BASICITY AND COMPLEXATION PROPERTIES OF SUBSTITUTED TETRAZOLES

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ABSTRACT

BASICITY AND COMPLEXATION PROPERTIES OF SUBSTITUTED TETRAZOLES

By Thomas C. Wehman

The complexing ability of the tetrazole ring was investigated in order to determine the π-doner ability of tetrazoles. It has been shown that 5-substituted and 1,5-disubstituted tetrazoles readily form charge-transfer complexes with π-acids such as tetracyanoethylene, tetracyanoquinodimethane, *p*-chloranil, 1,3,5-trinitrobenzene and 2,4,7-trinitrofleurenone. Formation constants of these complexes were measured spectrophotometrically in dichloromethane at 25°. There is a reasonable agreement between the magnitudes of the formation constants and the inductive effects of the substituent groups on the tetrazole ring. The formation constant of the pentamethylenetetrazole complex with 1,3,5-trinitrobenzene has also been measured by nuclear magnetic resonance techniques.

The proton accepting properties of tetrazole and substituted tetrazoles were studied using the protogenic solvent, formic acid. Conductance measurements made on formic acid solutions show that tetrazole, 5-methyl-, 5-phenyl-, and pentamethylenetetrazole behave as weak bases with pK_b values ranging from 1.78 to 2.06.

Precise conductance measurements were also carried out at 25° on solutions of twelve 1:1 electrolytes in anhydrous formic acid, in particular on alkali metal perchlorates, formates, chlorides and bromides. It was found that iodides, nitrates, thiocyanates and fluorides

were rapidly solvolyzed by formic acid. Most inorganic salts are completely dissociated in formic acid solution. Hydrogen chloride, however, behaves as a weak electrolyte with a dissociation constant of 1.1×10^{-2}. Single-ion limiting conductances were calculated from the conductance data. These data also indicate that the upper limit for the self-ionization constant of formic acid at 25° should be 2.2×10^{-7}.

Preliminary studies of pentamethylenetetrazole (PMT)-transition metal complexes were performed in formic acid to observe the effect of tetrazole protonation upon complex-coordination. The following seven perchlorate hexahydrate salts were used in this investigation: chromium(III), manganese(II), iron(III), iron(II), cobalt(II), nickel(II), and copper(II). It was found that the coordinating ligands about the transition metal ion are not PMT or protonated PMT molecules, but rather formate ions.

Since these investigations involved tetrazoles which could not be obtained commercially, several different syntheses were used in their preparation. The syntheses of thirteen 5-substituted tetrazoles, three 5,5-ditetrazolyls, five 1,5-disubstituted tetrazoles, and three substituted pentamethylenetetrazoles are described.

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By

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TABLE OF CONTENTS

Page

CHAPTER I

INTRODUCTION

CHAPTER II

SYNTHETIC WORK

CHAPTER III

STUDY OF π-COMPLEXATION OF SUBSTITUTED TETRAZOLES

CHAPTER IV

STUDIES IN FORMIC ACID SOLUTIONS

LIST OF TABLES

TABLE Page

LIST OF FIGURES

FIGURE Page

CHAPTER I

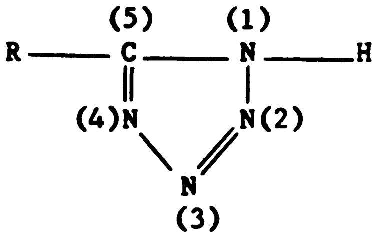
INTRODUCTION

TETRAZOLES

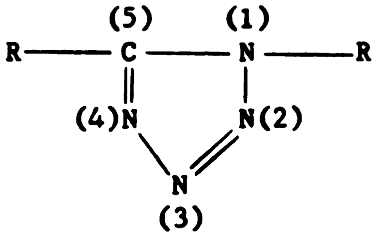
I. General

Substituted tetrazoles have been the object of numerous investigations because of their interesting physiological and physiochemical properties. Since the first tetrazole was prepared in 1885 by the Swedish chemist, J. A. Bladin (1), over 400 members of this class of nitrogen heterocycles have been synthesized and characterized (3).

The structures I, II and III represent 5-monosubstituted and 1,5-disubstituted tetrazoles of particular interest.



(I)



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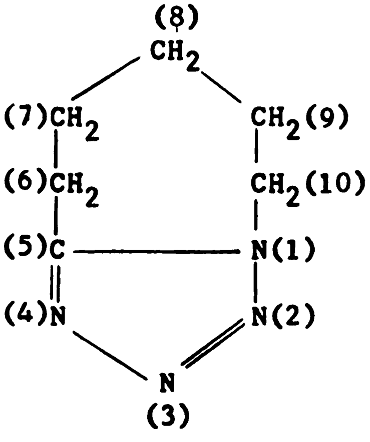


(III)

Pentamethylenetetrazole (PMT), structure III, represents a special case of the 1,5-disubstituted tetrazoles. In this structure a carbon and a nitrogen of the tetrazole ring are connected by a five membered methylene chain forming a fused ring system. The pharmacological and physiochemical properties are dependent upon the substituent groups on the tetrazole ring or the groups on the methylene chain of PMT.

In a series of studies, Gross and Featherstone (2) have shown that the neurological activity of these tetrazoles range from strong stimulation of the nervous system to a depressant action. It is conceivable that the neurological activity is related directly to the physiochemical properties of the tetrazoles.

II. Acid-Base Properties

The most comprehensive review of tetrazole chemistry to date was published in 1947 by F. R. Benson (3). A discussion of 2-substituted, 1-substituted, and 2,5-disubstituted derivatives is also included in this review.

The 5-monosubstituted tetrazoles were first shown to behave as weak acids in aqueous solution by Olivera-Mandala (4). He states that their acid strength is approximately equal to that of acetic acid ($Ka \approx 1 \times 10^{-5}$). Later investigations by Herbst and co-workers (5) were in fair agreement with Mandala's work. However, due to variation of the solvent mixtures in which pK_a values were determined, the relative acid strengths of the tetrazoles are in question. In a recent publication by Caruso et al., (6) the effect of substituent groups on 5-monosubstituted tetrazoles was studied by conductance methods. The basic solvent, 1,1,3,3-tetramethylguanidine, was used in order to enhance the acidity of the tetrazoles. Because of the low dielectric constant of this solvent ($\mu = 11.00$ at 25°) extensive ion-pair formation occured. As a consequence, the resulting acid-base equalibria were complex and only the overall dissociation constant could be calculated. The inductive effect of the substituent groups on the acidity of the 5-substituted tetrazoles is demonstrated by a linear Taft plot.

The disubstituted tetrazoles would be expected to have some proton affinity since all four nitrogen atoms in the ring contain an electron pair available for coordination. However, neither Dister (7) nor Zwikker (8) observed any basic character in aqueous PMT solutions. When PMT is dissolved in a strongly protogenic solvent, such as acetic acid, it behaves as a weak monoprotic base and can be titrated with perchloric acid (9). The basicity of PMT and other substituted tetrazoles is further accentuated by the stronger protogenic medium, formic acid (21).

III. Complexation-Coordination

Since the tetrazole ring itself has nucleophilic properties it is able to form moderately strong complexes with a number of Lewis acids. Various complexes have been reported with halogens (28) and transition metal ions (39). Also, salt-like compounds have been prepared with 5-substituted tetrazoles by simple neutralization with relatively strong bases (10).

The first silver and copper salts of tetrazole and 5-substituted tetrazoles were prepared by Bladin (11). Recently, transition metal complexes with 1-substituted and 5-substituted tetrazoles have been reported by Brubaker and co-workers (12, 13, 14). Brubaker and Daugherty (13) have suggested that the bonding in these complexes may occure either through one or two nitrogens of the tetrazole ring or that the central metal ion may coordinate to the π-electron system of the tetrazole ring. The last alternative was originally favored by Jonassen and co-workers (15) in their preparation of microcrystalline iron (II) complexes. However, in a more recent study of transition metal complexes, Jonassen (16) cites stronger evidence for a "σ" bond from a nitrogen to the metal ion.

The first crystalline halogen coordination compound to be reported was the iodine monochloride-PMT charge-transfer complex (40, 41). This complex was studied along with several other iodine monochloride complexes using infrared techniques by Person et al.(40). They noted systematic changes in infrared spectra of the iodine monochloride stretching vibrations as the halogen formed complexes of increasing stability. Using this relationship it was concluded that the donor properties of PMT were slightly weaker than those of pyridine. This study was expanded by Popov et al. (41) to include iodine and iodine monobromide complexes. The formation constants of these halogen-PMT complexes were determined spectrophotometrically in carbon tetrachloride solution. Although solid iodine monobromide-PMT and iodine-PMT complexes could not be obtained, their stoichiometry in solution was shown to be the same as the 1:1 iodine monochloride-PMT complex.

In a later paper by Vaughn et al. (42) the formation constants of iodine monochloride complexes of 7-methyl, 8-sec-butyl, and 8-t-butyl PMT were also determined spectrophotometrically. While solid compounds could not be prepared, the complexes were all shown to be more stable than the unsubstituted PMT complex.

Recently, two independent structure determinations have been carried out on the iodine monochloride-PMT complex by the use of X-ray crystallographic techniques (43). The two determinations are in complete agreement with regard to the overall structure and specific parameters. The PMT acts as a unidentate ligand with the iodine of the halogen molecule bound to 4-nitrogen of the tetrazole ring. The nitrogen-iodine monochloride group is linear and coplanar with the flat tetrazole ring, while the seven-membered methylene ring of PMT is in a chair conformation.

There have been several reported preparations of PMT-metal complexes(9) in acetonitrile solutions. Although all of these complexes had the same general formula, $(PMT)_2 M^+$, and approximately the same stability constants, only the unsubstituted PMT-silver nitrate complex could be prepared in solid form. Polarographic studies also showed that the cadmium-, thallium-, and cobalt-PMT complexes in aqueous solutions were almost completely dissociated.

In a recent series of papers by Popov and co-workers (39, 62), anhydrous transition metal complexes of PMT have been prepared and characterized. These complexes were prepared with iron(II), manganese(II), cobalt(II), nickel(II), and zinc(II) by treating PMT with the respective hexaaquo transition metal perchlorates in 2,2-dimethoxypropane solutions. The composition and structure of the complexes have been shown to be $M^{II}(PMT)_6(ClO_4)_2$ in an octahedral configuration. Electron spin resonance spectra of several of these complexes show that the metal-ligand bonds are highly ionic with only small distortions from the octahedral symmetry.

OBJECTIVES OF INVESTIGATION

With the exception of the iodine monochloride-PMT complex (43), the manner in which the tetrazole ligand is bonded to other Lewis acids is not clear (13, 16). It seemed to us that an investigation of the electron donor properties of the tetrazole ring would indicate the bonding nature of these complexes. Thus, a study of possible complex formation between various tetrazoles and Lewis π-acids should indicate the extent of the π-electron donor ability of the tetrazole ring. Chapter III of this thesis, then, deals with the complexes between substituted tetrazoles and a few strong π-electron acceptors. Complexation between several tetrazoles and tetracyanoethylene were studied since it is one of the strongest π-acids known (44). Also, for comparison, complexes with other π-acids such as tetracyanoquinodimethane (45); *p*-chloranil (46); 1,3,5-trinitrobenzene (46, 48); and 2,4,7-trinitrofluerenone (47) were investigated.

The proton accepting properties of tetrazole and substituted tetrazoles may be studied using a protogenic solvent to enhance their basicity. Anhydrous formic acid was chosen as the solvent in this study since it's properties remain largely unexplored. Thus, in Chapter IV, preliminary studies using this acidic medium were performed on PMT-transition metal complexes in order to observe the effect of tetrazole protonation upon complex-coordination. Also, described in Chapter IV, are conductance measurements which were carried out on solutions of 1:1 electrolytes and tetrazole derivatives.

Since the above investigations all involved tetrazoles which could not be obtained commercially, many had to be synthesized using the methods described in Chapter II of this thesis.

CHAPTER II

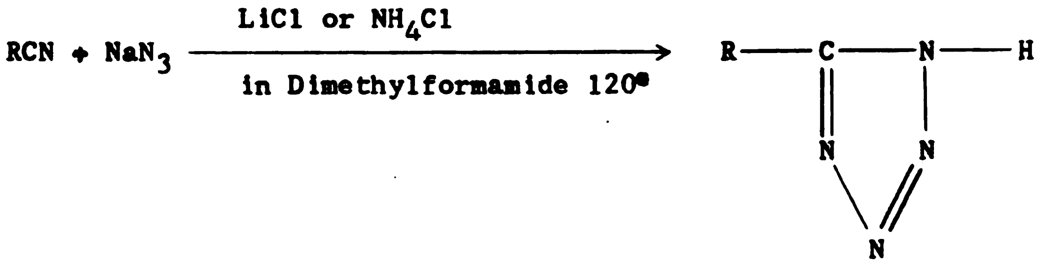
SYNTHETIC WORK

With the exception of pentamethylenetetrazole, all of the tetrazoles used in this investigation were synthesized by the following methods:

I. 5-Substituted Tetrazoles

A. Procedure (A)— Aromatic Substituents

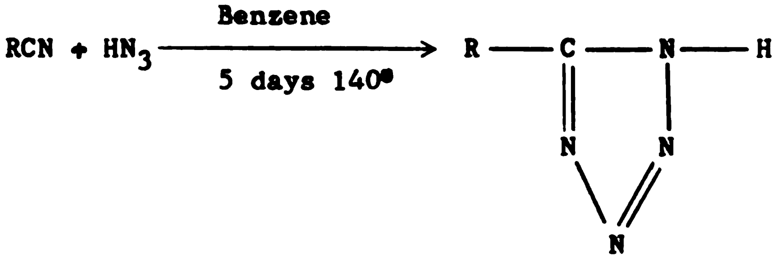
These tetrazoles were obtained by treating sodium azide with the corresponding nitriles following the general reaction (27):



The reactions were allowed to proceed in dimethylformamide for 20 to 40 hours using either lithium chloride or ammonium chloride as a Lewis acid catalyst. Since the synthesized tetrazoles were very insoluble in aqueous solution, they could be easily recovered from the reaction mixture by the addition of a dilute mineral acid. The crude product was filtered from the solution and purified by several recrystallizations.

B. Procedure (B)— Alkyl Substituents

Because of appreciable solubility of the 5-alkyl tetrazoles in aqueous solution, Procedure (A) could not be used for their preparation. A method described by Mihina and Herbst (38) which makes use of a sealed tube reaction was then successfully employed.



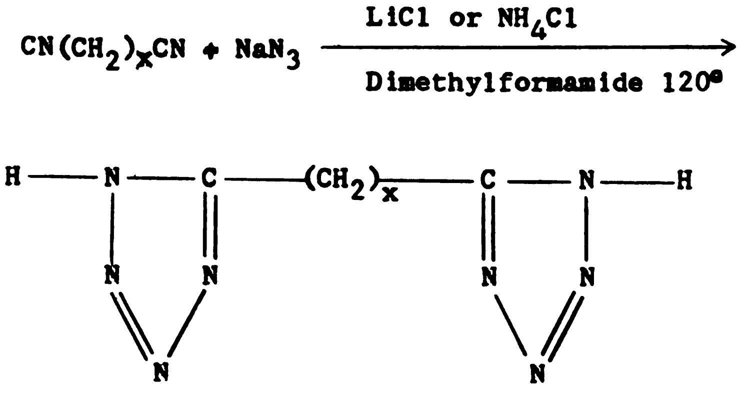
After the reaction was completed, the sealed tubes were opened and their contents poured into an evaporating dish. The mixture was then brought to dryness *in vacuo*, and, finally, the crude product was purified by sublimation at reduced pressure. The synthesized compounds and their properties are recorded in Table I. The two new compounds which had not been previously reported were sent out for elemental analysis.

Anal. Calcd for 5-*p*-Chlorobenzyltetrazole: C, 49.34; H, 3.62; N, 28.80. Found: C, 49.08; H, 3.61; N, 28.70.

Anal. Calcd for 5-*p*-Methylbenzyltetrazole: C, 62.07; H, 5.78; N, 32.15. Found: C, 62.04; H, 5.78; N, 32.10.

II. Ditetrazolyls

The ditetrazolyls-1,4, bis-(5-tetrazolyl)-butane and 1,3 bis (5-tetrazolyl) propane were prepared by procedure (A) above using adiponitrile and glutaronitrile respectively.



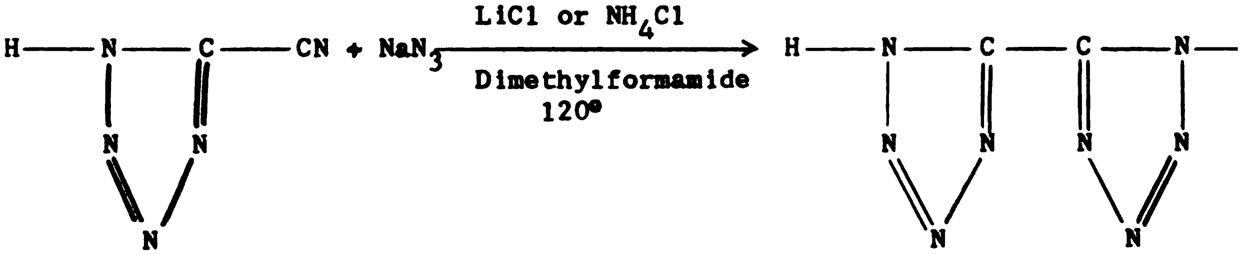
Where: x = 1, 2, 3 . . .

Table I. 5-Substituted Tetrazoles.

5-Substituent (R)	Procedure & Reference	mp	Lit. mp	Yield	Reaction Time	Recryst. Solvent
Benzyl	(A) 27	124-125°	123-125°	57%	9 hrs.	$EtCl_2$ [a]
8-Phenylpropyl	(A) 27, 38	89-91°	92.5-93.5°	10%	24 hrs.	$EtCl_2$
p-Chlorobenzyl	(A) 27	163-164°	NPP[a]	72%	12 hrs.	$EtCl_2$
p-Methylbenzyl	(A) 27	161-162°	NPP	75%	17 hrs.	$EtCl_2$
Methyl	(A) 27, 38	147-149°	148-148.5°	45%	48 hrs.	$EtCl_2$
Ethyl	(A) 27, 38	95-96°	98-99°	15%	24 hrs.	Subl.[a]
n-Propyl	(A) 27, 38	60-62°	63-64°	48%	30 hrs.	Subl.
n-Butyl	(B) 38	49-50°	47.5-48.5°	20%	7 days	Subl.
n-Pentyl	(B) 38	41-43°	41-42°	20%	7 days	Subl.
n-Hexyl	(B) 38	47-50°	46.5-47.5°	1%	7 days	Subl.
Monochloromethyl	(A) 27	NP[a]	NPP	NP	24 hrs.	Subl.
Dichloromethyl	(A) 27	NP	NPP	NP	24 hrs.	Subl.
B-Chloroethyl	(A) 27	NP	NPP	NP	24 hrs.	Subl.

[a] NP=no product; NPP=not previously prepared; $EtCl_2$=1,2-dichloroethane; Subl.=Sublimation.

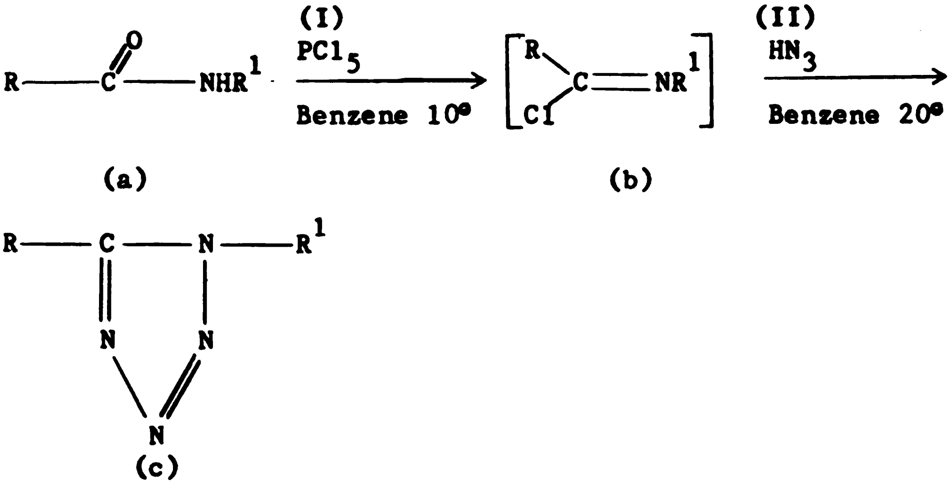
In order to prepare 5,5^1—ditetrazolyl, 5-cyanotetrazole was allowed to react with sodium azide using procedure (A). The 5-cyanotetrazole had been previously prepared in this laboratory from cyanogen, using a similar procedure.



The results are listed in Table II.

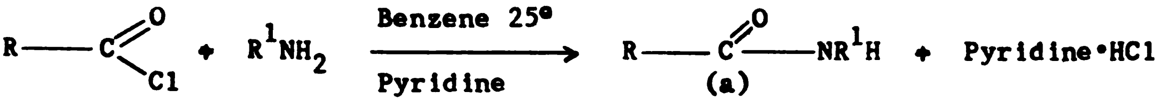
III. 1,5-Disubstituted Tetrazoles

The overall synthesis involved a two step procedure (29).



Step (I)

The starting amides (a), could either be purchased commercially or obtained by reacting an acid chloride with the appropriate amine.



The pyridine hydrochloride was filtered off, the solvent was evaporated

Table II. Ditetrazolyls.

Compound	mp	Lit. mp	% Yield	Recrys. Solvent
5,5^1-Ditetrazolyl	255°D	254°D (3)	42%	95% Ethanol
1,3-bis-(5-Tetrazolyl)-Propane	197-200°	Not prev. prep.	94%	95% Ethanol
1,4-bis-(5-Tetrazolyl)-Butane	205-206°	205-205°D (27)	89%	95% Ethanol

The following compounds were sent out for elemental analysis:

Anal. Calcd for 1,3-bis-(5-Tetrazolyl)-propane: C, 33.33; H, 4.48; N, 62.20. Found: C, 33.31; H, 4.50; N, 62.21.

Anal. Calcd for 1,4-bis-(5-Tetrazolyl)-butane: C, 37.11; H, 5.19; N, 57.70. Found: C, 37.10; H, 5.25; N, 57.90.

and the crude amide was purified by recrystallization.

Step (II)

The imide chlorides (b) were never isolated since upon completion of reaction (I), hydrozoic acid was immediately added to the mixture. Solutions of hydrozoic acid in benzene were prepared by reacting sulfuric acid with sodium azide in benzene.(30).

The final tetrazole was recovered and purified by repeated extractions and recrystallizations of the reaction mixture after step (II) was completed. The amides used in the syntheses are listed in Table III while the final tetrazoles are listed in Table IV.

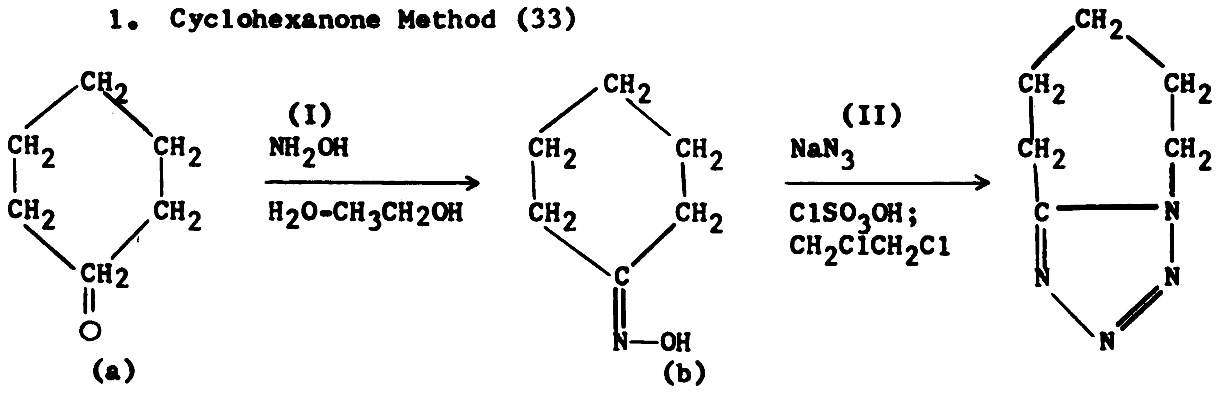
IV. Substituted Pentamethylenetetrazoles

Although many alkyl-substituted pentamethylenetetrazoles have been reported and characterized, (31, 32) no halogenated derivatives have been prepared. The following methods were used in an attempt to prepare monochlorinated PMT.

A. Preparation I — Pentamethylenetetrazole

In order to test several possible procedures for the synthesis of monochlorinated derivatives, the following methods were used to prepare unsubstituted PMT.

1. Cyclohexanone Method (33)



The overall synthesis involves a two step procedure. The purchased starting material, cyclohexanone (a), was converted into an oxime (b) by

Table III. N-Substituted Amides.

Amide	Preparation	% Yield	mp	Lit. mp	Recryst. Solvent
N-Ethylbenzamide	Benzoylchloride + Ethylamine	74%	67-68°	68.5°	Methanol-Water
Benzanilide	Commercial Source	--	159°	161°	--
Propionanilide	Commercial Source	--	102°	104°	--
N-Propyl-*n*-Propionamide	Propionyl Chloride + *n* Propyl Amine	90%	--	--	Used in impure form
N,*n*-Butylacetamide	Commercial Source	--	--	--	--

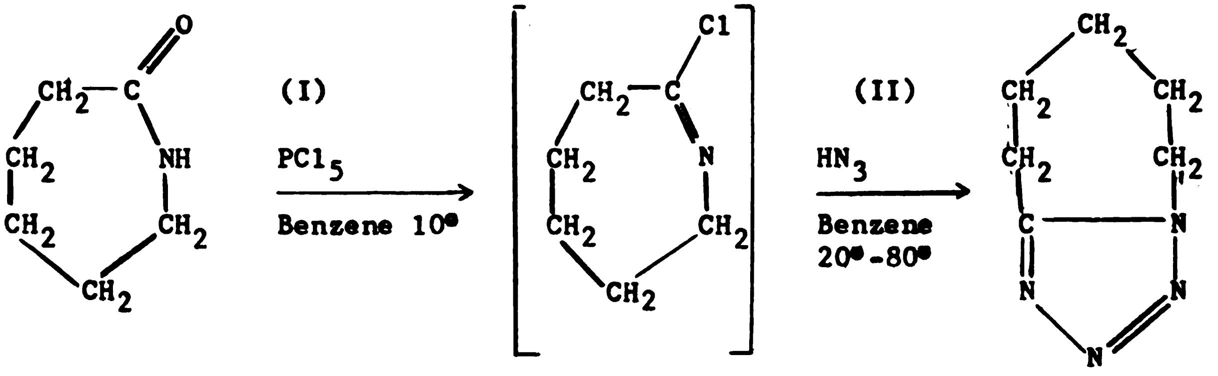
Table IV. 1,5-Disubstituted tetrazoles.

Tetrazole	Starting Amide	% Yield	mp	Lit. mp	Recryst. Solvent.
1-Ethyl-5-phenyl-	(1)	13%	67-68°	70-71° (29)	n-heptane
1,5-Diphenyl-	(2)	94%	144-146°	144-145° (29)	Methanol-Water
1-Phenyl-5-ethyl-	(3)	27%	46°	49° (29)	Ethyl Acetate-n-heptane
1-Propyl-5-ethyl	(4)		(Impure Oil Obtained)		Fractional Distillation
1-Butyl-5-methyl	(5)		(Impure Oil Obtained)		Fractional Distillation

treating it with hydroxylamine. The cyclohexanone oxime (b) was separated from the reaction mixture by filtration and was recrystallized from an ethanol-water mixed solvent before it was used in reaction (II) mp 88°-90° lit. mp 90° (34). Step (II) involved the slow addition of an 1,2-dichloroethane solution of the oxime to a mixture of sodium azide and chlorosulfonic acid in the same solvent. After the reaction was completed, the mixture was neutralized with aqueous sodium hydroxide solution. The 1,2-dichloroethane layer was separated and dried *in vacuo*. The final product was obtained from the remaining residue and purified by repeated extractions and recrystallizations with ethyl ether.

2. ε-Caprolactam Method

This synthesis involves a two step procedure which is similar to the preparation of 1,5-disubstituted tetrazoles described above.

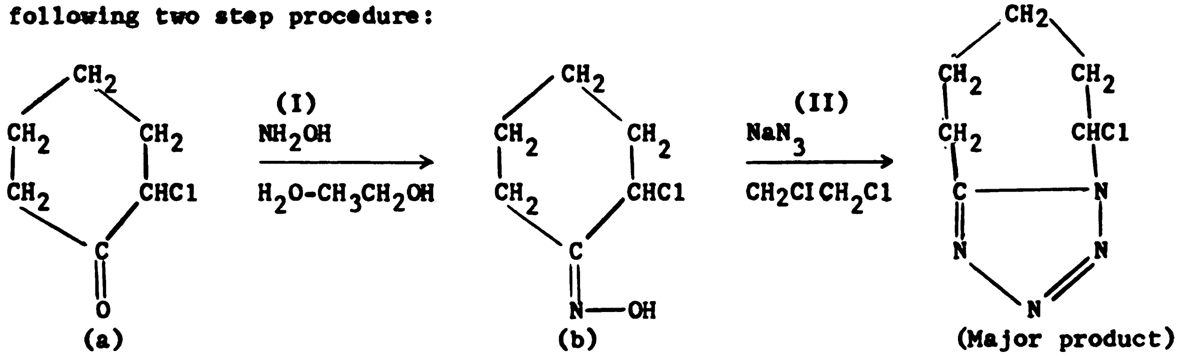


(a)

The starting material, ε-caprolactam (a), which may be purchased commercially, is a cyclic amide in contrast to the straight chain amides encountered previously. The reaction conditions were the same as those described for the 1,5-disubstituted tetrazoles. The final product was separated and purified by repeated extractions with ethyl ether and sublimation.

B. Preparation II — 10-Chloropentamethylenetetrazole

The same general method described in the cyclohexanone - PMT procedure was used for this synthesis. The overall synthesis involved the following two step procedure:

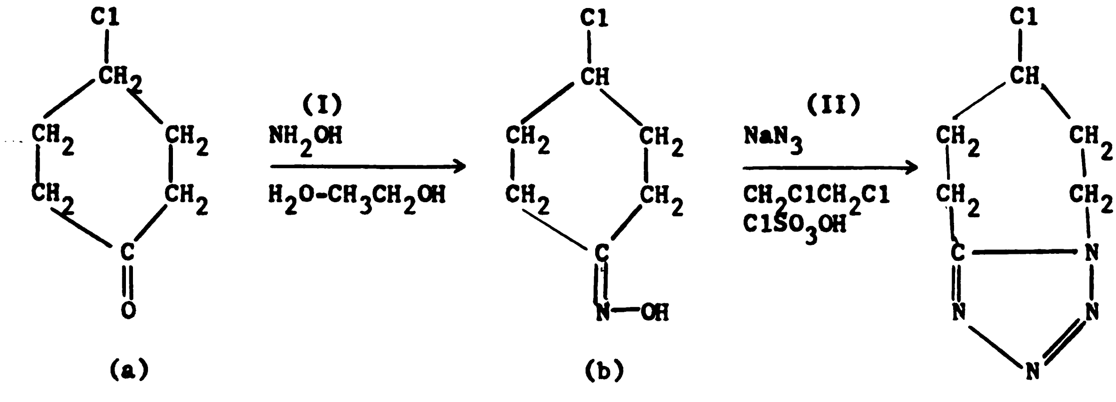


The starting material, 2-chlorocyclohexanone (a), was purchased from commercial sources. After reaction (I) was completed, the 2-chlorocyclohexanone oxime (b), was recovered but could not be purified. However, the oxime was used in its impure form for reaction (II).

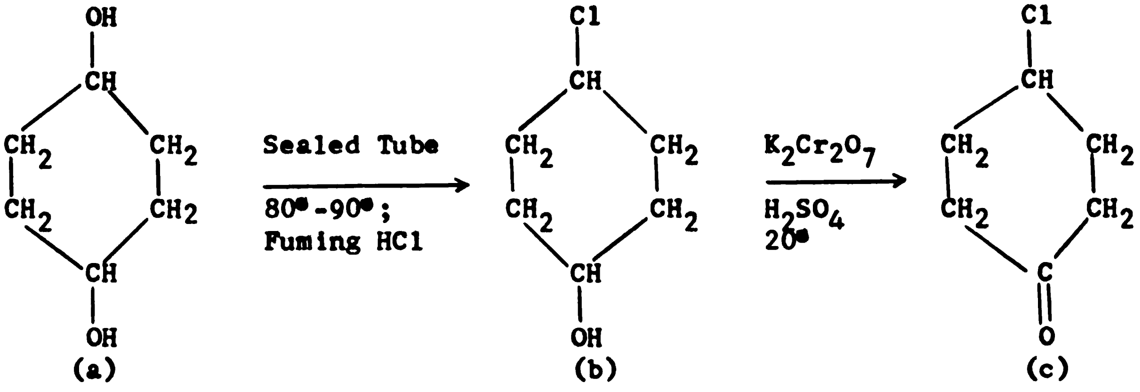
After reaction (II) was completed, the mixture was treated in the same fashion as described for the cyclohexanone-PMT preparation. Unfortunately, only a few grams of black oily material were obtained which could not be purified or identified.

C. Preparation III — 8-Chloropentamethylenetetrazole

The same general method described in the preparation of 10-chloropentamethylenetetrazole above was used for this synthesis.



Since 4-chlorocyclohexanone (a) could not be purchased from commercial sources, the following procedure was used in its preparation (35, 36).



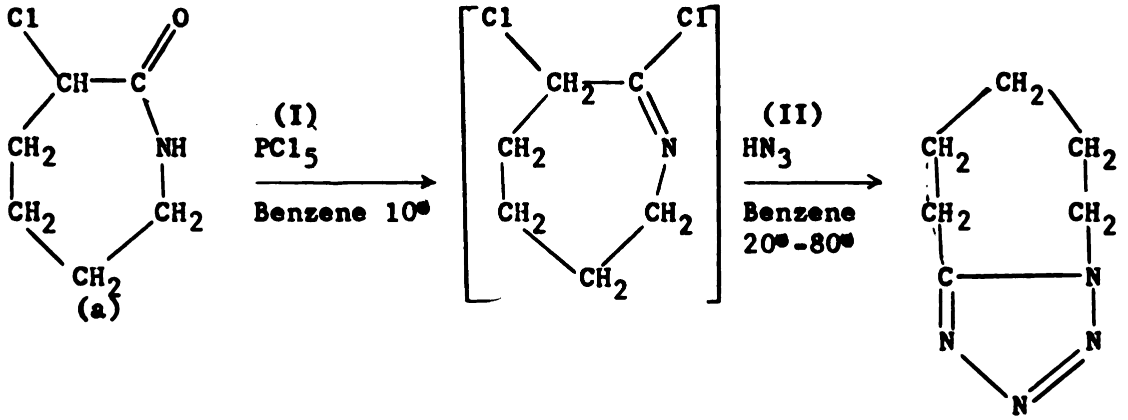
Commercial cyclohexane - 1:4 diol (a) was placed in a sealed tube with fuming hydrochloric acid at 90° for 24 hours. After reaction (I) was completed the 4-chlorocyclohexanol (b) was separated by fractional distillation under reduced pressure with a yield of 56%, $n^{16^\circ}\underline{\underline{D}}$ 1.4960; lit. (35) $\underline{n}^{16^\circ}\underline{\underline{D}}$ 1.4964. This material was then oxidized to 4-chlorocyclohexanone (c) by an acidic potassium dichromate solution, the final product being obtained by fractional distillation under reduced pressure with a yield of 14%, $n^{21^\circ}\underline{\underline{D}}$ 1.4878; lit, (36) $\underline{n}^{21^\circ}\underline{\underline{D}}$ 1.4867. Upon separation, the pure material was used to form 4-chlorocyclohexone oxime in Step I of the 8-chloropentamethylenetetrazole synthesis. Although the oxime could not be purified, it still was used in the final reaction (II).

After the final reaction (II) was completed, the end product was obtained by repeated extractions and a vacuum sublimation. Only a trace amount of an impure brown oil was recovered from the reaction mixture. However, an infrared spectrum of this material indicates that there is a tetrazole ring present because of the characteristic absorption in the 6μ to 12μ region. Also, strong absorption in the 13.3μ to 14.3μ region indicates an aliphatic carbon-chlorine stretching vibration.

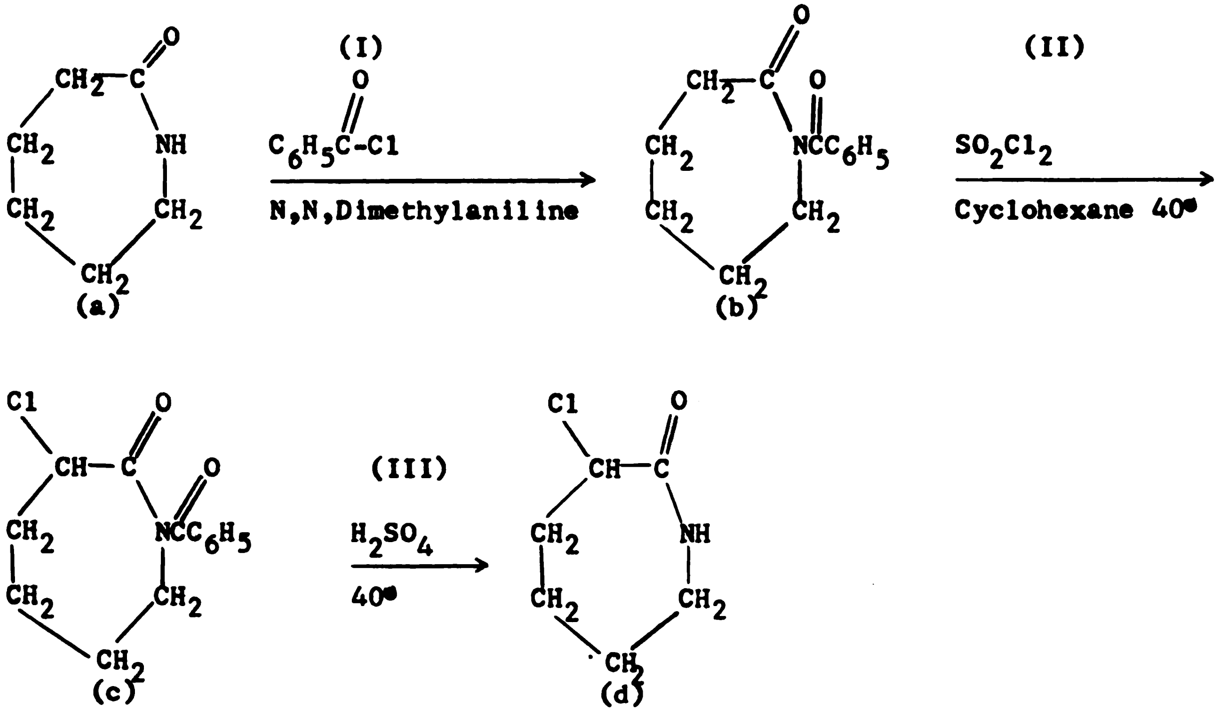
No further characterization of the final product could be made.

