.815
610		.665	.820
620		.650	.798
630	.032	.625	.768
640		.600	.735
650	.054	.568	.685

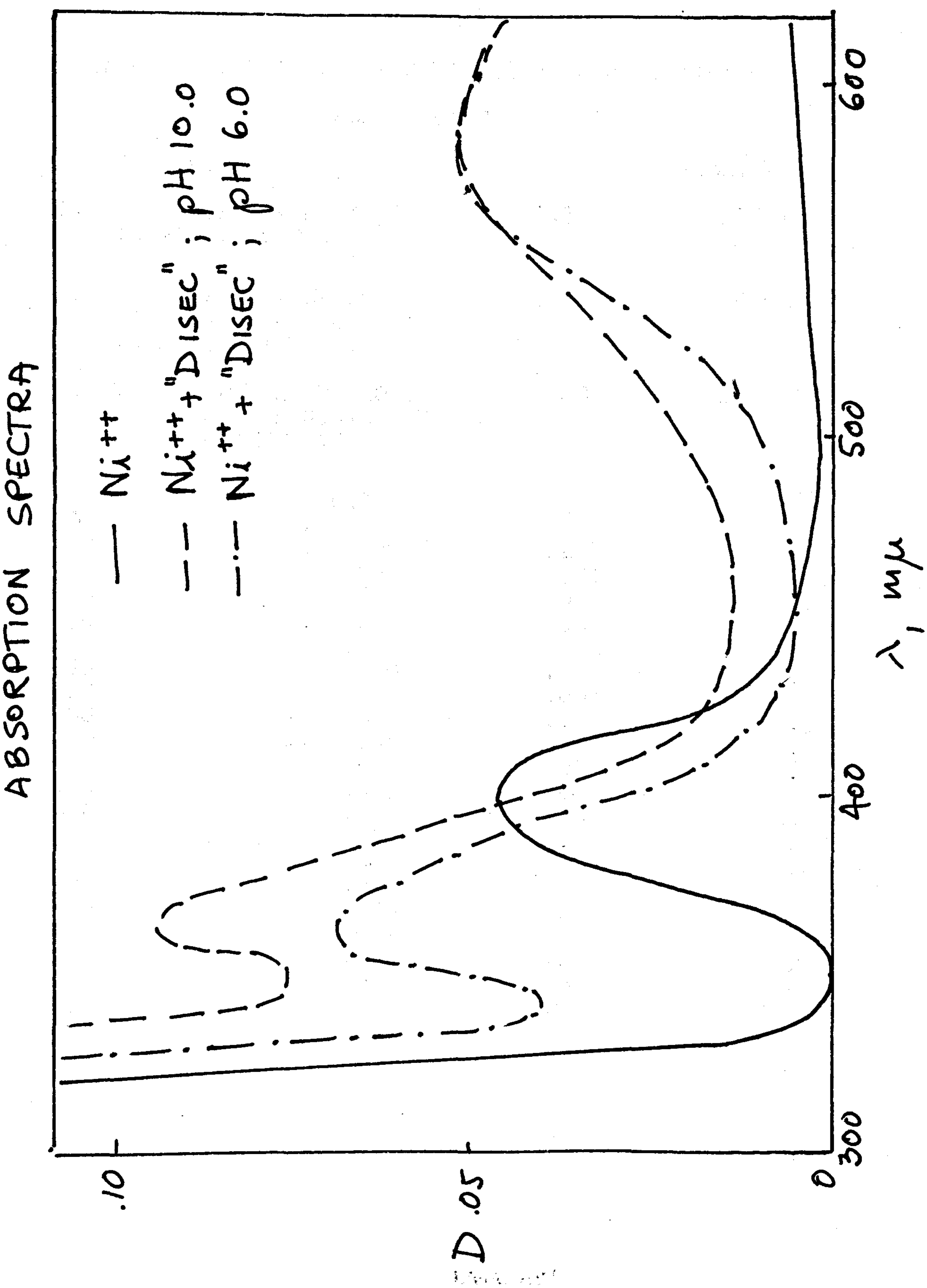

ABSORPTION SPECTRA

FIGURE 6

TABLE XI

Spectra of $Ni(NO_3)_2$ and Ni(II)-"Disec" chelate.

(Data for Figure 6)

	Solution	pH	Final Volume
1.	10 ml .101 M $Ni(NO_3)_2$ 10 ml 1.0 M $NaNO_3$	6.30	100 ml
2.	10 ml .101 M $Ni(NO_3)_2$ 20 ml .100 Disec 10 ml 1.0 M $NaNO_3$	6.04	100ml
3.	10 ml .101 M. $Ni(NO_3)_2$ 20 ml .100 M Disec 10 ml 1.0 M $NaNO_3$	10.00	100 ml

λ	9(1)	(2)	(3)
320	.208	.231	.318
330	.046	.074	.135
340	.000	.041	.080
350	.000	.057	.078
360	.000	.068	.093
370	.010	.064	.087
380	.028	.054	.072
390	.042	.041	.055
400	.044	.027	.039
420	.022	.008	.018
440	.007	.004	.012
460	.005	.004	0013
480	.004	.007	.017
500	.003	.010	.021
520	.004	.019	.028
540	.005	.033	.037
560	.007	.047	.048
580	.010	.053	.052
600	.018	.049	.049
650	.022	.037	.040

