SPECTROPHOTOMETRIC INVESTIGATION OF THE ANALYTICAL REAGENT 1-(2-PYRIDYLAZO)-2-NAPHTHOL, PAN, AND ITS COPPER, NICKEL AND PALLADIUM CHELATES

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BURTON FRANK PEASE

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Redacted for Privacy

Associate Professor of Chemistry

In Charge of Major

Redacted for Privacy

Chairman of Department of Chemistry

Redacted for Privacy

Chairman of School Graduate Committee

Redacted for Privacy

Dean of Graduate School

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CHAPTER I

INTRODUCTION

The use of metal chelates in analytical chemistry is a rapidly expanding field. The growing importance of these compounds may be visualized by surveying a recent representative issue of Analytical Chemistry (2). Out of a total of forty-seven articles in this issue, six are concerned either directly or indirectly with metal chelates. Another issue (1) of the same journal, published just six years previously, contains a total of forty-two articles of which only one is concerned with this type compound.

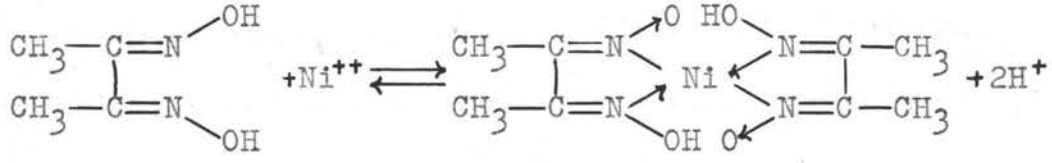
The term "chelate" was proposed by Morgan and Drew (21, p. 1456) to designate the cyclic structures which arise from the combination of metallic ions with inorganic or organic molecules.

In order for the formation of a metal chelate of an organic compound to occur the compound must contain two or more atoms, usually oxygen or nitrogen, capable of coordination with a metal ion; that is, it must be a base having a pair of unshared electrons available for coordination. These coordinating atoms are so arranged that rings of five or six atoms, including the metal,

will be formed in the process (30, p. 85).

In addition to having electrons available for coordination the organic molecule must also contain one or more replaceable hydrogens.

The coordination compound of nickel and dimethylglyoxime is a typical example.



dimethylglyoxime nickel dimethylglyoxime

The = NOH groups are both acidic and basic. One loses a proton while the other coordinates with the nickel through the nitrogen forming five-membered rings. Since hydrogen ions are released, the formation of the compound, as in other chelates, is dependent upon pH.

The stability of the complexes of a given chelating agent with various metal ions will depend on the size of the cation, its oxidation state, its coordination number and the geometric distribution of its valence bonds (30, p. 86).

An excellent discussion of the theory and uses of chelation is given by Martell and Calvin, Chemistry of the Metal Chelate Compounds (19) and more recently by Bailar, The Chemistry of the Coordination Compounds (3).

The metal chelates resulting from a combination of metal ions and organic molecules are largely organic in character. Their low solubility in aqueous solutions, high molecular weights, sensitivity and selectivity lead to widespread use as precipitating agents.

Many of these chelates have a characteristic color, thus their concentrations may be determined by colorimetric analysis. If the chelate is not water soluble it may be extracted by an organic solvent and determined photometrically in the latter.

Those metal chelates which are water soluble are also used to suppress the reaction of an interfering cation by the formation of a stable complex. They are frequently used to hold a metal ion in solution at pH values where the hydroxide or oxide would normally precipitate (30, p. 110).

Various organic dyes have been used as metal indicators in the titration of metal ions. In this procedure the dye and the metal form a colored complex. When a solution containing this complex is titrated with another stronger complexing agent the color will disappear or change depending upon whether the second complex is colorless or not. The most common use of this type reaction is the determination of calcium and magnesium in water. With the dye, Eriochrome Black T, magnesium forms a red complex

at pH 10 which is subsequently destroyed by versene, the tetrasodium salt of ethylenediaminetetraacetic acid (19, p. 811).

The versene complexes with the free calcium ions and then removes the magnesium from the Eriochrome Black T. Both the calcium and magnesium versene complexes are colorless but the solution at the end point of the titration is blue. This is the color of the Eriochrome Black T at this pH.

Although many reliable empirical procedures have been developed using metal chelates in colorimetric and titrimetric analysis it is nevertheless desirable and in many cases necessary to gain more fundamental knowledge regarding the nature of the processes involved. For this reason in recent years there has been a greater tendency toward studying the dye itself, the metal to dye ratios at various pH values and determining the dissociation constants of the dyes and their metal chelates.

A variety of procedures are available for the determination of these constants, for example; polarographic, ion exchange, spectrophotometric, oxidation potential and solubility measurements have all been used (19, pp. 76-133). The potentiometric procedures of Schwarzenbach (23) are perhaps the most popular and accurate but are unsatisfactory in many instances if the organic compounds or metal chelates

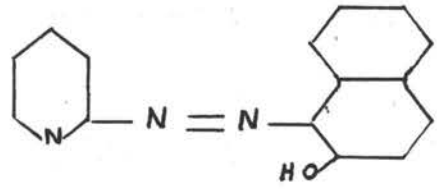
are but slightly soluble in water. The resulting solutions are often too dilute to be studied by this means. On the other hand, since many of the dyes and chelates are highly colored the more dilute solutions easily lend themselves to spectrophotometric studies either in aqueous media or by extraction with an organic solvent.

A typical study of this type was performed by Hildebrand and Reilley (16) on the o,o' dihydroxyazo napthalene dye, Calcon, and its calcium, magnesium and zinc complexes.

CHAPTER II

SURVEY OF PREVIOUS WORK ON PAN

Tschitschibabin (25, pp. 513-516 and 26, p. 1582) in 1915 and 1918 reported the synthesis of some o-hydroxyl compounds. One of these, 1-(2-pyridylazo)-2-naphthol, PAN, an orange-red dye was studied further by Liu (18).



Through magnetic measurements and elemental analysis it was found that the metal-dye ratio of the solid metal chelates was approximately 1 to 1 for Cu (II) and Ni (II) (18, pp. 22 and 43) and the ratio for Fe (III) was intermediate between 1 to 1 and 2 to 1 (18, pp. 43-44). All of these metal chelates were separated from alcohol solutions.

In addition to the work on the solid substances she also found that the ratio of metal to dye in 95% alcohol was 47 to 53 for Cu (II), and 31 to 69 for Ni (II) (18, pp. 35-36 and 41-42). Cheng and Bray (9, p. 783) have reported the existence of a 1 to 2 Co (III) chelate in aqueous solutions.

Since all of the metal chelates are highly colored

Cheng and Bray (9) recognized the possibility of using this dye for analytical purposes. It was applied by them as a metal indicator in the direct titration of copper, cadmium and zinc with ethylenediaminetetraacetic acid, EDTA (9, p. 783). It was later extended by Cheng (8, pp. 1582-1583) for the determination of indium and by Cheng and Williams (10, p. 96) for scandium. The latter workers also introduced the back titration of excess EDTA with standard copper solution (10, pp. 96-97) for the determination of scandium. Flaschka and Abdine have applied this back titration technique, using PAN as the indicator, to iron, copper, nickel, cobalt, zinc, cadmium, lead, gallium, calcium, magnesium, manganese, mercury and vanadium (12, pp. 2-3 and 13, pp. 58-61).

Cheng and Bray (9, p. 783) have suggested and surveyed the possibility of using PAN as a color forming agent for the spectrophotometric determination of Co (III), Co (II), Cu (II), Zn (II) and Ni (II). All of these metals, with the exception of Co (III), form red chelates with strong absorption bands in the 550 to 560 mu wavelength region. Co (III) and Pd (II) were reported to form green chelates. These workers formed the metal chelates in aqueous buffered solutions and extracted them with isoamyl alcohol. The approximate molar absorbancy

indices[1], calculated from Cheng and Bray's data (9, p. 784) are summarized in Table 1. For comparison, the molar absorbancy index of chromium diphenylcarbazide, one of the better known and more sensitive colored compounds, is included.

In addition to the previously mentioned work Cheng and Bray have also studied the effect of various masking agents on 16 different PAN chelates (9, p. 784).

[1] $A = abc$

$a_m = (A.W.)\ (a)$

A = absorbance

a = absorbancy index

a_m = molar absorbancy index

b = cell length in cm.

c = concentration in g/1000 g of solvent

A.W. = atomic weight of metal

TABLE 1

MOLAR ABSORBANCY INDICES OF PAN CHELATE

Metal ion	solvent	molar absorbancy index
Co(III)	water	36×10^3
Zn(II)	isoamyl alcohol	27×10^3
Cu(II)	" "	22×10^3
Co(III)	" "	17×10^3
Ni(II)	" "	9×10^3
Cr(VI)[a]	water	34×10^3

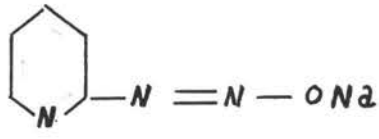
Reference (8, p. 784), a. Chromium diphenylcarbazide

CHAPTER III

THE PREPARATION AND PROPERTIES OF PAN

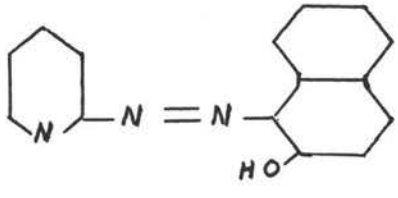
Preparation of PAN

The dye, 1-(2-pyridylazo)-2-naphthol, PAN, was not commercially available at the beginning of this investigation, therefore it was prepared according to the procedure of Tschtschibabin (25, pp. 513-516 and 26, p. 1582). The diazotate is obtained by the addition of a mixture of 2-aminopyridine and n-butyl nitrite in absolute ethanol to a solution of sodium alcoholate. After refluxing for several hours the diazotate precipitates.



sodium pyridyl diazotate

The resulting diazotate is coupled with 2-naphthol in absolute ethanol with the passage of carbon dioxide through the solution and the dye, 1-(2-pyridylazo)-2-naphthol is formed.



1-(2-pyridylazo)-2-naphthol

Reagents

Anhydrous ethyl alcohol.

The starting material used was 100% alcohol obtained from Commercial Solvents Corp., Agnew, California. This was further purified by distillation from magnesium ethoxide according to the procedure described in Fieser (11, pp. 358-359).

Anhydrous ethers.

The starting material was commercial grade ether obtained from Carbide and Carbon Chemical Company, 3404 4th Avenue, Seattle, Washington. It was further purified by refluxing and distilling from concentrated sulfuric acid according to the procedure described in Fieser (11, pp. 360-362) with one modification. The volumes of all reagents were cut 1 to 4.

Other reagents.

The n-butyl nitrite, 2-amino pyridine and 2-naphthol were Eastman grade chemicals, numbers 57, 4741 and 171 respectively, and were used without further purification.

Procedure

To a 500 ml. 3-necked flask, equipped with a reflux condenser and stirrer, was added, with constant stirring, 300 grams of absolute ethanol, 7.2 grams of sodium metal,

39.6 ml. of n-butyl nitrite, and 30 grams of 2-amino pyridine. This mixture was refluxed for 3.5 hours, allowed to cool to room temperature, diluted with approximately 1800 ml. of anhydrous ether and placed in the refrigerator (approximately 5°C.). After 48 hours the light yellow precipitate formed was separated from the solvent by decantation, filtered and dried in a stream of room temperature air for 3 hours. The yield was 33.1 grams before drying; 25.4 grams after drying.

Twenty-eight grams of 2-naphthol were dissolved in 75 ml. of absolute ethanol. This solution was then added to another solution containing all of the previously prepared diazotate in 600 ml. of absolute ethanol. After being stirred for two hours the resulting solution was allowed to stand overnight in the refrigerator. It was then divided evenly among four 250 ml. gas-washing bottles which were immersed in an ice bath while a stream of CO_2 gas was passed through them for 6 hours. The light yellow precipitate formed was mainly Na_2CO_3. The dark red supernatant liquid was decanted and the Na_2CO_3 precipitates were combined and extracted with four 50 ml. portions of boiling anhydrous ethanol.

This extract was added to the supernatant liquid and the resulting solution was evaporated to approximately 300 ml. with a stream of room temperature air. The dark

red crystals (13.3 grams) formed were separated from the mother liquor and redissolved in another 300 ml. of anhydrous ethanol. Upon standing at room temperature for three hours a sponge like mass of dark red crystals dropped out carrying the mother liquor with it. The resulting mass was separated from the liquor by filtration and the crystals were dried in a vacuum dessicator over P_2O_5 at 20 mm. pressure for two days.

The yield was 7.47 grams or 9.4% of the theoretical yield of 79.6 grams based upon the limiting quantity of 2-amino pyridine. An analysis of the prepared compound, 1-(2-pyridylazo)-2-naphthol, by Weiler and Straus, Microanalytical Laboratory, 164 Banbury Road, Oxford, England showed that the compound contained 71.3% carbon, 4.46% hydrogen and 16.7% nitrogen. The calculated values are 72.4%, 4.45% and 16.9% carbon, hydrogen and nitrogen respectively.

PROPERTIES OF PAN IN ALCOHOL

Since the dye is quite insoluble in H_2O it was desirable to check the suitability of methyl or ethyl alcohol as solvents for stock solutions. The dye became commercially available (4, p. 37) from the J. T. Baker Chemical Company, Phillipsburgh, New Jersey about 6 months after the start of this investigation, therefore a comparison

test between the author's and Baker's dye also seemed advisable. It will be shown later by spectrophotometric titrations with Cu (II) in 20% dioxane and absorbance values in methanol that the commercial dye is of slightly higher purity.

Reagents and Equipment

1-(pyridylazo)-2-naphthol.

Unless stated to the contrary the solid reagent prepared in this laboratory by the previously described procedure was used. The commercial sample was Baker Analyzed Reagent #8994.

Methyl alcohol.

The methanol was commercial grade obtained from Carbide and Carbon Chemicals Corporation, San Francisco, California. Samples were obtained from two separate 55 gallon drums of this solvent. For identification purposes they will be referred to as "drum" 1 and "drum" 2. In addition a portion of the "drum" 2 alcohol was redistilled and the 64° - 65° C. (uncorrected B.P.) fraction was used.

Ethyl alcohol.

The 95% U.S.P. ethanol obtained from Commercial Solvents Corp. was used without further purification.

Spectrophotometers.

The Beckman Model DK-2 Ratio Recording and the Beckman Model B Spectrophotometers were used with 1 cm. matched silica cells.

Procedure

Solutions of PAN in "drum" 1 methanol and in ethanol were obtained by the addition of 37.4 mg. of the dye to each of two 100 ml. volumetric flasks and diluting to volume with the respective solvents. Two ml. aliquots of each of these solutions were then transferred to other 100 ml. volumetric flasks. After diluting to volume with the alcohols the absorption spectra were obtained using the Beckman DK-2 Spectrophotometer. Although the curves are plotted on log scale paper with this instrument they have been transferred to a linear scale for ease of comparison. Figure 1 shows the resulting curves.

The presence of a slight absorption band at 550 millimicrons in the methyl alcohol dye solution prompted a further study on this solvent. A comparison of the author's and Baker's compounds was also made at the same time.

Six dye in alcohol solutions were prepared by the previously described procedure. Baker's dye was used in

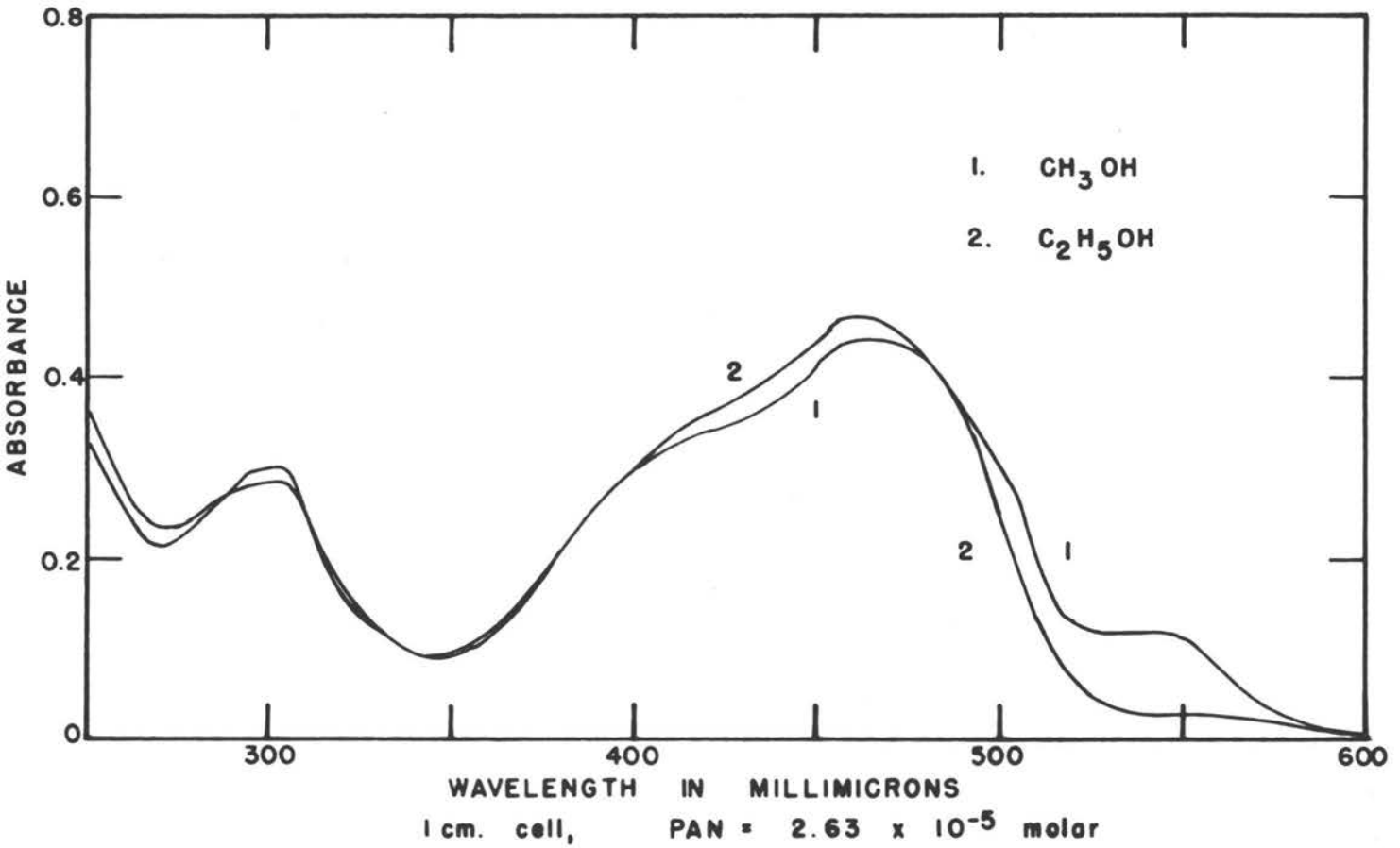


Figure 1. Absorption Spectra of PAN in Methyl and Ethyl Alcohols

three of these while the other three contained the author's compound. Three different methanol samples ("drum" #1, "drum" #2, and redistilled) were used for each solid reagent, i.e., there was prepared a total of six samples of PAN in methanol. All of these solutions were allowed to stand in the laboratory exposed to the normal amount of light. In addition to this, portions of the dye in redistilled methanol solutions were exposed to a 150 watt lamp for two hours.

The absorption spectra in Figure 2 and all of the resulting absorbance measurements in Tables 2 and 3 were obtained using matched, 1 cm. silica cells and the Beckman Model B Spectrophotometer, the instrument being balanced against a blank of redistilled methanol.

