1961

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Recommended Citation

Caskey, Albert Leroy, "2-nitroso-1-naphthol-4-sulfonic acid as a reagent for cobalt " (1961). *Retrospective Theses and Dissertations*. 2455.
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CASKEY, Albert Leroy, 1931-
2-NITROSO-1-NAPHTHOL-4-SULFONIC ACID
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Iowa State University of Science and Technology
Ph.D., 1961
Chemistry, analytical

University Microfilms, Inc., Ann Arbor, Michigan

2-NITROSO-1-NAPHTHOL-4-SULFONIC ACID AS A REAGENT FOR COBALT

by

Albert Leroy Caskey

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Analytical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

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Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

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TABLE OF CONTENTS

I. INTRODUCTION

The beginning student of chemistry usually first encounters the chemistry of the element cobalt early in the qualitative analysis of cation mixtures. He learns that the cobalt ion is a member of the aluminum-zinc group and that it follows the nickel(II) ion throughout the separations that take place within the group. He then finds that when 1-nitroso-2-naphthol is added to the solution containing the cobalt(II) and nickel(II) ions, a dark brown solid separates from the solution simultaneously with a red colored solid. He is told that the appearance of these red-brown solids is indicative of the presence of cobalt in the sample or unknown.

The chemistry of this test for cobalt is explained to him in this manner. The 1-nitroso-2-naphthol oxidizes the cobalt(II) ion to the cobalt(III) ion, and at the same time is reduced to a dark brown insoluble organic substance. The cobalt(III) ion immediately reacts with more 1-nitroso-2-naphthol to form a red colored solid, the formation of which indicates the presence of cobalt in the original sample or unknown.

Sulfonic acid derivatives of 1-nitroso-2-naphthol have effectively caused 1-nitroso-2-naphthol to become very water soluble and have also caused the reaction product between cobalt(III) and the water soluble 1-nitroso-2-naphthol to become water soluble. The 3,6-disulfonic acid derivative is utilized in the well known Nitroso-R salt method (41, 45, 58), which for a period of about the last twenty years has been the most popular analytical method for the spectrophotometric determination of cobalt. The cobalt(II) ion is oxidized to cobalt(III) in the presence of nitric acid and the cobalt(III) reacts with the Nitroso-R salt, to form a red colored solution. The oxidation is not instantaneous, and hence the intensity of the color depends upon the time of boiling of the reaction mixture as well as upon the amount of reagent and cobalt(II) originally present. The intensity of the color of the complex changes with the temperature, the time of heating, and upon the length of the time of standing after the formation of the color. After several hours, a solid is often found to be slowly coming out of solution. The chemical reactions involved in the oxidation are not definite and are not completely understood.

Suddenly, in 1954, 2-nitroso-1-naphthol-4-sulfonic was reported as a new spectrophotometric reagent for cobalt (61). In this reagent the nitroso and hydroxyl groups are in reverse positions as compared to the positions they occupy in 1-nitroso-2-naphthol and its sulfonic acid derivatives. The 2-nitroso-1-naphthol-4-sulfonic acid reacts with the cobalt(II) ion to instantaneously form a red colored complex. The red complex is reversibly decomposed with acid, without the formation of a dark brown color, showing that oxidation-reduction is not involved in the formation of the complex. The red complex is also found to be stable with respect to time and temperature.

By reversing the positions of the nitroso and hydroxyl groups on the naphthalene nucleus, a reagent is obtained that is extremely sensitive to cobalt(II) and yet does not oxidize it, that forms a stable complex with cobalt(II) and yet the formation is reversible with addition of acid, and that apparently reacts with the cobalt(II) in a definite stoichiometric manner and yet reacts with chemistry that is not known. The purpose of this dissertation is to study the reaction between cobalt(II) and 2-nitroso-1-naphthol-4-sulfonic acid that results in the formation of the red colored cobalt complex.

II. HISTORICAL REVIEW

The German dye industry was the first to report the preparation of 2-nitroso-1-naphthol-4-sulfonic acid and its metal complexes when a patent was obtained in 1884 (30). A method was given for the preparation of a series of dyes by the action of certain metals, or their salts, on certain nitrosonaphtholsulfonic acids. The dyes produced were described to be of such a nature that the metal was not detectable by the usual methods of precipitation as the hydroxide. The nitrosonaphtholsulfonic acids were prepared by treating the corresponding naphtholsulfonic acids with nitrite and hydrochloric acid. Water solutions of the nitrosonaphtholsulfonic acids and metal salts were mixed, the excess metal precipitated, the solution filtered and the filtrate evaporated to dryness yielding the various dyes. The iron(III) complexes were dyes that varied in color from green to a deep olive, while the cobalt dyes were brown-red. The patent indicated that all naphthol sulfonic acids could be utilized except the β-naphthol-α-monosulfonic acid and the β-naphthol-γ-disulfonic acid.

Later the same year, M. Ilinski (37) published his early studies on the nitroso derivatives of 1-naphthol and 2-naphthol. He showed that both 2-nitroso-1-naphthol and 1-nitroso-2-naphthol react with iron and cobalt salts to form green and red-brown precipitates, respectively. He also pointed out that 4-nitroso-1-naphthol did not react with cobalt chloride to give a precipitate.

A few months later another paper appeared in which the author, Hoffmann (35), discussed the results of some of his research which lead to the patent discussed above. This short communication gave several facts of importance. The compounds of 1-nitroso-2-naphthol and 2-nitroso-1-naphthol formed from iron and cobalt salts were green and red-brown, respectively, but they were also insoluble in water and hence were not of technical use in the dye industry and were not mentioned in the patent. The nitroso derivatives of Schaffer's acid and 1-naphthol-4-sulfonic acid were some of the acids that formed the dyes that were described by the patent. Last, but not least, realizing the relationships between the sulfonated and unsulfonated derivatives, he pointed out that only the ortho nitrosonaphthols react with the metal salts and then indicated that it was likely that the ortho position of the nitroso group to the hydroxyl group was essential to the reactions described above.

Later in the year, Ilinski and Knorre (38), published a rebuttal to Hoffmann's paper, claiming that the latter had republished Ilinski's work on the unsulfonated nitrosonaphthols. Nevertheless, Hoffmann's contribution, concerning the necessity of ortho positions for the nitroso group and the hydroxyl group, was not mentioned in Ilinski's earlier paper

(37).

The authors also gave details for the preparation of the cobalt(II) and the cobalt(III) derivatives of 1-nitroso-2-naphthol. The cobalt(II) complex was formed by treating a neutral cobalt(II) salt solution with a neutral solution of the sodium salt of 1-nitroso-2-naphthol. The red-brown, water insoluble solid contained two organic molecules per cobalt atom and could be transformed into the cobalt(III) complex by treatment with hot alkali or hot acid. The cobalt(III) complex was formed by treating a neutral or acid solution of a cobalt(II) salt with an acetic acid, alcohol, or alcohol-water solution of 1-nitroso-2-naphthol. The voluminous, purple-red solid complex was stable toward acids, bases, oxidizing agents and reducing agents and contained three molecules of the nitrosonaphthol per atom of cobalt. Thus it was possible to distinguish between the two possible oxidation states of cobalt, the complex of cobalt(II) being destroyed and the complex of cobalt(III) being stable when hydrochloric acid was added to each. In general complexes of cobalt(III) have been known for their great stability. A similar relationship between the properties of the 1-nitroso-2-naphthol complexes of nickel(II) and cobalt(III), led to a quantitative separation of nickel and cobalt, which was also described.

While reporting the characterization of 1-naphthol-4-sulfonic acid, Witt and Kaufmann (62), were the first to report the details of the preparation of 2-nitroso-1-naphthol-4-sulfonic acid. 1-Naphthol-4-sulfonic acid and its salts were described as being little inclined toward crystallization, with a tendency to become colored in air. This troublesome property they possessed of often being very modified in exterior appearance was said to be due to slight amounts of impurity which were stubbornly retained.

