THE PREPARATION AND STUDY OF 4,4'-DIHYDROXYBENZILDIOXIME FOR THE SPECTROPHOTOMETRIC DETERMINATION OF NICKEL II

by

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ABSTRACT

THE PREPARATION AND STUDY OF 4,4'-DIHYDROXYBENZILDIOXIME FOR THE SPECTROPHOTOMETRIC DETERMINATION OF NICKEL II

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This investigation is concerned with the applicability of an organic reagent for the determination of nickel in aqueous solutions. A four-step synthesis was utilized for the preparation of the organic reagent, 4,4'-dihydroxybenzildioxime (DHBD). Para-anisaldehyde was used to prepare anisoin. Anisil, obtained from the anisoin, was used to synthesize 4,4'-dihydroxybenzil which was the precursor to DHBD. Ethanol was selected as the solvent for DHBD and a DHBD-nickel complex was studied.

The optimum wavelength for the complex was 420 nm with the absorbance measurements being made after a twenty minute color development. The effect of water in ethanol was studied as well as the effect of pH in the diluent solution. The DHBD-nickel complex conforms to Beer's Law and the metal to ligand ratio was determined to be 1:1, although a 1:2 ratio was expected. The effect of foreign ions on the absorbance of the DHBD-nickel complex was studied.

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LIST OF SYMBOLS

Symbol	Definition	Units or Reference
$a = A/bc$	absorptivity	see Eq. (5)
b	sample path length	cm
c	concentration of the solute in the sample	g/l
e	base of the natural logarithm	none
k	constant	see Eq. (1)
k'	constant	see Eq. (2)
k''	constant	see Eq. (4)
$A = \log P_o/P$	absorbance of the sample	see Eq. (5)
DHBD	abbreviated form for 4.4'-dihydroxybenzildioxime	none
MW	molecular weight	none
P	intensity of transmitted light	see Eq. (1)
P_o	intensity of incident light	see Eq. (1)
$\varepsilon = A(MW)/bc$	molar absorptivity	see Eq. (6)

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CHAPTER I

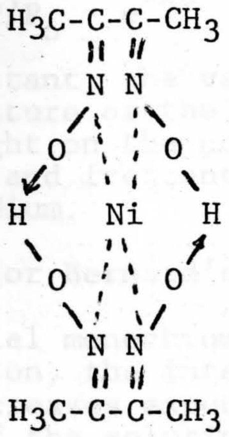
INTRODUCTION

A. Chelating Agents

Organic reagents which are used as chelating agents are characterized by an ability to form covalent bonds with inorganic ions. Another characteristic is the presence of nitrogen, oxygen, or sulfur atoms which have a free pair of electrons.[1] The chelate also has heterocyclic rings which are formed from a metal ion and at least two functional groups in a single ligand or electron-pair donating molecule.[2]

B. Dioxime Compounds

Dioxime compounds have undergone many analytical studies ever since Tschugoeff first used dimethylglyoxime for the gravimetric determination of nickel.[3] Dimethylglyoxime, which is an example of a 1,2-dioxime, is probably the most widely used organic precipitant and is certainly one of the most specific reagents. Dimethylglyoxime forms a chelate with nickel as shown in Figure 1.



STRUCTURE OF NICKEL-DIMETHYLGLYOXIME

Figure 1

Yamasaki and Banks synthesized many dioxime compounds and studied the reactions of their dioxime compounds with metal ions.[4,5] Kuse, Motomizu and Toei have reported that sixteen orthodiketonedioxime compounds showed high sensitivity for nickel and cobalt.[6] They have also reported that nickel chelates of benzildioxime derivatives provide a selective color reaction when extracted into an organic solvent. This gave rise to the use of an extraction-spectrophotometric method for the determination of nickel.[7]

C. Colorimetric Analysis

The importance of colored solutions is that the radiation absorbed is characteristic of the absorbing material.[8] In absorption methods, there are two fundamental laws. One is Lambert's (or Bouguer's) Law which states:

> In a homogeneous sample, the intensity of plane-parallel monochromatic light entering a sample normal to the surface is diminished exponentially as the path length of absorption increases arithmetically:

$$P/P_o = e^{-kb} \quad (1)$$

> where k is a constant, the value of which depends on the nature of the solute, on the wavelength of light, on the concentration of the solution, and frequently on the nature of the medium.

The other law is Beer's (or Bernard's) Law which states:

> When parallel monochromatic light passes through a solution, the intensity of the transmitted light decreases exponentially as the concentration of the solution increases arithmetically:
>
> $$P/P_o = e^{-k'c} \quad (2)$$
>
> where k' is a constant, the value of which depends on the nature of the solute, on the wavelength of the light, on the length of the absorbing layer, and on the nature of the medium.[9]

Equation (2) can be rewritten as

$$\ln P/P_o = -k'c \quad (3)$$

However, a more useful measure is the product of concentration and the path length so that

$$\ln P/P_o = -k''bc \quad (4)$$

By replacing k" with another constant, a, which includes a conversion factor for changing natural logarithms to common logarithms we have

$$\log P_o/P = A = abc \quad (5)$$

P_o/P has been inverted to remove the negative sign and the quantity $\log P_o/P$ has been given the symbol A and is called the absorbance. Equation (5) is commonly referred to as Beer's Law.

The absorptivity is characteristic of a particular combination of solute and solvent for a given wavelength. Its units are dependent upon the units chosen for pathlength and concentration.[10] Generally, the pathlength is expressed in centimeters and the concentration is expressed in grams per liter. When the concentration is expressed in molar units, the symbol ε is used in place of a and it is called the molar absorptivity.[11] Absorbance is an extensive property while absorptivity is an intensive property.

Beer's Law implies that the absorptivity is a constant that is not dependent upon the concentration of the absorbing species, the pathlength or the intensity of incident radiation. The law does not provide for the effect of temperature, wavelength or solvent nature. However, the temperature has been found to have only minor effects, unless varied over an unusually wide range. It has been found, even in a specified solvent at a constant temperature, that the absorptivity may vary. Deviations from the law are designated as positive or negative depending on whether the observed curve, when the absorbance is plotted as a function of concentration, is concave upward or concave downward. According to the prediction of equation (5), a straight line should intersect the origin if the absorbance is plotted as a function of the concentration of the absorbing species.[12]

D. Other Methods of Nickel Determinations

Nickel can also be determined by other methods. S. Vaeck has determined nickel concentrations in microgram quantities using paper chromatography.[13] A mercury cathode can be used for the electrolytic deposition of nickel from an acid solution.[14] Emission spectroscopy and atomic absorption spectroscopy are also used for nickel determinations.[15,16]

E. Statement of the Problem

While all of the above methods for determining nickel have their specific merits, they all have one of two common faults associated with them for the small industrial laboratory. The problems arise due to the cost of the instruments required or due to the amount of time required for the analysis. This investigation was undertaken to find a rapid and inexpensive method for determining nickel concentrations in aqueous solutions. A benzildioxime derivative that was not investigated by Kuse was selected as a possible complexing reagent for nickel because of the solubility of the nickel derivative in ethanol. The complexing reagent used, 4,4'-dihydroxybenzildioxime (DHBD), was prepared using a four-step procedure. The DHBD was then characterized and investigated for use as a complexing reagent for the analytical determination of nickel.

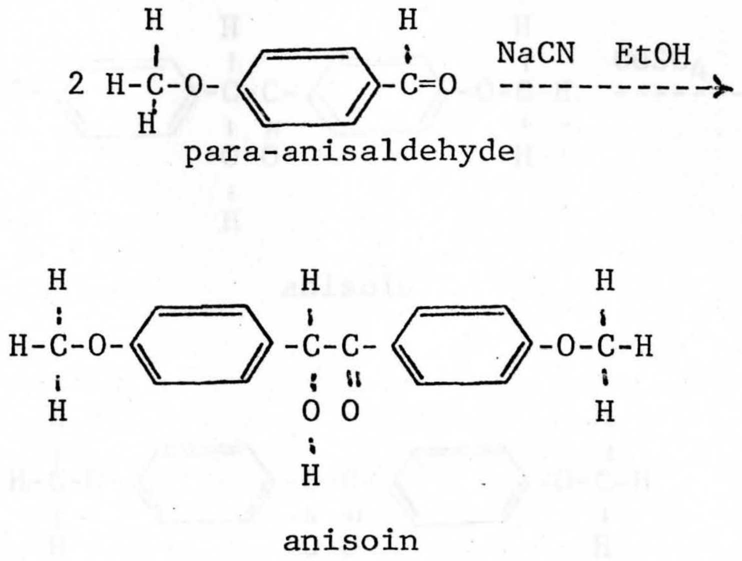
CHAPTER II

SYNTHESIS OF DHBD

A. Anisoin from Para-anisaldehyde

The synthesis of anisoin from para-anisaldehyde was performed according to the method of Dewar and Read.[17] A mixture, consisting of 120 g (0.88 moles) of para-anisaldehyde, 160 ml of absolute ethanol, 100 ml of distilled water and 20 g (0.41 moles) of sodium cyanide, was refluxed for two hours. An additional 20 g (0.41 moles) of sodium cyanide were added to the mixture and refluxing was continued for another two hours. The hot mixture was transferred to a 600-ml beaker and cooled in an ice bath for three hours and then placed in a refrigerator at 1°C for sixteen hours. The yellow crystaline precipitate that formed on cooling was filtered and washed with cold distilled water. The precipitate was recrystallized from boiling absolute ethanol.

The procedure was performed in duplicate and the yields were 28.2 g and 28.3 g of anisoin. This produced a percent yield of 23.5 and 23.7 percent respectively. The anisoin had a melting point of 109°C. The literature value for the melting point of anisoin is 113°C.[18] This reaction is shown in equation (6).



(6)

B. Anisil from Anisoin

The method outlined in Gilman and Broadbent was followed.[19] Anisil was synthesized from a mixture of 10g (36.7 mmoles) of anisoin, 30 g (120 mmoles) of copper sulfate pentahydrate, 30 ml of distilled water and 45 g (569 mmoles) of pyridine. The mixture was refluxed, with stirring, for twenty-four hours. The solution was then transferred to a 400-ml beaker and cooled in a refrigerator at 1°C for three hours. The bright yellow crystals that precipitated were filtered and washed with cold distilled water. The precipitate was recrystallized from boiling ethanol. The synthesis was performed in duplicate which produced yields of 93.7 and 100 percent. The melting point of anisil was 131.5°C and the literature value is 133°C.[20] This reaction is shown in equation (7).