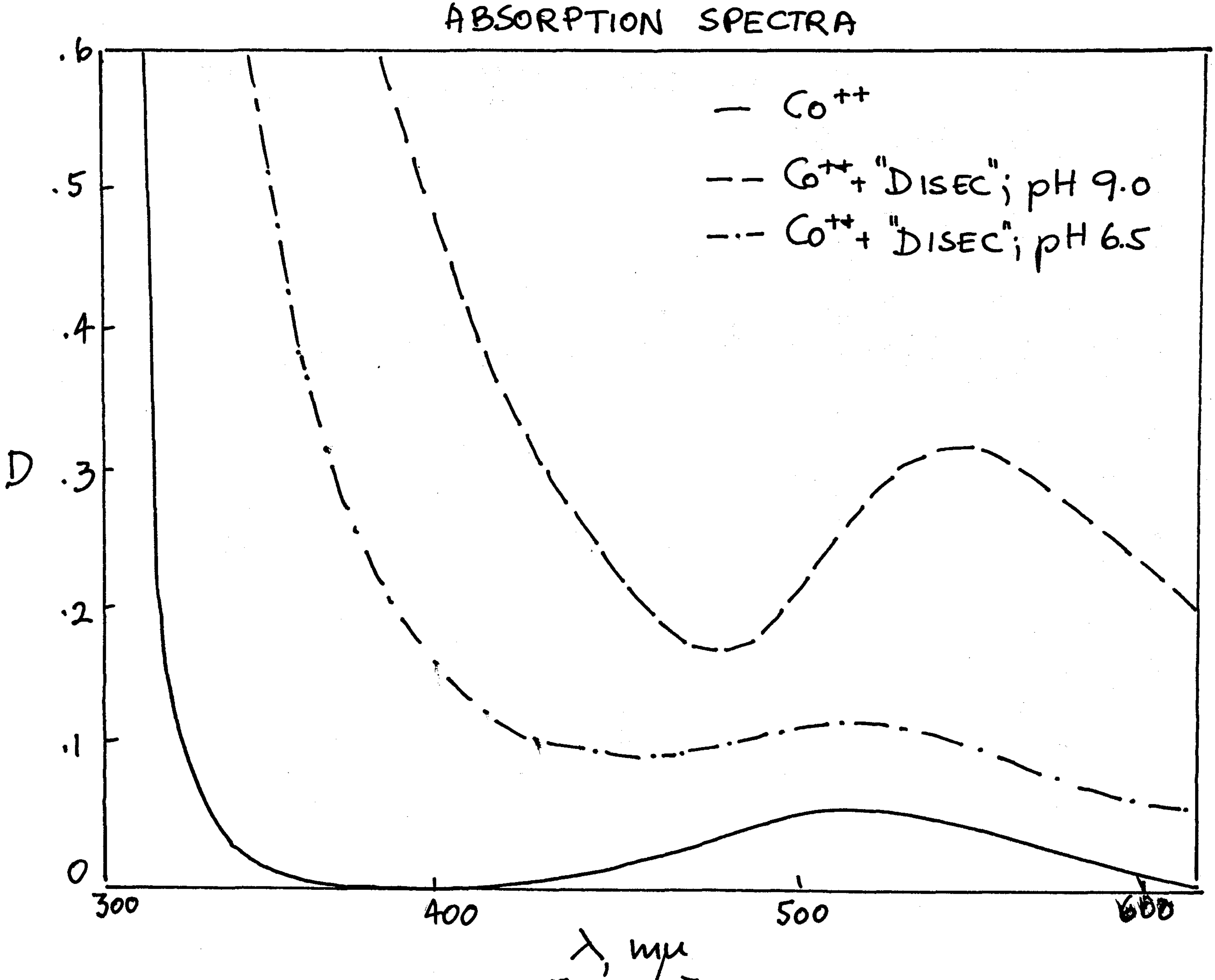

ABSORPTION SPECTRA
— Co^{++}
– – Co^{++} + "DISEC"; pH 9.0
–·– Co^{++} + "DISEC"; pH 6.5
D
.6
.5
.4
.3
.2
.1
0
300
400
500
600
λ, mμ

Figure 7

TABLE XII

Spectra of $Co(NO_3)_2$ and Co(II)-Dised Chelate.

(Data for Figure 7)

	Solution	pH	Final Volume
1.	10 ml .102 M $Co(NO_3)_2$ 10 ml 1.0 M $NaNO_3$	6.73	100 ml
2.	10 ml .102 M $Co(NO_3)_2$ 20 ml .100 M Disec 10 ml 1.0 M $NaNO_3$	6.53	100 ml
3.	10 ml .102 M $Co(NO_3)_2$ 20 ml .100 M Disec 10 ml 1.0 M $NaNO_3$	9.00	100 ml

λ	(1)	(2)	(3)
320	.236	1.15	∞
325	.137	.985	∞
330	.065	.850	∞
340 350	.011	.647	∞
350	.000	.495	∞
360	.000	.375	1.68
370	.000	.288	1.32
380	.001	.227	1.04
390	.002	.183	.806
400	.003	.148	.612
410	.005	.127	.464
420	.007	.110	.366
440	.015	.100	.270
460	.028	.095	.195
480	.037	.097	.170
500	.045	.108	.217
520	.047	.113	.277
540	.032	.099	.316
560	.015	.085	.305
600	.005	.062	.224
625	.006	.050	.184
650	.005	.041	.138

Solutions having a constant total concentration with varying amounts of metal ion and "Disec" were prepared. The pH of the solutions was adjusted with carbonate-free sodium hydroxide solution. Ionic strength was kept constant at 0.1 M $NaNO_3$. Spectrophotometric measurements were taken at the most favorable wave lengths for the different chelates.

Figures 8, 9 and 10 show the results obtained. The absorbancy of the solution was plotted against the ratio of the metal concentration to the constant total concentration. These graphs clearly show a maximum at $R = 0.5$, which correponds to the ratio of 1:1 of metal ion to "Disec".

Job's method required that the solutions should obey Beer's law. To test this, equimolar solutions of metal and "Disec" were prepared and the changes in absorbancy on dilution were measured. Figure 11 shows the results obtained at different wave lengths and different pH of the solution. It was found that cupric, nickelous and cobaltous ion solutions with "Disec" obey Beer's law.

These results together with results obtained by Job's method were used to calculate the stability constants of the corresponding metal chelates.

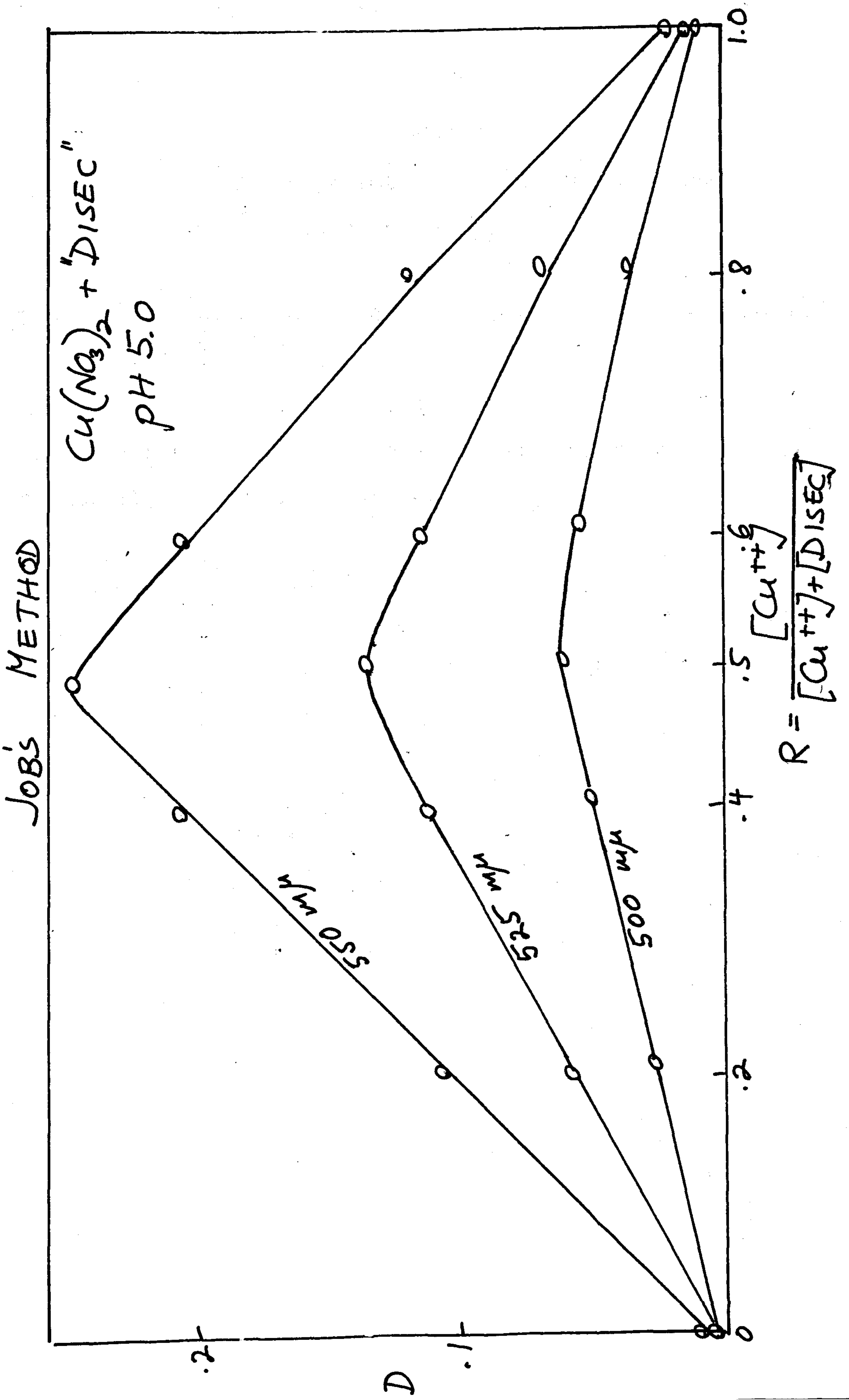

JOB'S METHOD
$Cu(NO_3)_2$ + "DISEC"
pH 5.0
550 mμ
525 mμ
500 mμ
D
.2
.1
0
.2
.4
.5
.6
.8
1.0
$R = \frac{[Cu^{++}]}{[Cu^{++}]+[DISEC]}$

Figure 8

TABLE XIII

Job's Method for Cu(II)-Disec System.

