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A spectrophotometric reagent for cobalt

Larry Keith Hunt
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A SPECTROPHOTOMETRIC REAGENT FOR COBALT

by

Larry Keith Hunt

A Dissertation Submitted to the
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DOCTOR OF PHILOSOPHY

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Approved:

Signature was redacted for privacy.

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Of Science and Technology
Ames, Iowa

1965

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INTRODUCTION

The growth and development of modern technology has resulted in the need for ever more versatile and sensitive analytical reagents. The determination of elements in the parts-per-million range and below has become a matter of considerable importance. The simplicity, reliability, and low cost of spectrophotometric methods of analysis have resulted in their continued use for the trace analysis of both metals and nonmetals. The analytical chemistry of the transition elements, particularly of manganese, iron, nickel, cobalt, and copper, has received considerable attention, but the need continues for more sensitive and selective reagents.

Much of the early work with organic analytical reagents was empirical and depended on testing many different compounds for a particular application. Present-day knowledge of the basic principles of chelate-ring chemistry and of the formation of nondissociated or "complex" compounds has helped greatly in the discovery of new reagents, making it possible to predict the possibilities for reaction, specificity, and sensitivity, as well as the effects of factors such as pH, equilibria, and solvent.

Numerous reagents have been proposed for the colorimetric determination of cobalt, the most important being thiocyanate, 3-nitrososalicylaldehyde, α -nitroso- β -naphthol, dimethylglyoxime, and diethyldithiocarbamate. All of these reagents suffer from lack of sensitivity and selectivity.

The thiocyanate method for cobalt has been used for many years (1). The compound formed is not very intensely colored in aqueous solution,

and extraction into organic solvents is generally used to concentrate the compound for final measurement. Many elements interfere, and the method has limited application.

3-Nitrososalicylic acid is useful for determining small amounts of cobalt (2). This reagent forms a brown compound with cobalt which is soluble in petroleum ether and also a red nickel compound which is soluble in aqueous solution; this makes possible the simultaneous determination of nickel and cobalt. Iron(II) and copper(II) interfere.

α -Nitroso- β -naphthol is the most commonly used of the cobalt reagents. Generally, one of its sulfonated derivatives such as 1-nitroso-2-naphthol-4-sulfonate is used. These reagents suffer from many interferences, especially nickel, and are not very sensitive (3).

Because of the limitations of sensitivity and specificity of the presently available reagents for cobalt, there is a real need for a reagent which can be used to determine small amounts of cobalt, particularly in the presence of the iron which occurs commonly in biological material and of course is the major component of cobalt-containing steels. An ideal colorimetric reagent for cobalt should be free of interferences from nickel and copper too since nickel is present in large amounts in some steels and copper is common in biological materials. Among the known reagents for cobalt there is not one which fulfills these requirements completely.

The determination of nickel is generally made with dimethylglyoxime or a related dioxime. Cobalt interferes seriously in the spectrophotometric determination of nickel with dimethylglyoxime by forming a highly

colored compound with the reagent. The molar extinction coefficients of nickel-dioxime compounds are low, and the dioxime reagents thus lack sensitivity (4).

Diethyldithiocarbamate forms intensely colored compounds with nickel which have been used for the determination of small amounts of the metal. This reagent forms colored compounds with many metals so that a preliminary separation of the nickel from interfering elements is always necessary (5).

The spectrophotometric determination of iron is usually made with 1,10-phenanthroline (6). This reagent has high sensitivity and specificity for iron, copper being the only serious interference.

The spectrophotometric determination of copper is quite simple, selective reagents being available in the 2,9-dialkyl-1,10-phenanthrolines (7). No metals interfere, and the sensitivity of one reagent, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine), is exceptionally high.

Schiff's bases having functional groups adjacent to the carbon-nitrogen bond so that chelation (ring formation) can occur with metal atoms are of interest because of the intense colors of many of the metal derivatives. Metal derivatives of Schiff's bases have been known for many years, but recently Lions and Martin (8) and Geldard and Lions (9) reported a Schiff's base with two pyridine groups that is of particular interest. The compound, 1,3-bis(2'-pyridine)-2,3-diaza-1-propene, abbreviated PDP, prepared by condensing 2-pyridinecarboxaldehyde with 2-pyridylhydrazine, was reported to form an intensely colored compound with cobalt. Lions and his co-workers actually prepared a considerable number of metal-PDP compounds of the transition elements and investigated the

properties of some, but the investigation of the cobalt compound was incomplete.

In the present work, the cobalt-PDP compound and the derivatives of PDP with iron(II), nickel(II), and copper(II) have been investigated in detail. The use of PDP as an analytical reagent for cobalt, in particular, has been developed.

The combining ratios and structures of the metal derivatives of PDP have been determined. Methods have been developed for the solvent extraction of the PDP compounds of iron, nickel, copper, and other divalent transition elements and their removal in this way from the cobalt-PDP compound, thus permitting a measurement of the cobalt compound.

A procedure which can be applied to biological materials and even to steels was developed for determining cobalt in small amounts.

Copper was found to form two compounds with PDP, and the formation constants for these compounds have been determined and their values explained in terms of structure.

Other Schiff's bases, particularly 1-(2'-hydroxyphenyl)-3-pyridyl-2,3-diaza-1-propene, designated later as HPDP, were also investigated as reagents for the transition metals. Alkaline earth metals also react with HPDP.

APPARATUS AND MATERIALS

Absorption spectra in this study were obtained on Beckman DK2 and DU spectrophotometers. All spectrophotometric data used in determining combining ratios were obtained on the DU spectrophotometer.

Thermogravimetric analyses were made using the instrument described by Diehl and Wharton (10).

Karl Fischer titrations for water were carried out by addition of excess Karl Fischer reagent and back titration with a standard methanol-water solution. The reagent was standardized against reagent-grade sodium acetate trihydrate. The end-point of the titration was determined by the "dead-stop" method. The visual end-point could not be used because of the dark-colored solutions of the compounds titrated.

The titration system was protected from moisture in the air by a calcium sulfate drying tube. The sample was added through a stopper in the top of the titration flask, and the transfer of sample was made as rapidly as possible to prevent entrance of moisture. The dead-stop electrodes were two bright platinum wires sealed into the bottom of the titration flasks.

All pH measurements were made using a Beckman Model G pH meter standardized against commercial buffers. A commercial-type saturated calomel electrode and glass electrode were used.

Paper electrophoresis experiments were conducted using a horizontal-type apparatus manufactured by the C-E Apparatus Co., Swarthmore, Pennsylvania. A 0.1 M potassium acid phthalate solution was used as buffer. The pH of this solution was approximately pH 7. A 500 volt, 10 mamp.

current was applied across the paper.

Electrical conductance was measured on an Industrial Instruments Co., Conductance Bridge, Model RC16B2. The cell constant was determined with 0.01 M potassium chloride at 25° using the value 0.0014087 for the specific conductance, data of Jones and Bradshaw (11). The cell constant was 0.062 from this measurement.

Nuclear magnetic resonance (NMR) spectra were obtained on a Varian spectrometer Model HR60 with a 60 Mc field. Tetramethylsilane was used as internal standard for all spectra.

Standard solutions of cobalt(II) were prepared by weighing out and dissolving appropriate amounts of cobalt(II) sulfate. The cobalt(II) sulfate was prepared from hexamminecobalt(III) oxalate and was free from iron and nickel impurities.

Iron(II) solutions were prepared from ferrous ethylenediammonium sulfate obtained from the G. Frederick Smith Chemical Company. Standard nickel(II) solutions were prepared by dissolving Mond nickel (International Nickel Company) in a minimum amount of nitric acid.

Constant ionic strength buffers were used in all spectrophotometric studies. The buffers were prepared by the directions of Bates (12), page 117, for buffers of ionic strength 0.1 in which an acid reagent containing 0.2 M hydrochloric acid and 0.1 M potassium chloride is added to a base stock solution 0.05 M in the sodium salt of a monobasic weak acid and 0.05 M in potassium chloride. It is necessary that the monobasic weak acid be so weak that the contribution of its ionization to the total ionic strength can be ignored. Since the hydrochloric acid solution added will dilute

the stock solution and lower the ionic strength, the acid reagent must contain a neutral salt to compensate exactly for this dilution. The weak acid sodium salts used in the base stock solutions are formate, acetate, and borate. The buffer ranges covered by these salts are formate, pH 3.0 to 4.5; acetate, pH 4.0 to 5.5; and borate, pH 9.0 to 10.0.

2-Pyridinecarboxaldehyde, 2-chloropyridine, and hydrazine hydrate were obtained from the Aldrich Chemical Company and were used without purification. Salicylaldehyde was obtained from the Eastman Kodak Company.

PREPARATION OF COMPOUNDS

2-Pyridylhydrazine: 2-Pyridylhydrazine was prepared by refluxing 10 ml. of 2-chloropyridine with excess hydrazine hydrate in 10 ml. of ethanol. The 2-pyridylhydrazine was not isolated but was used in further synthesis.

1,3-Bis(2'-pyridyl)-2,3-diaza-1-propene (PDP): PDP was prepared by refluxing a mixture of 2 ml. of 2-pyridinecarboxaldehyde, the crude 2-pyridylhydrazine as prepared in 10 ml. of ethanol, and several drops of glacial acetic acid. Pale yellow needles were obtained directly; recrystallization from hot ethanol gave pale yellow needles with melting point: 178-180°; reported: 179-180° (8). The solid PDP was not soluble indefinitely.

1-(2'-Hydroxyphenyl)-3-pyridyl-2,3-diaza-1-propene (HPDP): HPDP was prepared by refluxing a mixture of 1 ml. of salicylaldehyde, 1 ml. of 2-pyridylhydrazine in 10 ml. of ethanol, and several drops of glacial acetic acid. White needles recrystallized from ethanol; melting point: 123.5-124.5°; analysis: C, 67.91; H, 4.89; N, 19.17; calculated for C₁₂H₁₁N₃O: C, 67.60; H, 5.16; N, 19.72.

NATURE OF THE COBALT COMPOUND

Introduction

Lions and Martin (8) reported that cobalt(II) forms an intensely colored compound with PDP, and they isolated the compound as the dibromide. They showed that cobalt is present in the compound as diamagnetic cobalt(III) and suggested that the ligand is reduced by the oxidation of cobalt(II) to cobalt(III). Lions and Martin suggested that PDP might be of value as a colorimetric reagent for cobalt but reported no further work in this direction.

Work reported in this thesis has shown that PDP is indeed a useful colorimetric reagent for cobalt but has also shown the necessity for further work on the structure and properties of the cobalt compound. The research reported here differs in significant details from the work of Lions and Martin and does not support the conclusions of these workers with respect to the structure of the cobalt(III) compound of PDP and the mechanism of oxidation of the cobalt(II) compound to the cobalt(III) compound.

The cobalt(III) compound of PDP has now been isolated as the bromide salt, and the formula has been established by elemental analysis and thermogravimetric analysis. Molar conductance and migration studies were made to help explain the structure of the cobalt compound. An attempt was also made to determine the amount of water in the compound by the Karl Fischer titration.

Experimental Work

Preparation of the cobalt compound

The cobalt derivative of PDP was prepared as the bromide salt by addition of cobalt(II) perchlorate to an ethanol solution of PDP. An ice-cold, saturated solution of potassium bromide was added, and the precipitate which formed was filtered off. The product was recrystallized from an ethanol-water mixture. Iridescent-green plates were obtained: melting point 303-304° (8); analysis: C, 46.55; H, 4.10; N, 19.17; Br, 13.19; Co, 10.30; calculated for $C_{22}H_{18}N_8CoBr \cdot 3H_2O$; C, 44.99; H, 4.09; N, 19.08; Br, 13.62; Co, 10.04.

Characterization of the compound

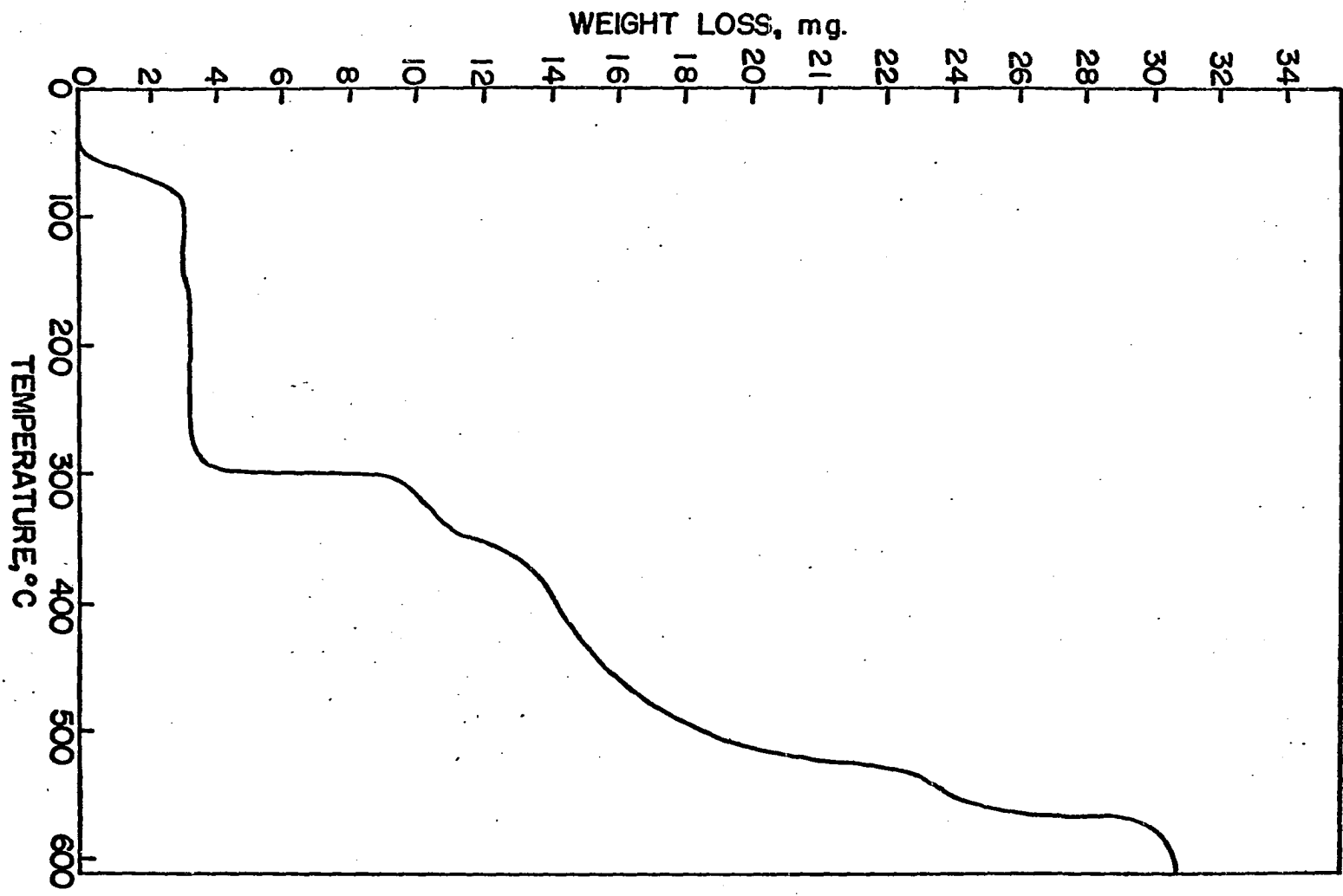
Thermogravimetric analysis of the compound showed the progressive loss of water, bromide, and PDP with increasing temperature. A graph of weight loss versus temperature is shown in Fig. 1.

The conductance of a 1.000×10^{-3} M solution of the cobalt compound was measured. The solution was prepared by weighing out the solid compound and dissolving it in conductivity water. The data are given in Table 1.

Table 1. Conductance of 1.000×10^{-3} M solutions of metal derivatives of PDP

Compound	Specific conductance	Molar conductance
$Co(NH_3)_6Cl_3$	4.575×10^{-4}	457.5
$Co(PDP)_2Br \cdot 3H_2O$	1.065×10^{-4}	106.5
$Fe(PDP)_2Br_2 \cdot 3H_2O$	2.020×10^{-4}	202.5
$Ni(PDP)_2Br_2 \cdot 3H_2O$	2.186×10^{-4}	220.0

Fig. 1. Theromgravimetric analysis of the cobalt compound of PDP



Migration of the compound was studied using paper electrophoresis. Two inch-wide strips of Whatman 3M filter paper were used for all experiments. The solvent was an aqueous solution of 0.1 M potassium hydrogen phthalate. A water solution of the cobalt compound was added as a spot on one end of the filter paper and allowed to migrate for four hours at 500 volts with a 10 mamp. current. The migration of the compound in the electric field could easily be followed because of the intense color of the ion.

Discussion

The thermogravimetric analysis (Fig. 1) shows a loss of 3.26 mg. of a 35.8 mg. sample when heated from 50 to 85°. This corresponds exactly to the loss of three water molecules from the compound. The second plateau from 280 to 320° corresponds to the loss of one bromide per atom of cobalt. The final loss in weight from 320 to 560° corresponds to the loss of two molecules of FDP per cobalt atom. Apparently, the FDP was not lost as an intact molecule but was degraded in several steps. The oxide residue was very close to the weight of Co_3O_4 expected for the sample.