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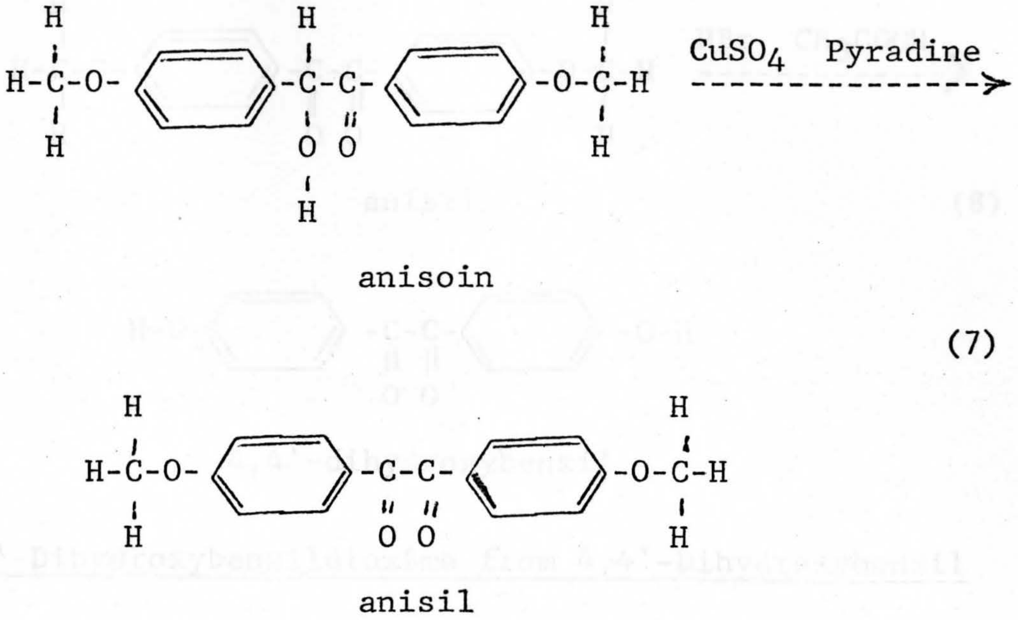
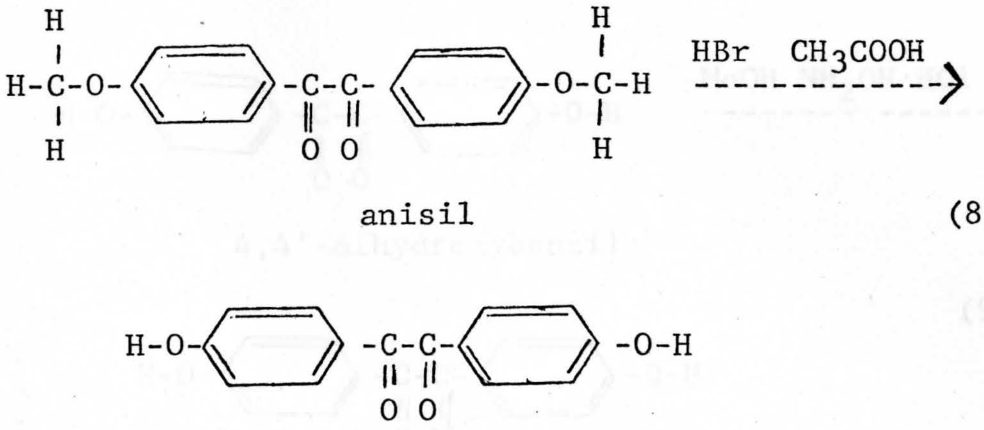


(7)

C. 4,4'-Dihydroxybenzil from Anisil

The method outlined in Leonard[21] was used as a guide in the preparation of 4,4'-dihydroxybenzil. A mixture of 6.2 g (22.9 mmoles) of anisil, 50 ml of 48 percent hydrobromic acid and 50 ml of glacial acetic acid was refluxed for twenty hours. The solution was transferred to a 250-ml beaker and cooled in an ice bath for one hour. The precipitate of pale yellow needles was washed with cold distilled water until the washings were no longer acidic. The precipitate was recrystallized from boiling distilled water. The synthesis was performed in duplicate which produced yields of 63.0 and 87.5 percent. The melting point was 246.5°C. The literature value for the melting point is 244-246°C.[22] This reaction is shown in equation (8).

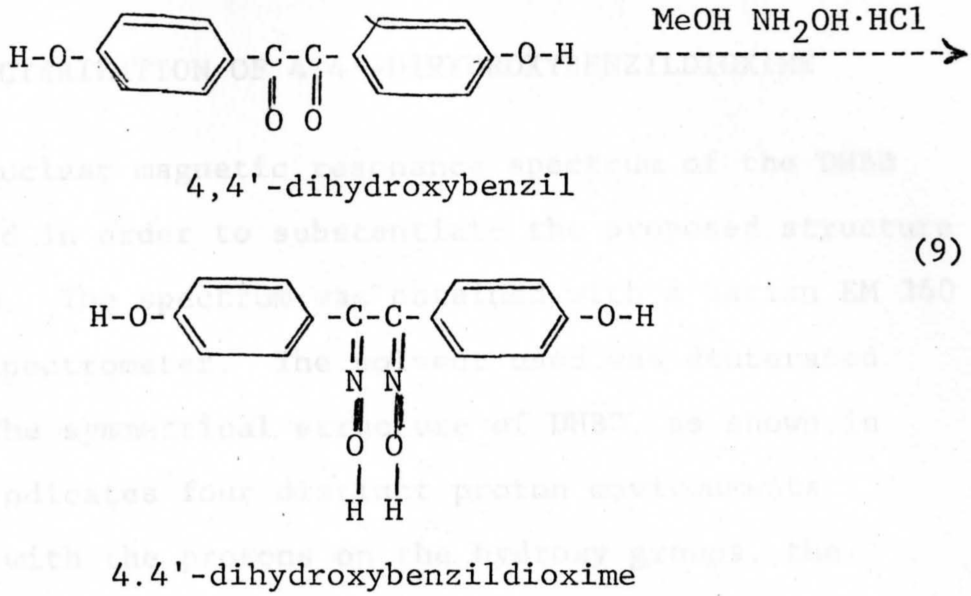


anisil (8)

4,4'-dihydroxybenzil

D. 4,4'-Dihydroxybenzildioxime from 4,4'-Dihydroxybenzil

The method described by Dobbelstein was used as a guide in the oximation of 4,4'-dihydroxybenzil.[23] A mixture of 2.0 g (8.26 mmoles) of 4,4'-dihydroxybenzil, 3.0 g (43.2 mmoles) of hydroxylamine hydrochloride and 100 ml of methanol was refluxed for twenty-two hours. The hot mixture was transferred into a 400-ml beaker and the methanol was evaporated until a final volume of 25 ml was obtained. To this, 200 ml of distilled water was added and the pH was adjusted to 7.0 with 2 M sodium hydroxide. The solution was cooled in a refrigerator at 1°C for three hours. The precipitate was filtered and washed with cold distilled water. A dark brown powder was obtained and the yield was 22.2 percent. The melting point was 242°C. The reaction is shown in equation (9).


MeOH $NH_2OH \cdot HCl$

4,4'-dihydroxybenzil

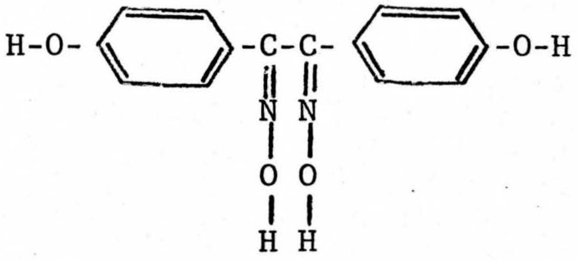
(9)

4.4'-dihydroxybenzildioxime

CHAPTER III

CHARACTERIZATION OF 4,4'-DIHYDROXYBENZILDIOXIME

A nuclear magnetic resonance spectrum of the DHBD was obtained in order to substantiate the proposed structure of the DHBD. The spectrum was obtained with a Varian EM 360 60MHz NMR Spectrometer. The solvent used was deuterated acetone. The symmetrical structure of DHBD, as shown in Figure 2, indicates four distinct proton environments associated with the protons on the hydroxy groups, the oxime groups and the two benzene rings.



Structure of DHBD

Figure 2

The NMR spectrum depicted in Figure 3 shows four distinct proton environments. The sharp singlet produced at 2.01 ppm was determined to be a solvent peak. There was a sharp singlet at 3.77 ppm which is probably produced by the hydroxy groups attached to the benzene rings. A doublet at 6.92 ppm and a doublet at 7.81 ppm indicates two benzene rings with a typical A2B2 pattern on each. The peak associated with the oxime protons appeared at 7.39 ppm.

The chemical shifts and peak integrals are consistent with the proposed symmetrical structure of the molecule.

NMR SPECTRUM OF DHBD

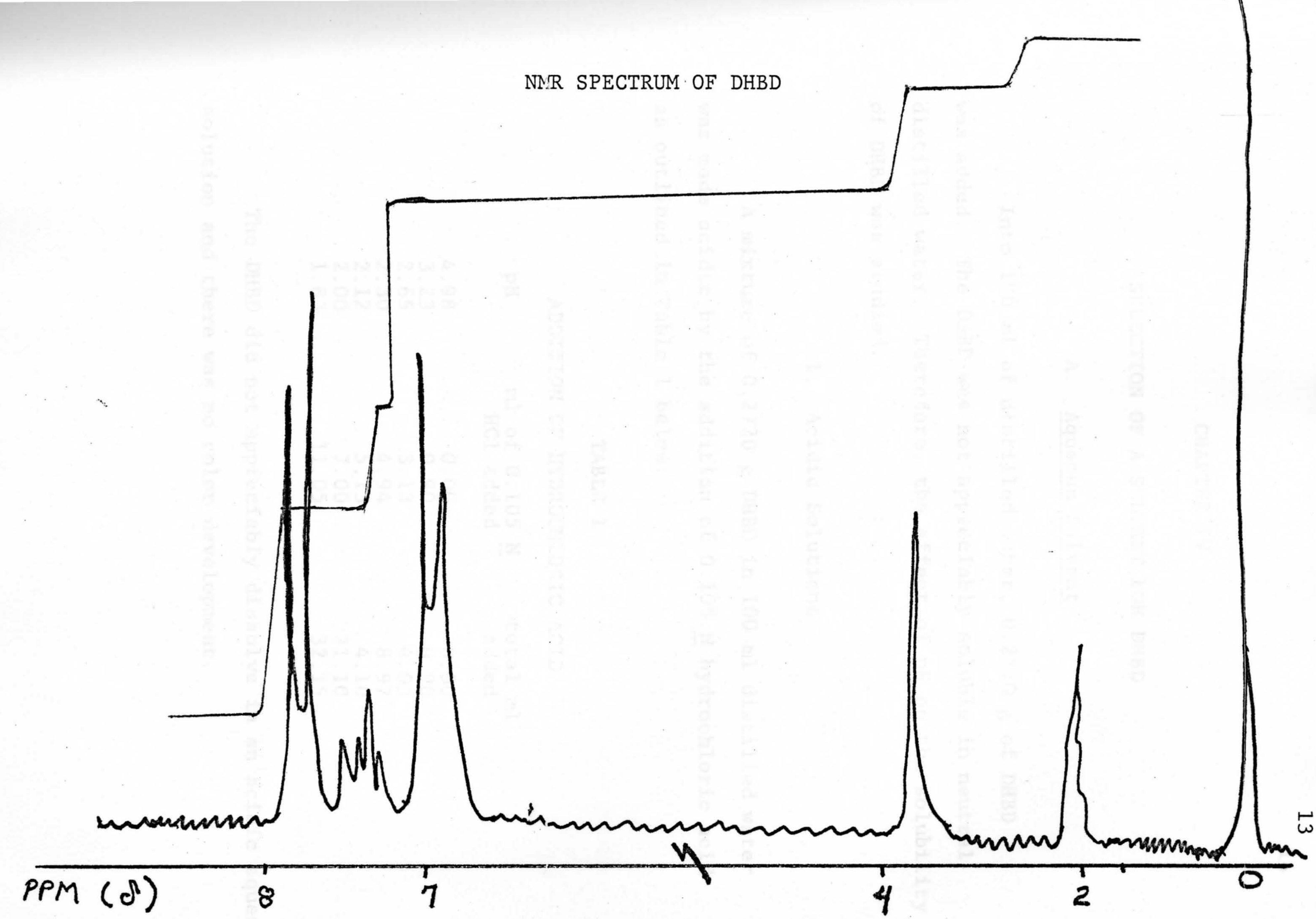


Figure 3

CHAPTER IV

SELECTION OF A SOLVENT FOR DHBD

A. Aqueous Solvent

Into 100 ml of distilled water, 0.2720 g of DHBD was added. The DHBD was not appreciably soluble in neutral distilled water. Therefore, the effect of pH on the solubility of DHBD was studied.

1. Acidic Solutions

A mixture of 0.2720 g DHBD in 100 ml distilled water was made acidic by the addition of 0.105 N hydrochloric acid as outlined in Table 1 below:

TABLE 1

ADDITION OF HYDROCHLORIC ACID

pH	ml of 0.105 N HCl added	total ml added
4.98	0.00	0.00
3.23	0.90	0.90
2.65	3.13	4.03
2.30	4.94	8.97
2.12	5.13	4.10
2.00	7.00	21.10
1.83	11.05	32.15

The DHBD did not appreciably dissolve in an acidic aqueous solution and there was no color development.

2. Basic Solution

The acidic DHBD in water mixture was made basic by the addition of 0.134 N sodium hydroxide as outlined in Table 2 below:

TABLE 2

ADDITION OF SODIUM HYDROXIDE

pH	ml of 0.134 N NaOH added	total ml added
1.83	0.00	0.00
2.00	5.35	5.35
2.15	6.50	11.85
2.40	6.05	17.90
7.65	8.05	25.95
8.85	3.80	29.75
9.50	4.65	34.40
10.55	3.60	38.00
11.15	3.90	41.90

The DHBD was only slightly soluble in a basic aqueous solution at a pH greater than 10. The solution had a faint yellowish color.