Discussion of Results

The solutions of the dye in the commercial solvents both show a strong absorption band at 550 mμ. It will be shown later in this work, in addition to the information of Cheng and Bray (9, p. 783), that most of the heavy metal chelates have a strong absorbance in this region. In addition to this it will also be shown that there is an increase in absorbance in this region with an increase in pH in aqueous and 20% dioxane solutions. Further work needs to be performed before the cause of

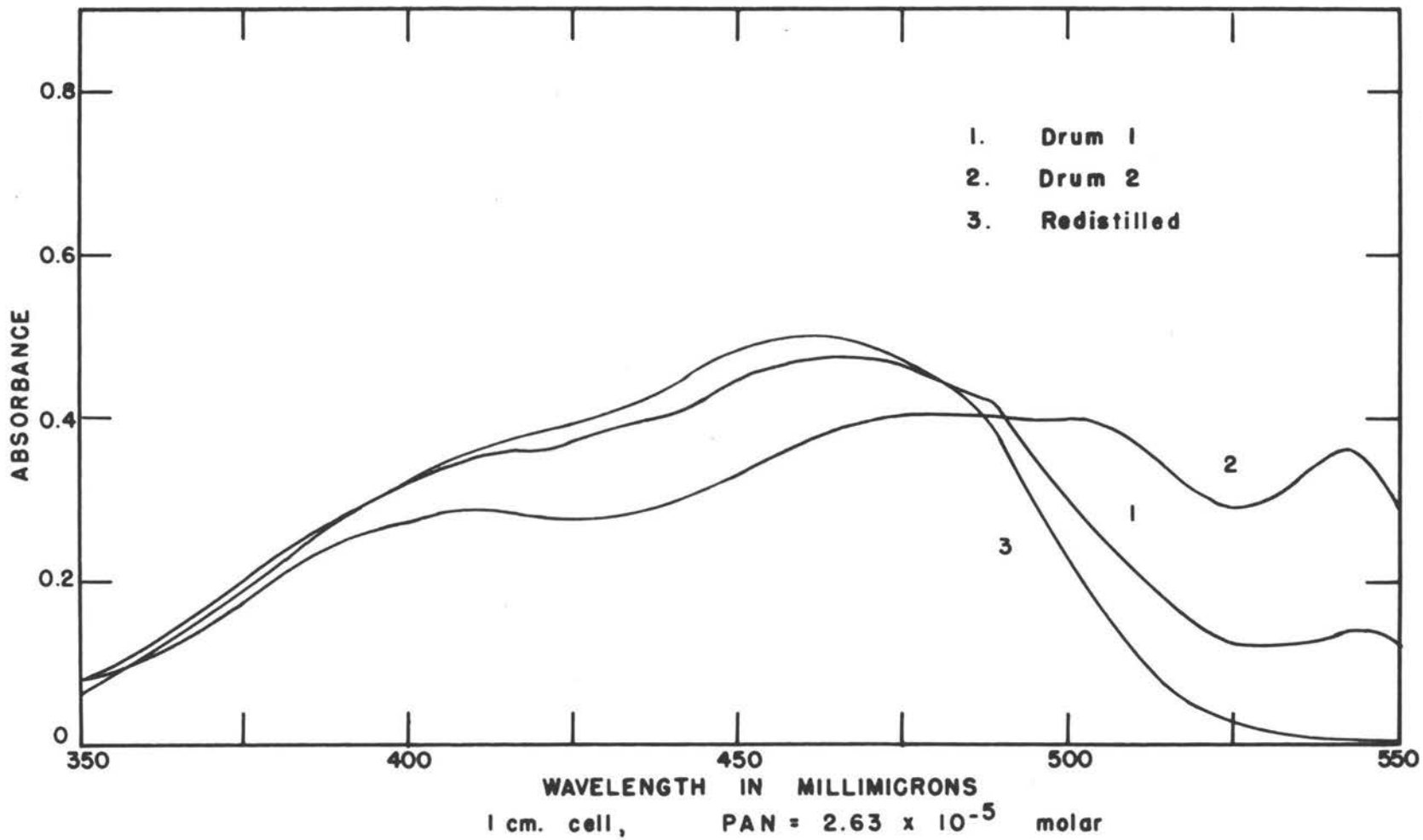


Figure 2. Absorption Spectra of PAN in Methanol

TABLE 2

COMPARISON OF METHANOL SAMPLES AND

DYE SAMPLES

Methanol sample	Absorbance of dyes at 550 millimicrons author's	Baker's
"drum" 1	0.118	0.104
"drum" 2	0.268	0.260
redistilled	0.005	0.002

time of standing	A at 460 mμ redistilled		A at 465 mμ "drum" 1		A at 475 mμ "drum" 2	
	author's	Baker's	author's	Baker's	author's	Baker's
1 hour	0.460	0.497	0.422	0.460	0.390	0.400
12 hours	0.464	0.500	0.423	0.462	0.390	0.400
24 hours	0.458	0.498	0.422	0.460	0.380	0.390
36 hours	0.458	0.496	0.420	0.457	--	--
1 month	0.462	0.502	--	--	--	--
6 months	--	--	0.424	0.464	--	--
2 hours[a]	0.462	0.498	--	--	--	--

a. These portions of the samples were exposed to a 150 watt light at a distance of 30 inches for 2 hours. All other samples were allowed to stand exposed to a normal amount of light.

TABLE 3

ABSORPTION SPECTRA OF PAN IN METHANOL

Wavelength in mu	Absorbance redistilled	Absorbance "drum" 1	Absorbance "drum" 2
350	0.067	0.083	0.080
360	0.109	0.120	0.105
370	0.164	0.170	0.150
380	0.220	0.228	0.202
390	0.278	0.278	0.248
400	0.320	0.318	0.272
405	0.343	0.338	0.282
410	0.361	0.348	0.285
415	0.370	0.358	0.282
420	0.382	0.361	0.281
430	0.413	0.382	0.282
440	0.438	0.403	0.297
450	0.482	0.448	0.333
455	0.496	0.462	0.350
460	0.500	0.470	0.363
465	0.496	0.472	0.380
470	0.488	0.472	0.398
475	0.472	0.465	0.405
480	0.450	0.450	0.403
485	0.420	0.430	0.402
490	0.367	0.397	0.400
495	0.305	0.351	0.395
505	0.172	0.261	0.395
515	0.072	0.175	0.340
525	0.030	0.130	0.288
535	0.018	0.134	0.328
545	0.014	0.140	0.350
550	0.013	0.124	0.298
555	0.010	0.094	0.210
565	0.005	0.004	0.078
580	0.002	0.010	0.016

this absorbance in the commercial methanol solutions can be specified. For the purposes of this investigation it is sufficient to redistill the alcohol before using it for a solvent for stock dye solutions.

As shown in Table 2 the Baker's dye has a greater absorbance in 460-470 mμ wavelength region. This would indicate that their dye is slightly more pure (about 8%) than the author's. This is also verified in Chapter IV by a titrimetric procedure. However much of the following work was performed with the author's dye before the commercial sample was available. The determination of the dissociation constants in the following sections depended upon the ratios of different forms of the dye rather than absolute concentrations, therefore the impurity present would not change the obtained values.

Table 2 also demonstrates that both of the dye solutions in redistilled methanol are stable to not only the normal but also to an abnormal amount of light.

In addition to the information on the dye in methanol solutions, melting point comparisons were made. The melting characteristics of the author's and Baker's dyes seemed to be identical. Both melt at 137-138°C. (uncorrected) and decompose around 141°C. The two solid samples appear the same reddish-orange color.

As a result of the study, it was concluded that redistilled methyl alcohol is a suitable solvent for stock solutions of the dye.

PROPERTIES OF PAN IN WATER

It has previously been reported by Cheng (8, p. 1583) that the dye, 1-(2-pyridylazo)-2-naphthol, is an acid-base indicator in aqueous media, being yellow in neutral solutions and red in the strongly basic range. Preliminary test tube experiments by the author indicated the existence of a third form of the dye below pH 2. This form is yellow green.

Reagents and Equipment

Buffers.

Standard pH and constant ionic strength (0.05 and 0.10) buffer solutions were prepared from reagent grade salts according to the procedure in Bates (5, pp. 117 and 118). The constant ionic strength solutions below pH 2 were prepared by varying the ratio of 0.100 N HCl and 0.100 N KCl solutions.

The Beckman Model H-2 pH meter equipped with glass and calomel electrodes numbers 4990-80 and 1170 respectively was used for all pH measurements. This instrument was calibrated against National Bureau of Standards buffers

(5, p. 118).

Stock dye solution.

The stock dye solution consisted of 37.4 mg. of PAN dissolved in 100 ml. of redistilled methyl alcohol. The concentration of this solution was 1.50×10^{-3} M based upon the weight of the dye taken. In the next chapter a standardization procedure for the dye will be given. This shows that the true concentration of the stock solution was 1.32×10^{-3} molar. All of the figures, tables and calculations in both the preceding and following portions of this thesis, with the exception of Job's method, have been corrected to this concentration.

Spectrophotometer cells and cell holders.

Five cm. cylindrical Teflon cells, equipped with silica windows were obtained from Microchemical Specialties Co., 1834 University Avenue, Berkeley 3, California, and were used to obtain all of the absorption spectra in water. In order to prevent the formation of air bubbles in the light path and reflection of the light from the white sides of the cells, the inside bore was increased to 1.1 cm. The bore in the cap of the cells was left at 0.6 cm, thus there was 0.25 cm. of solution between the edge of the light beam and the walls of the cell.

Since there was no 5 cm. cell holder available, it was necessary to devise one. It was found that a block

of wood with the dimensions of 16.0 cm. x 7.5 cm. x 6.2 cm. could be used in the Beckman Model B instrument. Several metal strips (7.0 cm. long and 1.2 cm. apart) were placed on the top of the block and parallel to the light path. The cells will lay in the groove formed by the strips and the entire apparatus will fit snugly in the cell compartment of the Beckman Model B.

The beam of light entering the cell compartment was larger than the outside diameter of the cells, therefore a portion of it was cut off by means of a piece of black electrician's tape. The cover for the cell compartment is the one devised for the spectrophotometric titrator described in the following section. It was found that absorbance readings in the 0.4 region could be reproduced to within 0.003 units using the 5 cm. cells and holder.

It was also necessary to make some slight modifications on the cell holder of the DK-2. Blocks of wood, 10.0 cm. x 1.8 cm. x 0.5 cm. were placed in the base of this cell holder in order to align the cell windows with the incoming beam of light. Again it is necessary to diminish the cross section area of the incoming beam. This was done in the previously described manner.

Spectrophotometric titrator.

The spectrophotometric titrator designed and built

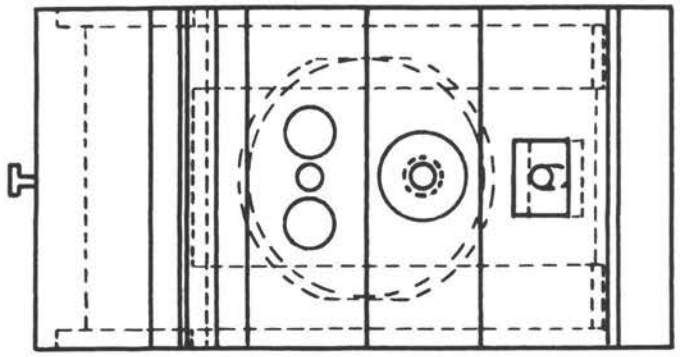
by the author is shown in Figure 3. A 250 ml. beaker, with the lips removed, was used as the cell. The electrodes and pH meter have been described. A constant rate of stirring is necessary and was attained by the use of a voltage regulator. Since Figure 3 is drawn to scale the dimensions will not be repeated here.

Procedures

Absorption spectra of PAN in H_2O.

To each of a series of 0.10 constant ionic strength buffered solutions in 100 ml. volumetric flasks was added 0.50 ml. of the stock dye solutions. They were then diluted to volume with the buffers and the absorption spectra were obtained within 3-5 minutes. The reference cell contained the respective buffers. The pH of all the solutions were measured. The resulting absorption spectra and pH measurements are shown in Figure 4.

Curve 6 of Figure 4, like all of the other curves, was obtained in 3-5 minutes, however it should be mentioned that the dye is slowly changing from one form to another at this 9.8 pH value. The spectrum of this solution showed an increase of absorbance with an increase in time in the wavelength region above 500 mμ and a corresponding decrease in absorbance in the 450 mμ region.



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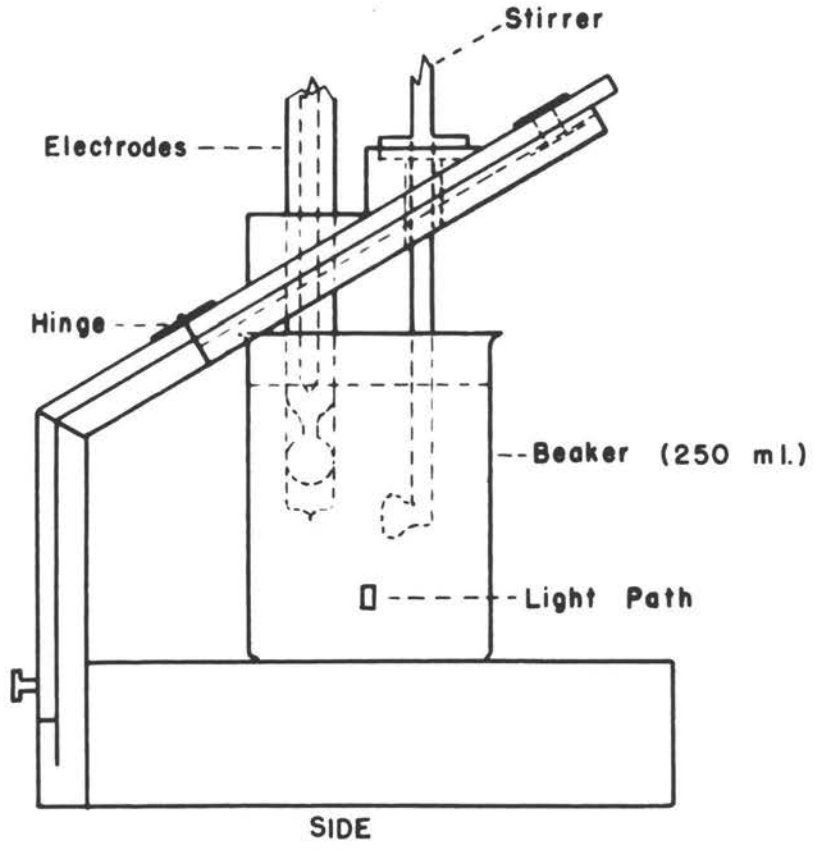

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Scale = 1/2

Figure 3. Spectrophotometric Titrator

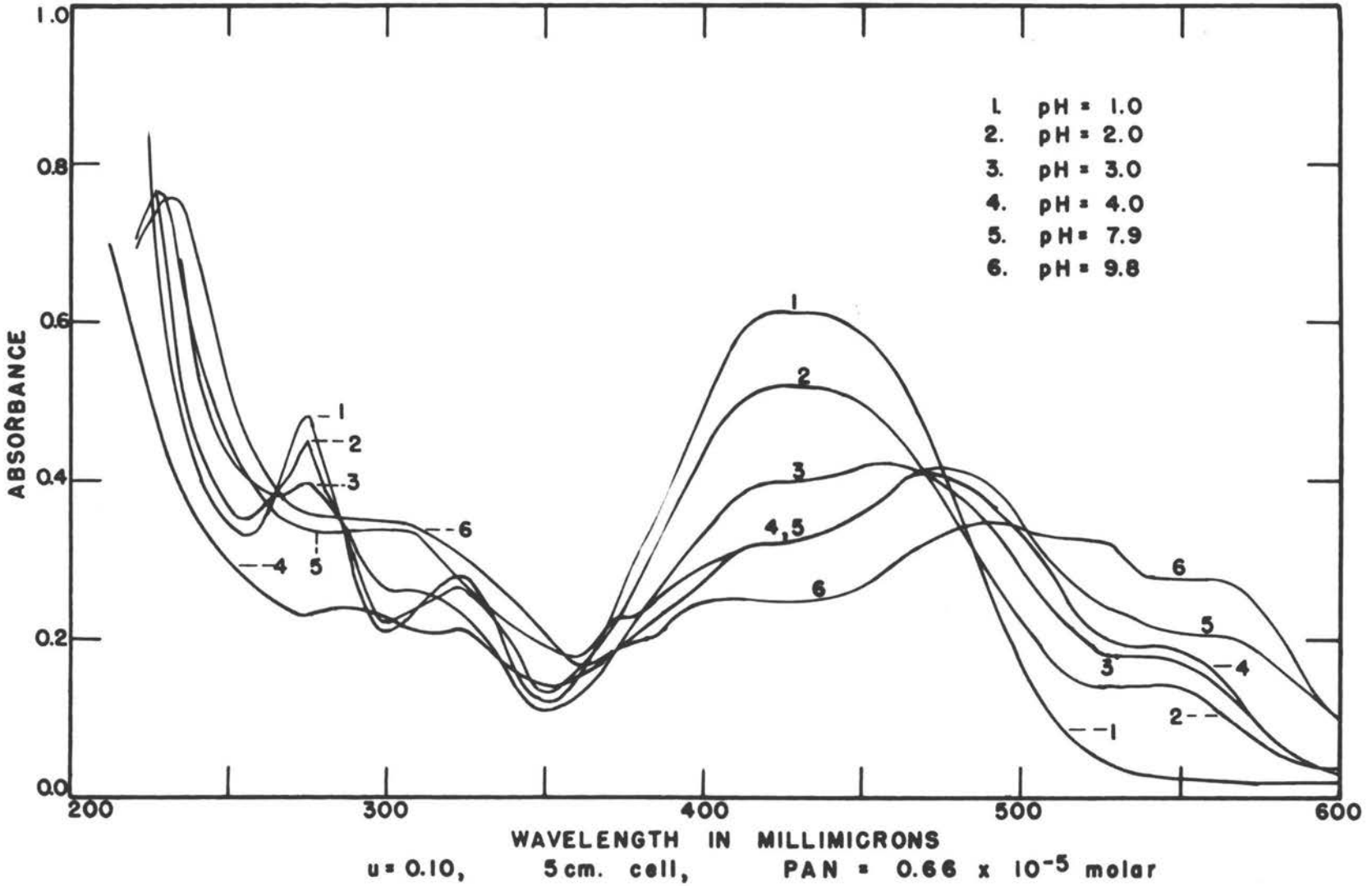


Figure 4. Absorption Spectra of PAN in Water

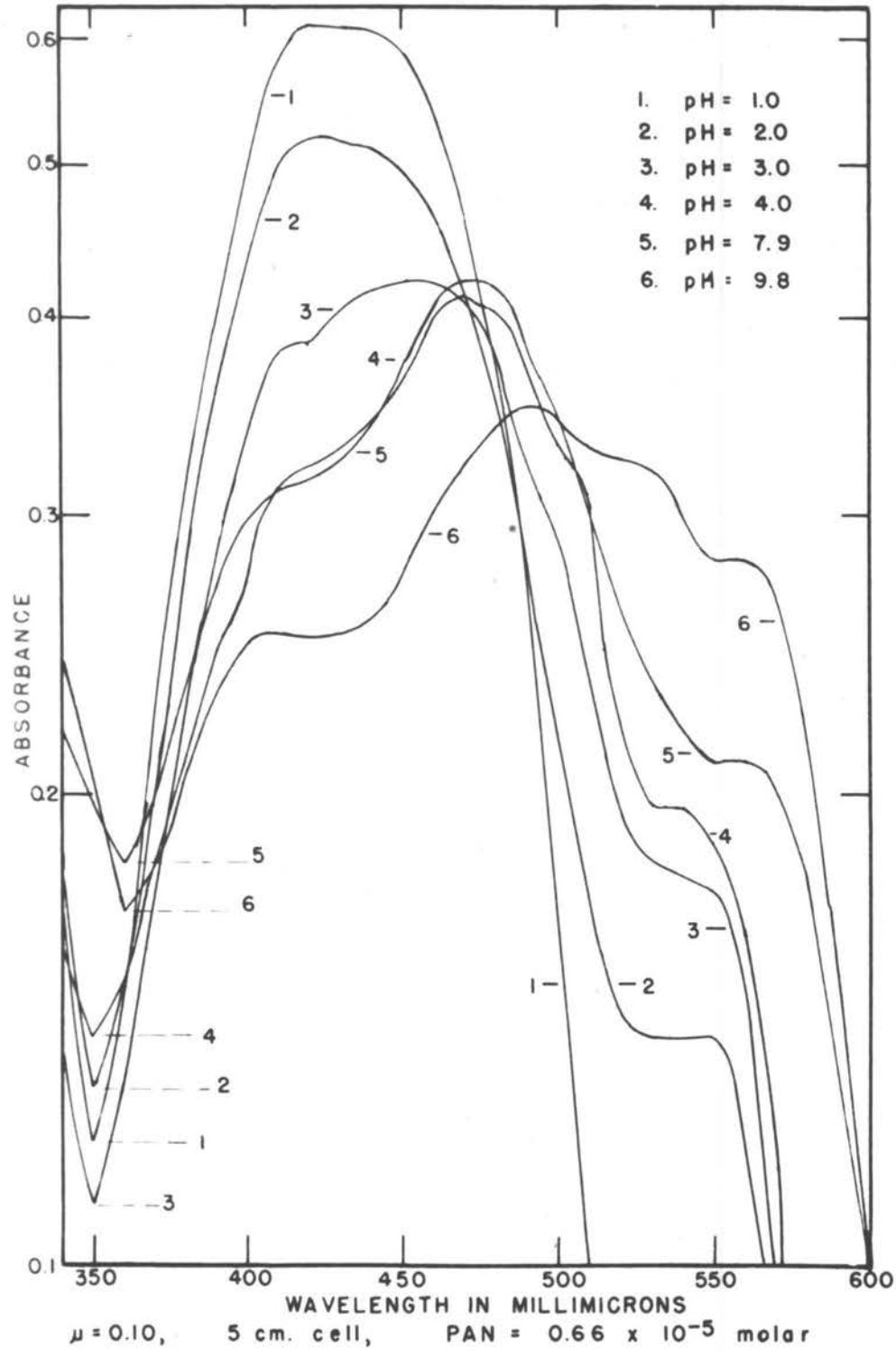


Figure 5. Log Absorbance Vs. Wavelength of PAN in Water

The absorbance at 500 mμ was constant with time, indicating an isosbestic at this wavelength. A total of 8 spectra of this solution were obtained within 30 minutes and during this time the absorbance at 530 mμ increased from 0.32 to 0.38. The strong absorbance bands at 530 and 580 mμ became much sharper and more pronounced when the solution was allowed to stand. This red form of the dye, like the strongly acid yellow-green form, and in contrast to the intermediate species, was found to be very soluble. More will be said concerning the spectra and species of the dye.

Dissociation constant of PAN in H_2O.