(Data for Figure 8)

$$R = \frac{(Cu^{++})}{(Cu^{++}) + (Disec)} \; ; \quad (Cu^{++}) + (Disec) = 2 \times 10^{-3} \text{ moles.}$$

R = 0, .2, .4, .5, .6, .8, 1.0

To all solutions 10 ml 1.0 M $NaNO_3$ were added and diluted to 100 ml; the pH of the solution was adjusted to 5.00.

λ	0	.2	.4	.5	.6	.8	1.0
500	.007	.023	.044	.054	.047	.029	.00
525	.008	.056	.108	.128	.105	.059	.000
550	.008	.103	.204	.242	.197	.110	.006
600	.009	.189	.373	.443	.360	.205	.015

JOB'S METHOD

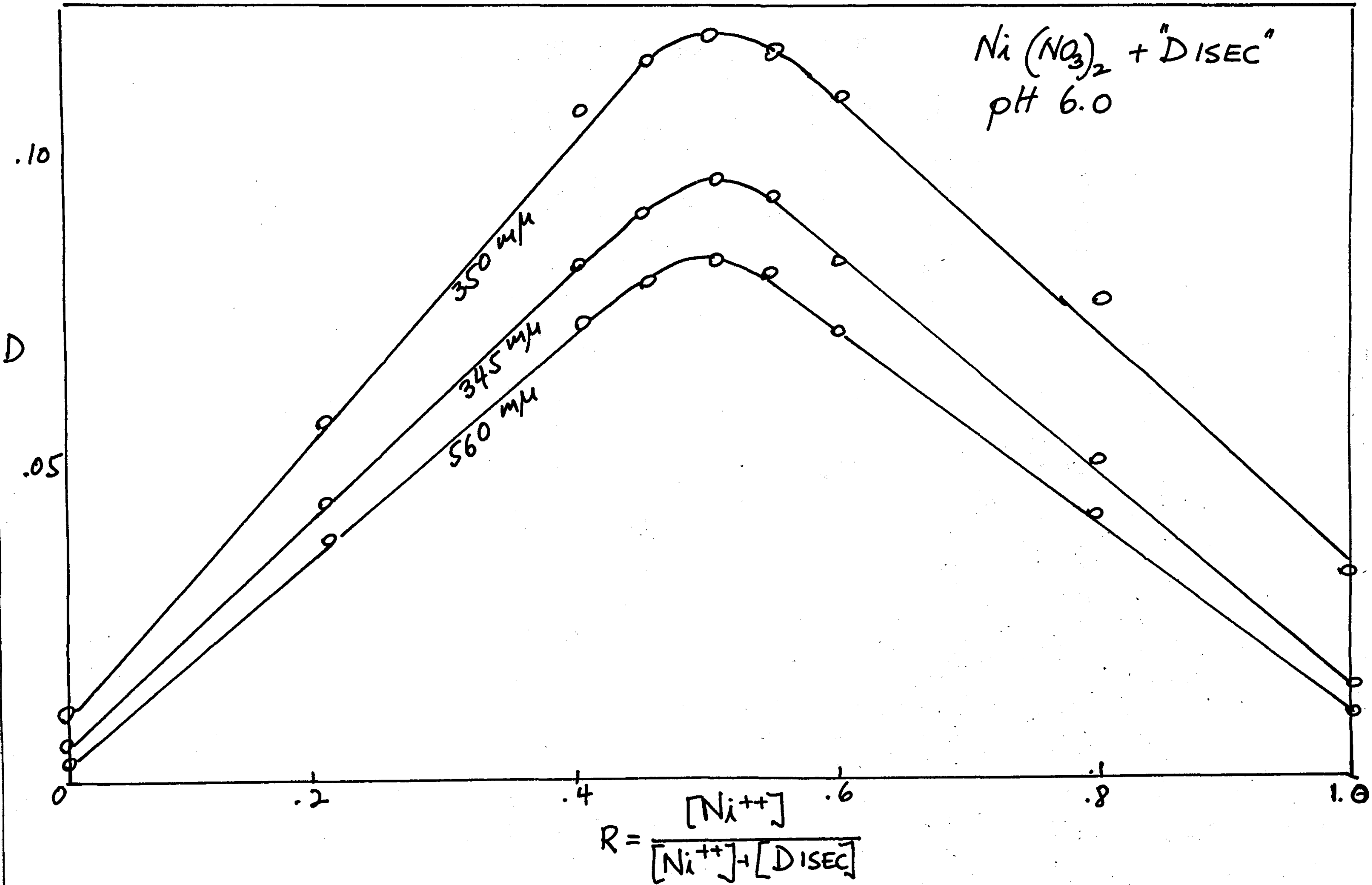


Figure 9

TABLE XIV

Job's Method for Ni(II)-Disec System.

(Data for Figure 9)

$$R = \frac{(Ni^{++})}{(Ni^{++}) + (Disec)} \quad ; \quad (Ni^{++}) + (Disec) = 4 \times 10^{-3} \text{ moles}$$

R = .0, .2, .4, .45, .5, .55, .6, .8, 1.0.

10 ml 1.0 M $NaNO_3$ were added to all solutions and then diluted to 100 ml.

pH 6.00

λ	0	.2	.4	.45	.5	.55	.6	.8	1.0
340	.020	.044	.077	.082	.086	.084	.082	.064	.038
345	.015	.048	.087	.095	.097	.097	.088	.065	.029
360	.011	.064	.121	.131	.137	.135	.125	.090	.045
560	.004	.038	.071	.077	.080	.080	.069	.042	.011
580	.006	.043	.080	.088	.092	.090	.080	.050	.018