B. Organic Solvents

Various organic solutions were tried as a suitable solvent for DHBD. DHBD was soluble in ethanol, methanol and acetone. DHBD was insoluble in chloroform, carbon tetrachloride and isopropyl ether. All of the remaining work was carried out with ethanol as the solvent. This selection was based upon the lower cost of ethanol and the availability of ethanol in the laboratory.

Moreover, ethanol was used as the solvent for thirteen dioximes studied by Kuse.[24] In addition, ethanol was used as a solvent for alpha benzildioxime as described by Scott and ethanol was also used as a solvent for dimethylglyoxime which was described by Fischer.[25,26]

CHAPTER V

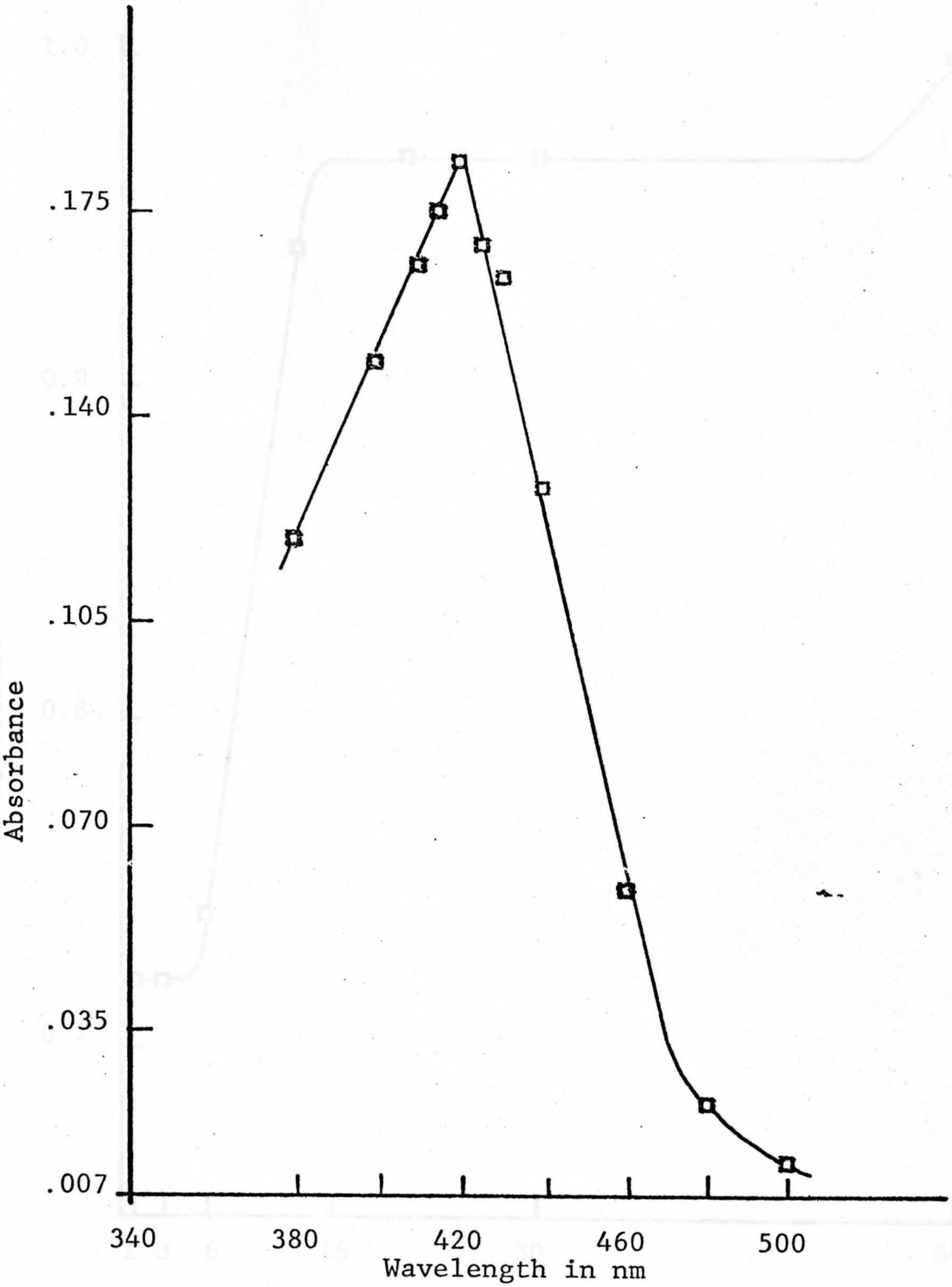
FACTORS AFFECTING ABSORPTIVITY

A. Wavelength Selection

A solution of 1×10^{-3} M nickel nitrate was prepared with distilled water and a 1×10^{-3} M solution of DHBD was prepared with ethanol. A 1.00-ml sample of the nickel solution and a 3.00-ml sample of the DHBD solution were pipetted into a 25-ml volumetric flask and diluted with ethanol. A yellow color developed and after 30 minutes, the absorbance was measured using a Bausch and Lomb Spectronic 20. The reference solution was 1×10^{-3} M DHBD in ethanol. The absorbance was plotted as a function of the wavelength as shown in Figure 4. The optimum wavelength is 420 nm and all subsequent investigations were performed at this wavelength.

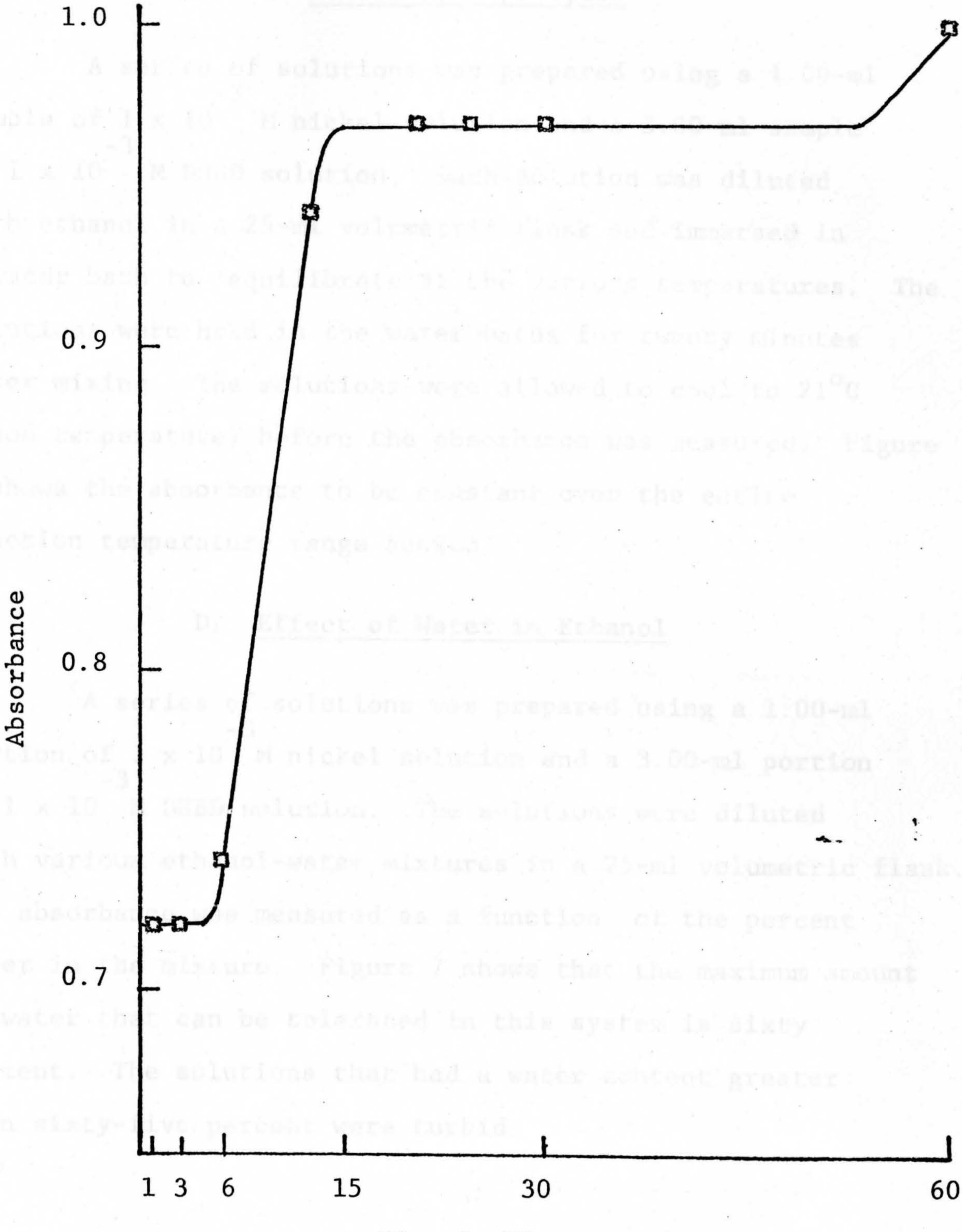
B. Reaction Time

The absorbance was measured as a function of elapsed time after mixing. A 2.00-ml sample of 1×10^{-3} M nickel solution and a 4.00-ml sample of 1×10^{-3} M DHBD solution were pipetted into a 25-ml volumetric flask and diluted with ethanol. As can be seen from Figure 5, a minimum of fifteen minutes must elapse after mixing in order to achieve a stable absorbance reading. Also, the reading must be taken prior to a sixty minute time lapse. All subsequent measurements were made with a twenty minute time lapse after mixing.