D. Preparation IV — 6-Chloropentamethylenetetrazole

The same general method described in the ε-caprolactam preparation of PMT was used for this synthesis.



Since α - chloro-ε-caprolactam (a), could not be purchased commercially, it was prepared by the following three step procedure (37):



Step (I) - Preparation of N-Benzoyl-ε-Caprolactam (b)

To a mixture of 90.4 g (0.80 mole) of ε-caprolactam and 114 ml (0.88 mole) of N,N-dimethylaniline was slowly added 102 ml (0.88 mole) of benzoyl chloride. The mixture was heated and stirred at 90° for four hours, cooled to 60°, and poured into 800 ml of dilute hydrochloric acid (0.05 molar). The crystalline lumps were broken up, filtered, air dried and recrystallized from a methanol-water solution giving 146 g (84%): mp 70.0-70.5°; lit. mp 68-70.5° (37).

Step (II) - Preparation of N-Benzoyl-α-Chloro-ε-Caprolactam (c)

To a suspension of 87 g (0.4 mole) of N-benzoyl-ε-caprolactam (b) in 22 ml of carbon tetrachloride and 66 ml of cyclohexane was added 34 ml (0.42 mole) of sulfuryl chloride. The mixture was heated and stirred at 40° for 36 hours. The material was then evaporated to dryness *in vacuo* and recrystallized from isopropyl alcohol giving 64 g (63%): mp 122-123°; lit. mp 120-121.5° (37).

Step (III) - Preparation of α-Chloro-ε-Caprolactam (d)

To 90 ml of concentrated sulfuric acid was added, in portions, 64 g (0.26 mole) of N-benzoyl-α-chloro-ε-caprolactam (c). The mixture was heated and stirred at 50° for three hours, cooled to 25° and poured onto 500 g of ice. After neutralization with concentrated ammonium hydroxide solution, the mixture was extracted with three 250-ml portions of chloroform. The chloroform solution was evaporated, and the residue was recrystallized from petroleum ether giving 33 g (88%): mp 90-92°; lit. mp 91.5-93°.

The 6-chloropentamethylenetetrazole was then prepared in the following manner: To a mixture of 140 ml of dry benzene and 29.6 g (0.20 mole) of α-chloro-ε-caprolactam (d) was added 41.7 g (0.20 mole) of phosphorus pentachloride over a period of one hour. The temperature was maintained at 15° by use of an ice bath. After all of the phosphorus pentachloride was dissolved, 360 ml of 0.67 *N* hydrazoic acid (0.24 mole) in benzene was slowly added. The mixture was allowed to stand overnight at room temperature and was then refluxed at 80° for two hours. The yellow solution was evaporated to dryness in vacuo, redissolved with 50 ml water and again brought to dryness. The residue was extracted several times with chloroform and a light brown oil was obtained. The final product, a clear viscous liquid, was obtained by fractional distillation of the oily residue at reduced pressure (70°, 0.2 mm pressure). Several attempts were made to crystallize this material by seeding and freezing, but, apparently, it is a liquid at room temperature. The boiling point at atmospheric pressure could not be determined because of extensive decomposition of the tetrazole at temperatures above 150°. The final yield was 5 g (14%):

Anal. Calcd for 6 -chloropentamethylenetetrazole: C, 41.75; H, 5.26; N, 32.46; Cl, 20.54. Found: C, 41.86; H, 5.36; N, 32.12; Cl, 20.60.

The ir spectrum of 6-chloropentamethylenetetrazole along with a spectrum of unsubstituted pentamethylenetetrazole may be seen in Figure I. A comparison of the two spectra show the similarity in the tetrazole region (6μ-12μ), while only in Spectrum (B) are there strong absorptions at 13.3μ to 14.3μ, presumably from a carbon-chlorine stretching vibration. Although nmr spectra show small amounts of impurities in the final product, they are in essential agreement with the 6-chloropentamethylenetetrazole structure. A summary of all the results may be seen in Table V.

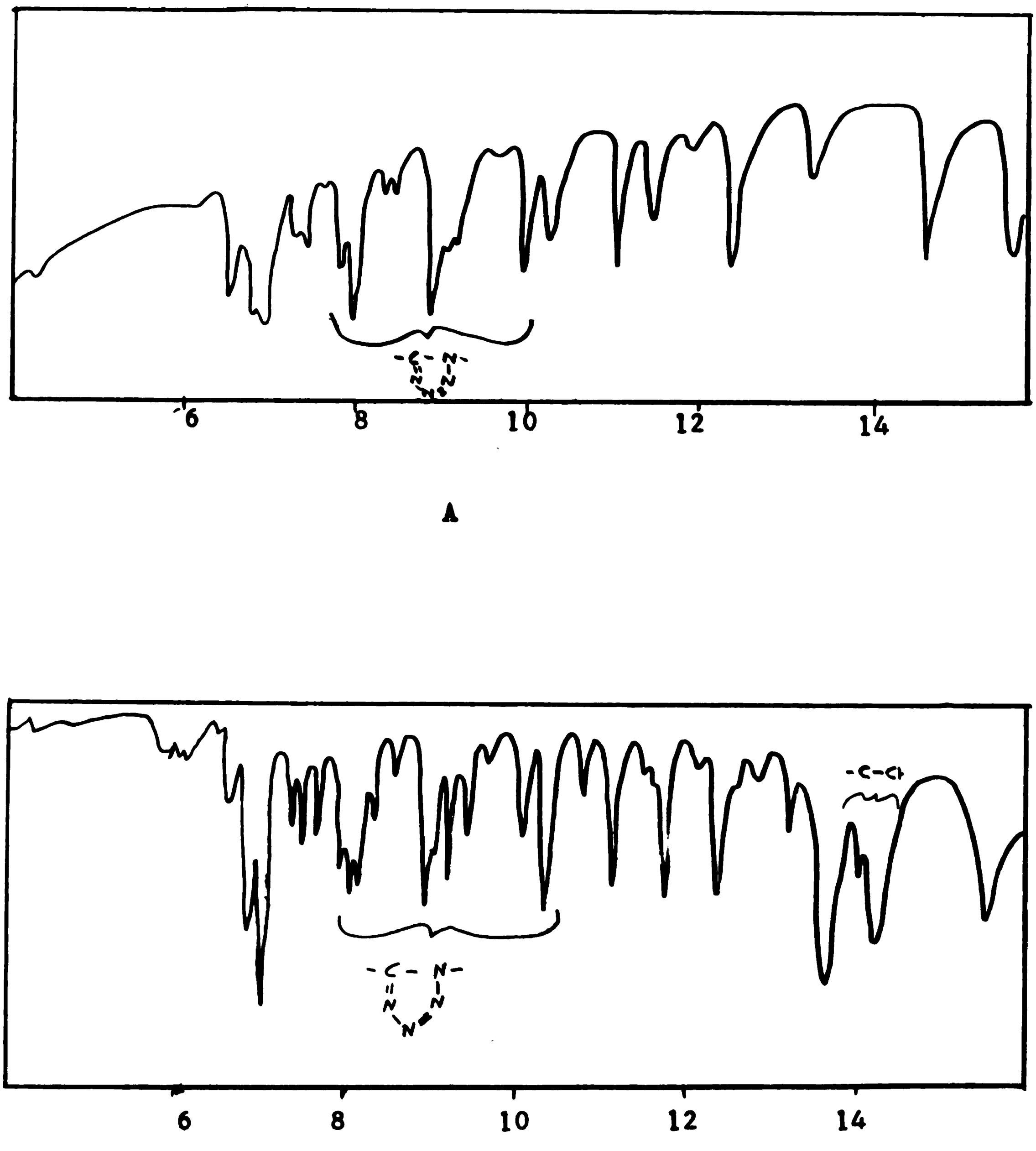


Figure 1. Infrared absorption spectra of A, PMT using a KBr pellet; B, 6-chloropentamethylenetetrazole using KBr plates. (wavelength in μ)

Table V. Substituted Pentamethylenetetrazoles.

Tetrazole	Synthesis	% Yield	mp	Lit. mp	Purification Recryst. Solvent
PMT	Cyclohexone Method	No attempted yield	59°	60°	Ethyl Ether
PMT	ϵ-caprolactam Method	No attempted yield	60°	60°	Ethyl Ether
10-ClPMT	Cyclohexone Method	No product	--	--	Sublimation
8-ClPMT	Cyclohexone Method	Small	--	--	Sublimation
6-ClPMT	ϵ-caprolactam Method	14%	--	--	Fractional distillation

CHAPTER III

STUDY OF π-COMPLEXATION OF SUBSTITUTED TETRAZOLES

HISTORICAL

In recent years there have been substantial developments in the investigation of molecular complexes, particularly for those that can be studied spectrophotometrically. These coordination compounds have stabilities which range from the very stable, predominately ionic complexes such as those found between ammonia and boron trifluoride (83) to the weak association complexes of solvent molecules found in liquid benzene and nitroanaline (84). These complexes are often referred to as donor-acceptor complexes with the donor molecules being grouped into two catagories (85); "n" donors, such as alcohols, organic sulfides, and nitrogen bases which donate a non-bonded electron pair and, secondly, "π" donors such as alkenes, alkynes and aromatic hydrocarbons which contain π-molecular orbitals. The acceptor component of the complexes, of which there are numerous types, include metal ions, halides (n- or π- bonding), and π-acids.

The nature of the intermolecular forces between the components of a molecular complex is a matter of considerable controversy. The heats of formation are generally small, and there is abundant evidence that the bonding forces are smaller than those of covalent bonds (85). The equilibria involved in complex formations are generally so rapid that kinetic studies can not be made by ordinary procedures (110). Bennett and Willis (86) were the first to note that the bonding forces in these complexes arose from some type of electron donor-acceptor interaction and proposed the actual formation of covalent bonds. However, it has since been shown that the bond distances are far greater than those corresponding to covalent bonds (87), but still less than those expected from Van der Wall's forces alone (96).

Pfeiffer (88), upon observing complexes of aromatic hydrocarbons with inorganic and organic compounds, assumed that the complex bond arose as a result of unsaturated secondary valences present in the aromatic ring. On the other hand, Lewis (89) treated these complexes in terms of acid-base theory and proposed that bonding occures by a base donating an electron pair to the recipient acid.

Briegleb and Schachowskoy (90) observed that the heats of formation for 1:1 complexes of nitro-compounds with aromatic hydrocarbons decreased with a decrease in the polarizability of the hydrocarbons. The above trend in the heats of formation led Briegleb (91, 92) to postulate that these complexes are formed as a result of electrostatic attraction between molecules with permanent dipoles and non-polar species which can be polarized by induction. However, this theory does not explain complexation involving substances lacking even partial dipole movements such as those found in iodine-benzene complexes.

It has long been noted that marked spectral changes accompany complex formation, especially in the case of aromatic complexes (93). Hammick and Yule (94) and Gibson and Loeffler (95) suggest that these spectral shifts arrise from electron transfer between the complex components during *normal* collisions if the molecules are properly oriented. Orgel and Mulliken (97) later expanded upon this work showing that in some cases spectral shifts do indeed arrise from short lived collision interactions which they called "contact charge-transfer" transitions.

Weiss (98) postulated that spectral shifts arrise by the formation of singly charged ions from the donor molecule (D:), and the acceptor (A), which are then held together by electrostatic forces, *i.e.*

$$D: + A \longrightarrow [D.]^{+}[A\cdot]^{-}$$

He suggested that the stability of the complex should be dependent on the ionization potential of the donor and the electron affinity of the acceptor. However, since the heats of complex formation are generally too low for ion formation (99), Brackmann (100), proposed that a complex formed from an electron-transfer is actually a resonance hybrid of a non-bonded and a dative bonded structure.

The most widely accepted theory of charge-transfer complexation is that proposed by Mulliken (101). Mulliken considers a 1:1 donor-acceptor complex to have a stable ground state, Ψ'_0, which is made up of contributions from a no-bond state, Ψ_0 (DA), and a dative polar state, Ψ_1 (D^+, A^-), and is given by the expression:

$$\Psi'_0 = \Psi_0 (DA) + a\Psi_1 (D^+, A^-). \qquad 1.$$

The complex in the excited state, Ψ'_1, is:

$$\Psi'_1 = \Psi_1 (D^+, A^-) + b\Psi_0 (DA) \qquad 2.$$

The coefficients a and b, which are approximately equal, are generally small when compared to unity. The charge-transfer absorption band of the complex arrises from the transition $\Psi'_0 \longrightarrow \Psi'_1$. The energy of this transition is related to the ionization potential of the donor (D) and the electron affinity of the acceptor (A).

Several semi-emperical relationships relating the charge-transfer absorption frequency (ν_{ct}) to the donor ionization potential (I_D) and the electron affinity of the acceptor (E_A) have been proposed (102-108). McConnell, Ham and Platt (102) found that the equation

$$h\nu_{ct} \doteq I_p - E_A - W \qquad 3.$$

where W = dissociation energy of charge-transfer excited state fits the data they obtained for a series of iodine complexes and a plot of $h\nu_{ct}$ *versus* I_p of the donors yields a straight line. Walkley *et al.* (107) expanded these studies to include iodine complexes of "n" donor and "π" donor solvents obtaining similar linear relationships.

Linear relationships between $h\nu_{ct}$ and donor I_p have also been reported for aromatic-π-acid complexes of *p*-chloranil (46), 1,3,5-trinitrobenzene (46, 48, 103-105), and 2,4,7-trinitrofluorenone (103-105). The equation suggested by Merrifield and Phillip (44), to fit the data they obtained from tetracyanoethylene-methylbenzene complexes,

$$h\nu_{ct} = 0.487\ I_p - 1.30 \qquad 4.$$

was later expanded to include other aromatics by Voigt and Reid (106). Mulliken and Person have recently published a very good review of charge-transfer complexes and related calculations (108).

THEORETICAL

The basic equation used in quantitative spectrophotometric calculation is Beer's law,

$$A = \epsilon b C \qquad 5.$$

where

A = absorbance at a given wavelength
ϵ = molar absorptivity at the same wavelength
b = pathlength in centimeters
c = concentration in moles per liter.

The importance of this relationship lies in the fact that at a given wavelength and pathlength the absorbance (A) is directly proportional to the concentration of the absorbing species.

In order to spectrophotometrically calculate equilibrium constants, or more accurately equilibrium quotients, since activity coefficients are not used, the method originally reported by Benesi and Hildebrand (111) or some variation (115) of this procedure is generally used. The method was originally derived for 1:1 complexes between iodine and organic solvents, but it can be altered to include complexes of different stoichiometries. For the donor-acceptor complex (DA) the equilibrium constant K is given by:

$$D + A \rightleftharpoons DA$$

$$K = \frac{(DA)}{(D)(A)} = \frac{C_{DA}}{(C_D - C_{DA})\,(C_A - C_{DA})} \qquad 6.$$

where

C_D = initial concentration of donor
C_A = initial concentration of acceptor
C_{DA} = concentration of complex at equilibrium.

let

$C_D >> C_A$; thus $C_D >> C_{DA}$

and

$$K = \frac{C_{DA}}{C_D(C_A - C_{DA})} \qquad 7.$$

from equation 5:

$$C_{DA} = \left[{}^{A}/_{\epsilon_{DA} b}\right] = \left[{}^{A}/_{\epsilon_{DA}}\right] \text{ for } = 1\text{cm}. \qquad 8.$$

If a wavelength is chosen such that

$$\epsilon_A = \epsilon_D = 0$$

then by substituting Equation 7 into Equation 6 and rearranging we obtain the final equation:

$$\frac{C_A}{A_T} = \frac{1}{\epsilon_D K \epsilon_{DA}} + \frac{1}{\epsilon_{DA}} \qquad 9.$$

where A_T = total absorbance of solution at same wavelength.

A plot of $\left[{}^{C_A}/_{A_T}\right]$ <u>versus</u> $\left[{}^{1}/_{C_D}\right]$ for a series of solutions gives a straight line with a slope of $\left[{}^{1}/_{K \epsilon_{DA}}\right]$ and an intercept of $\left[{}^{1}/_{\epsilon_{DA}}\right]$.

In cases where $\epsilon_A \neq 0$, a new equation, which is similar to Equation 9, can be derived (112):

$$\frac{1}{\epsilon_t - \epsilon_A} = \frac{1}{\epsilon_{DA} - \epsilon_A} \cdot \frac{1}{KC_D} + \frac{1}{\epsilon_{DA} - \epsilon_A} \qquad 10.$$

where

$$\epsilon_t = \frac{A_t}{(C_A + C_{DA})} \approx \frac{A_T}{C_A} \text{ for a weak complex.}$$

A plot of $(1/\epsilon_t - \epsilon_A)$ versus $(1/C_D)$ for a series of solutions gives a straight line with a slope of $(1/\epsilon_{DA} - \epsilon_A \cdot 1/K)$ and an intercept of $(1/\epsilon_{DA} - \epsilon_A)$.

Person (113) has shown that these equations give linear plots with meaningful slopes and intercepts only if the donor concentration (C_D) is greater than 0.1 (1/K). Also, Johnson and Bowen (114) have pointed out, by the use of synthetic data for the complex systems DA, D_2A and DA_2, that a linear plot from the Benesi-Hildebrand and Ketlelaar equations (Equations 9 and 10) is not always indicative of the complex stoichiometry assumed in the original derivation. The true test of complex stoichiometry is the agreement between calculated equilibrium constants at several different wavelengths.

Recently, a new method for the determination of complex formation constants in solutions using nuclear magnetic resonance spectroscopy has been proposed by Hanna and Ashbaugh (116). They have shown that for a 1:1 charge-transfer complex, the chemical shift of the acceptor protons is related to the strength of the donor-acceptor interaction. They derived a relationship analogous to that of Benesi and Hildebrand (Equation 9)

$$\frac{1}{\Delta} = \frac{1}{K\Delta_0 C_D} + \frac{1}{\Delta_0} \qquad 11.$$

where Δ is the difference between the observed shift of the acceptor protons in the presence of the donor and the chemical shift of the uncomplexed acceptor; Δ_0 is the difference between the shift of the acceptor protons in the pure complex and the shift of the uncomplexed acceptor; K is the formation constant of the complex; and C_D is the total concentration of the donor. Just as in the case of optical spectra, one measures the chemical shift of the acceptor protons in a series of solutions containing varying concentrations of the donor and plots $(1/\Delta)$ versus $(1/C_D)$. A straight-line plot is obtained in the case of 1:1 complexes and the values of Δ_o and K are obtained from the slope and the intercept. The NMR technique was used very successfully by Foster and Fyfe in the study of the dinitrobenzene and trinitrobenzene complexes with aromatic compounds (117).

EXPERIMENTAL

I. Solvents

The following five procedures were used to purify the solvents in this investigation.

Procedure A

Cyclohexane, 1,2-dichloroethane, carbon tetrachloride, dichloromethane, n-heptane, and benzene were purified in the following manner:

Step 1. The solvent was washed several times with concentrated sulfuric acid until the acid layer remained colorless.

Step 2. The acid was drained off and the solvent was washed with water, sodium bicarbonate solution (0.5 M) and, then, water again.

Step 3. The water was drained off, and the wet solvent was dried for two days over anhydrous barium oxide.

Step 4. The solvent was then refluxed for six hours over fresh barium oxide and fractionally distilled at atmospheric pressure through a 30 in. column packed with glass beads, collecting only the middle portion.

Procedure B

Triethylamine, piperidine, 2,6-lutidine, pyridine, and nitromethane were all purified by first drying the solvents over anhydrous barium oxide for two days. They were then vacuum (0.10 mm) fractionally distilled through a 30 in. Vigreaux column using fresh anhydrous barium oxide as the drying agent.

Procedure C

Acetone was purified by simply refluxing it for six hours over anhydrous calcium chloride and then fractionally distilling it at atmospheric pressure through a 30 in. column packed with glass beads, collecting only the middle portion. Stronger dehydrating agents could not be used because of possible acetone condensation.

Procedure D

Methanol was purified by the following procedure:

Step 1. Solid iodine and concentrated aqueous sodium hydroxide solution were added to the methanol and allowed to stand for several hours to remove any aldehydes or ketones present.

Step 2. A large excess of silver nitrate solution (0.1 m) was added to the mixture to remove the unreacted iodine and any other reducing impurities.

Step 3. The above mixture was fractionally distilled to remove most of the water present. The remaining solvent was refluxed over magnesium ribbon for six hours. It was then fractionally distilled at atmospheric pressure through a 30 in. column packed with glass beads, collecting only the middle portion.

Procedure E

Acetonitrile was purified in the following manner:

Step 1. The impure solvent was allowed to stand over calcium hydride for two days. It was then fractionally distilled at atmospheric pressure through a 30 in. column packed with glass beads, collecting only the middle portion.

Step 2. The distilled solvent was next refluxed for 24 hours over phosphorus pentoxide and finally fractionally distilled, collecting only the middle portion.

II. Reagents

Substituted tetrazoles used in this investigation were synthesized and purified according to the procedures described in Part II of this thesis. Pentamethylenetetrazole, however, was obtained from

Knoll Pharmaceutical Co. and purified by several recrystallizations with anhydrous ethyl ether: mp 60-61°; lit. mp 61° (28). The 1,2,4-triazole was purchased from Calbiochem and recrystallized twice from dichloromethane-methanol.

Tetracyanoethylene was originally obtained from the du Pont Co. and subsequently from Eastman. It was recrystallized twice from chlorobenzene and then sublimed twice in an inert atmosphere. The potassium salt of the tetracyanoethylene anion radical was prepared and purified using the method of Webster _et al._ (118). Tetracyanoethane was obtained by reducing tetracyanoethylene with hydrogen iodide and was purified by recrystallization from ethyl acetate-hexane (119). The remaining π-acids used in this study are listed in Table VI.

III. Apparatus

Absorption measurements in the visible and ultraviolet regions were made on a Cary recording spectrophotometer Model 14, in silica cells of 1.00, 5.00, and 10.00 ± 0.01 cm pathlengths. Measurements were done at room temperature of approximately 25°.

All NMR measurements were made on carbon tetrachloride solutions with a Varian Associates A-60 spectrometer operating at 60 Hz/sec. The probe temperature was approximately 35°. Tetramethylsilane was used as the reference for chemical shift measurements.

Infrared measurements were made on a Beckman recording spectrophotometer Model IR-5, using potassium bromide pellets.

Table VI. π-Acids.

Compound	Source	Purification	mp	Lit mp
Tetracyanoethylene (TCNE)	du Pont Co.	Recrystallized from Chlorobenzene and sublimed	199°	200° (44)
Tetracyanoquinodimethane (TCNQ)	du Pont Co.	Obtained in pure form	294°	294-296° (45)
p-chloranil (CA)	Eastman Co.	Recrystallized from Dichloromethane	292°	290° (46)
1,3,5-trinitrobenzene (TNB)	Eastman Co.	Recrystallized from Ethanol	63°	61° (48)
2,4,7-trinitrofluorenone (TNF)	Eastman Co.	Recrystallized from 3:1 nitric acid-water	173-174°	175-176° (47)

RESULTS AND DISCUSSION

The possible complex formations between tetrazoles and Lewis π-acids were studied in order to indicate the extent of π - electron donor ability of the tetrazole ring. The greater part of this work was performed using tetracyanoethylene (hereafter abbreviated as TCNE) since it has been shown to be one of the strongest π-acids available (44). However, the complexing tendencies of the tetrazoles were studied with other π-acids such as tetracyanoquinodimethane (TCNQ), p-chloranil (CA), 1,3,5-trinitrobenzene (TNB), and 2,4,7-trinitrofluorenone (TNB).

The choice of solvents for these studies had to take into account two major factors; the general insolubility of the substituted tetrazoles and the reactivity of the π-acids, especially TCNE. Solubility studies were made with various tetrazoles, and it was found that they dissolved to an appreciable extent in several chloronated hydrocarbon solvents and alcohols.

In order to test for π-acid— solvent interaction, Beer's law studies were preformed in the following solvents; dichloromethane, 1,2-dichloroethane, methanol, acetonitrile, and absolute ethanol (Figure 2). Solutions of TCNE in all five solvents adhered to Beer's law; spectra were obtained immediately after making up the solutions. However, drastic spectral changes were observed within a short period of time in methanol, ethanol and acetonitrile; thus, the use of these solvents was discontinued.

Because of greater solubility of the tetrazoles in dichloromethane than in 1,2-dichloroethane, the former solvent was chosen for the remainder of this study. Beer's law studies were run on the rest of the

Figure 2. Beer's law study of TCNE in: A, dichloromethane (268mμ); B, 1,2-dichloroethane (263 mμ); C, methanol (235 mμ); D, nitromethane (278 mμ), and E, ethanol (240 mμ) using 1-cm-pathlength cells.

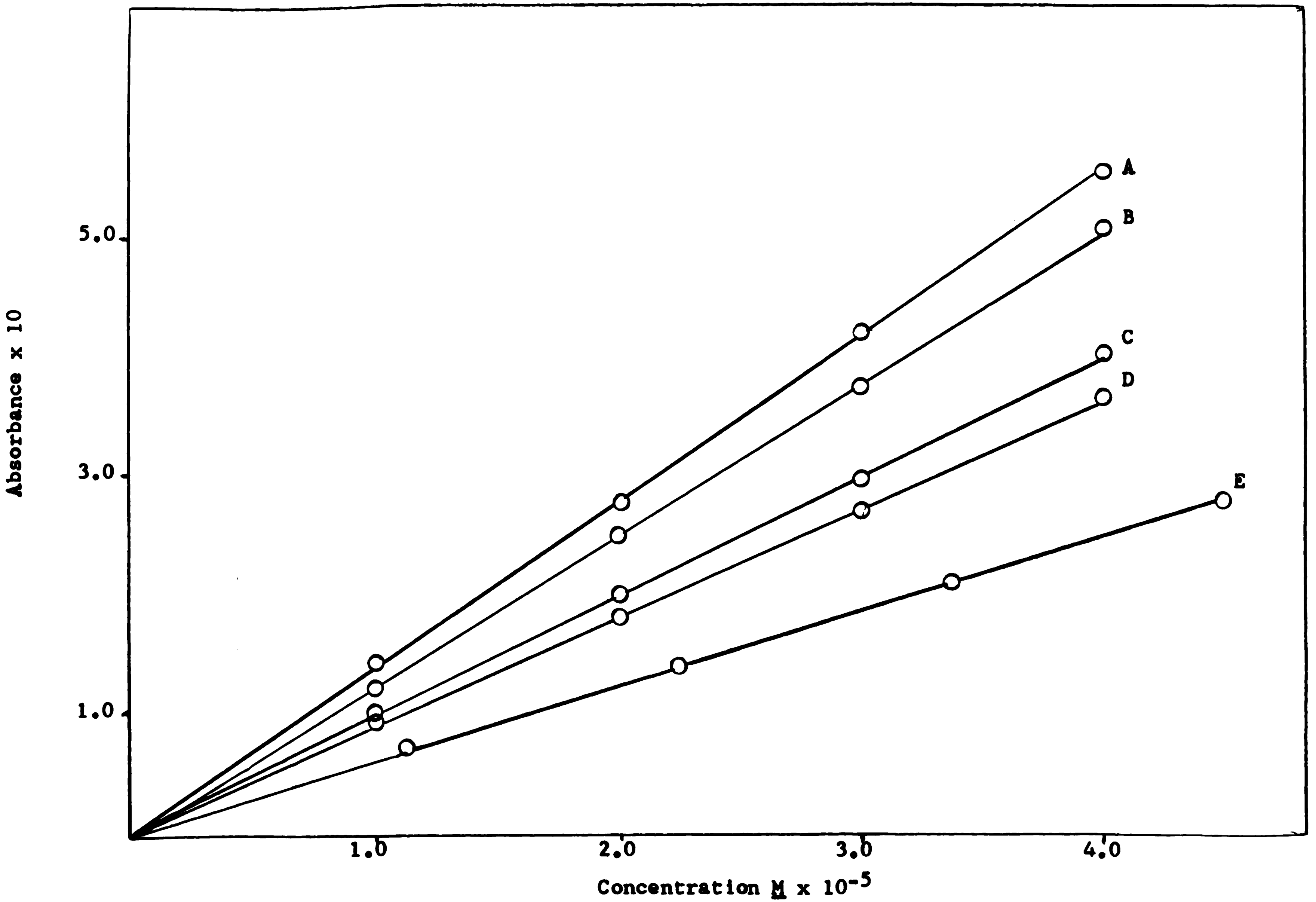

Absorbance x 10
5.0
3.0
1.0
1.0
2.0
3.0
4.0
Concentration $\underline{M}$ x 10^{-5}
A
B
C
D
E

Figure 2.

π-acids (TCNQ, CA, TNB, and TNF) in dichloromethane (Figures 3 and 4). All four compounds obeyed Beer's law and their solutions showed no spectral changes with time.

A series of solutions with TCNE and PMT were made in dichloromethane and their absorption spectra were determined. As the PMT/TCNE mole ratio increases, the TCNE absorption band at 268 mμ gradually decreases in intensity and broadens at the base. The series of curves (Figure5) pass through a rather poorly defined isobestic point, indicating the presence of only two absorbing species.

In order to make quantitative spectral measurements, higher concentrations of TCNE ($\approx 1 \times 10^{-3}$) had to be used. Since the tetrazoles did not absorb radiation in the region studied (300-450 mμ), spectral measurements were taken directly from the TCNE absorption band.

It is interesting to note that in all the tetrazole-TCNE complexes the absorption maxima of charge-transfer bands were not observed, but rather the absorption band of the TCNE broadened considerably and extended to lower frequencies (Figures 6-13). Absorption measurements were, consequently, carried out on the rather steep side of the new absorption band with consequent loss of accuracy. An absorption maximum, however, was obtained in the case of 5-benzyltetrazole (Figure 14).

The experimental data were evaluated according to the method of Kelelaar, _et_ _al_. (112) using Equation 10 p 31. Since this treatment involves the use of a least squares analysis, a Fortran computer program was used on a Control Data Corporation 3600 computer. The results plus their corresponding average deviations are listed in Table VII. The values of the formation constants are independent of the wavelength

Figure 3. Beer's law study of: A, TCNQ (400 mμ); B, TNF (280 mμ); and C, TNB (260 mμ) in dichloromethane using 1-cm-pathlength cells.

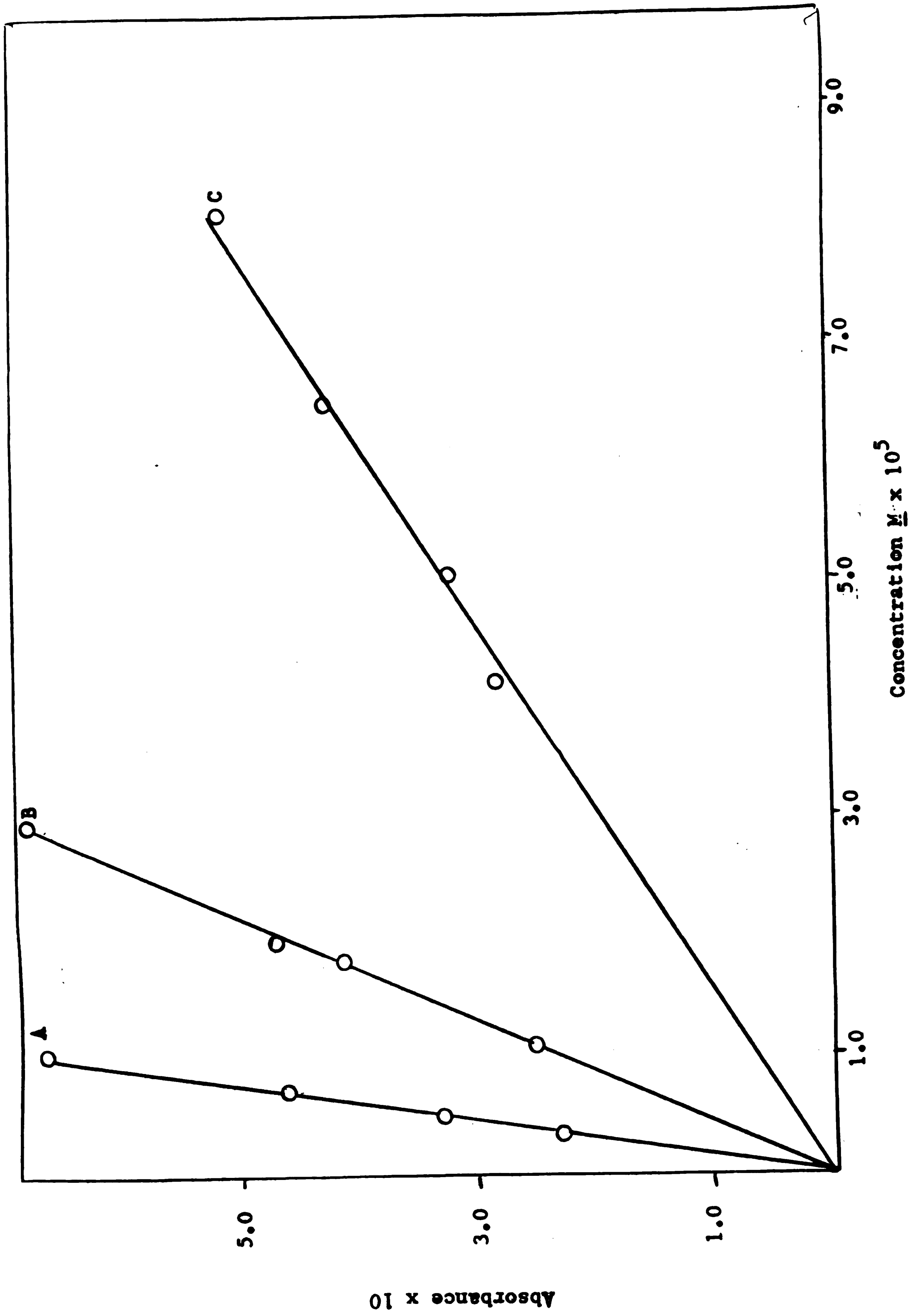

A
B
C
1.0
3.0
5.0
7.0
9.0
Concentration $\underline{M}$ x 10^5
1.0
3.0
5.0
Absorbance x 10

Figure 3.

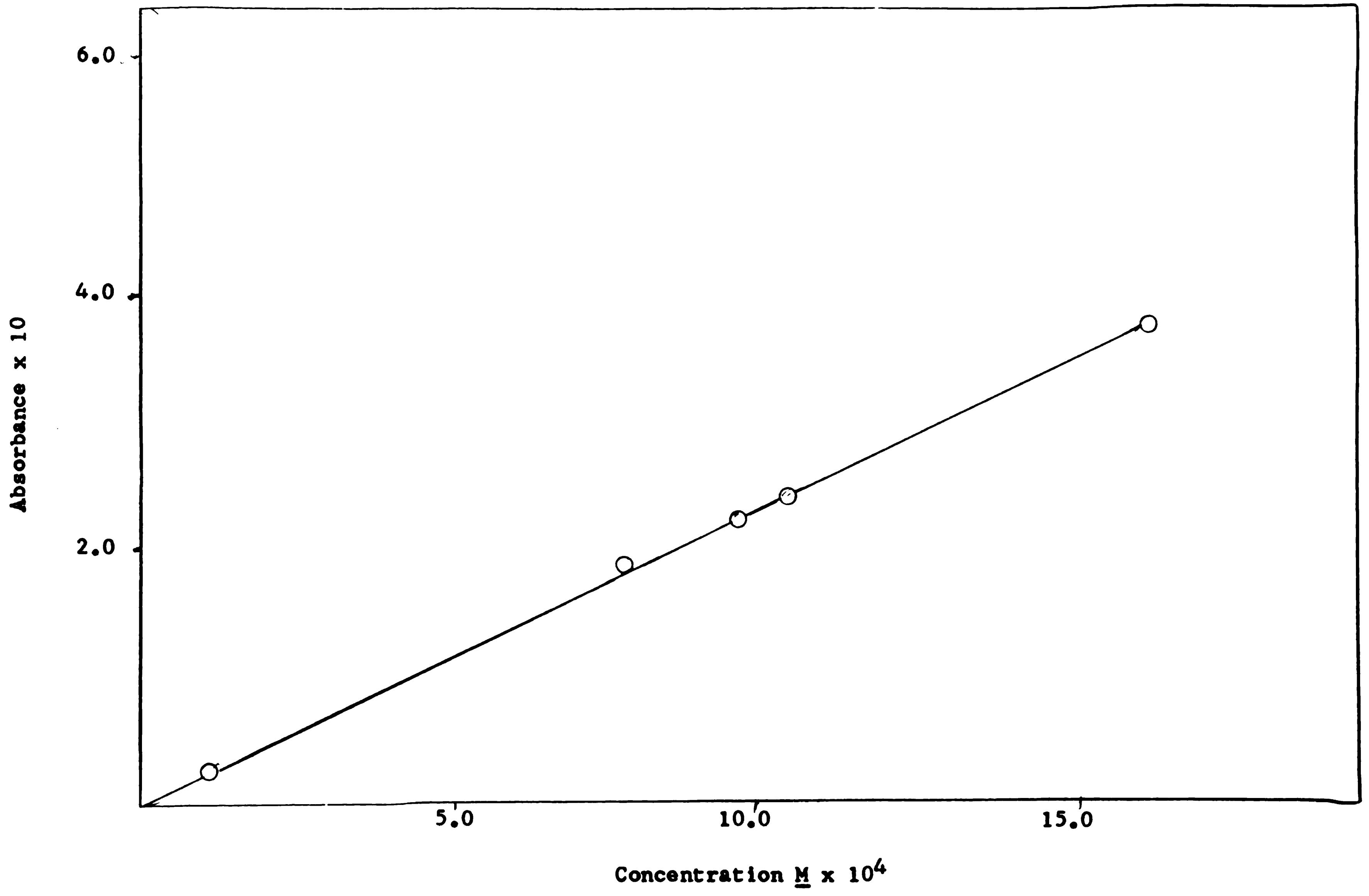


Figure 4. Beer's law plot of p-chloranil (373 mμ) in dichloromethane using a 1-cm-pathlength cell.