The preparation of 2-nitroso-1-naphthol-4-sulfonic acid: 24.6 g. of 1-naphthol-4-sulfonic acid (Na salt) from any method of preparation was dissolved in 300 ml. of water, and was mixed with 19 ml. of (39% by volume) hydrochloric acid; then as much concentrated sodium nitrite solution was introduced dropwise as corresponded to 6.9 g. of pure sodium nitrite. The solution was well cooled during the introduction of the nitrite solution. At once a crystalline precipitate separated. This was collected on a suction filter, dissolved in 500 ml. of hot water, and treated with 50 ml. of pure hydrochloric acid. Immediately the formation of yellow-brown, large, lustrous crystals began. A yield of 20 g. was obtained.

Witt and Kaufmann (62) indicated that the product obtained was the free acid and was easily recrystallized until it was free of ash. The crystals were efflorescent in a desiccator and could be dried to constant weight at 115°, leaving a vermilion colored residue, the water free acid, which was very hygroscopic. The air dried preparation, dried to constant weight at 115°, lost weight corresponding to 19.44 per cent water. The $3\frac{1}{2}$ hydrate would contain 19.94 per cent water. The following results were obtained upon analysis of the substance, dried at 115° to constant weight: C, 47.18; H, 3.6; N, 5.39; and S, 12.41 per cent. Theoretical results for the anhydrous acid were: C, 47.43; H, 2.77; N, 5.53; and S, 12.65 per cent. All of the results were below the theoretical except for H, which was high.

Two series of salts were prepared from 2-nitroso-1-naphthol-4-sulfonic acid, neutral salts and acid salts. The neutral sodium and neutral barium salts were prepared from basic alcohol solutions, while the corresponding acid salts were prepared from sodium acetate buffered water solutions. Witt and Kaufmann analyzed the two acid salts mentioned above and obtained results that were in good agreement with the theoretical. The colors formed when the free nitroso compound reacted with cobalt and iron salts were also observed.

The organic molecule was characterized in several ways. It was easily reduced by tin(II) and chloride in hydrochloric acid or by sodium hydrogen sulfite to 2-amino-1-naphthol-4-sulfonic acid. It also reacted with boiling dilute nitric acid to form 2,4-dinitro-1-naphthol (3). It was condensed with aniline to form the corresponding 2,4-dianilino derivative.

Several months later, Hoffmann published complete analyses on several other metal derivatives of 2-nitroso-1-naphthol-4-sulfonic acid and gave details for their preparation (36). The trisodium and tripotassium salts of the iron(III) complex contained three organic molecules per iron atom. The long, bronze needles of the copper(II) salt, were those of a trihydrate, and contained one organic molecule per copper atom. A copper ammine salt was discussed, which apparently differed from the simple copper salt only by the replacement of two of the water molecules by ammonia molecules. Zinc and cadmium ammine salts were also prepared, and were completely analogous to the copper ammine salt.

In 1893, Conrad and Fischer (20), prepared 2-nitroso-1-naphthol-4-sulfonic acid while studying 1-naphthol-4-sulfonic acid. They reported the green and red colors with iron and cobalt and also the brown-yellow needles of the copper(II) derivative. In addition, the potassium, lead and silver salts were prepared and all found to be yellow in color. The latter salt was analyzed, with the results indicating that it actually was just a salt and not a complex. It was noted that the potassium salt was insoluble in cold water.

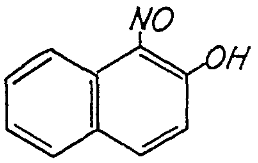
After nearly three decades had passed, in 1921 two British dye chemists, Morgan and Smith (47), prepared 2-nitroso-1-naphthol-4-sulfonic acid in solution followed immediately by the formation of its cobalt complex. They described the red complex as being very water soluble and precipitated it from a hot acid solution, by the addition of 2-naphthylamine, as tris-(naphthylammonium) tris-(2-nitroso-1-naphtholato-4-sulfonato)-cobaltate(III), $(C_{10}H_{10}N)_3[(C_{10}H_5O_5NS)_3Co]$, which formed as a crystalline bright red solid. The excess nitrite apparently acted as an oxidizing agent in the boiling acid solution to increase the oxidation state of the cobalt.

When a solution of the cobalt complex was neutralized with ammonia, cobalt(II) chloride and hydrogen peroxide added, the solution boiled, a purple solid precipitated. This solid was described by Morgan and Smith as being the pentamminecobalt(III) "lake" of the cobalt(III) complex of 2-nitroso-1-naphthol-4-sulfonic acid, with the sulfonic acid group completing the coordination sphere of the former cobalt(III) atom. In the presence of hydrogen peroxide, there was no doubt but that this giant molecule contained trivalent cobalt. The authors used the complexes as dyes.

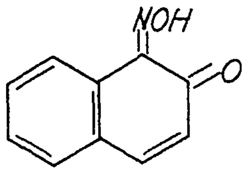
In the 1930's, 2-nitroso-1-naphthol-4-sulfonic acid was prepared by two other methods. The first of these methods (28), was rather quaint. Electrolysis of a neutral aqueous solution of 1-naphthol-4-sulfonic acid and sodium nitrite, yielded the 2-nitroso derivative of the sulfonic acid along with an appreciable amount of 2,4-dinitro-1-naphthol.

The second method of formation of 2-nitroso-1-naphthol-4-sulfonic acid lent some light on the answer to the question of why under simple mixing of aqueous solutions of the organic reagents and cobalt(II) salts, 2-nitroso-1-naphthol-4-sulfonic acid formed a cobalt(II) complex while 1-nitroso-2-naphthol formed a cobalt(III) complex. The transformation of 1-nitroso-2-naphthol and its sulfonated derivatives into sulfonated derivatives of 2-nitroso-1-naphthol has been studied extensively in a series of papers by Bogdanov, a Russian.

It has long been known that 1-nitroso-2-naphthol (I) existed in a tautomeric form, that of 1-oxime-1,2-naphthoquinone (II). The substance has been treated with aqueous sodium hydrogen sulfite, which transformed it into a soluble "bisulfite" addition compound (III) (4, 6, 14, 15, 59). The reaction that took place was the familiar nucleophilic attack of an α,β-unsaturated ketone. The N-methyl ether (37) of the oxime-quinone form underwent a similar reaction to form a compound that had similar properties (59). When the bisulfite adduct of 1-nitroso-2-naphthol was heated with hydrochloric acid, 1-amino-2-naphthol-4-sulfonic acid was formed (4, 14, 15, 59).



I.



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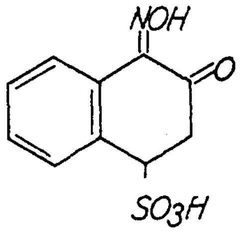
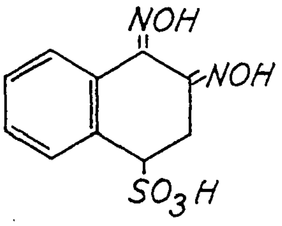


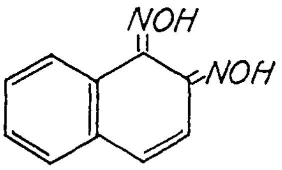
III.

While proving that the bisulfite adduct had the structure

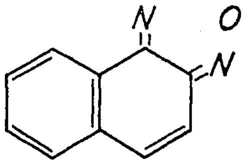
III, Bogdanov added hydroxylammonium chloride to an acid solution of the bisulfite adduct, and after the solution had been boiled, he was able to isolate in very good yield 2-nitroso-1-naphthol-4-sulfonic acid (4). Later (5), when the reaction was run in a solution that was buffered with sodium acetate, he was able to isolate the bisulfite adduct of 1,2-dioxime-1,2-naphthoquinone (IV), and hence he was able to show the presence of the carbonyl group. When the bisulfite adduct of 1,2-dioxime-1,2-naphthoquinone was boiled in dilute hydrochloric acid, it was converted to 2-nitroso-2-naphthol-4-sulfonic acid in near quantitative yields (5). When the same bisulfite adduct was carefully heated in a sodium carbonate solution, the bisulfite was removed leaving as a product the free 1,2-oxime-1,2-naphthoquinone (V), which in turn could be converted into its anhydride, 1,2-naphtho-3',4'-furazan (VI), in boiling alcoholic sodium hydroxide solution (5).