The molar conductance of the cobalt compound is that of a typical di-univalent electrolyte. The electrophoretic study showed that the highly colored species containing the cobalt migrated toward the negative electrode and is the cation.

Variable results were obtained by the Karl Fischer titration for water. Apparently, the cobalt compound reacts with the reagent in some way.

The empirical formula for the cobalt compound calculated from the

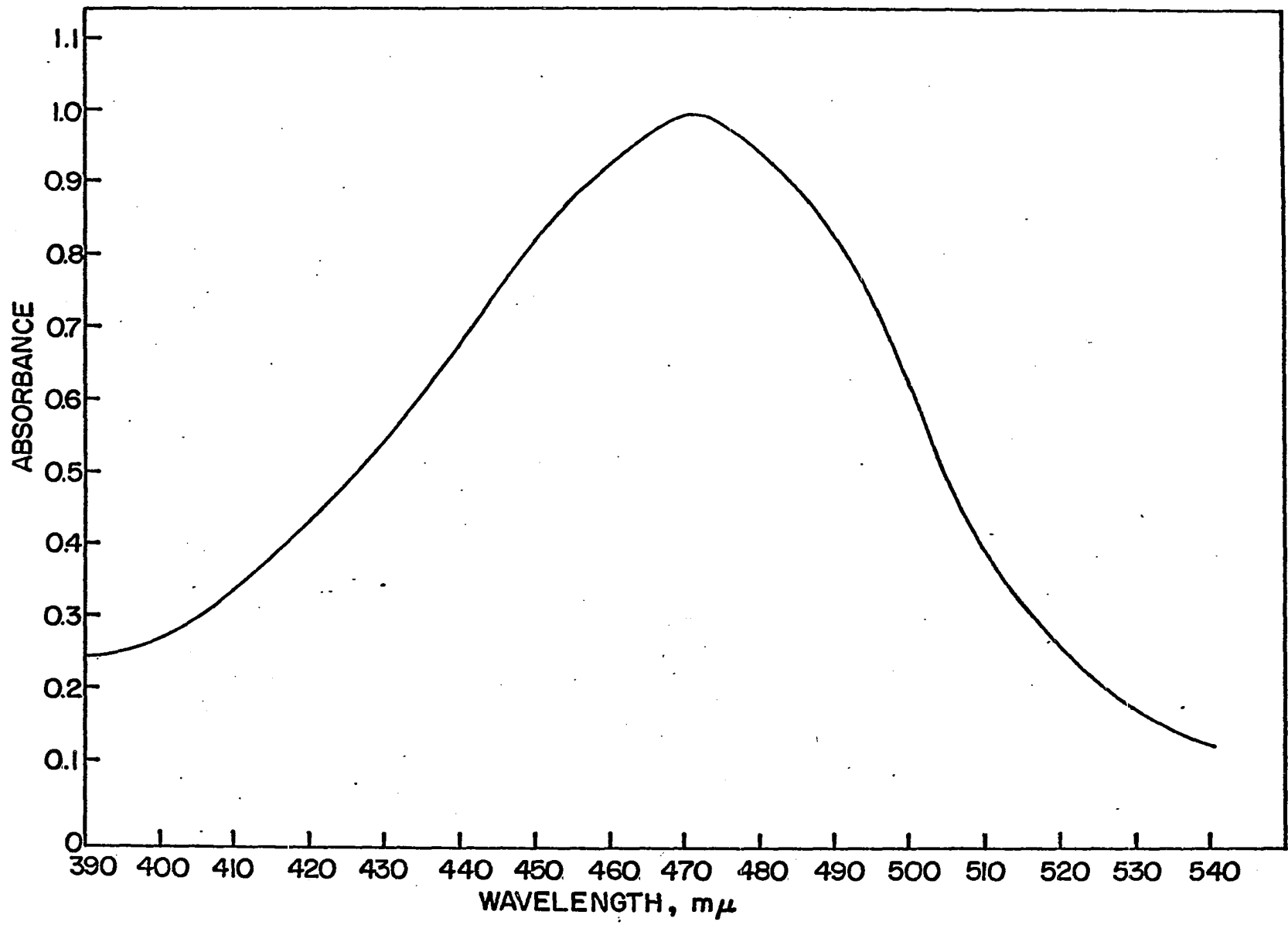
analytical data is $C_{22}H_{18}N_8CoBr \cdot 3H_2O$. This formula is supported by the thermogravimetric analysis and the conductance study as well as by the elemental analysis.

SPECTROPHOTOMETRIC STUDIES OF THE COBALT COMPOUND

Absorption spectra: Absorption spectra of the cobalt compound of PDP in aqueous buffered solutions, $\mu = 0.1$, were obtained using one-centimeter quartz cells. All solutions were blanked against distilled water. The spectrum of PDP alone shows so little absorbance in the 400 to 800 $m\mu$ region that no correction is necessary for the excess reagent. The solutions were prepared from standard $1.000 \times 10^{-3} M$ cobalt(II) sulfate and 0.0100 M PDP in ethanol solution. Constant ionic strength buffers were used. The spectrum of the cobalt compound is shown in Fig. 2. A broad peak occurs in the visible region of the spectrum with maximum absorbance at 480 $m\mu$ and molar extinction coefficient of $28,500 \text{ l cm}^{-1} \text{ mole}^{-1}$. The solution of the cobalt compound is stable indefinitely. No change was observed in the absorption spectrum with time after initial formation.

Combining ratio: The combining ratio of cobalt and PDP was determined by the method of continuous variations (13). To each of a series of ten 100-ml. volumetric flasks was added, in order, 0, 1, 2, 3, 4, 5, 6, 7, 8, and 9 ml. of standard $1.000 \times 10^{-3} M$ cobalt(II) sulfate solution and 9, 8, 7, 6, 5, 4, 3, 2, and 1 ml. of the $1.000 \times 10^{-3} M$ PDP solution. The solutions were then diluted to volume with pH 4.5, $\mu = 0.1$ buffer (sodium acetate-HCl buffer described by Bates) and allowed to equilibrate before measuring the absorbance. A similar continuous-variations study using pH 8.3, $\mu = 0.1$ buffer gave quite different results. The plot of absorbance versus milliliters of PDP is shown in Fig. 3. The combining ratios of cobalt to PDP are 1:2 at pH 8.3 and 1:3 at pH 4.5.

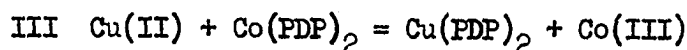
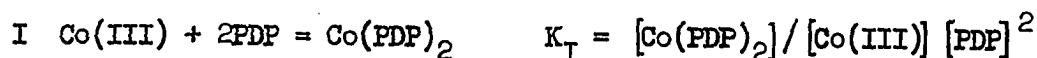
Fig. 2. Absorption spectrum for the cobalt (III)-PDP compound
 4×10^{-5} M Co (II), 2×10^{-4} M PDP, pH 8.65, $\mu = 0.1$



FORMATION CONSTANT OF THE COBALT(III)-PDP COMPOUND

Introduction

The formation constant of the cobalt(III)-PDP compound (reaction I) was determined from the individual formation constants of the compounds shown in reactions II and III.



$$K_{\text{III}} = [\text{Cu(PDP)}_2][\text{Co(III)}] / [\text{Cu(II)}] [\text{Co(PDP)}_2]$$

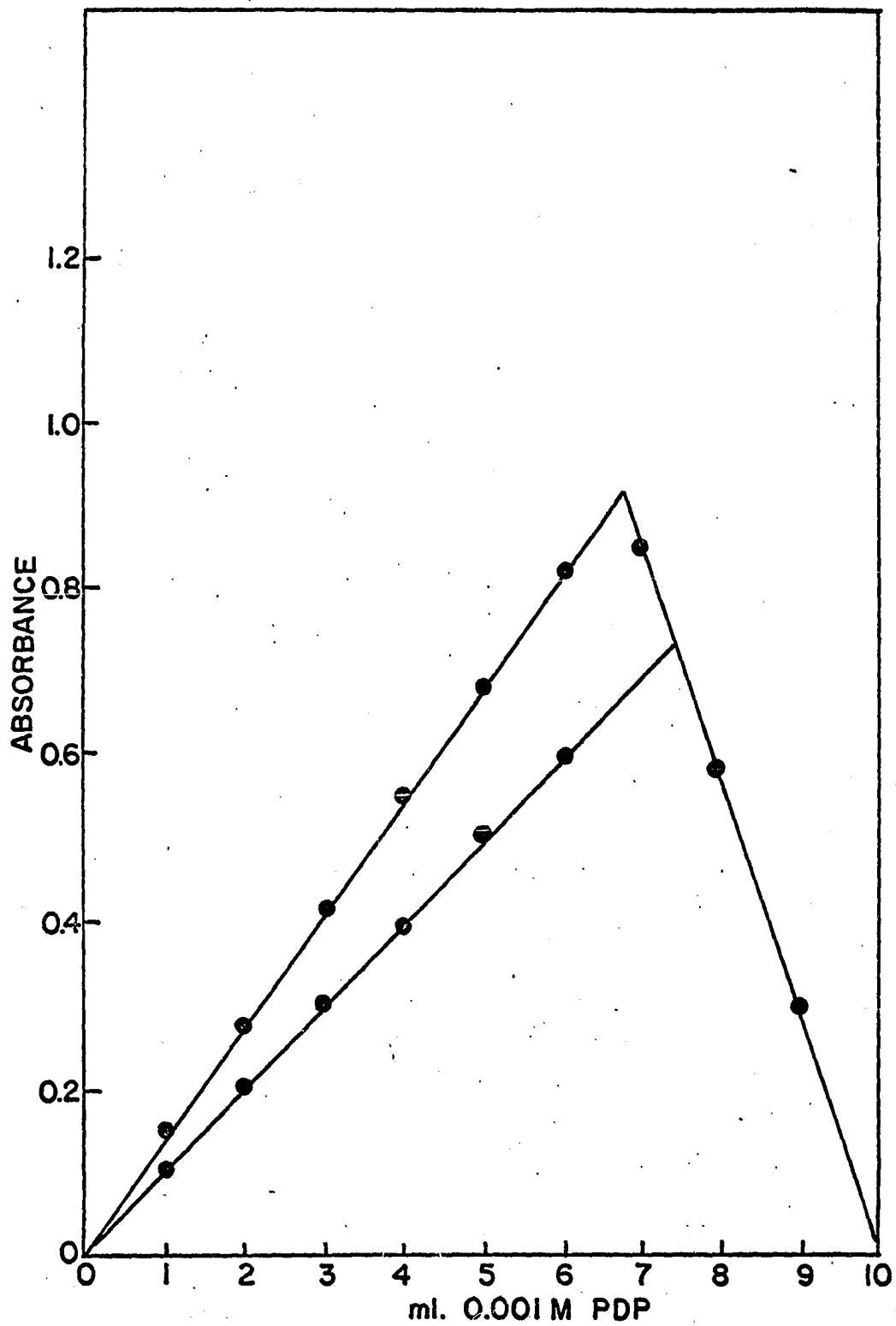
It is apparent that $K_{\text{II}} = K_{\text{I}} \cdot K_{\text{III}}$ for the above reactions. The experimental problem is to determine K_{II} and K_{III} . K_{II} can be determined potentiometrically and K_{III} spectrophotometrically.

Experimental Work

Formation constant for the copper compound

The formation constant for reaction II was determined potentiometrically using a copper-amalgam electrode. A solution was prepared containing 70 ml. of 1.000×10^{-3} M copper(II), 15 ml. 0.1000 M potassium sulfate, and 15 ml. 0.0100 M PDP so that the total volume of the solution was 100 ml. The final solution was 7.00×10^{-4} M in copper(II), 0.0150 M in potassium sulfate, and 1.50×10^{-3} M in PDP. The standard solution of PDP contained 75 ml. of ethanol per 250 ml. of solution. This solution was immersed in a constant temperature bath for 24 hours at $25.45 \pm 0.1^\circ$.

Fig. 3. Continuous variations plot for cobalt and PDP
A. pH 8.3
B. pH 4.6



The copper-amalgam electrode is shown in Fig. 4. The copper(II) sulfate solution above the amalgam electrode is to help prevent air oxidation of the amalgam. The copper amalgam was made by electrolysis. The mercury was saturated with respect to copper. The electrical connection to the amalgam was made through a platinum wire sealed into the glass.

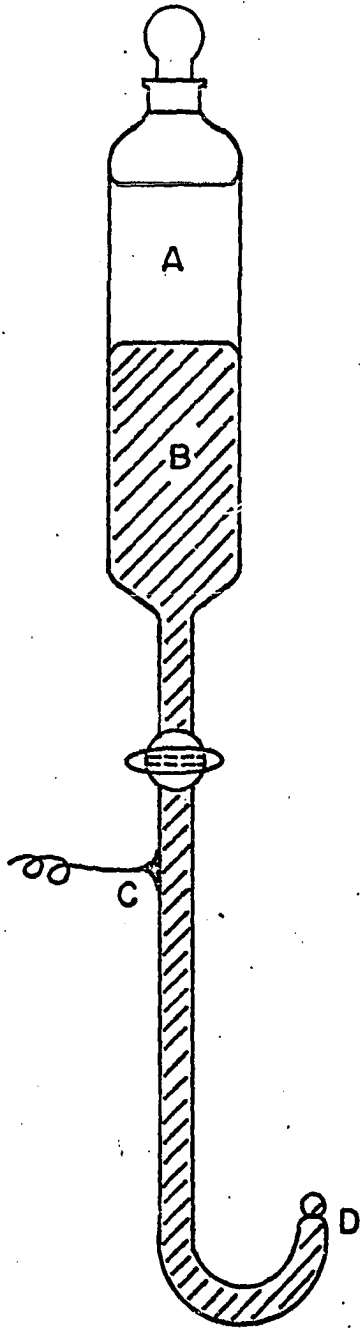
The lower end of the electrode was lowered into a solution of copper (II) and PDP, and a drop of amalgam was allowed to flow out by opening the stopcock. A commercial saturated calomel electrode was used as a potential standard. A high precision Leeds and Northrup potentiometer was used for null-point detection.

Considerable difficulty was experienced in obtaining reproducible results with the copper-amalgam electrode; but after careful attention to experimental details, values within three millivolts of the theoretical value were obtained with a standard copper solution.

The potential measured for the copper-amalgam electrode in the copper-PDP solution system using the technique described was +0.2358 volts versus the standard hydrogen electrode. Since the copper-amalgam electrode was saturated with respect to copper, it functions as a metallic-copper electrode; and the standard reduction potential +0.3448 for the reaction $\text{Cu}^{++} + 2e = \text{Cu}^0$ can be used. Substitution of the standard reduction potential and the potential observed for the copper-amalgam electrode in copper-PDP solutions into the Nernst equation gave a calculated free copper(II) concentration of 2.02×10^{-4} M. The approximations given by Rossotti and Rossotti (14) were used in calculation of the formation constant:

$$K = \frac{[\text{Cu}(\text{PDP})_2]}{[\text{Cu}(\text{II})] [\text{PDP}]^2},$$

- Fig. 4. Copper amalgam electrode
- A. CuSO_4 solution
 - B. Copper amalgam
 - C. Electrical contact through a platinum wire to the amalgam
 - D. Narrow opening to emit drops of amalgam



where: $(\text{PDP}) = (\text{PDP})_t - 2(\text{Cu})_t = 1.00 \times 10^{-4} \text{ M}$ free ligand concentration;

$$[\text{Cu}(\text{PDP})_2] = (\text{Cu})_t = 7.00 \times 10^{-4} \text{ M};$$

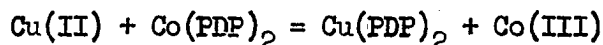
$[\text{Cu}(\text{II})] = 2.02 \times 10^{-4} \text{ M}$ unbound copper. The calculated formation constant is 3.50×10^8 .

Equilibrium constant for the displacement reaction

One milliliter of $1.00 \times 10^{-3} \text{ M}$ cobalt(II) sulfate, 2 ml. of $1.00 \times 10^{-3} \text{ M}$ PDP, and enough potassium chloride to give the solution an ionic strength of 0.1 were diluted to 100 ml. Another solution was prepared in exactly the same manner except 10 ml. of $1.00 \times 10^{-3} \text{ M}$ copper(II) solution was also added.

The solutions were allowed to stand in a constant temperature bath for 24 hours at $25.45 \pm 0.1^\circ$. The absorbances were measured at 470 m μ on a Beckman DU spectrophotometer. Absorbance readings of 0.242 for the cobalt-only solution and 0.143 for the solution containing both cobalt and copper were obtained.

On the assumption that the cobalt exactly reacted with the ligand with no excess of either reagent:



$$K_{\text{III}} = x^2 / [(\text{Cu}(\text{II})) - x] [(\text{Co}(\text{PDP})_2) - x] = 0.0256$$

where: $[\text{Cu}(\text{II})] = 1.00 \times 10^{-4} \text{ M}$

$$[\text{Co}(\text{PDP})_2] = 8.68 \times 10^{-6} \text{ M}$$

$$[\text{Cu}(\text{PDP})_2] = [\text{Co}(\text{III})] = x = 3.55 \times 10^{-6} \text{ M}.$$

Formation constant for the cobalt compound

Using the previously determined values for the formation constant for the copper compound K_{II} and the equilibrium constant for the displacement reaction K_{III} , the formation constant for the cobalt compound K_I is calculated to be 1.36×10^{10} .