To each of ten 250 ml. volumetric flasks containing about 200 ml. of the 0.10 ionic strength buffers was added 1.0 ml. of the stock dye solution. The flasks were then diluted to volume with the proper buffers, mixed thoroughly and read immediately at 430 millimicrons on the Beckman Model B instrument. The cell in this case was a 250 ml. beaker, i.e., the bottom part of the spectrophotometric titrator. Water was used as a reference solution. The results are summarized in Table 4 and Figure 6. It was noted that the greatest color change from the strongly acid yellow-green to the yellow color occurred between the pH 1.8 and 2.0. This

TABLE 4

VARIATION OF ABSORBANCE OF PAN WITH pH

Solution	pH	Absorbance at 430 mμ Run #1	Run #2
1	1.2	0.610	0.593
2	1.4	0.600	0.585
3	1.6	0.590	0.578
4	1.8	0.565	0.535
5	2.0	0.540	-
6	2.2	0.496	0.500
7	2.4	0.468[a]	0.432[a]
8	2.6	0.468[a]	0.462[a]
9	2.7	0.450[a]	-
10	2.8	0.450[a]	0.443[a]
11	2.9	0.420[a]	-

a. showed a colloidal suspension or precipitate

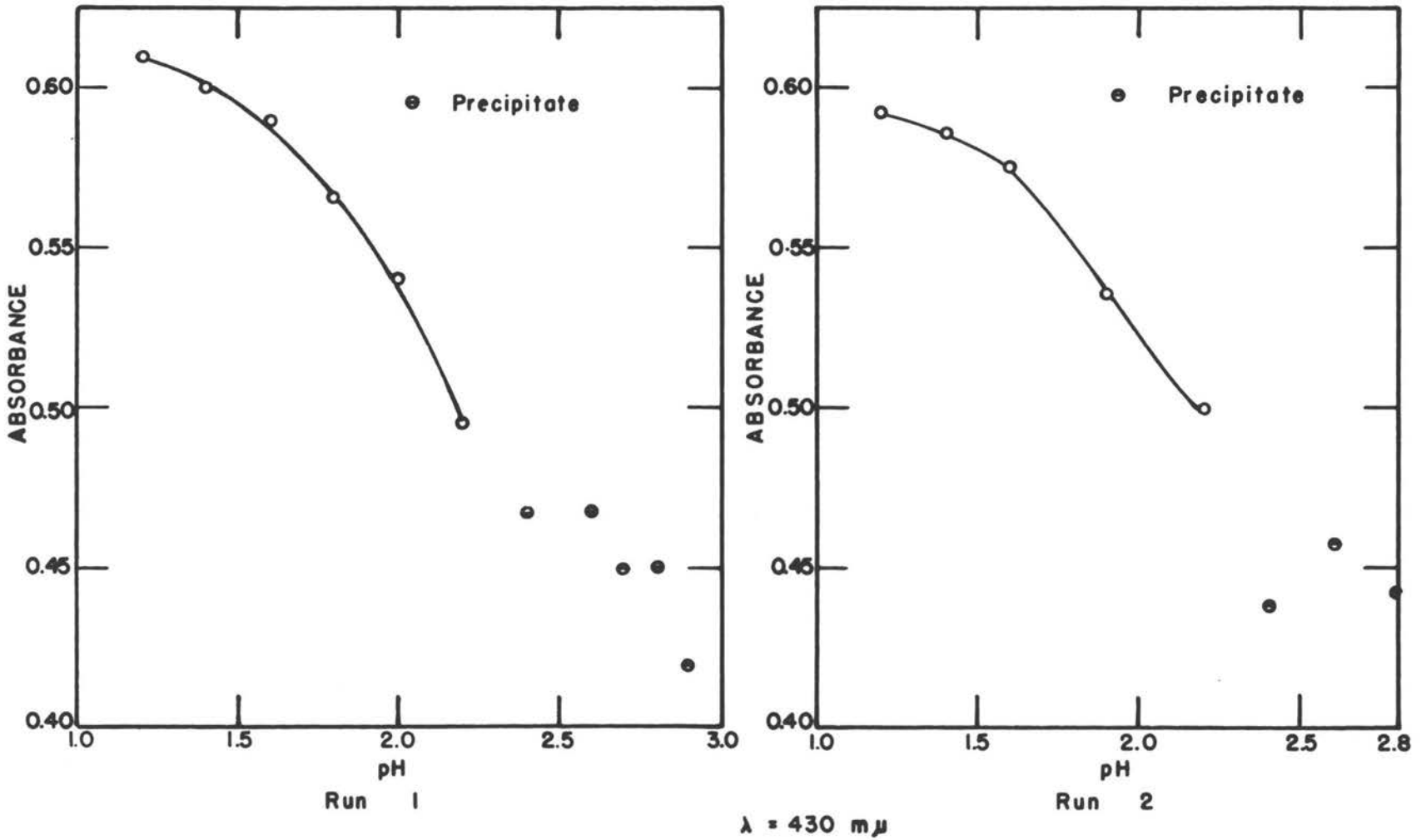


Figure 6. Variation of Absorbance of PAN with pH in Water

change in color was sharp enough to be easily detected by the eye.

The above experiment was repeated and these results are also given in Table 4 and Figure 6. It should be pointed out that there is a reason for the absorbance readings in this run being lower than those in the first. Remembering that the cell is a 250 ml. pyrex beaker, it is not expected that all portions of the sides will transmit the same amount of light. No attempt was made to replace the beaker in the second run to the exact position used in the former but the position of the beaker with respect to the light path was held constant for all the measurements within one run.

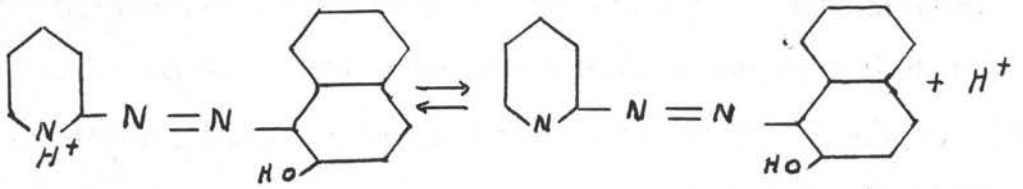
Discussion of Results

The resulting absorption curves shown in Figure 4 clearly show the existence of two forms of the dye in the 1 and 2 pH range. There is a decrease in absorbance with an increase of pH at 275, 323 and 425 millimicrons. There is a corresponding increase of absorbance at 540 millimicrons. It was observed that the dye is very soluble at pH of 1 and 2 but at a pH of 3 it forms a colloidal suspension and slowly starts to precipitate. This should not affect the general shape of the curve but it will lead to a decrease in absorbance and will

prevent the curve at pH 3 from crossing the isosbestic points at 312, 335, 360 and 485 millimicrons. The spectra also indicate the existence of the quite insoluble neutral form in the intermediate pH region. The spectrum obtained at pH 9.8 in 3-5 minutes, combined with the information obtained from the repeated runs at this pH and at various times up to 30 minutes points out the strong possibility of a third species in the strongly basic region. This species appears red in water solution, is soluble and has strong absorption bands at 530 and 580 mu. There is an isosbestic point for the second and third species at 500 mμ.

In order to compare absorption spectra of solutions which are different in concentrations it is common practice to plot the logarithm of absorbance against the wavelength (20, pp. 307-311). If the solutions are the same, but concentrations are different, the obtained curves will be identical but displaced. Since the intermediate form of the dye was coming out of solution, the concentration would be different than that in the solutions in the very low or high pH range. The plots of log A vs. wavelength for the same solutions have been plotted over the 350-680 millimicrons range. These plots, shown in Figure 5, demonstrate more clearly the existence of three forms of the dye.

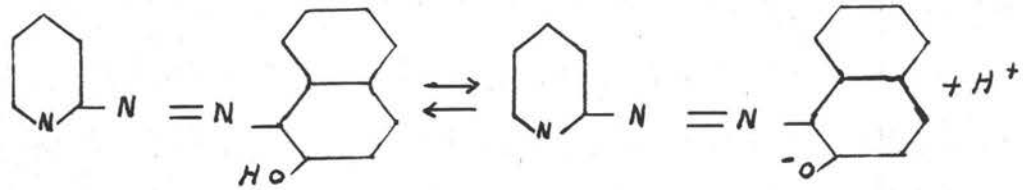
Concerning these three dye species, it is quite conceivable that the neutral yellow form (HKE) may add a hydrogen on the pyridine nitrogen to give the yellow-green acid form (H_2KE^+).



yellow green $\rightleftharpoons$ yellow

$$H_2KE^+ \rightleftharpoons HKE + H^+ \qquad (1)$$

Likewise, the yellow neutral form may dissociate to form the red basic species (KE^-).



yellow $\rightleftharpoons$ red

$$HKE \rightleftharpoons KE^- + H^+ \qquad (2)$$

The equilibrium constant, Ka_1 for equation (1) may be written

$$Ka_1 = \frac{[H^+]\,[HKE]}{[H_2KE^+]}$$

or $\log K_{a1} = \log [H^+] + \log \frac{[HKE]}{[H_2KE^+]}$.

At the point where $[HKE] = [H_2KE^+]$, $\log K_{a1} = \log [H^+]$ and $pH = pK_{a1}$.

Similarly, $K_{a2} = \frac{[H^+][KE^-]}{[HKE]}$ and when $[KE^-] = [HKE]$ the $pH = pK_{a2}$.

According to Figure 4, as the pH is raised from 1 to 4 there is a decrease of absorbance at 430 millimicrons and as the solution is made more basic, there is a further decrease in absorbance. It will be shown later that this is also true in 20% dioxane solutions of the dye.

At the point (Figure 6 and Table 4) where the change in absorbance per unit change in pH is the greatest, $[HKE] = [H_2KE^+]$ and $pH = pK_{a1}$ (6, p. 248). The attempts to determine the previously mentioned points and pK_{a1} spectrophotometrically in aqueous solutions were unsuccessful due to the precipitation of the neutral form of the dye.

Since the pH 1.8 buffer solution appeared yellow-green whereas the 2.0 solution appeared yellow, it is likely that the pK_{a1} of the dye in aqueous solutions is between these two numerical values.

PROPERTIES OF PAN IN 20% DIOXANE

Since the neutral form of the dye is quite insoluble and forms a colloidal suspension or precipitate in water, the previously mentioned curves in Figures 4 and 5, for this form can only be used for qualitative estimations. In order to obtain quantitative data and dissociation constants it was necessary to use a different solvent. Calvin and Wilson (7, p. 2003) and later Van Uitert and others (27, 28, and 29) have shown that it is possible to measure accurately the pH of aqueous-dioxane solutions by means of glass and calomel electrodes. For this reason and also since all three forms of the dye are soluble in 20% dioxane, giving absorption spectra similar to the water solutions, this was chosen as a convenient solvent for future experiments.

Reagents and Equipment

1,4 Dioxane.

Commercial grade dioxane, obtained from Carbide and Carbon Chemical Co, 3404 4th Avenue, Seattle, Washington, was purified as follows. To 1 kg. of dioxane was added 15 ml. of concentrated HCl and 70 ml. of H_2O. The solution was allowed to stand at room temperature for 1.5 hours, 15 g. of KI was added, the mixture was stirred well for 15 minutes and then

saturated with KOH pellets. The upper dioxane phase was separated by decantation through filter paper and the filtrate was distilled from KOH pellets. The tested peroxide-free dioxane fraction (B.P. 100-101°C., uncorrected) was used throughout all of the experiments.

All the other reagents and equipment have been previously described.

Procedure

Absorption spectra of PAN in 20% dioxane.

A series of unbuffered solutions were prepared by the addition of varying amounts of 0.10 N HCl or 0.10 N NaOH, 20 ml. of the repurified peroxide-free dioxane, 0.50 ml. of the stock dye solution and the dilution to 100 ml. with 0.100 N KCl. The spectra of the resulting solutions were then obtained using the recording spectrophotometer with the 5 cm. cells. The pH values of the solutions were obtained within an hour. The details of the composition of the solutions, measured pH values and time of standing before running are summarized in Table 5 and the resulting absorption spectra are shown in Figure 7. The spectra of the solutions in the lower wavelength region could not be obtained. Dioxane has an appreciable absorbance in the ultraviolet region (15, p. 412). This, coupled

TABLE 5

DATA FOR ABSORPTION SPECTRA OF

PAN IN 20% DIOXANE

Solution	ml. 0.10 HCl or 0.10 NaOH	Measured pH	Time of Standing minutes	Color
1	80 (HCl)	1.1	3 - 5	yellow-green
2	8.0 (HCl)	2.0	4 - 6	yellow
3	0.8 (HCl)	2.9	4 - 6	yellow
4	none	3.5	5 - 7	yellow
5	0.8 (NaOH)	4.2	4 - 6	yellow
6	2.0 (NaOH)	6.1	4 - 6	yellow
7[a]	80 (NaOH)	12.6	4 - 6	red

All solutions contained 20 ml. dioxane, 0.50 ml. stock dye, and were diluted to 100 ml. with 0.100 N KCl.

a. Fades rapidly upon standing.

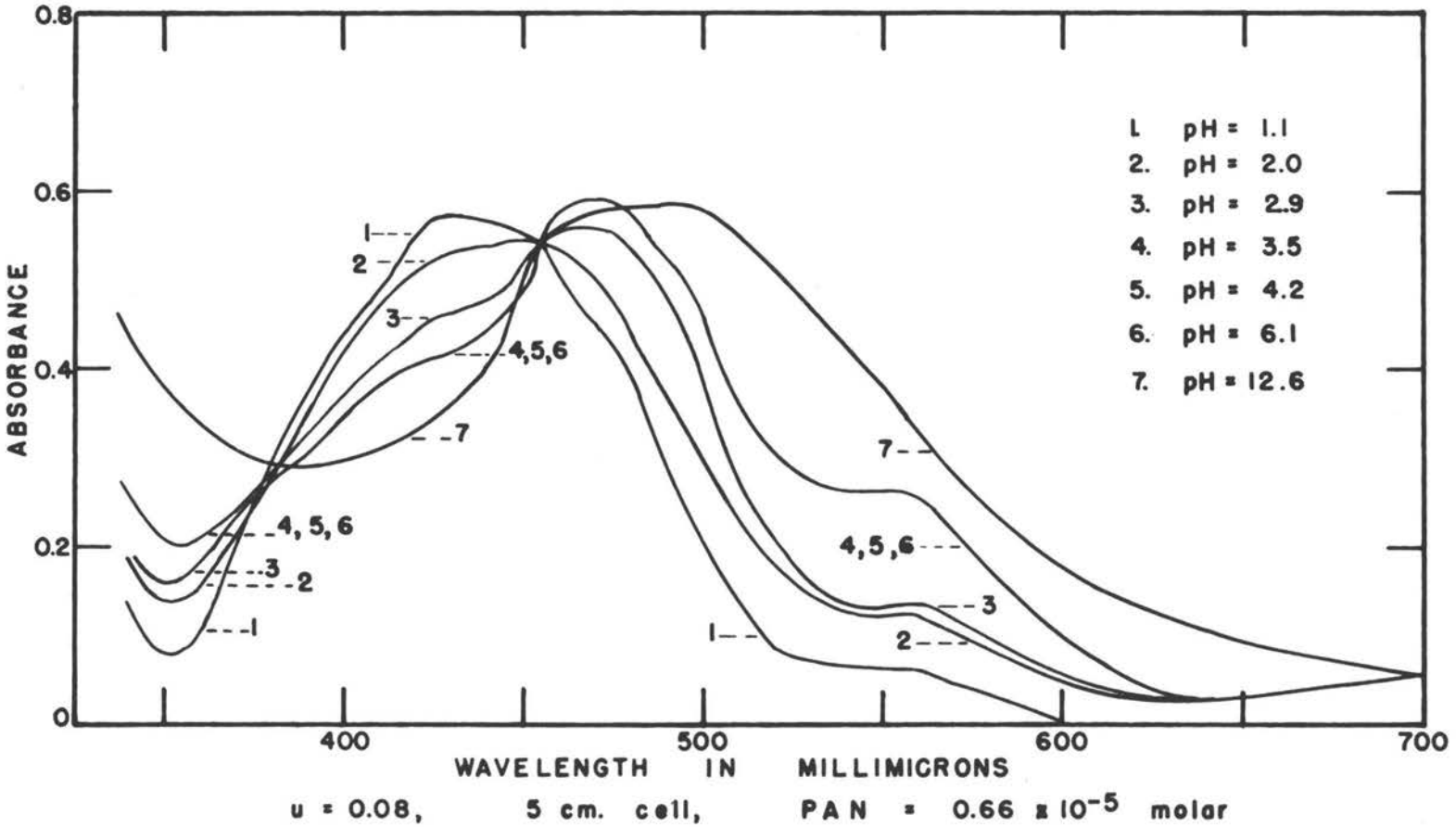


Figure 7. Absorption Spectra of PAN in 20% Dioxane

with the long 5 cm. light path, required greater slit widths than were available.

All of the solutions appeared stable except the red one obtained at pH 12.6. This solution faded rapidly upon standing and became clear and colorless within two hours.

Stability of PAN in 20% dioxane.

Since the previous experiment indicated the red strongly-basic form of the dye was unstable it was desirable to check the stability of all three forms.

To each of four 100 ml. volumetric flasks was added 20 ml. of dioxane, 1.0 ml. of the stock dye solutions and varying amounts of 0.10 N HCl or NaOH. The solutions were then diluted to volume with 0.100 N KCl and mixed thoroughly. Using as a reference, a solution containing 20 ml. of dioxane and 80 ml. of the HCl, the absorbances in 1 cm. cells were obtained through the use of the Beckman Model B operated at maximum sensitivity. The details of solution composition, pH values, absorbances, wavelengths and times are summarized in Figure 8 and Table 6.

Determination of dissociation constants.

Experiment 1

To a series of thirty-eight 25 ml. volumetric flasks was added 0.85 ml. of the stock dye solution, 20 ml. of

TABLE 6

STABILITY OF PAN IN 20% DIOXANE

Solution	1	2	3	4
Ml. 0.10 N HCl or 0.10 N NaOH	80(HCl)	0.8(HCl)	2 (NaOH)	15(NaOH)
Measured pH	1.0	2.8	4.5	12.2
Color	yel.-gr.	yellow	yellow	red
Wavelength, mμ	430	475	475	475
Time in min.	Absorbance	Absorbance	Absorbance	Absorbance
3	-	-	0.237	-
5	0.237	-	0.235	0.185
7	-	0.226	-	-
8	-	-	-	0.179
10	-	-	0.239	-
11	-	-	-	0.174
12	-	0.227	-	0.167
15	0.237	-	-	-
18	-	0.227	-	-
20	0.236	0.227	-	-
24	-	-	-	0.151
25	0.235	-	0.239	-
30	-	-	-	0.143
32	-	0.227	-	-
38	-	-	-	0.135
40	0.238	-	0.241	-
43	-	-	-	0.125
49	-	0.227	-	-
55	-	0.228	-	-
62	-	-	-	0.107
70	-	-	-	0.096
74	0.237	-	-	-
75	-	0.227	0.240	-
76	-	-	-	0.094
80	0.236	-	-	-
85	-	-	-	0.085
115	-	-	0.238	-
117	0.237	-	-	-
119	-	0.227	-	-

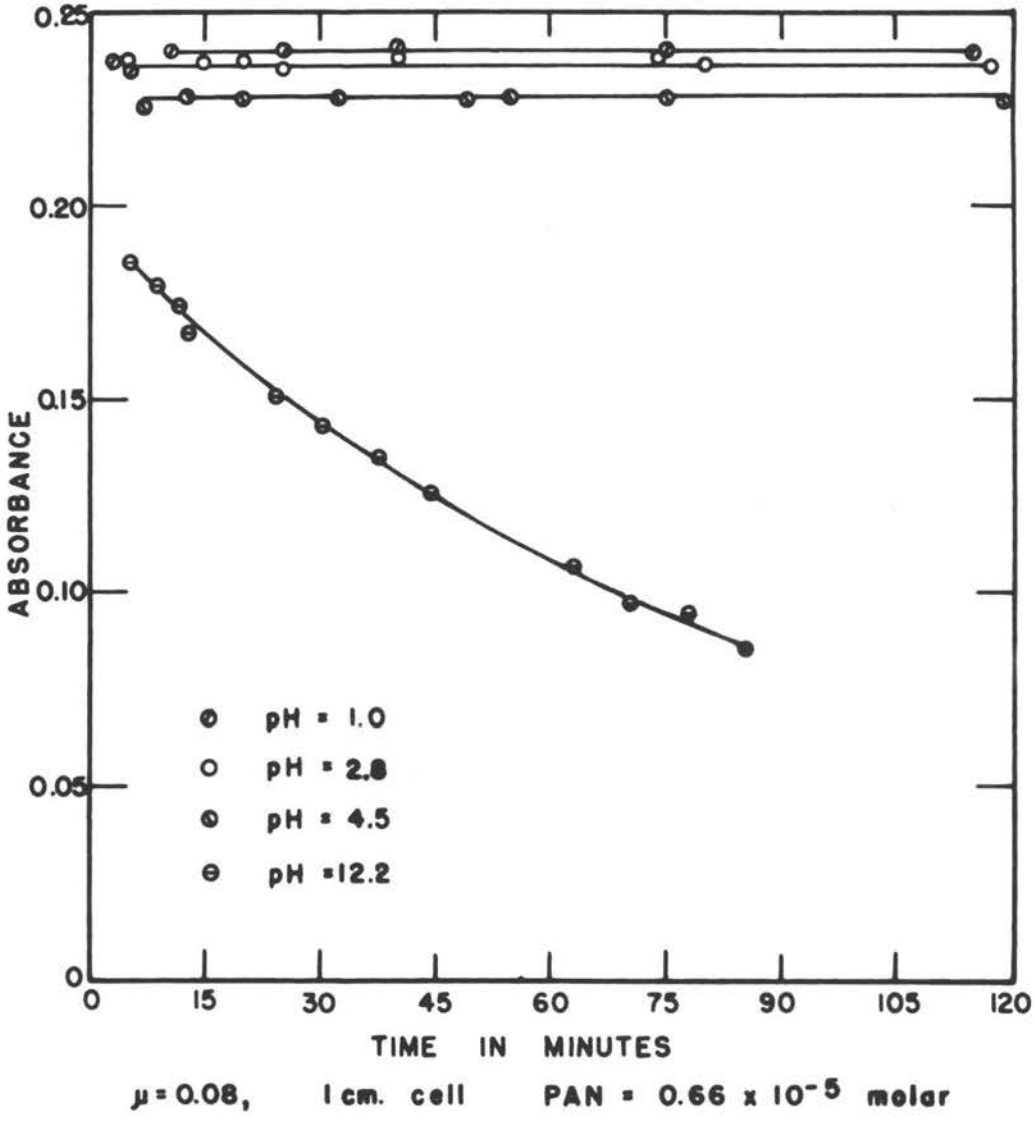


Figure 8. Stability of PAN in 20% Dioxane

dioxane and varying amounts of 0.10 N HCl, 0.10 N NaOH, 0.10 N KCl or buffered solutions. The absorbance values were obtained at 425 mμ every two minutes until the readings were constant. All of the solutions were read against a 20% dioxane in water reference on the Beckman Model B Spectrophotometer equipped with 1 cm. cells. The resulting absorbance, pH values and composition of the solutions are summarized in Table 7 and Figure 9.