IV.



V.



VI.

Bogdanov used similar reactions to prepare over a dozen mono- and di-sulfonic acids of 2-nitroso-1-naphthol (7, 8, 9, 10, 11, 12, 13). He found that even 1-amino-2-naphthol, 2-amino-1-naphthol and their sulfonic acid derivatives could be converted into corresponding 2-nitroso-1-naphthols.

This series of reactions in which the 1-oxime was converted into the 1,2-dioxime, which in turn was hydrolyzed back into a monooxime, the 2-oxime, indicated that the 2-oxime contained features that made it more stable. For a long time, the direct relationship between strength as an oxidizing agent and stability has been known, the more unstable of two oxides having the greater strength as an oxidizing agent. The 1-oximes were found to be more unstable and capable of oxidizing cobalt(II) to cobalt(III) under almost any aqueous conditions. The 2-oximes were apparently capable of this oxidation only under more strenuous conditions. The presence of a sulfonic acid group in the 4-position further enhanced the stability.

Sarver, in 1938, was the first to report the use of 2-nitroso-1-naphthol-4-sulfonic acid as an analytical reagent (51). He reported several qualitative tests, in which a 1 per cent aqueous solution of the organic acid was used as the color forming reagent. Such a solution, was stable for at least several months. Cobalt, copper and ferrous iron were identified by their red, orange and green color reactions, respectively. In concentrated solutions precipitates were formed, but in dilute solutions the colored derivatives did not settle out, and the solutions were stable over a period of months. It was indicated that the complexes were formed in neutral solutions, with an optimum pH of 5 for the ferrous complex and an optimum pH range of 7 to 8 for the cobalt complex. At higher and lower concentrations the complexes did not form well. The sensitivities of the tests were very great. The color reactions interfered with one another, but in the pure form it was comparatively easy to detect cobalt and iron in concentrations of one part in 20 million; the colors given by copper were only slightly less intense. Saver pointed out the fact that when a complex was formed, the hydrogen atom on the hydroxyl group was replaced by one equivalent of the metal, which in turn formed a coordinate bond with either the oxygen or nitrogen of the nitroso group, and therefore formed either a six or five membered ring, respectively. He indicated that it was uncertain which of the rings was formed and he did not indicate the ratio of organic ligand to metal atom.

The use of 2-nitroso-1-naphthol-4-sulfonic as a qualitative analysis reagent has been mentioned in several other papers (27, 49).

Three papers have been published concerning the details of the reactions of 2-nitroso-1-naphthol-4-sulfonic acid with metal ions. Wise and Brandt (61) used the reagent in the colorimetric determination of cobalt, but they did not consider the reactions involved in the determination. On the other hand, Tolmachev and Korobka (56) studied the reaction between the organic molecule and nickel(II) ions, but they did not study the spectrophotometric determination of nickel using the reagent. Later, Tolmachev and Tulchinskaya (57) studied the reaction of copper(II) with 2-nitroso-1-naphthol-4-sulfonic acid. Again, although the possibility of a spectrophotometric determination was mentioned, it was not studied in any way. These are the only papers dealing with the details of the chelometric reactions of 2-nitroso-1-naphthol-4-sulfonic acid.

The spectrophotometric determination of cobalt (61) using 2-nitroso-1-naphthol-4-sulfonic acid was found to be "convenient, sensitive, reproducible, accurate, and precise." The cobalt complex was found to be stable over a pH range 7-10, with the color of the reagent having little effect on the color of the complex. The effect of pH on the visible spectrum of the reagent is shown in Figure 1, while the effect of pH on the visible spectrum of the cobalt complex is shown in Figure 2. It is to be noted that the UV and IR spectra are not given in the literature. At 525 $m\mu$., the absorbance of the cobalt complex was found to be a maximum while the absorbance of the corresponding reagent solution was very small, and this wavelength was chosen for the spectrophotometric determination. The colored system was shown to obey Beer's Law over the range of 0.24 - 7.5 p. p. m. cobalt. The color formed was not so intense in the presence of ammonia, which was accredited to the formation of a cobalt ammine. Low concentrations of iron

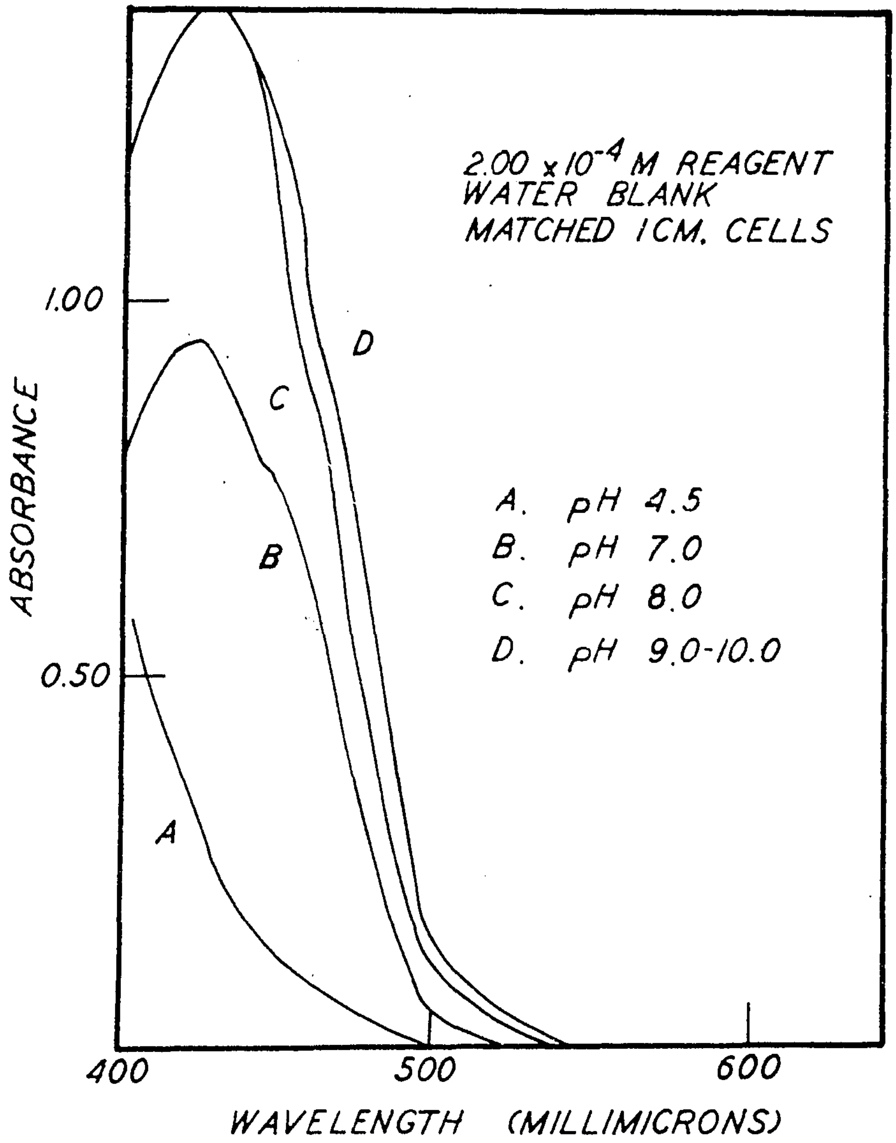
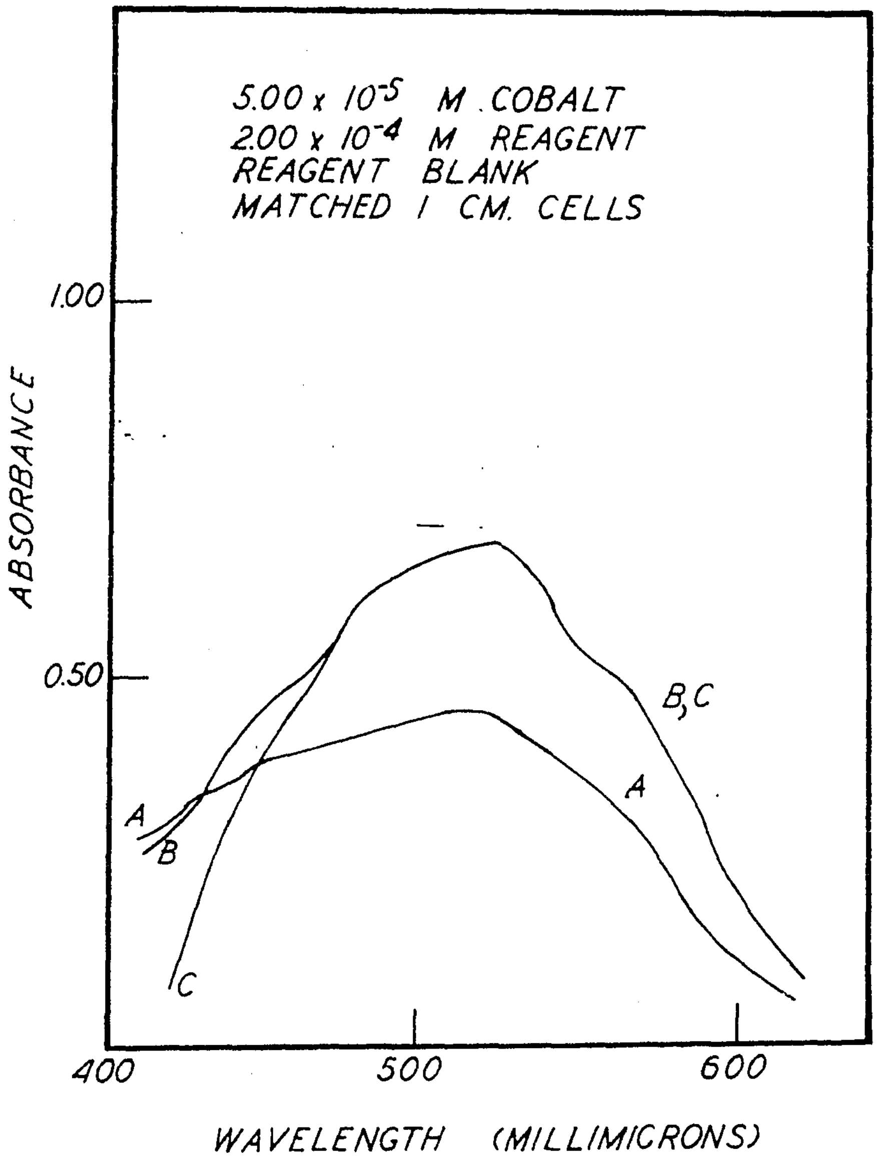