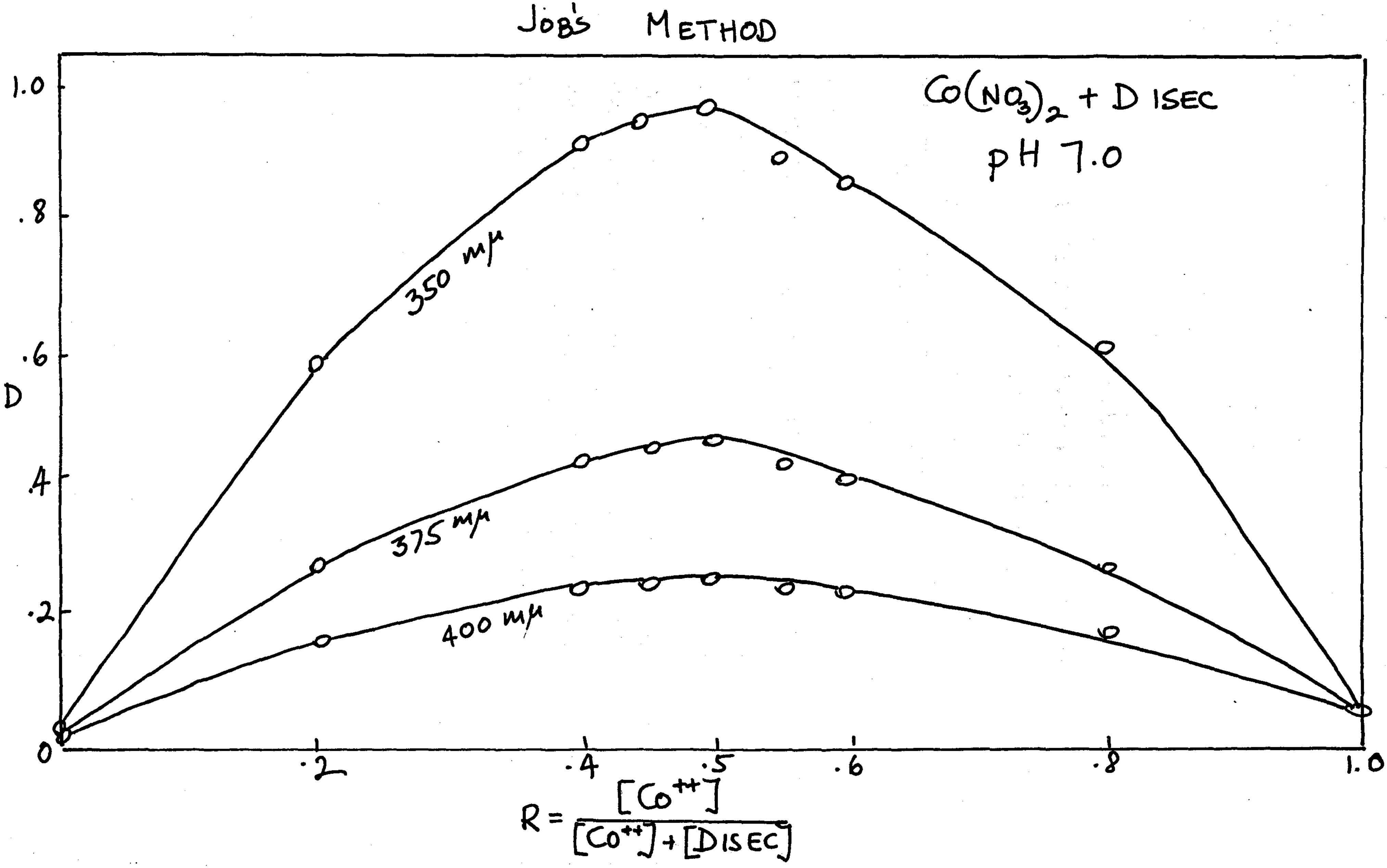

JOB'S METHOD
$Co(NO_3)_2$ + D ISEC
pH 7.0
D
1.0
.8
.6
.4
.2
0
.2
.4
.5
.6
.8
1.0
350 mμ
375 mμ
400 mμ
$R = \frac{[Co^{++}]}{[Co^{++}] + [DISEC]}$

Figure 10

TABLE XV

Job's Method for Co(II)-Disec System.

(Data for Figure 10)

$$R = \frac{(Co^{++})}{(Co^{++}) + (Disec)}; \qquad (Co^{++}) + (Disec) = 2 \times 10^{-3} \text{ moles}$$

R = 0, .2, .4, .45, .5, .55, .6, .,8, 1.0.

10 ml 1.0 M. $NaNO_3$ were added to all solutions and then diluted to 100 ml.

pH 7.00

λ	0	.2	.4	.45	.5	.55	.6	.8	1.0
350	.007	.575m	.900	.927	.960	.873	.841	.600	.026
375	.003	.267	.422	.434	.447	.406	.389	.273	.016
400	.002	.136	.222	.227	.238	.216	.212	.163	.017

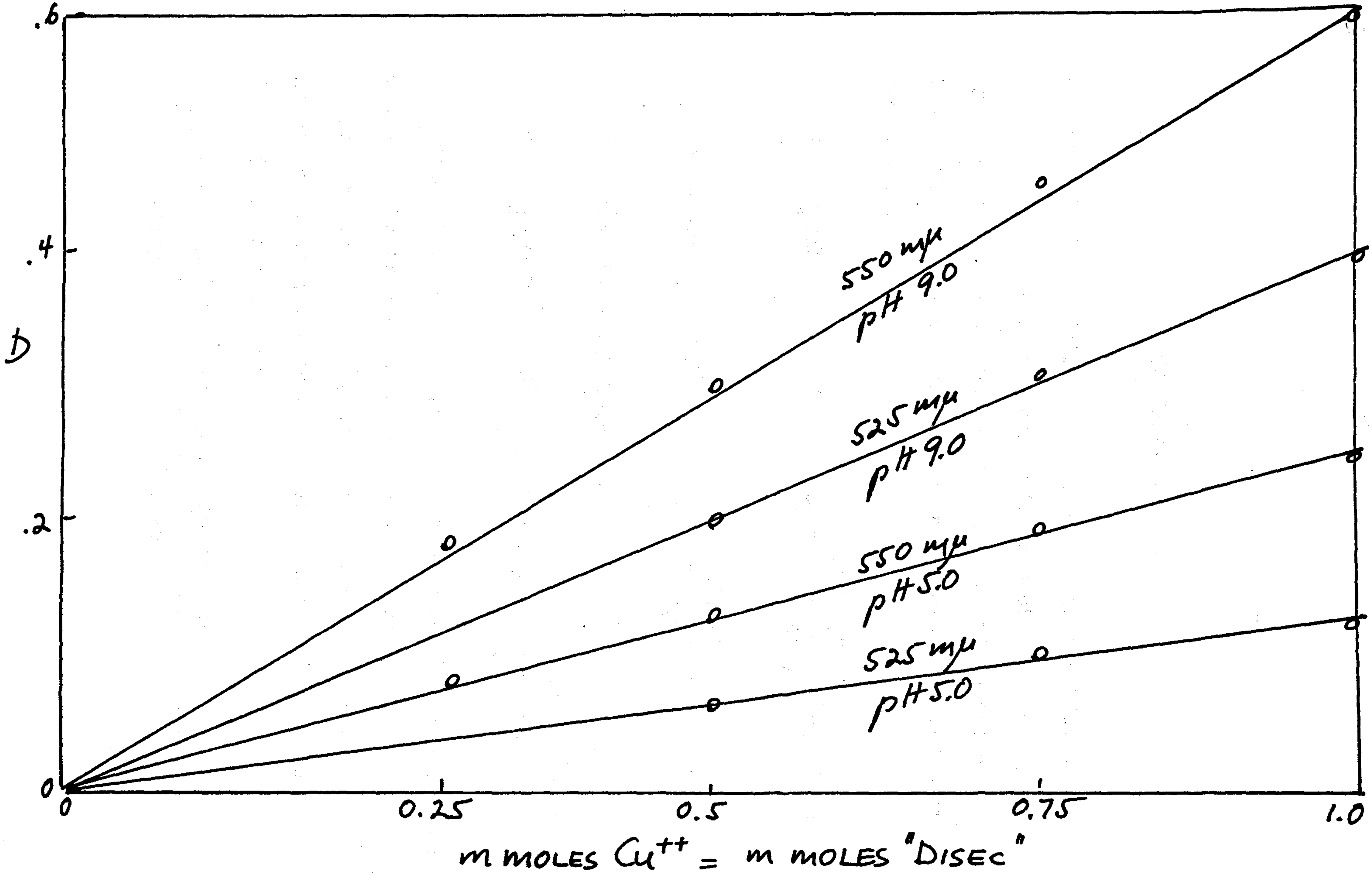

.6
.4
.2
0
D
0
0.25
0.5
0.75
1.0
m MOLES Cu++ = m MOLES "DISEC"
550 mμ
pH 9.0
525 mμ
pH 9.0
550 mμ
pH 5.0
525 mμ
pH 5.0

Figure 11

IV CALCULATIONS

A. Calculation of Dissociation Constants for "Disec".

"Disec" is the hydrochloride salt of a polyhydroxydiamine, and thus has two dissociable hydrogen ions. The following equilibria represents the salt form and the free amine:

$$H_2D^{++} \rightleftharpoons HD^+ + H^+ \qquad k_1 = \frac{(H^+)\ (HD^+)}{(H_2D^{++})} \qquad (21)$$

$$HD^+ \rightleftharpoons D + H^+ \qquad k_2 = \frac{(H^+)\ (D)}{(HD^+)} \qquad (22)$$

The overall equilibrium is

$$H_2D^{++} \rightleftharpoons D + 2H^+ \qquad K = k_1k_2 = \frac{(H^+)^2(D)}{(H_2D^{++})} \qquad (23)$$

Dissociation constants were determined by pH titration method. The free amine form was considered to be the central molecule, and $\bar{n}$, which represents the average number of hydrogen ions bound per "Disec" molecule was determined from the equation

$$\bar{n} = \frac{\text{bound } (H^+)}{(\text{Disec})} = \frac{2\ (\text{Disec}) - (\text{NaOH}) \text{ added} - (H^+)}{(\text{Disec})} \qquad (24)$$

The values of $\bar{n}$ calculated from equation (24) were plotted versus the corresponding pH values.

The shape of the Curve (Figure 12) indicates that the spreading factor between the two consecutive constants is sufficiently large to allow graphical determination of the two successive dissociation constants k_1 and k_2.