Experiment 2

To the previously described 250 ml. titrating vessel was added 36 cc. of peroxide-free dioxane, 0.61 grams of sodium formate, 130 cc. of 0.2 N HCl and 13 cc. of H_2O. The transmission of the resulting solution was set at 100% requiring a slit width of 0.56 mm. at sensitivity setting 2 and a wavelength of 550 millimicrons. To this was added 1.00 ml. of the stock dye in methanol solution.

The pH of the solution was varied by the addition of a titrant which contained 8 grams of NaOH and 20 ml. of dioxane per 100 ml. of solution. The pH values and absorbances were measured throughout the titration and are summarized in Table 8 and Figure 10. The above procedure was repeated. These results are also

TABLE 7

VARIATION OF ABSORBANCE OF PAN WITH pH

IN 20% DIOXANE; $\lambda = 425$ mμ

Solution	Measured pH	Absorbance	Ml. 0.10 N HCl or 0.10 N NaOH	Dilute to 25 ml. with
1	0.4	0.397	none	0.18 N HCl
2	0.96	0.389	to vol. (HCl)	---
3	0.98	0.393	to vol. (HCl)	---
4	1.70	0.352	15 ml. (HCl)	0.100 N KCl
5	2.15	0.342	10 ml. (HCl)	0.100 N KCl
6	2.18	0.330	10 ml. (HCl)	0.100 N KCl
7	2.58	0.298	7 ml. (HCl)	0.100 N KCl
8	3.08	0.289	1 ml. (HCl)	0.100 N KCl
9	3.52	0.287	none	0.100 N KCl
10	3.62	0.282	none	0.10 N KHP[a]
11	3.90	0.280	1 ml. (NaOH)	0.10 N KHP
12	5.10	0.280	5 ml. (HCl)	0.10 N NaAC[b]
13	5.45	0.282	2 ml. (HCl)	0.10 N NaAC
14	6.10	0.287	none	0.10 NaAC
15	7.25	0.280	2.0 ml. (HCl)	phosphate[c]
16	7.30	0.282	none	phosphate
17	7.30	0.287	none	phosphate
18	7.71	0.275	1.0 ml. (NaOH)	phosphate
19	7.78	0.280	1.8 ml. (NaOH)	phosphate
20	7.98	0.282	2.0 ml. (NaOH)	phosphate
21	8.18	0.282	2.5 ml. (NaOH)	phosphate
22	8.48	0.262	3.0 ml. (NaOH)	phosphate
23	8.90	0.282	0.10 ml. (NaOH)	0.100 N KCl
24	9.18	0.277	0.02 ml. (NaOH)	0.100 N KCl
25	9.30	0.260	0.03 ml. (NaOH)	0.100 N KCl
26	10.0	0.265	0.04 ml. (NaOH)	0.100 N KCl
27	10.3	0.262	0.05 ml. (NaOH)	0.100 N KCl
28	10.7	0.258	0.05 ml. (NaOH)	0.100 N KCl
29	10.9	0.254	0.05 ml. (NaOH)	0.100 N KCl
30	11.4	0.252	0.08 ml. (NaOH)	0.100 N KCl
31	11.5	0.253	0.10 ml. (NaOH)	0.100 N KCl
32	11.5	0.257	0.15 ml. (NaOH)	0.100 N KCl
33	11.7	0.252	0.20 ml. (NaOH)	0.100 N KCl
34	12.5	0.229	0.30 ml. (NaOH)	0.100 N KCl

TABLE 7 (continued)

VARIATION OF ABSORBANCE OF PAN WITH pH

IN 20% DIOXANE; λ = 425 mμ

Solution	Measured pH	Absorbance	Ml. 0.10 N HCl or 0.10 N NaOH	Dilute to 25 ml. with
35	12.5	0.220	1.0 ml. (NaOH)	0.100 N KCl
36	12.6	0.217	1.0 ml. (NaOH)	0.100 N KCl
37	13.2	0.208	none	1 N NaOH
38	13.8	0.187	none	1 N NaOH

a. KHP = 0.05 molar potassium acid pthalate

b. NaAC = 0.10 molar sodium acetate

c. phosphate = 0.025 molar potassium dihydrogen phosphate and 0.025 molar disodium hydrogen phosphate

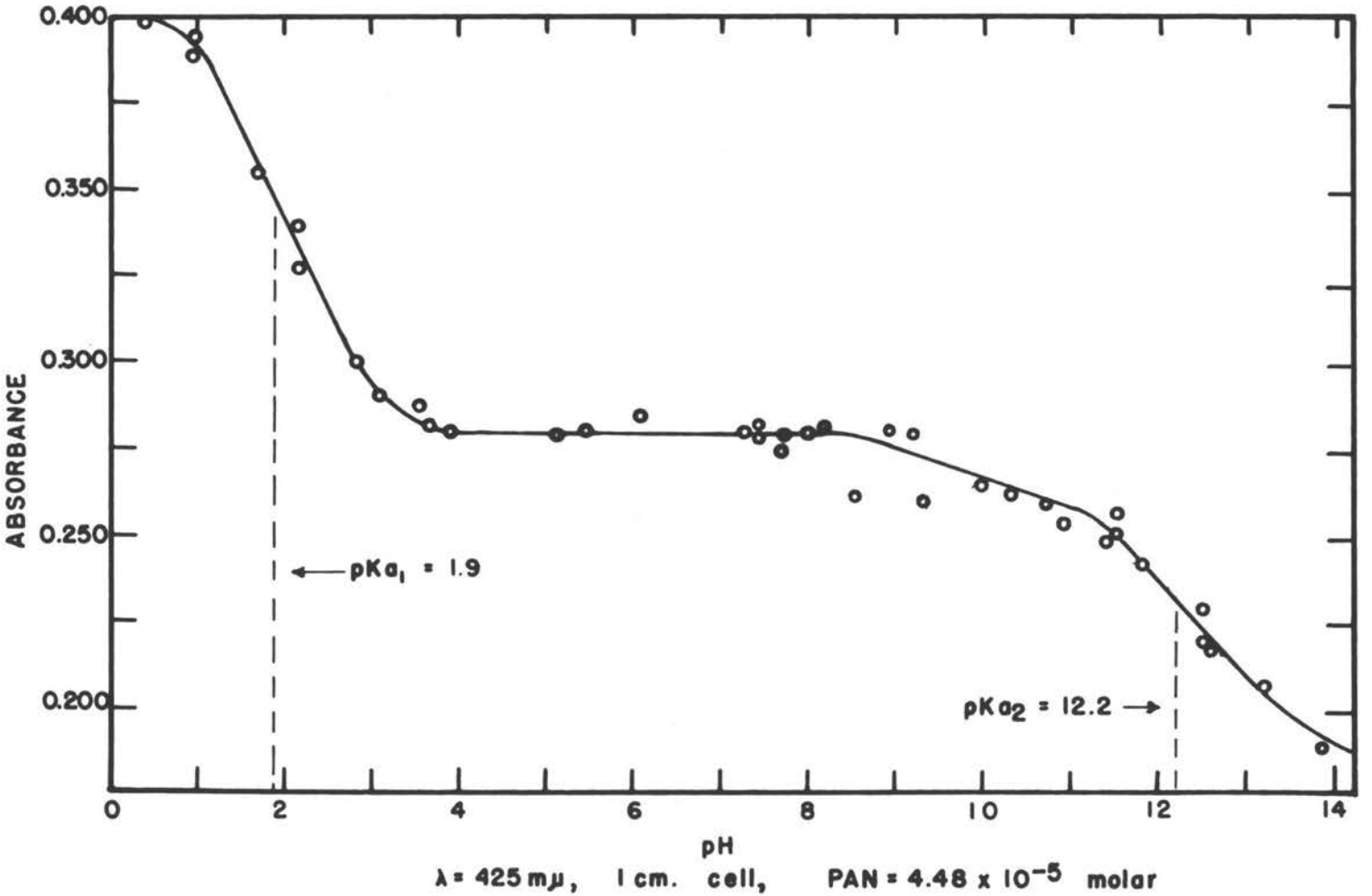


Figure 9. Absorbance Vs. pH of PAN in 20% Dioxane

TABLE 8

VARIATION OF ABSORBANCE OF PAN WITH pH

IN 20% DIOXANE, λ = 550 mμ

Run #1

pH	$\bar{A}$	pH	$\bar{A}$	pH	$\bar{A}$
1.29	0.025	1.68	0.090	2.12	0.172
1.35	0.032	1.75	0.098	2.26	0.186
1.41	0.038	1.82	0.110	2.36	0.198
1.43	0.043	1.83	0.117	2.45	0.210
1.46	0.047	1.91	0.131	2.63	0.222
1.51	0.053	1.95	0.137	2.71	0.232
1.57	0.064	1.98	0.152	2.77	0.238
1.63	0.076	2.08	0.167	2.85	0.244

A Absorbance corrected for dilution

pKa_1 = 1.86

Run #2

pH	$\bar{A}$	pH	$\bar{A}$
1.20	0.000	2.03	0.193
1.33	0.012	2.10	0.217
1.43	0.023	2.20	0.239
1.47	0.031	2.27	0.257
1.57	0.056	2.42	0.277
1.65	0.074	2.45	0.286
1.73	0.097	2.53	0.300
1.82	0.128	2.60	0.304
1.88	0.141	2.68	0.314
1.95	0.170	2.76	0.322

pKa_1 = 1.93

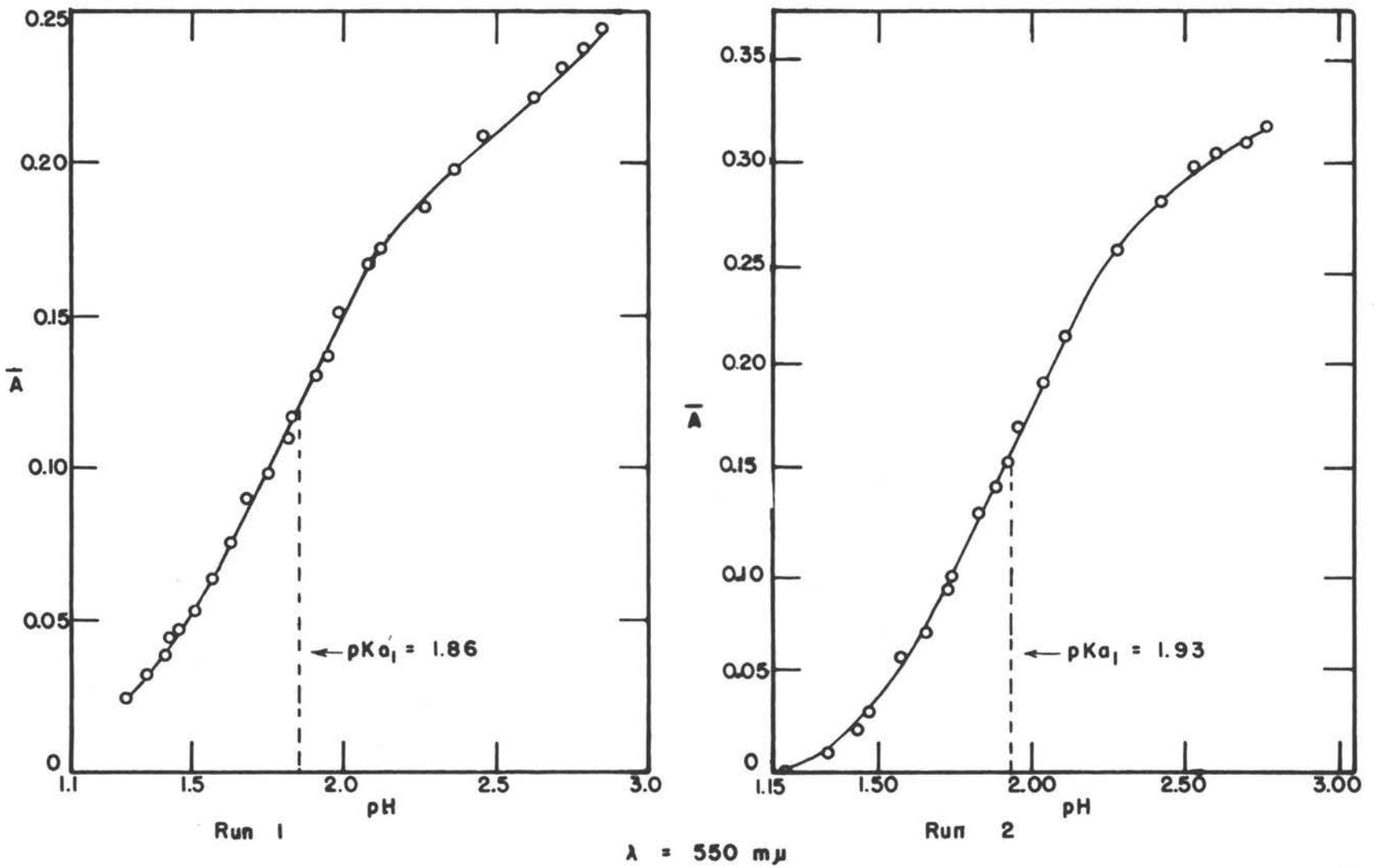


Figure 10. Variation of Absorbance of PAN with pH in 20% Dioxane

summarized in Table 8 and Figure 10.

Discussion of Results

It is interesting to note the similarities between the absorption spectra of the dye in 20% dioxane, Figure 7, and the corresponding spectra is aqueous media, Figure 4. Again the yellow-green species shows a strong absorption band around 425 millimicrons. As the pH is increased from 1.1 to 2.9 there is a decrease in absorbance with an increase in pH at this wavelength. There is also a corresponding increase in absorbance at the right of the 457 isosbestic point as well as an absorption band at 550 millimicrons.

The two isosbestic points, i.e. 457 and 382 mμ, are formed by the conversion of the H_2KE^+ to HKE (equation 1).

Since curves 4,5, and 6 of Figure 7 are identical, essentially all of the dye is in the neutral, HKE, form between the pH values of 2.9 and 6.1.

Curve 7 of Figure 7 was obtained at pH 12.5. This would represent the KE^- species.

It has been found that the acid and neutral forms are quite stable in 20% dioxane, however the negative species is unstable. This prevents the accumulation of reliable quantitative data in basic solutions.

The discussion concerning the three dye species and the determination of pK_{a1} and pK_{a2} has been given in the preceding section and will not be repeated here. The variation of pH with absorbance at 425 and 550 millimicrons has been studied in order to determine these constants. The average pK_{a1} of the three values determined graphically in Figures 9 and 10 is 1.9 and K_{a1} is 1.26×10^{-2}.

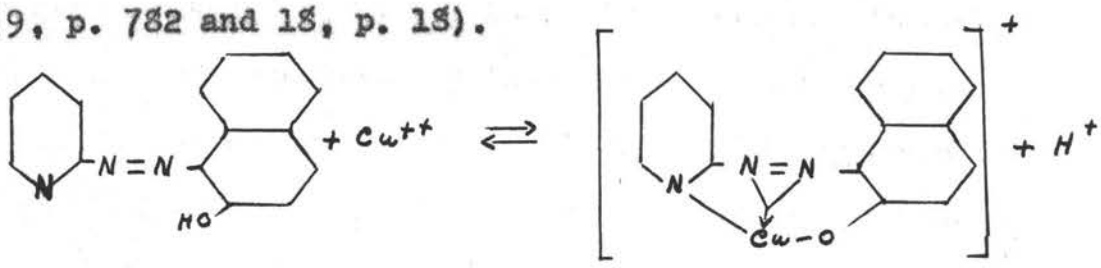
In addition to the instability of the KE^- specie there is another factor which makes it difficult to obtain an accurate value for K_{a2}. When using the glass and calomel electrodes in basic 20% dioxane solution, the pH scale must be calibrated (7, p. 2003 and 29, pp. 451-455). The approximate pK_{a2} as determined from Figure 9 is 12.2, corresponding to a value for K_{a2} of 6.3×10^{-13}, but further work must be performed in this range in order to obtain a more exact value.

In addition to the two inflection points determined on Figure 9, the possibility of a third one at pH 8 cannot be ignored. Further work must be done in this pH region before any definite conclusions can be drawn. All of the work in the following portions of this thesis has been done below pH 6 in order to avoid this region.

CHAPTER IV

PROPERTIES OF THE Cu (II)-PAN CHELATE

When Cu (II) is added to a solution of PAN in 20% dioxane, the light yellow color of the dye changes to a deep red due to the formation of the copper-PAN chelate. This color appears violet in very dilute solutions. The reaction is postulated as follows (9, p. 782 and 18, p. 18).



$$HKE + Cu^{++} \rightleftharpoons CuKE^{+} + H^{+} \qquad (3)$$

It is the purpose of this investigation to verify the formation of a 1 to 1 Cu-PAN chelate in aqueous and 20% dioxane solutions and to determine the equilibrium constant for reaction 3.

Reagents and Equipment

Standard Cu (II) solution.

This solution was prepared by dissolving 1.6143 grams of electrolytic copper in 25 ml. of 1-3 nitric acid. The solution was then boiled for 20 minutes to

eliminate oxides of nitrogen, cooled, and diluted to 500 ml. with distilled H_2O. This copper solution was standardized against both sodium thiosulfate and potassium ferrocyanide. An aliquot was diluted to form a 3.00×10^{-3} M stock Cu (II) solution.

Buffer solution.

Solution A. Sodium formate (6.801 grams) and 10.11 grams of KNO_3 were dissolved and diluted to 2 liters with water.

Solution B. Potassium nitrate (10.11 grams) and 16.6 ml. of 6 N HNO_3 were dissolved and diluted to 1 liter with water.

The constant ionic strength (0.10 in H_2O and 0.08 in 20% dioxane) buffer solution was prepared by adding 14 cc. of B to 1 liter of A.

All other reagents and equipment have been previously described.

Procedure

Determination of absorption spectra.

The absorption spectra for the copper chelate shown in Figure 11 were obtained through the use of the Beckman DK-2 Recording Spectrophotometer.

For each chelate spectrum, curves 1-5, 5.00 ml. of dioxane, 0.30 ml. of the standard copper solution and

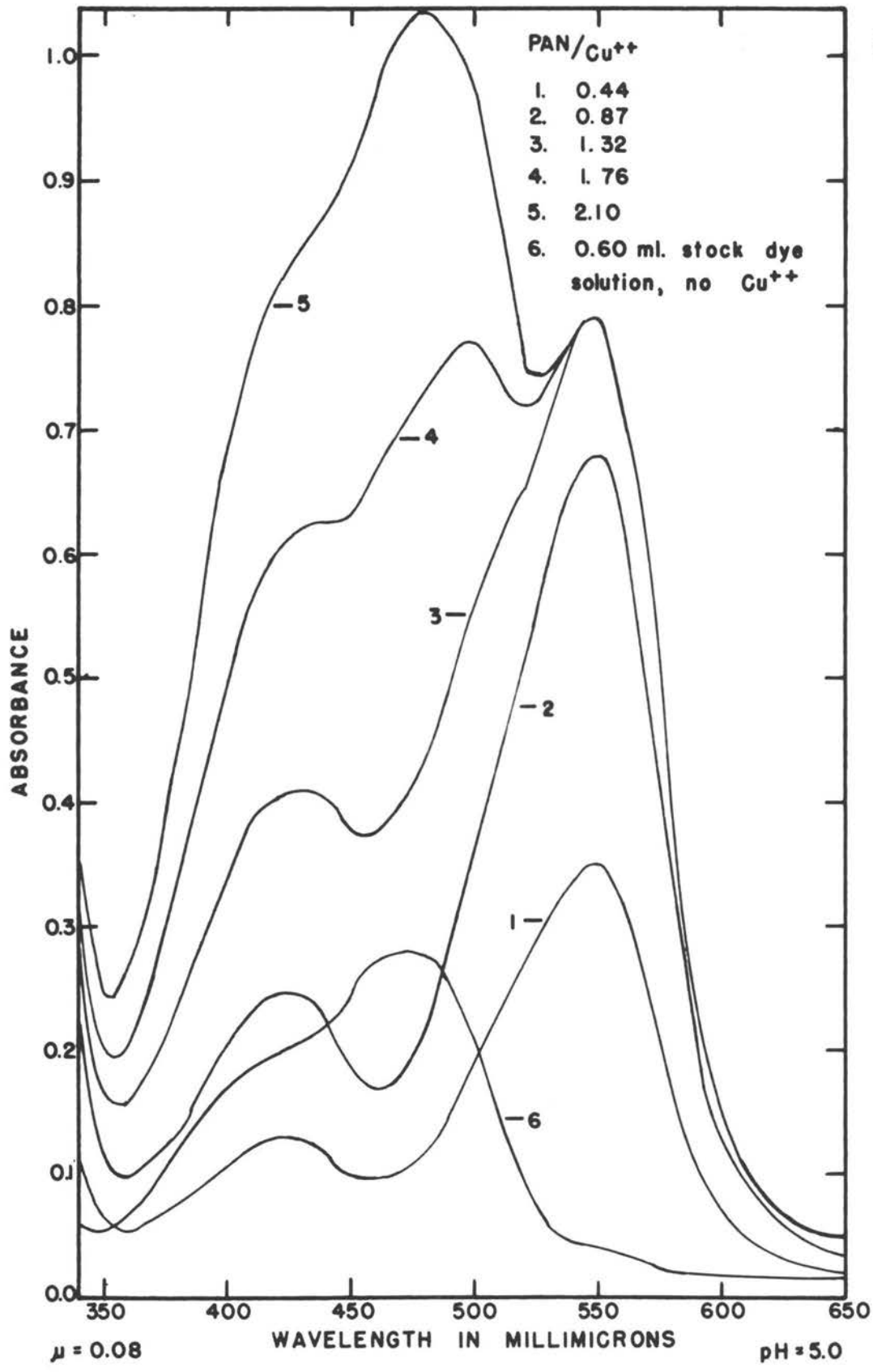


Figure II. Absorption Spectra of Copper Chelate in 20% Dioxane

0.15, 0.30, 0.45, 0.60, or 0.75 ml. of the stock dye in alcohol solutions were added to each of the respective flasks. Curve 6, the spectra of 0.60 ml. of the dye was prepared in exactly the same manner except the copper was omitted. These 6 solutions were then diluted to volume with the sodium formate buffer and the spectra were obtained.