POLAROGRAPHIC STUDY OF THE COBALT(III)-PDP COMPOUND

Introduction

The polarographic reduction of $\text{Co(III)(PDP)}_2\text{Br}\cdot 3\text{H}_2\text{O}$ was studied using potassium chloride as the supporting electrolyte. All polarographic data were obtained using a Leeds and Northrup Electrochemograph Type E polarograph. The same capillary was used for all work. The solutions were carefully deaerated with oxygen-free nitrogen before each reduction. All potentials were referred to the saturated calomel electrode. A 1.000×10^{-4} M solution of the cobalt compound was prepared by weighing out the solid and dissolving it in 0.1 M potassium chloride solution.

Experimental Work

Characteristics of the capillary

The data for the characteristics of the capillary shown in Table 2 are for a 0.1 M aqueous solution of potassium chloride using an open circuit. The constants K and r, the radius of the capillary orifice, are those suggested by Muller (15) for the characterization of the capillary from drop weight.

Table 2. Characteristics of the capillary used in the polarographic study of $\text{Co(III)(PDP)}_2\text{Br}$

K(P/M)	Drop weight(mg)	P(cm)	t(sec)	m(mg./sec.)	Time of measurement	Number of drops
102.3	6.37	80	8.14	0.782	602.7	74

Using a drop weight of 6.34 mg., the radius of the capillary orifice is given by: $r = (4.11)(6.34 \text{ mg./drop}) = 26.0 \mu$.

The radius of the capillary orifice was also determined using resistance measurements using the formula $r = \rho l/R\pi$ where ρ is the specific resistivity in ohms, l the length of the capillary in cm., and R the resistance of the capillary in ohms. The length of the capillary used was 21 cm. and the measured resistance through the capillary was 96.3 ohms. The radius of the capillary orifice using this method was 25.8 μ .

Evaluation of $m^{2/3}_t l^{1/6}$

The flow of mercury through the capillary was determined at -1.2 volts from the time required for a large number of drops to fall in a 0.1 M potassium chloride supporting electrolyte. The mercury was then weighed to determine the mass of the drops collected. The mg./sec. of mercury flowing from the capillary was then calculated. From the same experimental data, the drop time in seconds per drop was also calculated. The mercury flow was 0.785 mg./sec. and the drop time 4.67 sec./drop for a mercury head of 80 cm.

Evaluation of the diffusion coefficient

The diffusion coefficient for the cobalt compound of PDP was evaluated from conductance data. Electrical conductance was measured using the same instrument and cell previously used for conductance studies of PDP compounds. The cell constant was redetermined with 0.01 M potassium chloride at 25° using the value 0.0014087 for the specific conductance from the data of Jones and Bradshaw (11). The cell constant was 0.0566.

The conductance of a series of progressively more dilute solutions of $\text{Co(III)(PDP)}_2\text{Br}$ was measured, and the equivalent conductance of these solutions was plotted against the square root of concentration. The equivalent conductance at infinite dilution is 124.

The equivalent ionic conductance of bromide at infinite dilution is given by MacInnes (16) as 78.4. From the relationship $\lambda_{\infty} = \lambda_{+}^{\circ} + \lambda_{-}^{\circ}$, the equivalent ionic conductance of the $\text{Co(III)(PDP)}_2^{+}$ ion is 45.6. Using the formula $D = RT\lambda_{+}^{\circ}/zF^2$ for an infinitely dilute solution where R is 8.317 volt-coulomb deg.⁻¹; F is 96,500 coulombs; T is 298°K; z is the charge on the ion. Thus $D = 2.67 \times 10^{-7} \lambda_{+}^{\circ}/z \text{ cm}^2 \text{ sec}^{-1}$ at 25°C. Using the value of λ_{+}° calculated for $\text{Co(III)(PDP)}_2^{+}$, the diffusion coefficient is $1.2 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$.

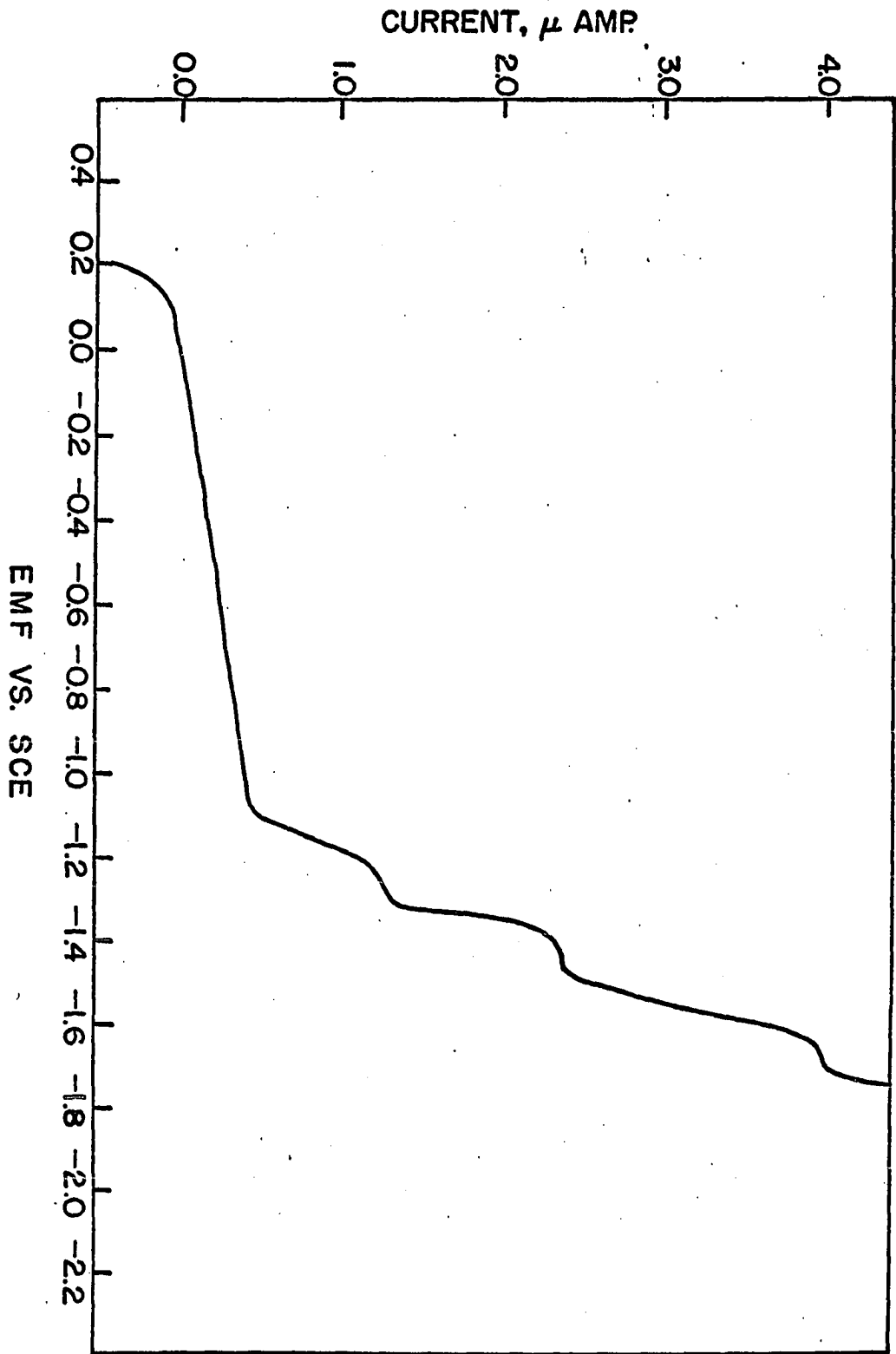
Calculation of the number of electrons

The diffusion currents of the three polarographic waves were 0.8, 1.2, and 1.4 μamp . The number of electrons calculated from the polarographic data and the Ilkovic equation are 2.96, 4.43, and 5.15 for the first, second, and third reductions, respectively.

Discussion

The polarogram of the cobalt compound shown in Fig. 5 has three distinct reduction waves--at -1.14, -1.34, and -1.55 volts versus the SCE. The number of electrons involved in the reductions were calculated from the Ilkovic equation $i_d = 706nD^{1/2}Cm^{2/3}t^{1/6}$ where i_d is the diffusion current in $\mu\text{amperes}$, 706 a constant, D the diffusion coefficient in $\text{cm}^2 \text{ sec}^{-1}$, C the concentration in millimoles per liter, m the flow of

Fig. 5. Polarogram of $\text{Co(III)(PDP)}_2\text{Br}$, 0.0001 M solution in 0.1 M KCl, pH 5.5; 25°C



mercury from the capillary in mg./sec., and t the drop time in seconds. The number of electrons involved in the polarographic reductions are 2.96, 4.43, and 5.15 for the first, second, and third reduction waves respectively. A plot of EMF versus $\log(i/i_d - i)$ for each of these reductions gave slopes corresponding to 0.811, 1.17, and 1.04 electrons. While these results are in complete disagreement with the number of electrons calculated from the Ilkovic equation, the slope method of calculation is known to be less reliable than direct calculation from the Ilkovic equation. It is necessary for the reduction to be reversible for the slope method to give meaningful results.

The first polarographic wave at -1.14 volts is apparently due to reduction of the cobalt in the cobalt-PDP compound. This is supported by the fact that addition of excess ligand does not change the height of the first wave but does change the other two waves. The first wave is a three electron reduction; and, apparently, cobalt(III) is reduced to cobalt(0). This is most unusual in the light of the observations of Jaselskis and Diehl (17) on the polarographic reduction of cobalt compounds. The number of electrons involved in the reductions of the second and third polarographic waves also indicates that they are reductions of the PDP molecules.

POTENTIOMETRIC TITRATION OF THE COBALT(II)-PDP COMPOUND

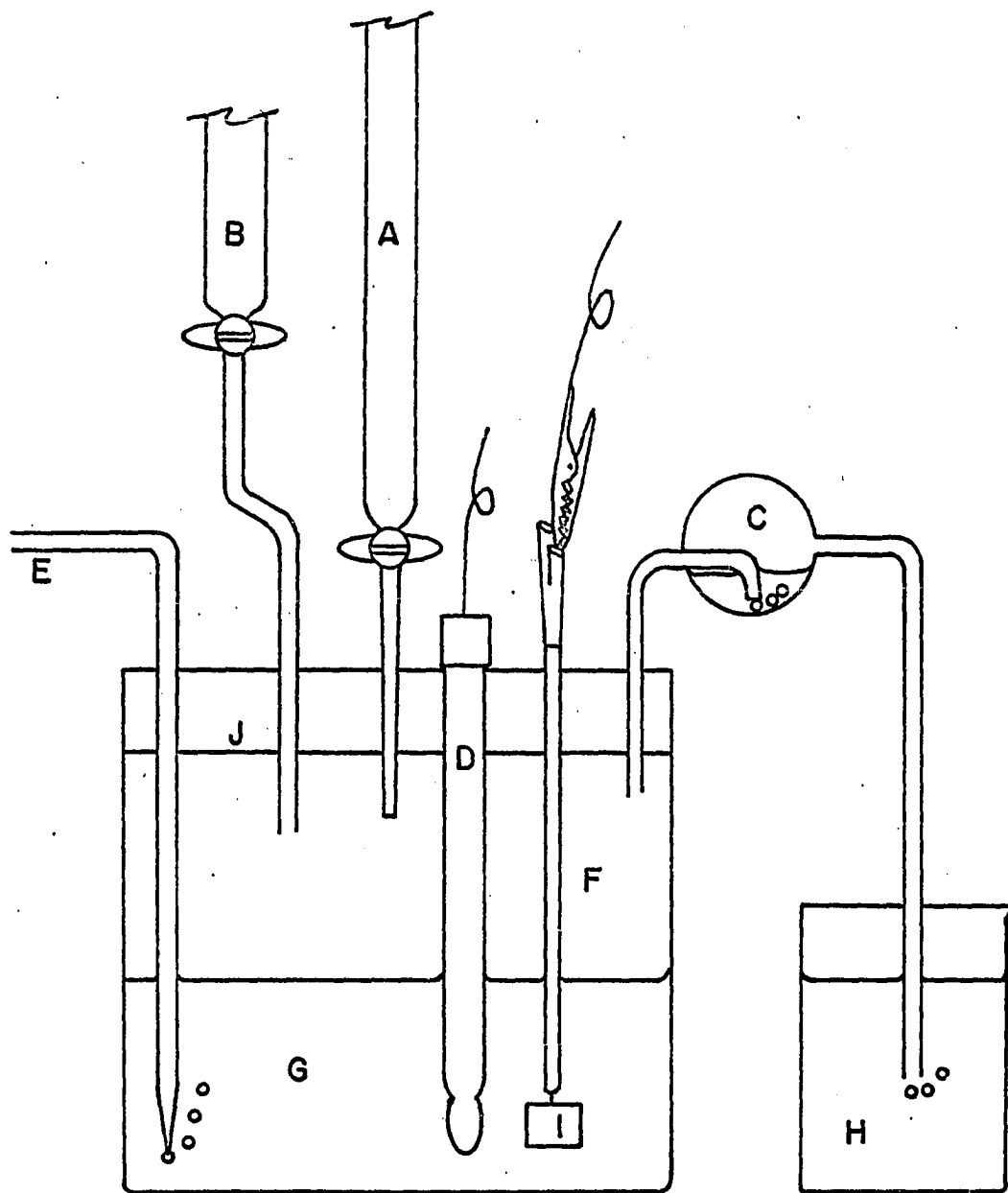
Introduction

The cobalt compound was not soluble enough in aqueous solution to permit a determination of the standard reduction potential by a potentiometric titration. Nevertheless, it was of interest to see if the compound could be titrated potentiometrically in nonaqueous solvents. A water-dimethylsulfoxide (DMSO) solvent mixture was used in this study primarily because of the satisfactory solubility of the cobalt compound in this mixed solvent. It was necessary to exclude atmospheric oxygen inasmuch as the cobalt(II) compound is easily oxidized. The solution was about 50 per cent DMSO.

Experimental Work

The apparatus for the titration is shown in Fig. 6. Nitrogen was bubbled through the apparatus to purge it of oxygen and to stir the solution during the titration. A trap allowed excess nitrogen to escape but excluded air. An aqueous solution of cobalt(II) sulfate was placed in the titration apparatus, and all oxygen removed by purging with nitrogen. The cobalt(II)-PDP compound was then formed by adding a solution of PDP in DMSO which had been previously freed of dissolved oxygen. The compound formed was titrated with 0.1 M potassium dichromate free of dissolved oxygen. A platinum foil indicator electrode and a commercial type SCE were used.

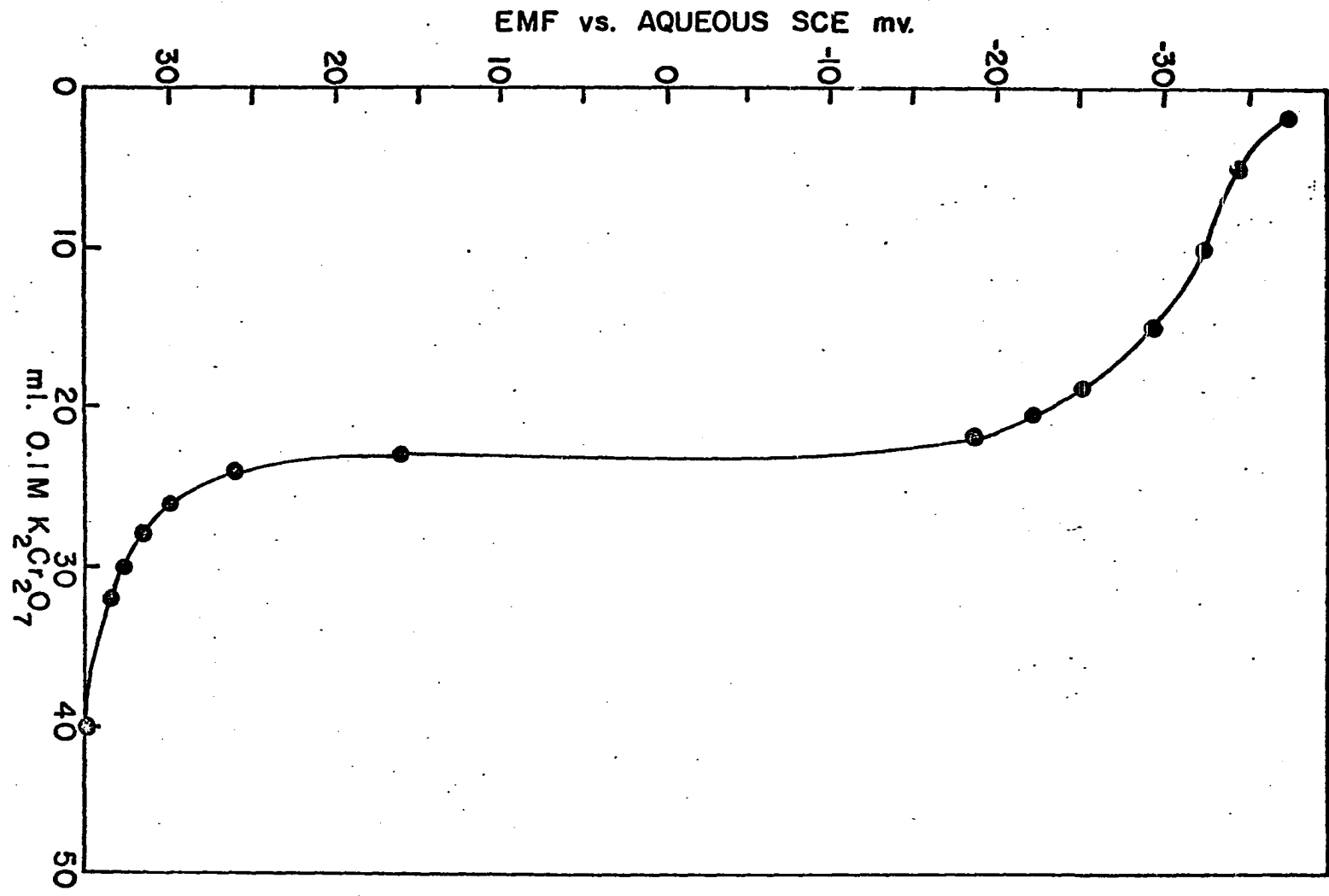
- Fig. 6. Apparatus for potentiometric titration in the absence of oxygen
- A. 0.1M $K_2Cr_2O_7$ solution
 - B. Solution of PDP in DMSO
 - C. Bubbler containing water
 - D. SCE
 - E. Nitrogen inlet
 - F. Glass tubing containing Hg for electrical contact
 - G. Aqueous solution of cobalt(II) sulfate
 - H. Water
 - I. Platinum foil
 - J. Rubber stopper with holes for entrance of tubes



Discussion

The potentiometric titration curve is shown in Fig. 7. A very sharp break was obtained with an apparent E° for the reaction of -0.312 volts versus the aqueous SCE. The E° is not the thermodynamic E° since the titration was not in aqueous solution under standard conditions. A titration carried out under the same conditions but omitting the cobalt compound showed no evidence that DMSO was being oxidized.