In this case the number of donor molecules N is two. The spreading factor is expressed by[44]

$$\frac{k_1}{k_2} = 4\,x^2 \tag{25}$$

As $k_1 k_2 = K$, then

$$k_1 = 2x\,K^{\frac{1}{2}} \tag{26}$$

$$k_2 = \frac{K^{\frac{1}{2}}}{2\,x} \tag{27}$$

Substituting these values in the general formation function, get

$$\bar{n} = \frac{2\,x\,K^{\frac{1}{2}}\,(H^+) + 2\,K\,(H^+)^2}{1 + 2\,x\,K^{\frac{1}{2}}\,(H^+) + K\,(H^+)^2} \tag{28}$$

When $\bar{n} = 1$, this relationship simplefies to

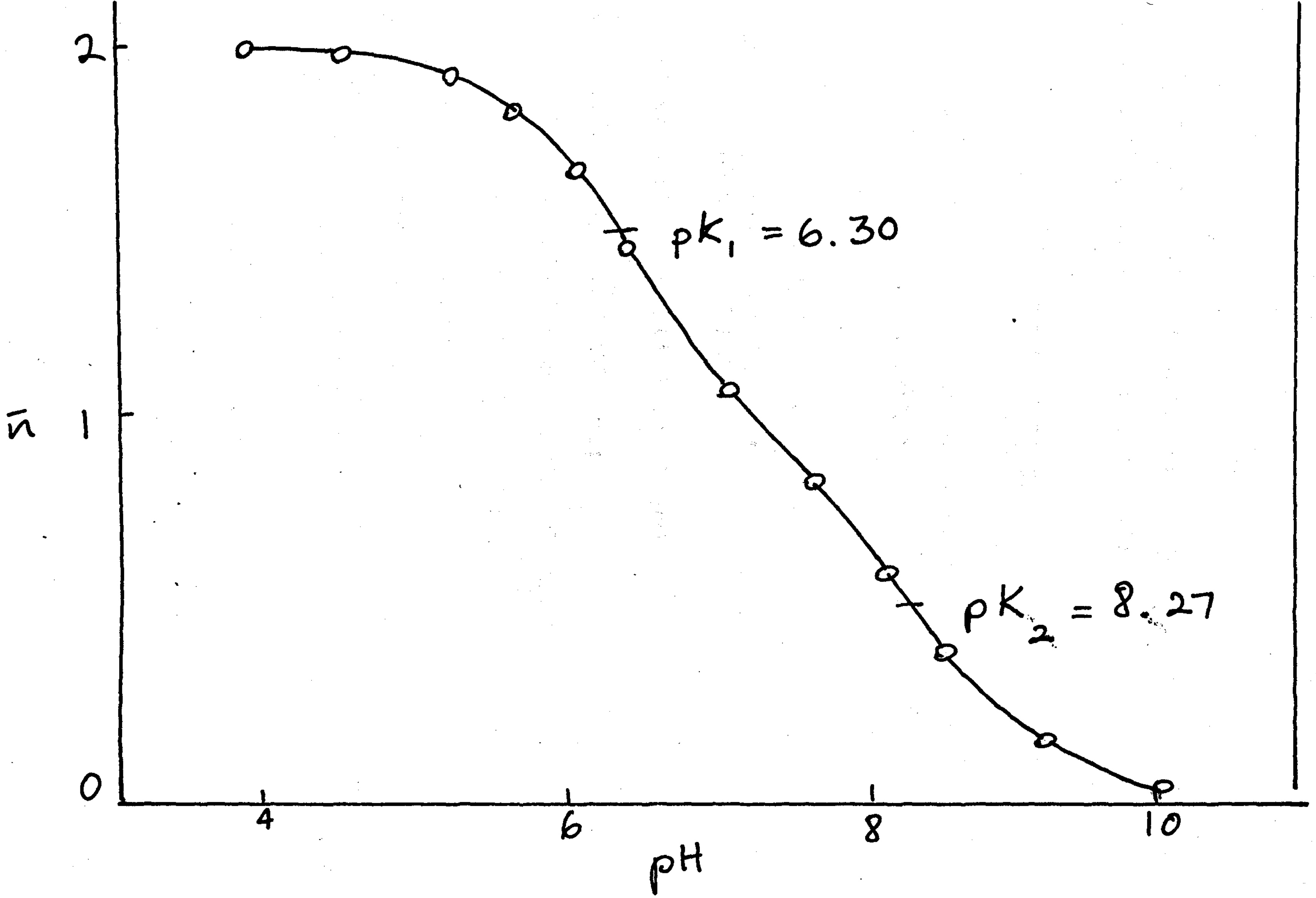
$$K = \frac{1}{(H^+)}\,.$$

When $\bar{n} = \frac{1}{2}$, on combining equation (28) and (26) get

$$k_1\,(H^+) + \frac{3\,(k_1(H^+))^2}{4\,x^2} = 1 \tag{29}$$

---

[44] Martell and Calvin, op. cit., p. 80.



DISSOCIATON CURVE OF "DISEC"

Figure 12

If $x >> k_1\ (H^+)$, the term $\frac{3\ (k_1(H^+))^2}{4\ x^2}$ becomes negligible, and

$$k_1 = 1/\ (H^+).$$

Similiarly, at $\bar{n} = 3/2$, by combining (28) and (27), the following expression is obtained:

$$k_2\ (H^+) - \frac{3}{4\ x^2\ (k_2\ (H^+))} = 1 \qquad (30)$$

Again, for large values of x it reduces to

$$k_2 = 1/(H^+).$$

Sample Calculation.

Sample : 50 ml .100 M "Disec"
10 ml 1.0 M $NaNO_3$

Titration performed with 1.152 N NaOH.

At pH 6.00: 1.57 ml NaOH used;

have $.050 \times .100 = 5 \times 10^{-3}$ moles "Disec"

$1.57 \times 10^{-3} \times 1.152 = 1.807 \times 10^{-3}$ moles NaOH

$(H^+) = 10^{-6}$ molar

Substituting these values in equation (24) get

$$\bar{n} = \frac{2 \times 5 \times 10^{-3} - 1.8 \times 10^{-3} - 10^{-6}}{5 \times 10^{-3}} = 1.65.$$

Stability Constants Calculated by Spectrophotometric Method.

Stability constants of cupric, nickelous and cobaltous chelates with "Disec" were determined by employing the method used by Turner and Anderson[45]. This method is discussed on p. 29 of this paper.

The equation used is the following:

$$K = \frac{(MKe)}{(C_{M1} - (MKe))\ (C_{Ke1} - (MKe))} = \frac{(MKe)}{(C_{M2} - (MKe))\ (C_{Ke2} - (MKe))} \qquad (31)$$

Solving for (MKe) get

$$(MKe) = \frac{C_{M2}\ C_{Ke2} - C_{M1}\ C_{Ke1}}{(C_{M2} - C_{M1}) + (C_{Ke2} - C_{Ke1})} \qquad (32)$$

Sample Calculation.

For the cupric ion-"Disec" chelate have the following data:

$C_{M1} = 6.74 \times 10^{-4}$ M

$C_{Ke1} = 6.72 \times 10^{-4}$ M

$C_{M2} = 1.40 \times 10^{-3}$ M

$C_{Ke2} = 6.56 \times 10^{-4}$ M

$$(MKe) = \frac{6.74 \times 10^{-4} \times 6.72 \times 10^{-4} - 1.40 \times 10^{-3} \times 6.56 \times 10^{-4}}{13.46 \times 10^{-4} - 20.56 \times 10^{-4}}$$

$$= 6.58 \times 10^{-4}$$

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[45] Turner and Anderson, J. Am.Chem. Soc., 71, 912 (1949).

$$K = \frac{6.58 \times 10^{-4}}{(6.74 - 6.58) \times 10^{-4}\ (6.72 - 6.58) \times 10^{-4}}$$

$$= 293.75 \times 10^{4}$$

$\log K = 6.47.$

V INTERPRETATION OF RESULTS

The aim of this study was to determine the chelating tendencies of Disec with various cations of the first transition series and calcium ion. Preliminary investigations were performed employing potentiometric determinations of hydrogen ion concentration. The hydrogen ion concentration of the water solution is directly affectedby chelate formation, since the formation of a metal-"Disec" chelate would result in liberation of hydrogen ions.