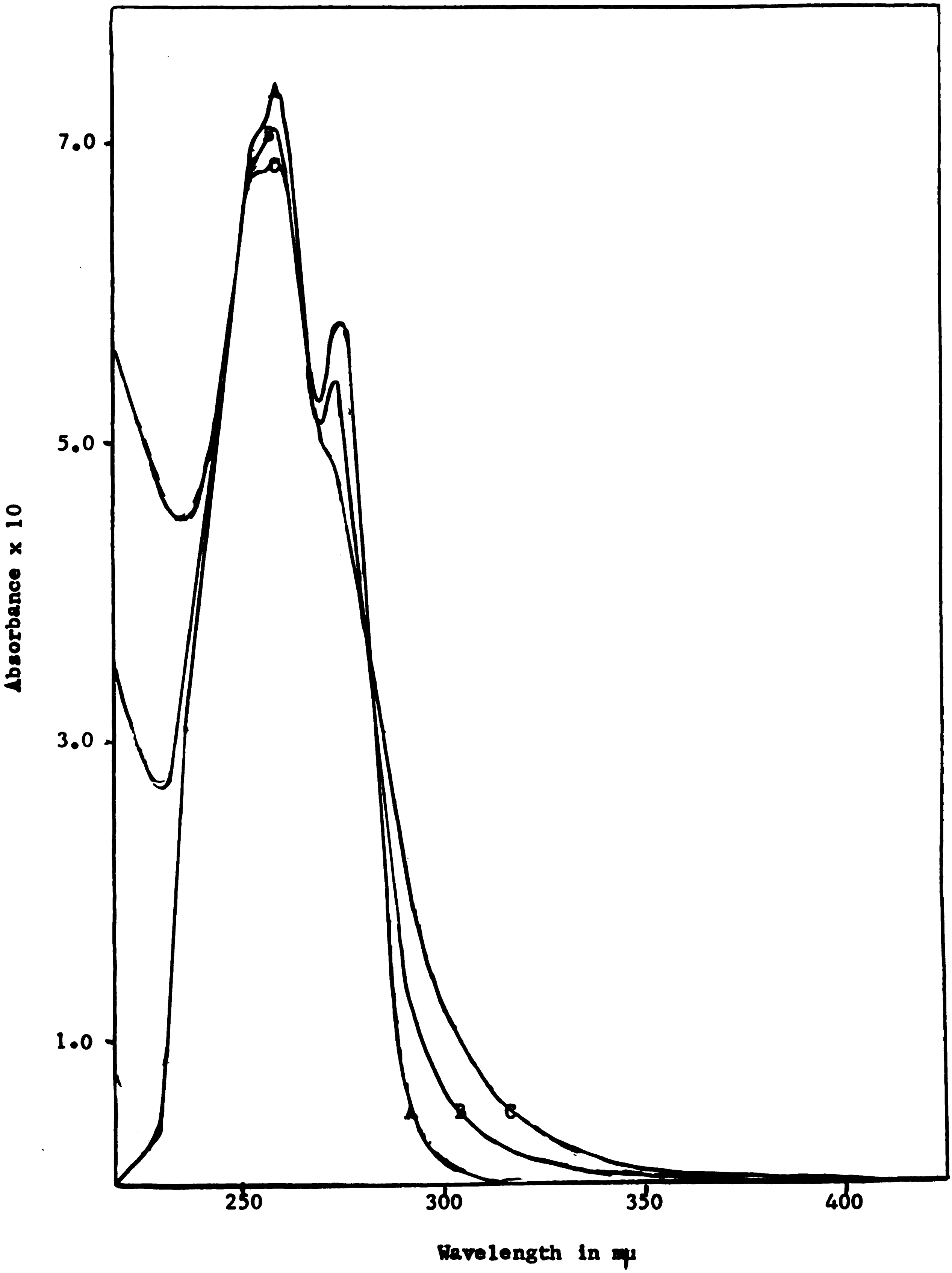


Figure 5. Spectrophotometric study of 5.0 x 10^{-5} M TCNE(A) with PMT mole ratios of B, 1085; and C, 4330, in dichloromethane using a 1-cm-pathlength cell.

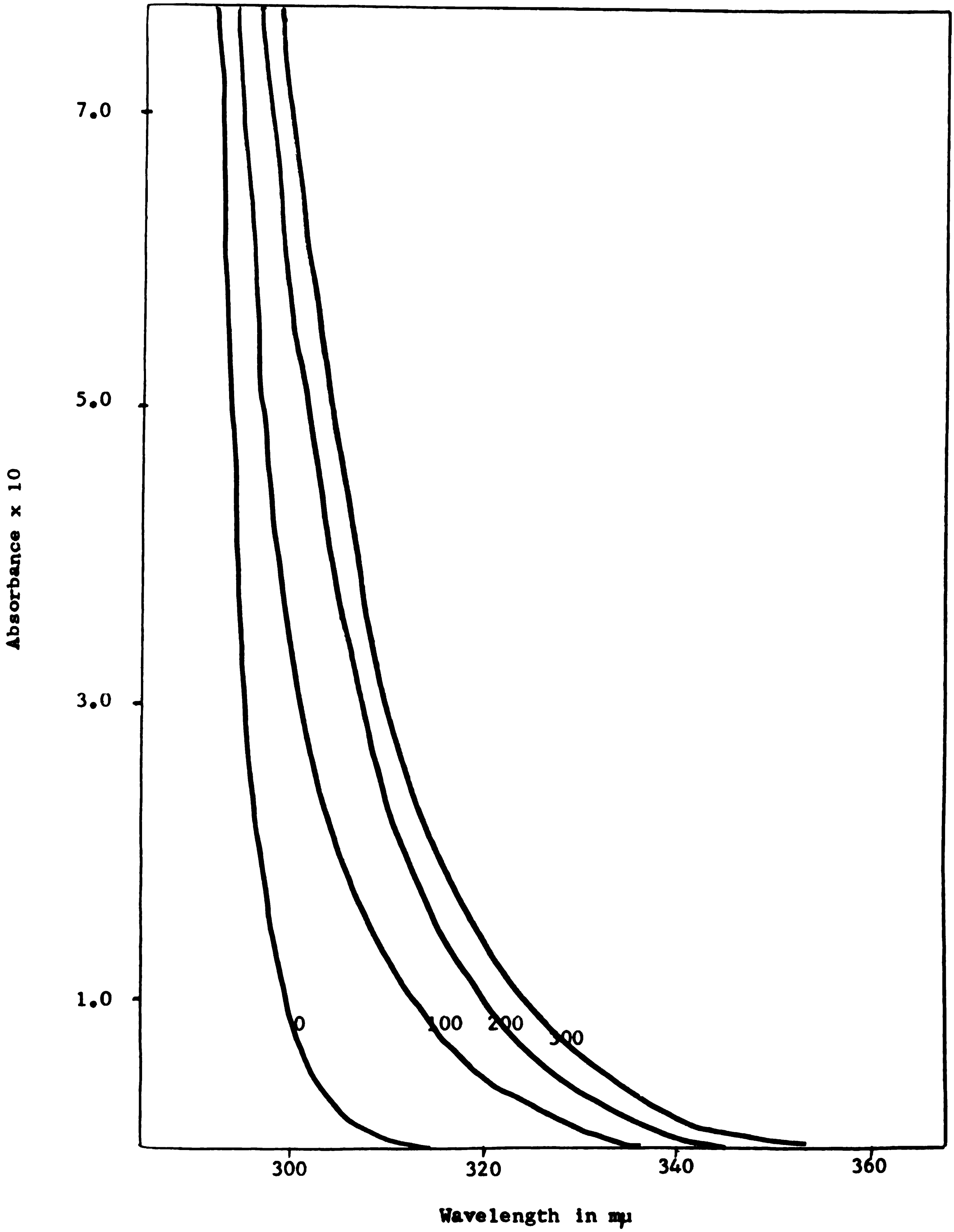


Figure 6. Spectrophotometric study of 1.0 x 10^{-3} M TCNE with various mole ratios of PMT in dichloromethane using a 1-cm-pathlength cell.

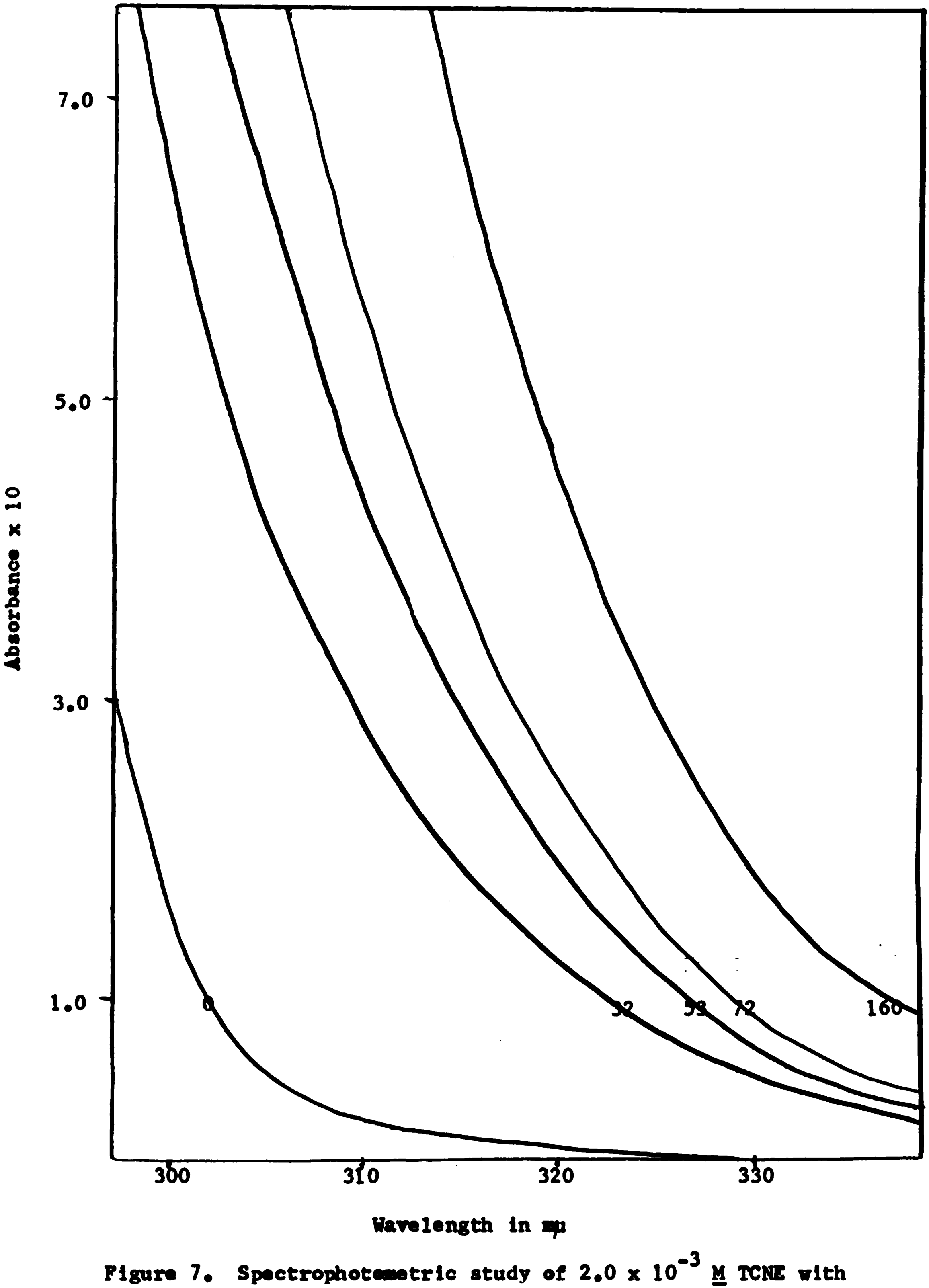


Figure 7. Spectrophotometric study of 2.0 x 10^{-3} M TCNE with various mole ratios of 1-cyclohexyl-5-ethyltetrazole in dichloromethane using a 1cm-pathlength cell.

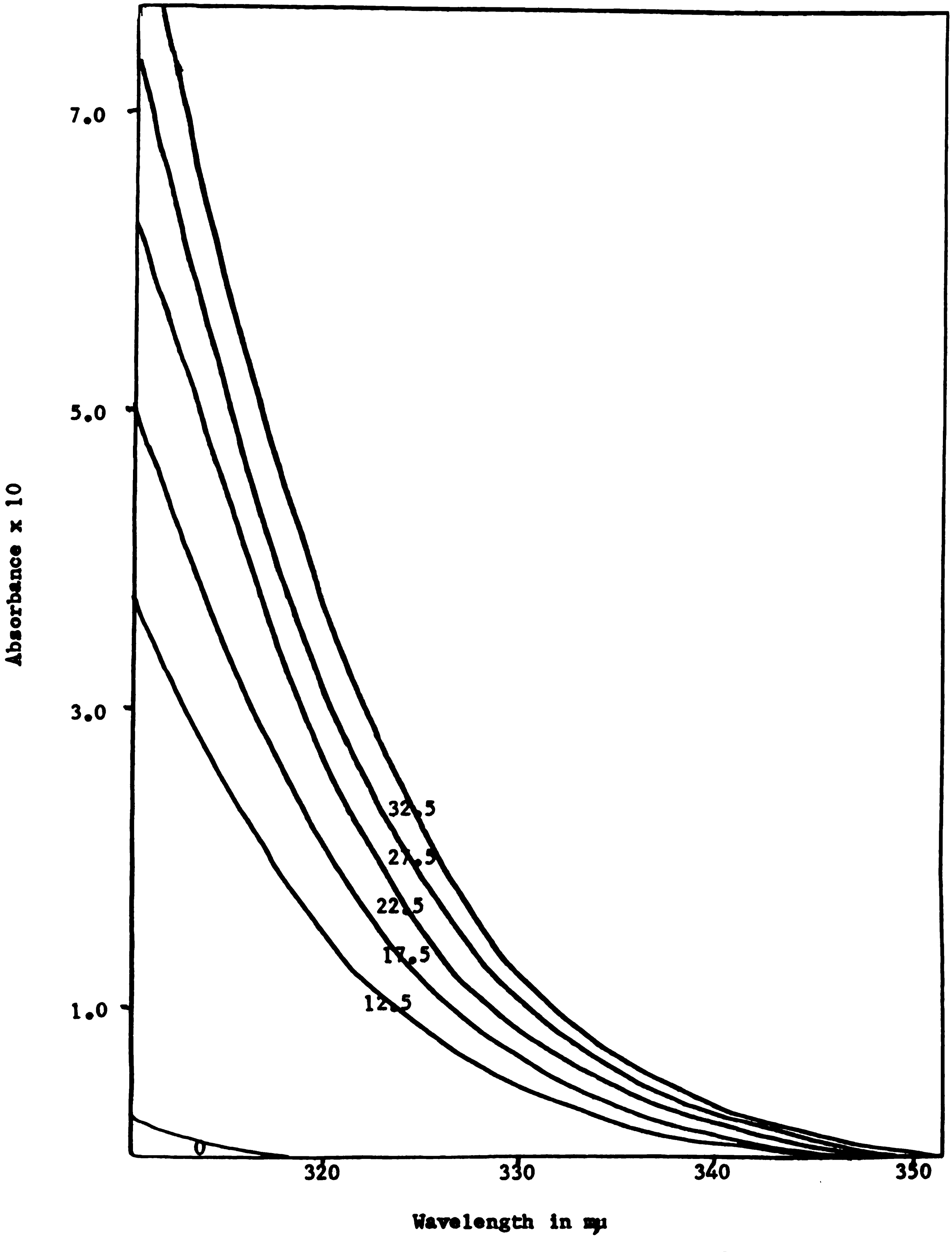


Figure 8. Spectrophotometric study of 4.0×10^{-3} M TCNE with various mole ratios of 1-cyclohexyl-5-methyltetrazole in dichloromethane using a 1cm-pathlength cell.

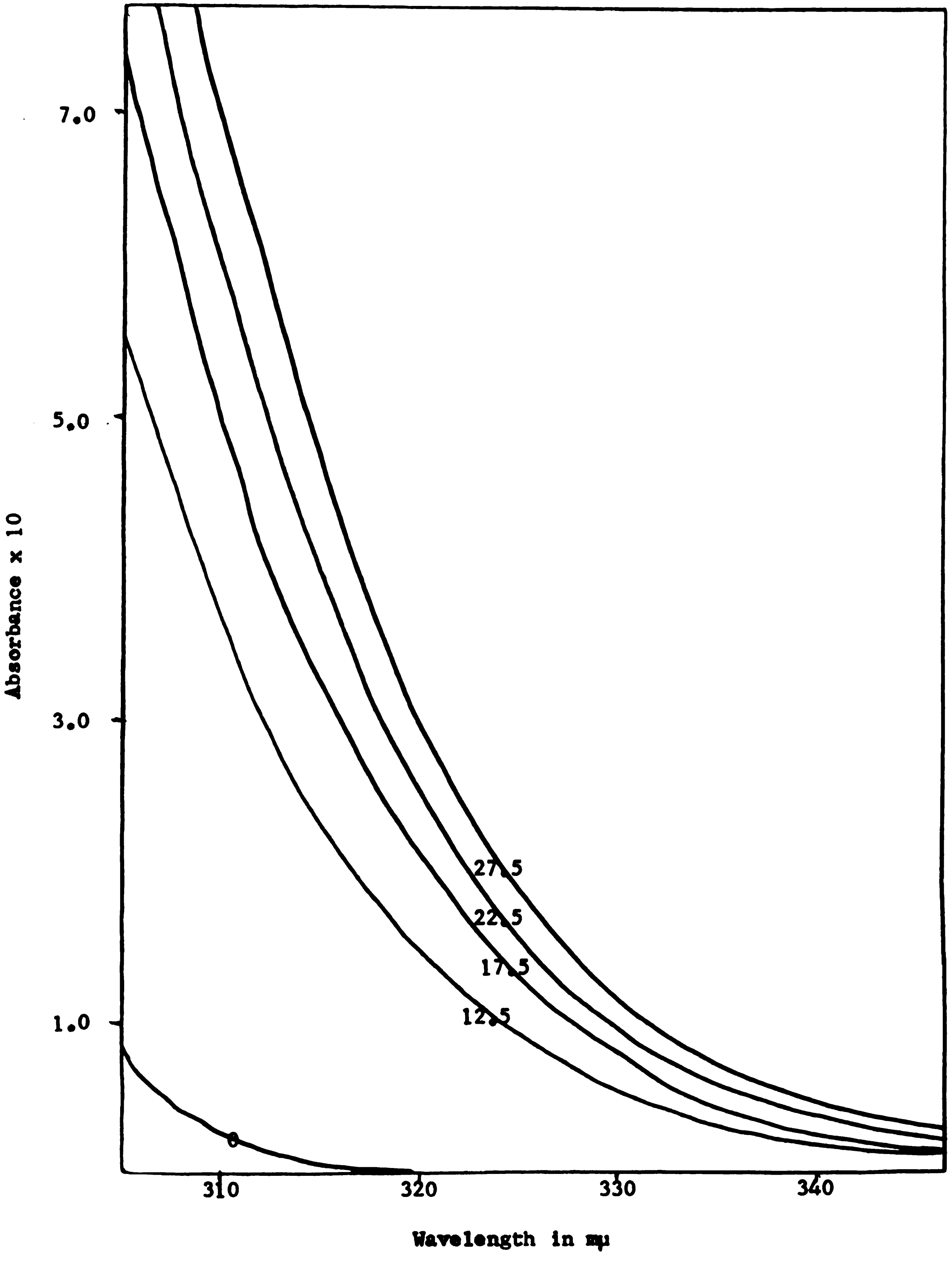


Figure 9. Spectrophotometric study of 4.0 x 10^{-3} M TCNE with various mole ratios of 1-methyl-5-cyclohexyltetrazole in dichloromethane using a 1cm-pathlength cell.

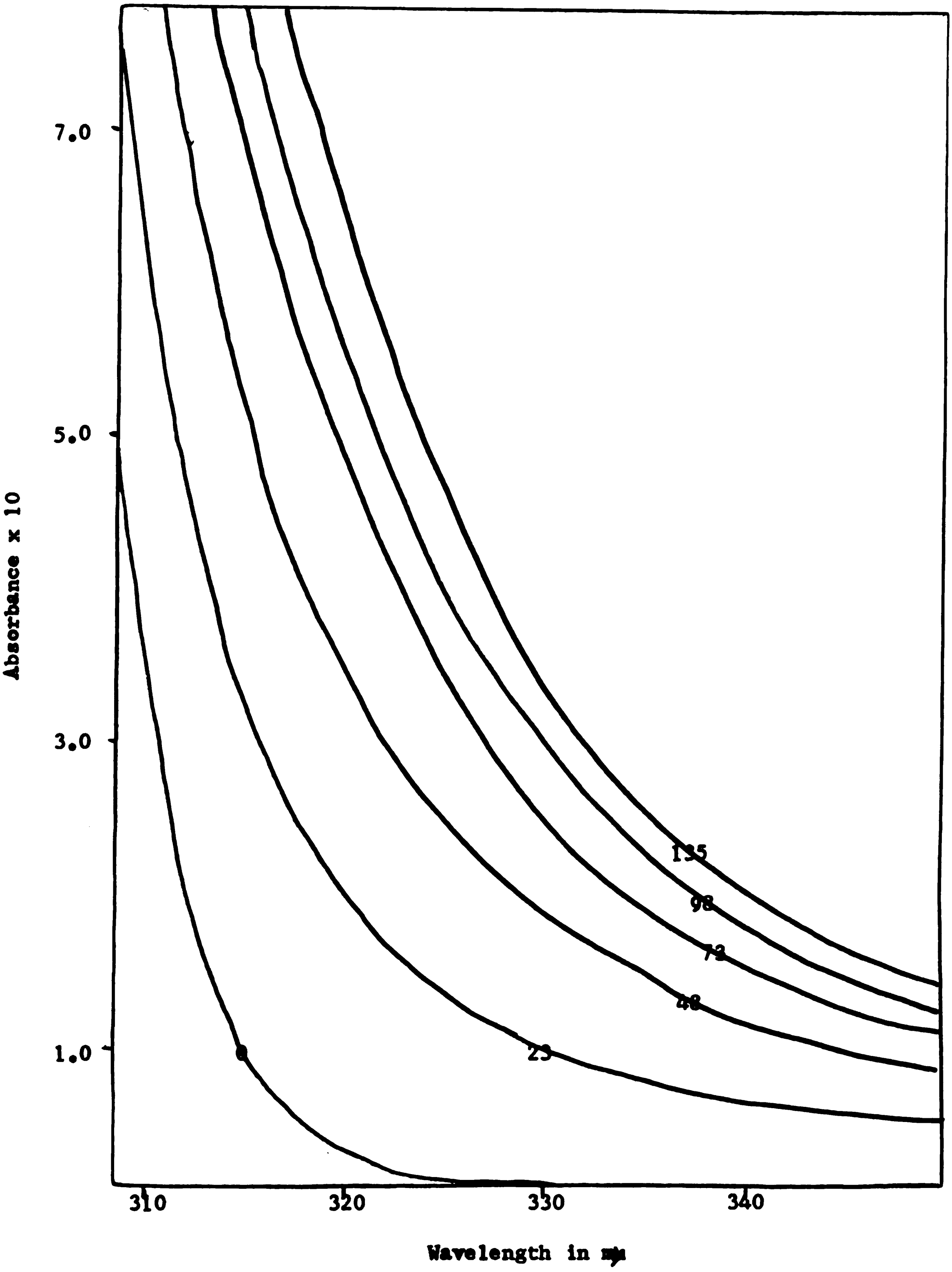


Figure 10. Spectrophotometric study of 4.0 x 10^{-3} $\underline{M}$ TCNE with various mole ratios of 5-propyltetrazole in dichloromethane using a 1-cm-pathlength cell.

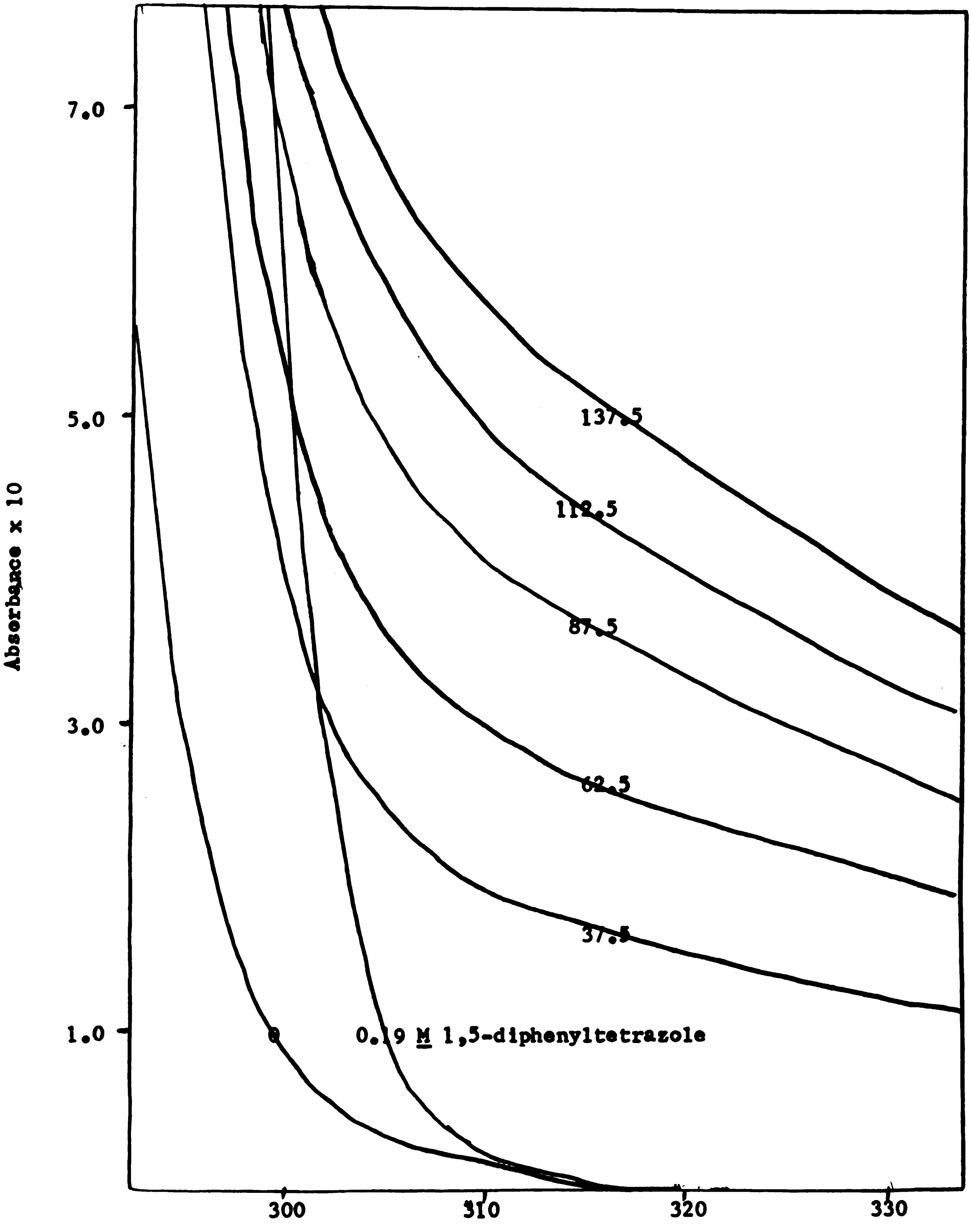


Figure 11. Spectrophotometric study of 1.0×10^{-3} M TCNE with various mole ratios of 1,5-diphenyltetrazole in dichloromethane using a 1-cm pathlength cell.

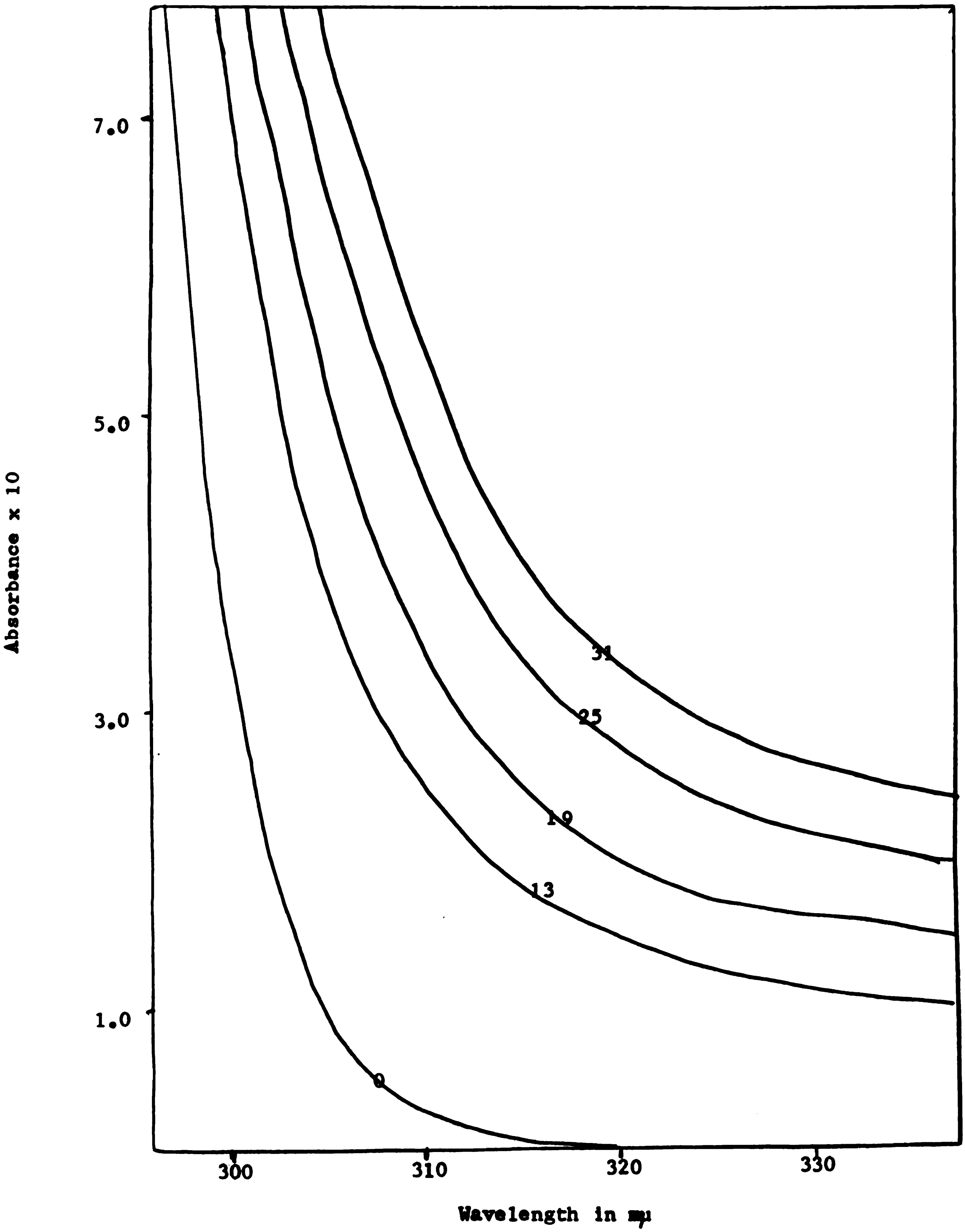


Figure 12. Spectrophotometric study of 4.00 x 10^{-3} M TCNE with various mole ratios of 1-ethyl-5-phenyl tetrazole in dichloromethane using a 1-cm pathlength cell.

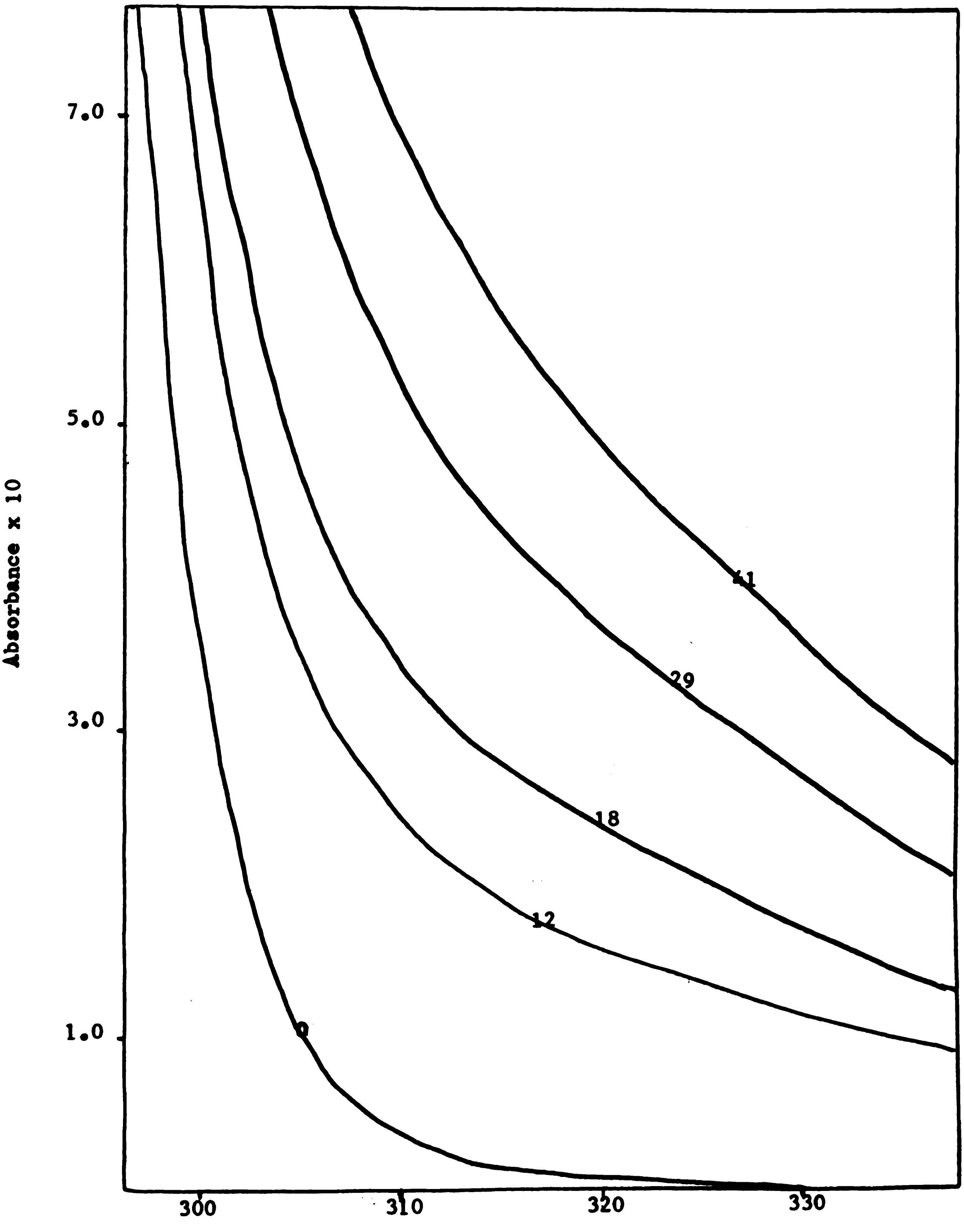


Figure 13. Spectrophotometric study of 4.0×10^{-3} M TCNE with various mole ratios of 1-phenyl-5-ethyltetrazole in dichloromethane using a 1-cm-pathlength cell.

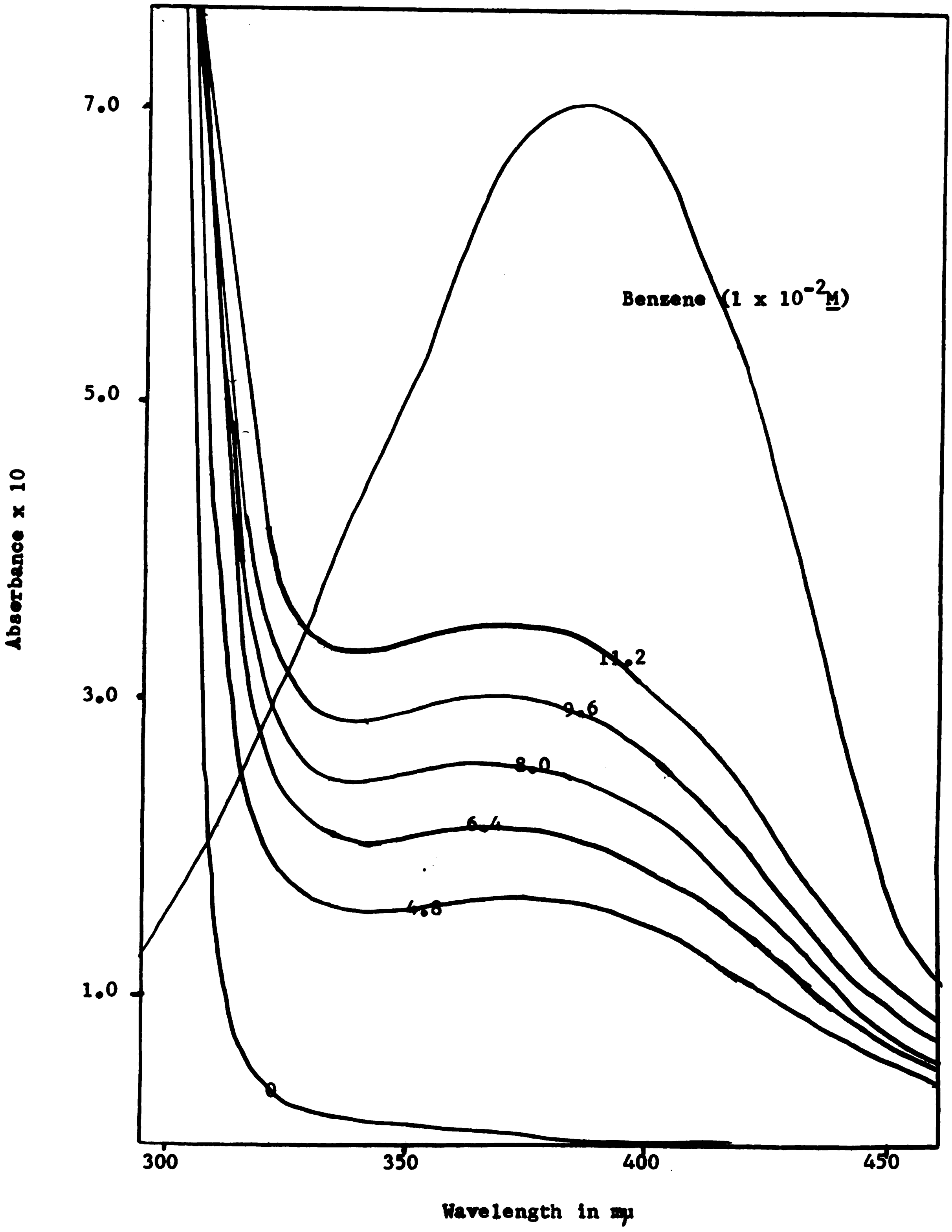


Figure 14. Spectrophotometric study of 5.00 x 10^{-3} M TCNE with various mole ratios of 5-benzyltetrazole in dichloromethane using a 5-cm-pathlength cell.

Table VII. Tetracyanoethylene Complexes with Tetrazoles.