FIGURE 1. THE EFFECT OF pH ON THE VISIBLE SPECTRUM OF 2-NITROSO-1-NAPHTHOL-4-SULFONIC ACID

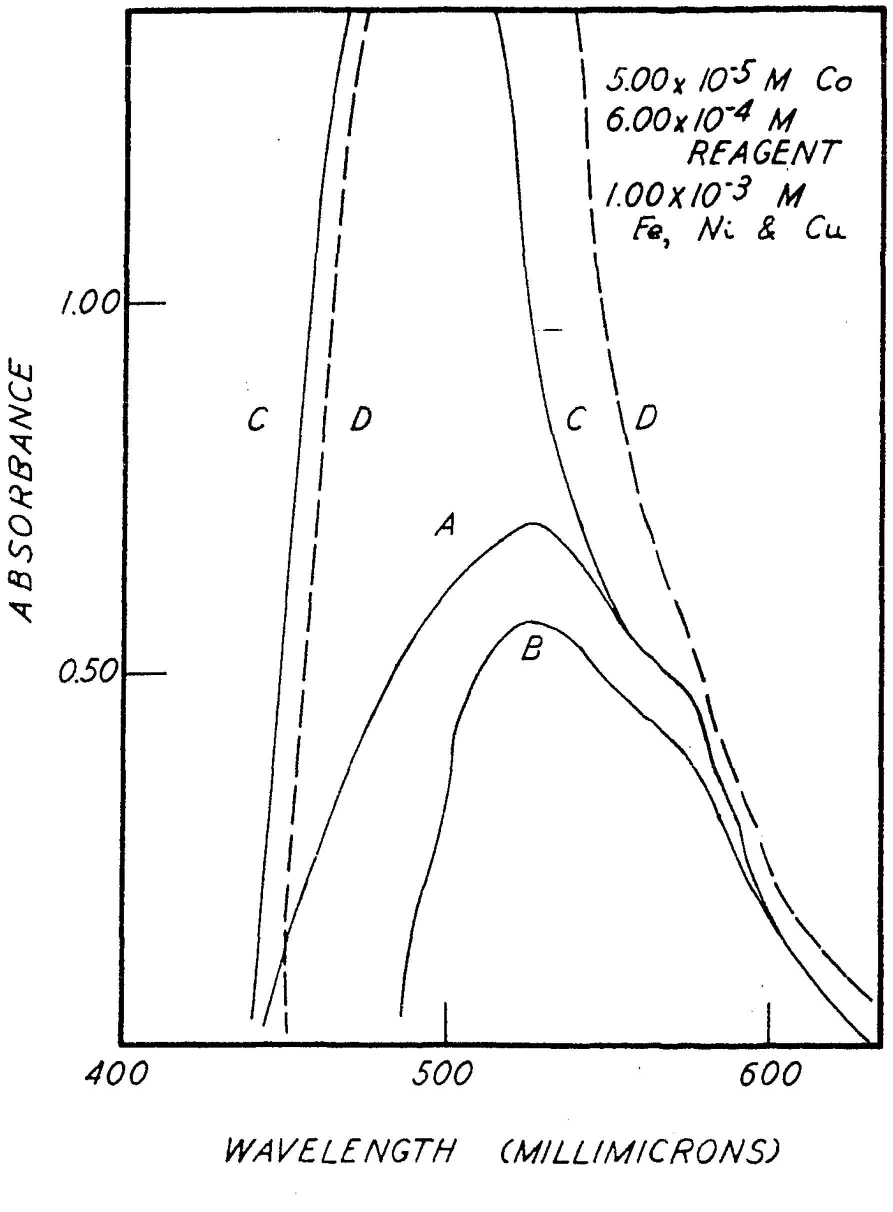


A. pH 4.5
B. pH 6.0
C. pH 7.0-10.0

FIGURE 2. THE EFFECT OF pH ON THE VISIBLE SPECTRUM OF THE COBALT COMPLEX

and copper, which interfered with the color formation, were controlled by the addition of citrate, which acted as a masking agent. The actual effects of iron, nickel and copper upon the spectrum of the cobalt complex were shown as in Figure 3. While the presence of iron decreased the absorbance of the solution measured, the presence of nickel or copper increased the absorbance of the solution. The copper and nickel complexes were thus shown to absorb very strongly at a wavelength of about 500 mμ. Other metals that formed insoluble hydroxides at pH 7, or that had the tendency to form complex ions also caused trouble in the determination of cobalt. The reagent was shown to provide a useful method for the quantitative spectrophotometric determination of cobalt. The system described, was stable, independent of reagent concentration and obeyed Beer's Law. This reproducible, sensitive, accurate, and precise method was considered to be very useful for determining minute amounts of cobalt.