Fig. 7. Potentiometric titration curve for cobalt(II) compound of PDP



THE OXIDATION STATE OF COBALT IN THE PDP COMPOUND

Introduction

The potentiometric titration of the cobalt(II)-PDP compound suggested that the assumption of Lions and co-workers (8) that the cobalt is oxidized by the ligand to cobalt(III) was incorrect. This work suggested that the cobalt(II) compound is stable in the absence of oxidizing agents and air. To answer this question, an all-glass apparatus was built in which PDP, cobalt(II) salts, and solvent could be mixed in the absence of oxygen under a nitrogen atmosphere. The cobalt(II)-PDP compound formed was then sealed into an NMR sample tube and the NMR spectrum measured. The NMR spectrum shows quite easily the presence or absence of paramagnetic material in the sample by the width of the absorption bands. Broadening of some of the absorption bands is an indication of the presence of paramagnetic materials.

Experimental Work

Stoichiometric amounts of PDP and cobalt(II) perchlorate were placed in the apparatus; and after purging the system of oxygen with pure nitrogen, DMSO which had also been purged of dissolved oxygen was admitted to the system. After thorough mixing, a sample of the solution containing the cobalt(II) compound was drawn into the NMR sample tube, and the tube was sealed with a torch.

The NMR spectrum of the cobalt(II) compound

The NMR spectrum of this sample showed typical broadening of the peaks characteristic of the presence of a paramagnetic material. Only those peaks which correspond to hydrogen atoms close to a paramagnetic center show noticeable broadening because nuclear-coupling effects decrease inversely with the third power of the distance between nuclei (18).

NMR spectrum after oxidation

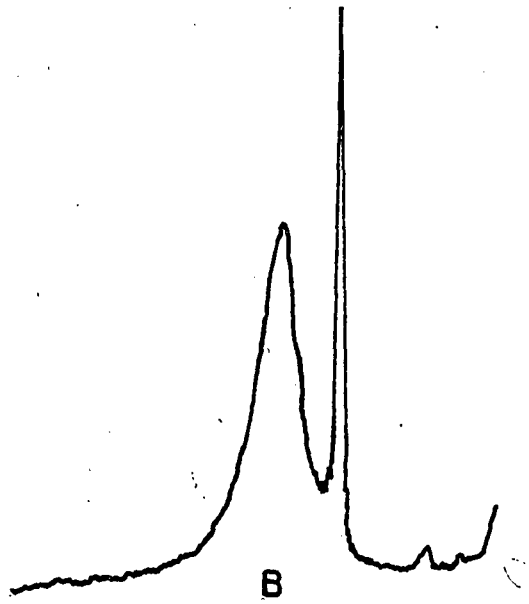
The sample tube was then opened, and oxygen was bubbled through the solution for several minutes. The sample was then purged of dissolved oxygen by the passage of a stream of oxygen-free nitrogen.

The absorption peaks now appeared quite sharp and showed quite strikingly that the compound was diamagnetic. The differences in the spectra may be seen in Fig. 8.

Discussion

Apparently, cobalt(II) readily forms a stable compound with PDP. This bivalent cobalt compound is immediately oxidized to the trivalent cobalt compound by air. It is apparent from this work that the cobalt(II) compound is stable in the absence of oxidizing agents and that PDP is not reduced by the oxidation of the cobalt.

Fig 8. NMR spectrum of the cobalt compound
A. After air oxidation
B. Before air oxidation



COLORIMETRIC DETERMINATION OF COBALT

Introduction

A number of colorimetric reagents for cobalt have been reported in the literature. 2-Nitroso-1-naphthol-4-sulfonate is the reagent most commonly employed and presumably the best of those known. The reagent has molar extinction coefficient of $14,400 \text{ l cm}^{-1} \text{ mole}^{-1}$, and the system conforms to Beer's law from 0.24 to 7.5 ppm cobalt. The method gives results accurately to plus or minus 2 per cent for concentrations of cobalt above 0.24 ppm. Below this concentration, the accuracy is plus or minus 20 per cent. The reagent is not specific and is subject to a number of interferences. Wise and Brandt (3) found that the following ions give errors in absorbancy of greater than 2 per cent when present in concentrations of greater than 0.001 M or more: Cu(II), Fe(II), Fe(III), Ni(II), Pb(II), Al(III), Cd(II), Hg(II), Bi(III), Sn(IV), Sb(III), Mn(II), As(III), $\text{UO}_2(\text{II})$, $\text{CrO}_4^{=}$, $\text{Cr}_2\text{O}_7^{=}$, and CN^- . They report that it is possible to mask Fe(III) or Cu(II) with citrate if these ions are present in concentrations of less than 0.001 M. Nickel must be absent in all cases.

The large number of interferences and the necessity of preliminary separations in the case of nickel has led to the need for a better colorimetric reagent for the cobalt. The large molar extinction coefficient of the cobalt(II)-PDP compound suggests its use in the colorimetric analysis of cobalt. A detailed study to determine the best conditions for analysis of cobalt with this compound was therefore undertaken.

Experimental Work

Effect of pH

A series of solutions containing the same amounts of cobalt(II) sulfate and FDP and buffered at various pH values with constant ionic strength buffers, $\mu = 0.1$, was prepared. Each solution was $2.00 \times 10^{-5} M$ in cobalt(II) and $2.00 \times 10^{-4} M$ in FDP. The constant ionic strength buffers were prepared by the directions of Bates described on page 6. The absorbances of these solutions were measured at 470 $m\mu$. The data are shown in Fig. 9. The absorption spectrum of the cobalt compound at pH 8.65 is shown in Fig. 2. These solutions were prepared in the same manner as those above.

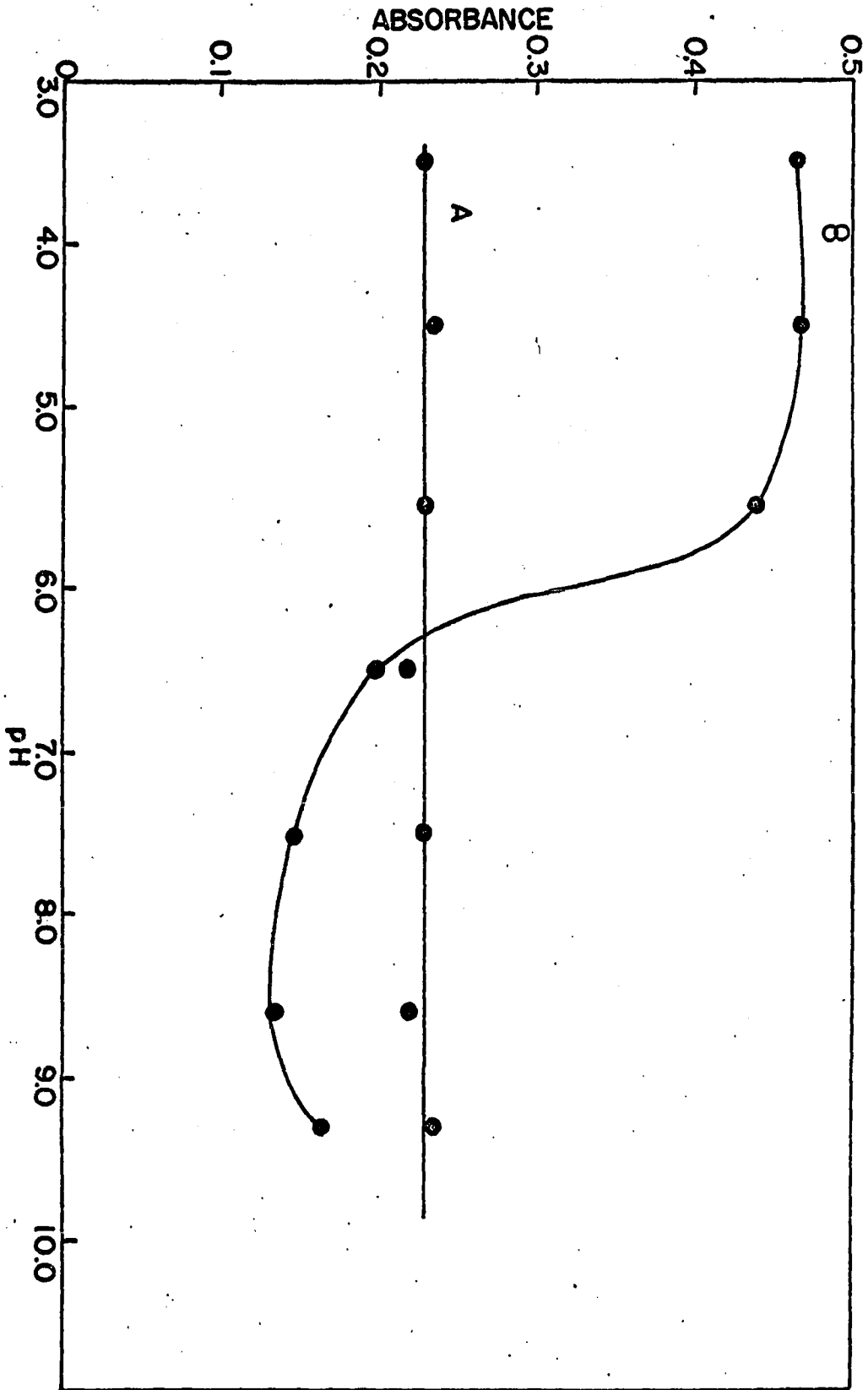
The effect of pH on the absorption of FDP alone was also studied at pH 5.6, 7.6, and 9.42. Three solutions of $8.00 \times 10^{-4} M$ FDP were prepared by diluting 0.0100 M FDP with the appropriate buffer of constant ionic strength (described on page 6). The absorbance of each solution was then measured at 480 $m\mu$, the wavelength of maximum absorbance for the cobalt-FDP compound. The data are given in Table 3.

Table 3. Effect of pH on the absorbance of $8.00 \times 10^{-4} M$ FDP at 480 $m\mu$ in $\mu = 0.1$ buffers

pH	Absorbance
5.60	0.025
7.60	0.049
9.42	0.034

The spectrum of FDP in pH 9.3 solution is shown in Fig. 12.

Fig. 9. Absorbance of cobalt(III)-PDP as a function of pH, 2×10^{-4} M Co(II), 4×10^{-4} M PDP
A. 470 m μ
B. 420 m μ



Effect of oxidizing agents

It was shown in an earlier part of this thesis that cobalt(II) is oxidized to cobalt(III) in the cobalt-PDP compound by atmospheric oxygen. Shaking the solutions in air for a few minutes proved sufficient for the development of maximum color. Strong oxidizing agents destroyed the color.

Effect of excess reagent

The effect on the absorbance of the cobalt-PDP solutions of excess reagent was studied by preparing solutions containing the same amount of cobalt(II) sulfate and buffered at the same pH but containing varying amounts of PDP. All solutions were buffered at pH 9.42 and contained 1 ml. of 1.000×10^{-3} M cobalt(II) sulfate per 25 ml. of solution. Two to ten milliliters of 0.0100 M PDP per 25 ml. of solution were added. The results are given in Table 4.

Table 4. Absorbance of cobalt(II) solutions containing varying amounts of excess PDP buffered at pH 9.43, $\mu = 0.1$

ml. of 0.0100 M PDP per 25 ml. added	Absorbance at 480 m μ
2	0.951
5	0.976
10	0.988

Interferences

The colorimetric determination of cobalt with PDP has a number of interferences. Strong complexing agents such as cyanide react with cobalt ions to form coordination compounds which are inert with respect to

substitution. In the presence of such agents, the PDP compound with cobalt(II) can not form.

Iron(II), nickel(II), and copper(II) give highly colored solutions with PDP which interfere in the colorimetric determination of cobalt. The visible spectra of these compounds are shown in Fig. 10, 11, and 12.

Interference of iron(II) Since both iron and cobalt-PDP compounds absorb light strongly in the same spectral region, both can not be present if one or the other is to be determined spectrophotometrically with PDP. Two approaches to the elimination of the interference of iron in the determination of cobalt were investigated: oxidation of the iron(II)-PDP compound to the slightly colored iron(III)-PDP compound, and the extraction of the iron(II)-PDP compound into organic solvents.

Oxidation of the iron(II) compound A series of solutions containing the same amount of cobalt(II) sulfate and varying amounts of iron(II) was prepared. To each of five 50-ml. volumetric flasks was added 1 ml. of 1.000×10^{-3} M cobalt(II) sulfate and varying amounts of 1.000×10^{-3} M ferrous ethylenediammonium sulfate. Two milliliters of 0.0100 M PDP in 95 per cent ethanol were added to each flask. A few drops of 30 per cent hydrogen peroxide and 1 ml. of 0.1 M sodium tartrate were added and the solutions heated to destroy the excess peroxide. After dilution of the solutions, the absorbances were measured. The data are given in Table 5. The iron(III)-PDP compound was not stable and ferric hydroxide precipitated from solution after standing.

Table 5. Effect of oxidation on the absorbances of the iron(II)-PDP compound at 480 m μ in solutions containing 1 ml. of $1.000 \times 10^{-3} \text{M}$ Co(II) per 50 ml.

ML. $1.000 \times 10^{-3} \text{M}$ Fe(II)	Absorbance
0	0.286
1.00	0.331
3.00	0.294
5.00	0.071
10.00	0.021

Extraction Three solutions of different pH values were prepared by addition of $1.000 \times 10^{-3} \text{M}$ ferrous ethylenediammonium sulfate and excess 0.0100 M PDP to each of three 50-ml. volumetric flasks. The solutions were diluted to mark with 0.1 constant ionic strength buffers of pH 9.1, 8.2, or 5.2 (described on page 6). The iron(II) concentration in each solution was $4.00 \times 10^{-5} \text{M}$. Ten milliliters of each of the buffered solutions were then extracted with 10 ml. of water-saturated octyl alcohol. The aqueous phase was drained off and diluted to 25 ml., and the absorbance measured. At pH 9.1, the absorbance before extraction was 0.290 and 0.010 after; at pH 8.2, 0.248 before and 0.026 after; at pH 5.2, 0.030 before and 0.010 after.

A series of four solutions containing a constant amount of the cobalt-PDP compound and varying amounts of the iron compound was prepared. To each of four 25-ml. volumetric flasks were added 1 ml. of $1.000 \times 10^{-3} \text{M}$ cobalt(II) sulfate and, in order, 0, 2, 5, and 8 ml. of $1.000 \times 10^{-3} \text{M}$ ferrous ethylenediammonium sulfate. Two milliliters of 0.0100 M PDP in 95 per cent ethanol were added to each flask. The solutions were diluted to

mark with a pH 9.1 buffer. Ten milliliters of each solution were extracted once with 10 ml. of water-saturated octyl alcohol, and the aqueous layer was then separated and diluted to 50 ml. The absorbances of the aqueous solutions are given in Table 6.