Tetrazole		300	305	310	315	320	325	330	335	340	K_{av}[a]	
		Wavelength, mμ										
PMT	K	1.33	1.32	1.32	1.30	1.28					1.31	0.02
	ε	2260	1630	1120	760	490						
1-Cyclohexyl-5-EtTz[b]	K			1.90	1.94	1.80					1.88	0.07
	ε			250	850	600						
1-Cyclohexyl-5-MeTz	K		1.30	1.50	1.38						1.39	0.10
	ε		2030	1250	900							
1-Me-5-cyclohexylTz	K		1.94	2.20	1.93						2.02	0.14
	ε		1430	900	400							
5-PrTz	K		2.00	1.59	1.85						1.81	0.20
	ε		3.60	2.60	1.80							
1,5-DiPhTz	K	1.08		0.84		0.89		0.78			0.90	0.15
	ε	1690		1250		1190		1090				
1-Et-5-PhTz	K						1.44	1.39	1.48	1.53	1.46	0.07
	ε						470	440	390	350		
1-Ph-5-EtTz	K			1.21	1.22	1.24	1.20	1.18			1.21	0.03
	ε			1000	850	720	630	540				

[a] Formation constants are given in liters per mole. [b] Me = methyl; Et = ethyl; Pr = propyl; Ph = phenyl; Tz = tetrazole.

at which the measurements were made indicating the presence of a 1:1 complex (see p 32 for discussion). The only exception seems to be the complex of the 1,5-diphenyltetrazole, but here again the trend is not outside the expected experimental error.

In the case of the complex between TCNE and 5-benzyltetrazole it was noted that there were spectral shifts with time, possibly from an addition reaction. However, for short periods of time (approx. one hour) the absorption maximum was stable and was similar to the maximum obtained for the benzene-TCNE complex (Figure 14). The experimental data are given in Table VIII. While there is little doubt that the appearance of the new band is due to complex formation, in view of relatively low molar absorptivity it is doubtful that this is a charg-transfer band.

In all cases the Ketelaar plots were linear as may be seen in the representative graphs of Figure 15.

Since TCNE is very reactive chemically, it was important to determine whether the spectral changes observed in the TCNE-tetrazole systems were not due to side reactions. Tetracyanoethylene readily forms the radical anion $TCNE^{\cdot -}$ or it can undergo a reduction to H_2TCNE. Both of these substances were synthesized, and their spectra were determined. Their spectra (Figure 16) showed good agreement with the data in the literature (118). From comparison of these spectra with the results obtained in the TCNE-tetrazole systems it is evident that the spectral changes observed in these systems are not due to the formation of either the radical anion or of the reduction product.

It is also known that TCNE can react irreversibly with strong bases (118). Solutions of TCNE were prepared in methylene chloride containing piperidine, triethylamine, or pyridine. The spectra of these

Table VIII. Charge-transfer complex of TCNE with 5-Benzyltetrazole.

	Wavelength, mμ					
	350	370	390	410	K_{av}	
K	2.26	2.27	2.31	2.28	2.28	0.02
C	77	89	98	89		

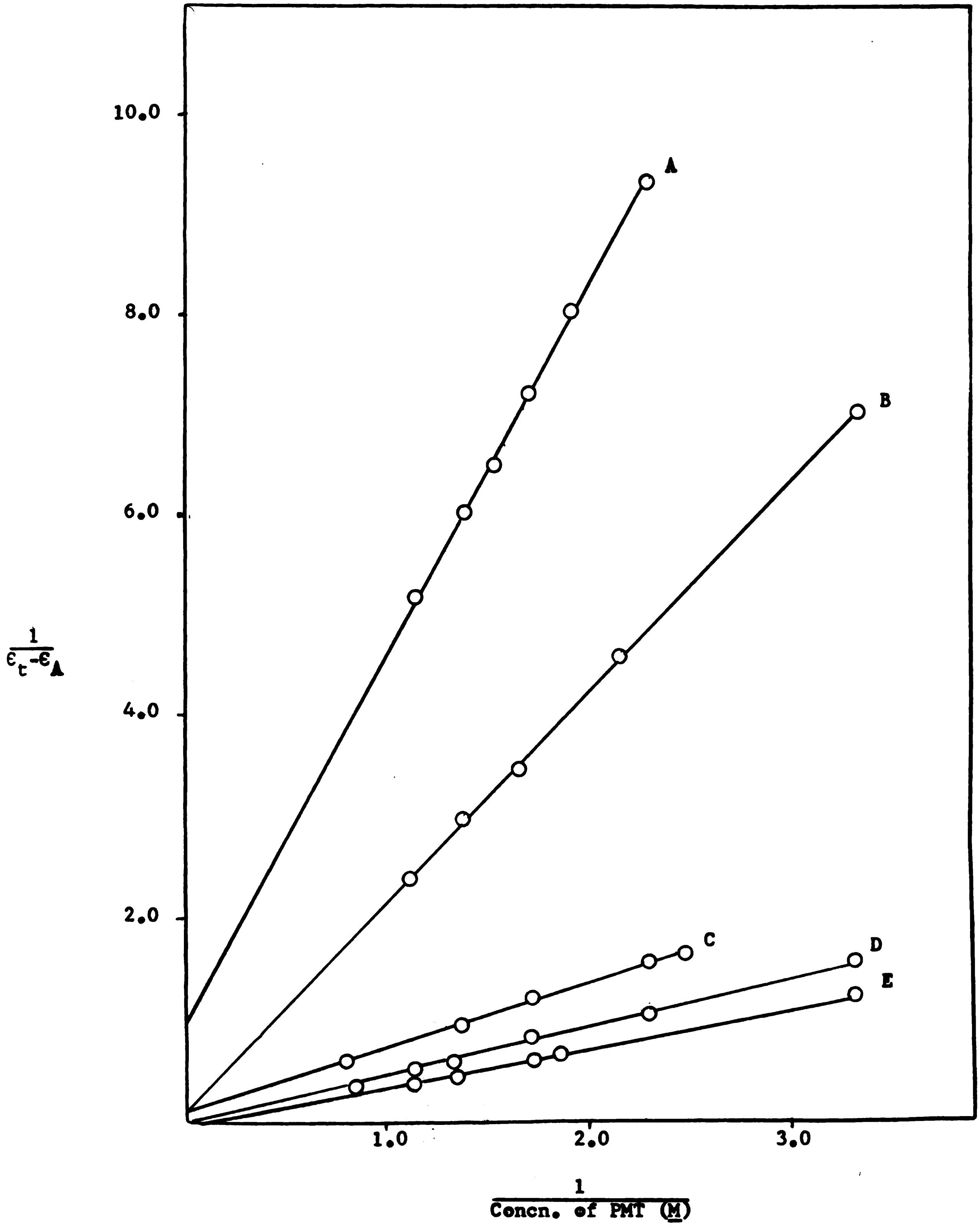


Figure 15. Ketelaar plots for PMT complexes of: A, TCNQ (283 mμ); B, CA (315 mμ); C, TNB (270 mμ); D, TNF (300 mμ); and E, TCNE (293 mμ) in dichloromethane.

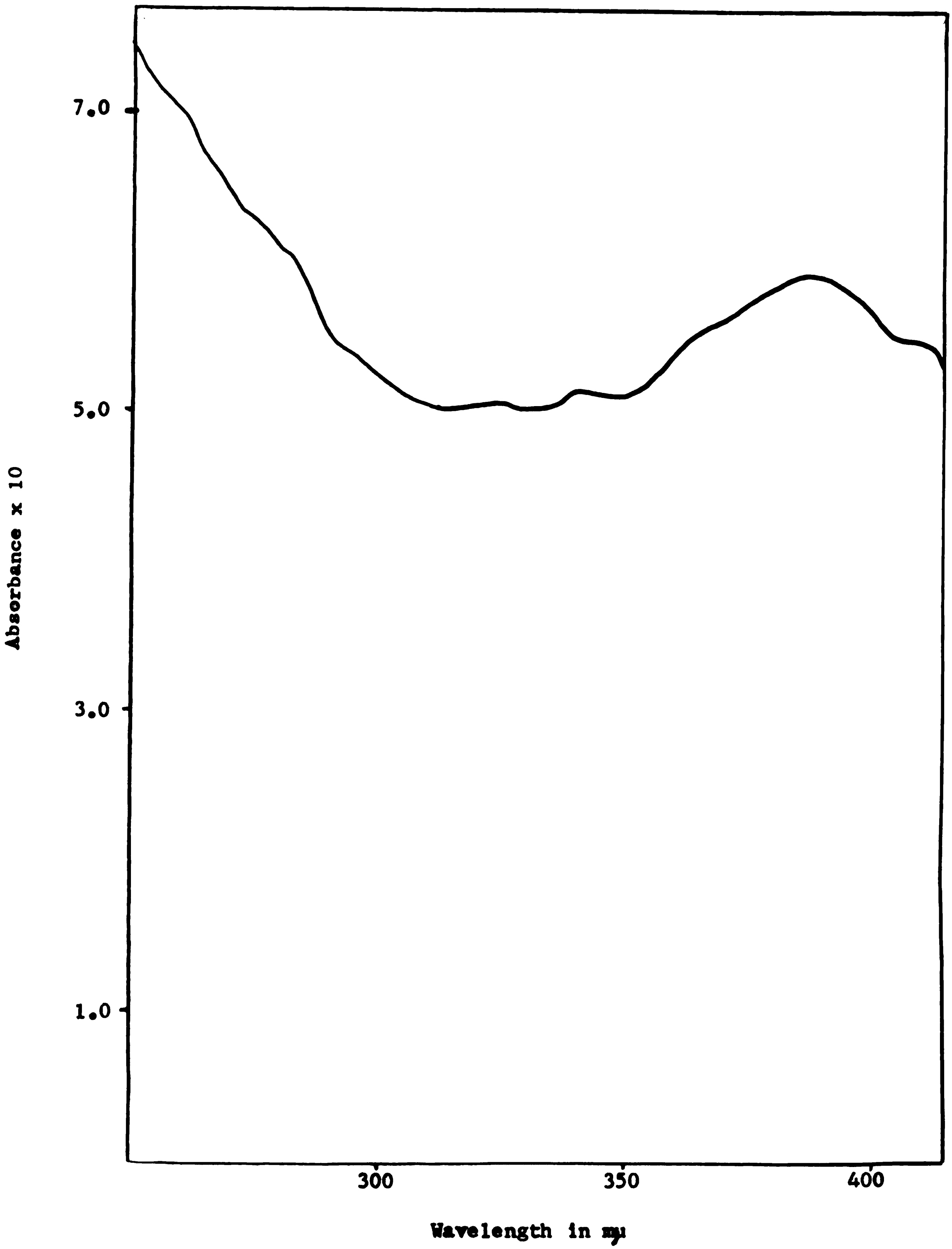


Figure 16. Spectrophotometric study of ≈ 1 x 10^{-4} M TCNE$^-$ in acetonitrile using a 1-cm-pathlength cell.

solutions were found to be time dependent and irreversible formation of colored adducts were noted. The spectral changes were entirely different from those observed with the tetrazoles.

An attempt to study TCNE-1,2,4-triazole complexation was not successful because of insolubility of the triazole in any of the non-donor solvents.

Spectral shifts similar to those obtained in TCNE-tetrazole systems were also observed when PMT was added to solutions of other π-acids, namely trinitrobenzene (TNB), p-chloranil (CA), trinitrofluorenone (TNF), and tetracyanoquinodimethane (TCNQ), (Figures 17-20). Formation constants of the resulting complexes were calculated by the same technique and the results are given in Table IX.

It is obvious from Table IX that the π-acids listed are much weaker π-electron acceptors than TCNE. The absolute values of formation constants of the PMT complexes with CA, TNB, and TNF are not very accurate and should not be heavily weighted. Since the formation constants are small, measurable spectral changes can only be obtained with very large excesses of one of the reagents, and this greatly magnifies the experimental error (113). However, the data at least indicate the relative strengths of the PMT complexes. As seen from Table IX the strength of the PMT complexes follows closely the trends of the other two donors, benzene and hexamethylbenzene. This is another indication that tetrazoles form π-complexes with π-acids.

The nuclear magnetic resonance method of Hanna and Ashbaugh (116), described on p 32 of this thesis, was used in the determination of the PMT-TNB complex formation constant in carbon tetrachloride solutions. A plot of $(1/\Delta)$ <u>versus</u> $[1/(\mathrm{PMT})]$ gave a satisfactory straight line (see Figure 21). All chemical shifts were measured from the standard

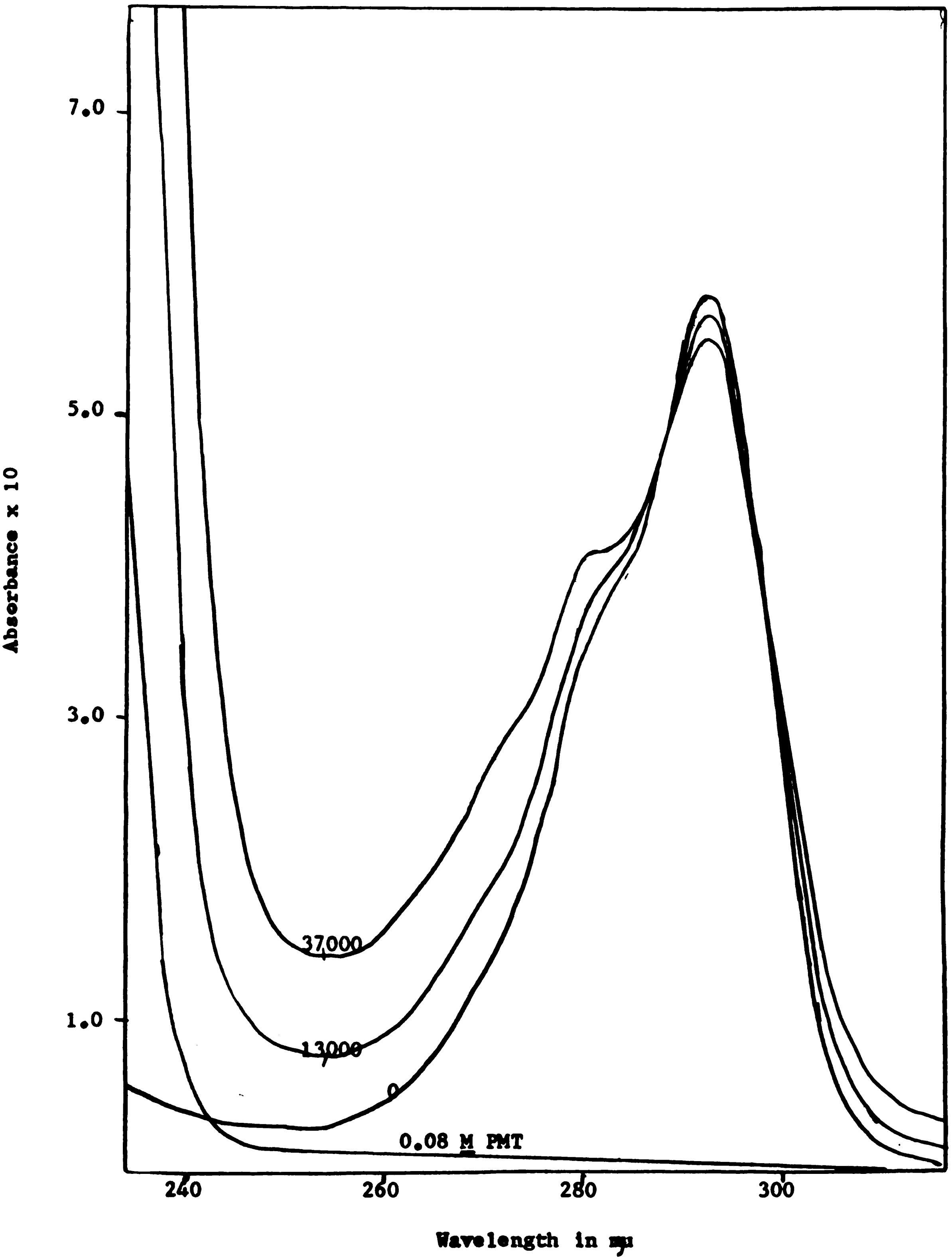


Figure 17. Spectrophotometric study of 2.5 x 10^{-5} M p-chloranil with various mole ratios of PMT in dichloromethane using a 1-cm-pathlength cell.

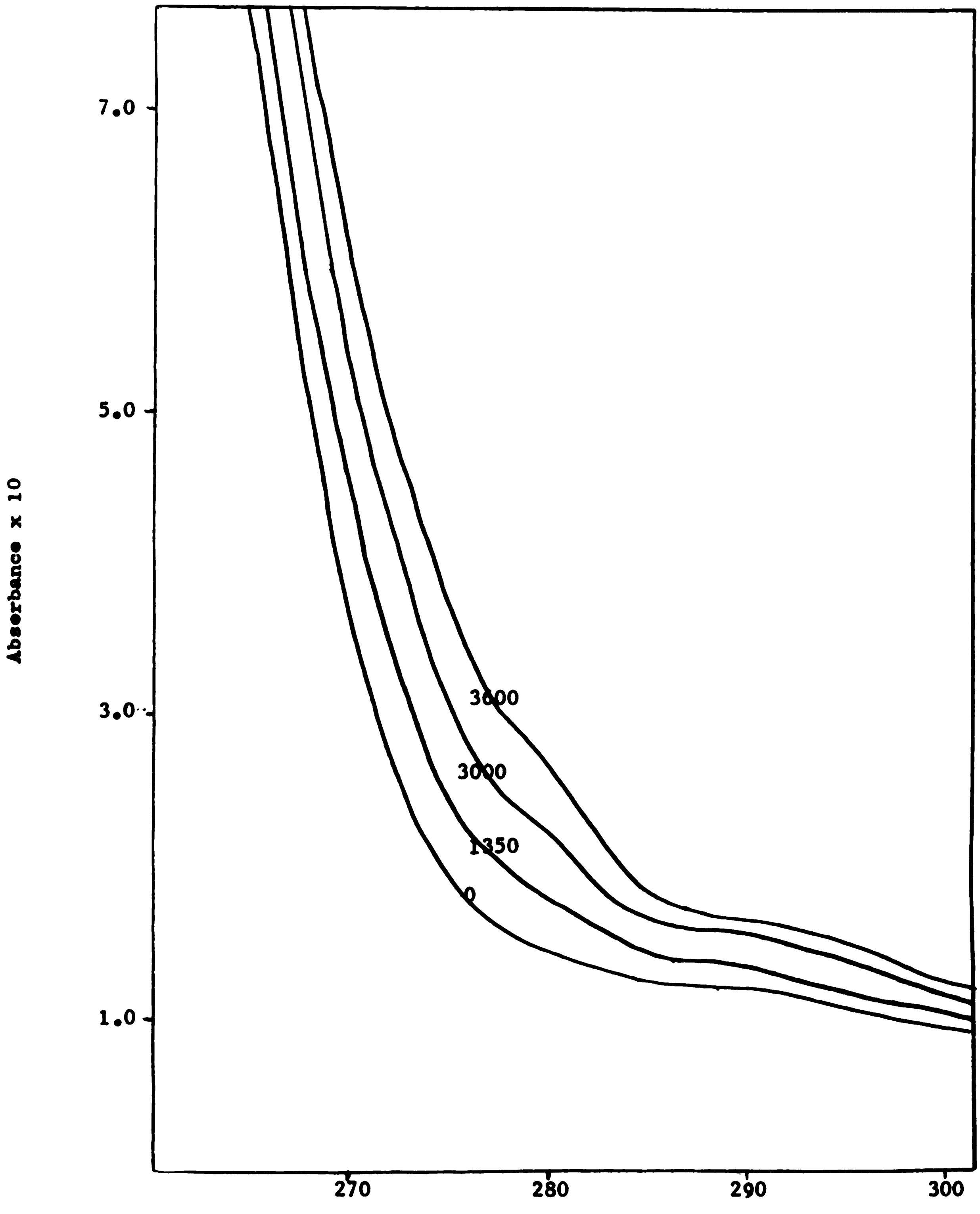


Figure 18. Spectrophotometric study of 2.0 x 10^{-4} M 1,3,5-trinitrobenzene with various mole ratios of PMT in dichloromethane using a 1-cm-pathlength cell.

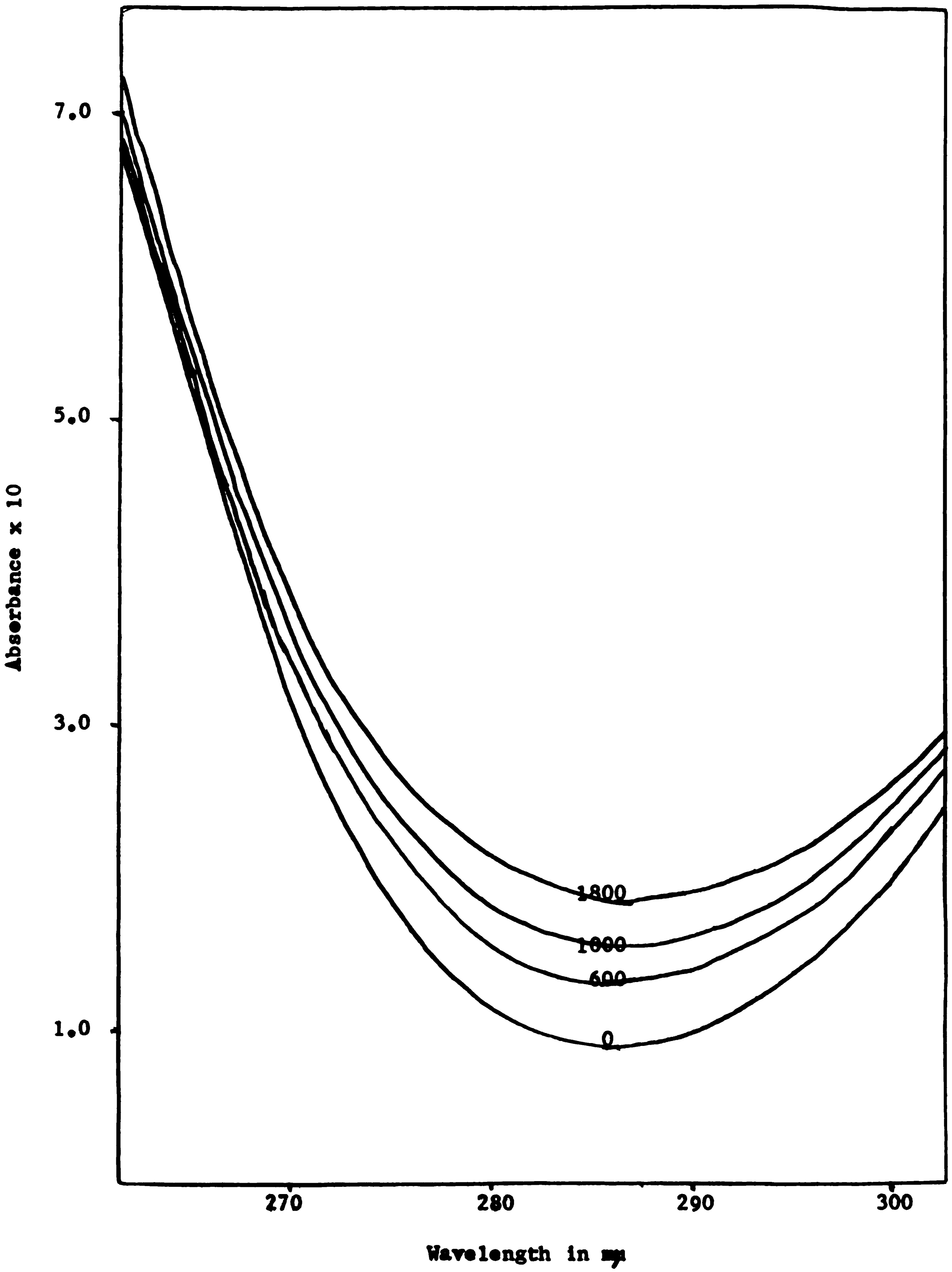


Figure 19. Spectrophotometric study of 5.1 x 10^{-4} M tetracyanoquinedimethane with various mole ratios of PMT in dichloromethane using a 1-cm-pathlength cell.

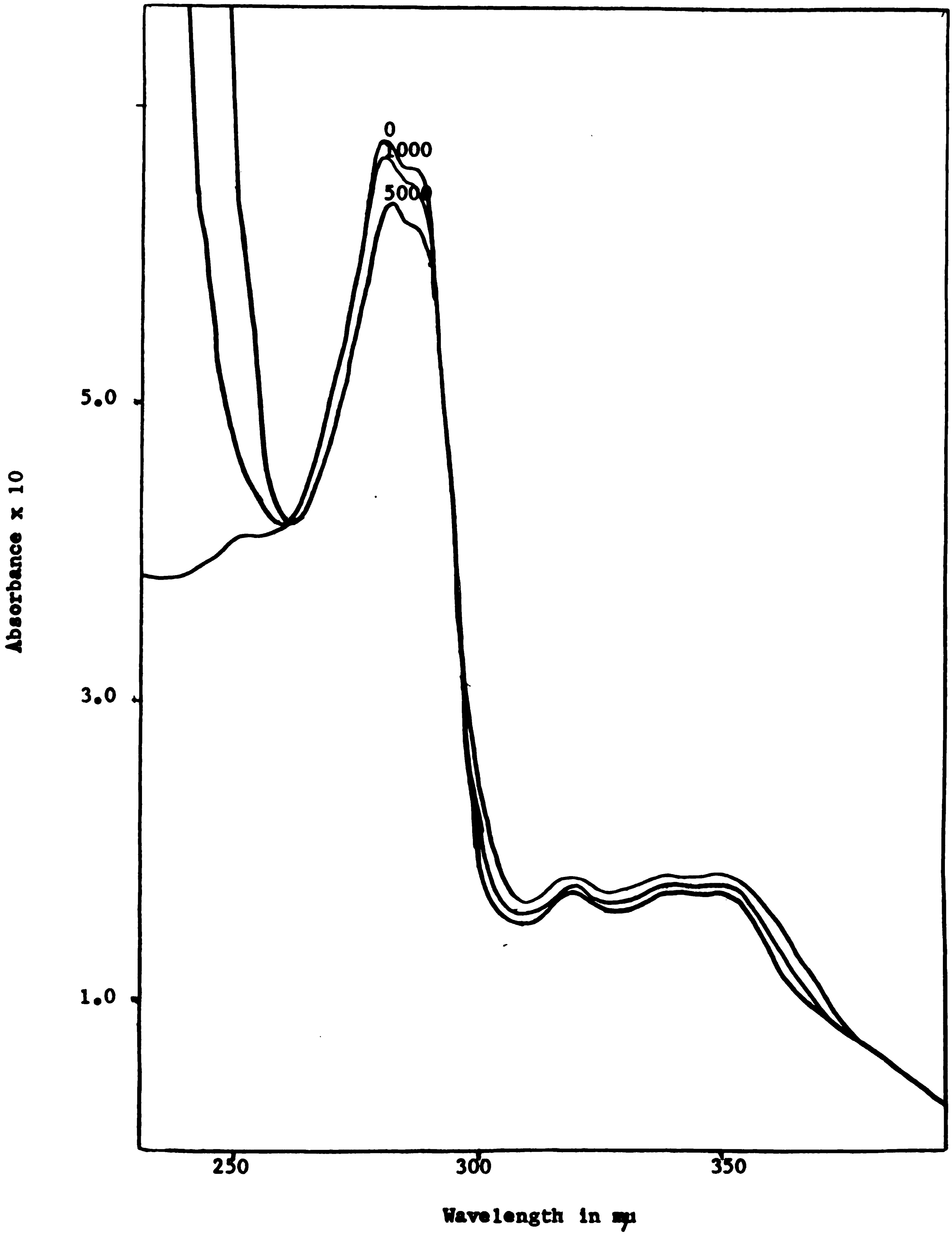


Figure 20. Spectrophotometric study of 2.0 x 10^{-5} M 2,4,7-trinitrofluerenone with various mole ratios of PMT in dichloromethane using a 1-cm-pathlength cell.

Table IX. Comparison of Complex Strengths.

	Formation constants					
Donors	TCNE	TCNQ	CA	TNB	TNF	I_2
PMT						
(K in CH_2Cl_2)	1.31	0.22	0.16	0.10	0.06	7.5[b]
Benzene[a]						
(K in CCl_4)	1.03		0.33	0.23	(very small)	0.15
Hexamethylbenzene[a]						
(K in CCl_4)	2.54	1.40	---	0.55	(very small)	1.52

[a] Values from L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, p 97. The values of formation constants given in the references are converted to liter $mole^{-1}$ units to compare with our values. [b] Reference (28)

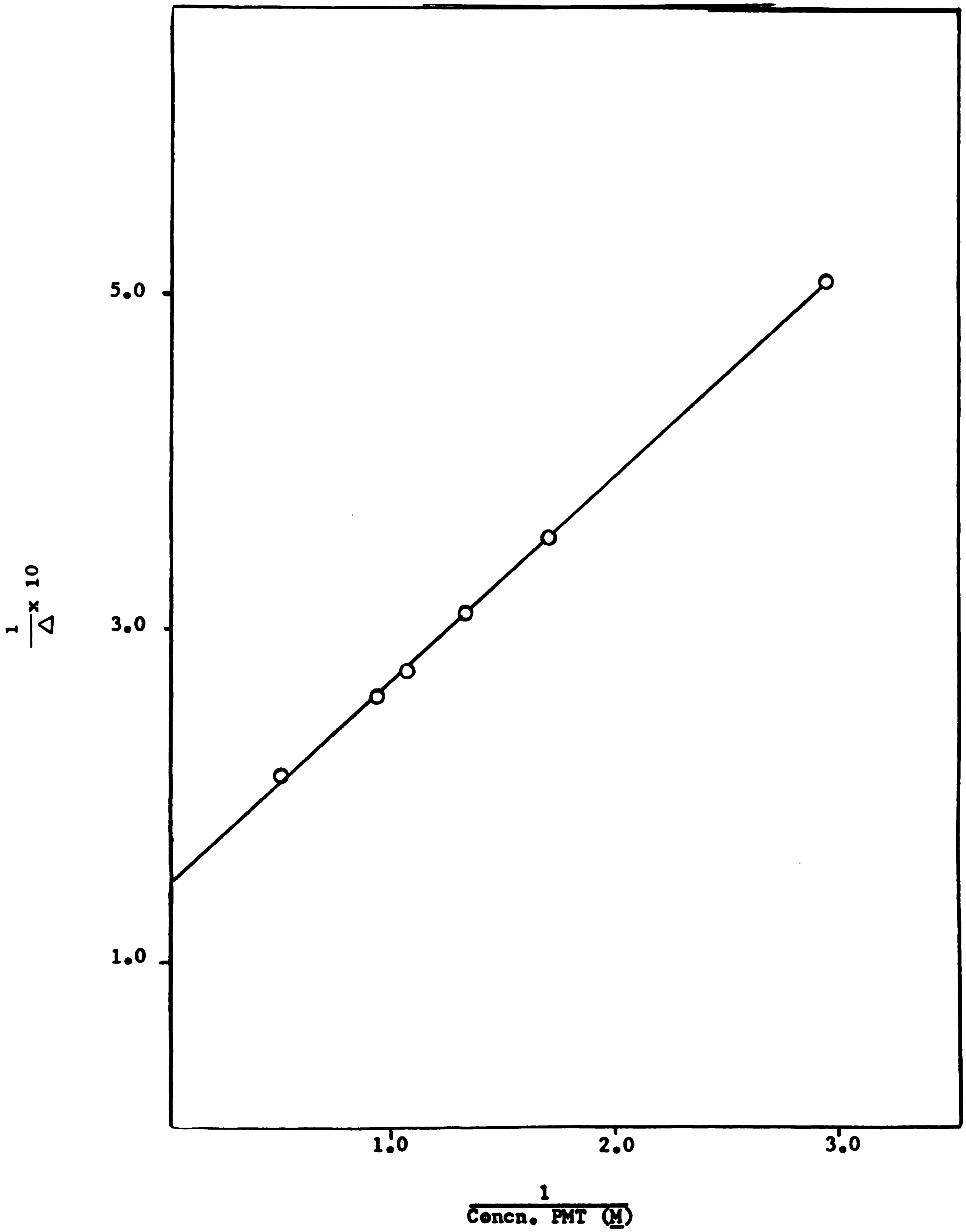


Figure 21. NMR spectroscopic study of TNB proton shift with increasing concentration of PMT in carbon tetrachloride.

tetramethylsilane signal with an estimated accuracy of ± 0.5 cps. The formation constant of the complex was found to be K = 1.3, which is higher by an order of magnitude than the constant determined spectrophotometrically. This is not surprising, however, since the latter was determined in dichloromethane which is a polar solvent, as compared to carbon tetrachloride, and can itself participate in the complexation reaction (120). In order to verify this point, the formation constant of the complex was also determined spectrophotometrically in carbon tetrachloride solutions. Once again, no charge transfer band was observed and the measurements had to be made at the broad absorption tail as in the case of TCNE-tetrazole complexes. The results are summarized in Table X. Good agreement of the two values obtained by quite different techniques seems to confirm the validity of our assumption that the increase in absorption such as shown in Figures 5-20 is due to complex formation.

It seems reasonable to conclude from the above data that the tetrazole ring does indeed possess some π-donor ability and is capable of forming charge-transfer complexes with π-acids. As seen from Table VII, VIII, and IX there is a reasonable agreement between the electron inductive effect of the substituent groups and the stability of the complexes.

It is also interesting to compare the formation constants of the 1-cyclohexyl-5-methyltetrazole-TCNE complex with that of 1-methyl-5-cyclohexyltetrazole-TCNE complex as well as the complexes formed by 1-phenyl-5-ethyltetrazole and 1-ethyl-5-phenyltetrazole. It is seen that when the larger group is in the 1-position of the tetrazole ring, the stabilities of the complexes are less than when the groups are reversed.

Table X. Spectrophotometric determination of K for the trinitrobenzene-pentamethylenetetrazole complex in carbon tetrachloride.

	Wavelength, mμ			
	267.5	272.5	277.5	K_{av}
K	1.67	1.52	1.73	1.64 0.10
C	7550	4300	2160	

It has been shown that the nitrogen and carbon bonds which extend from the 1- and 5- positions of the tetrazole ring respectively, are coplanar with the ring itself in PMT (43). However, it seems reasonable to assume that these bonds, particularly the nitrogen bond, become slightly distorted and consequently out of plane with the tetrazole ring when large groups such a cyclohexyl- and phenyl- are substituted on the 1- or 5- positions. Thus, a large substituent group in the 1- position would extend above and below the tetrazole ring to a greater degree than in the 5- position. This large group would then partially shield the ring from TCNE or other π-acids with corresponding lowering of the stability of the complex.

It is interesting to note that the formation constants of the benzene-TCNE and PMT-TCNE complexes are comparable (Table IX). On the other hand the formation constant of iodine monochloride complexes with PMT is larger by three orders of magnitude than that of benzene-ICl complex (28). These results indicate that in the former case, the complexation occures through one of the nitrogen atoms on the PMT ring. The crystal structure of the PMT-ICl complex has been recently resolved (28), showing unambiguously that the complexation does indeed occur through one of the nitrogen atoms on the PMT ring.

CHAPTER IV

STUDIES IN FORMIC ACID SOLUTIONS

HISTORICAL

I. General

The use of formic acid as a non-aqueous media offers several advantages when compared to other acidic solvents. It has a convenient liquid range and readily dissolves most organic and many inorganic compounds (17, 49). It is one of the strongest carboxylic acids known, being a much stronger acid than glacial acetic acid (18). A high dielectric constant of 56.1 at 25° (19) essentially eliminates formation of ion-pairs in dilute solutions. Thus, the ionic equilibria in formic acid are much less complex than those in acetic acid ($\mu = 6.13$) (20), or in many other acidic solvents. Unfortunately, a relatively large self-ionization constant narrows its "pH" range as compared with that of water or of acetic acid (18).

There are several inherent problems involved in the use of this solvent. It is difficult to purify initially and to retain in the purified state due to spontaneous decomposition by the following mechanisms:

$$HCOOH \longrightarrow H_2 + CO_2$$

$$HCOOH \longrightarrow H_2O + CO$$

Hinshelwood, Hartley and Topley (22) studied the influence of temperature on these two decompositions and found that formic acid is best purified and stored at lower temperatures. Since the anhydrous acid is extremely hygroscopic, caution must be excercised to minimize its contacts with the atmosphere. The reader is refered to the Vol. 4 of "Chemistry in nonaqueous solvents" (54) for a complete discussion of the solvent properties and chemistry in anhydrous formic acid.

II. Purification

The first discussion of purification methods is given by Garner (23) and co-workers in 1911. They suggested that the solvent be distilled at 50° under reduced pressure from anhydrous copper sulfate. Several authors state (23, 24) that the use of phosphorus pentoxide and sulfuric acid as drying agents should be avoided in the purification procedures because of excessive formic acid decomposition. A review of several other procedures (25) indicates that the limiting factor involved in the purification of formic acid is the retardation of spontaneous decomposition. This may be done by avoiding strongly acidic or basic drying agents and maintaining a temperature close to the freezing point of formic acid, 8.4° (21).

A promising purification was reported recently by Popov and Marshall (21). This procedure involves a double vacuum distillation of previously dried (by anhydrous $CuSO_4$) formic acid from boric anhydride at room temperature. Although this method was quite time consuming and cumbersome, it did yield a product of very high purity. The acid obtained consistently melted between 8.3°C and 8.5°C with an average specific conductivity of 6.6×10^{-5} mho/cm. These results are in essential agreement with the best previously reported values (24, 26).

III. Acid - Base Equilibria

The strong protogenic nature of formic acid renders it quite useful for the study of solutions of very weak bases. The first study of acid - base equilibria in anhydrous formic acid was reported by Hammett and Dietz in 1930 (18). Using a quinhydrone electrode for titration measurements these authors showed that sodium formate, triphenyl carbinol and urea act as strong bases in formic acid while benzenesulfonic acid behaves as a strong acid. In a later study by Hammett and Deyrup (51) the pK_b values of several weak bases were determined using a system of indicators.

In a series of papers by Shkodin, Izmailov, and Dzyuba (50) the authors point out that formic acid both enhances and levels the strength of weak bases. Using quinhydrone and glass indicator electrodes with aqueous calomel as the reference electrode they titrated several weak acids and bases. They found that most inorganic acids in formic acid solutions remain largely dissociated while most of the organic acids were too weak to be titrated. The pK_a and pK_b values that they determined for the weak acids and bases are questionable because of the method of calculation that was used.

The titration curves of several weak organic bases in formic acid were also studied by Tomicek and Vidner (52) using indicators to determine the endpoints. However, their results are questionable because of the use of acetic anhydride to remove water in the purification of formic acid.

The most recent work reported using formic acid as the solvent media for acid - base study was that of Popov and Marshall (21, 53). The purification and use of anhydrous formic acid was done using a closed glass system in an inert atmosphere. Potentiometric titrations were successfully carried out on several substituted tetrazoles using quinhydrone electrodes and p-toluenesulphonic acid as the titrant. Attempts to use hydrogen electrodes yielded erratic results because of catalized decomposition of formic acid. Using a quinhydrone - sodium formate concentration cell the relative basicity constants were obtained for caffeine, theobromine, urea, sodium sulphate, pentamethylenetetrazole and nine substituted pentamethylenetetrazoles.

IV. Electrolytic Conductance

The first conductance measurements in formic acid were reported by Zinninovitch-Tessarin in 1896 (55). He found that most inorganic salts were completely ionized while solutions of hydrochloric acid were not dissociated to any measurable degree. However, Schlesinger and Calvert (26) showed that Tessarin's results were in error because of improperly purified solvent. These authors studied the conductance of ammonia solution and concluded that ammonia is completely converted to the dissociated ammonium formate salt. They also showed, contrary to Tessarin's results, that hydrochloric acid was dissociated to a moderate degree in formic acid.