Absorbance as a function of wavelength

FIGURE 4



Absorbance as a Function of Elapsed Time After Mixing

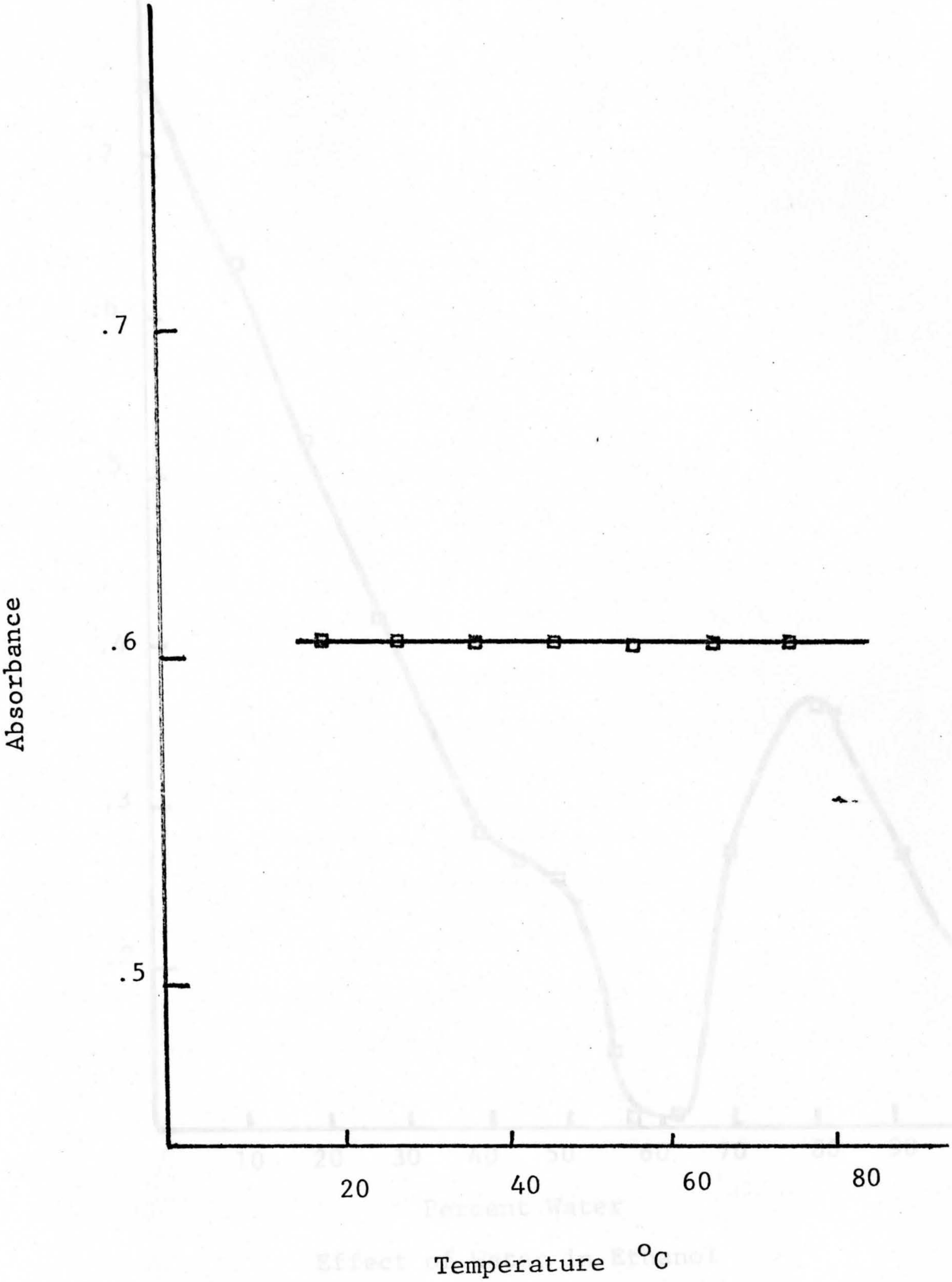
FIGURE 5

C. Reaction Temperature

A series of solutions was prepared using a 1.00-ml sample of 1 x 10^{-3} M nickel solution and a 3.00-ml sample of 1 x 10^{-3} M DHBD solution. Each solution was diluted with ethanol in a 25-ml volumetric flask and immersed in a water bath to equilibrate at the various temperatures. The solutions were held in the water baths for twenty minutes after mixing. The solutions were allowed to cool to 21°C (room temperature) before the absorbance was measured. Figure 6 shows the absorbance to be constant over the entire reaction temperature range tested.

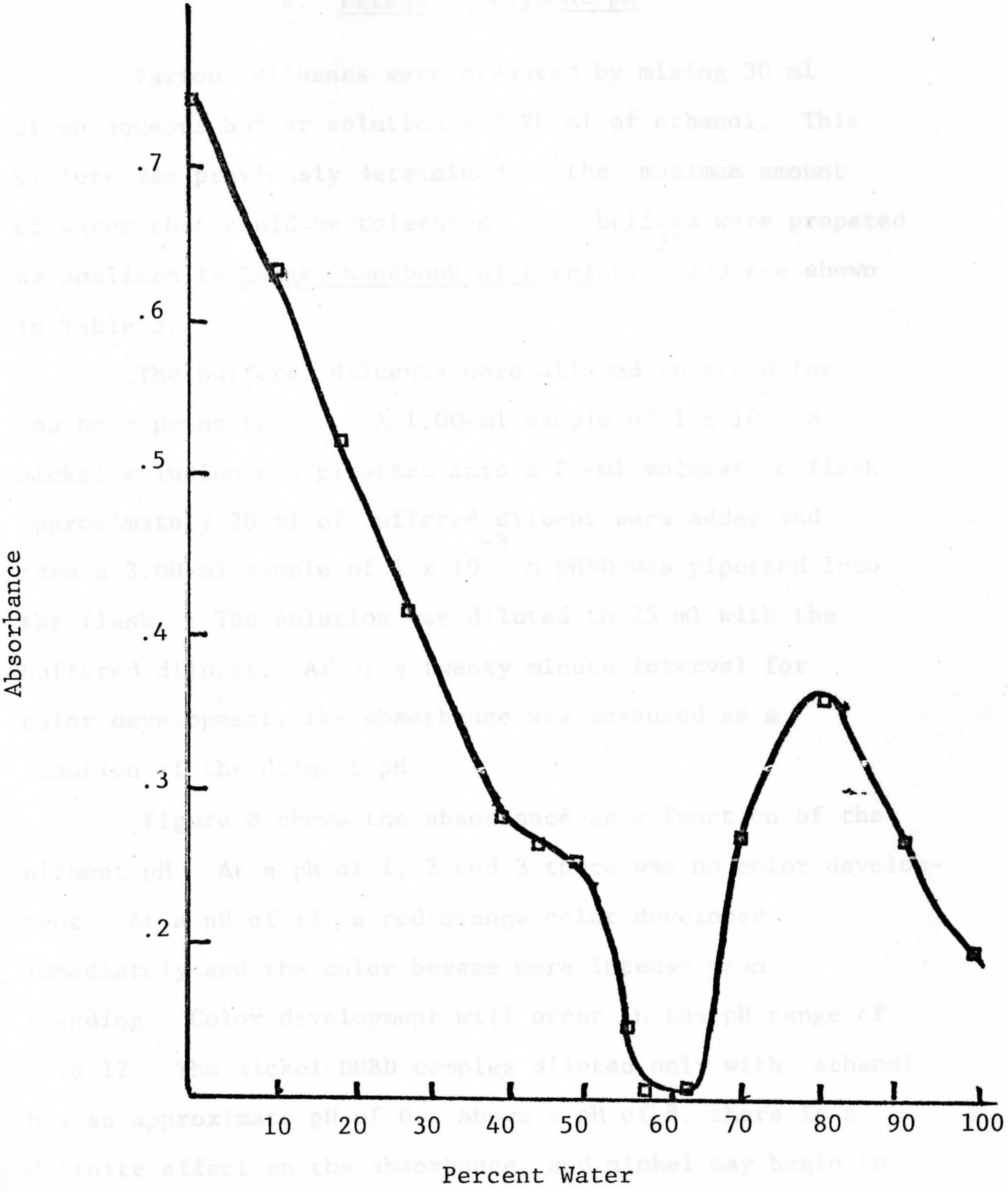
D. Effect of Water in Ethanol

A series of solutions was prepared using a 1.00-ml portion of 1 x 10^{-3} M nickel solution and a 3.00-ml portion of 1 x 10^{-3} M DHBD solution. The solutions were diluted with various ethanol-water mixtures in a 25-ml volumetric flask. The absorbance was measured as a function of the percent water in the mixture. Figure 7 shows that the maximum amount of water that can be tolerated in this system is sixty percent. The solutions that had a water content greater than sixty-five percent were turbid.



Absorbance as a Function of Reaction Temperature

FIGURE 6



Effect of Water in Ethanol

FIGURE 7

E. Effect of Diluent pH

Various diluents were prepared by mixing 30 ml of an aqueous buffer solution and 20 ml of ethanol. This mixture was previously determined as the maximum amount of water that could be tolerated. The buffers were prepared as outlined in Lange's Handbook of Chemistry[27] and are shown in Table 3.

The buffered diluents were allowed to stand for one hour prior to use. A 1.00-ml sample of 1×10^{-3} M nickel solution was pipetted into a 25-ml volumetric flask. Approximately 20 ml of buffered diluent were added and then a 3.00-ml sample of 1×10^{-3} M DHBD was pipetted into the flask. The solution was diluted to 25 ml with the buffered diluent. After a twenty minute interval for color development, the absorbance was measured as a function of the diluent pH.

Figure 8 shows the absorbance as a function of the diluent pH. At a pH of 1, 2 and 3 there was no color development. At a pH of 13, a red-orange color developed immediately and the color became more intense upon standing. Color development will occur in the pH range of 4 to 12. The nickel-DHBD complex diluted only with ethanol has an approximate pH of 6. Above a pH of 8, there is a definite effect on the absorbance, and nickel may begin to precipitate.

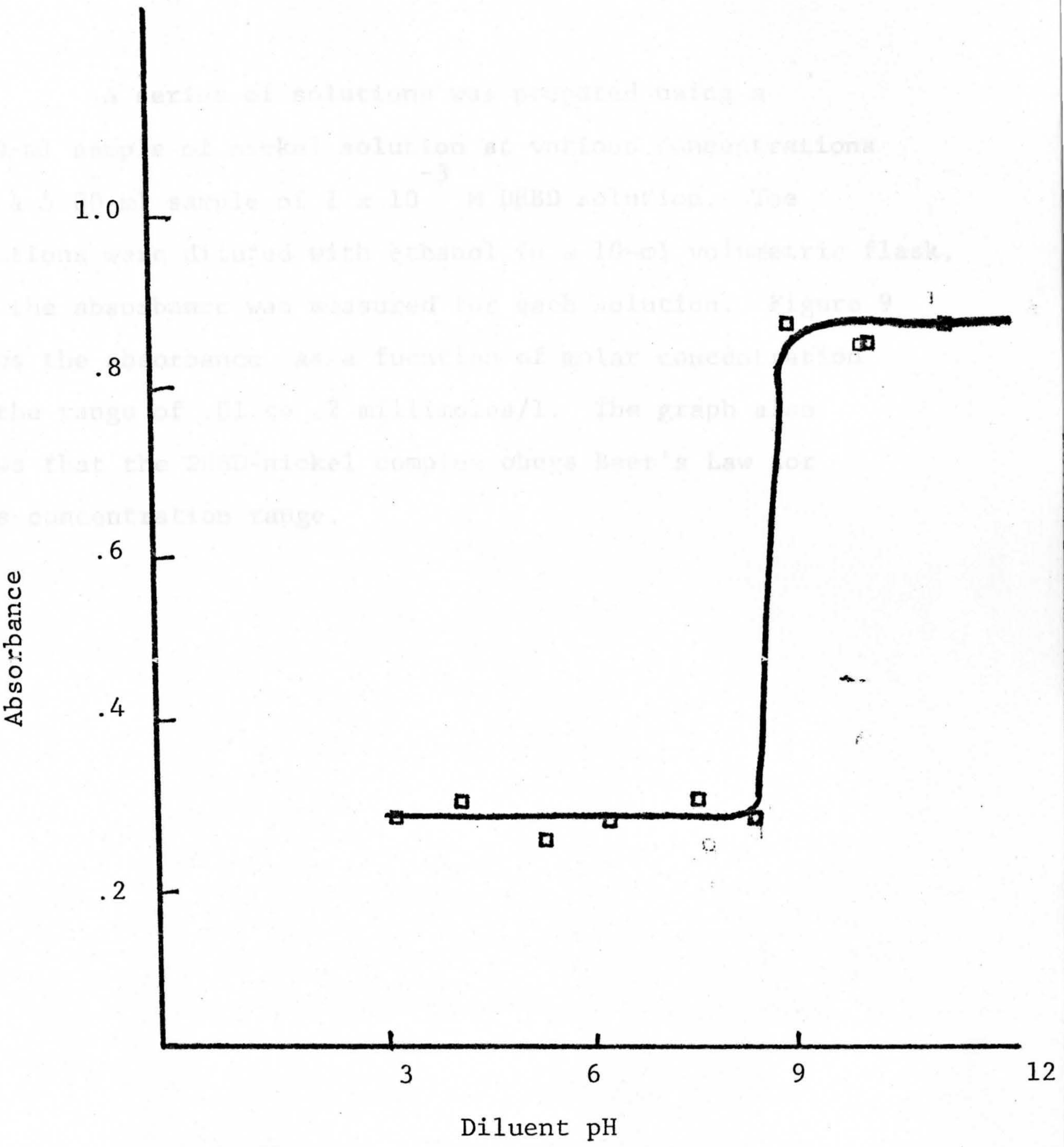
When using DHBD for nickel determinations, all standard solutions and unknown solutions must be in the pH range of 4 to 7 in order to avoid a pH effect on the absorbance.