In the same year that Wise and Brandt published their work on the cobalt complex, Tolmachev and Korobka published their study (56) of the reaction of nickel(II) with the sodium salt of 2-nitroso-1-naphthol-4-sulfonic acid, which was prepared by the method of Witt and Kaufmann. In their study, Tolmachev and Korobka used spectrophotometric data, supplemented by pH measurements with a glass electrode and the quinhydrone electrode. The effect of pH on the spectrum of



A. COBALT(II)
B. COBALT(II) AND IRON(III)
C. COBALT(II) AND NICKEL(II)
D. COBALT(II) AND COPPER(II)

FIGURE 3. EFFECTS OF SEVERAL METAL IONS ON THE SPECTRUM OF THE COBALT COMPLEX

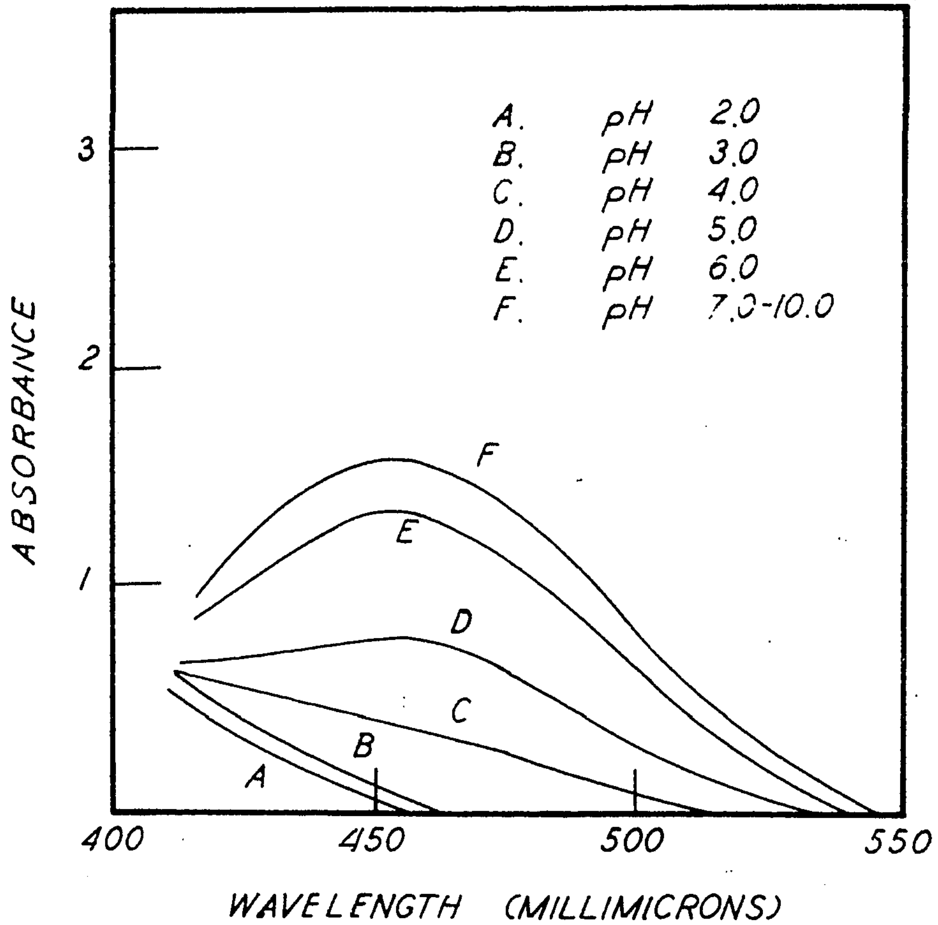


FIGURE 4. THE EFFECT OF pH ON THE SPECTRUM OF THE NICKEL COMPLEX

the nickel complex was given as in Figure 4. Information was not given in the paper concerning the blank solution used in the determination. Continuous variations plots were used to show the possibility of three complexes, 1:1, 1:2, and 1:3 at pH 4, 5, and 6, respectively. Four wavelengths near the maximum shown in Figure 4 were used.

The authors first studied the 1:1 complex over a pH range of 3.5 to 4.0 and then they studied the 1:3 complex at pH 6 or above. Using the spectrophotometric data that they obtained, they calculated the spectra of the two complexes and obtained the results given in Figure 5. It is to be noticed that these spectra do not agree with the spectrum of the nickel(II) complex at pH 7 as given by Wise and Brandt (Figure 3).

In the experimental work, series of pairs of solutions were prepared. When the 1:1 complex was studied, nickel(II) and the organic reagent were used in the same mole ratio. When the 1:3 complex was studied, three moles of reagent were used to each mole of nickel(II). Of each pair of solutions, one differed from the other only in having a larger concentration of both the nickel and organic reagent. From the absorbance data from each pair of solutions the molar absorptivity of the corresponding nickel complex was calculated. Using these values, the authors calculated equilibrium constants, K_1 and K_2 respectively, for the following reactions:

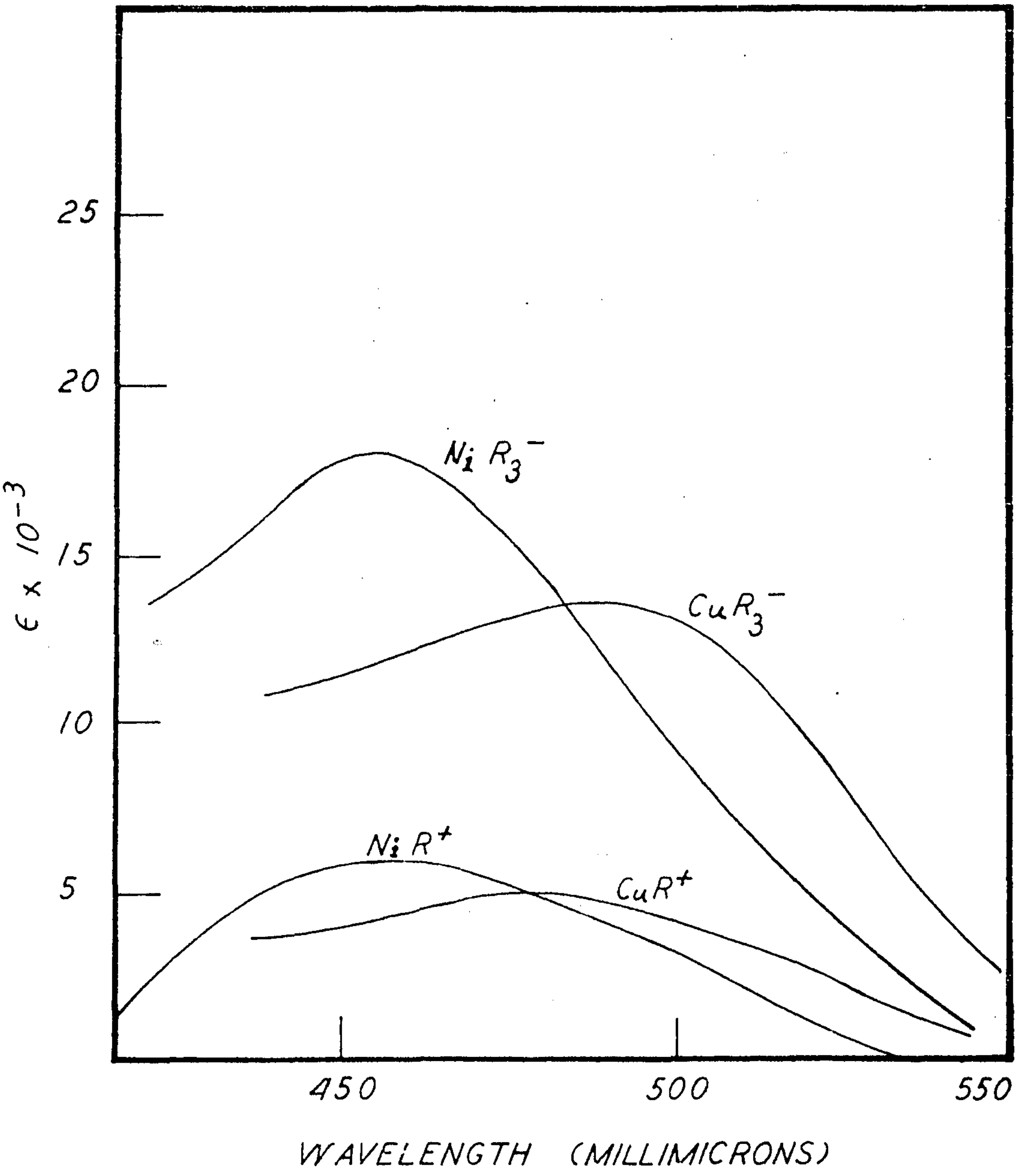


FIGURE 5. SPECTRA OF THE NICKEL(II) AND COPPER(II) COMPLEXES

$$RH + Ni^{++} = NiR^{+} + H^{+} \tag{1}$$

$$3RH + Ni^{++} = NiR_3^{-} + 3\ H^{+} \tag{2}$$

where RH was used as a symbol for the organic molecules, with the ionization of the sulfonic acid being completely disregarded. Then, using a value of 8.2×10^{-7} for the second ionization of the organic acid, instability constants, K_1 and K_2 respectively, were calculated for the following reactions:

$$NiR^{+} = Ni^{++} + R^{-} \tag{3}$$

$$NiR_3^{-} = Ni^{++} + 3\ R^{-} \tag{4}$$

The results of the calculations are given in Table 1.