When "Disec" was titrated with sodium hydroxide in the presence of a divalent cation, in the region where chelate formation occured, more moles of sodium hydroxide were required to reach a given pH value than were required in the absence of the metal ion. The greater the tendency for the metal ion to form a chelate with "Disec", the greater was the observed drop in the pH of the solution.

Titration curves indicated that the most stable chelate was formed with cupric ion, with nickelous, cobaltous and zinc ions following in the corresponding order. Manganous and calcium ions showed very little tendency for chelation. This is clearly shown by Figure 13.

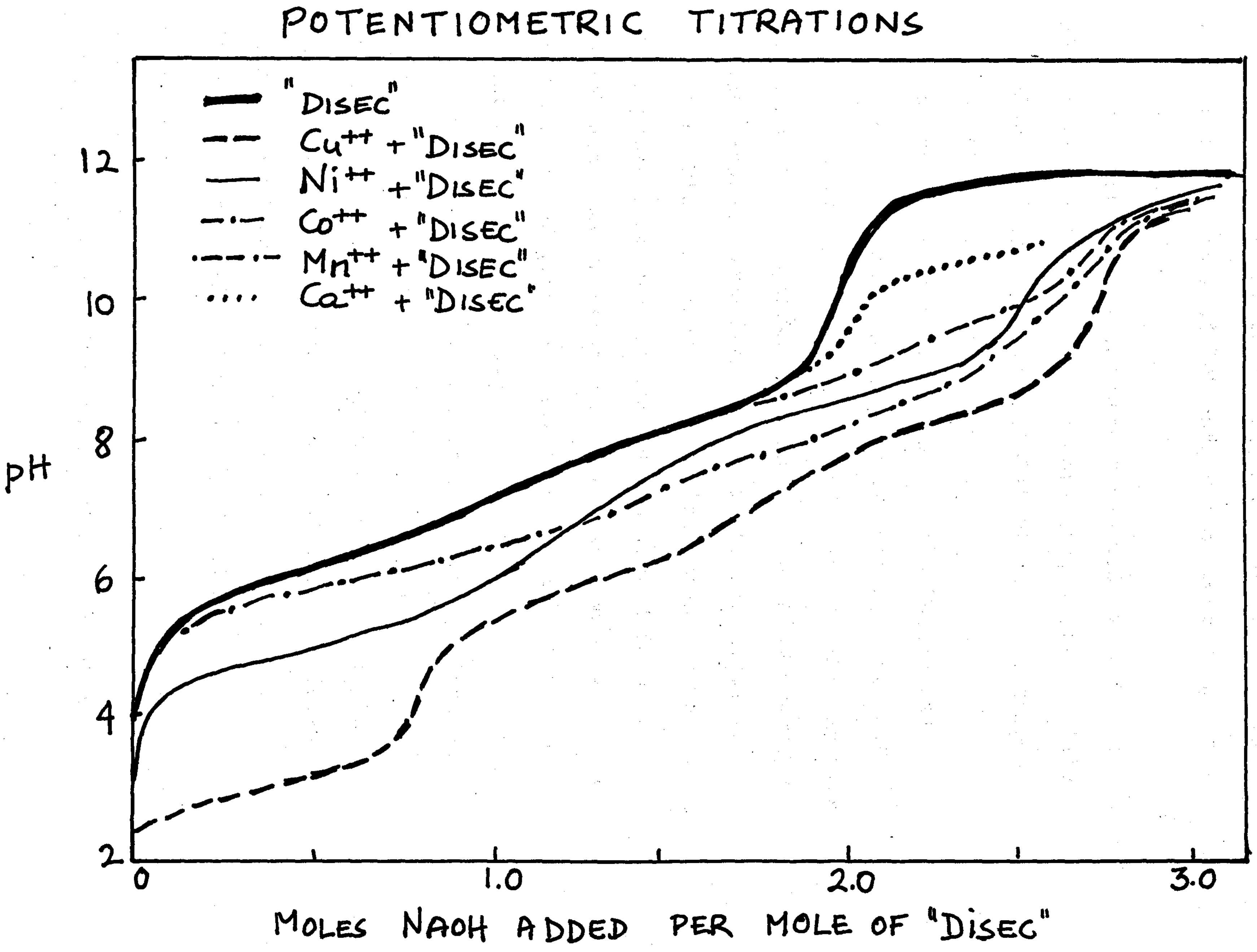
POTENTIOMETRIC TITRATIONS
"DISEC"
Cu++ + "DISEC"
Ni++ + "DISEC"
Co++ + "DISEC"
Mn++ + "DISEC"
Ca++ + "DISEC"
pH
12
10
8
6
4
2
0
1.0
2.0
3.0
MOLES NAOH ADDED PER MOLE OF "DISEC"

Figure 13

When the metal salt solutions were titrated with base in the absence of "Disec", the correponding metal hydroxydes were formed.

The following colors were exhibited by the metal chelates: Co(II) chelate was dark red, Ni(II) chelate lavender and Cu(II) chelate violet blue. Zinc formed a colorless chelate with "Disec".

No precipitation was observed with Cu(II) and Ni(II) chelates on standing for two weeks, while Co(II) chelate solution showed formation of the metal hydroxide in 24 hours. Manganous and calcium ion solutions with "Disec" showed formation of hydroxides immediately.

The ratio of Disec to metal ion concentration in these potentiometric titrations was varied from 1:1 and to 1:5 and qualitatively similiar graphs were obtained. With a ratio of less that 1:1 of metal ion to "Disec", formation of metal hydroxides was observed.

It was decided to concentrate investigations on cupric, nickelous and cobaltous chelates, as these seemed to form stable chelates and could be helpful in determining the structure and nature of chelates formed with "Disec". The behavior of ferric ion with "Disec" was studied by Mrs. J. B. Gladding[45] at the same time.

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(45) J. B. Gladding, Thesis, University of Richmond, August 1955.

The compositions of the colored cupric, nickelous, and cobaltous chelates were determined by the method of continuous variation, which was discussed previously on p. 28. Investigation of the spectra of the metal salt solutions and"Disec" separately showed no appreciable absorption at the wave lengths used. If Beer's law is obeyed, the absorbancy is directly proportional to the chelate concentration. Spectrophotometric measurements showed that the water solutions of the metal chelates obeyed Beer's law.

Figure 14 shows that when the absorbance of the metal chelate solutions at a certain wave length was plotted versus the composition ratio, a maximum resulted at the concentration ratio of 0.5, which corresponds to a 1:1 chelate compound. The fact that the experimental cuarves are lower than the theoretical curves indicate that the chelates are partly dissociated. As expected, cobaltous chelate shows more dissociation than nickelous chelate, while cupric chelate is the most stable.

Originally it was planned to determine the chelate stability constants by potentiometric titration methods, developed by Bjerrum[46] and further developed by others[47, 48].

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(46) Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

(47) H. Irving and H. S. Rossotti, J. Chem. Soc., 1953, 2904.

(48) J. C. Sullivan and J. C. Hindman, J. Am. Chem. Soc., 74, 6091 (1952).