Job's method in 20% dioxane at pH of 5.0.

To each of a series of ten 25 ml. volumetric flasks was added 5 ml. of the dioxane and varying volumes of the stock dye and copper solutions. They were all diluted to the mark with the sodium formate buffer and the absorbance values at 550 mμ were obtained on the Beckman Model B Spectrophotometer using 1 cm. cells. The data is summarized in Table 9 and Figure 12.

Job's method in water at pH of 3.0.

To each of a series of twenty-one 100 ml. flasks, was added 20 ml. of the dioxane and varying volumes of the stock dye solution, copper solution, and methyl alcohol. These flasks were then diluted to the mark with the sodium formate buffer and the absorbance values at 550 mμ were obtained through the use of the 5 cm. cells and the Model B spectrophotometer. These results are summarized in Table 10 and Figure 13.

TABLE 9

ABSORBANCE VS. Cu(II) AND PAN VARIATION IN 20% DIOXANE; pH = 5.0

Solution	ml. CuII	ml. PAN	A at 550 mμ	$\bar{A}$	$\frac{Cu^{++}}{Cu^{++} + PAN}$
1	0.00	0.72	0.047	0.000	0.00
2	0.04	0.64	0.128	0.087	0.11
3	0.08	0.56	0.250	0.214	0.22
4	0.12	0.48	0.338	0.307	0.33
5	0.16	0.40	0.448	0.422	0.44
6	0.20	0.32	0.388	0.368	0.56
7	0.24	0.24	0.309	0.294	0.67
8	0.28	0.16	0.207	0.197	0.78
9	0.32	0.08	0.103	0.097	0.89
10	0.36	0.00	--	0.000	1.00

λ = 550 mμ, Total volume = 25 ml, 1 cm. cells.

$\bar{A}$ = Absorbance corrected for line of no reaction

PAN = 1.50×10^{-3} molar before dilution.

Cu^{++} = 3.00×10^{-3} molar before dilution

sodium formate buffer

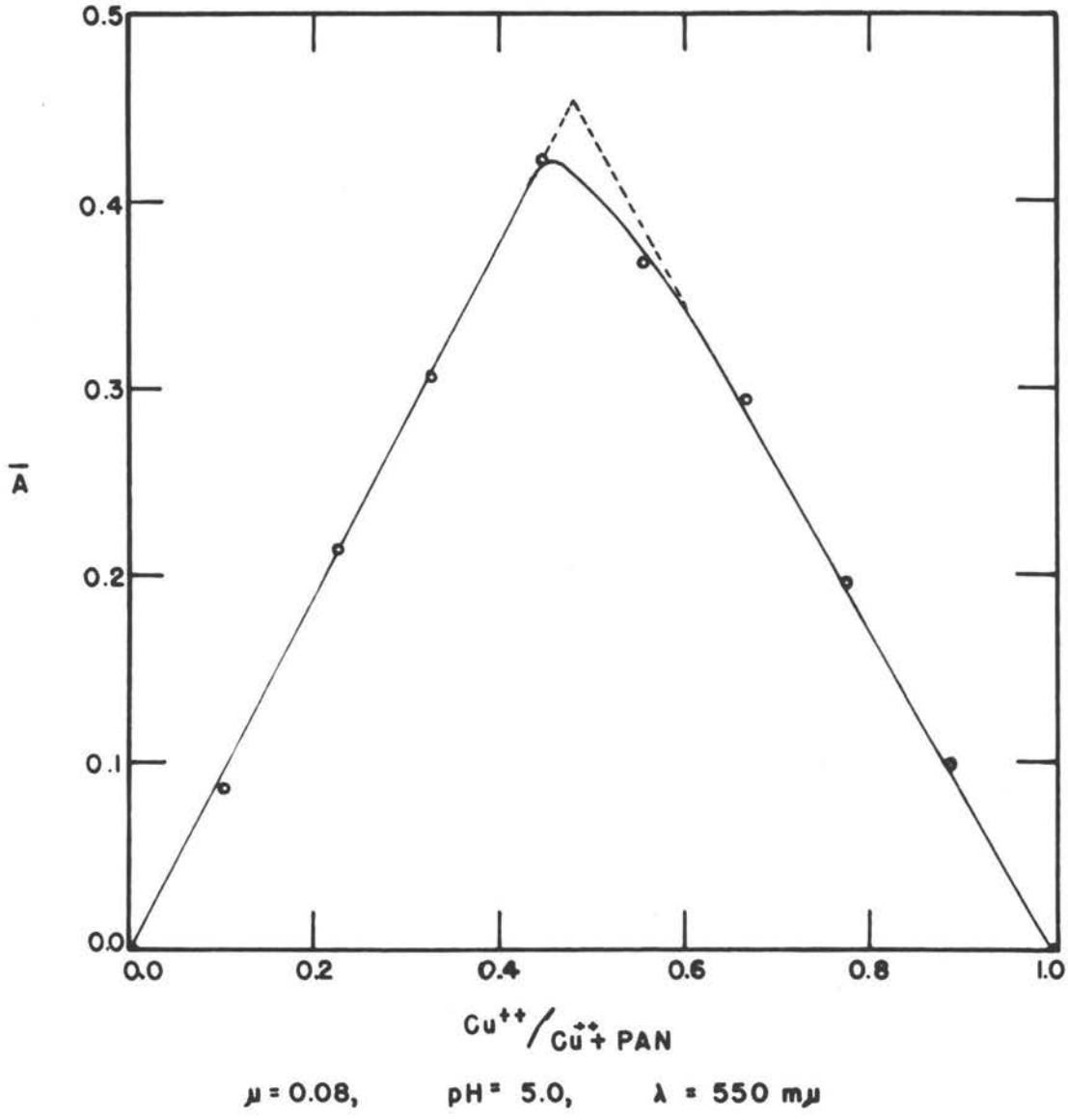


Figure 12. Absorbance Vs. Variation of Cu (II) and PAN in 20% Dioxane

TABLE 10

ABSORBANCE VS. Cu(II) AND PAN VARIATION

IN WATER; pH = 3.0

Solution	ml. Cu(II)	ml. PAN	ml. MeOH	A at 550 mμ	$\bar{A}$	$\frac{Cu^{++}}{Cu^{++} + PAN}$
1	1.00	0.00	2.00	0.000	0.00	1.00
2	0.95	0.10	1.90	0.150	0.13	0.95
3	0.90	0.20	1.80	0.296	0.25	0.90
4	0.85	0.30	1.70	0.418	0.38	0.85
5	0.80	0.40	1.60	0.570	0.52	0.80
6	0.75	0.50	1.50	0.720	0.63	0.75
7	0.70	0.60	1.40	0.850	0.76	0.70
8	0.65	0.70	1.30	0.972	0.88	0.65
9	0.60	0.80	1.20	1.139	1.02	0.60
10	0.55	0.90	1.10	1.240	1.13	0.55
11	0.50	1.00	1.00	1.390	1.26	0.50
12	0.45	1.10	0.90	1.467	1.31	0.45
13	0.40	1.20	0.80	1.417	1.25	0.40
14	0.35	1.30	0.70	1.282	1.10	0.35
15	0.30	1.40	0.60	1.176	0.97	0.30
16	0.25	1.50	0.50	1.000	0.78	0.25
17	0.20	1.60	0.40	0.834	0.60	0.20
18	0.15	1.70	0.30	0.710	0.46	0.15
19	0.10	1.80	0.20	0.522	0.26	0.10
20	0.05	1.90	0.10	0.451	0.18	0.05
21	0.00	2.00	0.00	0.281	0.00	0.00

PAN = 1.50×10^{-3} molar before dilution

Cu^{++} = 3.00×10^{-3} molar before dilution

sodium formate buffer, 5 cm. cells.

Total volume 100 ml.

$\bar{A}$ = absorbance corrected for line of no reaction

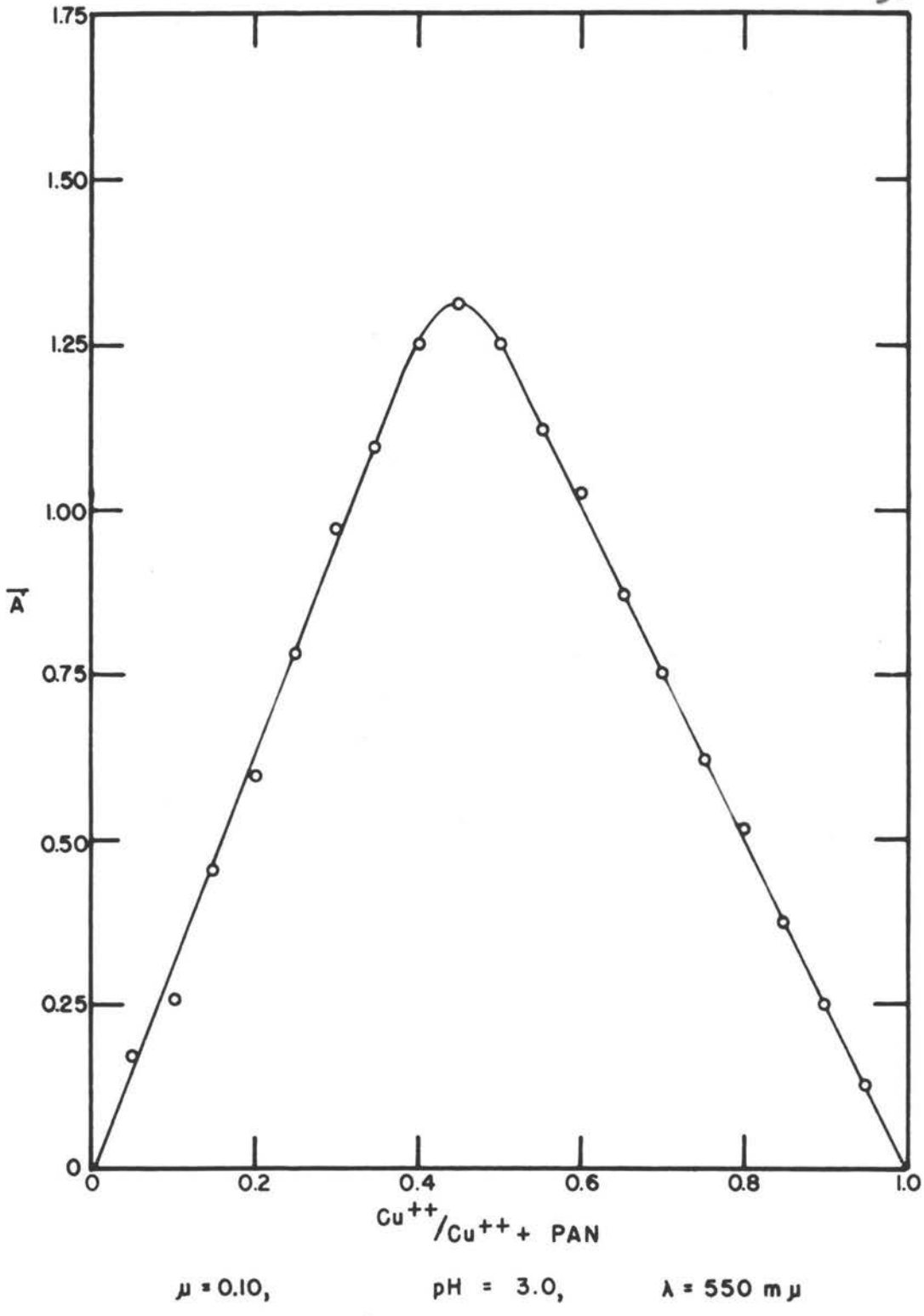


Figure 13. Absorbance Vs. Variation of Cu(II) and PAN in Water

Job's method in water at pH of 6.0 and pH of 8.25.

These two runs were made similar to the preceding one. The results are summarized in Tables 11 and 12 respectively.

Stability of the copper chelate.

Solutions number 5 of Table 9 and number 12 of Table 10 were used for stability measurements. The absorbances were obtained every 2 hours for the first 12 hours and at longer intervals thereafter. It was found that both solutions were stable for at least 5 days. No maximum time limit has been obtained on the stability of the copper chelate.

Spectrophotometric Titration of Cu (II).

1) pH 3.0 in water.

To the 250 ml. titrating beaker was added 0.50 ml. of the stock copper solution and 200 ml. of the sodium formate buffer. The transmission at 550 millimicrons was then set at 100% at sensitivity setting of 1, requiring a slit width of 0.57 on the Beckman Model B spectrophotometer. The absorbance values obtained upon the addition of increment portions of the stock dye in methanol solution are shown in Table 13 and Figure 14. The absorbance values have not been corrected for dilution. This is not necessary since even at the

TABLE 11

ABSORPTION VS. Cu(II) AND PAN VARIATION

IN WATER; pH = 6.0

Solution	ml.Cu(II)	ml.PAN	ml. MeOH	A at 550 mμ	$\bar{A}$	$\frac{Cu^{++}}{Cu^{++} + PAN}$
1	1.00	0.00	2.00	0.000	0.00	1.00
2	0.90	0.20	1.80	0.212	0.16	0.90
3	0.80	0.40	1.60	0.504	0.42	0.80
4	0.70	0.60	1.40	0.762	0.60	0.70
5	0.65	0.70	1.30	0.875	0.70	0.65
6	0.60	0.80	1.20	1.052	0.85	0.60
7	0.55	0.90	1.10	1.132	0.91	0.55
8	0.50	1.00	1.00	1.242	0.98	0.50
9	0.45	1.10	0.90	1.350	1.06	0.45
10	0.40	1.20	0.80	1.342	1.02	0.40
11	0.30	1.40	0.60	1.132	0.78	0.30
12	0.20	1.60	0.40	0.933	0.51	0.20
13	0.10	1.80	0.20	0.676	0.26	0.10
14	0.00	2.00	0.00	--	0.00	0.00

5 cm. cells, Sodium acetate buffer

$\bar{A}$ = Absorbance corrected for line of no reaction

PAN = 1.50×10^{-3} molar before dilution, total vol. = 100 ml.

Cu^{++} = 3.00×10^{-3} molar before dilution

TABLE 12

ABSORBANCE VS. Cu(II) AND PAN VARIATION

IN WATER, pH = 8.25

Solution	ml. Cu(II)	ml. PAN	Ml. MeOH	A at 550 mμ	$\bar{A}$	$\frac{Cu^{++}}{Cu^{++} + PAN}$
1	1.00	0.00	2.00	0.000	0.00	1.00
2	0.90	0.20	1.80	0.255	0.20	0.90
3	0.75	0.50	1.50	0.610	0.47	0.75
4	0.60	0.80	1.20	0.937	0.73	0.60
5	0.50	1.00	1.00	1.116	0.93	0.50
6	0.40	1.20	0.80	1.261	1.00	0.40
7	0.30	1.40	0.60	1.176	0.88	0.30
8	0.20	1.60	0.40	0.968[a]	0.62	0.20
9	0.10	1.80	0.20	0.750[a]	0.36	0.10
10	0.00	2.00	0.00	0.430[a]	0.00	0.00

λ = 550; pH = 8.25, 5 cm. cells a. colloidal

$\bar{A}$ = corrected for line of no reaction, phosphate buffer

PAN = 1.50×10^{-3} molar before dilution

Cu^{++} = 1.00×10^{-3} molar before dilution, total vol. = 100 ml.

TABLE 13

SPECTROPHOTOMETRIC TITRATION OF Cu(II)

WITH PAN IN H_2O, pH = 3.0

ml. PAN	Absorbance	ml. PAN	Absorbance
0.00	0.000	1.10	0.907
0.10	0.094	1.20	0.968
0.20	0.188	1.30	1.01
0.30	0.276	1.40	1.06
0.40	0.362	1.50	1.09
0.50	0.447	1.60	1.12[a]
0.60	0.520	1.70	1.14[a]
0.70	0.602	1.80	1.16[a]
0.80	0.684	1.90	1.17[a]
0.90	0.762	2.00	1.18[a]
1.00	0.837	2.10	1.19[a]

λ = 550, Sodium formate buffer

a. precipitate

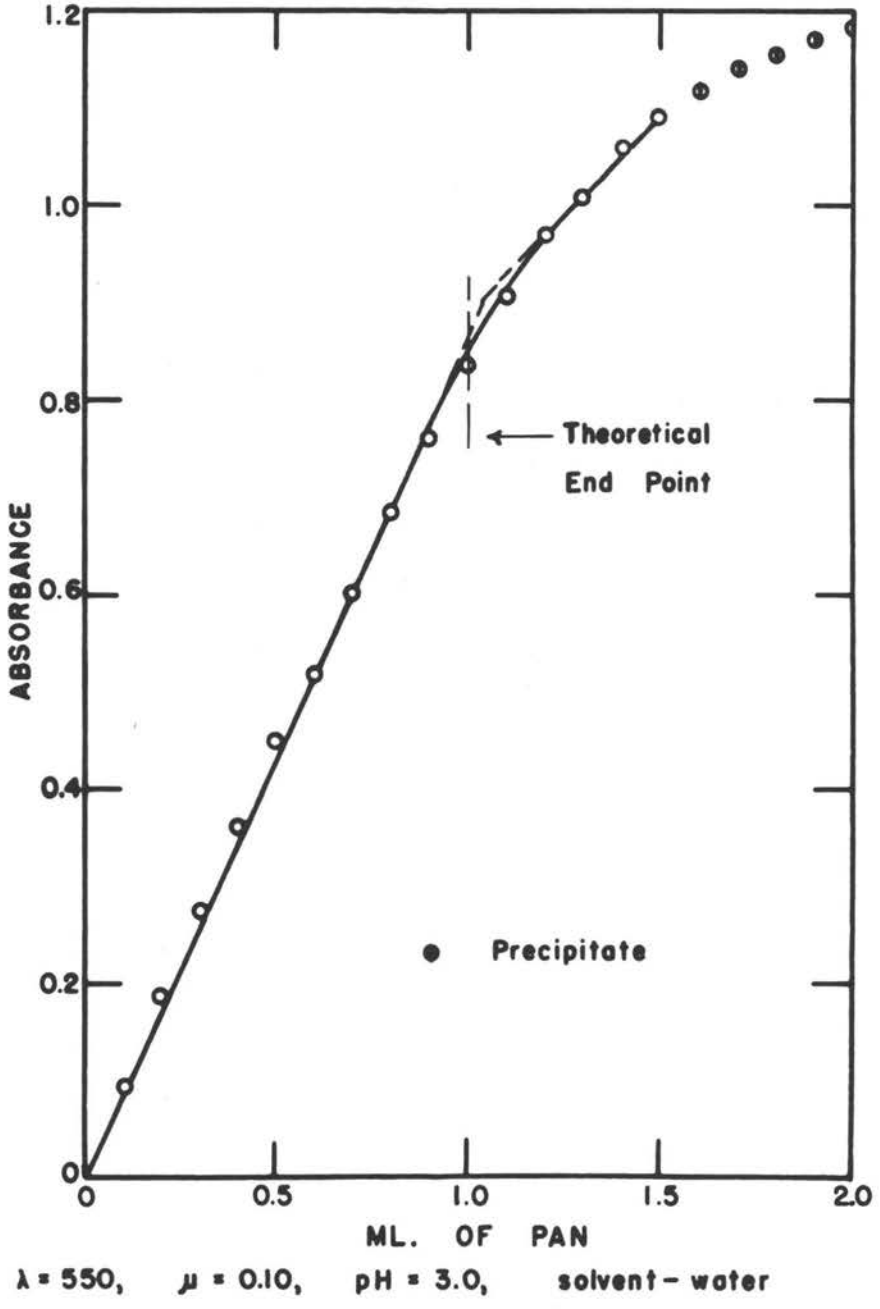


Figure 14. Spectrophtometric Titration of Cu (II) with PAN

end of the titration there would only be a 1% correction.

2) pH 8.25 in water.

The above procedure was repeated except that a phosphate buffer, pH 8.25, was substituted for the sodium formate buffer used in the preceding run. These results are summarized in Table 14 and Figure 15.

3) pH 5.0 in 20% dioxane.

The titrating cell contained 143 cc. of the sodium formate buffer, 36 cc. of dioxane and 0.5 cc. of the standard copper solution at the start of the run. This was titrated with the stock dye in methanol solution as previously described. The results are shown in Figure 16 and Table 15. This procedure was used to standardize the dye in methanol.

After the commercial dye became available an estimate of the purity of it was made. An insufficient number of points were obtained for a very accurate value but it was found to be between 92 and 95% pure. The author's dye was found to be 87.7% pure.

Variation of absorbance of the copper chelate with pH.