The authors were able to show that the presence of a 1:2 complex was unlikely and if it did exist it was present to only 4-5 per cent of the total complex present. This was said to be in the order of the error of the spectrophotometric

Table 1. Results of the study on the nickel(II) complexes

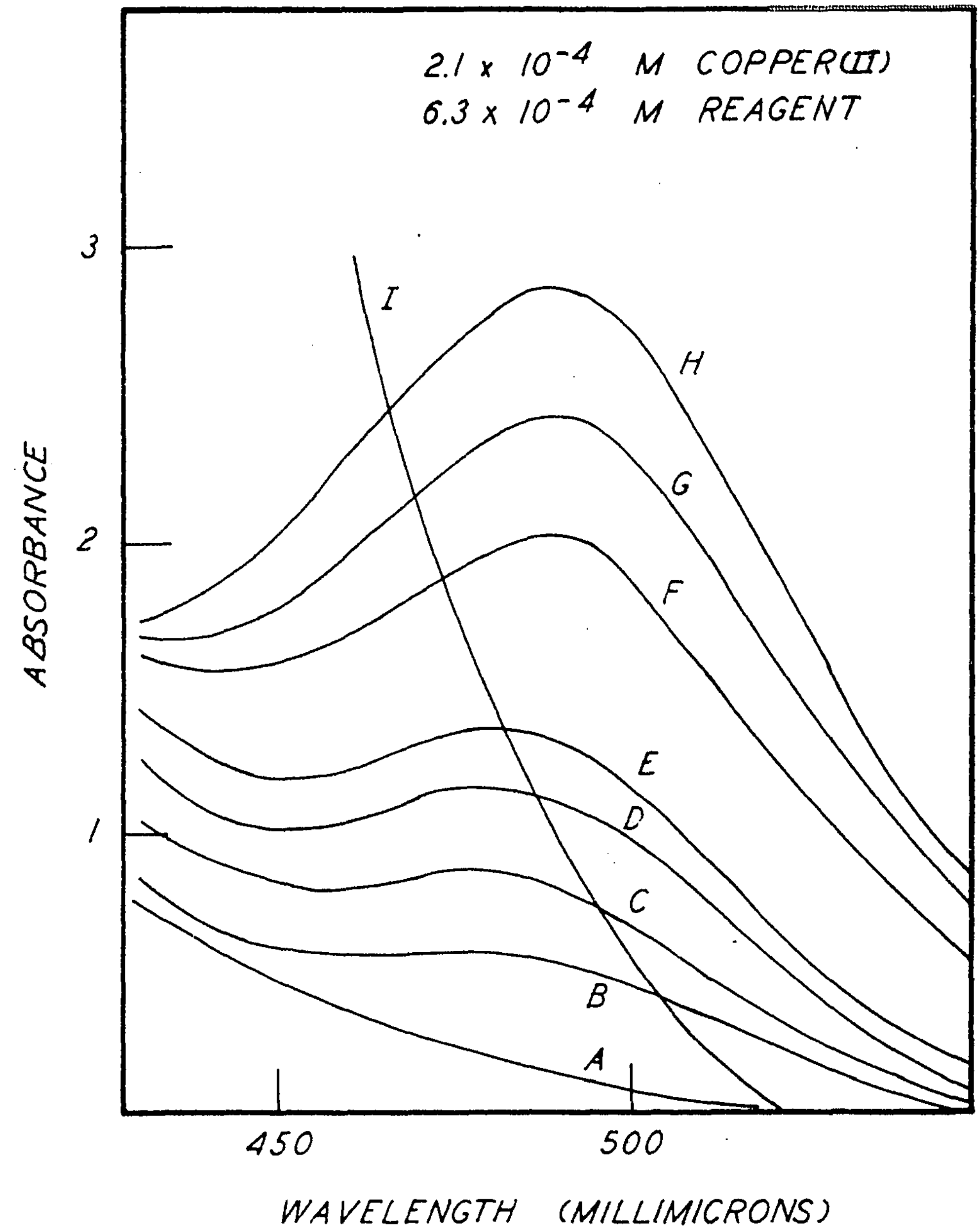
	1:1 Complex			1:3 Complex	
	Value	Relative error--%		Value	Relative error--%
^{490}	3240	18	^{500}	8650	3
^{500}	2800	19	^{510}	7370	5
K_I	0.74	7	K_{II}	3.6×10^{-5}	33
^{490}	3680	2			
^{500}	2960	6			
K_I	0.65	4			
K_1	1.3×10^{-6}	--	K_2	1.5×10^{-14}	--

measurements.

Although all of their measurements were based upon Beer's Law, no where in the paper was it shown that any of the chemical species actually obey Beer's Law. The use of 2-nitroso-1-naphthol-4-sulfonic acid as a colorimetric or spectrophotometric reagent for nickel(II) was suggested, but not studied in any way.

The study of the reaction of the sodium salt of 2-nitroso-1-naphthol-4-sulfonic acid with copper(II) ions (57) was almost a duplicate of the study done previously on the reaction previously described with nickel(II) ions. The data were taken in exactly the same manner, under the same conditions, and the calculations and results were presented in the same way. The effect of pH on the spectrum of the copper(II) complex was given as in Figure 6. From spectrophotometric measurements, with the use of continuous variations plots, the possibility of 1:1, 1:2, and 1:3 complexes was shown. Again, it was later shown that the 1:2 complex was present to only a slight extent. Calculated spectra of the 1:1 and 1:3 complexes were given as shown in Figure 5.

Several values of the molar extinction coefficients of the 1:1 complex were given as follows: $_{540} = 1050 \pm 180$; $_{530} = 1850 \pm 270$; $_{520} = 3030 \pm 320$; $_{510} = 3560 \pm 475$. The error acknowledged to be present in these measurements and the results calculated from them, indicated most probably



A. pH 1.95
B. pH 2.50
C. pH 3.00
D. pH 3.50
E. pH 3.95
F. pH 5.00
G. pH 6.10
H. pH 7.30
I. pH 10.00

FIGURE 6. THE EFFECT OF pH ON THE SPECTRUM OF THE COPPER(II) COMPLEX

the amount of error present in the results in both of Tolmachev's papers.

The values given for the formation constants for the copper(II) complexes that correspond to the reactions given by Equations 1 and 2 were given as 7.5 ± 0.5 and 3.9×10^{-2}, respectively. The values given for the instability constants for the copper(II) complexes that correspond to the reactions given by Equations 3 and 4 were given as 1.1×10^{-7} and 1.4×10^{-17}. The copper complexes were thus found to be slightly more stable than the corresponding nickel complexes.

The authors noted that from the spectra of the complexes (Figure 5), it may be possible to determine nickel(II) in the presence of copper(II) by the use of 2-nitroso-1-naphthol-4-sulfonic acid.

III. EXPERIMENTAL WORK

When this project was started 2-nitroso-1-naphthol-4-sulfonic acid was not commercially available. The first task that was therefore necessary was to prepare the organic compound. The next task of course was to carefully analyze the substance and determine the purity. Impure material would of course need further purification before it would be possible to do careful studies on the reaction of cobalt(II) with 2-nitroso-1-naphthol-4-sulfonic acid.

A. Preparation of 2-Nitroso-1-Naphthol-4-Sulfonic Acid

1. Reagents

Reagent grade hydrochloric acid, sodium hydrogen sulfite, sodium hydroxide and sodium nitrite were used in the preparation.

Deionized water was used. It was obtained by passing distilled water through a column of Amberlite MB-2, and was then stored in the absence of carbon dioxide. The Amberlite MB-2 that was used was a mono-bed ion exchange resin consisting of a sulfonic acid cation exchanger and a quaternary ammonium anion exchanger.