METHOD OF CONTINUOUS VARIATION

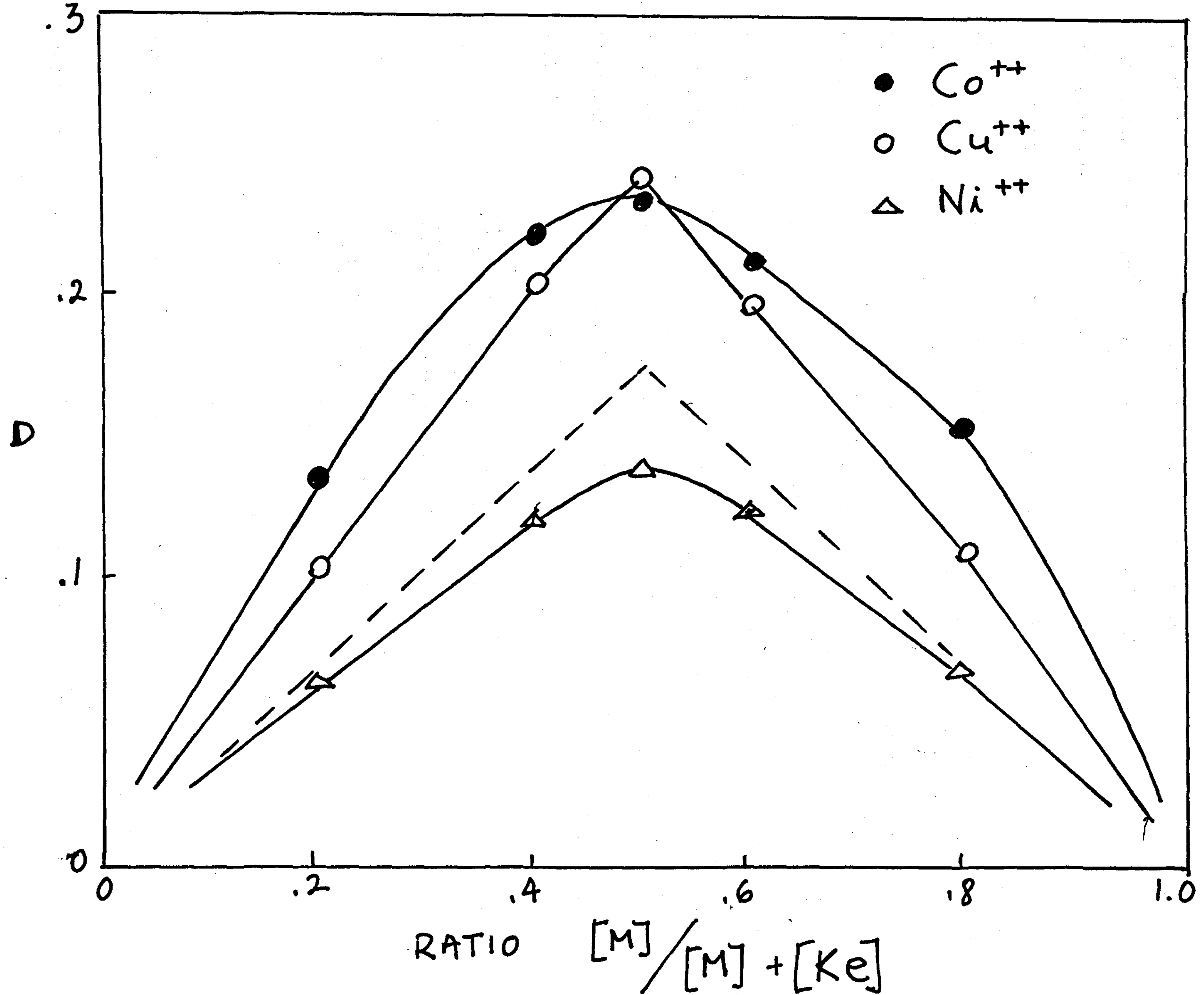
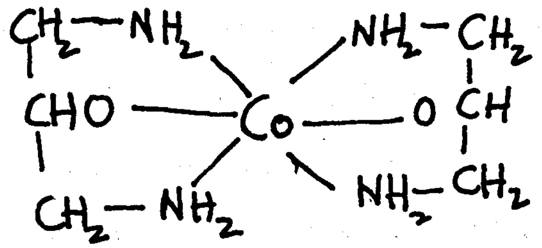


Figure 14

Uncertainty about the number of donor atoms forming links to the central ion, and thus the number of hydrogen ions liberated favored a spectrophometric determination of stability constants.

Structural considerations led to assmption that the two secondary amino groups in "Disec" would chelate with the metal ion to form a six-membered ring. Also, the possibility that some of the alcohol groups could take part in chelation was assumed.

Breckenridge and Hodgins[49] had prepared the coordination compounds of 1,3-diaminoisopropanol with cobaltous, cupric, zinc and silver salts. They analyzed the crystalline compounds and found the general formula $((C_3H_9N_2O)_2Co)X$ for the cobaltous compound. The following structural formula was proposed:



XXV

Cupric compound was found to have the formula

$$CuX_2(C_3H_{10}N_2O)_2,$$

which shows that two molecules of the chelating agent

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(49) Breckenridge and Hodgins, C. A., 34, 1269^4.

combine with the cupric ion. The two amino groups take part in the chelate formation by coordinating with the cation, while no coordination seems to take place between the hydroxyl group and cupric ion.

It is interesting to note, that the zinc-amino alcohol crystalline product did not correspond to any simple formula.

"Disec" is a NN-disubstituted 1,3-diaminoisopropanol, and, steric factors permitting, should be expected to chelate with cupric ion through the amino nitrogens. However, pH titration curves of the cupric ion-"Disec" solution show almost identically the same buffer reagion as Disec alone. This might be explained by assuming that the amino nitrogens do not take part in chelate formation and thus will impart the same buffering action as in absence of metal ion. Explanation predicting that copper forms only oxygen links with "Disec" seems rather improbable because of the rather great affinity of cupric ion for nitrogen.

The possibility of steric hindrance was considered, but, though it probably decreases the stability of the chelate, it does not seem likely that it will prevent chelation through the nitrogen atoms.

Mrs. J. B. Gladding(50) suggested another possible

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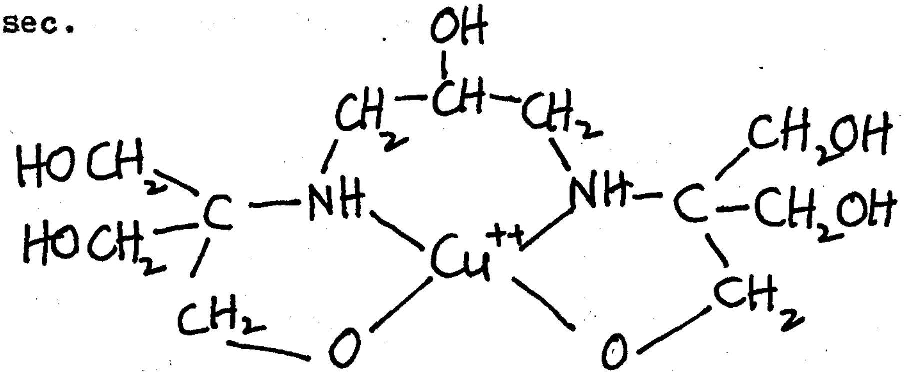
(50) Mrs. J. B. Gladding, Thesis, University of Richmond, August, 1955.

explanation by considering the stabilities of the metal chelate and Disec. If the chelate has exactly the same stability as that of the hydrogen ion with the amino groups, then the same buffering action could be accounted for the metal chelate solution.

Thus, the following structure is proposed as possible for a square-planar cupric ion chelate with Disec.



XXVI

Justification for the alcohol groups entering into chelate formation is found in the pH titration curves. At the end of titration a total of four moles of hydrogen ion were liberated, two coming from the amino groups and two from two alcohol groups.

Nickel and cobalt chelates probably have a structure similiar to copper chelate. The approximately same amount of hydrogen ion is liberated at the end of the titration with all three metal ions, while the difference in the shapes of the titration curves could be interpreted as a weaker chelating tendency of nickel and cobalt as compared to copper.

The stability constants of the chelates formed were determined by spectrophotometric methods. Two separate determinations were made at different concentrations of the reacting species - the metal ion and Disec. The agreement of the constants calculated for both determinations was found to be rather close. The following values were obtained:

Table XVI

Metal Ion	Log K	Color	Ionic Strength
Cu^{++}	6.47 6.43 > 6.45	deep blue	0.1
Ni^{++}	4.83 4.90 > 4.86	lavender	0.1
Co^{++}	3.65 3.66 > 3.66	deep red	0.1

These values for formation constants are in agreement with the Irving-Williams[51] series predicting that the chelate stability with the same chelating agent is as follows: Cu^{++} $>$ Ni^{++} $>$ Co^{++}.