TABLE 3

Buffer Solutions

Literature pH	Reagents Used			Actual pH
1.00	25 ml 0.20 M KCl	+	67.00 ml 0.20 M HCl	0.91
2.00	25 ml 0.20 M KCl	+	6.50 ml 0.20 M HCl	1.95
3.00	50 ml 0.10 M KHP	+	22.30 ml 0.10 M HCl	2.94
4.00	50 ml 0.10 M KHP	+	2.95 ml 0.10 M NaOH	4.01
5.00	50 ml 0.10 M KHP	+	22.60 ml 0.10 M NaOH	5.02
6.00	50 ml 0.10 M $Na_2C_4H_4O_6.2H_2O$	+	0.20 ml 0.20 M HCl	5.99
7.00	50 ml 0.10 M $Na_2C_4H_4O_6.2H_2O$	+	0.10 ml 0.10 M NaOH	7.02
8.00	50 ml 0.10 M $Na_2C_4H_4O_6.2H_2O$	+	0.60 ml 0.10 m NaOH	8.08
9.00	50 ml 0.05 M $NaHCO_3$	+	1.00 ml 0.10 M NaOH	8.91
10.00	50 ml 0.05 M $NaHCO_3$	+	10.70 ml 0.10 M NaOH	9.99
11.00	50 ml 0.05 M $NaHCO_3$	+	23.00 ml 0.10 M NaOH	10.88
12.00	25 ml 0.20 M KCl	+	12.00 ml 0.10 M NaOH	12.10
13.00	25 ml 0.20 M KCl	+	24.38 ml 0.54 M NaOH	13.10

All solutions were diluted to 100 ml



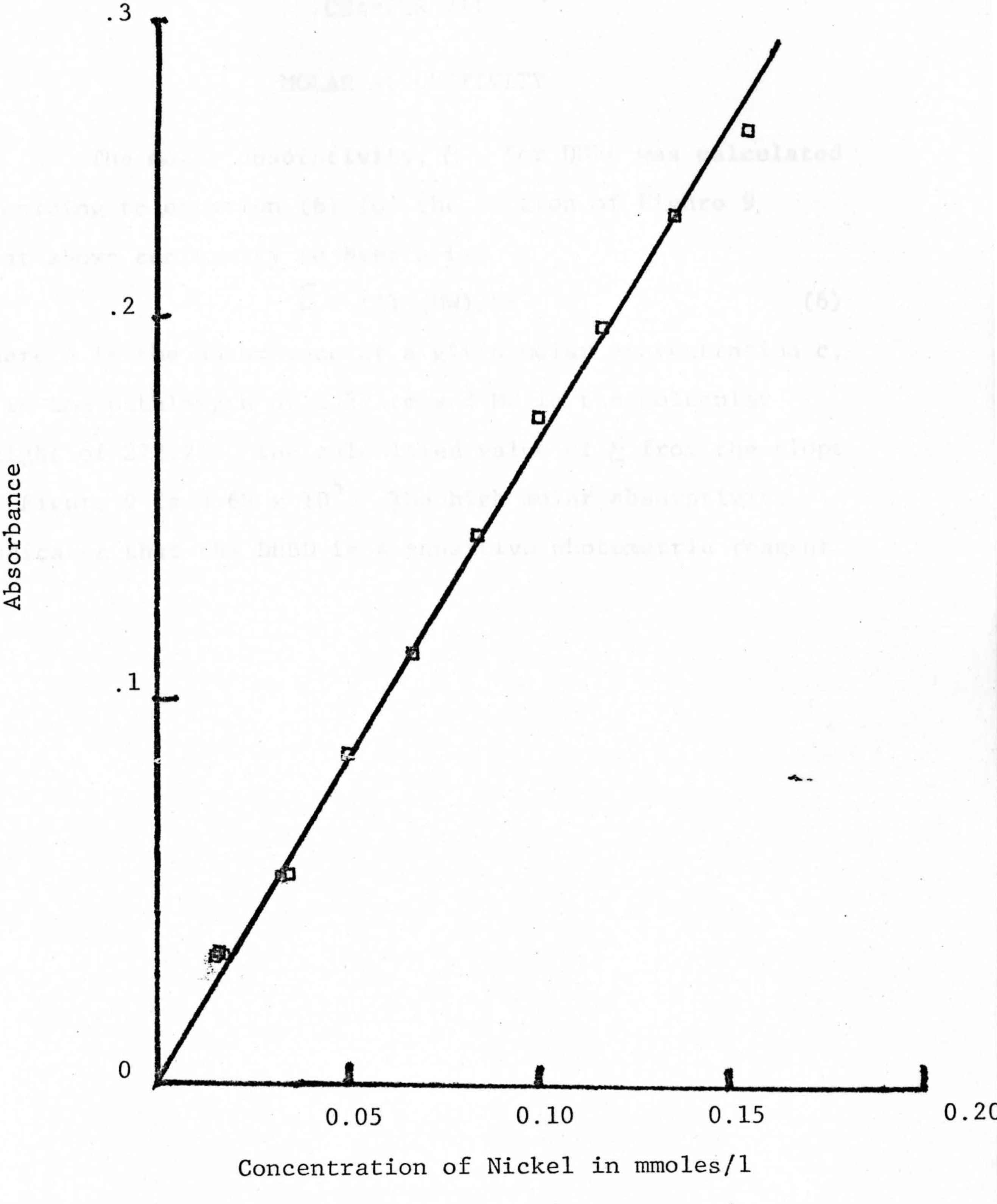
Absorbance as a Function of Diluent pH

FIGURE 8

CHAPTER VI

CONFORMITY TO BEER'S LAW

A series of solutions was prepared using a 1.00-ml sample of nickel solution at various concentrations and a 5.00-ml sample of 1 x 10^{-3} M DHBD solution. The solutions were diluted with ethanol in a 10-ml volumetric flask, and the absorbance was measured for each solution. Figure 9 shows the absorbance as a fucntion of molar concentration in the range of .01 to .2 millimoles/l. The graph also shows that the DHBD-nickel complex obeys Beer's Law for this concentration range.



Absorbance as a Function of Concentration

FIGURE 9

CHAPTER VII

MOLAR ABSORPTIVITY

The molar absorptivity, ε, for DHBD was calculated according to equation (6) for the section of Figure 9 that shows conformity to Beer's Law

$$\varepsilon = (A)\ (MW)/bc \qquad (6)$$

where A is the absorbance at a given molar concentration c, b is the pathlength of 1.27 cm and MW is the molecular weight of 272.26. The calculated value of ε from the slope of Figure 9 is 3.68×10^5. The high molar absorptivity indicates that the DHBD is a sensitive photometric reagent.

CHAPTER VIII

METAL-LIGAND RATIO

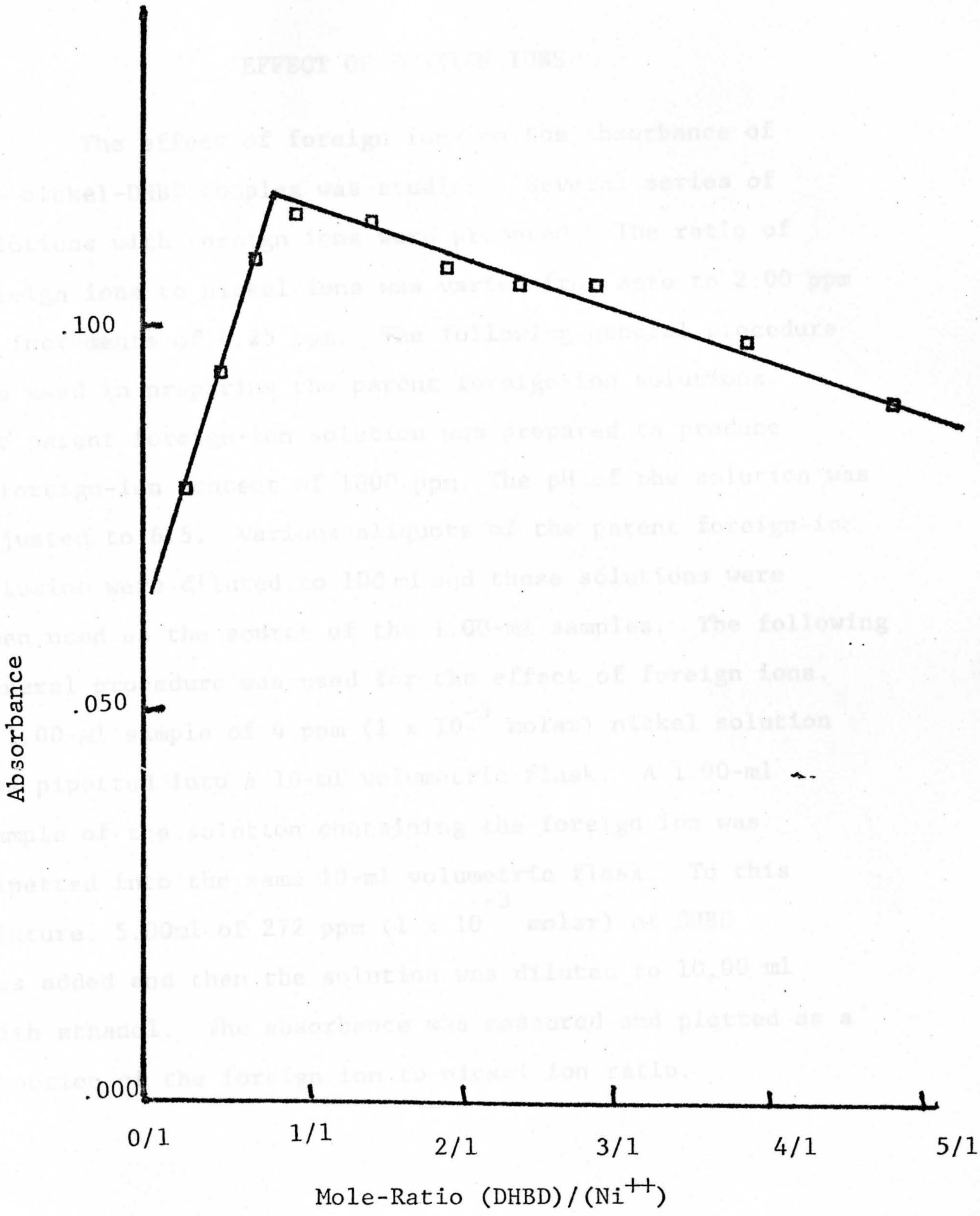
The molar ratio of metal to ligand can be determined by the mole ratio method.[28] A series of solutions was prepared with a constant amount of complexing reagent and varying amounts of the metal ion. The complexing reagent was held constant at 2.00 ml of 1 x 10^{-3} M DHBD. The amount of nickel was varied as outlined in Table 4 and the solution was diluted to 25 ml with ethanol.

TABLE 4

MOLE RATIO METHOD

ml of 1 x 10^{-3} M DHBD	ml of 1 x 10^{-3} M Ni^{++}	$\frac{(DHBD)}{(Ni^{++})}$	A
2.00	8.00	0.25	.079
2.00	4.00	0.50	.094
2.00	2.66	0.75	.109
2.00	2.00	1.00	.112
2.00	1.33	1.50	.111
2.00	1.00	2.00	.105
2.00	0.80	2.50	.103
2.00	0.66	3.00	.103
2.00	0.50	4.00	.096
2.00	0.40	5.00	.087

The absorbance is plotted as a function of the mole ratio of DHBD to nickel. As can be seen in Figure 8, the metal to ligand ratio has been determined to be one mole of nickel to one mole of DHBD. The anticipated metal to ligand ratio was 1:2 based upon the study reported by Kuse and his co-workers on their ortho-diketonedioxime compounds.[29] Repeated mole-ratio studies of the metal to ligand ratio for the nickel-DHBD complex substantiated the 1:1 ratio. The plot does not go through the origin because the aqueous nickel nitrate-ethanol solution has an appreciable absorbance relative to the ethanol-DHBD reference solution.



Absorbance as a Function of Mole-Ratio of DHBD to Nickel

FIGURE 10

CHAPTER IX

EFFECT OF FOREIGN IONS

The effect of foreign ions on the absorbance of the nickel-DHBD complex was studied. Several series of solutions with foreign ions were prepared. The ratio of foreign ions to nickel ions was varied from zero to 2.00 ppm in increments of 0.25 ppm. The following general procedure was used in preparing the parent foreign-ion solutions. The parent foreign-ion solution was prepared to produce a foreign-ion content of 1000 ppm. The pH of the solution was adjusted to 6.5. Various aliquots of the parent foreign-ion solution were diluted to 100 ml and these solutions were then used as the source of the 1.00-ml samples. The following general procedure was used for the effect of foreign ions. A 1.00-ml sample of 4 ppm (1 x 10^{-5} molar) nickel solution was pipetted into a 10-ml volumetric flask. A 1.00-ml sample of the solution containing the foreign ion was pipetted into the same 10-ml volumetric flask. To this mixture, 5.00ml of 272 ppm (1 x 10^{-3} molar) of DHBD was added and then the solution was diluted to 10.00 ml with ethanol. The absorbance was measured and plotted as a function of the foreign ion to nickel ion ratio.