Table 6. Absorbance of 2.00×10^{-5} M cobalt(III)-PDP compound after extraction of the iron(II)-PDP compound into octyl alcohol

ml. of 1.000×10^{-3} M Fe(II) added per 25 ml.	Absorbance
0	0.162
2	0.165
5	0.169
8	0.170

The efficiency of the extraction for large amounts of iron in the presence of small amounts of cobalt was studied. To each of five 60-ml. separatory funnels were added 1 ml. of 1.000×10^{-3} M cobalt(II) sulfate and varying amounts of 0.0982 M ferrous ethylenediammonium sulfate so that the iron to cobalt ratios are 3, 50, 100, 500, and 1000. A stoichiometric amount of 0.1000 M PDP was added in each case. To insure that all the iron was reduced to iron(II), 0.1 g. ascorbic acid was added and the solutions made basic with 10 ml. of 0.1 M sodium hydroxide. The solutions were then extracted twice with an equal volume of chloroform, and the aqueous phases were drained off and diluted to 50 ml. The absorbance of the aqueous solutions were measured at 480 m μ . The data are given in Table 7.

Table 7. Absorbance of pH 10 solutions of varying iron to cobalt ratios after extraction of the iron-PDP compound into chloroform

Iron to cobalt ratio(Fe/Co)	Absorbance
3	0.201
50	0.211
100	0.215
500	0.202
1000	0.202

Better extractions were obtained if chloroform was used instead of octyl alcohol because of the sharper phase separations after extraction with chloroform. The aqueous phase which had been extracted with octyl alcohol was often cloudy.

Interference of copper(II) and nickel(II) Solutions of the nickel(II) and copper(II) compound of PDP were prepared by addition of 1 ml. of 1.000×10^{-3} M copper(II) or nickel(II) and 1 ml. of 0.0100 M PDP and pH 9.43 buffer to a 25-ml. volumetric flask. Five milliliters of this solution were then extracted with 10 ml. of xylene, and the aqueous phase was diluted to 25 ml. with buffer. The absorbances of the aqueous solutions were then measured. The absorbance of copper and nickel-PDP solutions before and after extraction with xylene are given in Table 8.

Table 8. Absorbance of aqueous pH 9.43 solutions before and after extraction of the Cu(II) and Ni(II)-PDP compounds into xylene

	Absorbance	
	Before extraction	After extraction
Cu(II)-PDP compound	0.824	0.027
Ni(II)-PDP compound	0.417	0.020

Similar results were obtained for extractions with chloroform.

Discussion

In Fig. 9, it is shown that the change in pH has little effect on the intensity of the absorption peak at 470 m μ of the cobalt(III)-PDP compound between pH 3.0 and pH 9.5.

Oxidizing agents other than air are not required to develop the maximum color of the cobalt compound within a very few minutes. Very strong oxidizing agents may adversely effect the results by destroying the reagent.

Attempts to oxidize the iron(II) compound to the colorless iron(III) compound were not successful as can be seen from the data given in Table 5.

The interference of iron(II), nickel(II), and copper(II) may be circumvented by extraction of the PDP compounds of these metals into a non-aqueous solvent such as octyl alcohol, xylene, or chloroform. Table 6 and Table 7 show that very large amounts of iron(II) can be separated from small amounts of cobalt by the extraction from basic solution. No iron was extracted from acid solutions. In Table 8, it is shown that the nickel(II) and copper(II) compounds of PDP are completely extracted into xylene from pH 9.43 solution. Similar results are obtained with extractions with chloroform. Although no separations of cobalt and nickel or copper were made separately, the data in Table 8 and Table 10 indicate that this separation works. In Table 10, cobalt is separated quantitatively from several metals, including nickel, by extraction of divalent

metal-PDP compounds into chloroform leaving the cobalt(III)-PDP compound in the aqueous phase.

Chloroform is the least unpleasant solvent to use for extractions and also has the added advantage of being more dense than water so that repeated extractions may be carried out leaving the aqueous layer in the separatory funnel each time. Chloroform also gives sharper phase separations than octyl alcohol. The aqueous phase is often cloudy after extraction with octyl alcohol.

The ease with which iron, nickel, and copper compounds of PDP may be extracted into nonpolar solvents such as chloroform may be explained as the selective extraction of an uncharged compound into the organic phase leaving a charged cobalt species in the aqueous phase. Earlier work in this thesis has shown that cobalt is present as cobalt(III) in the PDP compound and that other metal ions are present as bivalent ions. Removal of the two acidic protons from the coordinated PDP molecules, as would occur in basic solution, would give a charged species for cobalt but an uncharged compound for the bivalent transition metals which would be preferentially extracted into low dielectric constant solvents. Cobalt(II) can thus be determined in the presence of more than 1000 times as much iron using the extraction procedure.

PDP itself has only a low absorbance in the 470 m μ region, and no correction for excess reagent is necessary. Large excess of reagent is not required to convert all the cobalt to the colored compound.

DETERMINATION OF COBALT IN STEELS

Introduction

The determination of small amounts of cobalt in the presence of large amounts of iron, nickel, manganese, or other divalent transition metals such as would be expected in steels requires extensive separations using presently available analytical reagents. Great advantages in the simplicity and rapidity of the analysis would result if preliminary separations could be avoided. The ease with which the PDP compounds of bivalent transition elements may be extracted into nonpolar solvents such as chloroform offers a technique whereby the formation of the transition-metal compounds and their separation from the cobalt(III)-PDP compound may be easily and rapidly made. The method was first applied to known solutions of cobalt and comparable amounts of iron. Solutions containing iron, cobalt, nickel, and manganese similar to a solution of a steel sample in dilute acid were then analyzed by the extraction method. Finally, the technique was applied to the analysis of a National Bureau of Standards steel sample.

Recommended Procedure for the Determination of Cobalt in Steel

Reagents

Preparation of the reagent PDP has been described, page 8. Prepare a 0.1 M solution of PDP in ethanol by dissolving 1.9800 g. of the solid compound in ethanol and then diluting to 100 ml. with ethanol.

Prepare a standard solution of cobalt(II) sulfate containing 1.48 mg.

of cobalt per 25 ml. from anhydrous, reagent-grade cobalt(II) sulfate free from iron and nickel impurities.

Prepare a pH 10 borate buffer by the directions given on page 6. Approximately 25 ml. will be needed for each aliquote of the unknown solution taken.

Preparation of the calibration curve

Pipette 0.1, 0.2, 0.3, and 0.4 ml. of the standard cobalt(II) sulfate solution into separate 25-ml. volumetric flasks. Add 0.1 ml. of the PDP reagent. Mix thoroughly. Dilute to mark with pH 10 buffer. This gives solutions containing 5.9, 11.8, 17.7, and 23.6 $\mu\text{g.}$ of cobalt per 25 ml. Measure the absorbance of these solutions at 480 $\text{m}\mu$. Construct a calibration curve by plotting absorbance versus concentration in $\mu\text{g.}$ of cobalt per 25 ml.

Procedure

Weigh out a sample of the steel to be analyzed of such size as to contain approximately 0.7 mg. of cobalt. Dissolve the steel in a minimum amount of nitric acid with heating. Transfer the solution to a 250-ml. volumetric flask and dilute to mark with distilled water. Pipette 5 ml. of this solution into a 60-ml. separatory funnel. Add approximately 5 mg. of sodium hydrosulfite on the tip of a spatula. Shake the solution to mix. Add 2 ml. of 0.1 M PDP solution and shake to mix. Add 10 ml. of pH 10 borate buffer. Extract this solution twice with 20-ml. portions of chloroform. Discard the chloroform layers. Dilute the solution to 25 ml. with the pH 10 borate buffer and measure the absorbance of the solution at 480 $\text{m}\mu$.

Experimental Work

Analysis of known solutions

A series of known solutions containing up to twice as much iron as cobalt was prepared by addition of appropriate amounts of standard 1.000×10^{-3} M cobalt(II) sulfate and 1.000×10^{-3} M ferrous ethylenedimmonium sulfate and 0.0100 M FDP to 25-ml. volumetric flasks and diluting with distilled water and enough 0.1 M potassium hydroxide to make the solution pH 10. Ten milliliters of each solution was then extracted with 10 ml. of water-saturated octyl alcohol and the alcohol layer discarded. The aqueous layer was then diluted to mark with distilled water, and the absorbance was measured at 480 μ . A standard curve was prepared in exactly the same way with solutions containing only cobalt(II) sulfate. The results are given in Table 9.

Table 9. Analysis of solutions containing varying ratios of Co(II) and Fe(II)

Solution number	Co/Fe	μ g. Co taken	μ g. Co found
1	3/1	23.6	24.3
2	1/2	47.2	46.5
3	2/3	70.9	72.5

A known solution prepared to simulate a steel sample was analyzed by the recommended procedure. The sample solution contained 234.9 μ g. cobalt, 164.8 μ g. manganese, 29.3 mg. nickel, and 55.85 mg. iron per 100 ml. Six 5-ml. aliquotes were taken and treated by the standard procedure. The results are given in Table 10.

Table 10. Analysis of a known sample for cobalt with PDP by extraction of the PDP compounds of bivalent metals into octyl alcohol; sample contains 234.9 μg . cobalt, 164.8 μg . manganese, 29.3 mg. nickel, and 55.85 mg. iron

μg . of cobalt found
230
236
262
231
218
<u>219</u>
233 average

Analysis of cobalt steel, NBS 126a

The National Bureau of Standards sample of high nickel steel was analyzed by the suggested procedure. The results on ten aliquotes taken from the sample solution are given in Table 11.

Table 11. Determination of cobalt in NBS 126a

Cobalt found, per cent
0.304
0.298
0.303
0.317
0.309
0.317
0.306
0.318
0.317
<u>0.304</u>
average: 0.309, $\sigma = 0.0067$

Better results were obtained when the aqueous phase was made basic with the pH 10 borate buffer than if the solution was made basic with potassium hydroxide. Results of 0.329 per cent cobalt for NBS 126a were obtained on eight aliquotes taken from the same stock solution with a standard deviation of 0.017 where the pH was adjusted with base instead of buffer.

Sodium hydrosulfite was found to give better results than ascorbic acid when used to reduce the iron to iron(II). For fourteen aliquotes taken, results of 0.470 per cent cobalt were found using ascorbic acid as reducing agent on NBS 126a.

Discussion

The analysis of known solutions gives accurate results with small amounts of cobalt in the presence of small amounts of iron. The average value for the simulated high-nickel steel shows quite good results, but the precision is not as good as hoped.

Analysis of NBS 126a high-nickel steel gave high results when sodium hydroxide was used to adjust the pH. Results of 0.329 per cent cobalt with a standard deviation of 0.017 were obtained. High results were also obtained when ascorbic acid was used to reduce the iron to iron(II).

Using sodium hydrosulfite to reduce the iron and pH 10 borate buffer to adjust the pH on the solution gave results of 0.309 per cent cobalt for analysis of NBS 126a with a standard deviation of 0.0067. The precision of this method of analysis is not easy to compare with that of other methods since workers for the most part only report the average of several analyses. The Bureau value for NBS 126a is 0.308.

NATURE OF THE IRON(II) DERIVATIVE OF PDP

Introduction

Lions and co-workers reported the preparation of the iron(II) compound of PDP and studied some of the properties of the compound (8). In the work presented here, the spectrum and structure of the iron(II) compound are described. The compound has been characterized by spectrophotometric studies, thermogravimetric analysis, molar conductance, and Karl Fischer titration for water. The NMR spectrum has shown the compound to be diamagnetic.

Experimental Work

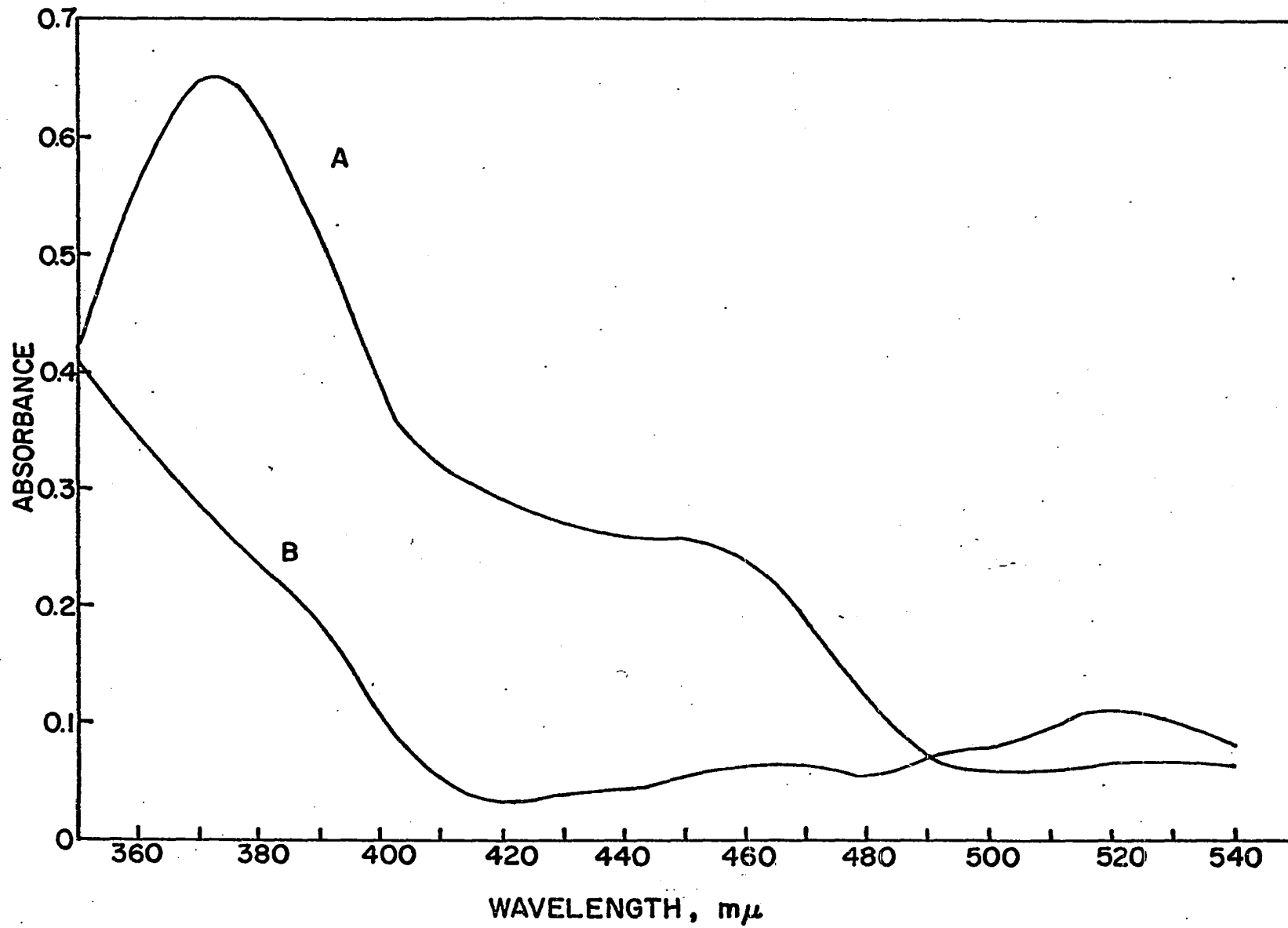
Preparation of the iron compound

The iron(II) derivative of PDP was prepared by addition of an aqueous solution of ferrous ammonium sulfate to an ethanolic solution of PDP. An ice-cold, saturated solution of potassium bromide was then added. The iron(II)-PDP compound crystallized in dark red-brown plates from ethanol, melting point 189-191°. The iron compound dissolves in water to give a dark-red solution.

Spectrophotometric studies of the iron compound

A continuous variations study of the iron compound in aqueous solution was made in the same manner as for the cobalt compound. The absorption spectrum of the iron compound in solutions buffered at pH 8.3 and 5.2 are shown in Fig. 10. The solutions were all ionic strength 0.1.

Fig. 10. Absorption spectrum of Fe(II)-PDP, $4 \times 10^{-5} \text{M}$
A. pH 9.1, $\mu = 0.1$
B. pH 5.2, $\mu = 0.1$



Characterization of the compound

Water in the iron compound was determined by Karl Fischer titration using the apparatus previously described. The visual end-point detection could not be used because of the dark color of the solutions titrated.

Thermogravimetric analysis of the iron compound gave weight losses at about the same temperatures as those for the cobalt compound. The data are given in Table 12.

Table 12. Thermogravimetric analysis of the iron(II)-PDP compound, sample: 30.5 mg.

Weight loss, mg.	Material lost	Calculated loss, mg.
2.5	3H ₂ O	2.5
7.6	Br ₂	7.4
17.7	2(C ₁₁ H ₁₀ N ₄)	17.7

The conductance of a 1.000×10^{-3} M solution of the iron compound was measured in the same conductance cell described under the section on the cobalt compound. The data are given in Table 1.

The NMR spectrum of the compound was run in DMSO using tetramethylsilane as internal standard.

Discussion

The combining ratios of iron to PDP was shown to be 1:2 by the method of continuous variations. The peak was quite sharp and occurred at a PDP mole ratio of 0.63.