The second paper (37) in a series of studies by Schlesinger and co-workers describes the conductances of sodium, potassium, phenylammonium and ammonium formate in anhydrous formic acid. Also, the dissociation constant for hydrochloric acid in formic acid was calculated using the Ostwald dilution law. This work was later re-evaluated by Schlesinger and Coleman (58) who again showed that these data obeyed the mass action law only if corrections for viscosity were not made.

The conductances of alkaline earth formates in formic acid were studied by Schlesinger and Mullinix (56) and later by Schlesinger and Reed (59). The latter authors also developed a method for calculating the degree of dissociation for mixed electrolytes in solution.

The transference numbers of several ions in solution were determined in the last study of the series (60). In this paper, Schlesinger and Bunting used the transference numbers to calculate single-ion equivalent conductances at infinite dilution. Kendall, Adler and Davidson (63) extended the conductance work in formic acid to include 1:2 electrolytes such as magnesium and barium formates.

A later conductance study by Lange (61) deals with the comparison between formic acid solutions and aqueous solutions. Equivalent conductances of several electrolytes including potassium chloride, tetramethylammonium chloride, potassium picrate, and methylene blue were determined at infinite dilution. Lange also calculated the partial molal volumns of these solutions.

In the latest conductance study to appear in the literature, written by Johnson and Cole (19), a proton transfer mechanism is postulated to explain the large equivalent conductance of pure formic acid. Also, a large dielectric constant of 56 at 25° indicates that the molecules of formic acid do not exist as non-polar dimers in solution. This is in contrast to acetic acid solutions where the molecules exist mainly as non-polar dimers.

THEORETICAL

I. General Conductance

The high dielectric constant of formic acid, 56.1 at 25° (19), essentially eliminates formation of ion-pairs in dilute solutions. Thus, the dissolution of a weak base in formic acid may be treated by simply assuming the following equilibria

$$B + HCOOH \rightleftharpoons HB^{+} + HCOO^{-}$$

where the basicity constant, K_b, is given by:

$$K_b = \frac{(HB^{+})(HCOO^{-})}{(B)} \qquad 1.$$

If we let

$$(HB^{+}) = (HCOO^{-}) = \alpha C_B; \text{ and } (B) = (C_B - \alpha C_B)$$

where C_B equals the initial molal concentration of the base, B, we can then substitute these values into Equation 1 to obtain the Ostwald dilution law:

$$K_b = \frac{\alpha^2 C_B}{1-\alpha} \qquad 2.$$

The basic equation used to calculate equivalent conductances is given by:

$$\Lambda = \frac{1000 Ls}{C} \qquad 3.$$

The specific conductance, Ls, is defined as

$$Ls = \frac{K}{R} \qquad 4.$$

where K is the cell constant and R is the resistance in ohms. Arrhenius was the first to show that the degree of dissociation, α, of a weak binary electrolyte can be approximately obtained from the expression

$$\alpha = \frac{\Lambda}{\Lambda_o} \qquad 5.$$

where Λ_o is the equivalent conductance at infinite dilution. Substituting Equation 5 into Equation 2 we obtain the following relationship:

$$K_b = \frac{\Lambda^2 C}{\Lambda_o(\Lambda_o - \Lambda)} \qquad 6.$$

By rearranging Equation 6 we get:

$$\Lambda C = \frac{(K_B \Lambda_o^{\,2})}{\Lambda} - K_B \Lambda_o \qquad 7.$$

It then follows that a plot of (ΛC) *versus* $(1/\Lambda)$ should give a straight line, and the values of Λ_o and K_B can be obtained from the slope and intercept. However, this treatment is only valid for very dilute solutions since it does not take into account interionic effects.

Kohlrausch postulated the following imperical relationship

$$\Lambda = \Lambda_o - b\sqrt{C} \qquad 8.$$

and showed that for strong electrolytes when Λ is plotted against $\sqrt{C}$ the curve (phoreogram) approaches linearity. In 1927 Onsager (64) derived an equation which was similar to Equation 8 above, taking into account relaxation, electrophoretic and Brownian effects in solution:

$$\Lambda = \Lambda_o - (\alpha\Lambda_o + \beta)\sqrt{C} \qquad 9.$$

α and β are defined as

$$\alpha = (\text{relaxation effect}) = \frac{8.204 \times 10^{-5}}{\eta(DT)^{3/2}} \qquad 10.$$

$$\beta = (\text{electrophoretic effect}) = \frac{82.43}{\eta(DT)^{1/2}} \qquad 11.$$

where D is the dielectric constant, η the viscosity, and T the absolute temperature. However, Shedlovsky, in 1932 (65) showed that Λ_0 was not constant over any appreciable concentration range. Consequently, he rearranged Equation 8 defining a new function Λ_0' given as:

$$\Lambda_0' = \frac{\Lambda + \beta C^{1/2}}{1 - \alpha C^{1/2}} \qquad 12.$$

A new value of Λ_0, which he called the true limiting equivalent conductance, was then obtained by plotting Λ_0' *versus* C from the equation:

$$\Lambda_0' = \Lambda_0 + \beta C \qquad 13.$$

II. Shedlovsky Iteration Technique

In 1938 Shedlovsky expanded the work of Fuoss and Kraus (66) and proposed the following equation for weak electrolytes (67)

$$\Lambda = \gamma\Lambda_0 - S\,\frac{\Lambda}{\Lambda_0}(\gamma C)^{1/2} \qquad 14.$$

the Onsager slope, S, is given by

$$S = \alpha\Lambda_0 + \beta$$

where α and β are described in Equations 10 and 11 respectively. The function S_z, was defined as

$$S_z = 1 + Z + \tfrac{1}{2}Z^2 + \ldots \qquad 15.$$

where Z is given as:

$$Z = \frac{S(C\quad)^{\frac{1}{2}}}{\Lambda_o^{\frac{3}{2}}} \qquad 16.$$

Substituting these equations into Equation 14 and rearranging we get:

$$\gamma = \frac{S_Z \Lambda}{\Lambda_o} \qquad 17.$$

Equation 17 may be combined with Ostwald's dilution law, Equation 2, and rearranged to give the final equation:

$$\frac{1}{\Lambda S_Z} = \frac{1}{\Lambda_o} + \frac{C S_Z f^2 \Lambda}{K_B \Lambda_o^2} \qquad 18.$$

If $(1/\Lambda S_Z)$ is plotted <u>versus</u> $(C\Lambda S_Z f^2)$ a straight line is obtained with an intercept of $(1/\Lambda_o)$ and a slope of $(1/K_b \Lambda_o^2)$. In order to use this treatment a value for Λ_o is assumed, and the corresponding values of Z and S_Z are calculated. These values are used in Equation 18 to obtain a new value of Λ_o which is then used to recalculate Z and S_Z. The process is repeated until consecutive Λ_o values agree within set limits. This procedure was used quite effectively by Fuoss and Shedlovsky (68) for the evaluation of Λ_o values and dissociation constants for several weak electrolytes.

More recent conductance treatments by Fuoss and Onsager (69) and Fuoss and Accascina (70) take into account two additional interionic forces. These two corrections deal with osmotic and static viscosity effects in the solution due to the presence of ions. However, in dilute solutions their results are in essential aggreement with those obtained by the Shedlovsky iteration method.

All of these conductance methods are best handled by using the method of least squares. Hence evaluation of Λ_o and K_B are easily obtained by use of modern digital computers.

EXPERIMENTAL

I. Solvent

Formic acid (98^+ percent, Baker and Adamson) was dried for 24 hours over anhydrous copper (II) sulfate. The solvent was then fractionally distilled through a 30 in. Vigreaux column under 1 mm pressure at room temperature. In order to keep the vapor pressure of the distilled solvent low, the receiving vessel was cooled with dry ice. The distilled product was further purified, under a dry nitrogen atmosphere, by batch fractional freezing. A modified, six-liter, separatory funnel with provisions for vacuum removal of impure solvent was used for this process. Usually five or six successive fractional freezings were required to obtain a product with a constant mp range of 8.25° to 8.30° (ave. 8.27°). Specific conductance of the purified formic acid varied between 5.9×10^{-5} to 6.3×10^{-5} ohm^{-1} cm^{-1} with an average value of 6.08×10^{-5} ohm^{-1} cm^{-1} compared to the best literature value of 6.6×10^{-5} ohm^{-1} cm^{-1} (21). The solvent was recovered for reuse by distillation.

Cyclohexane, nitromethane and pyridine were all purified by vacuum fractional distillation through a 30 in. Vigreaux column using anhydrous barium oxide as the drying agent.

II. Reagents

The inorganic salts used for conductance work, with the exception of sodium formate, were of reagent quality and were used without further purification. They were, however, dried before use at 110°. Sodium formate was recrystallized three times from conductance water. Anhydrous hydrogen chloride was prepared by slowly dropping concentrated sulfuric acid on to analytical grade sodium chloride. The gas was dried by passage through several magnesium perchlorate drying columns and then bubbled into the anhydrous formic acid. The concentration of the stock solution was determined by the standard silver chloride precipitation (82).

The organic salts, triisoamylbutylammonium iodide (TABI) and triisoamylbutylammonium tetraphenylborate (TABTPB), were prepared and purified using the method of Coplan and Fuoss (71). Eastman Grade tetramethylammonium bromide was used without purification but was dried in vacuo at 50° for two hours.

Triisoamylbutylammonium perchlorate ($TABClO_4$) was prepared by a metathetical reaction between silver perchlorate and the iodide of the organic salt. The obtained material was recrystallized three times from a methanol-water mixture. The final product melted at 94-96°.

Substituted tetrazoles used in this investigation were synthesized, and purified according to the procedures described in Part II of this thesis. Conductance water for potassium chloride solutions was prepared by passing distilled water through a mixed resin bed obtained from Crystalab Research Laboratories. Matheson, Coleman and Bell "Reagent A.C.S." grade potassium chloride was fused in a platinum crucible, ground in an agate mortar and dried at 110°.

The transition metal perchlorate hexaquo salts used in the complexation study were reagent grade, purchased from G. Frederick Smith Chemical Co. These salts were dried in vacuo at 20° to constant weight prior to their use in the preparation of stock solutions. The waters of hydration were removed when necessary by the addition of calculated amounts of Fisher Certified Reagent grade acetic anhydride.

III. Apparatus

The A. C. conductance bridge used in this investigation has been previously described (72). It was operated at a frequency of 1000 cps. The conductance cells were similar to those described by Daggett, Bair, and Kraus (73). Platinum electrodes were used but they could not be platinized since platinum black catalyzed the decomposition of formic acid. All equipment used for conductance work was cleaned with sodium hydroxide solution to remove traces of oil, thoroughly rinsed with hot distilled water and then steamed for one half hour on a steaming apparatus. After steaming, the cells were rinsed with pure acetone and dried in a stream of purified nitrogen. The constants of the three cells used in this investigation were measured by the standard procedure using KCl solutions and the Lind, Zwolenik, and Fuoss equation (74). They were found to be: 0.4427 ± 0.0012; 1.446 ± 0.005; 3.988 ± 0.013.

The temperature of the cell solution was maintained at 25.00 ± 0.02° by a Sargent S-84805 thermostatic bath assembly filled with light mineral oil. All melting points were taken on a Fisher-Jones melting point block for which the usual stem corrections were made.

Absorption measurements in the visible, ultraviolet and near-infrared regions were made on a Cary recording spectrophotometer Model 14, in glass stoppered cells of 1.00, 5.00 and 10.00 ± 0.01 cm-path-lengths. Measurements were done at room temperature of approximately 25°.

Infrared measurements were made on a Beckman recording spectrophotometer, Model IR-5, using potassium bromide pellets.

IV. Procedures

A given amount of pure formic acid was weighed into each conductance cell, allowed to equilibrate, and its specific conductance determined. Next, known amounts of a stock solution were added to the formic acid from a weight buret and the contents of the cells were thoroughly mixed. After temperature equilibration, the resistance was recorded, the solutions were then remixed and the resistance taken a second time. The addition of stock solutions to the conductance cells were made under normal laboratory conditions since brief exposure to the atmosphere caused no observable changes in resistance readings.

The concentration range of solutions used in the conductance studies varied from $5 \times 10^{-3}\underline{M}$ to $2.0 \times 10^{-1}\underline{M}$. The upper limit of concentration was determined by the Fuoss equation. $C_{max} = 3.2 \times 10^{-7}D^3$, where D is the dielectric constant, since at higher concentrations the simple laws of dilute solutions of electrolytes are no longer obeyed (75). The lower limit was taken such that the specific conductance of the solvent would be less than 10% of the specific conductances of the most dilute solution. The solvent correction was made by subtracting the specific conductance of the solvent from that of the respective solution.

The spectrophotometric methods, including mole ratio and continuous variation studies were preformed in a manner which has been previously described (76) in Part III of this thesis.

RESULTS AND DISCUSSION

I. Conductance

Conductance data in formic acid were obtained for eleven salts, four substituted tetrazoles and anhydrous hydrochloric acid. Attempts to study several other salts and tetrazoles were not successful either due to their reaction with formic acid or to the lack of solubility. The measured equivalent conductances of the solutions and their respective concentrations are given in Table XI.

The experimental conductance data were evaluated according to the method of Fuoss and Shedlovsky (67, 68). Since this treatment involves the use of an iteration procedure and a least squares analysis, a Fortran computer program was used on a Control Data Corporation 3600 computer. The results and the corresponding average deviations are listed in Table XII. It should be noted that the precision of the results is not as great as those often found in conductance measurements. At least in part the experimental scatter is due to the difficulties encountered in working with formic acid as a solvent, namely, its instability, especially in the presence of platinum, its extreme hygroscopicity and its high degree of self-ionization.

The Shedlovsky data, which were taken directly from the computer print-out, are plotted in Figures 22 to 25. It should be noted that while all the graphs are linear, the reproducibility varied between two extremes as represented in Figure 22. In the one case, the points from separate runs fall on the same line as seen in the sodium chloride and sodium formate plots. In the other case the two sets of data formed separate lines as demonstrated by the potassium chloride plots. No explaination, other than experimental error, is presented for

Table XI. Equivalent conductances in anhydrous formic acid. (Superscripts designate series of determinations)

10^2c	Λ	10^2c	Λ	10^2c	Λ
TABTPB		$TABClO_4$		NH_4Cl	
0.3023	24.60^{a}	0.4502	38.11^{a}	1.167	47.88^{a}
0.3773	24.51	0.6317	37.37	2.289	45.68
0.4345	24.44	0.8683	36.57	3.350	44.23
0.4853	24.31	1.051	36.06	4.204	43.27
0.5464	24.23	1.226	35.60	5.141	42.42
0.5858	24.16	1.389	35.20	5.957	41.69
0.6431	24.04	1.519	34.92	6.771	41.02
0.6855	23.93	1.684	34.58	7.470	40.53
0.7333	23.80	1.928	34.09	8.180	40.07
0.7720	23.57	2.047	33.86	9.466	39.23
0.3034	24.62^{b}	0.5458	36.90^{b}	10.035	38.94
0.3597	24.51	0.7651	36.25	1.180	47.00^{b}
0.4003	24.42	0.9789	35.65	2.189	44.84
0.4429	24.35	1.146	35.26	3.266	43.18
0.4887	24.29	1.313	34.93	4.205	42.18
0.5237	24.24	1.474	34.45	5.135	41.15
0.5690	24.13	1.638	34.09	5.881	40.48
0.6035	24.04	1.761	33.82	7.418	39.41
0.6338	23.91	1.890	33.53	8.155	38.87
0.6790	23.77	2.019	33.27	9.456	38.04
		2.171	32.99	10.165	37.67

continued

Table XI--- Continued.

10^2c	Λ	10^2c	Λ	10^2c	Λ
$NaClO_4$		NaHCOO		HCl	
1.899	42.24[a]	2.450	63.87[a]	0.6400	75.06[a]
3.429	39.94	32.60	63.26	1.388	65.79
5.683	37.74	4.169	62.47	2.006	60.18
7.458	36.50	4.738	62.04	2.509	56.50
8.995	35.54	5.351	61.73	3.086	53.23
10.314	34.81	5.963	61.14	3.557	50.94
11.023	34.47	6.549	60.66	3.997	49.05
1.229	43.30[b]	7.109	60.33	4.860	45.97
2.644	40.37	7.621	59.90	5.238	44.75
3.876	38.65	8.022	59.71	5.576	43.74
5.209	37.20	2.694	62.28	5.947	42.74
6.323	36.25	3.658	60.99	0.6828	72.18[b]
7.022	35.69	4.183	60.38	1.374	63.43
7.593	35.29	5.277	59.28	2.072	57.27
0.0590	49.04[c]	5.740	58.81	2.628	53.47
0.1350	48.17	6.194	58.36	3.159	50.71
0.2260	47.58	6.460	58.12	3.513	49.12
0.3610	46.68	6.937	57.71	4.027	46.99
0.4930	45.96	7.408	57.36	4.479	45.88
0.6080	45.49	2.313	63.46[c]	4.835	44.16
0.0830	48.79[d]	3.256	62.63	5.210	43.09
0.1670	47.76	4.062	61.91	5.566	42.09
0.2600	47.15	4.725	61.28	5.962	41.03
0.3980	46.35	5.365	60.82		
0.5300	45.76	2.011	64.89[d]	HCl (Schlesinger)	
0.6680	45.17	3.176	64.19		
0.7800	43.23	4.166	63.48	0.8000	70.00
		5.039	62.82	1.100	69.20
NaHCOO (Schlesinger)		5.791	62.28	1.500	62.30
		2.530	64.10[e]	1.950	58.90
6.418	61.70	3.364	63.51	2.760	53.70
8.375	60.54	4.323	62.78	3.280	51.80
9.682	59.75	5.061	62.20	5.180	45.20
7.550	55.94	5.706	61.79	9.510	37.40
20.68	54.67			10.10	35.40
23.37	53.72			17.40	30.00
25.28	53.00			18.10	26.00
27.34	52.28				
31.53	50.94				

continued

Table XI ---Continued.

10^2c	Λ	10^2c	Λ	10^2c	Λ
NaBr		KBr		KCl	
1.877	42.57[a]	1.029	47.52[a]	1.621	43.86[a]
2.695	41.45	2.018	45.43	2.314	42.58
3.404	40.64	2.833	44.26	3.176	41.30
4.056	40.01	3.515	43.43	3.853	40.54
4.786	39.31	4.222	42.73	4.649	39.68
5.496	38.76	4.827	42.20	5.169	39.18
6.048	38.35	5.514	41.56	5.941	38.57
6.660	37.95	6.105	41.13	6.426	38.25
7.194	37.56	6.766	40.67	7.067	37.92
7.694	37.28	7.242	40.43	7.853	37.39
8.225	36.97	7.784	40.20	8.531	36.92
1.863	41.83[b]	8.272	39.85	1.534	44.56[b]
2.635	40.60	1.376	45.83[b]	2.394	43.27
3.379	39.56	2.327	43.81	3.049	42.48
3.943	38.98	3.294	42.36	3.625	41.87
4.556	38.36	3.995	41.62	4.298	41.29
5.212	37.78	4.942	40.61	4.776	40.87
5.840	37.27	5.543	40.03	5.401	40.36
6.300	36.93	6.243	39.42	5.898	40.00
6.868	36.54	6.942	39.17	6.290	39.71
7.260	36.27	7.492	38.78	7.216	39.11
7.926	35.80	8.204	38.46	7.639	38.87
		8.733	38.25	1.533	43.05[c]
		9.345	37.73	3.122	41.14
				4.593	39.91
				6.228	38.85
				7.160	38.56
				7.479	38.16
				8.267	37.86
				8.667	37.53
				9.420	37.19
				9.731	37.08

continued

Table XI --- Continued.

10^2c	Λ	10^2c	Λ	10^2c	Λ
NaCl		Me_4NBr		LiCl	
1.568	41.23^{a}	0.9590	46.94^{a}	0.8872	41.72^{a}
3.134	39.64	2.370	44.05	1.701	40.22
4.830	38.09	3.134	42.94	2.487	39.18
6.215	37.10	3.860	42.08	3.317	38.29
8.713	35.62	4.419	41.54	3.932	37.71
9.434	35.24	5.002	40.96	4.512	37.24
1.664	41.17^{b}	5.571	40.52	5.162	36.77
3.032	39.26	6.065	40.10	5.752	36.42
4.467	37.70	6.578	39.81	6.161	36.17
5.632	36.71	7.057	39.49	6.743	35.80
6.874	35.84	7.451	39.20	7.143	35.57
7.737	35.33	1.260	45.67^{b}	7.571	35.27
8.548	34.90	2.100	43.78	1.520	40.18^{b}
1.053	42.17^{c}	3.043	42.27	2.341	38.77
2.072	40.36	3.669	41.48	3.259	37.68
2.926	39.29	4.270	40.90	4.113	36.73
4.068	38.06	5.035	40.00	4.965	36.01
5.187	37.09	5.692	39.43	5.589	35.59
6.016	36.52	6.241	39.03	6.423	35.13
6.822	36.03	6.788	38.65	6.978	35.00
		7.323	38.60	7.624	34.60
		7.831	38.23	8.334	34.37
		8.392	37.89	8.916	34.30
				9.545	33.31

continued

Table XI ---Continued.

10^2c	Λ	10^2c	Λ	10^2c	Λ
Tetrazole		5-Methyl Tetrazole		5-Phenyl Tetrazole	
0.7413	11.76[a]	1.428	28.15[a]	1.742	8.898
1.593	9.947	1.698	26.76	2.305	8.196
2.458	8.754	3.091	22.54	2.606	7.886
3.188	8.038	3.691	21.13	3.131	7.422
3.624	7.700	4.346	20.08	3.497	7.148
4.227	7.301	5.028	19.01	3.914	6.875
4.848	6.955	5.456	18.53	4.345	6.619
5.407	6.726	6.298	17.60	4.940	6.315
5.889	6.468	6.481	17.36	5.183	6.206
6.311	6.304	7.136	16.81	1.595	9.079[b]
6.862	6.114	7.723	16.27	2.050	8.439
7.192	6.008	8.813	15.51	2.520	7.907
1.738	9.641[b]	0.9373	30.57[b]	2.956	7.498
2.462	8.682	1.846	25.84	3.376	7.155
3.161	7.993	2.209	24.44	3.782	6.886
3.708	7.574	3.215	21.64	4.030	6.725
4.317	7.185	3.663	20.81	4.347	6.538
4.816	6.904	4.130	19.85	4.661	6.373
5.333	6.648	4.993	18.57	4.969	6.225
5.793	6.442	5.153	18.47		
6.241	6.267	5.741	17.64		
6.703	6.107	6.366	17.10		
7.097	5.975	7.725	15.91		
		8.849	15.17		

continued

Table XI ---Continued.

10^2c	Λ	10^2c	Λ	10^2c	Λ
PMT		PMT		PMT	
0.8592	36.75[a]	1.485	31.62[b]	1.288	34.15[c]
1.350	33.42	2.063	30.17	1.511	32.67
2.732	28.13	2.825	26.83	3.019	28.33
3.034	26.74	4.063	24.46	3.183	26.48
4.358	24.24	4.401	23.44	4.343	24.61
5.151	22.36	5.404	22.13	4.713	23.65
5.585	22.25	5.620	21.62	5.661	21.90
6.511	20.51	6.708	20.39	6.182	21.49
6.955	20.53	6.826	20.19	6.618	20.57
7.665	19.24	7.673	19.37	7.194	20.32
8.006	19.48	8.012	19.11	7.518	19.63
8.856	18.19	8.190	18.92	7.927	19.25
8.963	18.65	9.153	18.12	8.163	19.36
		10.20	17.33		

Table XII. Limiting equivalent conductances in anhydrous formic acid.

Salt	Run No. 1	No. 2	No. 3	No. 4	No. 5	Average	Ave. Dev.
TABTPB	24.61	24.71				24.66	0.05
$TABClO_4$	42.03	41.33				41.68	0.35
$NaClO_4$	50.33	50.90	49.63	50.01		50.22	0.04
NaHCOO	70.74	70.38	71.04	71.59	70.83	70.92	0.32
NaHCOO	Schlesinger and Reed Value (57)					66.23	(69.39)[a]
NaCl	47.34	47.10	47.73			47.39	0.23
NaBr	49.03	49.31				49.17	0.15
KBr	51.88	52.69				52.29	0.40
KCl	49.66	50.60	50.58			50.28	0.41
LiCl	46.16	45.60				45.88	0.28
NH_4Cl	53.89	53.16				53.53	0.36
Me_4NBr	52.22	51.61				51.92	0.30
HCl	107.75	104.55				106.15	1.60
HCl	Schlesinger and Martin Value (59)					80.0	(104.99)[a]

[a] Recalculated values are given in parenthesis

Figure 22. Shedlovsky plots: A, sodium chloride; B, sodium perchlorate; C, potassium chloride; D, potassium bromide; E, sodium formate, in formic acid.

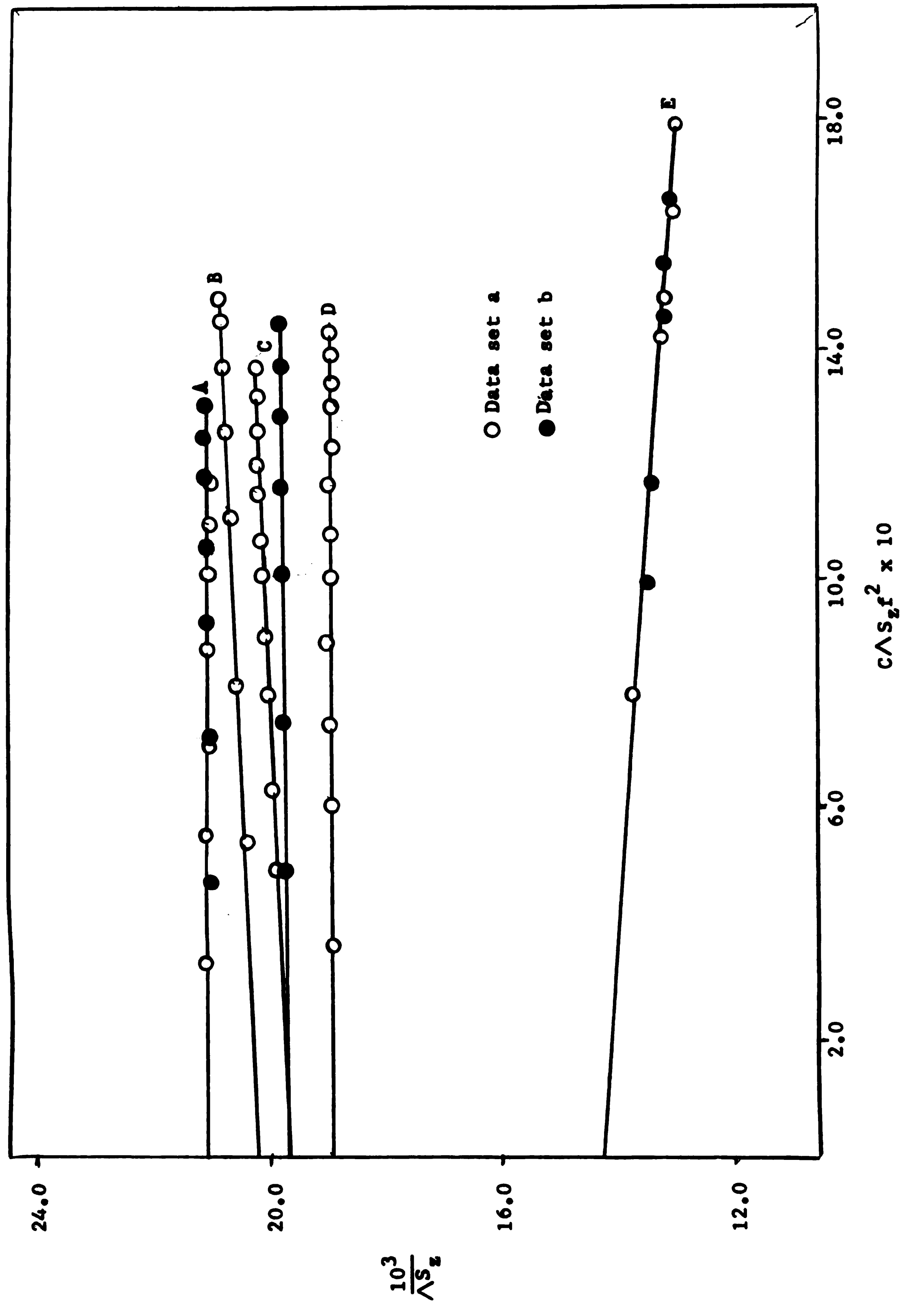

A
B
C
D
E
○ Data set a
● Data set b
$\frac{10^3}{\Lambda S_z}$
24.0
20.0
16.0
12.0
2.0
6.0
10.0
14.0
18.0
$C\Lambda S_z f^2 \times 10$

Figure 22

Figure 23. Shedlovsky plots: A, lithium chloride; B, sodium bromide; C, hydrochloric acid; D, tetramethylammonium bromide; and E, ammonium chloride, in formic acid.

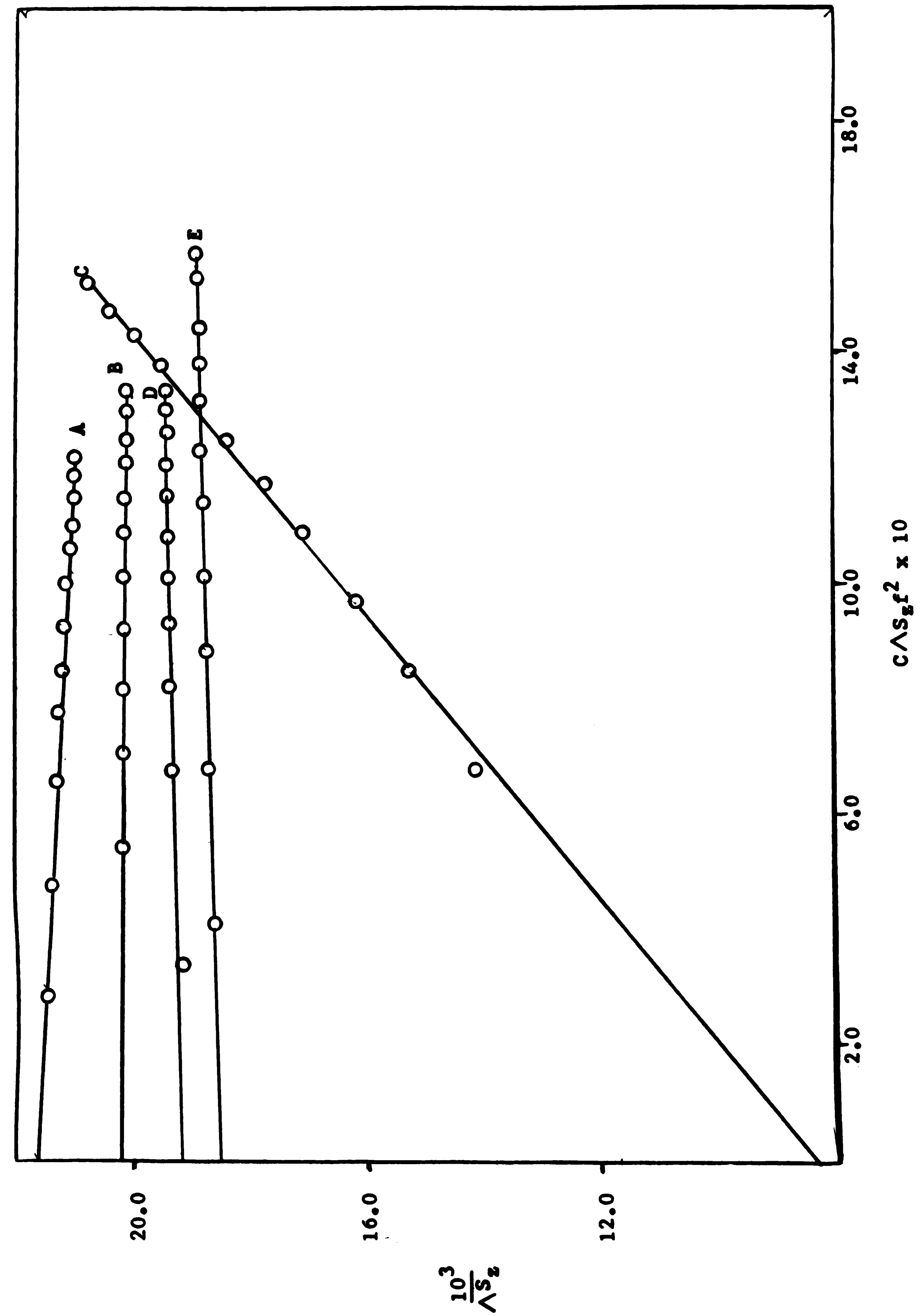

A
B
C
D
E
2.0
6.0
10.0
14.0
18.0
$C\Lambda S_z f^2 \times 10$
20.0
16.0
12.0
$\frac{10^3}{\Lambda S_z}$

Figure 23

Figure 24. Shedlovsky plots: A, triisoamylbutylammonium tetraphenylborate; and B, triisoamylbutylammonium perchlorate, in formic acid.

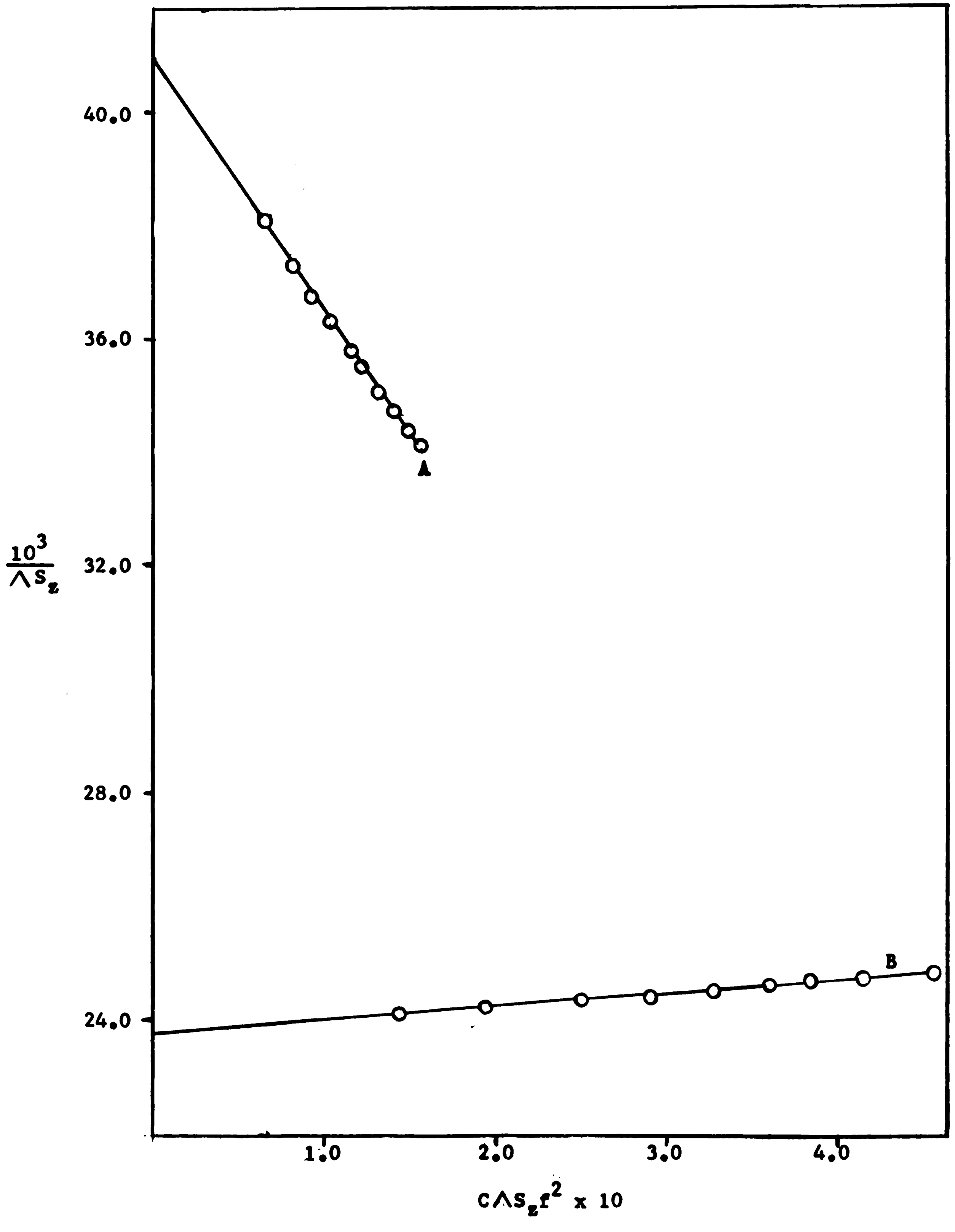
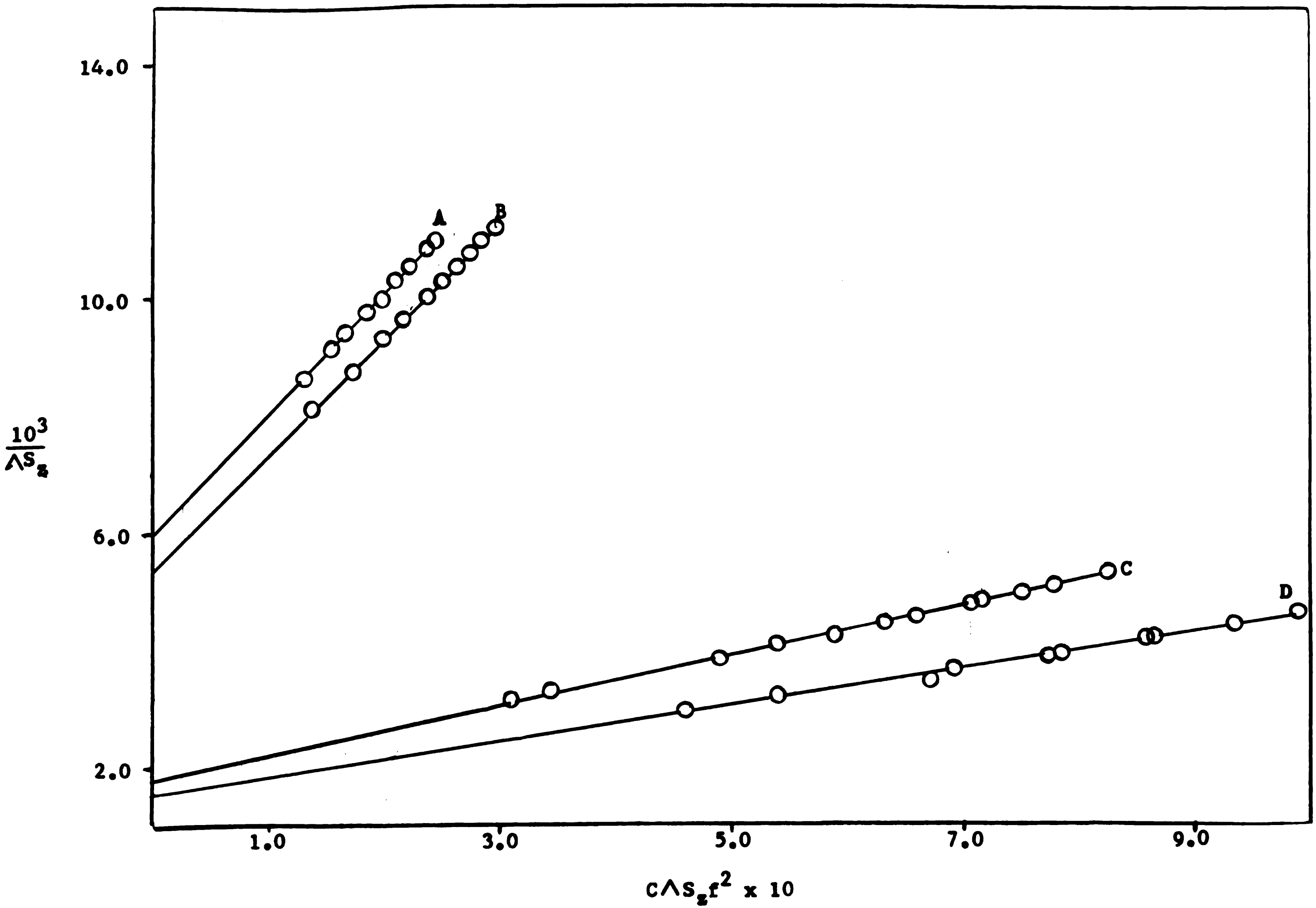

40.0
36.0
32.0
28.0
24.0
$\frac{10^3}{\Lambda S_z}$
A
B
1.0
2.0
3.0
4.0
$C\Lambda S_z f^2 \times 10$

Figure 24

Figure 25. Shedlovsky plots: A, 5-phenyltetrazole; B, tetrazole; C, 5-methyl tetrazole; and D, pentamethylenetetrazole, in formic acid.