To each of a series of 25 ml. volumetric flasks was added 5 ml. of dioxane, 0.40 ml. of the previously standardized dye solutions, 0.22 ml. of the standard Cu (II) solution and varying amounts of 0.10 N nitric

TABLE 14

SPECTROPHOTOMETRIC TITRATION OF Cu(II)

WITH PAN IN H_2O, pH = 8.25

ml.PAN	Absorbance	ml.PAN	Absorbance	ml.PAN	Absorbance
0.00	0.000	0.54	0.511	1.06	0.990
0.10	0.095	0.62	0.586	1.12	1.01
0.14	0.133	0.71	0.675	1.18	1.05
0.20	0.194	0.74	0.700	1.30	1.11
0.26	0.247	0.82	0.771	1.40	1.16
0.30	0.290	0.90	0.845	1.50	1.21
0.34	0.337	0.94	0.873	1.60	1.26
0.38	0.371	0.96	0.896	1.80	1.32[a]
0.42	0.408	0.98	0.919	1.90	1.36[a]
0.50	0.480	1.00	0.940	2.00	1.40[a]

λ = 550, phosphate buffer

a. precipitate

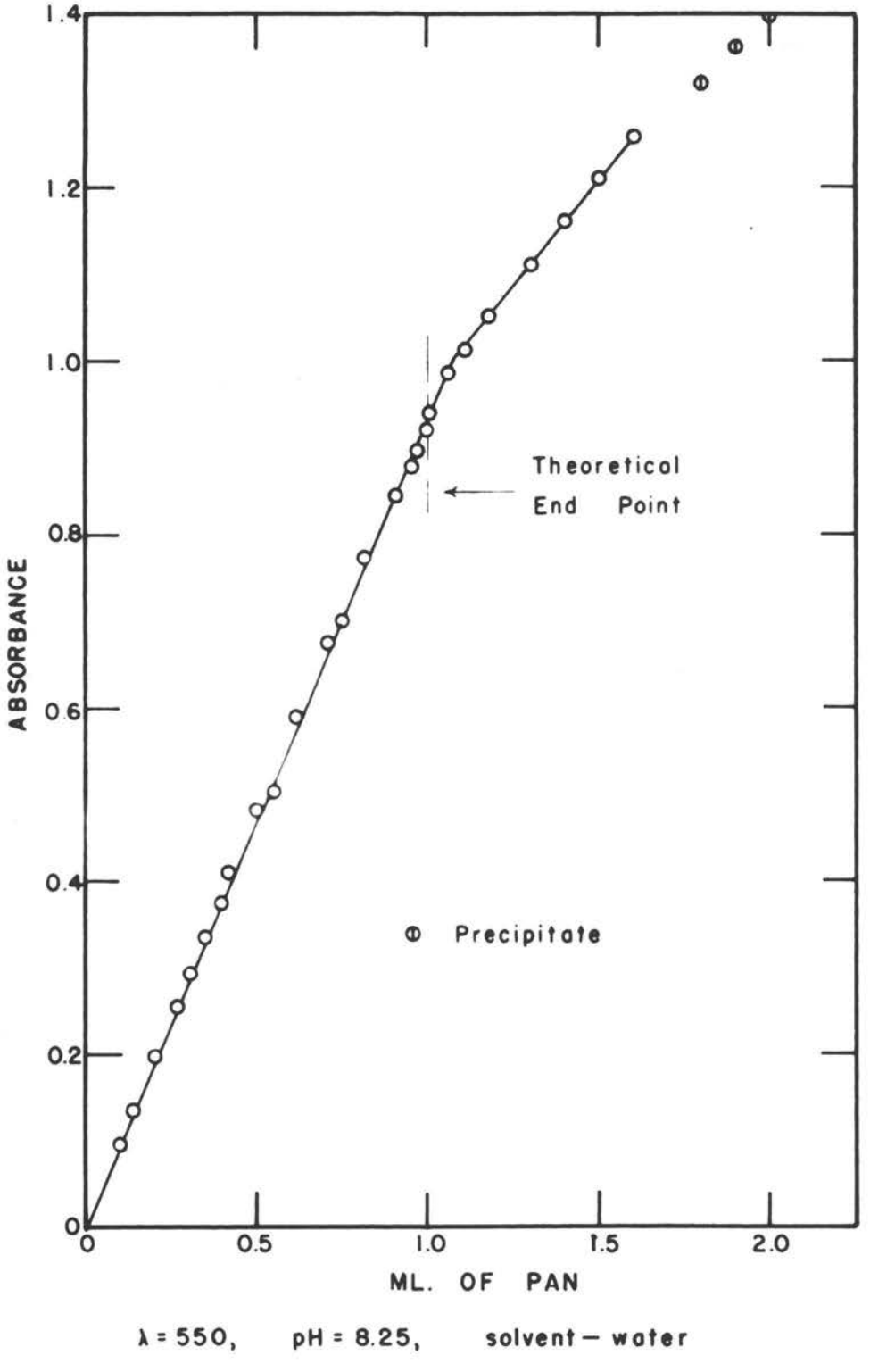


Figure 15. Spectrophotometric Titration of Cu (II) with PAN

TABLE 15

SPECTROPHOTOMETRIC TITRATION OF Cu(II)

WITH PAN IN 20% DIOXANE, pH = 5.0

ml.PAN	Absorbance	ml.PAN	Absorbance	ml.PAN	Absorbance
0.00	0.000	0.60	0.643	1.20	1.232
0.05	0.056	0.65	0.698	1.30	1.238
0.10	0.109	0.70	0.752	1.40	1.242
0.15	0.164	0.75	0.807	1.50	1.242
0.20	0.220	0.80	0.860	1.60	1.244
0.25	0.272	0.85	0.915	1.70	1.246
0.30	0.330	0.90	0.967	1.80	1.248
0.35	0.382	0.95	1.015	1.90	1.250
0.40	0.441	1.00	1.065	2.00	1.251
0.45	0.492	1.05	1.120	2.10	1.251
0.50	0.539	1.10	1.170	2.20	1.252
0.55	0.591	1.15	1.212	2.30	1.253

λ = 550, sodium formate buffer

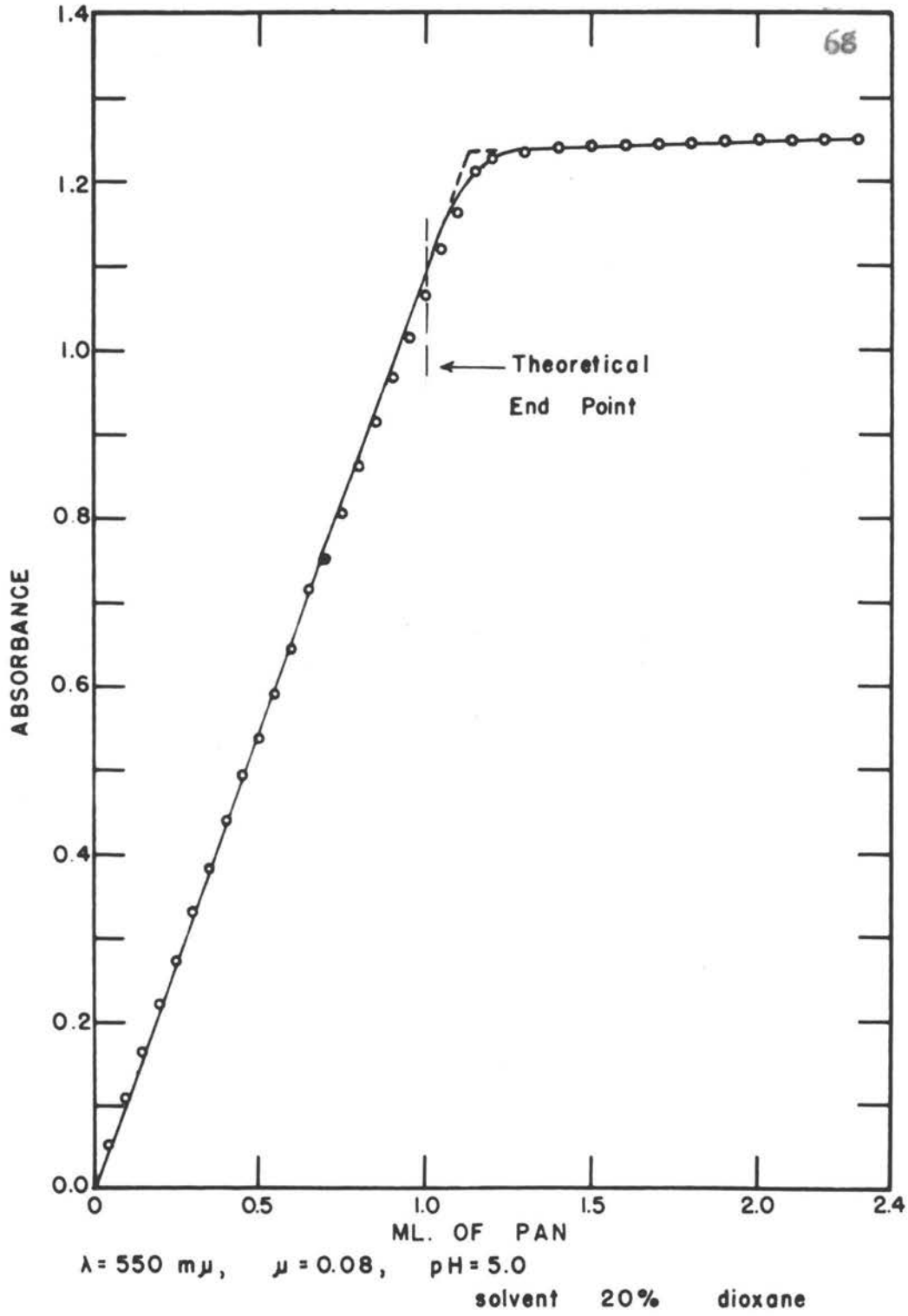


Figure 16. Spectrophometric Titration of Cu (II) with PAN (Standardization of PAN)

acid. The flasks were then diluted to the mark with 0.10 N potassium nitrate in order to maintain the ionic strength at 0.08. The absorbance and pH values were obtained, the data being summarized in Table 16 and Figure 17.

The absorbance values of dye alone, with no copper added, obtained in a like manner are also shown in Figure 17.

Discussion of Results

With respect to Figure 11 it is seen that at 550 mμ the copper chelate has a strong absorbance while that of the dye alone is very small. The free dye at this pH has its maximum absorbance at 470 mμ. Curve 1 is essentially the chelate curve since excess Cu (II) exists in solution and most of the dye is complexed.

The 550 mμ absorption peaks for curves 3, 4, and 5 are nearly the same since in these cases most of the copper is complexed with the excess dye and further addition of dye would form no additional chelate. The peaks of these curves are not identical, of course, because of the small contributions of the free dye. At 470 mμ for these latter curves, the absorbance increases markedly because of the increase in concentrations of free dye. From an examination of Figure 11, it seems

TABLE 16

VARIATION OF ABSORBANCE OF

COPPER CHELATE WITH pH

Solution	Ml. HNO_3	Absorbance	pH	K X 10^3
1	15.0	0.181	1.32	5.0
2	13.0	0.202	1.38	4.9
3	12.0	0.220	1.40	4.0
4	11.0	0.236	1.43	3.6
5	10.0	0.257	1.47	6.5
6	9.0	0.264	1.45	7.6
7	8.0	0.292	1.53	7.7
8	7.0	0.316	1.62	7.2
9	5.0	0.359	1.77	9.7
10	4.0	0.392	1.88	7.1
11	3.0	0.413	2.01	7.7
12	2.0	0.445	2.20	9.0
13	1.0	0.472	2.48	3.5
14	0.3	0.493	2.98	-
15	0.1[a]	0.497	3.64	-
16	0.2[a]	0.497	4.16	-

Total Cu^{++} = 2.62×10^{-5} Molar Mean 6.4×10^3

Total PAN = 2.11×10^{-5} Molar Avg. Dev. 1.7×10^3

HNO_3 = 0.10 Normal

a 0.10 Normal NaOH

$$K = \frac{[CuKE^+]\,[H^+]}{[Cu^{++}]\,HKE}$$

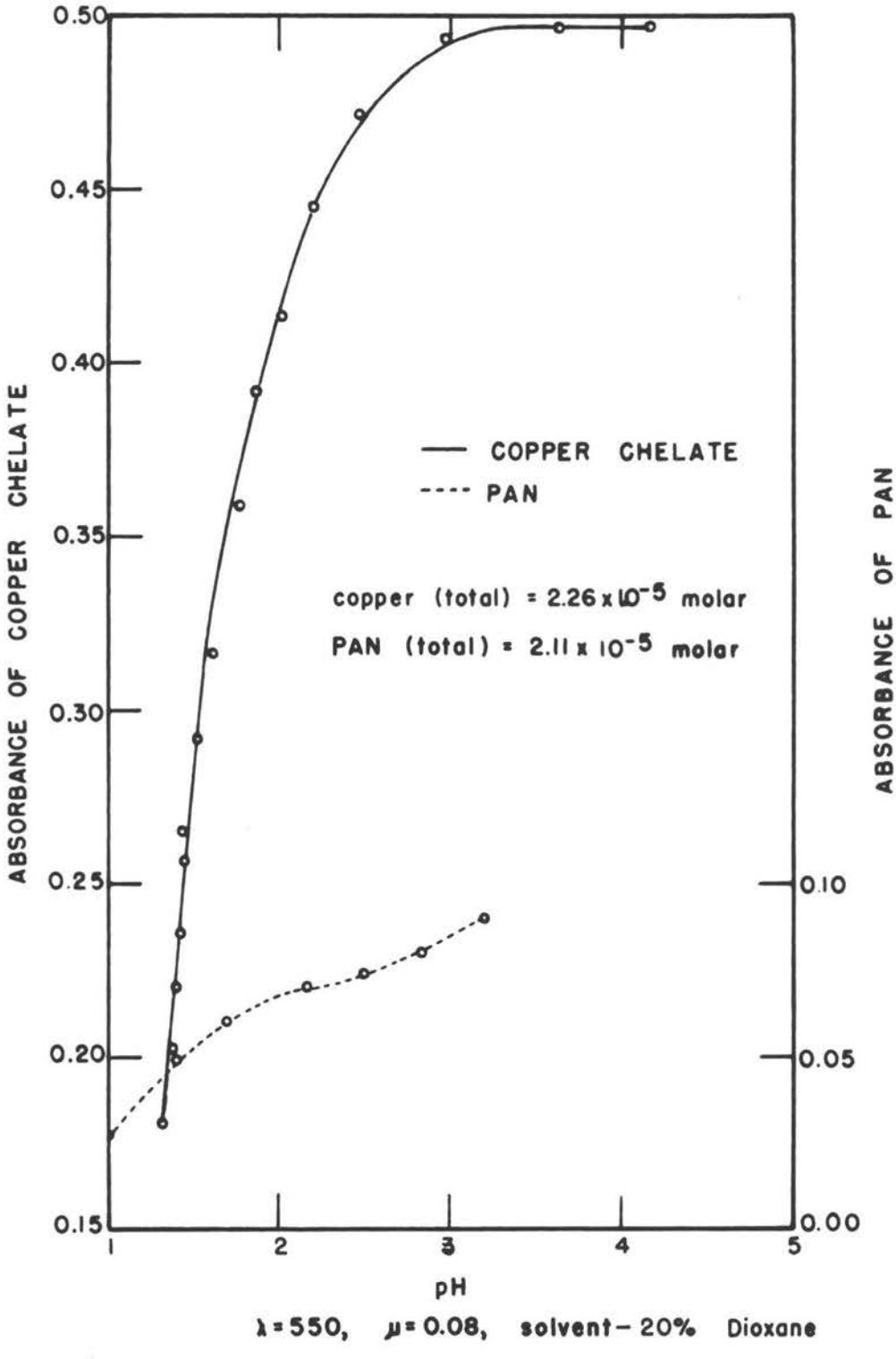


Figure 17. Variation of Absorbance of Copper Chelate and PAN with pH

likely that the Cu-PAN chelate forms in a 1 to 1 ratio.

This has been verified through Job's method of continuous variation in aqueous buffered solutions at pH of 3.0, (Figure 13 and Table 10), as well as at pH of 6.0 and 8.25 (Tables 11 and 12). In addition it was found that similar results were obtained by this method in 20% dioxane at a pH of 5.0 (Figure 12 and Table 9). The presence of a 1 to 1 copper chelate in the aqueous and dioxane solutions has been further verified by the spectrophotometric titrations which are summarized in Tables 13, 14 and 15 and Figures 14, 15 and 16.

Liu (18, p. 19) has also found that Cu (II) forms a 1 to 1 chelate with the dye in 95% alcohol.

Neither the PAN prepared in this laboratory nor that obtained commercially are pure. The spectrophotometric titration in 20% dioxane at pH 5.0 was chosen as a standardization procedure. The dye and the copper chelate are both soluble and stable in this solvent at this pH. Furthermore the hydrogen ion concentration is low enough so that the formation of the copper chelate is essentially complete.

$$HKE + Cu^{++} \rightleftharpoons CuKE^{+} + H^{+} \qquad (3)$$

That this is the case may be seen by examining Figure 16. The sharp rise in absorbance at 550 mμ in the spectrophotometric titration is due to the formation of the

highly colored copper chelate, while the sharp end point indicates that reaction 3 is predominately to the right. The slight rise in absorbance after the end point is due to the excess of dye being added. This also has a a very slight absorbance at 550 mμ.

If the dye were pure, the PAN concentration in the stock solution would be 1.50×10^{-3} molar and the end point of the titration would correspond to the addition of 1.00 ml. of dye. It is seen from the figure that the actual end point is reached when 1.14 ml. of dye is added. The purity of the dye therefore is 87.7%. All dye concentrations except for Job's method have been corrected on this basis. Similar results were obtained with the commerical sample of dye.

In order to calculate K_1 for reaction (3) it is necessary to obtain the concentrations of Cu^{++}, HKE, $CuKE^{+}$ and H^{+}.

With reference to Figure 17 and Table 16, all of the copper is present either as free Cu^{++} or $CuKE^{+}$. Therefore it may be said that

$$[Cu_{Total}] = [Cu^{++}] + [CuKE^{+}] \qquad (4)$$

Because pK_{a2} is approximately 12.2 and the experiments are being conducted at pH values below 4.2, it may be assumed that

$$[PAN_{Total}] = [CuKE^+] + [HKE] + [H_2KE^+] \qquad (5)$$

For solutions 15 and 16, Table 16, the absorbance is due almost entirely to the $CuKE^+$ species at a concentration of 2.11×10^{-5} molar. This absorbance of 0.497 was also obtained at a pH of 2.2, with the same concentration of dye as previously used and a thousand-fold excess of copper. The molar absorbancy index of the copper chelate calculated from this data is $2.4 \times 10^{+4}$.

Since the unchelated PAN, i.e. HKE and H_2KE^+, also make a slight contribution to the total absorbance at 550 mμ, the absorbances of a series of dye solutions has also been determined at various pH values and are plotted in Figure 17.

Using the known absorbance of the copper chelate and the absorbance of the dye alone, the contribution of the chelate and of the free dye to the total absorbance may be calculated. From this may be calculated the $[CuKE^+]$ and also the sum of $[H_2KE^+]$ and $[HKE]$.

Using equations (4) and (5) and the known Ka_1 from equation (1), K_1 for reaction (3) may be computed. The results are summarized in Table 16. The mean value of 13 determinations for K_1 is 6.4×10^3 with an average

deviation of 1.7×10^{3}.

The stability constant, K_2, for the reaction

$$Cu^{+} + KE^{-} \rightleftarrows CuKE \qquad (6)$$

is represented by the expression

$$K_2 = \frac{[CuKE^{+}]}{[Cu^{++}][KE^{-}]}$$

and may be obtained by dividing K_1 by Ka_2. Because of the uncertainty in the determination of Ka_2 only an approximate value for K_2 of 10^{16} has been obtained. This indicates that the copper chelate is very stable, but not as stable as the comparable copper-versene complex which has a stability constant 2.0×10^{18} (19, p. 538). This is one reason that the Cu-PAN indicator may be successfully used in complexometric titrations of metals with versene (8, 9, pp. 782-784; 10, 11, 12 and 13).

CHAPTER V

PROPERTIES OF THE Ni (II)-PAN CHELATE

Upon the addition of Ni (II) to a solution of PAN in 20% dioxane the light yellow color of the dye slowly changes to red due to the formation of the nickel-PAN chelate. It was felt that perhaps the experimental methods employed in the study of the copper compound could also be used with the nickel chelate.

Reagents and Equipment

Standard Ni (II) solution.

Baker's analyzed $Ni(NO_3)_2$ was used to prepare a 0.10 molar Ni (II) solution. This in turn was diluted to form a 1.53×10^{-3} molar solution. Another dilution was made to give a 2.63×10^{-4} molar standard nickel solution. The two weaker solutions were standardized with KCN by the procedure of Soine and Freund (24).

Standard dye solutions.

Dye solutions of 1.26×10^{-3} and 2.63×10^{-4} molar were prepared and standardized with Cu (II) in 20% dioxane by the previously described procedure.

Procedure

Determination of the absorption spectra.

Curves 1 to 4 of Figure 18 were obtained from a

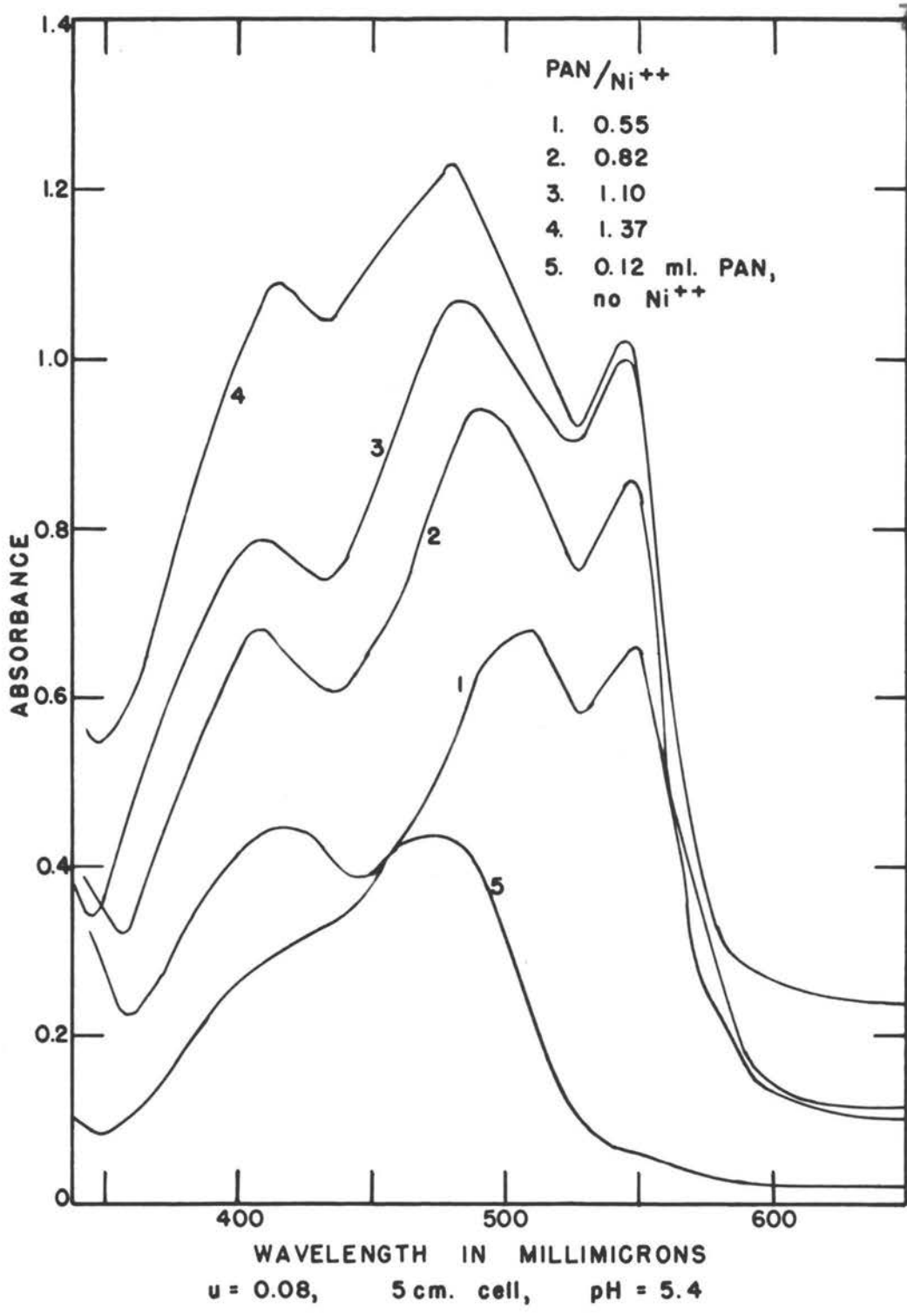


Figure 18. Absorption Spectra of Nickel Chelate in 20% Dioxane

series of solutions containing nickel and dye. For each of these curves, 5.00 ml. of dioxane, 0.30 ml. of the 1.53×10^{-3} molar nickel solution and 0.20, 0.30, 0.40 or 0.50 ml. of 1.26×10^{-3} molar stock dye solution were mixed. Sufficient volume of the sodium formate buffer solutions were used to bring the total volume to 25.00 ml. The measured pH of the resulting solutions was 5.4 and the ionic strength was 0.08. After allowing the solutions to stand for 25 minutes after mixing the absorption spectra were obtained with the Beckman DK-2 Recording spectrophotometer and 5 cm. cells. The reference solution contained the buffer, dioxane, and nickel.