The water in the iron compound was determined by Karl Fischer titration. A 10 mg. sample of the iron compound required 0.3695 ml. of Karl Fischer reagent. The reagent was found to correspond to 0.00224 g. of water per ml. of Karl Fischer reagent. The water in the iron compound is very close to three molecules of water per atom of iron (8.28 per cent water as compared to 8.12 per cent theoretical). The dead-stop end-point gave very satisfactory end-point detection. The visual end-point could not be used because of the intense color of the solutions titrated.

The molar conductance of a $1.000 \times 10^{-3} \text{ M}$ solution of the iron compound in conductivity water was 202.5. This is the conductance expected in water solutions for a typical di-univalent electrolyte.

The NMR spectrum of the iron compound was run in DMSO using tetramethylsilane as internal standard. The absorption bands were all quite sharp. The absence of any line broadening in the NMR spectrum shows that iron(II) is present in the compound. Paramagnetic iron(III) would give significant line broadening as in the case of the cobalt(II) compound.

The spectrum of the iron compound is quite interesting. A very intense peak at $375 \text{ m}\mu$ appears in the solution of pH 9.1. Only part of this peak appears at low pH and then as a shoulder on a large peak appearing in the UV region of the spectrum. This very broad shoulder on the ultra-violet band extends into the visible region of the spectrum to about $450 \text{ m}\mu$. Because of the intense charge-transfer bands all through this region, none of the small ligand-field transitions could be seen.

The thermogravimetric analysis and Karl Fischer titration for water support the results of the continuous variations study and lead to the

conclusion that the iron compound is $\text{Fe}(\text{C}_{11}\text{H}_{10}\text{N}_4)_2\text{Br}_2 \cdot 3\text{H}_2\text{O}$. The PDP compound is apparently a tridentate chelating agent since the bromides are shown not to be in the coordination sphere of the iron atom by the conductance study. Apparently, three nitrogens on the PDP molecule are coordinated to the iron. This suggests that the two PDP molecules are planar and at right angles to each other around the iron atom. Since the magnetic study showed that the iron is present as iron(II), and the conductance experiment showed that two anionic bromides are present for each iron, none of the acidic hydrogens on the PDP molecules have been displaced in isolating the solid iron compound. The experimental work with cobalt in which iron is extracted into chloroform from basic solution suggests that these hydrogens are removed in basic solution to give a neutral compound.

THE NICKEL(II) COMPOUND OF PDP

Introduction

A nickel(II) compound of PDP was also reported by Lions and his co-workers (9); but as with the cobalt and iron compounds, the nature of the compound was only partially established. In the work reported here, the compound has been characterized by elemental analysis, spectrophotometric studies, molar conductance, and thermogravimetric analysis. The effect of pH on the absorption spectrum of the compound and also on the extraction of the compound into nonaqueous solvents has been investigated.

Experimental Work

Preparation of the compound

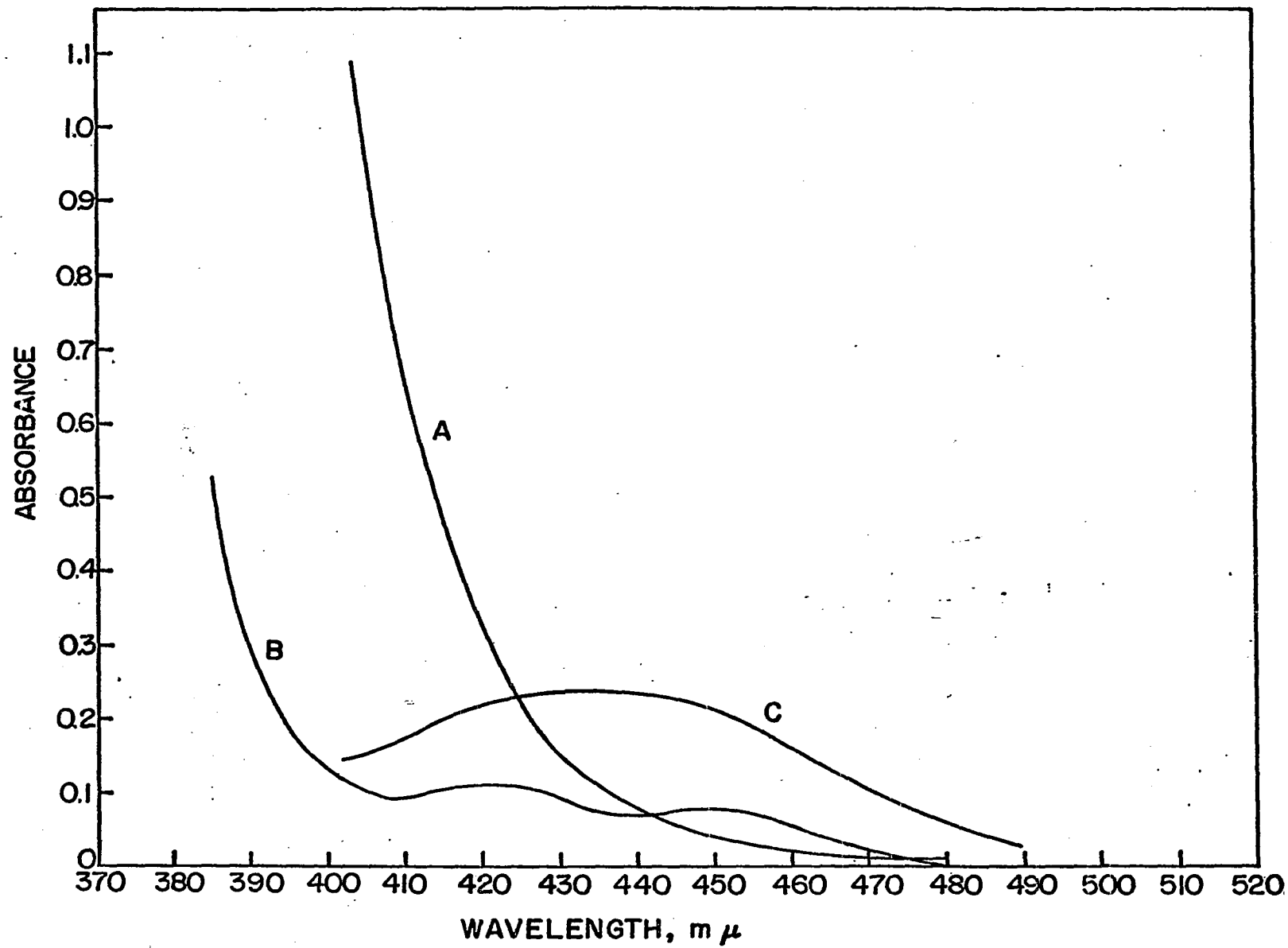
The nickel(II) compound of PDP was prepared by addition of an ethanol solution of PDP to an aqueous solution of nickel(II) nitrate. The bromide salt was precipitated by addition of an ice-cold, saturated solution of potassium bromide to the nickel-PDP solution. The compound was recrystallized from hot ethanol to give red-orange plates, melting point 264-265°.

Characterization of the compound

The spectrum of the nickel-PDP compound in the visible region of the spectrum is shown in Fig. 11. Maximum absorbance in this region occurs at 440 m μ with a molar extinction coefficient of 20,000 l cm^{-1} mole $^{-1}$ depending on the pH of the solution. The combining ratio of the compound in aqueous solution has been determined by both the molar-ratio and the continuous-variation methods. (13, 19).

Fig. 11. Spectra of the nickel-PDP compound, 2×10^{-5} M Ni(II), 4×10^{-5} M PDP

- A. pH 3.5
- B. pH 8.9
- C. pH 9.42



The elemental analysis of the compound gave the composition: C, 41.17; H, 3.64; N, 16.52; Br, 23.31; Ni, 8.75; calculated for $\text{Ni}(\text{C}_{11}\text{H}_{10}\text{N}_4)_2\text{Br}_2 \cdot 3\text{H}_2\text{O}$: C, 39.50; H, 3.89; N, 16.75; Br, 23.90; Ni, 8.78.

The molar conductance of a $1.000 \times 10^{-3}\text{M}$ solution of the nickel(II)-PDP compound was measured. The solution was prepared by weighing out the solid compound and dissolving in conductivity water. The data are given in Table 1.

The effect of pH on the absorption spectrum of the nickel compound was studied in constant ionic strength buffers from pH 3.5 to 8.9. The effect of pH on the extraction of the nickel compound into nonaqueous solvents was also studied.

Discussion

The elemental analysis of the compound indicates that the formula of the compound is $\text{Ni}(\text{C}_{11}\text{H}_{10}\text{N}_8)_2\text{Br}_2 \cdot 3\text{H}_2\text{O}$. The reason the analysis gave high results for carbon is not known. The results for the other elements are quite close to the theoretical per cent and leave no doubt that the empirical formula is correct.

The thermogravimetric analysis supports the results of the elemental analysis and confirms the presence of three molecules of water per nickel. A 39.7 mg. sample of the nickel compound shows a weight loss below 100° of 3.22 mg. which is 8.12 per cent. This corresponds very closely to the theoretical 8.08 per cent for three water molecules.

The continuous-variations plot shows very concave slopes on both sides of the maximum which are characteristic of the presence of more than

one species in solution (13). Also, the molar-ratio plot gave a mole ratio between one and two moles of FDP per nickel. This is a clear indication that more than one compound is formed in solution. Probably the 1:1 and the 2:1 ligand to metal compounds are both formed in aqueous solutions of approximately equal FDP and nickel concentrations. Since the 2:1 compound was the compound actually isolated from solution, the 2:1 FDP to nickel compound is probably more stable than the 1:1 compound.

The molar conductance of the solid nickel compound ($\text{Ni}(\text{C}_{11}\text{H}_{10}\text{N}_8)_2\text{Br}_2$) was measured in conductivity water. The molar conductance of a $1.000 \times 10^{-3} \text{ M}$ solution of the compound is 220. This is typical of a di-univalent electrolyte. The molar conductance suggests that the 2:1 FDP to nickel compound has little tendency to dissociate to the 1:1 compound once it is formed in aqueous solution.

The NMR spectrum of the 2:1 nickel compound in DMSO shows very broad peaks. The solid bromide salt was dissolved in the DMSO, and the spectrum was measured using tetramethylsilane as internal standard. The presence of the broad peaks in the NMR spectrum indicates the presence of paramagnetic nickel(II) in the compound.

The presence of bivalent nickel in the compound allows the complete extraction of the compound into chloroform from basic solution in the same manner as for the iron compound, Table 7.

THE NATURE OF THE COPPER COMPOUND

Introduction

Lions and co-workers (20) reported the preparation of a copper-PDP compound with a ligand to metal ratio of 1:1 and also one with a ligand to metal ratio of 1:2. The addition of an alcoholic solution of PDP to an aqueous solution of copper(II) sulfate gives an intensely yellow solution from which either the 1:1 or the 1:2 compounds may be precipitated depending on the PDP to copper ratio. The intense color of the compounds makes PDP of interest as a colorimetric reagent for copper.

Experimental Work

Spectrum of the copper compound

The effect of varying pH on the spectrum was studied from pH 3.0 to 9.3 in constant ionic strength buffers. Known amounts of a 1.000×10^{-3} M copper(II) solution and 0.1000 M PDP were diluted with the buffers. The data are shown in Fig. 12.

Combining ratios

The combining ratios of the copper compound were studied by the molar-ratio method (19). To each of five 50-ml. volumetric flasks was added a constant amount of 0.1000 M PDP in ethanol. Varying amounts of standard copper(II) solution were added to a given amount of ligand so that the ratio of copper(II) to PDP increased from 0.25 to 1.5. The solutions were then diluted with pH 9, $\mu = 0.1$ buffer. The data are given in Fig. 13. In a second experiment, the same procedure was used except a

Fig. 12. Absorption spectra of Cu(II)-PDP and of PDP

A. 4×10^{-5} M Cu(II), 2×10^{-5} M PDP in 0.1 M $\text{Na}_2\text{B}_2\text{O}_7$

B. 2×10^{-5} M PDP in 0.1 M $\text{Na}_2\text{B}_2\text{O}_7$

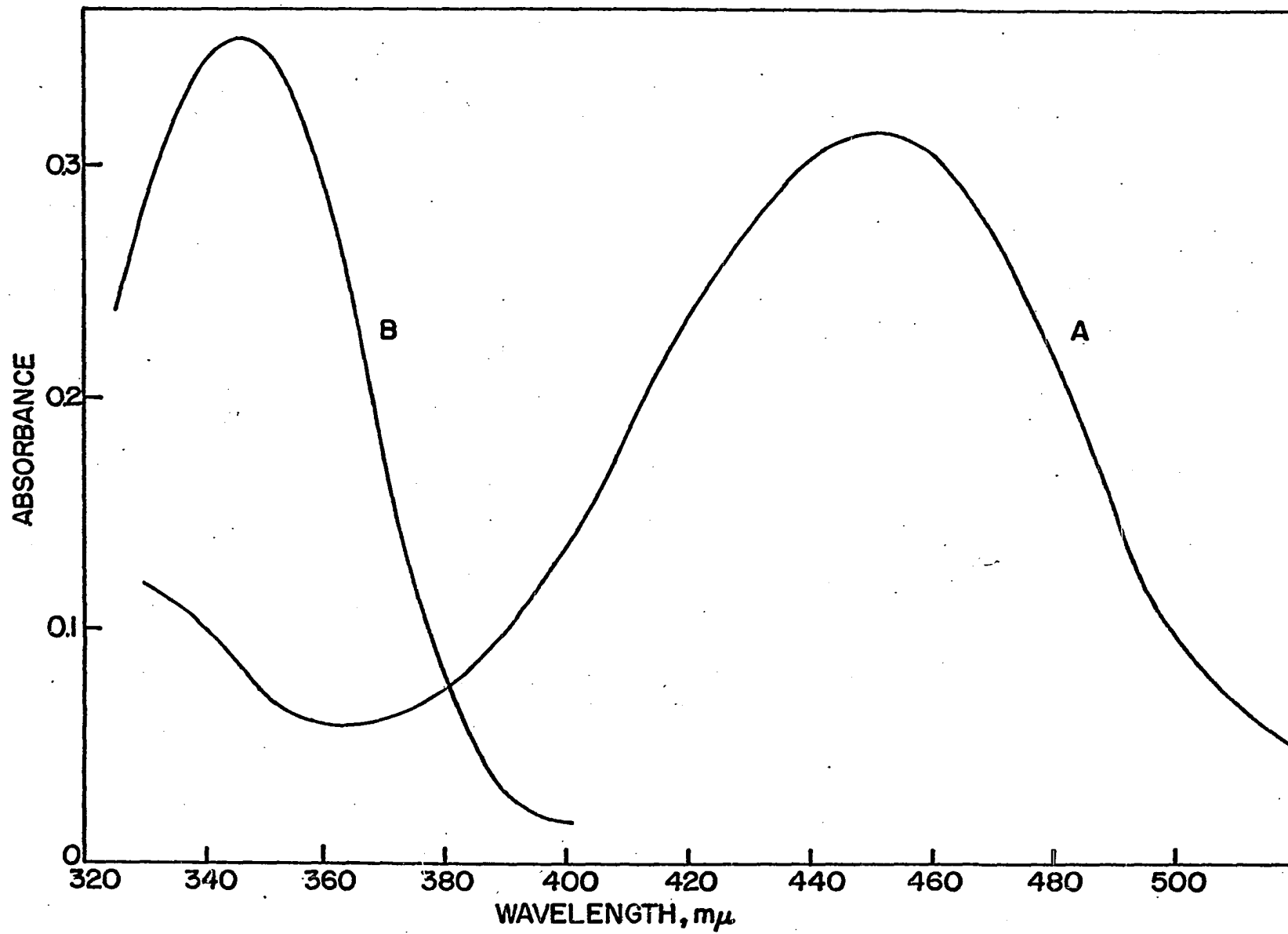
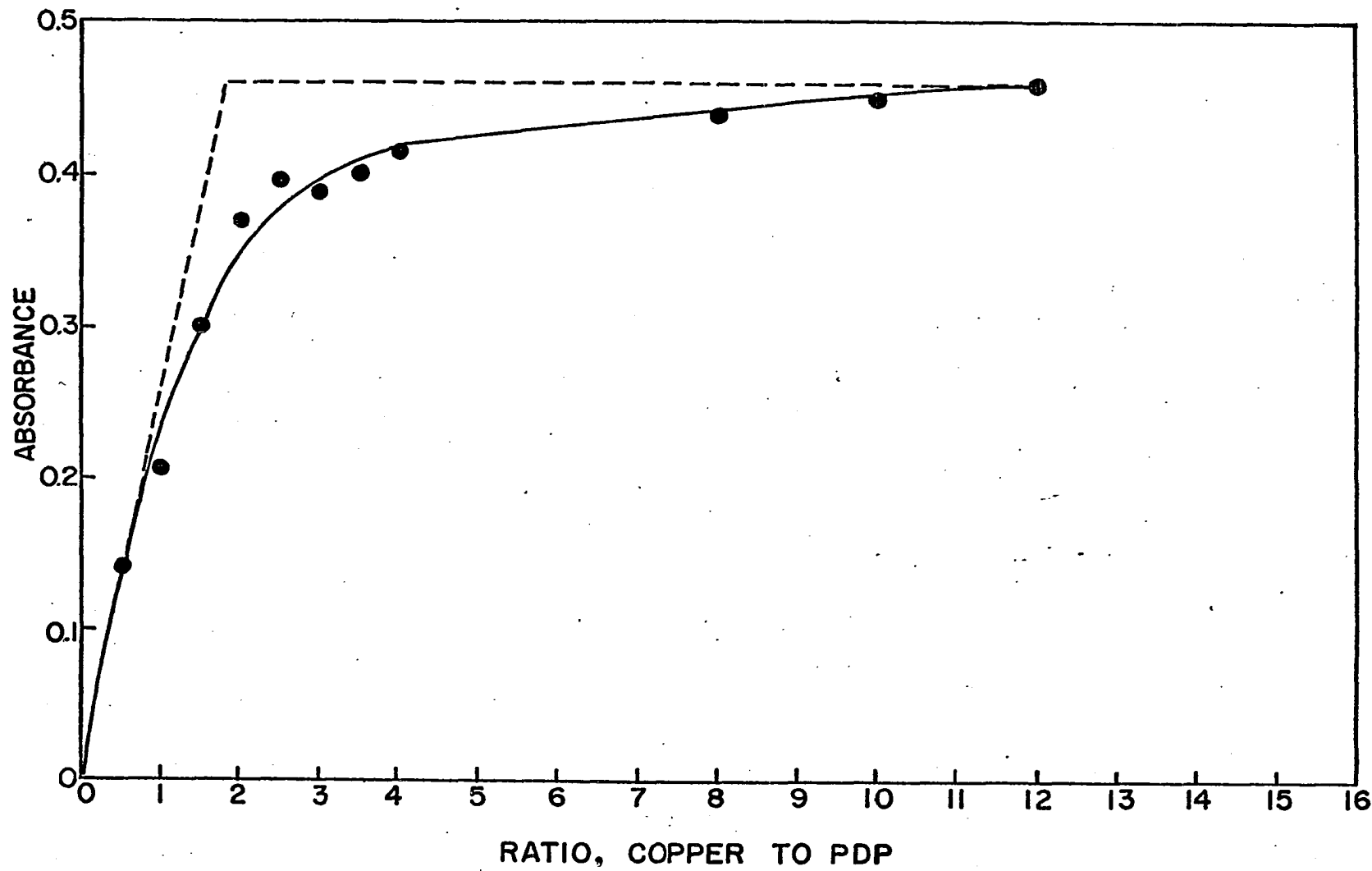


Fig. 13. Absorbance versus ratio of copper to PDP, 2×10^{-5} M PDP and varying copper concentration



constant amount of copper(II) was taken and varying amounts of FDP added. The data are shown in Fig. 14.