A. Manganese

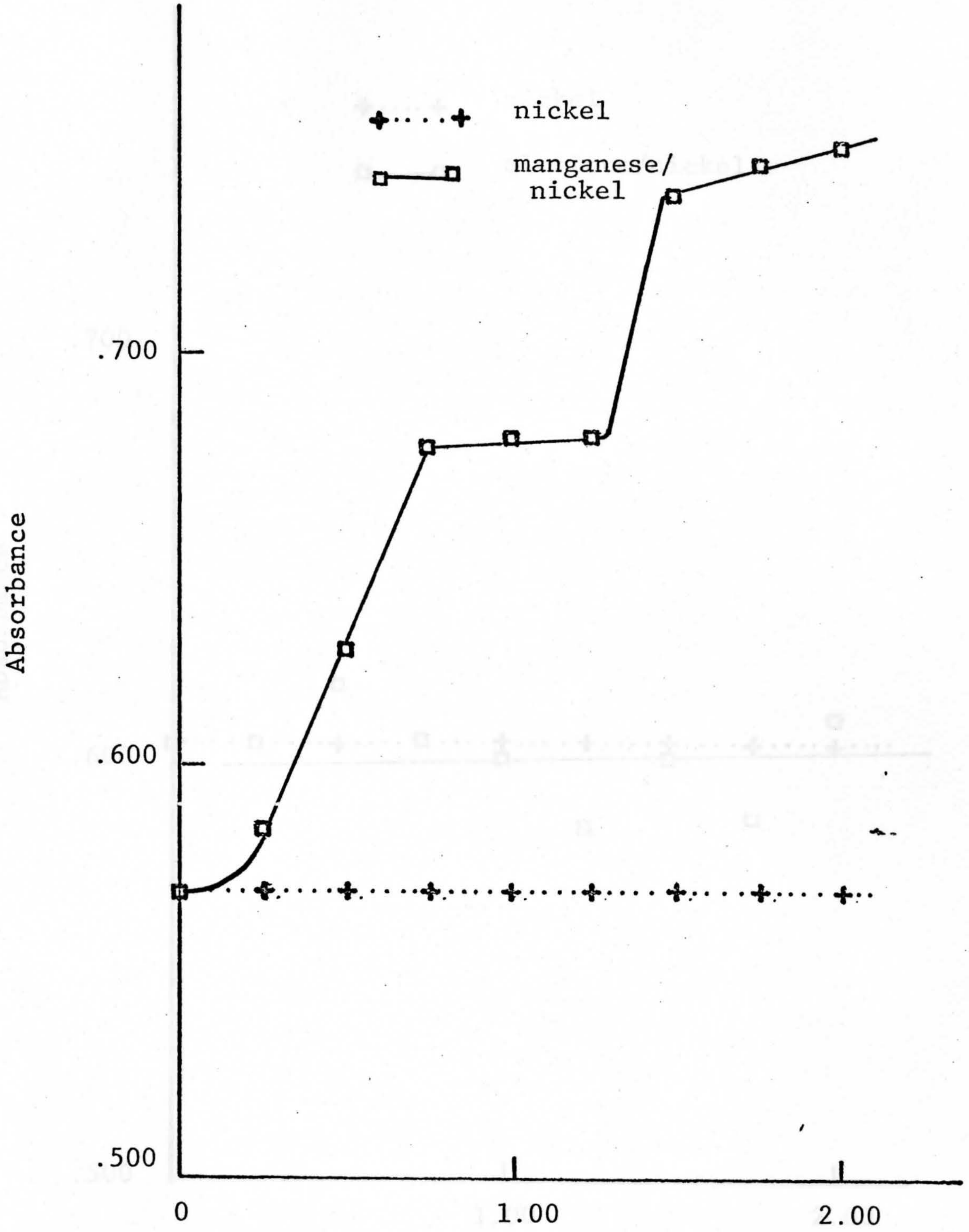
A solution of manganous chloride in dilute hydrochloric acid was used. DHBD did not form a colored complex with manganese. As can be seen from Figure 11, manganese did have a severe interference with the determination of nickel.

B. Aluminum

A solution of aluminum chloride in dilute aqua regia was used. After the pH adjustment, the solutions were allowed to stand and a white fluffy precipitate settled to the bottom. The 1.00-ml samples were pipetted from the clear supernatent liquid. DHBD does not form a colored complex with aluminum. When the fluffy precipitate was introduced into a DHBD-alcohol solution, a dense white precipitate of $Al(OH)_3$ formed. Figure 12 shows that the aluminum remaining in solution, after the pH adjustment, does not have an experimentally significant interference with the determination of nickel.

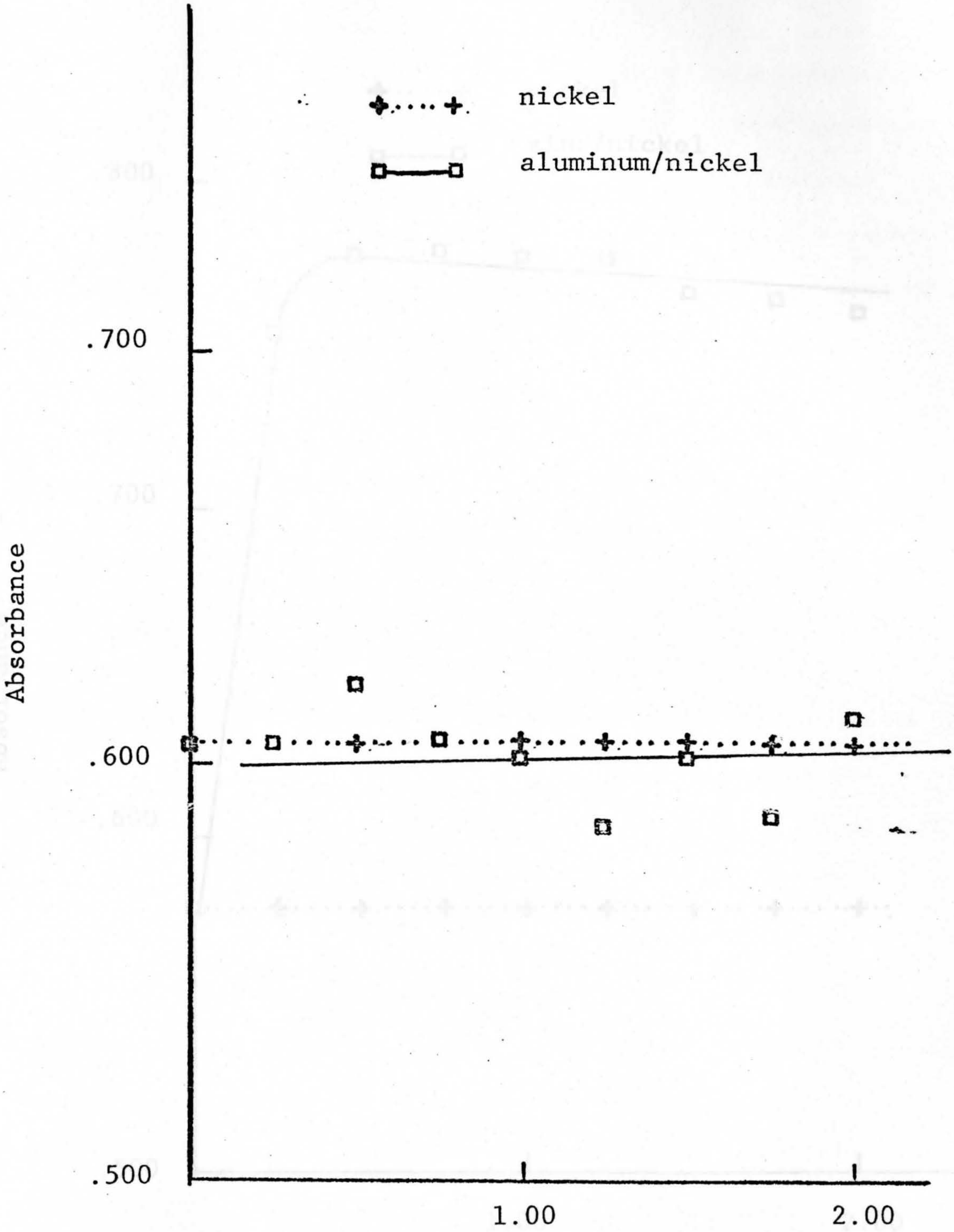
C. Zinc

A solution of zinc nitrate in dilute nitric acid was used. DHBD did not form a colored complex with zinc. Figure 13 indicates that zinc enhances the absorbance of the nickel-DHBD complex. This enhancement is fairly constant throughout the range of the zinc/nickel ratios tested.