Curve 5 is the absorption spectra of a solution prepared in the same manner but containing 0.12 ml. of dye and no nickel. This was obtained for comparison purposes.

Variation of absorbance of nickel chelate with time.

To a 25 ml. volumetric flask was added 5 ml. of the dioxane, 0.48 ml. and 0.42 ml. of the 2.63×10^{-4} molar nickel and dye solutions respectively. The flasks were then diluted to volume with the sodium formate buffer and the absorbance values obtained on the Beckman Model B Spectrophotometer with 5 cm. cells, the reference

solution being the buffer, nickel, and dioxane. The results are given in Table 17.

Determination of molar absorbancy index of the nickel chelate.

To each of three 100 ml. volumetric flasks was added 20 ml. of dioxane followed by 0.10, 0.20 and 0.30 ml. of 2.63×10^{-4} molar dye respectively, and 1 ml. of 0.1 N $Ni(NO_3)2$. The solutions were then diluted to volume with the sodium formate buffer and the absorbances were obtained in 5 minutes on the Model B with 5 cm. cells.

The three values, 0.140, 0.282 and 0.419, corresponding to 1.26×10^{-6}, 2.52×10^{-6} and 3.78×10^{-6} molar nickel chelate concentrations were used to calculate the molar absorbancy index for the nickel chelate. The average value, based upon a 1-1 nickel-PAN chelate and the above dye concentrations was found to be 2.2×10^{4}.

4) Job's method of continuous variation.

To each of a series of 25 ml. volumetric flasks was added 5.00 ml. of dioxane and varying amounts of 2.63×10^{-4} molar dye and nickel solutions, at all times maintaining the sum of the dye and nickel concentrations constant. The resulting absorbance values were obtained with 5 cm. cells.

TABLE 17

VARIATION OF ABSORBANCE OF NICKEL CHELATE WITH TIME

Time in minutes	Absorbance at 550 mμ
9	0.209
11	0.229
19	0.295
20	0.296
24	0.310
30	0.312
35	0.312
40	0.310
44	0.295

Since the absorbance changes with time, it was read every three minutes. The maximum absorbances obtained are shown in Table 18 and after being corrected for the line of no reaction are plotted in Figure 19 against the molar ratio of

$$\frac{Ni^{++}}{Ni^{++} + PAN.}$$

Determination of the dissociation constant of the nickel chelate.

To a series of four 100 ml. volumetric flasks was added 0.30 of the 1.53×10^{-3} molar nickel nitrate, 0.30 ml. of previously standardized 1.26×10^{-3} molar dye solutions, 20 ml. of dioxane and varying amounts of a solution which was 0.2 M HNO_3 and 0.1 M KNO_3. The solutions were then diluted to volume with the sodium formate buffer. The ionic strength was maintained at 0.08. The maximum absorbance values obtained and pH readings are shown in Table 19 along with the calculated values for the dissociation constant of the nickel chelate.

To another series of four 100 ml. volumetric flasks was added the 20 ml. of dioxane and varying amounts of the same nickel and dye solutions. These were also diluted to volume with the sodium formate buffer maintaining the pH and the ionic strength constant at

TABLE 18

ABSORBANCE VS. Ni(II) AND PAN VARIATION

IN 20% DIOXANE, pH = 5.5

Solution	ml.Ni(II)	ml.PAN	A	$\bar{A}$	$\frac{Ni^{++}}{Ni^{++} + PAN}$
1	0.00	0.90	0.124	0.000	0.000
2	0.06	0.84	0.184	0.070	0.066
3	0.12	0.78	0.244	0.167	0.133
4	0.18	0.72	0.290	0.190	0.200
5	0.24	0.66	0.310	0.220	0.266
6	0.30	0.60	0.309	0.227	0.333
7	0.36	0.54	0.309	0.235	0.400
8	0.42	0.48	0.304	0.238	0.467
9	0.48	0.42	0.290	0.232	0.533
10	0.54	0.36	0.271	0.220	0.600
11	0.60	0.30	0.232	0.187	0.667
12	0.66	0.24	0.215	0.182	0.733
13	0.72	0.18	0.163	0.137	0.800
14	0.78	0.12	0.131	0.112	0.867
15	0.84	0.06	0.048	0.035	0.933
16	0.90	0.00	0.000	0.00	1.000

PAN = 2.63×10^{-4} molar before dilution

λ = 550 mμ

Ni^{++} = 2.63×10^{-4} molar before dilution 5 cm. cell

ionic strength = 0.08

total volume = 25 ml.

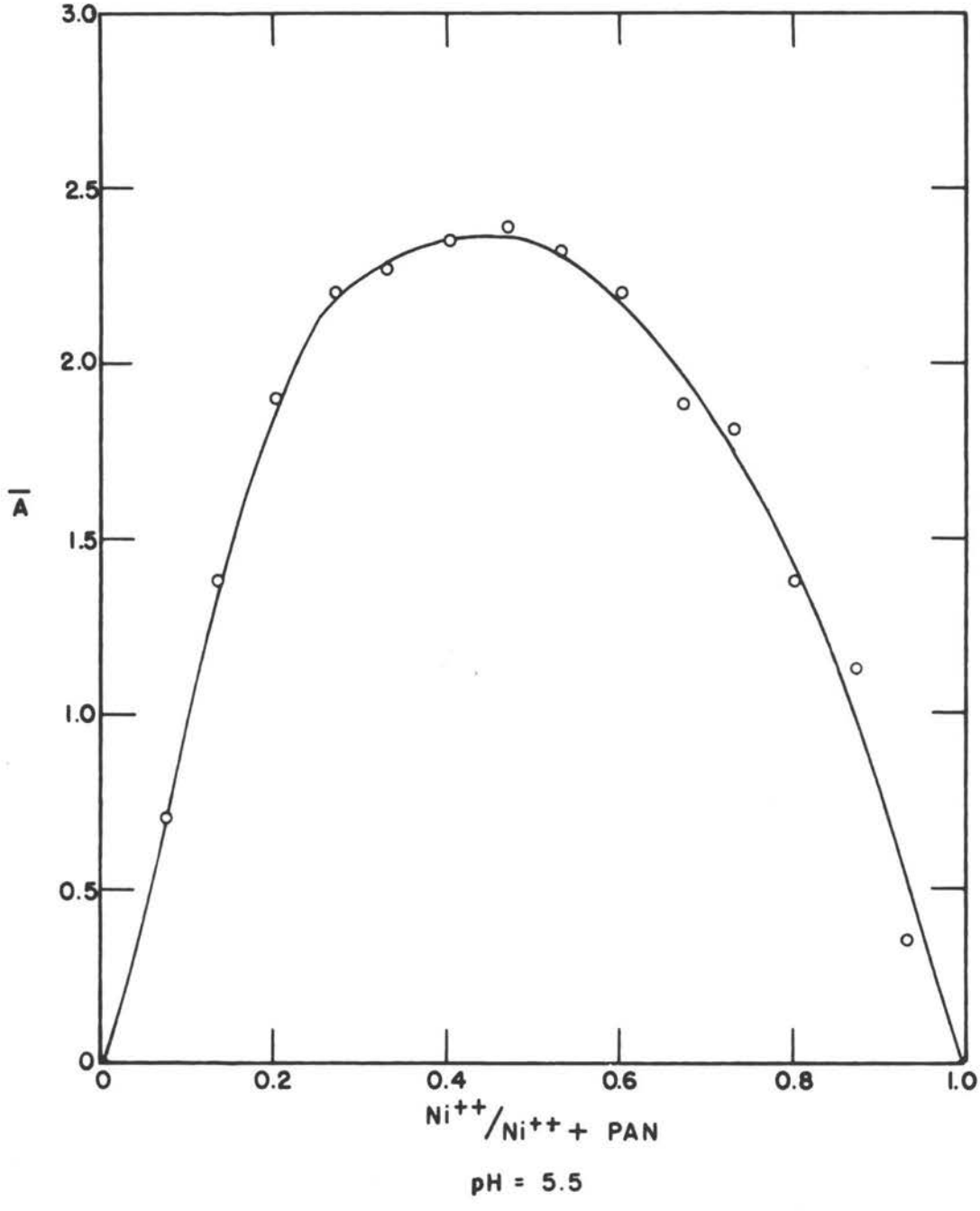


Figure 19. Absorbance Vs. Variation of Ni (II) and PAN in 20 % Dioxane

TABLE 19

VARIATION OF ABSORBANCE OF

NICKEL-PAN SOLUTIONS

Solution No.	pH	Absorbance at 550 mμ	ml. PAN	ml. Ni(II)	K
1	5.40	0.245	0.30	0.30	1.28
2	5.18	0.234	0.30	0.30	1.98
3	5.06	0.223	0.30	0.30	2.05
4	4.94	0.217	0.30	0.30	2.48
5	5.39	0.255	0.31	0.40	0.91
6	5.38	0.276	0.30	0.50	1.00
7	5.39	0.243	0.30	0.30	1.00
8	5.38	0.294	0.30	0.60	1.00

Total volume = 100 ml.

Ni^{++} = 1.53 x 10^{-3} molar before dilution

PAN = 1.29 x 10^{-3} molar before dilution

$$K = \frac{[NiKE^{+}]\,[H^{+}]}{[Ni^{++}]\,[HKE]}$$

5.39 and 0.08 respectively. These results are also summarized in Table 19.

Discussion of Results

Since the nickel is in excess and most of the dye is complexed, Curve 1 of Figure 18 is essentially that of the nickel chelate. This chelate has strong absorption bands at 410, 510 and 550 mμ.

Solutions 1, 2, and 3 show an increase in absorbance because the amount of dye added is increased followed by a subsequent increase in nickel chelate concentration. However, with respect to solutions 3 and 4 there is only a slight difference in absorbance at 550 mμ. There is a strong increase at both 410 and 510 mμ because the free dye has an appreciable absorbance at both of these wavelengths. An examination of Figure 18 seems to indicate that nickel and PAN combines in a 1-1 ratio.

Job's method of continuous variation shown in Figure 19 and Table 18 verifies the formation of a 1 to 1 nickel-PAN chelate. The fact that this curve is rounded at the top, instead of being a sharp peak, indicates considerable dissociation of the nickel complex at pH 5.5. It should be pointed out that Liu (18, p. 21) found the nickel-PAN ratio in 95% alcohol to be

0.31 to 0.69. She has also found that a 1-1 nickel-PAN ratio existed when the solid nitrate complex was precipitated. The possibility of a 1-2 complex or even a mixture of 1-1 and 1-2 complexes cannot be dismissed.

Although the nickel compound requires a higher pH for formation than does the corresponding copper chelate, it was felt that perhaps the constant for equation 7 might be determined by the same procedure

$$Ni^{++} + HKE \rightleftarrows NiKE^{+} + H^{+} \qquad (7)$$

as previously used. When the dye and nickel are in approximately equal molar amounts the chelate will not form to any extent below pH 4.5. On the other hand it is very desirable to perform the work below pH 8 until more is understood about the dye in this region.

It is interesting to note in Table 19 that the values obtained for equation 7 are constant, within experimental error, with constant pH but with a variation of nickel and dye concentrations. On the other hand those obtained at constant dye and nickel concentrations but varying pH show an increase in K with a decrease in pH. Further work must be performed before any definite conclusions can be made regarding the composition of the nickel chelate or the equilibrium constant for equation 7.

CHAPTER VI

COLORIMETRIC PALLADIUM

Cheng and Bray (9, p. 782) observed that all of the common metal ions, with the exception of Pd (II) and Co (III) form a red complex with PAN, these two being green. Since they also found that rhodium, iridium and osmium gave no detectable precipitate or coloration upon the addition of PAN it was felt by the author that perhaps a colorimetric procedure for Pd (II), in the presence of the other Group (VIII) precious metals could be developed.

Reagents and Equipment

Standard metal solutions.

Dry $PdCl_2$ (0.416 g.) obtained from Fisher Scientific Company was dissolved in 12 N HCl and brought to volume in a 250 ml. flask to give a Pd (II) solution which was 9.35×10^{-3} molar (1000 γ/ml.) in Pd (II).

$RuCl_3$, $RhCl_2$ (dry) and $IrCl_3$ were all obtained from Fisher Scientific Company. Solutions containing 1000 γ/ml. of Ru (III), Rh (II), and Ir(III) were prepared by placing 103.0 mg., 102.5 mg. and 73.0 mg. of the respective chlorides in 50 ml. volumetric flasks and diluting to volume with water. A solution containing 1000 γ/ml. of Os (III) was prepared by dissolving 150.9 mg.

of potassium osmium chloride, $2(OsCl_3 \cdot 3KCl) \cdot 6H_2O$, in 50 ml. of water. This solid reagent was obtained from the American Platinum Works, Newark, New Jersey.

A 5% platinum chloride solution, $PtCl_4$, was obtained from the General Chemical Company, New York, New York. This solution was diluted 1-10 to yield a solution which was 2.9×10^{-3} γ/ ml. in Pt (IV).

0.1% dye solution.

The 0.1% dye in methanol solution was prepared from the author's dye and redistilled methanol.

Solvents.

All of the extracting solvents of Table 20 were commercial grade and were used without further purification.

Spectrophotometer.

The Beckman Model D-U Spectrophotometer was used for all of the experiments in this chapter. Matched 1 cm. silica cells were used below 320 mμ and matched 1 cm. Pyrex cells in the visible region.

Procedure

Choice of extracting solvent.

It is necessary in choosing an organic extracting solvent to consider the solubility of the dye and chelate in it as well as the resulting molar absorbancy index

of the chelate. In order to obtain some qualitative data the following preliminary experiment was performed.

To each of ten 6 inch test tubes was added 10 ml. of H_2O, 0.14 ml. of the stock palladium solution (5.6 γ of Pd) and 1 ml. of the 0.1% dye in methanol solution. The solutions in the tubes were then mixed and allowed to stand for 1 hour. To each was added 10 ml. of one of the more common organic extracting solvents. The test tubes were shaken vigorously, allowed to stand 15 minutes, and the relative depth of colors and solubilities in the aqueous as well as organic layers was observed. The results are summarized in Table 20.

Of the ten solvents used, chloroform was chosen for future experiments. It not only exhibited the deepest green color in the organic phase but the resulting aqueous phase was colorless. In addition it was found that the chelate was more soluble in chloroform than in any of the other solvents.

Absorption spectra of palladium chelate and PAN.

Three solutions were prepared as follows. To one 60 ml. separatory funnel was added 10 ml. of H_2O and 0.20 ml. of the 1000 γ/ ml. Pd (II) solution. After mixing the above reagents, 0.15 ml. of the 0.1% dye solution was added. The funnel was shaken, heated at 80 ± 2°C. for 10 minutes and extracted with two 10 ml.

TABLE 20

CHOICE OF EXTRACTING SOLVENT FOR

PALLADIUM CHELATE

Solvent	color of [a] aqueous phase	color of [a] organic phase	Amount of [b] ppt.present
xylene	2	8	2
benzene	3	9	3
carbon tetrachloride	6	4	6
chloroform	1	10	1
isoamyl alcohol	7	5	7
diethyl ether	4	7	4
cyclohexane	8	2	8
methylcyclohexane	9	1	9
toluene	5	6	5
n-amyl acetate	10	3	10

a. The depth of the green color was estimated and scaled 1-10, 1 being the lightest green and 10 the darkest.

b. 1 corresponds to the least amount of precipitate or scum at the interface; 10 corresponds to the most.

portions of chloroform. The chloroform extract was run into a 25 ml. volumetric flask and enough chloroform was added to bring the solution in the flask to volume. To the flask was added 0.3 grams of anhydrous Na_2SO_4 for drying and the absorption spectrum was obtained against a chloroform blank. The measured pH of the aqueous phase was 0.8.

An absorption spectrum of the dye solution at the same pH was obtained in a like manner. The same procedure was used except 0.20 ml. of 12 N HCl was substituted for the 0.20 ml. of palladium solution.

The absorption spectrum of the dye solution at pH 10.1 was obtained in a like manner. In this case 10 ml. of 0.1 N NaOH was used instead of water, 0.15 ml. of the dye solution and no HCl or palladium solutions were added. All of the obtained absorption spectra and data are shown in Figure 20 and Table 21.

No absorption curve for the palladium chelate in basic solution has been obtained but it was observed that the chelate does form in basic solution and is also green in the chloroform extract.

Order of addition of reagents.

To a 60 ml. separatory funnel was added 10 ml. of H_2O and 0.10 ml. of the stock Pd (II) solution. These were mixed thoroughly and followed immediately with

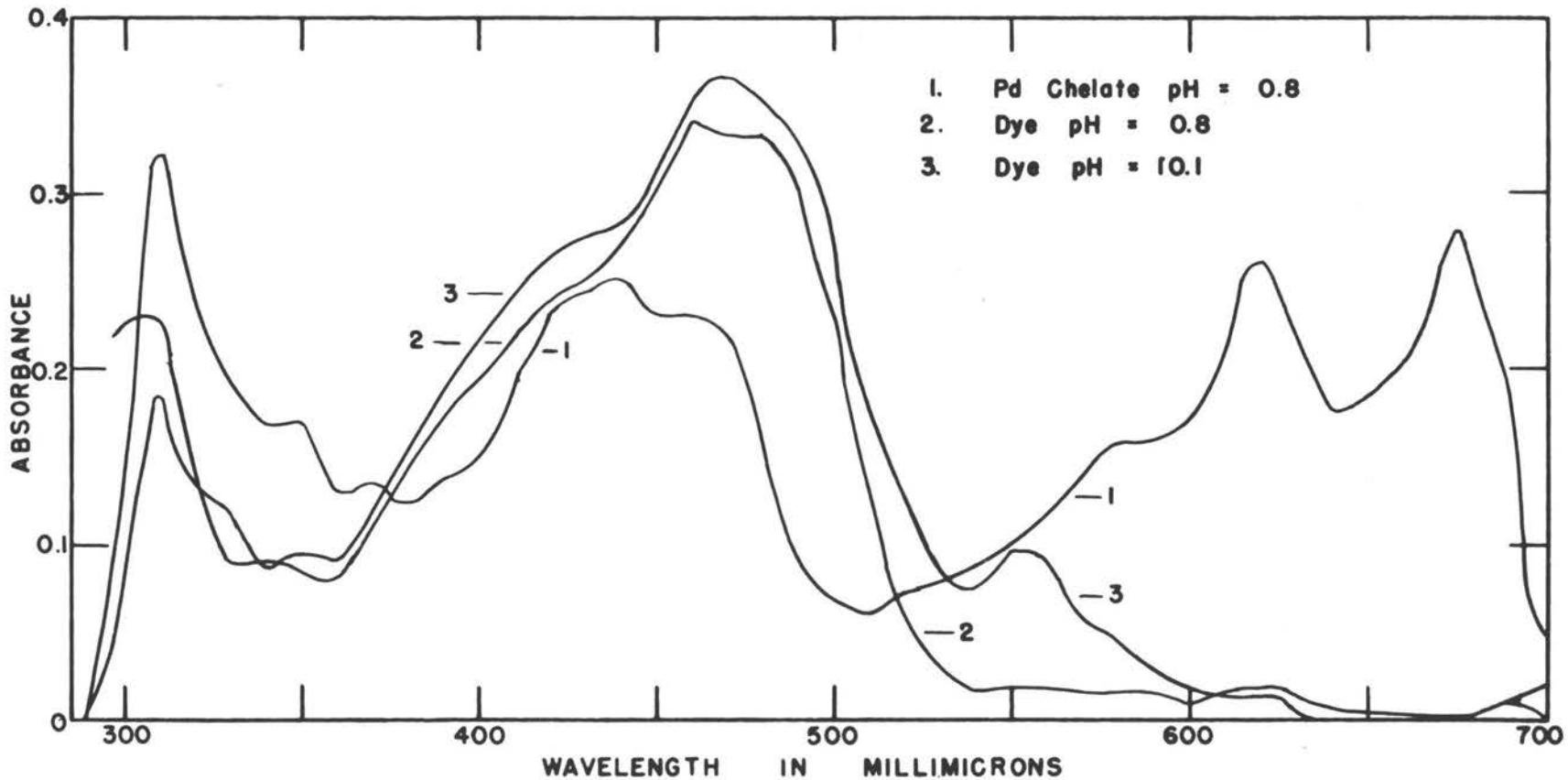


Figure 20. Absorption Spectra of Palladium Chelate and PAN in $CHCl_3$

TABLE 21

ABSORPTION SPECTRA OF PALLADIUM CHELATE AND PAN

Wavelength in mμ	Slit in mm	A #1	A #2	A #3
720	0.045	0.012	0.010	0.000
710	0.046	0.020	0.012	0.000
700	--	0.052	0.012	0.022
690	0.047	0.068	0.003	0.010
680	--	0.242	0.007	0.003
675	--	0.270	0.004	0.002
670	0.053	0.262	0.003	0.007
660	--	0.203	0.004	0.004
650	--	0.186	0.007	0.007
640	0.065	0.179	0.006	0.008
630	--	0.217	0.011	0.007
625	--	0.243	0.014	0.007
620	0.075	0.260	0.021	0.015
615	--	0.252	0.020	0.027
610	--	0.213	0.017	0.015
600	0.087	0.174	0.013	0.017
590	0.030	0.160	0.017	0.028
580	"	0.157	0.016	0.045
570	"	0.137	0.017	0.053
560	"	0.117	0.020	0.092
550	"	0.103	0.023	0.097
540	"	0.087	0.018	0.077
530	"	0.077	0.032	0.082
520	"	0.075	0.056	0.128
510	"	0.062	0.127	0.182
500	"	0.070	0.227	0.276
490	"	0.092	0.298	0.332
480	"	0.153	0.333	0.353
470	"	0.221	0.333	0.367
460	"	0.232	0.342	0.355
450	"	0.232	0.307	0.312
440	"	0.253	0.277	0.282
430	"	0.243	0.253	0.275
420	"	0.234	0.238	0.263
410	0.038	0.196	0.218	0.243
400	--	0.152	0.196	0.218
390	0.088	0.138	0.173	0.191

TABLE 21 (continued)

ABSORPTION SPECTRA OF PALLADIUM CHELATE AND PAN

Wavelength in mμ	Slit in mm	A #1	A #2	A #3
380	--	0.124	0.147	0.151
370	--	0.135	0.111	0.118
360	0.12	0.128	0.082	0.090
350	0.10	0.173	0.083	0.098
340	0.17	0.173	0.090	0.087
330	0.22	0.193	0.090	0.117
320	0.42	0.242	0.144	0.137
310	0.52	0.323	0.227	0.185
305	--	0.232	0.227	0.143
302	--	0.173	0.227	0.117
300	0.74	0.132	0.227	0.087
290	1.4	0.000	0.220	0.000

1 Palladium chelate at pH = 0.8

2 PAN at pH = 0.8

3 PAN at pH = 10.1

All absorption spectra are for chloroform extracts.