Effect of pH

The effect of pH on the copper-FDP compound was studied at varying pH values from pH 3 to 9. Each solution was $2.00 \times 10^{-5} \text{M}$ in copper(II) and $2.00 \times 10^{-4} \text{M}$ in FDP. All solutions were 0.1 ionic strength. The absorbances were measured at 450 μ . The data are shown in Fig. 15.

Discussion

The copper(II)-FDP compound shows intense absorption in the visible region of the spectrum at 440 μ . The variation in absorbance with pH of the 440 μ peak is shown in Fig. 15. The curve shows a large break at pH 6.5. This break may correspond to the removal of the two acidic hydrogen atoms from the coordinated FDP molecules. There is no shift in the absorption maximum with pH.

The molar-ratio plot gives quite interesting results for the combining ratio of copper(II) with FDP. The plots show that either the 1:1 or the 2:1 compound is formed in solution depending on the ratio of copper(II) to FDP. Most likely, the 1:1 compound is the predominant species in solutions of equal FDP and copper concentrations.

It is interesting that both the 2:1 and the 1:1 compounds have maximum absorbance at about 440 μ , but the 2:1 compound has the larger molar extinction coefficient, 22,450 as compared to 15,104 $\text{lcm}^{-1} \text{mole}^{-1}$ for the 1:1 compound.

Fig. 14. Absorbance versus PDP to copper ratio, 2×10^{-5} M copper and varying PDP concentration

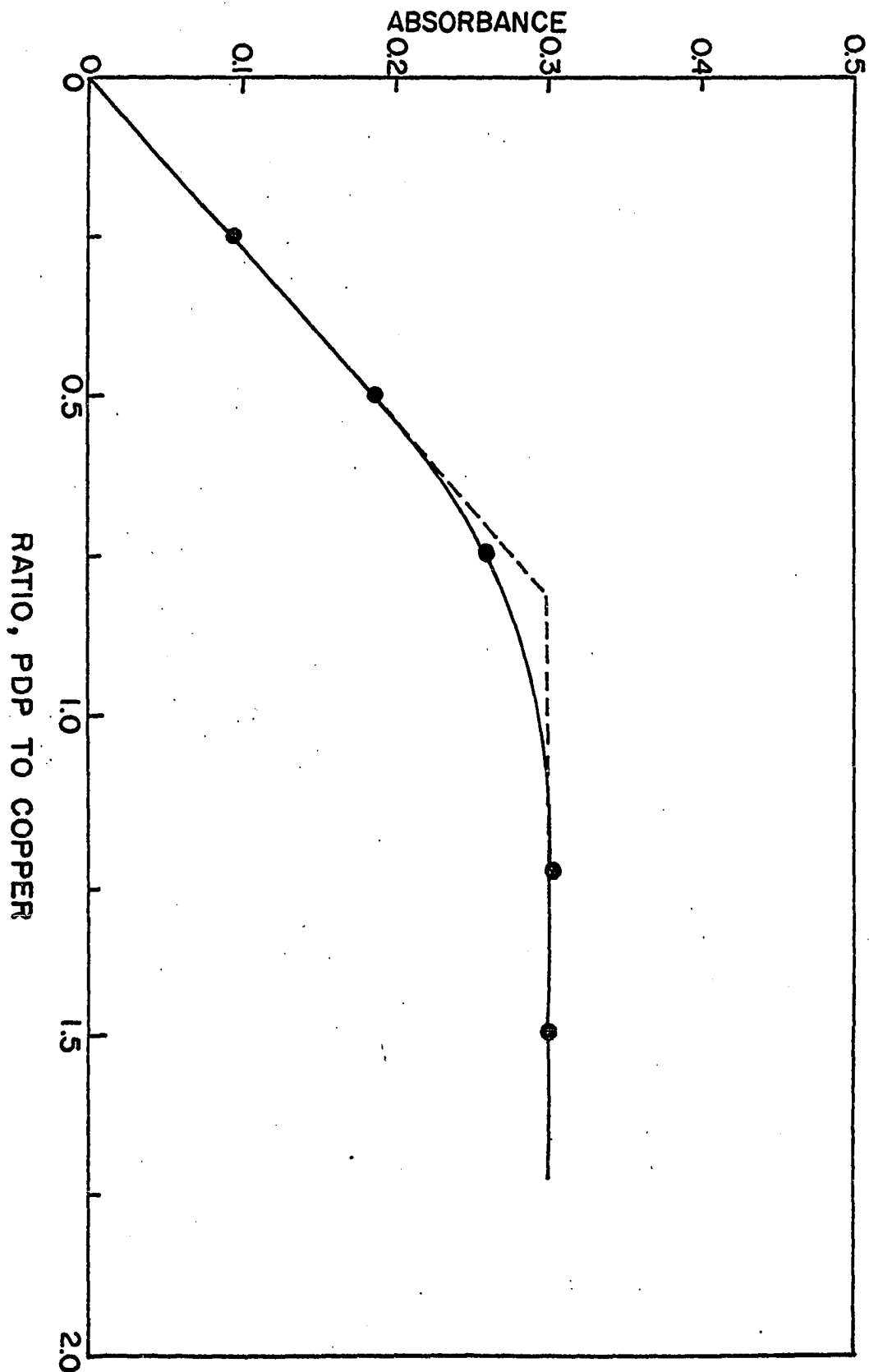
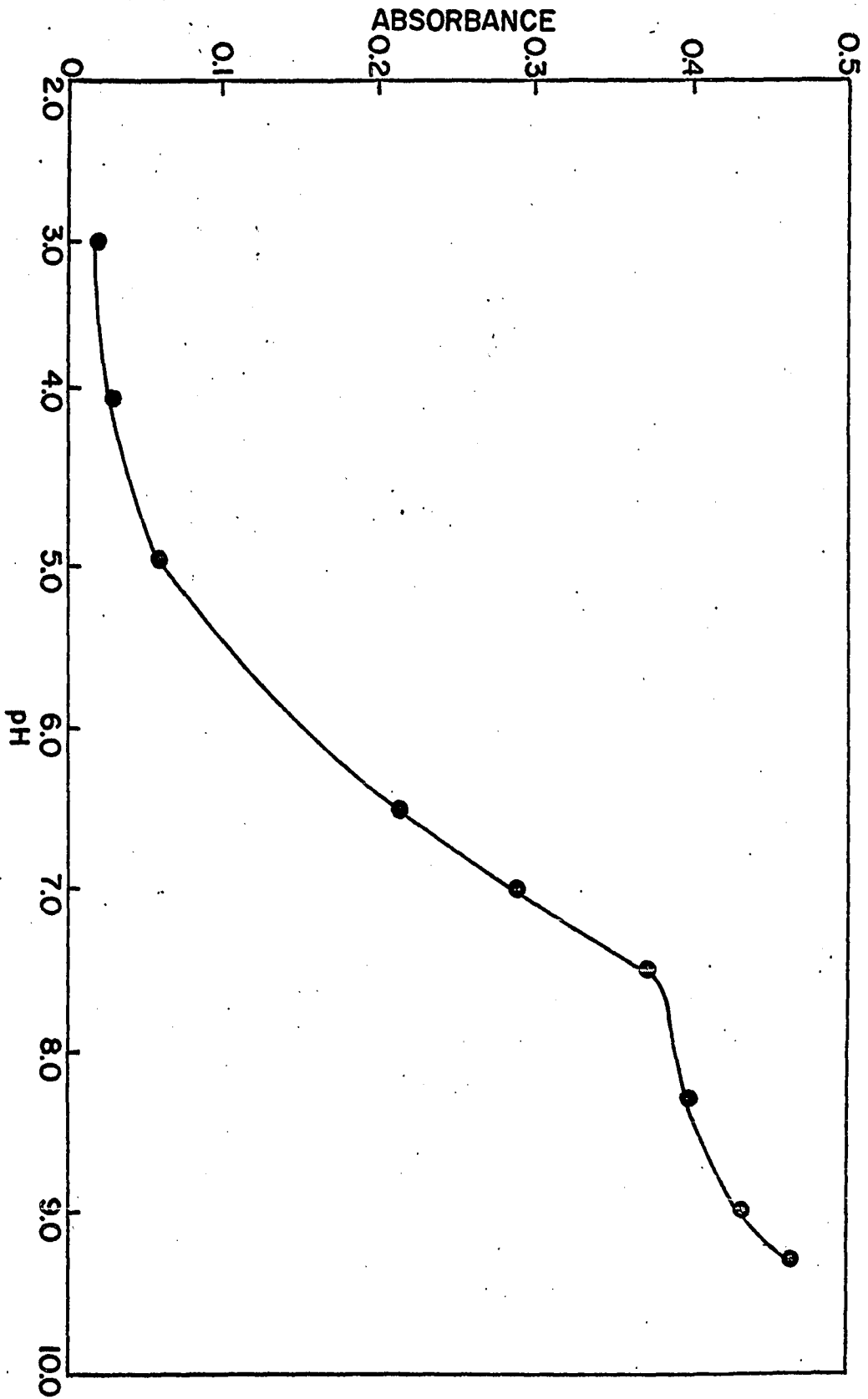


Fig. 15. Absorbance of the Cu(II)-PDP system as a function of pH
 $2 \times 10^{-5} \text{M Cu(II)}$, $2 \times 10^{-4} \text{M PDP}$, $\mu = 0.1$ at $450 \text{ m}\mu$



DETERMINATION OF THE FORMATION CONSTANTS
OF THE COPPER(II)-PDP COMPOUNDS

Introduction

Copper has been shown to form both 2:1 and 1:1 PDP to metal compounds in aqueous solution (20). As described in the previous section, the absorption bands in the visible region of the spectrum of both copper compounds show maximum absorbance at 440 μ . Comparison of the spectrum of the copper(II)-PDP solution and that of PDP alone showed that only the PDP solution has an absorption peak in the UV region of the spectrum at 345 μ . Preliminary work suggested that this peak is due to the free or unbound PDP. Since knowledge of the free ligand concentration allows calculation of the formation constants by Bjerrum's method (21), it was of considerable interest to test this hypothesis.

Experimental Work

Spectrophotometric studies

A series of eight solutions was prepared. To each of eight 25-ml. volumetric flasks was added 0.100 ml. of 0.1000 M PDP and varying amounts of 1.000×10^{-3} M copper(II) solution. The solutions were diluted to mark with pH 8.45, $\mu = 0.1$ buffer. The absorbances of these solutions were measured at 440 and 345 μ . The data are given in Table 13.

A calibration curve of PDP alone in pH 8.45, $\mu = 0.1$ solution was prepared covering the concentration range 8.0×10^{-6} to 3.2×10^{-5} M PDP.

Table 13. Change in the absorbance spectrum of the copper-PDP system with varying ratio of copper to PDP

(Cu) x 10 ⁵	Absorbance, 345 mμ	Absorbance, 440 mμ
0.80	0.699	0.171
1.20	0.606	0.244
2.00	0.485	0.407
2.80	0.331	0.513
3.60	0.213	0.642

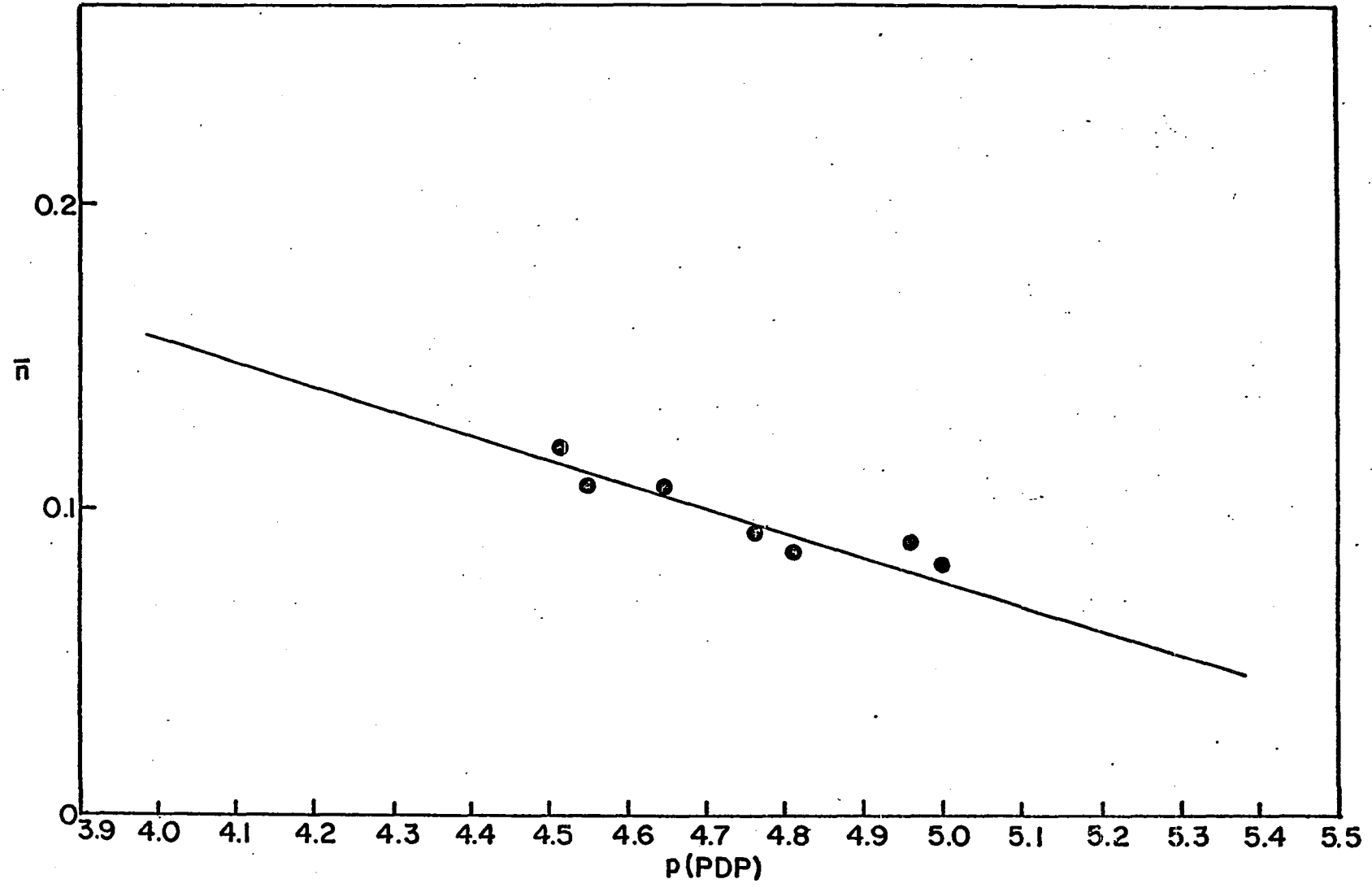
Calculation of \bar{n}

Bjerrum's \bar{n} function was calculated directly from the measured values of the absorbance of the copper-PDP solutions using the equation $\bar{n} = C_a - (\text{PDP})/C_m$, in which C_a is the total concentration of PDP in solution; (PDP) is the concentration of unbound or free PDP; and C_m is the total concentration of copper(II) in solution. C_a and C_m are known from the amounts of these materials added to the solution and (PDP) is obtained from the absorbance of the 345 mμ peak and the Beer's law plot for PDP alone in buffered solutions. A plot of \bar{n} versus $-\log(\text{PDP})$ or $p(\text{PDP})$ is shown in Fig. 16.