EFFECT OF MANGANESE

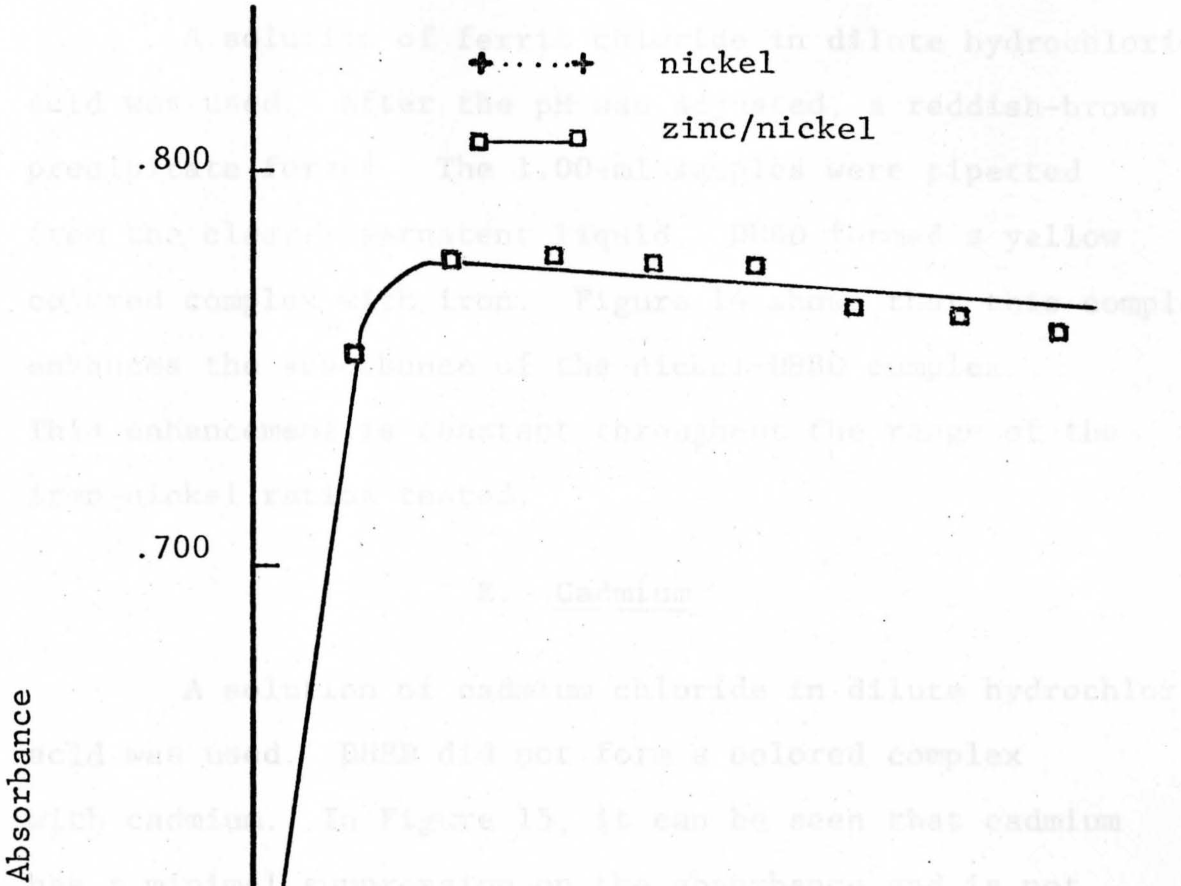
FIGURE 11



Aluminum/Nickel mass ratio

EFFECT OF ALUMINUM

FIGURE 12



EFFECT OF ZINC

FIGURE 13

D. Iron

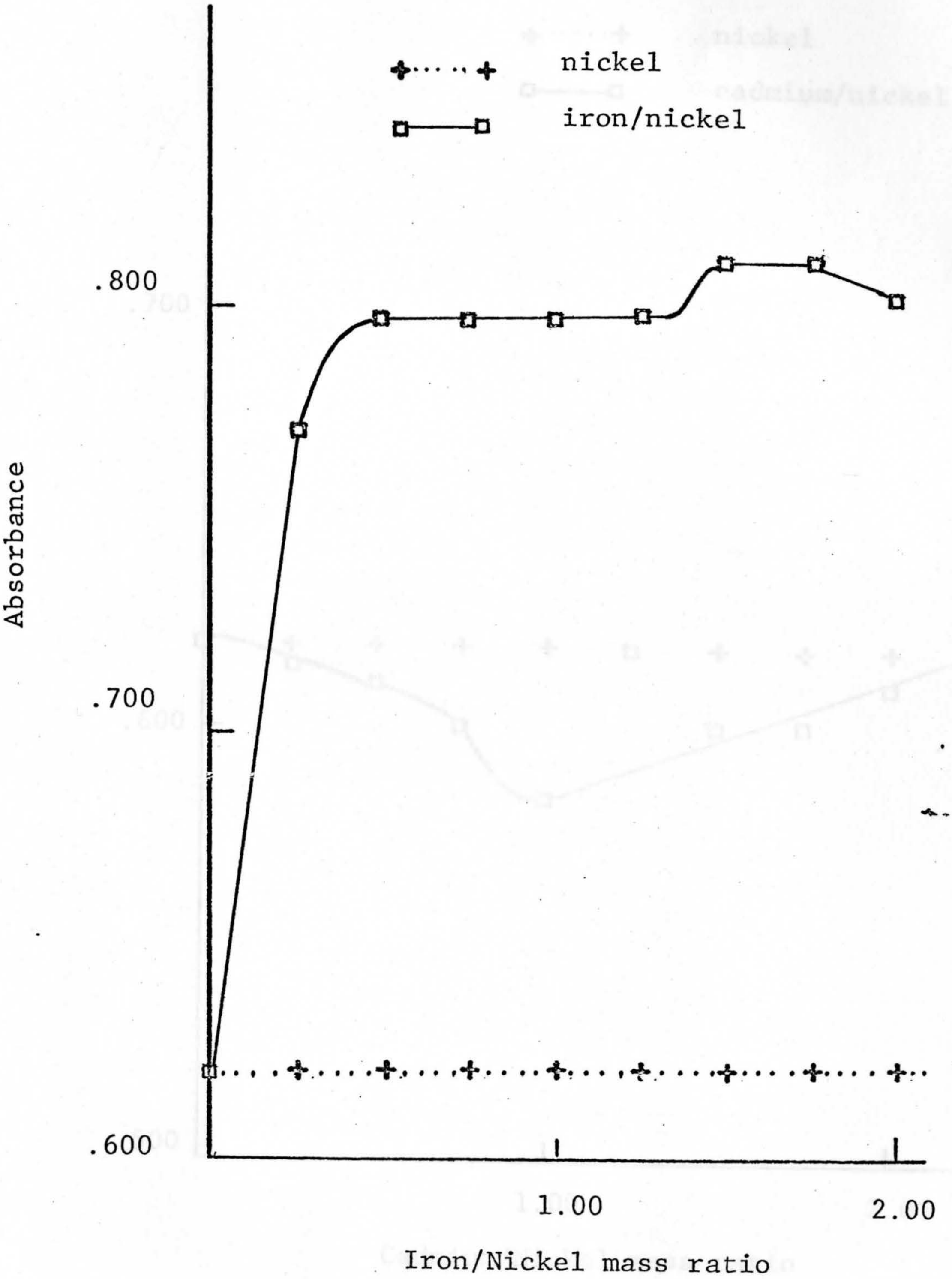
A solution of ferric chloride in dilute hydrochloric acid was used. After the pH was adjusted, a reddish-brown precipitate formed. The 1.00-ml samples were pipetted from the clear supernatent liquid. DHBD formed a yellow colored complex with iron. Figure 14 shows that this complex enhances the absorbance of the nickel-DHBD complex. This enhancement is constant throughout the range of the iron-nickel ratios tested.

E. Cadmium

A solution of cadmium chloride in dilute hydrochloric acid was used. DHBD did not form a colored complex with cadmium. In Figure 15, it can be seen that cadmium has a minimal suppression on the absorbance and is not experimentally significant for the determination of nickel.

F. Copper

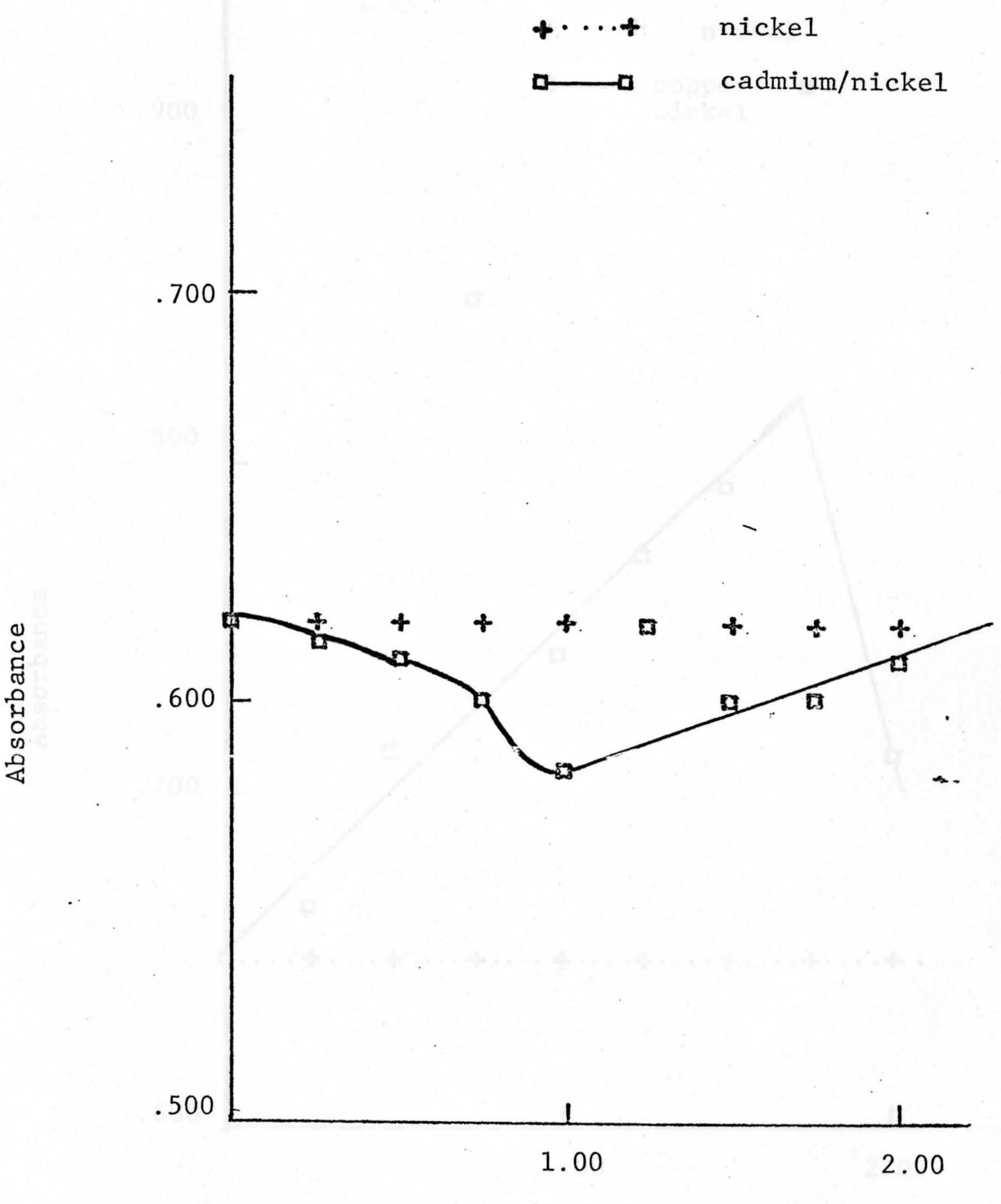
A solution of cupric sulfate in dilute sulfuric acid was used. The solution was light blue in color. Copper formed a white colored solution and a white precipitate when a DHBD-alcohol solution was added. The absorbance of the DHBD-nickel complex is enhanced by the presence of copper as can be seen in Figure 16.