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(51) H. Irving and R. J. P. Williams, J. Chem. Soc., 1953, 3192.

VI SUMMARY

1,3-bis-(tris-(hydroxymethyl)-methylamino)-2-propanol dihydrochloride chelates with calcium, manganous, cobaltous, nickelous, cupric and zinc ions were studied by potentiometric and spectrophotometric methods. An increase in hydrogen ion concentration was observed on chelation.

It was found:

1. calcium and manganous ions showed little tendency to chelate with the chelating agent regardless of the ratio of the metal ion concentration to the chelating agent concentration; above pH 9 some chelate formation was observed, but the chelate was too unstable to prevent metal hydroxide formation.

2. Cobaltous and zinc ions formed moderately stable chelates when the ratio of the chelating agent concentration to the metal ion concentration was 1:1 or more. Chelation started above pH 5.5; metal hydroxide formation was observed on standing with solutions of high pH.

3. Cupric and nickelous ions formed stable chelates when the ratio of chelating agent and metal ion concentrations was 1:1 or higher. No hydroxide formation was observed on standing. Chelation of

of cupric ion took place between pH 2.5 and 4.0. Nickelous ion chelate showed increased stability with increased basicity.

4. The compositions of cupric, nickelous and cobaltous chelates were determined by Job's method, and were found to be 1:1 complexes.

5. Chelate stability constants for cupric, nickelous, and cobaltous chelates were determined spectrophotometrically:

Metal ion	Log K
Cu(II)	6.45
Ni(II)	4.86
Co(II)	3.66

These stability values agree with the Irving-Williams stability series based on the central metal ion.

VII ACKNOWLEDGEMENT

I wish to express my sincere thanks to Dr. W. E. Trout, Jr. for the constant encouragement and invaluable advice given throughout this investigation. I am also indebted to Dr. J. Stanton Pierce for his advice and help in the purification of "Disec" and to Dr. W. Allan Powell and Dr. James E. Worsham, Jr. for encouragement and helpful suggestions.

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VIII BIBLIOGRAPHY

1. Bjerrum, J., Chem. Revs., 46, 381 (1950).
2. Bjerrum, J., "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.
3. Boeseken, Ber., 46, 2612 (1913).
4. Brandt, W. W.m, Dwyer, F. P., Gyarfas, E. C., Chem. Revs., 54, 959 (1954).
5. Breckenridge and Hodgins, C. A., 34, 1269^4.
6. Calvin, M. and Bailes, J., J. Am. Chem. Soc., 68, 949 (1946).
7. Calvin, M. and Wilson, K. W., J. Am. Chem. Soc., 67, 2003 (1945).
8. Carlson, G. A., McReynolds, J. P. and Verhoek, F. H., J. Am. Chem. Soc., 67, 1334 (1945).
9. Chabarek, Jr., S. and Martell, A. E., J. Am. Chem. Soc., 74, 5052, 5057, 6021, 6228 9 (1953).
10. Dwyer, F. P. and Mellor, D. P., J. Am. Chem. Soc., 63, 81 (1941).
11. Foley and Anderson, J. Am. Chem. Soc., 70, 1195 (1948).
12. Foley and Anderson, J. Am. Chem. Soc., 71, 909 (1949).
13. Gladding, J. B. G., Thesis, University of Richmond, August, 1955.
14. Harvey, Jr., A. E. and Manning, D. L., J. Am. Chem. Soc., 74, 4744.
15. Irving, H., Butler, E. J., Ring, M. F., J. Chem. Soc., 1949, 1489.
16. Irving, H. and Griffiths, M. M., J. Chem. Soc., 1954, 213.
17. Irving, H. and Rossotti, H. S., J. Chem. Soc., 1954, 2910.
18. Irving, H. and Rossotti, H. S., J. Chem. Soc., 1953, 2904.
19. Irving, H. and Williams, R. J. P., J. Chem. Soc., 1953, 3192.

20. Irving, H., Williams, R. J. P., Ferrett, D. F., Williams, A. E., J. Chem. Soc., 1954, 3494.

21. Job, Ann. Chim., (10) 9, (1928).

22. Jaeger, F. M. and Van Dijk, J. A., Chem. Abs., 29, 1352 (1935).

23. Jonassen, H. B. and Dexter, T. H., J. Am. Chem. Soc., 71, 1553 (1949).

24. Lanford, O. E. and Quinan, J. R., J. Am. Chem. Soc., 70, 2900 (1948).

25. Laitinen, H. A., Onstott, E. I., Bailar, Jr., J. C., Swann, Jr. S., J. Am. Chem. Soc., 71, 1551 (1949).

26. Mann, F. G., Purdie, D. and Wells, A. F., J. Chem. Soc., 1936, 1503.

27. Martell, A. E. and Calvin, M., "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, 1953.

28. Mellor, D., Chem. Revs., 33, 137 (1943).

29. Mellor and Maley, Nature, 159, 370 (1947).

30. Morgan and Drew, J. Chem. Soc., 117, 1456 (1920).

31. Nyholm, R. S., Chem. Revs., 53, 263 (1953).

32. Onstott, E. I., Laitinen, H. A., J. Am. Chem. Soc., 72, 4724 (1950).

33. Pauling, L., J. Am. Chem. Soc., 53, 1367 (1931).

34. Pauling, L., J. Am. Chem. Soc., 54, 994 (1932).

35. Pauling, L., "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1941.

36. Pierce, W. C. and Haenisch, E. L., "Quantitative Analysis,", John Wiley & Sons, Inc., New York, 1948.

37. Pierce, J. S. and Wotiz, J., J. Am. Chem. Soc., 66, 879 (1944).

38. Scott's Standard Methods of Chemical Analysis, N. H. Furman, Editor, D. Van Nostrand Co., Inc., New York, 1946, Vol. 1.

39. Sidgwick, J. Chem. Soc., 1941, 433.

40. Simms, H. S., J. Am. Chem. Soc., 48, 1239 (1926).

41. Sullivan, J. C. and Hindman, J. C. , J. Am. Chem. Soc., 74, 609, (1952).

42. Turner and Anderson, J. Am. Chem. Soc., 71, 913 (1949)

43. Van Uitert, L. G., Fernelius, W. C., J. Am. Chem. Soc., 75, 2739 (1953).

44. Van Uitert, L. G., Fernelius, W. C., J. Am. Chem. Soc., 76, 375 (1954).

45. Vickery, J. Chem. Soc., 1952, 1895.

46. Vosburgh and Cooper, J. Am. Chem. Soc., 63, 437 (1941).

47. Werner, A., "Beitrag zur Konstitution Anorganischer Verbindungen," Akademische Verlagsgesellschaft M. B. H., Leipzig, 1924.

48. Yaffe, R. P., Voigt, A. F. , J. Am. Chem. Soc., 74, 5043 (1952).

IX AUTOBIOGRAPHY

I, Velta Erdmanis, was born on June 25, 1930, in Riga, Latvia. In 1944 I graduated from the elementary school. At this time, because of war conditions, I and my family were forced to leave Latvia.

The years 1944 and 1945 I spent in Poland, Austria and Germany. After the end of the Second World War I lived in a Displaced Person Camp in Esslingen, Germany.

In 1948 I graduated from the Latvian Gymnasium in Esslingen.

I came to the United States in 1950. Through the World Student Service Fund I was awarded a scholarship at Westhampton College.

In June, 1953 I graduated from the University of Richmond with a Bachelor of Science degree.

From June, 1953 until September, 1954 I was employed as a chemist with E.I. du Pont de Nemours & Co., Inc. in Richmond, Virginia.

In September, 1954 I became a full-time graduate student at University at Richmond, and was awarded a Research Corporation of America fellowship.

At present I am a candidate for the degree of Master of Science in Chemistry at the University of Richmond.