14.0
10.0
6.0
2.0
$\frac{10^3}{\Lambda S_z}$
1.0
3.0
5.0
7.0
9.0
$C \Lambda S_z f^2 \times 10$
A
B
C
D

'Figure 25

this deviation. The remaining plots are taken from computer averaged data.

The Ostwald conductance Equation 7, p 77, was also applied to the conductance data but the resultant plots were curved, causing the extrapolated values of Λ_o and K_B to be inaccurate.

A comparison of our values with those of Schlesinger et al. (57, 59), showed considerable divergence. However, when their experimental results were treated according to the Fuoss-Shedlovsky method, a much better agreement was obtained. Two typical examples are given in Table XII.

With exception of hydrochloric acid, all of the electrolytes were dissociated to a very high degree. The dissociation constant obtained for hydrochloric acid showed, however, that there is a moderate amount of association in solution. This association of hydrochloric acid is caused by the protogenic nature of formic acid, which suppresses the ionization of dissolved acids. The hydrochloric acid solutions in general were difficult to work with because of their extremely volatile and hygroscopic nature. Treatment of data by the Fuoss-Shedlovsky method gave a value of 1.1×10^{-2} for the dissociation constant of hydrochloric acid. Schlesinger and Martin (57) report the value of 4.0×10^{-2} but recalculating their value by the Shedlovsky method gives 1.2×10^{-2}, which is in good agreement with our results.

A number of inorganic salts were found to react with formic acid and conductance measurements were not possible. As may be seen in Table XIII, these salts generally contain an anion which can be easily oxidized or reduced. Coupled redox reactions between formic acid and dissolved nitrates, sulfides, and cyanides have also been

Table XIII. Salts which react with formic acid.

Salt	Main Reaction Product
KI	I_2
NaI	I_2
$NaNO_3$	NO_2
KNO_3	NO_2
NaSCN	Elemental S
KSCN	Elemental S
KF	HF
NaF	HF

previously reported (54).

Single-ion limiting equivalent conductances were obtained by the method of Coplan and Fuoss (71) who made the assumption that in methanol the limiting conductance of the triisoamylbutylammonium (TAB^+) ion is equal to that of the tetraphenylborate ion (TPB^-). That is:

$$\lambda_{o\ (TABN^+)} = \lambda_{o\ (TPB^-)} = 1/2\Lambda_{o\ (TABN^+TPB^-)}.$$

It seems reasonable to assume that the above condition would also hold for formic acid solutions since it is highly doubtful that solvation effects would be larger than those in the methanol solutions.

Using the data for salts with common ions, the limiting equivalent conductance of 12 ions in formic acid have been calculated and are shown in Table XIV. As an experimental check, two values of the limiting equivalent conductance of potassium chloride were obtained. The first value can be calculated using the method described above while the second was obtained directly from conductance measurements (Table XII),

$$\Lambda_{oKCl} = \lambda_{oK+} + \lambda_{oCl^-} = 50.51; \text{ experimental value for KCl is } \Lambda_o = 50.28.$$

The agreement between the two values is within experimental error.

Schlesinger and Bunting (60) used Hittorf's method to determine the transference numbers of sodium and potassium ions in solutions of corresponding formates. Using their value of 0.220 for the sodium ion, the corresponding limiting equivalent conductance of 15.6 was calculated from our sodium formate data. The discrepancy between

Table XIV. Limiting equivalent conductances of single ions.

Ion	λ_o	Ion	λ_o
TAB^+	12.33	$HCOO^-$	50.05
Li^+	19.36	ClO_4^-	29.35
Na^+	20.97	Br^-	28.30
K^+	23.99	Cl^-	26.52
NH_4^+	27.01	TPB^-	12.33
Me_4N^+	23.62		
H^+	79.63		

their value and our value of 20.97 may be explained by the fact that they used Ostwald's method (Equation 7, p 77) to treat their conductance data in order to calculate the original transference numbers.

Comparison of the limiting ionic conductances in Table XIV leads to some interesting observations. It is seen that both H^+ and $CHOO^-$ have abnormally high conductances, which is indicative of a proton-jump conductance mechanism similar to the one found in aqueous solutions. On the other hand, the mobility of the alkali metal cations do not differ appreciably from that of the tetramethylammonium ion--or, for that matter, among themselves. While the limiting ionic conductance of Li^+ in aqueous solution is only half of that of K^+ in the same solvent, the respective values are 19.36 and 23.99 in formic acid. It seems reasonable to conclude that this fact is due to the much smaller ability of formic acid to solvate ions. These conclusions are in essential agreement with those postulated by Johnson and Cole (19).

Based upon the limiting equivalent conductances of the formate and hydrogen ions from Table XIV along with the average value of the specific conductivity of pure formic acid (6.08×10^{-5} $ohm^{-1}cm^{-1}$), the autoprotolysis constant of the pure solvent was calculated. The obtained value of 2.2×10^{-7} seems to indicate a purer solvent than the value of 5×10^{-7} reported by Hammett and Dietz (18). The value of 2.2×10^{-7} at least represents the upper limit of the autoprotolysis constant of formic acid.

In a continuing study of the physicochemical properties of substituted tetrazoles, the investigation of their pK_b values in formic acid appeared to be of interest. The pK_b's and limiting equivalent conductances of several tetrazoles were determined using Equation 1, p 76. It should be noted that in view of the high dielectric constant of formic acid the concentration of ion-pairs should be quite insignificant and, in contrast to acetic acid solutions, there is no distinction between the ionization and the dissociation constants. The results are listed in Table XV.

It is interesting to compare the value of the pK_b for pentamethylenetetrazole obtained from conductance work to the value obtained potentiometrically (21). The agreement between the two values is exceptionally good considering that two different methods were used in their determination. It is surprising to note that the five-substituted tetrazoles act as bases of approximately the same strength as the 1,5-disubstituted tetrazoles. This fact indicates that not only is the dissociation of the acidic proton on the tetrazole ring suppressed but the ring itself or a nitrogen atom on the ring acts as a proton acceptor.

Table XV. Basicity constants of some tetrazoles in anhydrous formic acid solutions.

Tetrazoles	Const.	Run No. 1	No. 2	No. 3	Average	Ave. Dev.
Tetrazole	Λ_o	17.80	18.53		18.17	0.36
	pK_b	1.74	1.82		1.78	0.04
5-Methyltetrazole	Λ_o	52.76	51.65		52.20	0.55
	pK_b	2.06	2.06		2.06	0.00
5-Phenyltetrazole	Λ_o	17.26	16.99		17.13	0.13
	pK_b	1.82	1.78		1.80	0.02
Pentamethylenetetrazole	Λ_o	59.58	60.82	59.09	59.83	0.66
	pK_b	2.03	2.03	2.00	2.02	2.02
Pentamethylenetetrazole	pK_b				2.03[a]	

[a] Potentiometric measurement, (21).

II. Complexation

A systematic study involving the first row transition metal perchlorates was made in order to observe any complex formation with PMT in anhydrous formic acid. The following seven perchlorate hexahydrate salts were used in this investigation: chromium(III), manganese(II), iron(III), iron(II), cobalt(II), nickel(II), and copper(II). These salts were dried in vacuo at room temperature to remove absorbed water, care being taken not to remove any water of hydration.

Since iron perchlorate salts could not be dried without undergoing partial decomposition, they were not included in this study.

Solutions of the five remaining perchlorate salts were made in both formic acid and water to note any spectral differences. The small spectral shifts between the two solvents are recorded in Table XVI. Due to the low molar absorptivity of manganese(II) perchlorate hexahydrate, its visible spectrum could not be obtained without recourse to extremely high concentrations.

In order to observe the effects of hydration upon the perchlorate salts in formic acid, spectra were obtained for anhydrous and hydrated solutions of each salt. The waters of hydration were removed from the anhydrous solutions by adding calculated amounts of acetic anhydride. The results may be seen in Table XVII. Although the peak shifts between the anhydrous and hydrated solutions are negligible, there is a small change in the molar absorptivities. Also, a study was made with the solutions containing acetic anhydride to see if there were any spectral changes with time. The reaction between the anhydride and water appeared to be complete within a few minutes after mixing. No spectral changes were observed after several days of standing.

Table XVI. Transition metal spectra in formic acid and water.

Salt	Solvent	λ max (mμ)	ε
$Cu(ClO_4)_2 \cdot 6H_2O$	H_2O	813	12
$Cu(ClO_4)_2 \cdot 6H_2O$	HCOOH	820	22
$Ni(ClO_4)_2 \cdot 6H_2O$	H_2O	405	5
		660	2
		725	3
		1170	4
$Ni(ClO_4)_2 \cdot 6H_2O$	HCOOH	400	8
		670	3
		730	4
		1180	5
$Co(ClO_4)_2 \cdot 6H_2O$	H_2O	276	3
		459	3
		511	5
$Co(ClO_4)_2 \cdot 6H_2O$	HCOOH	<250	
		468	7
		520	12
$Cr(ClO_4)_3 \cdot 6H_2O$	H_2O	408	15
		576	12
$Cr(ClO_4)_3 \cdot 6H_2O$	HCOOH	426	24
		586	29

Table XVII. Transition metal perchlorate spectra in formic acid.

Salt	max (mμ)	ε
$Cu(ClO_4)_2 \cdot 6H_2O$	820	22
$Cu(ClO_4)_2 \cdot 6H_2O^a$	820	23
$Ni(ClO_4)_2 \cdot 6H_2O$	400	8.6
	670	3.2
	730	3.4
	1190	4.6
$Ni(ClO_4)_2 \cdot 6H_2O^a$	400	8.7
	669	3.3
	729	3.5
	1190	4.7
$Co(ClO_4)_2 \cdot 6H_2O$	520	12
	1300	2.7
$Co(ClO_4)_2 \cdot 6H_2O^a$	520	12
	1300	2.7
$Cr(ClO_4)_3 \cdot 6H_2O$	420	32
	587	44
$Cr(ClO_4)_3 \cdot 6H_2O^a$	425	37
	590	52

[a] Acetic anhydride added to remove water.

A series of solutions with varying concentration was made for each transition metal salt. Calculated amounts of acetic anhydride were added to each solution and their spectra were determined. As may be seen in Figure 26 all four of the salts obey Beer's law at the concentration range studied.

Spectral studies were performed on solutions with and without the addition of acetic anhydride. Since only minute differences were observed, all of the remaining work was performed without the addition of acetic anhydride.

A. Copper(II) Perchlorate studies

In order to insure that the hydrated perchlorate salt did not lose any waters of hydration during drying, copper was determined using a standard iodometric procedure (82).

Anal. Calcd for $Cu(ClO_4)_2 \cdot 6H_2O$: Cu, 17.15.
Found: Cu, 17.11.

Hypsochromic spectral shifts were noted when PMT was added to copper(II) perchlorate hexahydrate solutions in formic acid (Figures 27 & 28). The absorption maxima progressively changed from 12,300 cm^{-1} (813 mμ) for the copper(II) perchlorate hexahydrate to 14,000 cm^{-1} (695 mμ) at a PMT/Cu(II) mole ratio of 10:1.

These spectra are typical of copper(II) complexes which theoretically have only one allowed transition $[{}^2Eg \rightarrow {}^2T_2\ (D)]$.

The absorbance maximum remained unchanged from a mole ratio of 10:1 up to a ratio of 50:1. However, at mole ratios of 50:1 and greater, the maximum again progressively changes to shorter wavelengths (Figure 29).

Figure 26. Beer's law plots: A, chromium(III) perchlorate hexahydrate (420 mμ); B, copper(II) perchlorate hexahydrate (815 mμ); C, cobalt(II) perchlorate hexahydrate (520 mμ); and D, nickel(II) perchlorate hexahydrate (397 mμ), in formic acid.

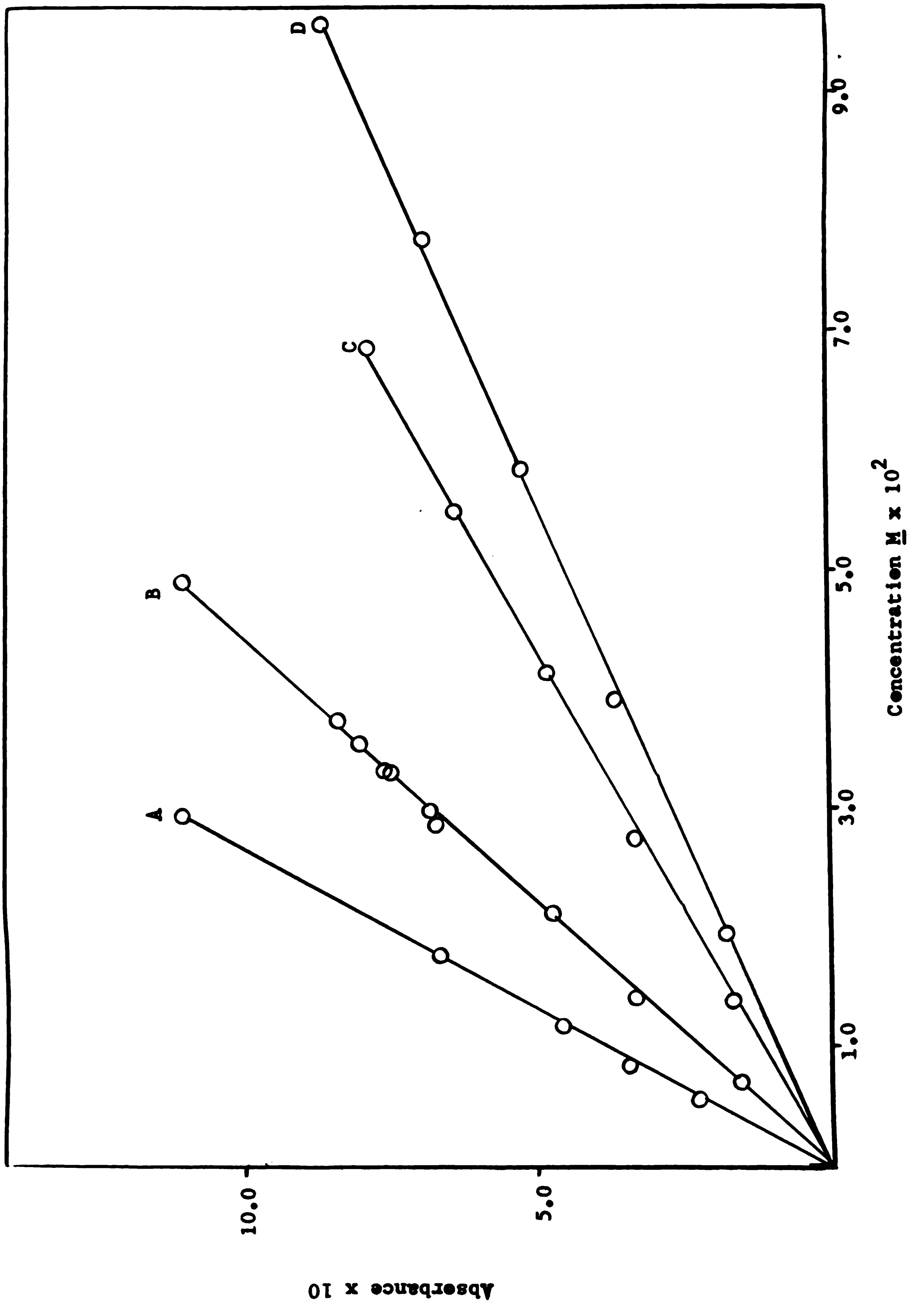

A
B
C
D
1.0
3.0
5.0
7.0
9.0
Concentration $\underline{M}$ x 10^2
10.0
5.0
Absorbance x 10

Figure 26

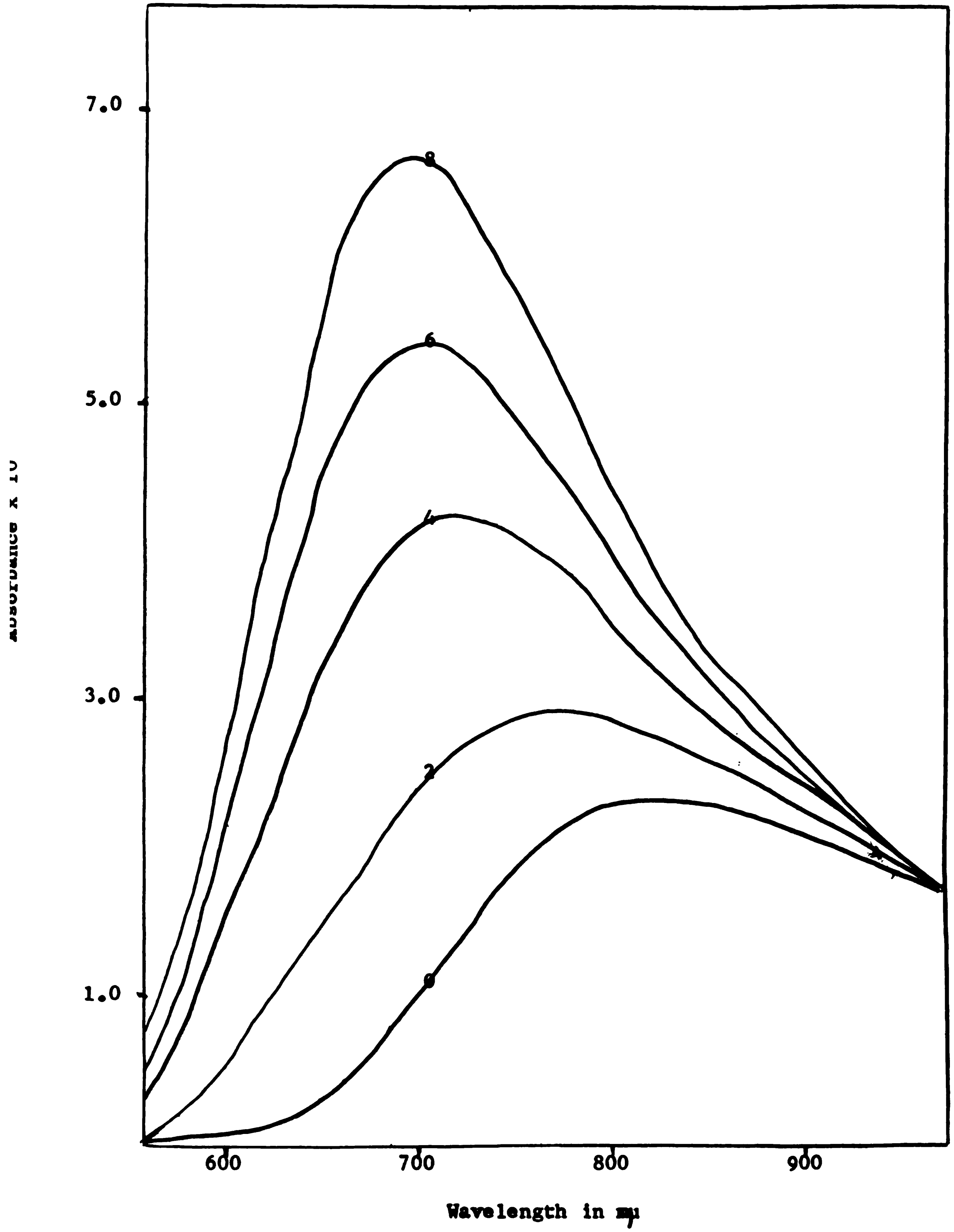


Figure 27. Spectrophotometric study of 1.0×10^{-3} $\underline{M}$ $Cu(ClO_4)_2 \cdot 6H_2O$ with various mole ratios of PMT in formic acid using a 10-cm cell.

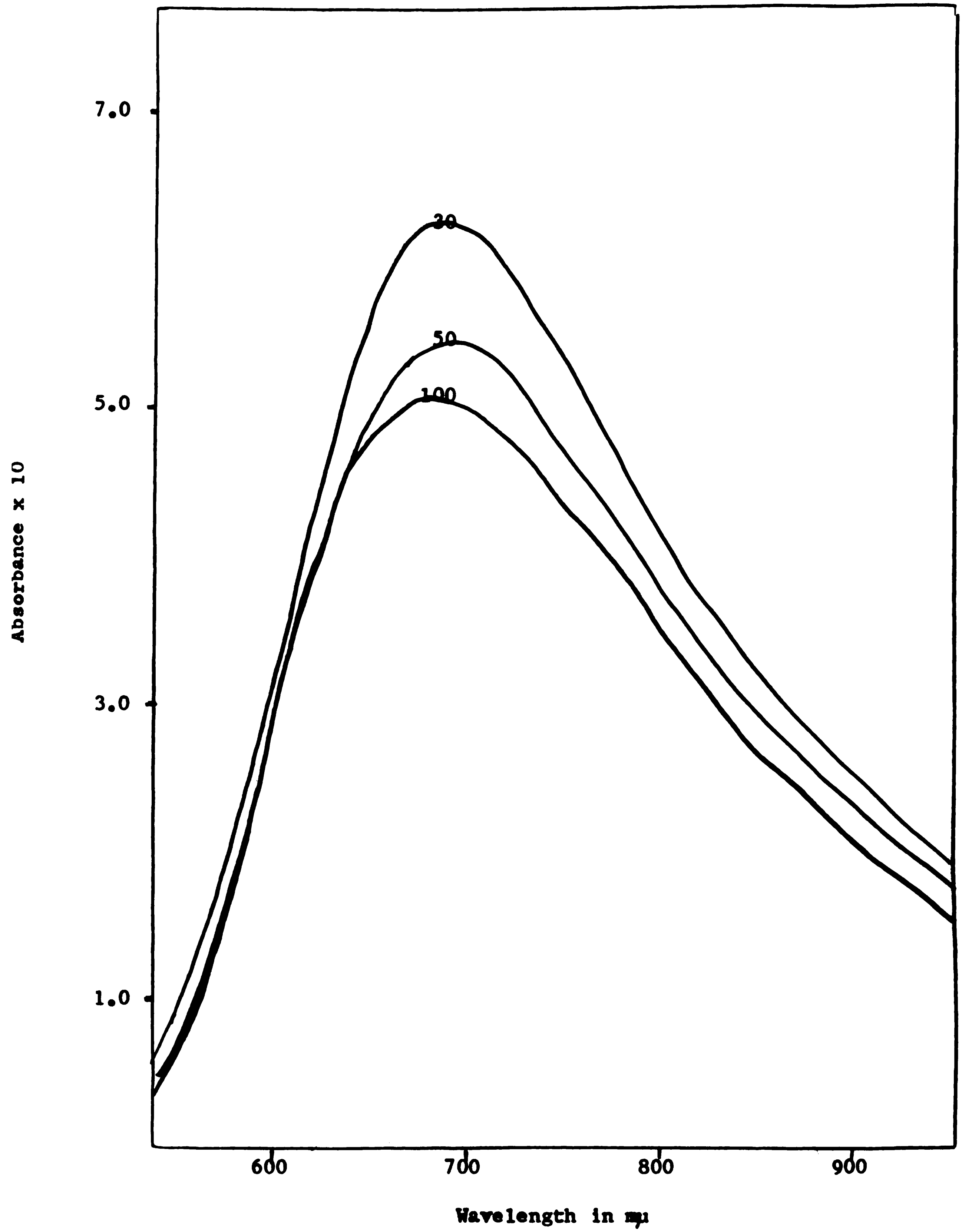


Figure 28. Spectrophotometric study of 1.0 x 10^{-3} $\underline{M}$ $Cu(ClO_4)_2 \cdot 6H_2O$ with various mole ratios of PMT in formic acid using a 10-cm cell.

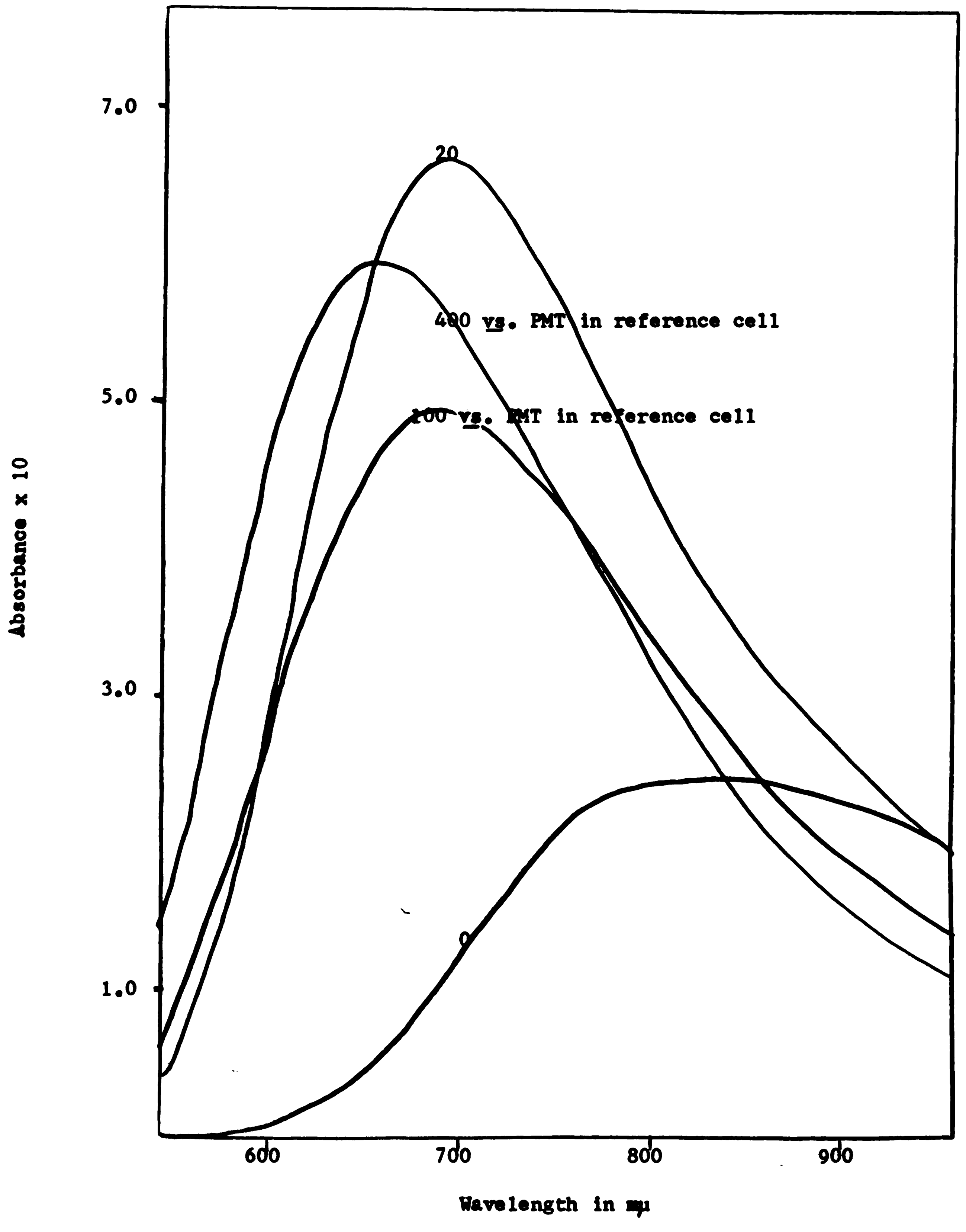


Figure 29. Spectrophotometric study of 1.0×10^{-3} M $Cu(ClO_4)_2 \cdot 6H_2O$ with various mole ratios of PMT in formic acid using a 10-cm cell.

These absorbance shifts were accompanied by a hyperchromic effect up to a mole ratio of 20:1 at which point a maximum absorptivity was obtained. At higher concentrations of PMT the absorptivity passed through a minimum and then slowly increased (Figure 29). These results were totally reproducible and may be seen by comparing Figures 27, 28, and 29. Maximum absorptivity at a 20 fold excess of PMT is clearly seen in a plot of molar absorptivity *versus* mole ratio PMT (Figure 30).

A continuous variation study (76) of PMT with copper(II) perchlorate hexahydrate shows a maximum at a ligand mole fraction of approximately 0.67 (Figure 31). This would correspond to a stoichiometry of 2:1 (ligand/metal) for the solution complex.

In several of the above solutions a light blue crystalline material precipitated out after 24 hours. This precipitate could be redissolved by the addition of dilute perchloric acid. Larger quantities of this material were prepared by carefully controlling the concentration and temperature of the PMT-copper(II) perchlorate solution in order to avoid super-saturation. An infrared spectrum of the precipitate, after it had been filtered and dried *in vacuo* (Figure 32A) showed no evidence of a tetrazole ring (cf. Figure 1, p.23). However, a comparison of this spectrum with those of copper(II) formate tetrahydrate, water and formic acid (Figures 33A, B and C) shows that the precipitate is copper(II) formate without any solvated water or formic acid. The loss of solvation molecules is also substantiated by the fact that the precipate's weight decreased as it changed from a light blue to a light green material upon drying. The dried material was analized for copper using a standard iodometric procedure (82).

Anal. Calcd for $Cu(HCOO)_2$: Cu, 41.38.
Found: Cu, 41.41.

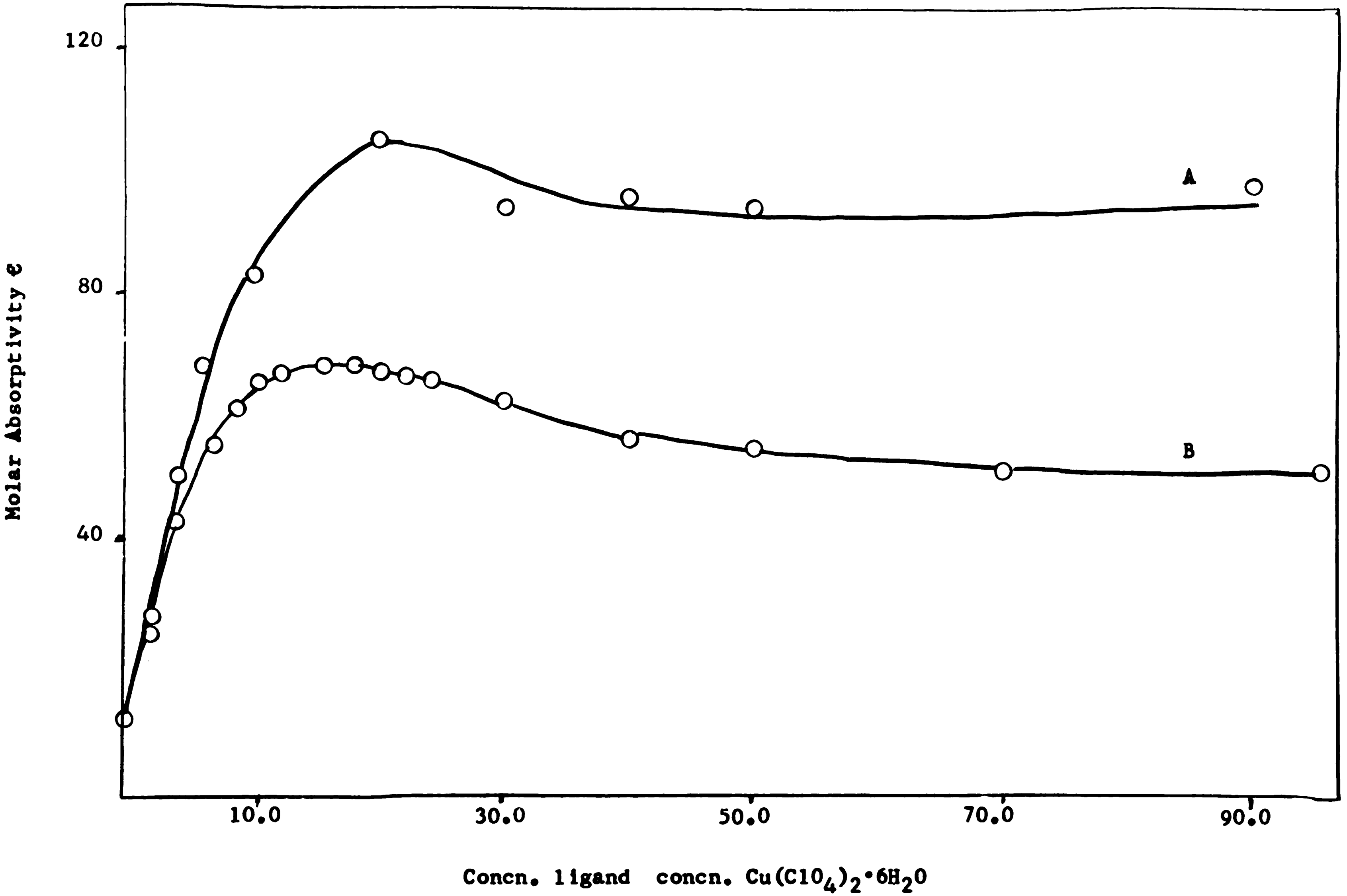


Figure 30. Mole ratio study of A, sodium formate; B, PMT with copper(II) perchlorate hexahydrate in formic acid (700 mμ).

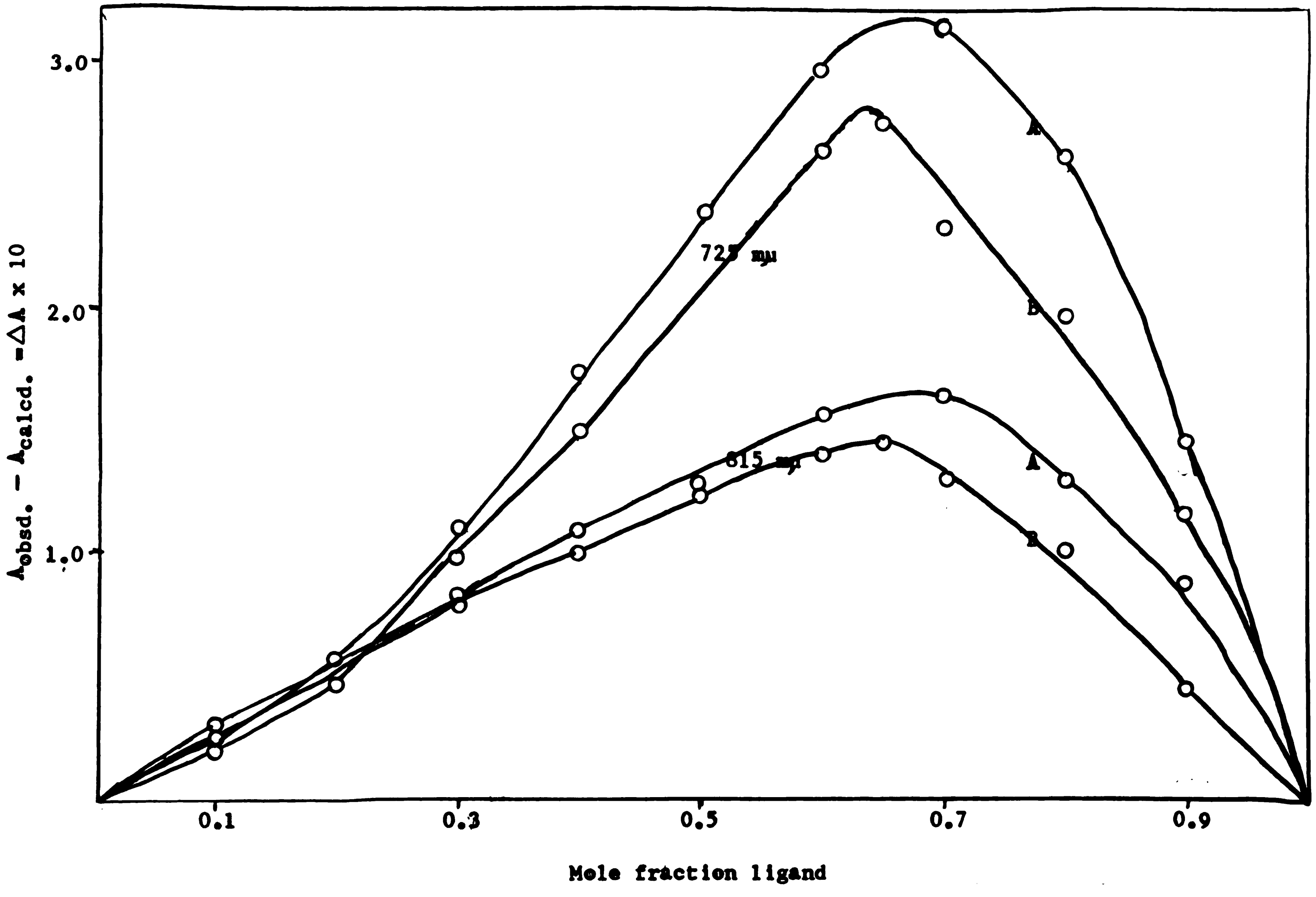


Figure 31. Continuous variation study of copper(II) perchlorate hexahydrate with A, sodium formate (2.0×10^{-3} M); B, PMT (4.5×10^{-3} M) in formic acid using a 1 cm cell.