Calculation of the step formation constants

Using Bjerrum's method, $k_1 = 1/(\text{PDP})$ where $\bar{n} = 1/2$ and $k_2 = 1/(\text{PDP})$ where $\bar{n} = 3/2$. The values of k_1 and k_2 obtained from the plot of \bar{n} versus $p(\text{PDP})$ in Fig. 16 were treated by successive approximation using the equation $\mathcal{E} = A_s - \epsilon_a a/Bl = (\epsilon_0 + \epsilon_1 \beta_1 a + \epsilon_2 \beta_2 a^2)/(1 + \beta_1 a + \beta_2 a^2)$, where A_s is the absorbance of the complex species, ϵ_a , ϵ_0 , ϵ_1 , ϵ_2 , the molar extinction coefficients of the PDP, the metal ion, and the 1:1 and 2:1

Fig. 16. \bar{n} versus $p(\text{PDP})$ for Cu-PDP, $p(\text{PDP}) = -\log(\text{PDP})$

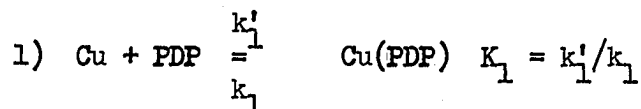


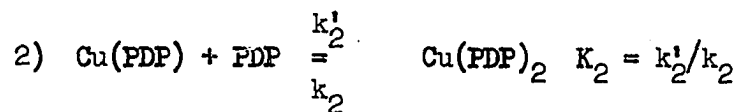
compounds of copper respectively. β_1 and β_2 are the over-all formation constants, l the cell length, and B the total concentration of copper(II). In this case, ϵ_0 and ϵ_a are zero. Refinement of the data by successive approximation gives $\beta_1 = 2.385 \times 10^5$ and $\beta_2 = 6.693 \times 10^{10}$ and $\epsilon_1 = 15,104$ and $\epsilon_2 = 22,450 \text{ l cm}^{-1} \text{ mole}^{-1}$ from which $k_1 = 2.4 \times 10^5$ and $k_2 = 2.8 \times 10^5$. These constants allow calculation of the absorbance of any copper solution at $440 \text{ m}\mu$ from the total copper(II) and the PDP in solution and the free ligand concentration measured at $345 \text{ m}\mu$.

Discussion

It is clear from the data in Table 13 that the absorption peak at $345 \text{ m}\mu$ is indeed a measure of the free PDP concentration. The fact that the constants obtained from this treatment give values of the absorbance of $440 \text{ m}\mu$ peak is confirmation that the constants are valid and accurate. Interestingly enough, the over-all formation constant determined potentiometrically of 3.5×10^8 (page 24) does not agree with the value of 6.69×10^{10} obtained spectrophotometrically. This is not unexpected since rather drastic approximations were made in calculation of the formation constant from potentiometric data.

The fact that $k_2 > k_1$ is unusual and implies that some kind of special interaction is present. Consider the following reactions where PDP is a tridentate chelating agent, and it is assumed that all three of the coordinating nitrogen atoms are attached simultaneously:





where the charges on the ions have been omitted for simplicity. From the mass action principle, the ratio of the kinetic constants $k_1' : k_2'$ is 1:1/12 and $k_1 : k_2 :: 1/12:1$. From this $K_1 : K_2 :: 1:1/12$. Actually, however, $K_1 : K_2 :: 1:1.17$. Obviously, some stabilizing force is present on addition of the second ligand molecule.

The formation constant may be used to calculate the free energy of the reactions:

$$\Delta F_1 = \Delta H_1 - T\Delta S_1$$

$$\Delta F_2 = \Delta H_2 - T\Delta S_2$$

Assuming that the bonds formed for the 1:1 and the 2:1 compounds are similar, $\Delta H_1 \approx \Delta H_2$ as a first approximation and $\Delta S_2 - \Delta S_1 = \Delta F_1 - \Delta F_2/T = 0.305$ eu.

This positive entropy for the system implies that an increase in the ordered structure of the system has occurred. In basic solution, the acidic hydrogen atoms of PDP have been removed, and this increases the color of the system greatly. This suggests that a resonating double-bond system exists between the two pyridine rings. Double bonding between ligand and the metal ion could give a quasi-aromatic five-membered ring system. Such "cyclic conjugation" involving the metal ion has been suggested by Bayer (22) as the reason for the unusual stability of similar chelate compounds. This hypothesis is supported by the fact that zinc forms a compound with PDP in basic solution with a spectrum similar to transition metal-PDP compounds. Since zinc has filled d-shells, $d^2 sp^3$ or

other hybrid bonding orbitals can not form; and the absorption peak in the visible region of the spectrum must be associated with the five-membered conjugated ring formed by the metal ion and the ligand. The iron, nickel, cobalt, and copper compounds of PDP all have similar visible spectra and pi-bonding is probably also important in these compounds too.

While coordination compounds with k_2 greater than k_1 are not unknown, they are very uncommon and usually occur in compounds with unusual steric hindrance or with change in bonding type. Irving and Mellor (23) have reported that k_3 for the addition of a third 2,2'-bipyridine or 1,10-phenanthroline molecule to the bis(2,2'-pyridine)-iron or 1,10-phenanthroline compound is greater than either k_1 or k_2 . An even more closely related situation occurs for the copper-2,9-dimethyl-1,10-phenanthroline compound. For the addition of a second molecule of 2,9-dimethyl-1,10-phenanthroline to the 1:1 compound, k_2 is greater than k_1 (24).

Irving and Mellor explain the value of k_3 for the iron compound as being due to crystal-field stabilization. They suggest that k_2 for the copper compound may be explained as resulting from repulsion between the first ligand molecule and the water shell around the compound so that the entry of the second molecule in a plane at right angles to itself is facilitated (by sp^3 orbitals) and k_2 is greater than k_1 . They call this effect "orbital stabilization."

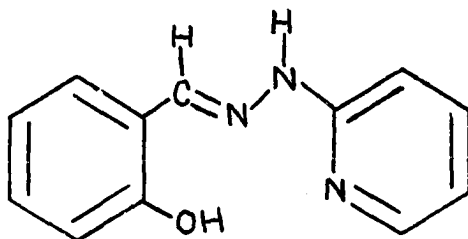
The 1:1 copper-PDP compound is probably planear and the 2:1 octahedral in structure. It is well known that the octahedral structure or a distorted octahedral structure is the most stable for copper(II). Thus, the d^2sp^3 hybrid orbitals for the 2:1 compound are more stable than the

dsp^2 planear orbitals, and the copper has a greater tendency to add the second molecule of PDP and achieve the more stable octahedral structure.

THE SCHIFF'S BASE OF SALICYLALDEHYDE AND 2-PYRIDYLHYDRAZINE

Introduction

The preparation of 1-(2'-hydroxyphenyl)-3-pyridyl-2,3-diaza-1-propene, abbreviated HPDP, was described earlier in this thesis on page 8. HPDP differs from PDP only in having a 2'-hydroxyphenyl group in place of the pyridine group on carbon one of 2,3-diaza-1-propene. The structural formula below shows this similarity.



Because of this similarity, it was of interest to compare the properties of metal derivatives of HPDP with those of PDP.

Experimental Work

Spectrophotometric studies

The absorption spectrum for the cobalt-HPDP compound was measured in pH 8.20, $\mu = 0.1$ buffered solution. The solution was $2.00 \times 10^{-5} M$ in cobalt(II) sulfate and $6.00 \times 10^{-5} M$ in HPDP. The HPDP was added as an alcoholic solution. The cobalt compound of HPDP showed maximum absorption at 430 m μ with molar extinction coefficient of 24,000 $lcm^{-1}mole^{-1}$. The absorption peak was very broad and rounded.

HPDP itself has little or no absorption in the visible region of the spectrum from 400 to 800 μ . HPDP gives compounds with cobalt, iron, or nickel only in basic solution.

Combining ratio

The combining ratio of cobalt(II) and HPDP was studied by the method of continuous variations. Solutions of 1.00×10^{-3} M cobalt(II) sulfate in aqueous solution and 1.00×10^{-3} M HPDP in ethanol were prepared by weight. To nine 25-ml. volumetric flasks were added, in order, 1, 2, 3, 4, 5, 6, 7, 8, and 9 ml. of the 1.00×10^{-3} M cobalt(II) solution and 9, 8, 7, 6, 5, 4, 3, 2, and 1 ml. of the 1.00×10^{-3} M HPDP solution in ethanol. The solutions were then diluted to mark with pH 8.20, $\mu = 0.1$ buffer solution (described on page 6). The absorbances of the solutions were then measured at 430 μ .

HPDP did not form colored compounds in neutral or acid solution with iron, nickel, or cobalt. The iron and nickel compounds formed in basic solution were not very intensely colored and so were not investigated.

Fluorometric studies

It was found that HPDP formed fluorescent compounds with calcium and magnesium. A large excess of the metal over HPDP was necessary to form the compounds. The maximum wavelength for the excitation spectrum of the magnesium-HPDP compound occurred at 400 μ , and the maximum wavelength for the emission spectrum occurred at 450 μ . The relative intensity of the emission peak was 12 in the absence of magnesium and 99 with a threefold excess of magnesium over HPDP. The excitation and emission spectra for the calcium compound are quite similar.

Discussion

The absorption spectrum of the cobalt-HPDP compound is similar to that for the cobalt(III)-PDP compound except the maximum absorption occurs further toward the UV region of the spectrum for the HPDP compound.

The combining ratio of HPDP with cobalt was shown to be 2:1 ligand to metal by the method of continuous variations. The continuous variations plot was quite sharp, and all experimental points lie on straight lines. Apparently, the compound formed is quite stable, or the plot would have had a rounded maximum. The maximum occurs at an HPDP mole ratio of 0.66.

HPDP forms compounds with cobalt, iron, or nickel only in basic solution. Acidic or neutral solutions of HPDP and metal ions are colorless. The molar extinction coefficient of the HPDP-cobalt compound in basic solution is $24,000 \text{ l cm}^{-1} \text{ mole}^{-1}$ which is smaller than that for the cobalt (III)-PDP compound.

It is particularly interesting that HPDP forms fluorescent calcium and magnesium compounds. This is not unexpected, however, since the Schiff's base is similar in over-all structure to o,o'-dihydroxyazobenzene used by Diehl and co-workers (25) in the fluorometric determination of magnesium. Unfortunately, HPDP formed alkaline earth compounds only with a very large excess of the metal ion; it appears not to offer possibilities as an analytical reagent.

In view of the fact that HPDP shows no particularly outstanding characteristics and no advantages over PDP as a colorimetric reagent for cobalt, the compound was not investigated further as an analytical reagent.

SUMMARY

The iron, cobalt, nickel, and copper compounds of 1,3-bis(2'-pyridyl)-2,3-diaza-1-propene (abbreviated PDP), first described by Lions and Martin, have been investigated in detail with respect to composition, structure, and possible use in the analytical chemistry of these metals, particularly cobalt.

PDP has been shown to form an intensely colored compound with cobalt in aqueous solution. The maximum absorption occurs in the visible region of the spectrum, at 480 m μ , and the molar extinction coefficient has the very high value of 28,500 l cm^{-1} mole $^{-1}$. The combining ratio in aqueous solution has been shown to be three molecules of PDP to one atom of cobalt at pH 4.5 and two molecules of PDP to one atom of cobalt at pH 8.3.

The cobalt(II)(PDP) $_2$ has been shown to be oxidized by air immediately on formation to give a cobalt(III) compound. The cobalt(II) compound has been shown to be stable in the absence of oxidizing agents or atmospheric oxygen; and under oxygen-free conditions, it can be titrated quantitatively with dichromate.

The cobalt(III) compound of PDP has been isolated as the bromide salt, melting point 303-304 $^{\circ}$, and characterized by elemental analysis, thermogravimetric analysis, molar conductance in aqueous solution, migration in an electrical field, and NMR spectroscopy. The compound has the composition $\text{Co(III)(C}_{22}\text{H}_{18}\text{N}_8\text{)Br}\cdot 3\text{H}_2\text{O}$.

The over-all formation constant of the cobalt(III)-PDP compound, determined by the competitive reactions of copper(II) and cobalt(II) for PDP, is 1.36×10^{10} .

The electrochemical properties of the cobalt(III) compound of PDP have been studied by polarography. A reduction of the cobalt(III) compound to a compound of cobalt(0) apparently occurs.

The effects of pH, excess reagent, time, and interfering ions have been investigated in a study of the use of PDP as an analytical reagent for cobalt. The interference of iron(II), which also forms a highly colored compound with PDP, has been circumvented by extracting the iron (II)-PDP compound from an alkaline solution into chloroform or other non-polar solvent. This extraction has been shown to be quantitative in one or two extractions with a volume of chloroform equal to the volume of the aqueous layer, presumably because the cobalt-PDP compound is a charged species whereas the iron(II)-PDP compound has zero charge. The extraction step also separates copper, nickel, and manganese from the cobalt and thus removes the interference of these ions.

A procedure has been developed for the spectrophotometric determination of cobalt in steel or other materials containing small amounts of cobalt. National Bureau of Standards 126a, a high-nickel steel, has been analyzed for cobalt using the recommended procedure; an average value of 0.309 per cent was obtained which is close to the NBS value of 0.308 per cent.

The nature of the iron(II) compound of PDP has been investigated by the method of continuous variations and by thermogravimetric analysis. The combining ratio is two molecules of PDP per atom of iron. A solid iron(II)-PDP compound has been isolated as the dark-red bromide and shown to correspond to the formula $\text{Fe}(\text{C}_{11}\text{H}_{10}\text{N}_4)_2\text{Br}_2 \cdot 3\text{H}_2\text{O}$ by thermogravimetric

analysis, spectrophotometric studies, molar conductivity in aqueous solutions, NMR spectroscopy, and Karl Fischer titration for water. The effect of pH on the absorption spectrum of the iron compound and also on the extraction of the compound into nonpolar solvents from basic aqueous solution has also been investigated. The extraction has been shown to be quantitative at pH 9 and above.

The nickel compound of PDP has been isolated as the bromide from aqueous solution as red-orange plates, melting point 264-265°. The compound has been shown to correspond to the formula $\text{Ni(II)(C}_{11}\text{H}_{10}\text{N}_8)_2\text{Br}_2 \cdot 3\text{H}_2\text{O}$ by elemental analysis, thermogravimetric analysis, and spectrophotometric analysis by the method of continuous variations. The molar conductance of the compound in aqueous solution has been shown to be that of a typical di-univalent electrolyte. The bromide atoms are therefore not coordinated with the nickel.

Copper(II) has been shown to form two compounds with PDP, the ratio of PDP to metal being 1:1 and 2:1. The wavelength of maximum absorption of the two compounds is the same, 440 m μ , the molar extinction coefficients being 15,100 and 22,450 $\text{lcm}^{-1}\text{mole}^{-1}$ respectively at pH 8.45. The absorption was shown to be dependent on the pH and to become much more intense in basic solution. This effect has been explained as the result of the removal of the acidic hydrogen atoms of the PDP molecules and the formation of a resonating double-bond system between the two pyridine rings of the PDP.

The formation constants for the copper(II)-PDP compounds have been determined by Bjerrum's method using spectrophotometric data. The function

$\bar{n} = C_a - (\text{PDP})/C_m$, where C_a is the total PDP concentration, (PDP) the free PDP concentration, and C_m the total metal ion concentration in solution, has been calculated from the absorbance of the free PDP at 345 m μ and the analytical concentrations of total PDP and metal ion in solution. The absorption peak at 345 m μ has been shown to be due only to the concentration of free PDP and not to the PDP bound to the copper. The formation constants obtained by this method are $k_1 = 2.4 \times 10^5$ and $k_2 = 2.8 \times 10^5$. The unusual situation in which k_2 is greater than k_1 has been explained as being due to the additional stability of the d^2sp^3 hybrid bonding orbitals for copper(II) and also additional possibilities for resonance stabilization of the system on addition of the second molecule of PDP.

Transition metal compounds with 1-(2'-hydroxyphenyl)-3-pyridyl-2,3-diaza-1-propene (abbreviated HPDP), the Schiff's base of salicylaldehyde and pyridylhydrazine, are formed with cobalt, iron, and nickel, but only the cobalt compound is intense enough in color to be useful for colorimetric determination of the metal. HPDP appears to offer no advantages over PDP as an analytical reagent for cobalt.

The Schiff's base has also been shown to form fluorescent compounds with calcium and magnesium in the presence of a large excess of the alkaline earth metal ions. The compound has not proven useful as an analytical reagent.

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