Iron/Nickel mass ratio

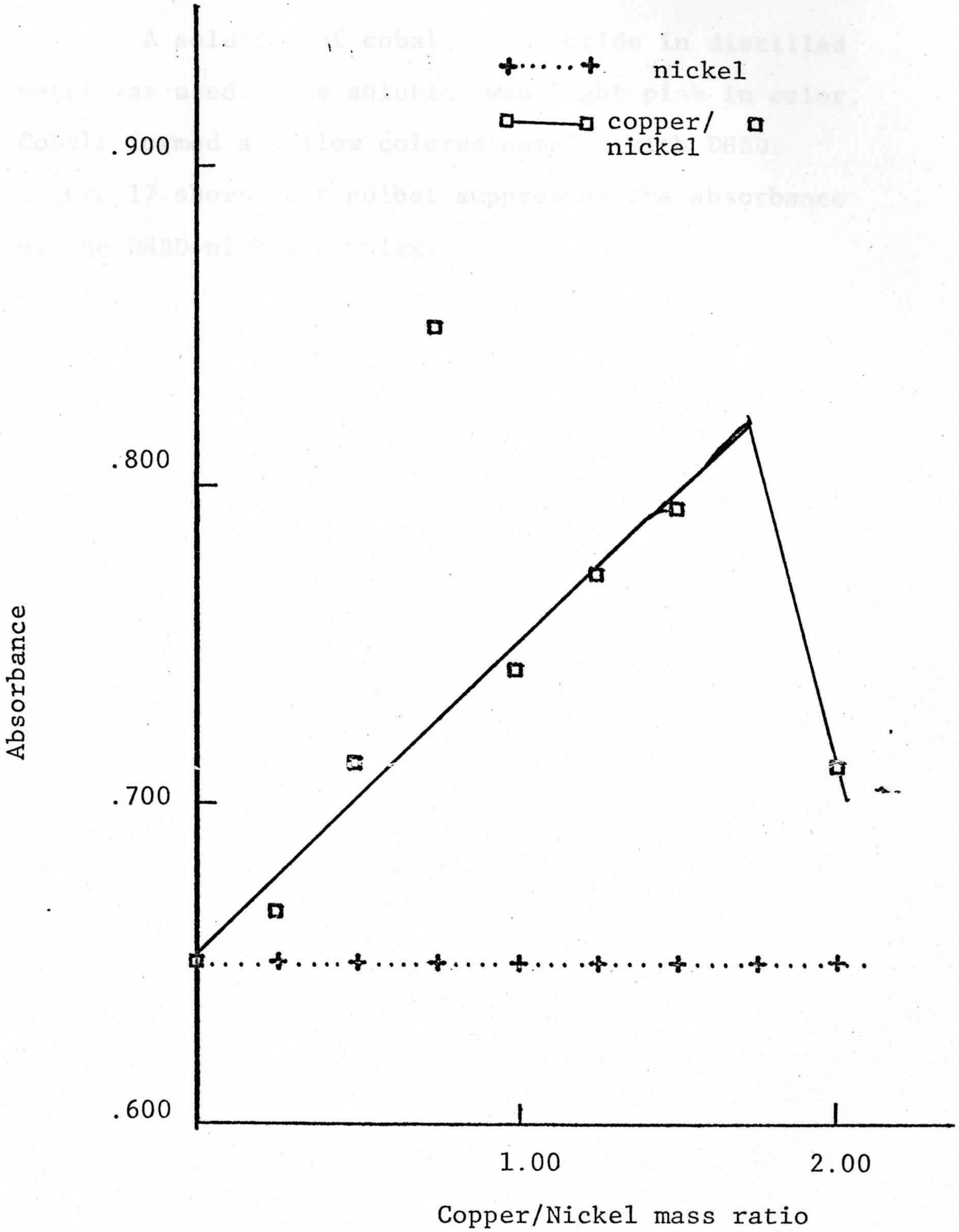
EFFECT OF IRON

FIGURE 14



EFFECT OF CADMIUM

FIGURE 15

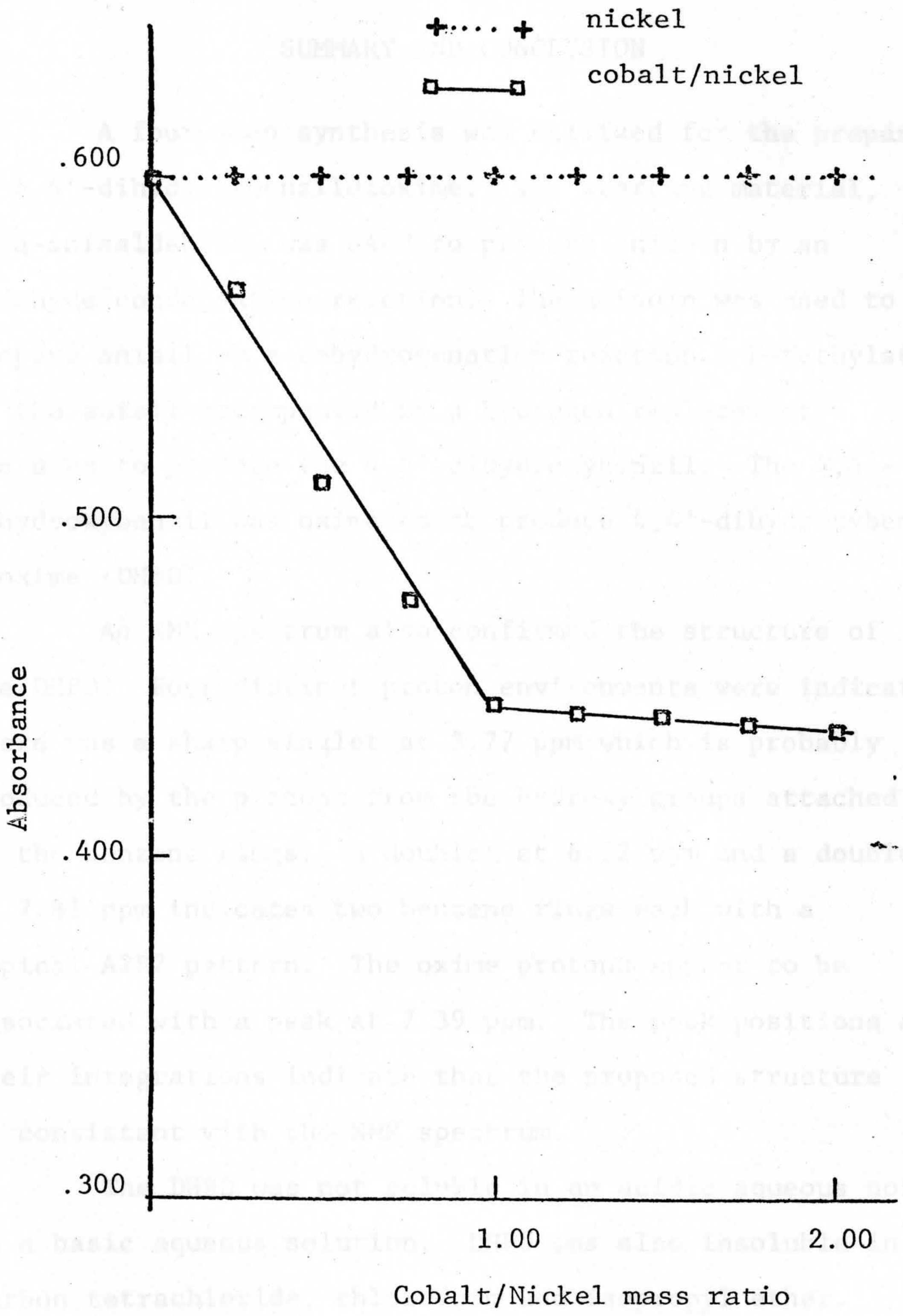


EFFECT OF COPPER

FIGURE 16

G. Cobalt

A solution of cobaltous chloride in distilled water was used. The solution was light pink in color. Cobalt formed a yellow colored complex with DHBD. Figure 17 shows that colbat suppresses the absorbance of the DHBD-nickel complex.



EFFECT OF COBALT

FIGURE 17

CHAPTER X

SUMMARY AND CONCLUSION

A four-step synthesis was utilized for the preparation of 4,4'-dihydroxybenzildioxime. The starting material, para-anisaldehyde, was used to prepare anisoin by an aldehyde condensation reaction. The anisoin was used to prepare anisil by a dehydrogenation reaction. Demethylation of the anisil accompanied by a hydrogen replacement was used to prepare the 4,4'-dihydroxybenzil. The 4,4'-dihydroxybenzil was oximated to produce 4,4'-dihydroxybenzil-dioxime (DHBD).

An NMR spectrum also confirmed the structure of the DHBD. Four distinct proton environments were indicated. There was a sharp singlet at 3.77 ppm which is probably produced by the protons from the hydroxy groups attached to the benzene rings. A doublet at 6.92 ppm and a doublet at 7.81 ppm indicates two benzene rings each with a typical A2B2 pattern. The oxime protons appear to be associated with a peak at 7.39 ppm. The peak positions and their integrations indicate that the proposed structure is consistant with the NMR spectrum.

The DHBD was not soluble in an acidic aqueous nor in a basic aqueous solution. DHBD was also insoluble in carbon tetrachloride, chloroform and isopropyl ether.

DHBD was soluble in ethanol, methanol and acetone. Ethanol was selected as the solvent for DHBD because of its low cost and availability. A literature search also revealed that ethanol was used as a solvent for thirteen dioximes as well as for alpha benzildioxime and for dimethylglyoxime.

A 1.00-ml portion of an aqueous solution of 1×10^{-3} M nickel nitrate was mixed with a 3.00-ml portion of 1×10^{-3} M DHBD in ethanol and this mixture was diluted to 25 ml with ethanol. The mixture produced a yellow colored solution. The wavelength of maximum absorbance for the yellow colored DHBD-Nickel complex is 420 nm. In order to achieve a stable absorbance reading, a color development time of twenty minutes is required. The absorbance reading is stable for an additional twenty-five minutes. After the total elapsed time of forty-five minutes, there is a slight increase in the absorbance.

Absorbance measurements are not affected by the reaction temperature. After mixing, the solutions were held at various temperatures in a water bath for twenty minutes. After the twenty minute color development in the water bath, the solutions were allowed to cool to room temperature (21°C) and absorbance measurements were taken.

The effect of water in ethanol was studied to determine whether or not an aqueous sample of nickel in an ethanol matrix would affect the absorbance. It has been determined that the water content does affect the absorbance. When the water content exceeded sixty-five percent, the solutions became turbid. At sixty percent water content, the solutions had the lowest absorbance reading. Various diluents were prepared consisting of an ethanol-water mixture. The water portion of the mixtures were prepared at various pH levels. At a pH of 1, 2 and 3 there was no color development. At a pH of 13, a red-orange color developed immediately and the color became more intense upon standing. Color development will occur in the pH range of 4 to 12. Above a pH of 8, there is a definite effect on the absorbance and the nickel as well as other metallic ions will begin to precipitate.

The absorbance is a linear function of the concentration in the millimole/l range and the yellow-colored DHBD-nickel complex conforms to Beer's Law. The high molar absorptivity indicates that the DHBD is a sensitive photometric reagent. The metal to ligand ratio was determined to be one mole of nickel to one mole of DHBD.

The effect of the presence of foreign ions on the absorbance of the nickel-DHBD complex was studied. Manganese as manganous chloride and copper as cupric sulfate have a negative interference on the absorbance readings. Iron as ferric chloride and zinc as zinc nitrate enhance the absorbance readings and they reach a relatively stable enhancement when their ppm concentration is at least one-half the ppm concentration of nickel. The remaining aluminum in solution causes only a minor deviation in the absorbance readings which is not experimentally significant. Cadmium as cadmium chloride suppresses the absorbance readings but the suppression is not considered to be experimentally significant. Cobalt as cobaltous chloride also suppresses the absorbance readings but when the cobalt is at least equal to the ppm concentration of the nickel, the suppression becomes relatively stable. The effect of the presence of anions was not studied and further investigation should be carried out in this area.

DHBD can be adapted for nickel determinations in aqueous solutions. By judiciously choosing pretreatment methods for the removal of interfering ions or by extracting the water-soluble DHBD-nickel complex into an organic solvent, DHBD can be used for the selective determination of nickel. Unfortunately, the necessity of pretreatment for the removal of these interfering ions and/or a solvent extraction nullifies the use of DHBD as an expeditious method for the analytical determination of nickel.

APPENDIX A

Equipment Used

EQUIPMENT USED

Bausch and Lomb Spectronic 20
Beckman Zeromatic II pH Meter
Beckman Model 26 Spectrophotometer
Varian EM 360 60MHz NMR Spectrometer
Thomas Hoover Melting Point Apparatus

APPENDIX B

Reagents Used

REAGENTS USED

All Reagents Used Were of A.C.S. Quality

Material	Manufacturer
Para-anisaldehyde	J.T. Baker
Pyridine	J.T. Baker
Absolute Ethanol	Commercial Solvents Corp.
Sodium Cyanide	J.T. Baker
95% Ethanol	Thomas Scientific
Cupric Sulfate	Fisher Scientific
48% Hydrobromic Acid	Mallinckrodt
Acetic Acid	DuPont
Hydroxylamine Hydrochloride	J.T. Baker
Nickel Nitrate	Fisher Scientific
Carbon Tetrachloride	Fisher Scientific
Chloroform	Fisher Scientific
Isopropyl Ether	Fisher Scientific
Acetone	Fisher Scientific
Hydrochloric Acid	Fisher Scientific
Sodium Hydroxide	Fisher Scientific
Potassium Acid Phthalate	Fisher Scientific
Potassium Chloride	Fisher Scientific
Sodium Bicarbonate	Fisher Scientific
Sodium Tartrate	Fisher Scientific

REAGENTS USED

All Reagents Used Were of A.C.S. Quality

Material	Manufacturer
Para-anisaldehyde	J.T. Baker
Pyrideine	J.T. Baker
Absolute Ethanol	Commercial Solvents Corp.
Sodium Cyanide	J.T. Baker
95% Ethanol	Thomas Scientific
Cupric Sulfate	Fisher Scientific
48% Hydrobromic Acid	Mallinckrodt
Acetic Acid	DuPont
Hydroxylamine Hydrochloride	J.T. Baker
Nickel Nitrate	Fisher Scientific
Carbon Tetrachloride	Fisher Scientific
Chloroform	Fisher Scientific
Isopropyl Ether	Fisher Scientific
Acetone	Fisher Scientific
Hydrochloric Acid	Fisher Scientific
Sodium Hydroxide	Fisher Scientific
Potassium Acid Phthalate	Fisher Scientific
Potassium Chloride	Fisher Scientific
Sodium Bicarbonate	Fisher Scientific
Sodium Tartrate	Fisher Scientific

REAGENTS USED (Continued)

All Reagents Were Standard Solutions
Purchased From Varian

Material	Manufacturer
Cd^{+2} as $CdCl_2$ in dilute HCl	Varian AA Standard
Cu^{+2} as $CuSO_4$ in dilute H_2SO_4	Varian AA Standard
Al^{+3} as $AlCl_3$ in dilute aqua regia	Varian AA Standard
Fe^{+3} as $FeCl_3$ in dilute HCl	Varian AA Standard
Mn^{+2} as $MnCl_2$ in dilute HCl	Varian SS Standard
Zn^{+2} as $Zn(NO_3)_2$ in dilute HCl	Varian AA Standard
Co^{+2} as $CoCl_2$ in water	Varian AA Standard

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