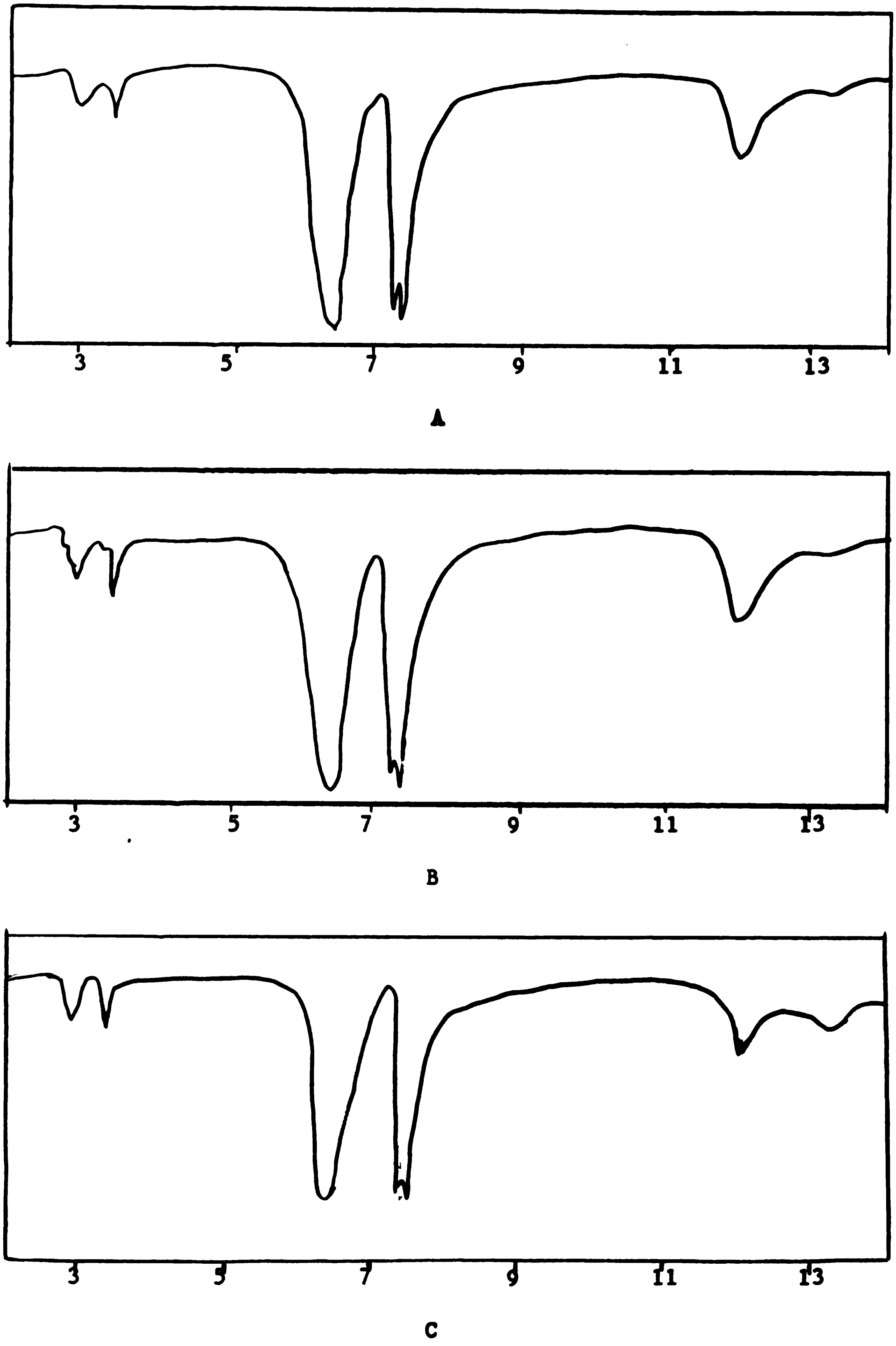


Figure 32. Infrared absorption spectra using KBr pellets of copper(II) precipitate from $Cu(ClO_4)_2 \cdot 6H_2O$ solutions of: A, PMT; B, sodium formate; and C, pyridine, in formic acid. (wavelength in μ)

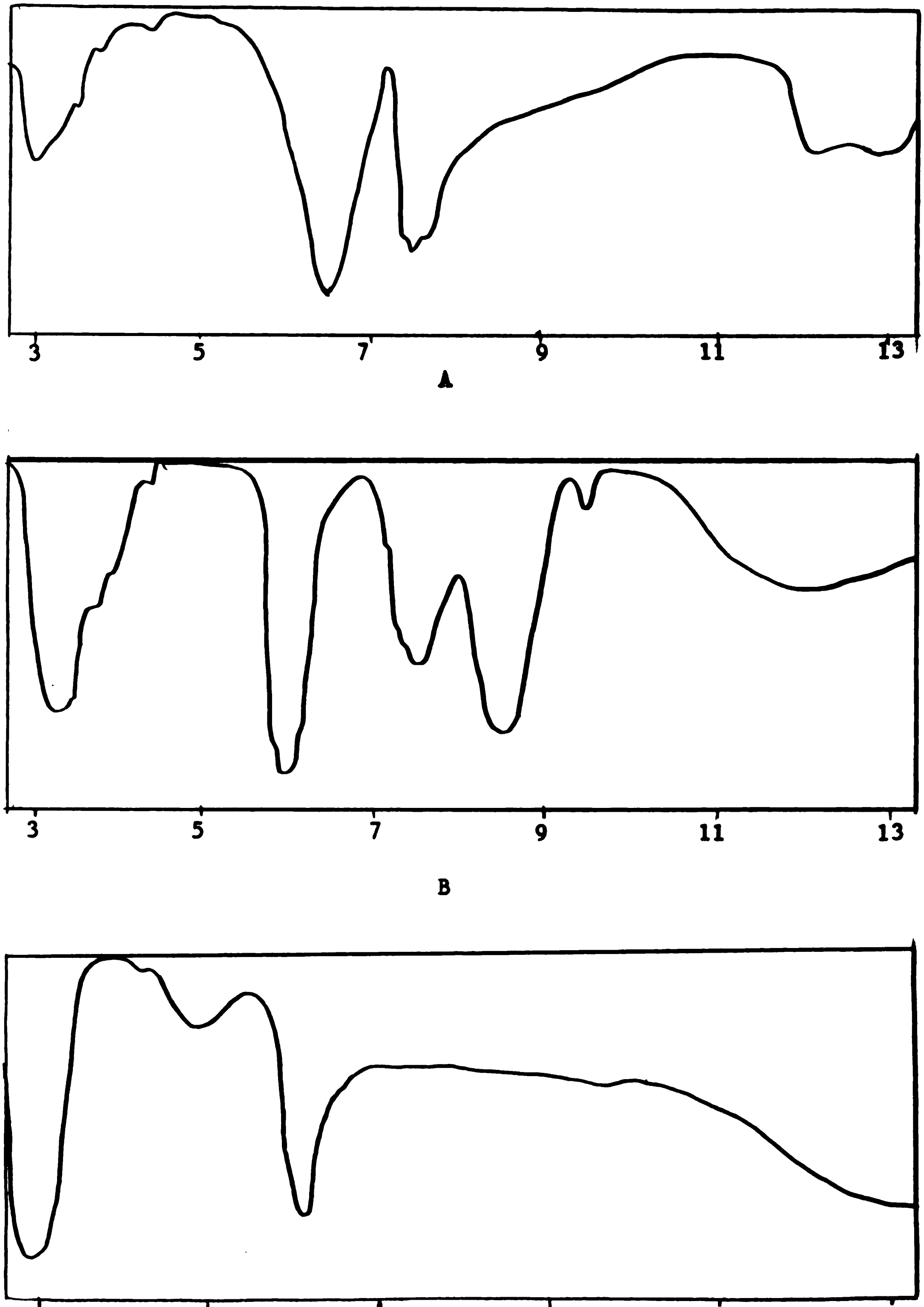


Figure 33. Infrared absorption spectra using KBr pellets of A, $Cu(HCOO)_2 \cdot 4H_2O$. B, HCOOH and C, H_2O, in the liquid state. (wavelength in μ)

Copper analysis of the solvated copper(II) formate salt could not be obtained because of interferences from reduction of the formic acid molecules.

A mole ratio study was run on the copper(II) perchlorate hexahydrate-sodium formate system in formic acid (Figure 34). A comparison of the results with those of the PMT system (Figures 27 and 30) shows a striking similarity. Just as in the PMT study, hypsochromic shifts were noted with increasing concentration of sodium formate--changing progressively from 12,300 cm^{-1} (813 mμ) for the uncomplexed solution to 14,400 cm^{-1} (695 mμ) at a sodium formate/Cu(II) mole ratio of 10:1. Again, a maximum absorptivity was obtained at a 20 fold excess of sodium formate (Figure 30). At higher concentrations of sodium formate an absorptivity decrease and a new hypsochromic shift was noted.

Upon standing, a light blue precipitate was obtained from a concentrated solution of copper(II) perchlorate hexahydrate and sodium formate. The precipitate turned from a light blue to green upon drying <u>in vacuo</u>. An ir spectra (Figure 32B) showed that it was copper (II) formate. A standard iodometric procedure was used to analyze the percent copper in the sample (82):

<u>Anal</u>. Calcd for $Cu(HCOO)_2$: Cu, 41.38.
Found: Cu, 41.36.

It appears, therefore, from the above observations that the addition of either PMT or sodium formate to Cu(II) solutions in formic acid causes the formation of copper(II) formate.

A continuous variation study of sodium formate and copper(II) perchlorate (Figure 31) shows a sharp peak at a ligand mole fraction of 0.67. This would correspond to a stoichiometry of 2:1 (ligand to metal) for the complex.

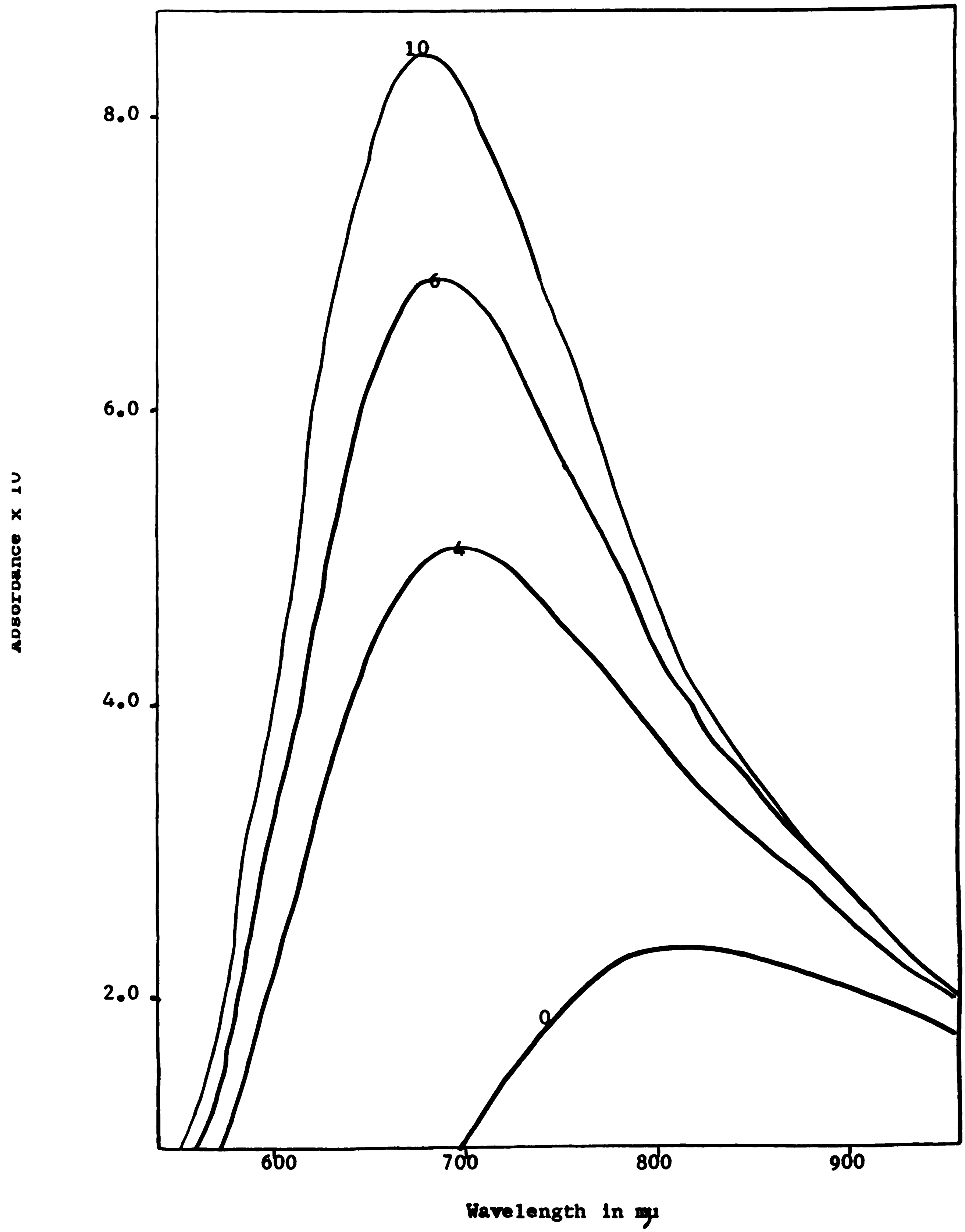


Figure 34. Spectrophotometric study of 1.0 x 10^{-3} M $Cu(ClO_4)_2 \cdot 6H_2O$ with various mole ratios of sodium formate in formic acid using a 10-cm cell.

A further comparison of mole ratio studies (Figure 30) shows that the sodium formate complex solutions have a greater molar absorptivity than the PMT solutions. This seems reasonable if the following equilibria are assumed:

1. $\text{PMT} + \text{HCOOH} \xrightarrow{K_b \approx 10^{-2}} \text{HPMT}^{+} + \text{HCOO}^{-}$

2. $2\text{HCOO}^{-} + \text{Cu}^{++} \xrightarrow{\text{HCOOH}} \text{Cu}^{++}(\text{HCOO}^{-})_2 \cdot x\ \text{HCOOH}$

Thus, at equal molar concentrations of PMT and sodium formate, there would be fewer formate ions available for coordination in the PMT solutions due to the ionization equilibrium of PMT (Step 1). The coordination of the formate ions to copper(II) ion in formic acid solutions should be suppressed by addition of a strong acid. The effect of perchloric acid additions to PMT solutions of copper(II) perchlorate hexahydrate may be seen in Figure 35. As small amounts of perchloric acid are added to these solutions, the spectra are progressively shifted back to that of the copper(II) perchlorate hexahydrate solution (Spectrum C). However, the absorptivities of the perchloric acid solutions are slightly less than that of the original copper(II) perchlorate hexahydrate solution. This indicates that a solution of copper(II) perchlorate hexahydrate in formic acid is coordinated by formate ions which arise in small concentrations from the autoprotolysis of the solvent.

Pyridine in formic acid solution should act as a strong base and be leveled to an equivalent amount of formate ion. Thus, we would expect to obtain similar spectral shifts to those observed above for solutions of sodium formate and copper(II) perchlorate. Indeed, inspection of Figure 36 shows that pyridine solutions behave in exactly the same

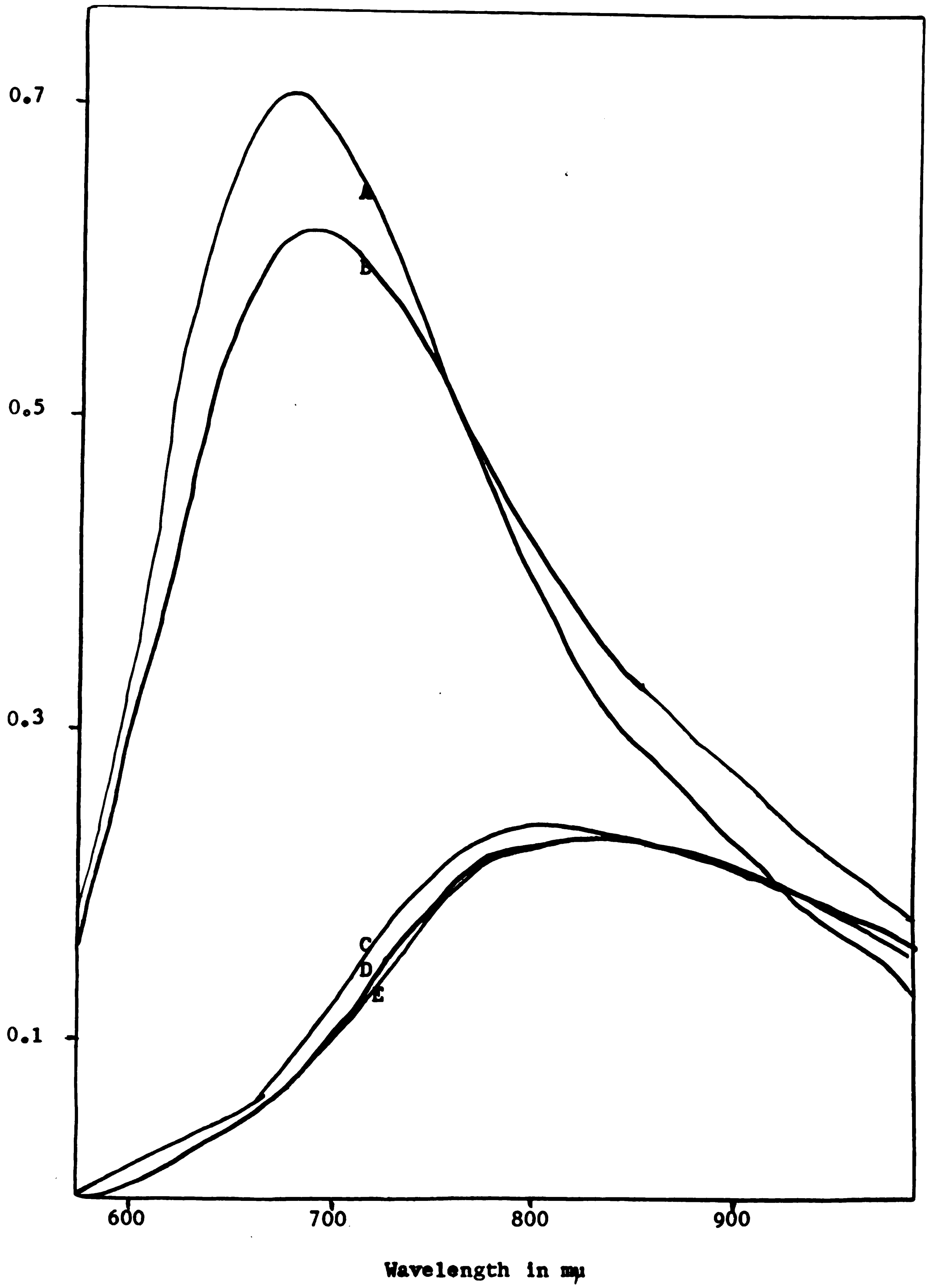


Figure 35. Spectrophotometric study of 2.0 x 10^{-3} $\underline{M}$ $Cu(ClO_4)_2 \cdot 6H_2O$ (C) with: A, 8.0 x 10^{-3} $\underline{M}$ sodium formate; B, 8.0 x 10^{-3} $\underline{M}$ PMT; D, 8.0 x 10^{-3} $\underline{M}$ sodium formate + 8.0 x 10^{-3} perchloric acid; E, 8.0 x 10^{-3} $\underline{M}$ PMT + 8.0 x 10^{-3} $\underline{M}$ perchloric acid in formic acid using a 5-cm cell.

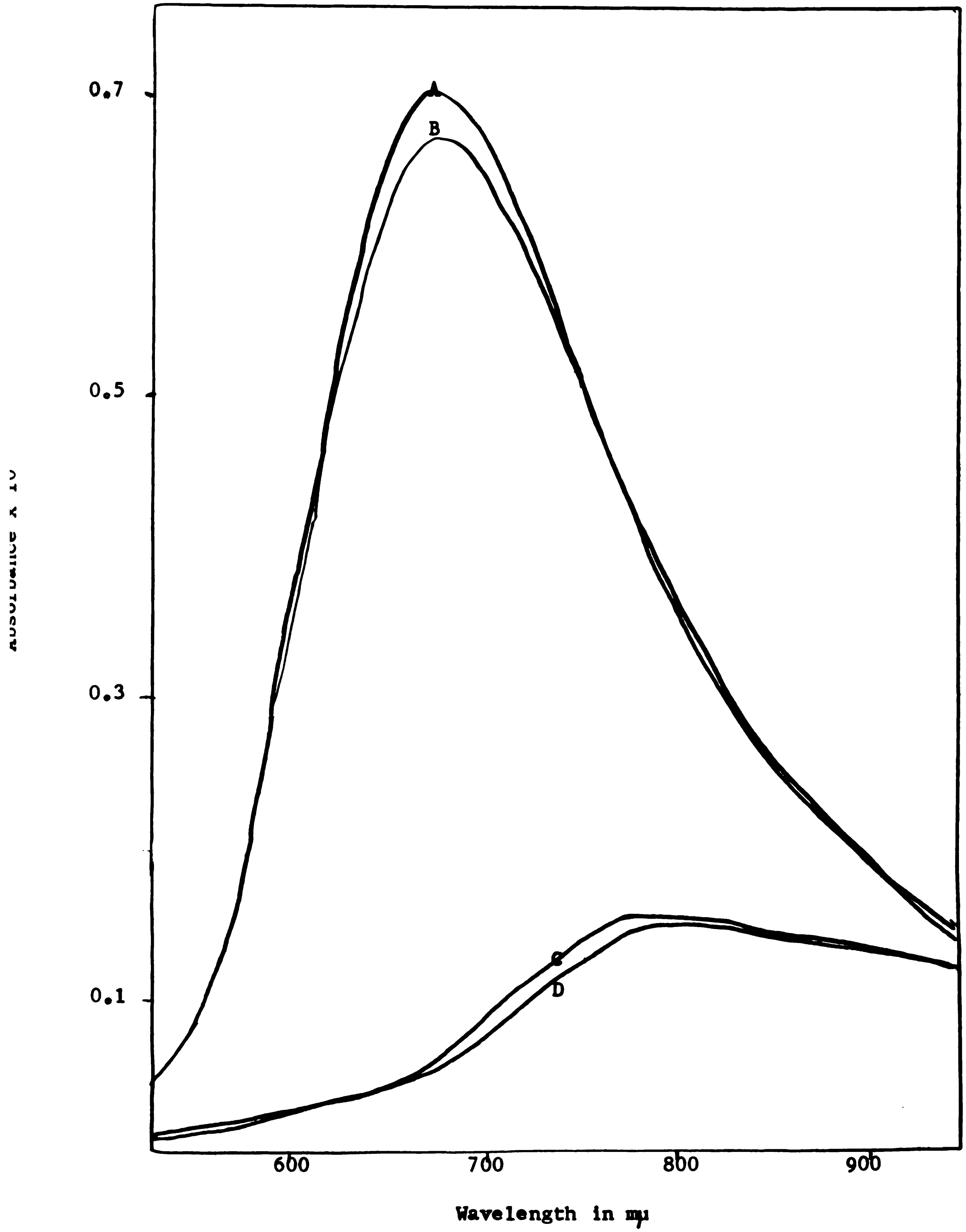


Figure 36. Spectrophotometric study of 1.2×10^{-3} $\underline{M}$ $Cu(ClO_4)_2 \cdot 6H_2O$ (C) with: A, 2.4×10^{-2} $\underline{M}$ pyridine; B, 1.2×10^{-1} $\underline{M}$ pyridine; D, 2.4×10^{-2} $\underline{M}$ pyridine + 2.4×10^{-2} $\underline{M}$ perchloric acid in formic acid using 5-cm cells.

manner as sodium formate and PMT solutions of copper(II) perchlorate. Again a precipitate was obtained which upon drying was found to be copper(II) formate (Figure 32C).

<u>Anal.</u> Calcd for $Cu(CHOO)_2$: Cu, 41.38.
Found: Cu, 41.35.

Attempts to study solutions of copper(II) formate in several polar non-donor solvents such as nitromethane were not successful due to lack of solubility.

To summarize, it appears that PMT or protonated PMT does not coordinate with copper(II) perchlorate hexahydrate in formic acid. Apparently the spectral shifts in these solutions at low ligand concentrations are caused by the coordination of two formate ions with each copper(II) ion. However, as the mole ratio excess of the ligand is increased to larger values (Figure 29), new spectral shifts indicate the presence of a different absorbing species. This species is probably a copper(II) ion with additional formate ions coordinated about it.

B. <u>Nickel(II) Perchlorate studies</u>

In order to insure that there was no water of hydration loss upon drying, a Karl Fisher water determination (81) was run on the vacuum dried nickel(II) perchlorate hexahydrate salt.

<u>Anal.</u> Calcd for $Ni(ClO_4)_2$: H_2O, 29.6%.
Found: H_2O, 29.5%.

A mole-ratio study of the PMT-nickel(II) perchlorate hexahydrate system is shown in Figure 37. The spectrum obtained from nickel(II) perchlorate hexahydrate solution (Spectrum A) is characteristic of a weakly coordinated octahedral complex (77). This spectrum shows the following absorption bands: (ν_1) 8,500 cm^{-1} (1180 mμ) arising from a $^3A_{2g} \longrightarrow {}^3T_{2g}$ transition; (ν_2) which is split into two bands, 13,700 cm^{-1} (730 mμ) and 14,900^{-1} (670 mμ) arising from a $^3A_{2g} \longrightarrow {}^3T_{1g}$

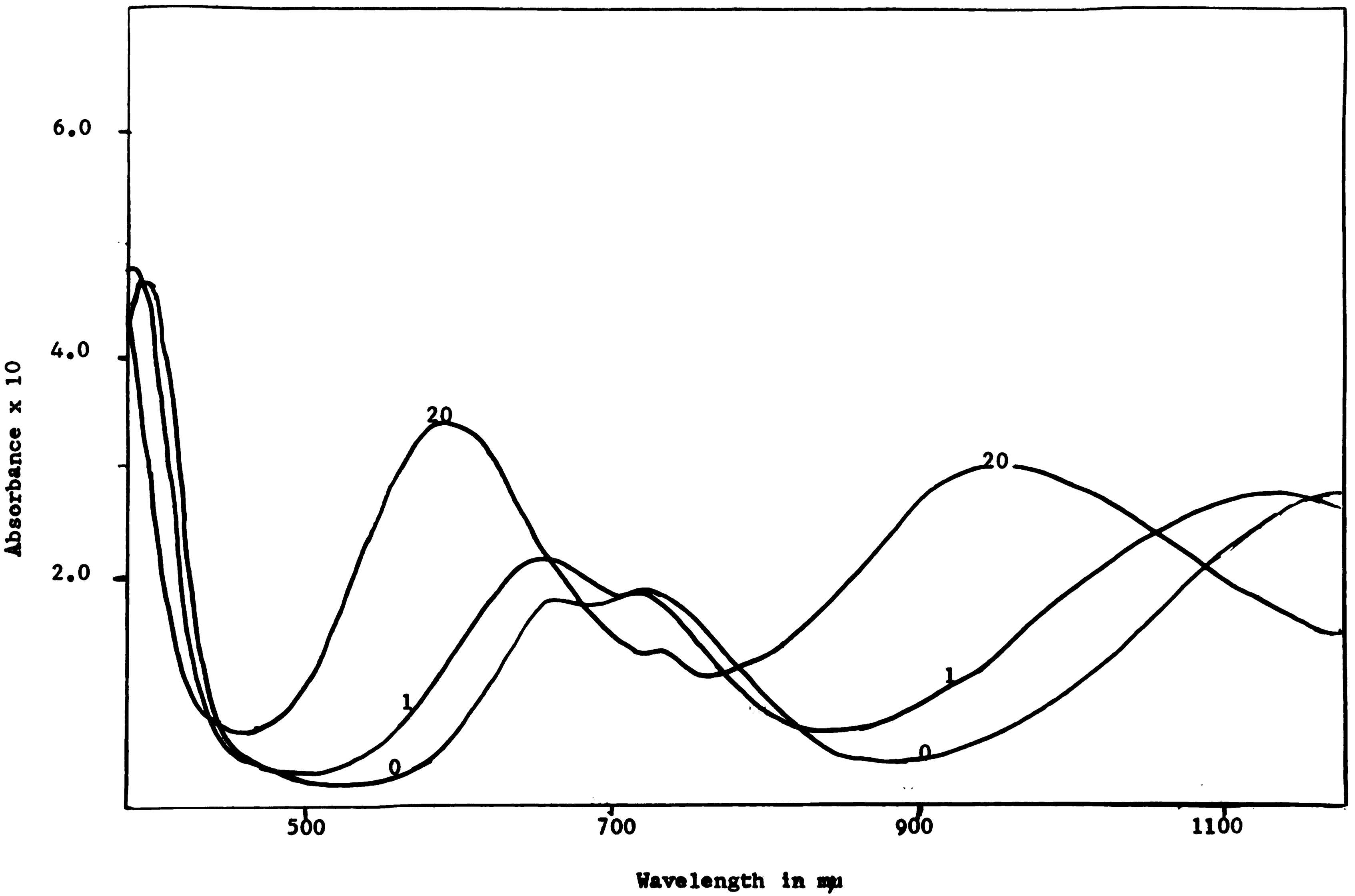


Figure 37. Spectrophotometric study of 5.5 x 10^{-2} M nickel(II) perchlorate hexahydrate with various mole ratios of PMT in formic acid using a 1-cm-pathlength cell.

transition. This band is split into two bands in weak complexes because of spin - orbit coupling between the $^3T_{2g}(F)$ and ^1E_g states which are very close in energy (78). The last band, (ν_3) 9,000 cm^{-1} (400 mμ) is due to a $^3A_{2g} \longrightarrow {}^3T_{2g}$ transition.

As PMT is added to nickel(II) perchlorate hexahydrate solution, hypsochromic spectral shifts occur (Figure 37). The absorption bands of the weakly coordinated hydrated salt (ν_1) 8,500 cm^{-1} (1180 mμ), (ν_2) 13,700 cm^{-1} (730 mμ) and 14,900 cm^{-1} (670 mμ), and (ν_3) 9,000 cm^{-1} (400 mμ) progressively changed to 10,300 cm^{-1} (975 mμ), 17,000 cm^{-1} (590 mμ), and 27,400 cm^{-1} (365 mμ) respectively. The $^3A_{2g} \longrightarrow {}^3T_{2g}$ transition (ν_2) is no longer split into two absorption bands since the nickel(II) ion is now in a stronger ligand field (no $^2T_{2g(F)}$-^1E_g spin-orbit coupling). Even at high mole ratio excesses of PMT (300:1) limiting absorbances could not be obtained for any of the absorption peaks (Figure 38). When perchloric acid was added to these solutions, all of the spectra shifted back to the original spectrum of nickel(II) perchlorate hexahydrate. The above results indicate that just as in the copper(II) solutions, coordination of the metal ion takes place with formate ions, and not with protonated PMT molecules.

A continuous variation study of PMT and nickel(II) perchlorate hexahydrate in formic acid showed a clear minimum at a PMT mole fraction of 0.67 (Figure 39). These results would correspond to a stoichiometry of 2:1 (ligand to metal) for the complex.

Solid nickel(II) formate was obtained by carefully controlling the concentrations of the nickel(II) perchlorate hexahydrate-PMT solutions in formic acid. This light green precipitate, which could be redissolved by the addition of dilute perchloric acid, was filtered and dried *in vacuo*. The infrared spectrum of the dried material (Figure 40A)

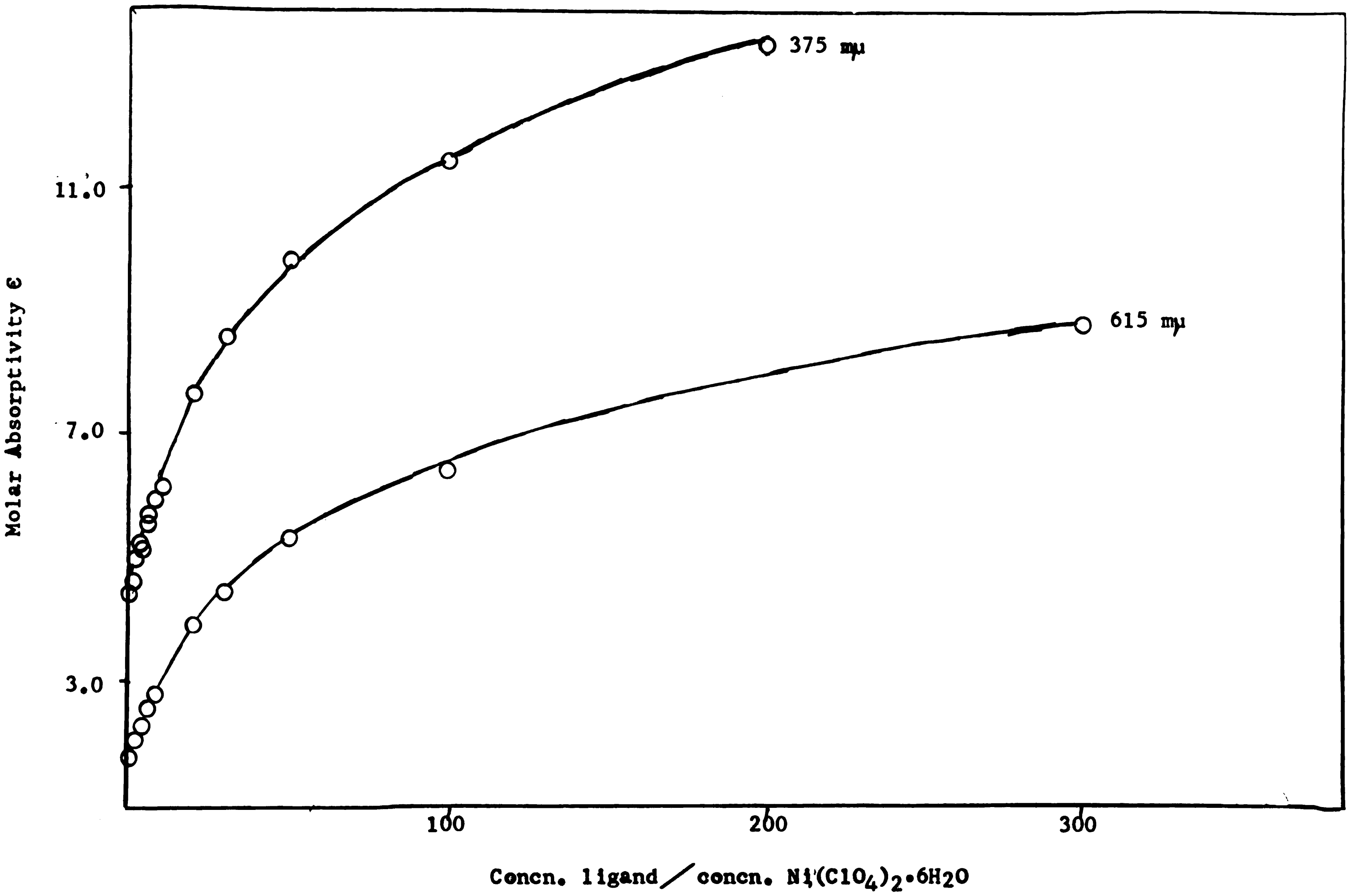


Figure 38. Mole ratio study of PMT – nickel(II) perchlorate hexahydrate in formic acid.

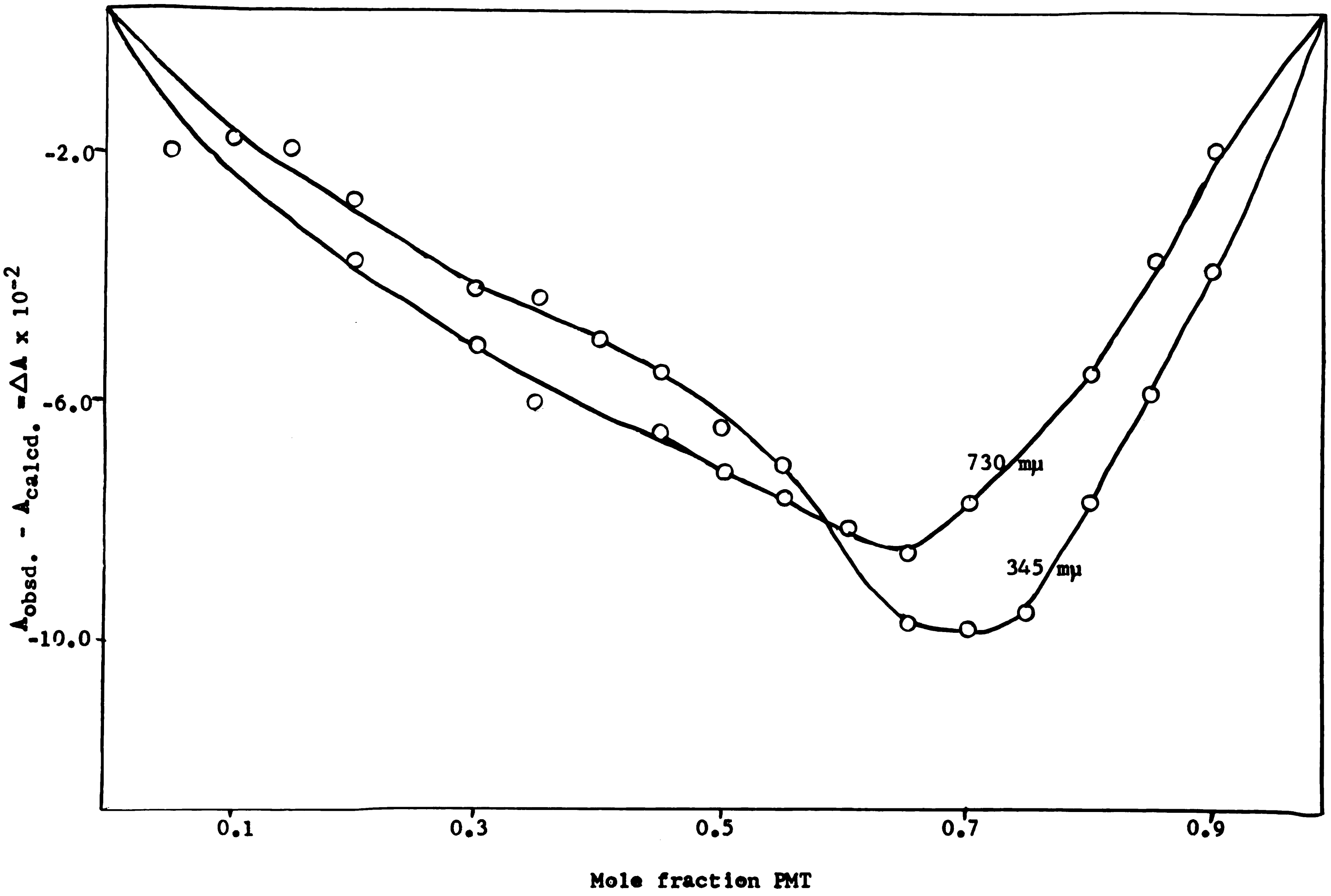


Figure 39. Continuous variation study of nickel(II) perchlorate hexahydrate - PMT with a total concentration of (2.2×10^{-1} M) in formic acid using a 1-cm-pathlength cell.