The 4-amino-1-naphthalenesulfonic acid used was Eastman Kodak "white label" No. 169.

The 1-naphthol-4-sulfonic acid used was obtained from several sources. It was first prepared by heating 4-amino-1-naphthalenesulfonic acid in an aqueous solution of sodium hydrogen sulfite and then making the resulting solution strongly basic with sodium hydroxide following the Bucherer Reaction (31). Some of the material used was obtained from the "organic chemical reserves" and was of unknown quality. These two portions, along with some obtained from Matheson Co., T1316 (Technical Grade), were used for Synthesis I below, while only the latter was used for Syntheses II and III below. These probably were actually the mono sodium salts.

Norite-A, commercially available decolorizing charcoal was used.

Practical grade p-toluidine was obtained from the Matheson Co. (P2715). It was suspended in water, treated with hydrochloric acid until it dissolved, and then the resulting solution was decolorized with Norite-A. Upon cooling the hydrochloride salt precipitated. This salt was dried and was used in the following experiments.

Reagent grade organic solvents were used. No particular effort was made to use the anhydrous solvents, nor was there any effort made to use thiophene free benzene.

2. Synthesis I

This method was essentially that of Witt and Kaufmann (62), with several slight modifications to reduce side reactions. It was the method that was mentioned in the literature. 1-Naphthol-4-sulfonic acid, from any of the sources, was suspended in water and enough sodium hydroxide was added to dissolve the organic acid. Sodium nitrite was added to this solution such that there was about a 15 mole per cent excess over the 1-naphthol-4-sulfonic acid. Ice, prepared from distilled water, was added directly to this solution to cool it to near 0°, with enough being added to maintain the solution at that temperature upon neutralization of the base with hydrochloric acid. 2-Nitroso-1-naphthol-4-sulfonic acid precipitated at once in the form of fine glistening yellow-brown needles, in near quantitative yields from the 1:5 hydrochloric acid solution. The material was easily recrystallized by dissolving it in hot water containing a trace of hydrochloric acid and then precipitating it again upon the addition of enough additional acid to make the solution about 1:5 in hydrochloric acid. Upon cooling to near 0°, nearly quantitative yields were obtained again. The solid so obtained was washed with ice cold dilute hydrochloric acid and allowed to air dry.

The formation of by-products was decreased by filtering the product from the reaction mixture shortly after acidification and before the temperature of the mixture rose above 5°. The filtered product in turn was suspended in cold dilute hydrochloric acid, washed thoroughly and then again filtered from the liquor to remove the necessary, but now harmful, excess sodium nitrite before any recrystallization. Failure to do this caused considerable coupling to take place and several times completely destroyed all of the product that was desired.

The filtrates from the recrystallizations were invariably red in color, even after several dozen recrystallizations. A red colored material was carried along with the 2-nitroso-1-naphthol-4-sulfonic acid. The organic acid precipitated first from the solvent as extremely fine needles. As this mixture was digested to purify the solid, the red material also settled from the solvent in just large enough quantity to "color" the yellow brown needles. Although this red material was low enough in concentration to not interfere with a spectrophotometric determination, and could cause only a shift in the position of the calibration curve, it was in high enough concentrations to interfere in any study in which the absolute value of the absorbance was of importance, such as in a continuous variations study. It was therefore deemed necessary to find a method to eliminate the impurity.

Both Norite-A and chromatography with alumina columns failed to remove the impurity without themselves destroying the 2-nitroso-1-naphthol-4-sulfonic acid.

3. Synthesis II

The most obvious change that could be made in the synthesis was a change in the solvent from which the recrystallization was done. Many solvents and solvent pairs were tried, but all were without success except one, the acetone-benzene solvent pair.

The impure material was dissolved in boiling acetone and then an equal volume of hot benzene was added to it. The same yellow-brown needles of 2-nitroso-1-naphthol-4-sulfonic acid precipitated very slowly from the solution, often taking 12 to 15 hours to complete precipitation even when the solution was cooled in an ice bath. With several recrystallizations the red material was completely removed and near quantitative yields were obtained. The filtrates were a pale yellow in color after the impurity was removed. The product was allowed to air dry.

This method of recrystallization was first extensively used during the month of June. When it was tried again during the following February, the middle of the winter, it did not work. The material would readily dissolve, but it would not precipitate again.

4. Synthesis III

All of the starting materials used in the preparation were highly pure except the 1-naphthol-4-sulfonic acid. If it in turn were purified, the amount of impurities present in the product should be decreased. A search of the literature, however, did not yield a method of purification. The sodium salt, the usual commercial form, was always obtained by salting it from solution with sodium chloride. It was felt that perhaps one of the solids formed in the characterization of sulfonic acids might be useable as a means of purification. The derivative had to be such that the original organic acid could again be readily obtained. The p-tolylammonium salt (p-toluidine salt) was chosen as a derivative that would meet those characteristics (17, 18, 23).

Equimolar quantities of 1-naphthol-4-sulfonic acid and p-tolylammonium chloride were dissolved in hot, dilute hydrochloric acid. This solution was treated with Norite-A, boiled, filtered hot to remove the carbon, and then allowed to cool. The p-tolylammonium 1-naphthol-4-sulfonate precipitated as long white needles in near quantitative yields by the time the mixture was cooled to near 0°. One recrystallization from dilute hydrochloric acid gave a white solid that slowly turned color in the presence of light, but that remained unchanged in the dark. This solid was then dissolved in dilute sodium hydroxide and gave a colorless solution which was extracted three times with diethyl ether. The resulting aqueous solution of the disodium salt of 1-naphthol-4-sulfonic acid was then treated with sodium nitrite and the preparation was completed as described in Synthesis I above. Several recrystallizations of the 2-nitroso-1-naphthol-4-sulfonic acid from 1:5 hydrochloric acid yielded a product that was free of the red impurity and that was obtained from filtrates that were yellow-brown in color.

5. Results

The original procedure of Witt and Kaufmann for the preparation of 2-nitroso-1-naphthol-4-sulfonic acid has been modified so that commercially available starting material could be readily used and so that a highly pure product could be obtained. The 1-naphthol-4-sulfonic acid was purified by precipitation with p-toluidine in a hydrochloric acid solution as p-tolylammonium 1-naphthol-4-sulfonate. After this material was dissolved in alkali, the p-toluidine was removed by extraction with diethyl ether.

Instead of treating a cold acid solution of 1-naphthol-4-sulfonic acid with sodium nitrite, it was found to be better to treat a basic solution of 1-naphthol-4-sulfonic acid with sodium nitrite and to then acidify that cold solution to cause the nitrosolation to occur. The product so obtained was first washed with cold dilute hydrochloric acid, before recrystallization was attempted.

Recrystallization from either 1:5 hydrochloric acid or 1:1 acetone-benzene yielded a pure product. The 1:1 acetone-benzene solvent pair was found to work only when the absolute humidity was high, since it was necessary for the 2-nitroso-1-naphthol-4-sulfonic acid to precipitate as a hydrate, water being extracted from the atmosphere during the process. It worked during the moist Iowa summer but failed to work during the dry winter that followed.

B. Characterization and Analysis

1. Analytical methods

Several determinations were carried out in the analysis and characterization of 2-nitroso-1-naphthol-4-sulfonic acid. Derivatives were made and melting points were taken and compared to those in the literature whenever it was possible to do so.

Air dried material was dried further to constant weight under three different sets of conditions; a) at 110° in a drying oven, b) at 110° in a drying oven, but under a vacuum of about 17-18 mm. Hg pressure as supplied by an aspirator, and c) at room temperature under a similar vacuum supplied by an aspirator in a vacuum desiccator over anhydrous magnesium perchlorate.

The familiar semimicro Kjeldahl method was used to determine nitroso nitrogen. After the nitroso compound was reduced to the amine in a dilute sulfuric acid solution using Devarda's alloy as the reducing agent, the amine was digested with concentrated sulfuric acid to form ammonium ion. The copper from the alloy acted as a catalyst and an indicator to show when the digestion was complete. The ammonia was distilled into boric acid and titrated with standard hydrochloric acid.