5 ml. of the 0.1% PAN solution. The chelate was extracted in 5 min. with two 10 ml. portions of $CHCl_3$ and the extracts were combined in a 25 ml. volumetric flask. The solution was then diluted to the mark with $CHCl_3$. Anhydrous Na_2SO_4 (0.3 g.) was added, the solutions were mixed thoroughly and the absorbances were obtained.

Another sample of the palladium chelate was obtained in exactly the same manner except that the dye was added before the palladium. The third procedure was the same as the first two except that the order of addition was H_2O, Pd, $CHCl_3$, and the dye. A blank was prepared by adding to a 60 ml. separatory funnel, 10 ml. of H_2O, 0.10 ml. of 12 N HCl, 5 ml. of the 0.1% PAN solution, the rest of the procedure being the same as in the preceding experiment.

The absorbance readings obtained at 675 mμ when the order of addition was H_2O, Pd, PAN, $CHCl_3$ was 0.455. When the order of addition was H_2O, PAN, Pd, $CHCl_3$ an absorbance of 0.226 was obtained and when the order was H_2O, Pd, $CHCl_3$, PAN the absorbance was 0.125.

It is not surprising that a very low absorbance value was obtained when the order of addition was H_2O, Pd, $CHCl_3$ and PAN. Both PAN and the metal chelate are soluble in chloroform. The PAN was extracted by the chloroform before it had reacted with Pd to form

the chelate. The author has no reason for the higher absorbance value which was obtained when the order of addition was H_2O, Pd, PAN, $CHCl_3$ in contrast to H_2O, PAN, Pd and $CHCl_3$.

In the following work, the order of addition was H_2O, Pd, PAN and $CHCl_3$

Choice of extraction procedures.

In order to find out if there was any practical advantage to be gained from using two 10 ml. portions of the extracting solvent in contrast to one 20 ml. or one 15 ml. portion, the following three procedures were run.

Ten ml. of H_2O, 0.18 ml. of the standard palladium solution and 0.02 ml. of concentrated HCl were added to each of three 60 ml. separatory funnels and thoroughly mixed. Exactly 5.0 ml. of the 0.1% PAN solution was added to these three funnels plus a fourth containing everything except the palladium. After thorough mixing they were all allowed to stand for exactly 1 hour. The solution in the first funnel was extracted with two 10 ml. portions of $CHCl_3$, that in the second with one 15 ml. portion and the one in the third with one 20 ml. portion. The total shaking time, using a mechanical shaker, was in all cases 6 minutes. In the first case, each of the 10 ml. extractions were shaken for 3 minutes

whereas the one 15 and one 20 ml. portions were shaken for 6 minutes each. The chloroform extracts in all three funnels, in addition to the blank, were brought to volume with the solvent in a 25 ml. volumetric flask and dried with 0.3 g. anhydrous Na_2SO_4. Upon reading the absorbance against the blank at 620 mμ, it was found that the two 10 ml. $CHCl_3$, one 15 ml. $CHCl_3$ and one 20 ml. $CHCl_3$ procedure yielded absorbance values of 0.858, 0.800, and 0.842 respectively.

To each of the remaining aqueous solutions was added 20 ml. of chloroform. These were shaken vigorously for 3 minutes, separated, brought to volume in 25 ml. flasks, dried with anhydrous Na_2SO_4 and the absorbance values at 620 mμ were obtained. The same blank as that used in the preceding part was also used here. It was found that there was the least amount of chelate remaining in the solution which had been extracted with the two 10 ml. portions, in fact, no absorbance could be measured. On the other hand, there was enough palladium chelate remaining in those solutions which had been extracted with one 15 ml. and one 20 ml. portions to yield absorbances of 0.010 and 0.008 respectively.

The first procedure, i.e. extraction with two-10 ml. portions, was chosen for all of the following work.

Effect of shaking an extraction.

The following procedures were run as a means of determining the minimum shaking time required.

To each of four 60 ml. separatory funnels was added 10 ml. of H_2O, 0.10 ml. of stock Pd solution and 0.10 ml. of concentrated HCl. The resulting solutions were shaken vigorously for a few seconds and then to each was added one 5 ml. portion of the 0.1% PAN. Again the solutions were shaken vigorously and 10 ml. $CHCl_3$ portions were added after they were allowed to stand for one hour. The first funnel was shaken vigorously by hand for 30 seconds. The second, third and fourth were placed on the mechanical shaker and shaken for 5, 10, and 15 minutes respectively. The above extraction process was repeated. These extracts were combined with the original 10 ml. portions from the same funnels, brought to volume in 25 ml. volumetric flasks, dried with anhydrous Na_2SO_4 and read against a blank dye extraction at 675 mμ. The first, second, third and fourth procedures yielded absorbances of 0.532, 0.530, 0.531 and 0.529 respectively.

Since there was obviously no advantage to be gained from using either the mechanical shaker or long extraction times these were dispensed with.

TABLE 22

CALIBRATION DATA FOR Pd(II) DETERMINATION

(EFFECT OF STANDING)

$\frac{\gamma \text{ Pd}}{\text{ml. } CHCl_3}$	ml. Pd (1000 /ml.) added	Pd added	A 620 mμ	a 620 mμ
0.8	0.02	20	0.102	127
1.6	0.04	40	0.195	122
2.4	0.06	60	0.297	124
3.2	0.08	80	0.394	123
4.0	0.10	100	0.472	118
4.8	0.12	120	0.566	118
5.6	0.14	140	0.655	117
6.4	0.16	160	0.740	115
7.2	0.18	180	0.826	115

$$a = \frac{A}{c\ b}$$

All solutions were allowed to stand for 1 hour before extraction.

Calibration curve for Pd (II) determination.

A calibration curve was prepared by transferring 20, 40, 60, 80, 100, 120, 140, 160 and 180 γ samples of Pd to 60 ml. separatory funnels containing 10 ml. of H_2O. To each funnel was then added enough concentrated HCl to bring the total volume of HCl plus palladium solution to 0.20 ml. These solutions were thoroughly mixed and to each was added 5 ml. of 0.1% PAN in methanol. They were again thoroughly mixed, allowed to stand for 1 hour, and extracted with two 10 ml. portions of $CHCl_3$. The extracts were brought to volume in 25 ml. flasks, dried with Na_2SO_4, and read against the blank at 620 mμ. The results are summarized in Table 22. The absorbancy indices have also been calculated and are shown in this table.

The calibration curve for determination of Pd was prepared in almost the same manner as the preceding. The only exception was that all of the solutions were heated at 80 ± 2° C. for 10 minutes, cooled and extracted with chloroform instead of being allowed to stand for 1 hour at room temperature. These results are summarized in Table 23. The average results of the two 80° runs at both 620 and 675 mμ are shown in Figure 21.

TABLE 23

CALIBRATION DATA FOR Pd(II) DETERMINATION

(EFFECT OF HEAT)

γ Pd / ml. $CHCl_3$	A Run #1	a Run #1	A Run #2	a Run #2
0.8	0.105	131	0.102	127
1.6	0.195	122	0.190	119
2.4	0.293	122	0.288	120
3.2	0.396	124	0.397	124
4.0	0.474	119	0.484	121
4.8	0.595	124	0.590	123
5.6	0.673	120	0.665	119
6.4	0.765	120	0.775	121
7.2	0.862	120	0.850	119

a = 122

λ = 620 mμ

All solutions were heated for 10 min. at 80°C before extraction.

TABLE 23 (continued)

CALIBRATION DATA FOR Pd(II) DETERMINATION

(EFFECT OF HEAT)

γ Pd / ml. $CHCl_3$	A Run #1	a Run #1	A Run #2	a Run #2
0.8	0.108	135	0.113	141
1.6	0.216	135	0.224	140
2.4	0.320	133	0.323	134
3.2	0.432	135	0.438	137
4.0	0.530	132	0.540	135
4.8	0.659	137	0.645	134
5.6	0.755	135	0.762	136
6.4	0.850	133	0.833	130
7.2	0.975	135	0.948	132

$a = 135$

$\lambda = 675$ mμ

All solutions were heated for 10 min. at 80°C before extraction.

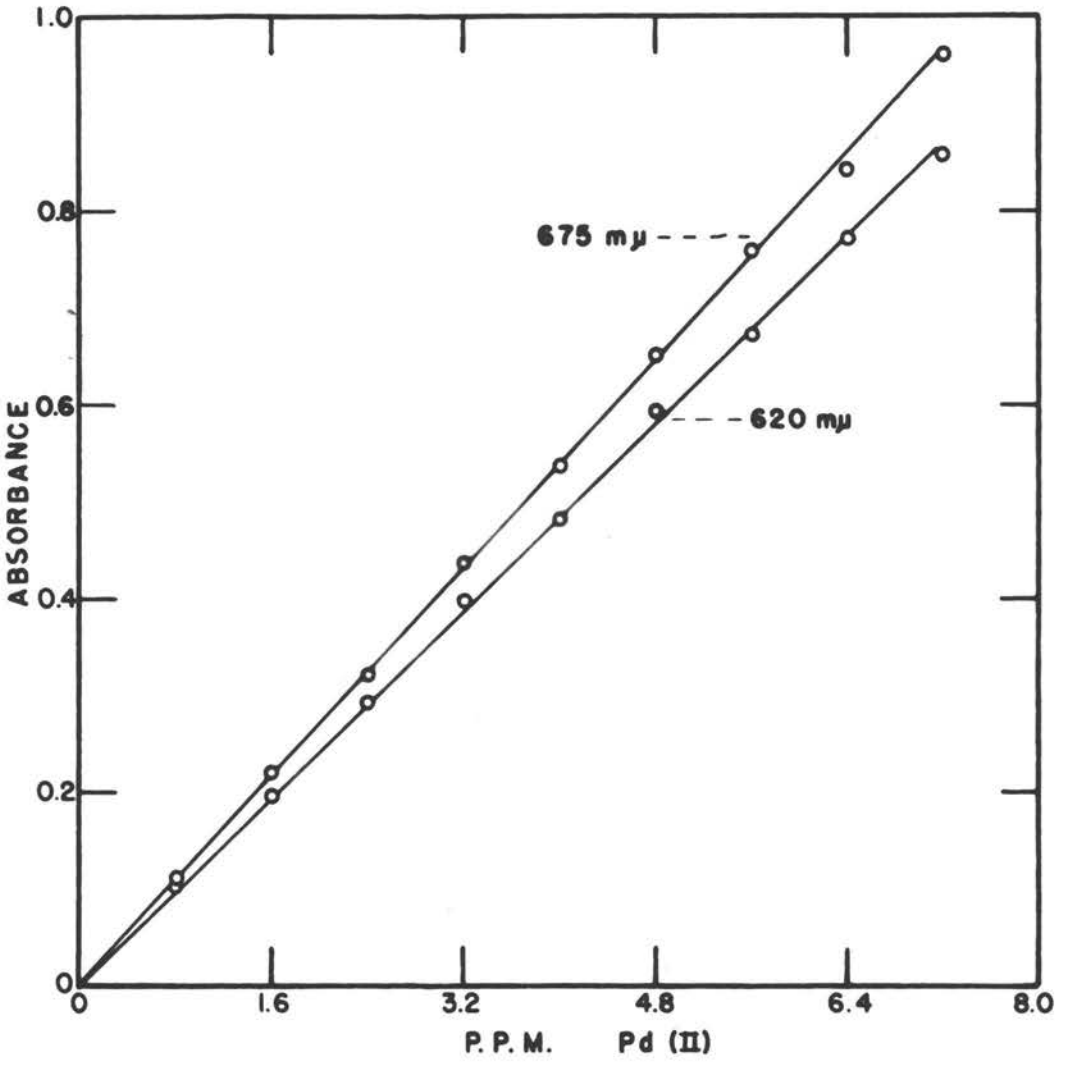


Figure 21. Palladium Calibration Curve

The aqueous layer of the heated solutions of both the palladium chelate and dye blank was a light yellow color. This color could not be extracted with chloroform. The possibility of this being due to methanol was eliminated by running a methanol and HCl solution with no Pd (II) or dye. It was found that the aqueous and organic layers were clear and colorless.

Interfering ions.

The following procedure was used to determine the effect of other Group VIII precious metals on the palladium chelate absorbances.

To 60 ml. separatory funnels was added 10 ml. of H_2O, 0.10 ml. of the stock Pd (II) solution, 0.10 ml. of 12 N HCl and various volumes of the previously described interfering ion solutions which contained 1000 γ/ ml. of Os (III), Ru (III), Rh (II), or Ir (III). The Pt (IV) solution used contained 2,896 γ/ ml. The separatory funnels were shaken vigorously and to each was added 5 ml. of the 0.1% PAN in methanol solution. After thorough mixing they were heated at 80 ± 2°C. for 10 min., cooled and extracted with two 10 ml. portions of chloroform. The chloroform extracts were combined, diluted to volume in a 25 ml. flask, dried, and the absorbances obtained at 620 and 675 mμ. The

TABLE 24

EFFECT OF GROUP VIII IONS

ml. of interfering ion solutions		Os(III)	Ru(III)	Rh(II)	Ir(III)	Pt(IV)
0.10	A_{620}	0.488	0.491	0.478	0.481	0.478
	a_{620}	122	122	120	120	120
	A_{675}	0.531	0.533	0.532	0.532	0.533
	a_{675}	133	133	133	133	133
0.20	A_{620}	0.507	0.522	0.478	0.476	0.488
	a_{620}	127	130	120	119	122
	A_{675}	0.568	0.565	0.538	0.532	0.534
	a_{675}	142	141	134	133	133
0.30	A_{620}	0.517	0.523	0.478	0.449	0.493
	a_{620}	129	130	120	112	123
	A_{675}	0.562	0.548	0.533	0.503	0.554
	a_{675}	140	137	133	126	138
0.40	A_{620}	0.529	0.558	-	0.490	-
	a_{620}	132	139	-	122	-
	A_{675}	0.570	0.567	-	0.535	-
	a_{675}	142	142	-	134	-
0.50	A_{620}	-	0.564	0.496	-	0.495
	a_{620}	-	141	124	-	124
	A_{675}	-	0.558	0.536	-	0.552
	a_{675}	-	139	134	-	138
0.70	A_{620}	-	-	-	-	0.495
	a_{620}	-	-	-	-	124
	A_{675}	-	-	-	-	0.535
	a_{675}	-	-	-	-	134

TABLE 24 (continued)

EFFECT OF GROUP VIII IONS

ml. of interfering ion solutions		Rh(II)	Ir(III)	Pt(IV)
0.80	A_{620}	0.488	-	-
	a_{620}	122	-	-
	A_{675}	0.536	-	-
	a_{675}	134	-	-
1.00	A_{620}	0.492	0.493	-
	a_{620}	123	123	-
	A_{675}	0.533	0.542	-
	a_{675}	133	137	-
2.00	A_{620}	0.527	0.480	0.495
	a_{620}	131	120	124
	A_{675}	0.571	0.538	0.535
	a_{675}	143	135	134
20.00	A_{620}	-	-	0.552
	a_{620}	-	-	138
	A_{675}	-	-	0.568
	a_{675}	-	-	142

blank was prepared in a like manner except that no metal ions were added and the HCl volume was increased to 0.20 ml. The measured pH of the aqueous phase was always between 0.8 and 1.0.

The results are summarized in Table 24. For convenience the absorbancy indices of the solutions, based upon the amount of known Pd (II) present, have been calculated. When using this table, it should be kept in mind that the average absorbancy indices of 122 and 135 were obtained from palladium chelate solutions at 620 and 675 mu respectively. These are the ideal values and if the presence of a foreign metal does not cause a significant deviation from these it is assumed that the ion will not interfere at that concentration.

Discussion of Results

The green palladium chelate shown in Curve 1 of Figure 20 has strong absorption bands at 310, 475, 620 and 675 mμ. The dye at the same pH of 0.8 also has strong absorption bands (Curve 2 of Figure 20) at 310 and 475 mμ but has only a very slight absorbance at 620 and 675. Since the molar absorbancy index of the chelate at 675 mμ is about 10% higher than at 620 mμ it is recommended that the former wavelength be used for a colorimetric palladium procedure. The molar absorbancy

index of the dye at 675 mμ is less than at 620 mμ giving one a further incentive to use the longer wavelength.

When the solutions containing the Pd and dye were allowed to stand one hour before extraction a straight line was obtained in a Beer's Law plot. Above 4.0 ppm. Pd there was a slight deviation from this line. The results are shown in Table 22. It has been found the range may be extended to at least 7.2 ppm by heating the solutions to 80° C. for 10 minutes. These results are summarized in Table 23 and Figure 21. No upper limit of concentration of palladium has been determined. The molar absorbancy indices of the Pd (II)-PAN chelate are 1.31×10^4 and 1.44×10^4 at 620 and 675 mμ respectively.

Table 24 lists results of the interference tests. Both Os (III) and Ru (III) were found to interfere seriously with the palladium determination. A ten-fold excess Rh (III) showed no appreciable interference but a twenty-fold excess did. On the other hand no interference was obtained with a twenty-fold excess of Ir (III). The Pt (IV) concentrations was increased until it was approximately 60 times that of the Pd (II) and there was still no serious interferences but when it is increased to approximately 600 times that of Pd (II) it does cause an increase in absorbance.

CHAPTER VII

SUMMARY

The dye 1-(2-pyridylazo)-2-naphthol, PAN, has been prepared and studied. It has been shown that it is an acid-base indicator which may exist in three forms. Absorption spectra of these forms have been obtained in water and 20% dioxane at various pH values and dissociation constants have been determined to be 1.26×10^{-2} and 6.3×10^{-13} in the latter solvent. Absorption spectra of the dye in methanol and ethanol were found to be similar to those obtained for the neutral form in 20% dioxane and water.

The copper-PAN chelate has been shown by Job's method of continuous variation to be a 1 to 1 complex at various pH's in aqueous and 20% dioxane solutions. This has been verified by spectrophotometric titrations. The dye prepared in this laboratory as well as commercial samples are impure and were standardized by a spectrophotometric titration with Cu (II) in 20% dioxane. The absorption spectrum of the copper chelate has been obtained and the equilibrium constant for the reaction, $HKE + Cu^{++} \rightleftarrows CuKE^{+} + H^{+}$, was found to be 6.4×10^{3} giving a stability constant for the copper chelate of approximately 10^{16}. The molar absorbancy index of the

copper chelate is 2.4×10^4. This coupled with the stability of the chelate suggests the possibility of an excellent colorimetric copper procedure.

The absorption spectrum of the nickel chelate has also been determined. This as well as Job's method indicates the presence of a 1 to 1 nickel-PAN complex. The molar absorbancy index of this complex based, upon the limiting concentration of the dye, was found to be 2.2×10^4 at 550 millimicrons. The attempts to determine the equilibrium constant for the reaction $HKE + Ni^{++} \rightleftharpoons NiKE^{+} + H^{+}$ were not completely successful. Further work must be done before any definite conclusions can be made.

A colorimetric palladium procedure has been developed. This procedure is based upon the chloroform extraction of the green complex. The molar absorbancy indices of the palladium chelate in chloroform are 1.31×10^4 and 1.44×10^4 at 620 and 675 millimicrons respectively.

The relative permissible concentrations of other Group VIII precious metals have been determined. It was found that only Os (III) and Ru (III) seriously interfere.

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