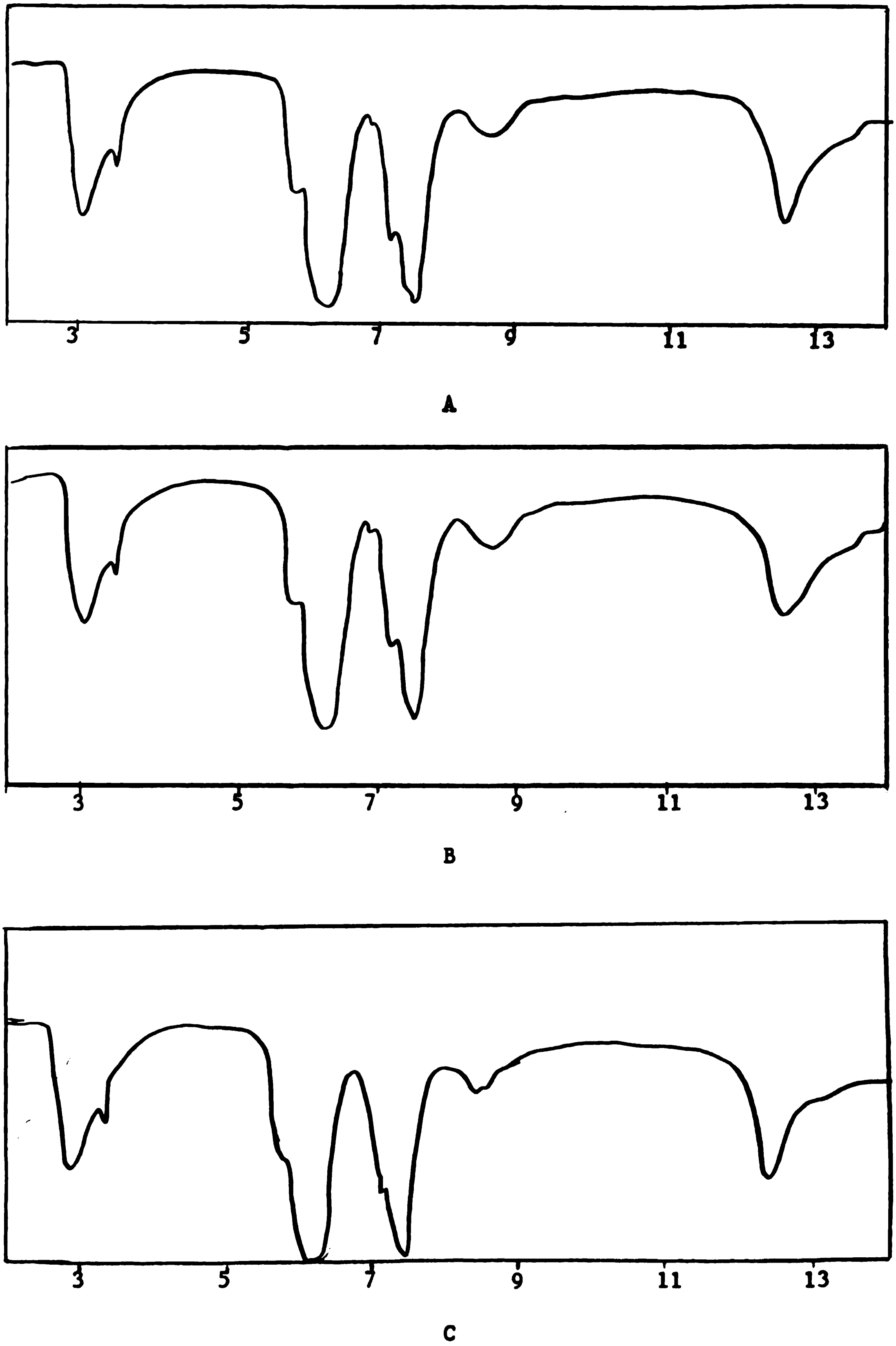


Figure 40. Infrared absorption spectra using KBr pellets of nickel(II) precipitate from $Ni(ClO_4)_2 \cdot 6H_2O$ solutions of: A, PMT; B, sodium formate; and C, pyridine, in formic acid. (wavelength in μ).

shows the presence of formate ions. No further analysis was preformed on this material.

Mole-ratio studies could not be obtained for sodium formate-nickel(II) perchlorate solutions even in very dilute solutions because of nickel (II) formate precipitation. An ir spectrum (Figure 40B) of the precipitate shows that it is nickel(II) formate. However, by the use of 10-cm-pathlength absorbance cells and extremely dilute solutions a continuous variation study was performed. Unfortunately, the absorbance difference between the various solutions were so small that meaningful results could not be obtained. Similarly, solubility difficulties were observed for the pyridine-nickel(II) perchlorate system. An infrared spectrum of the precipitate obtained from pyridine-nickel(II) solutions (Figure 40C) is identical to that of nickel(II) formate.

C. Cobalt(II) Perchlorate studies

A mole ratio study of PMT-cobalt(II) perchlorate hexahydrate is shown in Figure 41. These spectra are indicative of an octahedrally coordinated cobalt(II) ion, giving the following absorption bands: (ν_1) 7,700 cm^{-1} (1130 mμ) arising from a $^4T_1(F) \longrightarrow {}^4T_2$ transition; (ν_2) 19,200 cm^{-1} (520 mμ) arising from a $^4T_1(F) \longrightarrow {}^4A_2$ transition; and (ν_3) 21,300 cm^{-1} (470 mμ) arising from a $^4T_1(F) \longrightarrow {}^4T_1(P)$ transition (79). As PMT is added to solutions of cobalt(II) perchlorate hexahydrate, slight hypsochromic spectral shifts with corresponding increases of absorptivity occur. Even at high mole ratios of PMT to cobalt(II), a limiting absorptivity is not reached (Figure 42).

Continuous variation studies give a peak at a ligand mole fraction of 0.67 (Figure 43), indicative of a 2:1 stoichiometry (ligand:metal) for the complex. Although solid cobalt(II) formate

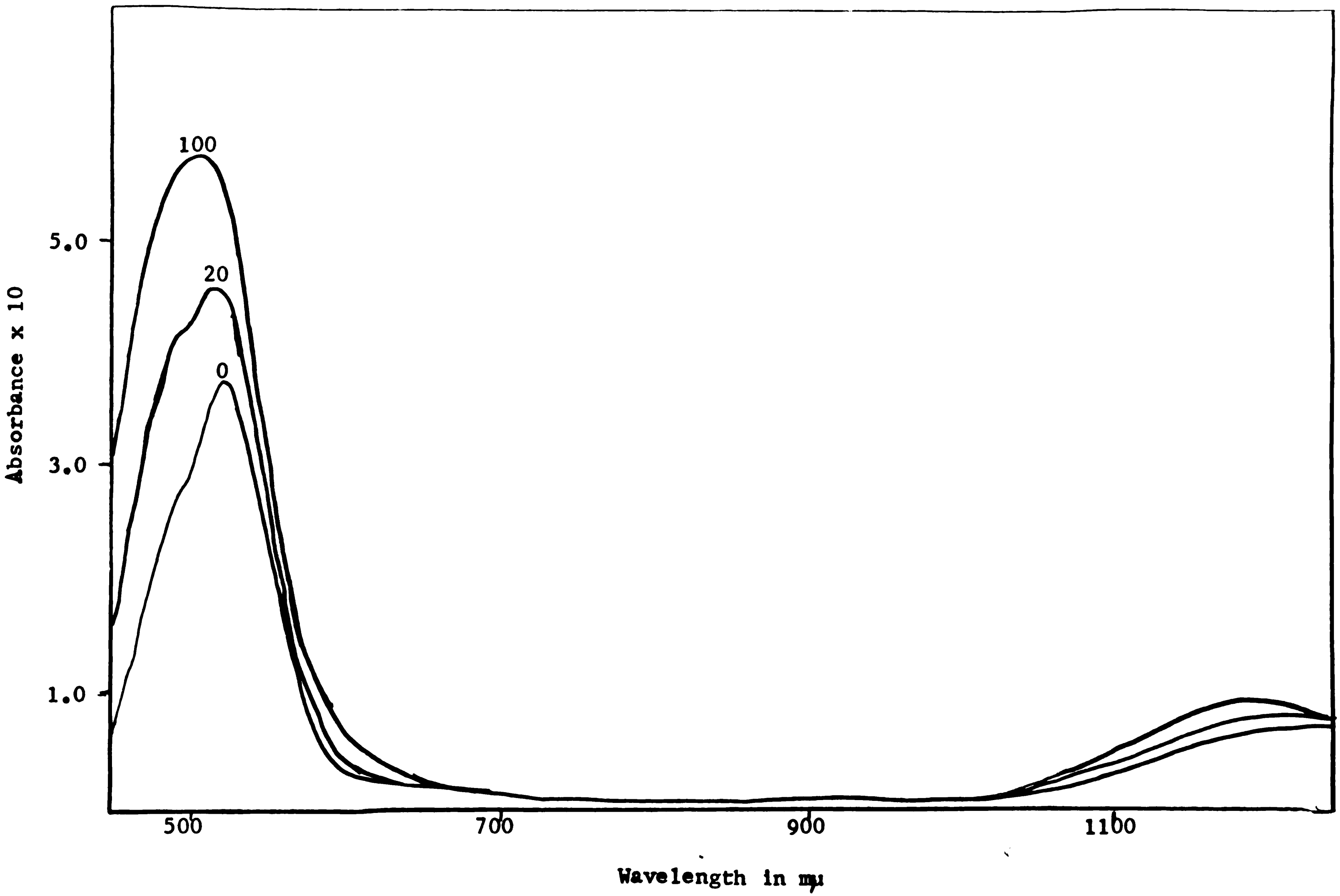


Figure 41. Spectrophotometric study of 6.0 x 10^{-3} M cobalt(II) perchlorate hexahydrate with various mole ratios of PMT using 5-cm-pathlength cells in formic acid.

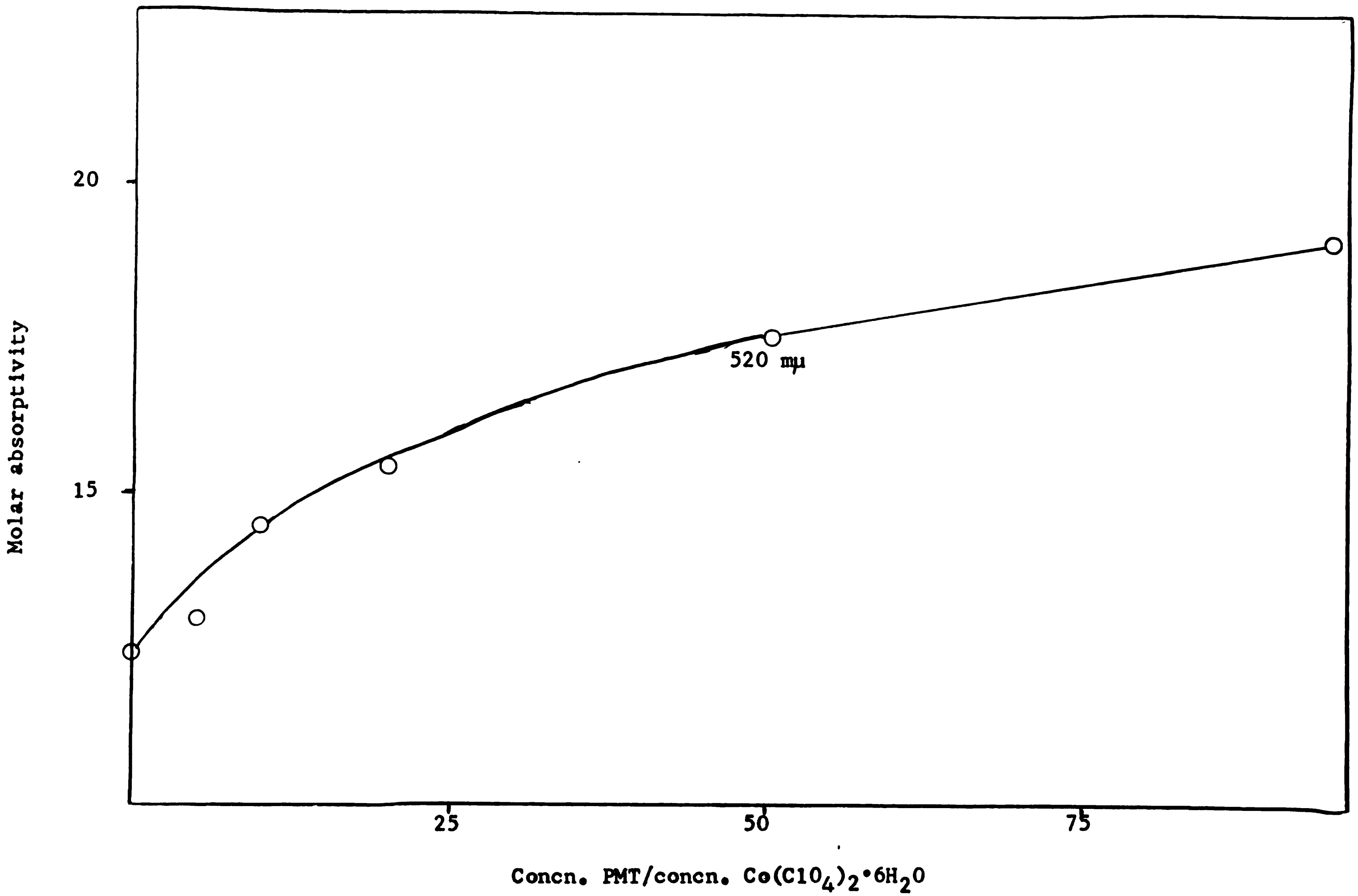


Figure 42. Molar ratio study of PMT with cobalt(II) perchlorate hexahydrate in formic acid.

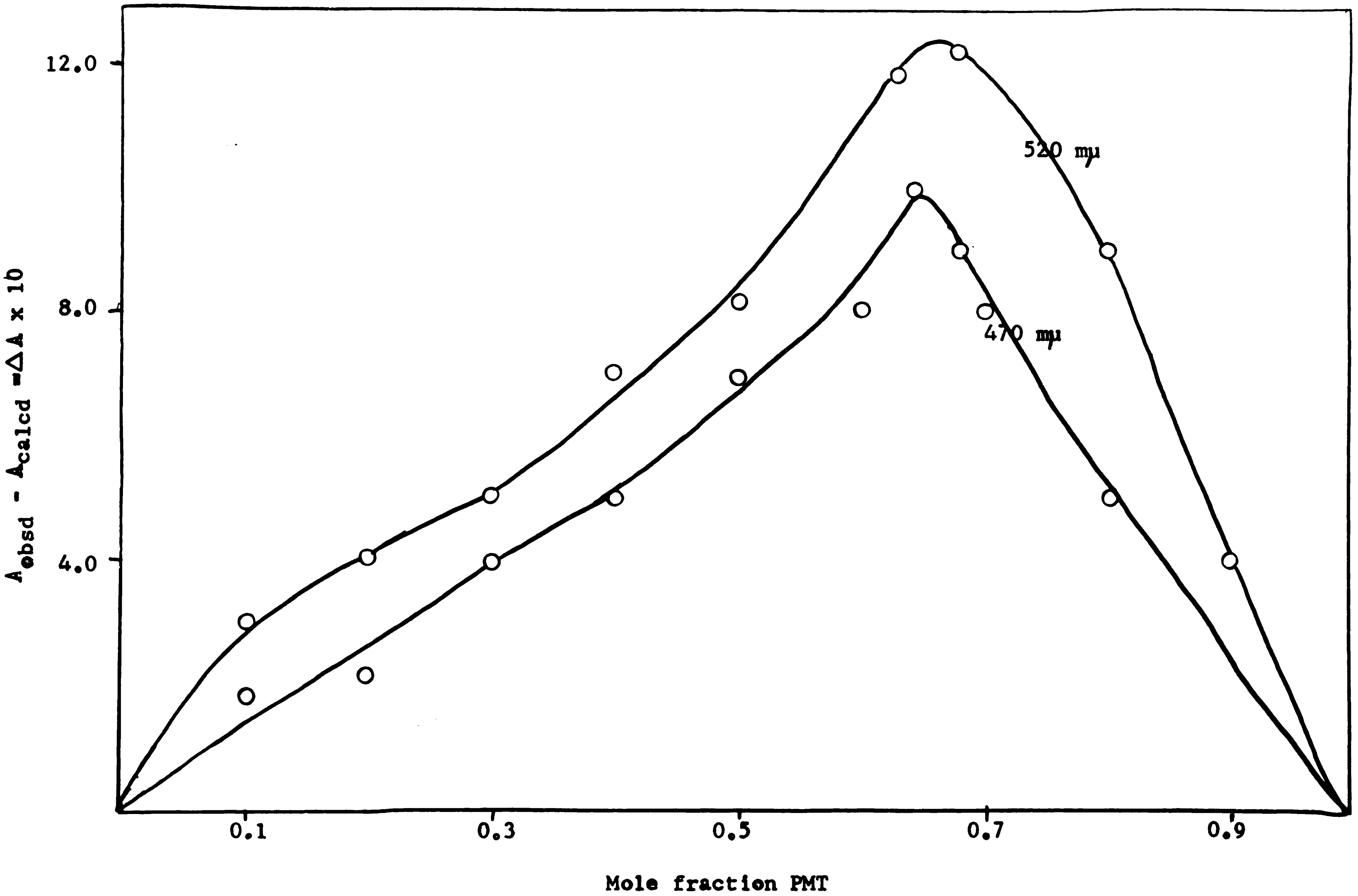


Figure 43. Continuous variation study of cobalt(II) perchlorate hexahydrate — PMT with a total concentration of (7.5×10^{-2} M) in formic acid using a 1-cm-pathlength cell.

could not be recovered from the PMT solutions, addition of perchloric acid showed that these spectral shifts were reversible.

In pyridine and sodium formate solutions of cobalt(II) perchlorate hexahydrate a pink precipitate was obtained which could be redissolved by addition of dilute perchloric acid. The infrared spectra of the two precipitates are identical (Figure 44), both showing the presence of cobalt(II) formate.

D. Chromium(III) Perchlorate studies

A mole ratio study of the chromium(III) perchlorate hexahydrate-PMT system (Figure 45) shows octahedral coordination with the following absorption bands: (ν_1) 17,400 cm^{-1} (585 mμ) arising from a $^4A_2g \rightarrow {}^4T_{2g}$ transition; and (ν_2) 23,800 cm^{-1} (420 mμ) arising from a $^4A_{2g} \rightarrow {}^4T_{1g}$ transition (80).

There are only slight hypochromic spectral shifts and hyperchromic effects upon addition of PMT to chromium(III) solutions. These same phenomena, which are reversible upon addition of dilute perchloric acid, are also noted for sodium formate-chromium(III) solutions in formic acid (Figure 46). A plot of molar absorptivity *versus* the mole-ratio excess of ligand shows no limiting absorptivity (Figure 47). Although several attempts were made to prepare solid chromium(III) formate from PMT, sodium formate, or pyridine solutions of chromium(III) perchlorate hexahydrate in formic acid, they were unsuccessful.

In summary, nickel(II), cobalt(II) and chromium(III) perchlorate-PMT solutions in formic acid behave in the same manner as copper(II) perchlorate-PMT solutions, *i.e.* the coordinating ligands about the transition metal ion are not PMT or protonated PMT molecules, but rather formate ions. However, there is no evidence of multiple

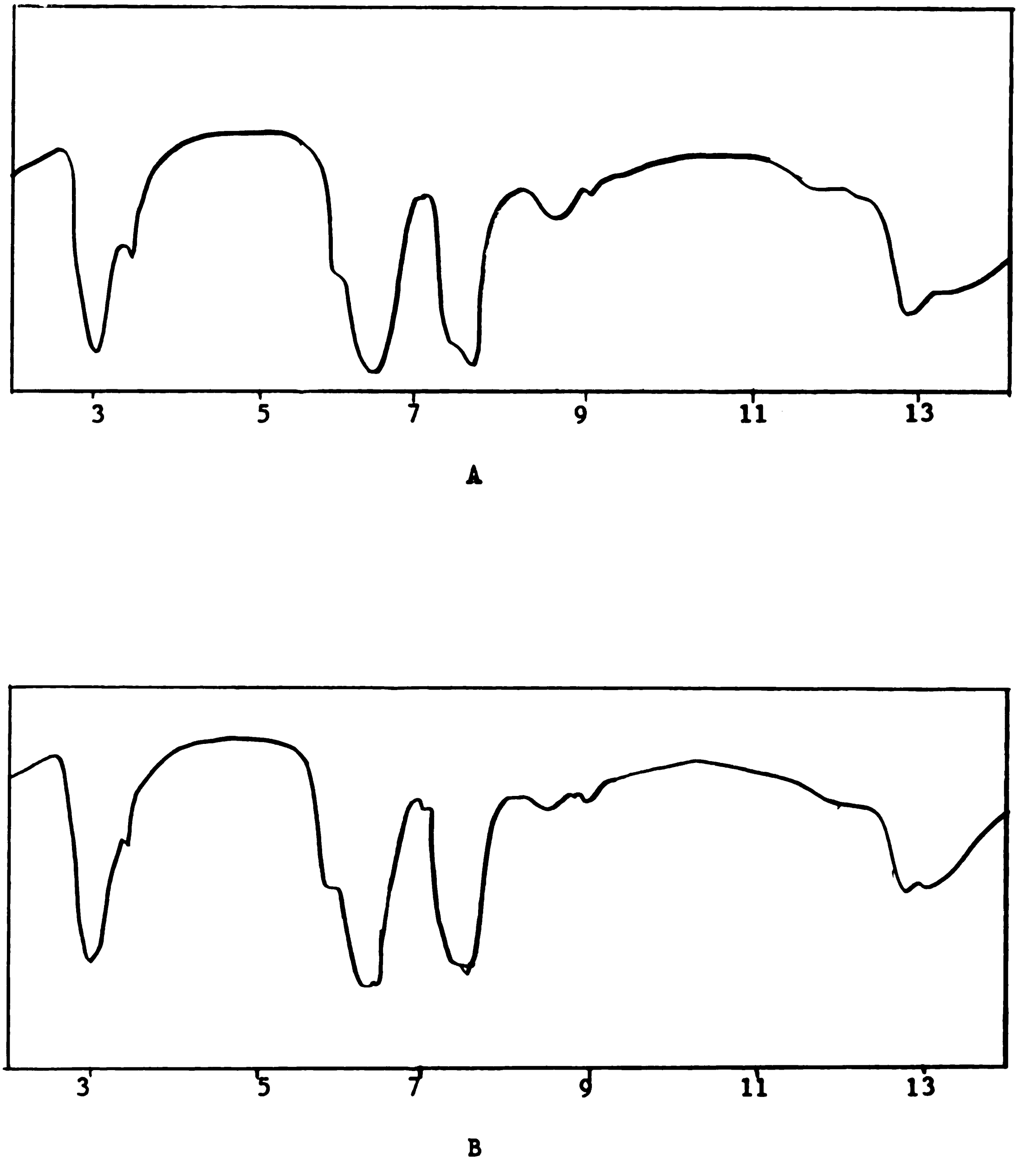


Figure 44. Infrared absorption spectra using KBr pellets of Cobalt(II) precipitate from $Co(ClO_4)_2 \cdot 6H_2O$ solutions of: A, sodium formate, and B, pyridine in formic acid (wavelength in μ).

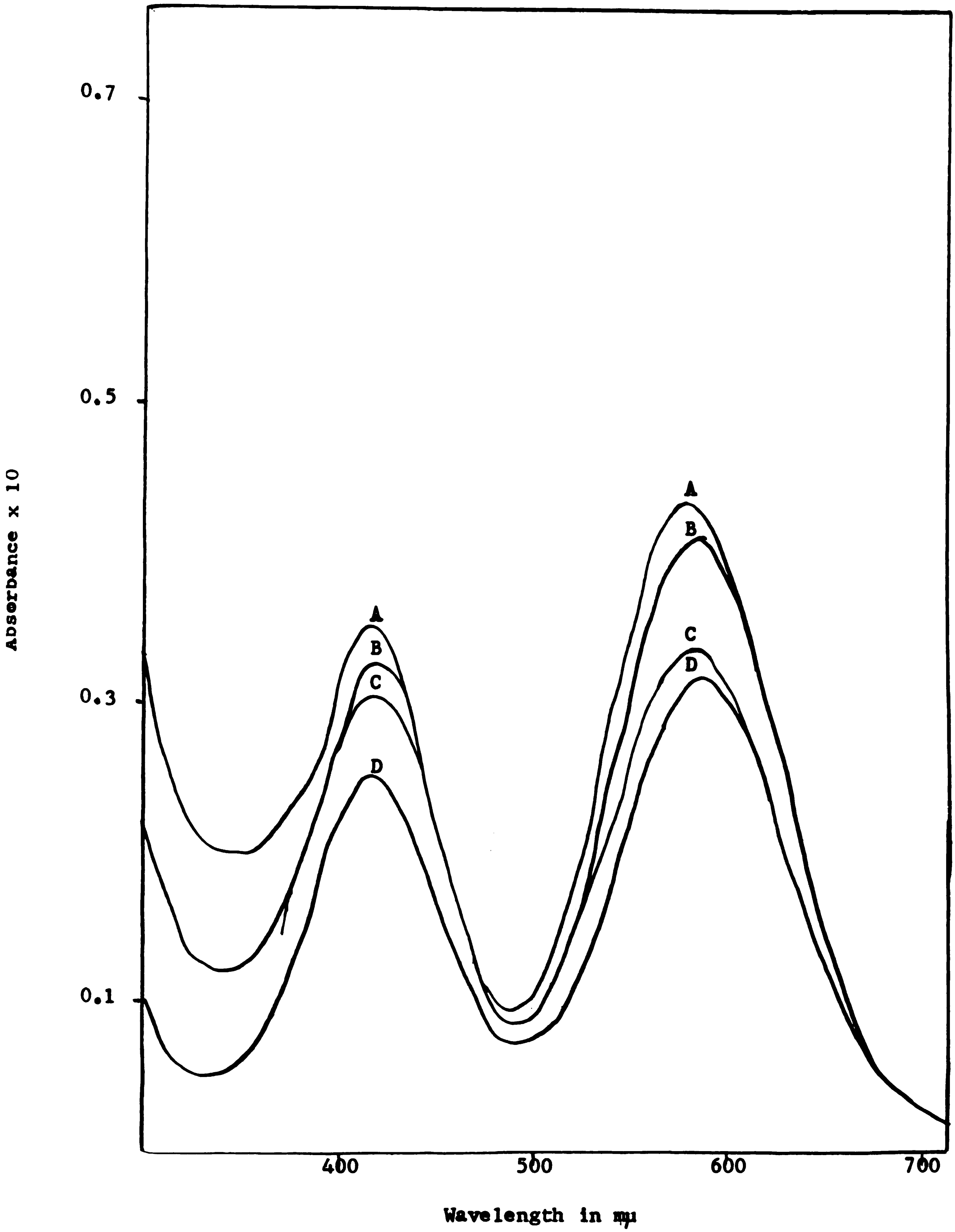


Figure 45. Spectrophotometric study of 2.0 x 10^{-3} $\underline{M}$ $Cr(ClO_4)_3 \cdot 6H_2O$ (C) with: A, 2.0 x 10^{-1} $\underline{M}$ PMT; B, 4.0 x 10^{-2} $\underline{M}$ PMT; D, 4.0 x 10^{-2} $\underline{M}$ PMT + 4.0 x 10^{-2} perchloric acid in formic acid using a 5.0-cm cell.

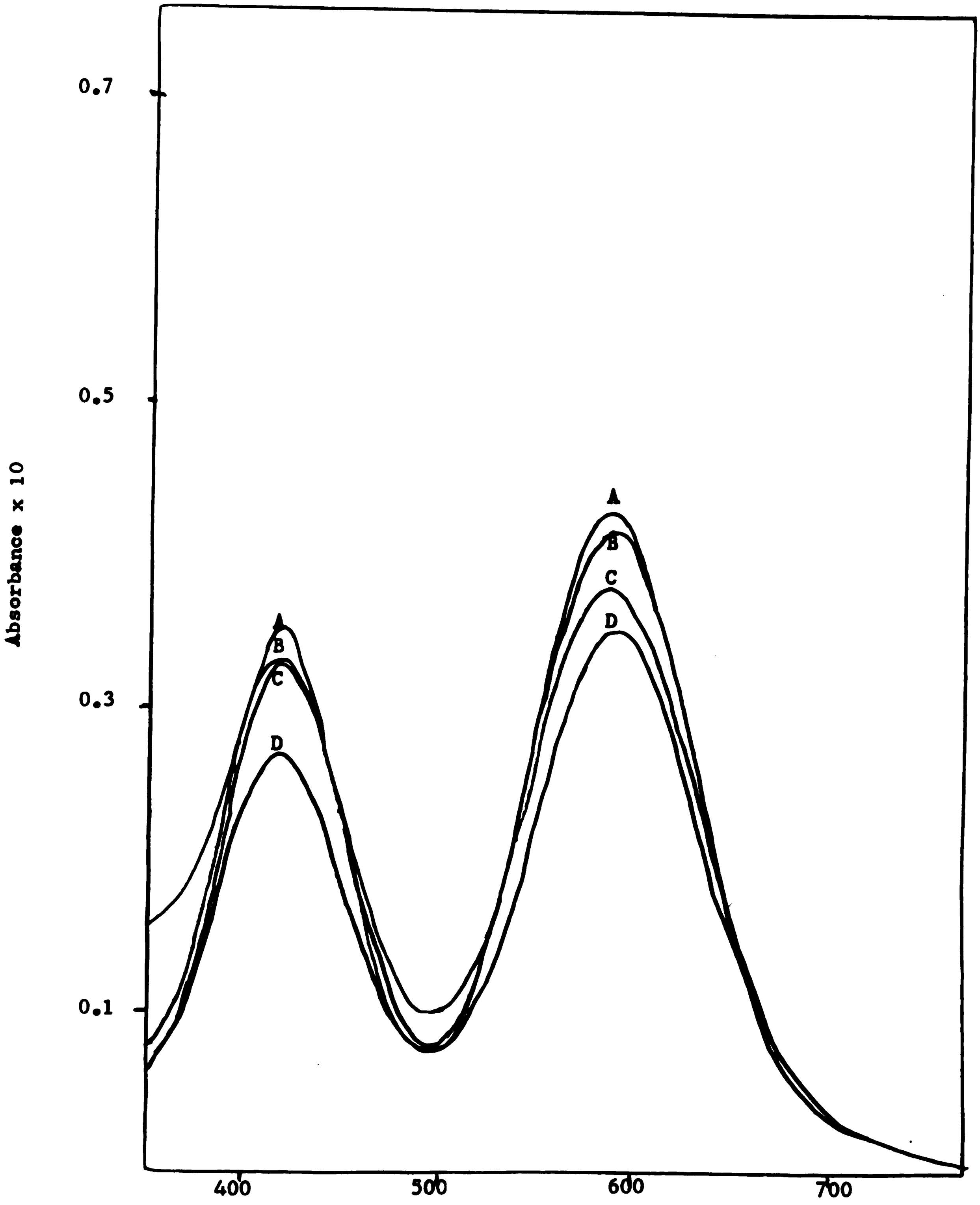


Figure 46. Spectrophotometric study of 2.0 x 10^{-3} M $Cr(ClO_4)_3 \cdot 6H_2O$ (C) with: A, 2.0 x 10^{-1} M sodium formate; B, 4.0 x 10^{-2} M sodium formate; D, 4.0 x 10^{-2} M sodium formate + 4.0 x 10^{-2} M perchloric acid in formic acid using 5-cm cells.

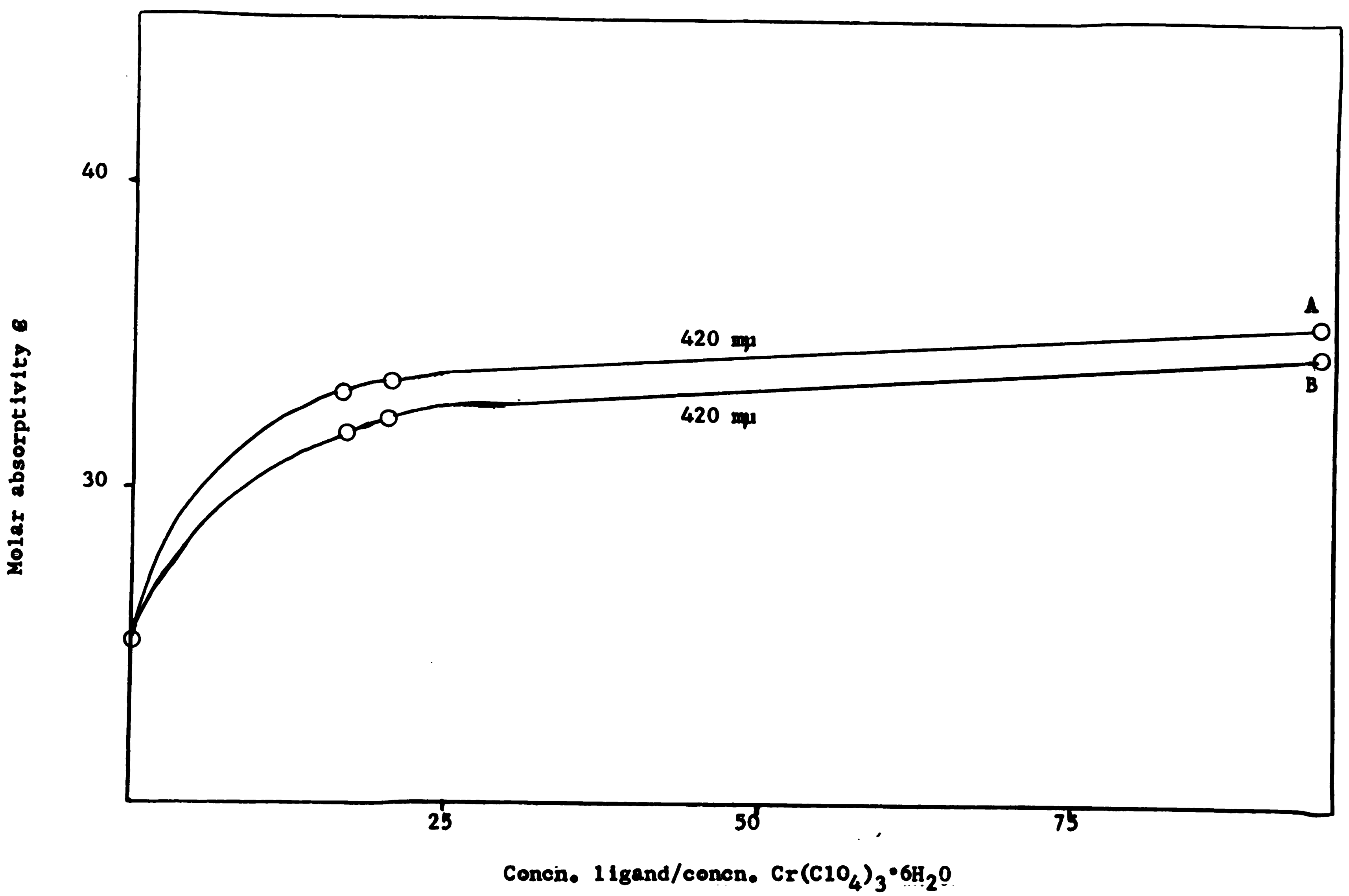


Figure 47. Mole ratio study of A, sodium formate; B, PMT; with chromium(III) perchlorate hexahydrate in formic acid.

complexation as there is in the copper(II) perchlorate hexahydrate systems.

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APPENDIX

COMPUTER PROGRAM

A. Explaination

The Ketelaar method, used for the spectrophotometric study of charge-transfer complexes, involves determination of the slope and intercept of a straight line. This is conveniently done by using the following modified least-squares Fortran computer program.

The data are read into the program in the following manner: Card 1, name card; Card 2, the number of data sets read in; the remaining cards are used for data in the form of donor concentration and corrected total solution absorbance at same wavelength. The output consists of the printed slope, intercept, molar absorptivity, and formation constant of the complex along with their standard deviations.

B. Computer Program

```
    PROGRAM LSTSQRS
    DIMENSION X(50),Y(50),YCALC(50),DEV(50),T(50)
 10 READ11,N,J
 11 FORMAT(212)
    IF(N)12,16,12
 12 READ13,(X(I),Y(I),I=1,N)
 13 FORMAT(F10,4,F7.5)
    READ 500,C
500 FORMAT(F20.10)
    DO 501 I=1,N
501 Y(I)=C/Y(I)
 14 SUMX=0
    SUMY=0
    SUMXY=0
    SUMX2=0
    SUMY2=0
    IF(J)30,30,40
 30 DO31I=1,N
 31 X(I)=1.0/X(I)
 40 DO50I=1,N
    SUMX=SUMX+X(I)
    SUMY=SUMY+Y(I)
    SUMXY=SUMXY+X(I)+Y(I)
    SUMX2=SUMX2+X(I)**2
 50 SUMY2=SUMY2+Y(I)**2
    FN=N
A=(FN*SUMXY-SUMX*SUMY)/(FN*SUMX2-SUMX**2
    B=(SUMY*SUMX2-SUMXY*SUMX)?(FN*SUMX2-SUMX**2
    PRINT60,A,B
 60 FORMAT(1HO,2X,6HSLOPE=,E12,6,5X,10HINTERCEPT=,E12.6)
    XXC=1./B $ XXD=1./S $ PRINT 999,XXD,XXC
999 FORMAT(1HO,*KONSTANT=*,E15.8,15X,*MOLAR ABSORPTIVITY=*,E15,8)
    XXE=XXD/XXC $ PRINT 998,XXE
998 FORMAT(1HO,*CONSTANT=*,E15.8)
```

continued

```
      FRACT=((SUMXY-SUMX*SUMY/FN)**2)/(SUMX2-SUMX**2/FN)
      E=SUMY2-(SUMY**2/FN)-FRACT
      S2=E/(FN-2.0)
      S=SQRTF(S2)
      SA2=S2/(SUMX2-SUMX**2/FN))
      SA=SQRTF(SA2)
      SB2=S2*SUMX2/(FN+SUMX2-SUMX**2)
      SB=SQRTF(SB2)
      PRINT70,S,SA,SB
   70 FORMAT(1H0,2X,22HSTD DEV OF A SINGLE Y=,E14.8,/,
      117HSTD DEV OF SLOPE=,E14.8,/,
      221HSTD DEV OF INTERCEPT=,E14.8)
      S08)I=1,N
   80 YCALC(I)=A*X(I)+B
      DO90I=1,N
      T(I)=ABSF(Y(I)-YCALC(I))
      DEV(I)=T(I)-3.0*S
      IF(DEV(I))90,100,100
   90 CONTINUE
      GO TO 115
  100 PRINT200,Y(I)
  200 FORMAT(1H0,2X,14HREJECTED POINT,5X,E14.8)
      FTN5.11
      M=1
      DO110I=M,N
  110 Y(I)=Y(I+1)
      N=N-1
      TO TO 14
  115 PRINT120,(Y(I),YCALC(I),T(I),(=1,N)
  120 FORMAT(1H0,2X,2HY=,E14.8,4X,6HYCALC=,E1418,4X,2HT=,E14.8)
      GO TO 10
   16 STOP
      END
```