Titration with standard sodium hydroxide was used for the determination of acid neutralization equivalents. A commercially available, Beckman Model G, pH meter was used to follow the titration.

The nitroso group was titrimetrically reduced to the corresponding amine by titanium(III) chloride. A sample of the nitroso compound was dissolved in 1:10 hydrochloric acid, excess standard 0.04 M titanium(III) chloride was added, and the excess was backtitrated with standard 0.04 M iron(III) perchlorate solution using potassium thiocyanate as the indicator and published techniques (42). The titrations were carried out in a closed vessel under an atmosphere of carbon dioxide.

2. Reagents

-- Several of the reagents that were used were previously mentioned, in section A.

The potassium hydroxide phthalate used was of primary standard grade and was obtained from the Mallinckrodt Chemical Works, catalog number 6704.

A saturated solution of NaOH, carbonate free, was prepared by dissolving sodium hydroxide, 60 g., in 60 ml. of deionized water. The solution was cooled and filtered through a pyrex filtering crucible before storage.

An approximately 1 per cent solution of phenolphthalein was prepared by dissolving 1 g. of the solid reagent (Baker and Adamson, C. P. Grade) in 70 ml. of 95 per cent ethyl alcohol. The solution was filtered to remove small black particles that were left undissolved.

Several standard solutions of carbonate free sodium hydroxide were prepared at different times by placing 7 ml. portions of the saturated solution of sodium hydroxide in 1 liter portions of deionized water. These solutions were standardized against potassium hydrogen phthalate using phenolphthalein as the indicator.

A 40 per cent solution of sodium hydroxide was prepared by dissolving the base, 400 g., in 600 ml. of deionized water.

A 4 per cent solution of orthoboric acid was prepared by dissolving 40.0 g. of the acid (Baker and Adamson, reagent grade) in about 150 ml. of deionized water and then pouring the resulting hot solution into about 800 ml. of deionized water.

Fleicher's "Methyl-purple" indicator was used.

Low nitrogen Devarda's alloy (Baker and Adamson) was used.

A standard solution of 0.1 N hydrochloric acid was used. It had been prepared in a 20 liter carboy and standardized by a fellow graduate student, Frederick Lindstrom. Using primary standard sodium carbonate and methyl-red as the indicator, he found a value of 0.09701 for the normality. A 2 liter flask was filled with the acid, which in turn was again standardized.

The sulfuric acid used for the digestion step in the Kjeldahl method for nitrogen was prepared for use in the Quantitative Organic Microanalysis laboratory by doubly distilling reagent grade sulfuric acid in an all glass apparatus. Unnecessary contact with the atmosphere was avoided.

Reagent grade hydrogen peroxide, nitric acid, potassium chloride, potassium hydroxide, potassium thiocyanate, and titanium(III) chloride solution were used.

A National Bureau of Standards standard buffer solution for pH 4.01 was prepared as described in the literature (1). Potassium hydrogen phthalate, 10.2115 g., which had been previously dried at 110° for several days, was dissolved in deionized water and the resulting solution was diluted to a volume of 1 liter. This 0.05 M solution has been defined to have a pH_s = 4.00 and 4.01 at 20° and 25°, respectively.

A standard solution of iron(III) perchlorate was prepared by dissolving electrolytic iron, 2.2379 g., in several ml. of boiling perchloric acid (G. F. Smith Chemical Co., Reagent grade) and then diluting the resulting solution to 1 liter. The solution was 0.04007 M.

A 1 per cent solution of potassium thiocyanate in water was prepared for use as an indicator solution.

A 0.03291 M solution of titanium(III) chloride was prepared by diluting the reagent solution with 1:10 hydrochloric acid and standardizing the resulting solution against the 0.04007 M iron(III) perchlorate using the latter as the titrant and potassium thiocyanate as indicator (48). The standardization was checked by Frederick Lindstrom. The solution was stored under carbon dioxide.

A tank of commercially available carbon dioxide was used in the experiments involving titanium(III) chloride.

3. Equipment

Borosilicate glassware was used. The volumetric glassware used met the specifications of Class A of the National Bureau of Standards.

Polyethylene containers were used instead of glass containers to store the basic solutions that were used.

All glassware and other containers were washed with soap (or detergent) and water, rinsed with tap water and then with distilled water. If droplets of water still had a tendency to cling to the walls of the container an alcoholic solution of potassium hydroxide was used to "cut" the grease and oil that could not be washed away. This treatment was of course followed by the one described above.

A Beckman Model G pH meter was used, along with a "general use" glass electrode and a saturated calomel reference electrode.

A Cary Recording Spectrophotometer, Model 12, was used to determine ultraviolet and visible spectra. Matched, silica, 1.000 cm. cells were used in the spectrophotometer. The slit control was set at 10.

The infrared spectra were run on a Baird-Atomic, Inc., I. R. Spectrophotometer using a sodium chloride prism. A technician, assigned to use the instrument, ran the spectra.

Magnetic stirrers, commercially available from the G. F. Smith Chem. Co., and teflon covered stirring bars were used to stir solutions, particularly during titrations.

A Fisher-Johns melting point apparatus was used to take melting points. A 115 volt variac was used to control the input voltage and hence the temperature. This particular hot stage had been demonstrated numerous times in the Quantitative Organic Microanalysis Laboratory to be correct within 1° from room temperature to near 300°.

Pyrex vacuum desiccators, filled with a desiccant of anhydrous magnesium perchlorate (G. Frederick Smith Chem. Co.), were used throughout this work.

The 110° drying oven was a commercial oven of standard make that was readily controlled to within 1°.

The vacuum drying oven used was a "Precision" - Thelco vacuum oven Model 19.

4. Experimental procedure

Melting points of p-tolyl-ammonium chloride, p-tolylammonium 1-naphthol-4-sulfonate and air dried 2-nitroso-1-naphthol-4-sulfonic acid were taken.

2,4-Dinitro-1-naphthol was prepared by dissolving 2-nitroso-1-naphthol-4-sulfonic acid in water, adding several ml. of nitric acid, and then boiling the resulting solution for 10 to 15 minutes. The insoluble 2,4-dinitro-1-naphthol readily precipitated from the hot solution, as fine red-brown crystals that melted sharply. It is to be noted that this reaction in which the sulfonic acid group is replaced by the nitro group is characteristic of many naphthol-sulfonic acids.

Air dried 2-nitroso-1-naphthol-4-sulfonic acid was dried to constant weight at 110°, and then the dried solid was dissolved in deionized water and titrated with standard sodium hydroxide to determine the neutralization equivalent of the solid. After the sodium hydroxide was standardized against the dried potassium hydrogen phthalate, the standardization was checked by titration against the hydrochloric acid, again using phenolphthalein as the indicator.

Nitrogen was determined in the 2-nitroso-1-naphthol-4-sulfonic acid that had been only air dried and also in the same material that had previously been dried to constant weight at 110°.

Air dried 2-nitroso-1-naphthol-4-sulfonic acid was dried at 110° in a vacuum drying oven in an attempt to obtain the anhydrous material. A pressure of 15-20 mm. Hg was obtained by the use of an aspirator. The dried material was titrated with standard sodium hydroxide to obtain the neutralization equivalent.

Air dried 2-nitroso-1-naphthol-4-sulfonic acid was dried to constant weight over magnesium perchlorate in a vacuum desiccator that had been evacuated by the use of an aspirator during a period of nearly five months. The material so obtained was titrated with standard sodium hydroxide to obtain its neutralization equivalent. The standardization of the sodium hydroxide against dry potassium hydrogen phthalate was checked against the standard hydrochloric acid.

Air dried 2-nitroso-1-naphthol-4-sulfonic acid was titrated with standard sodium hydroxide to determine its neutralization equivalent. The sodium hydroxide used was the same as before.

Air dried 2-nitroso-1-naphthol-4-sulfonic acid was titrated with standard titanium(III) chloride under an atmosphere of carbon dioxide. The nitroso group was quantitatively reduced to the corresponding amine in this titration.

The ultraviolet-visible spectra of the acid and dibasic forms of 2-nitroso-1-naphthol-4-sulfonic acid were determined for aqueous solutions.

The infrared spectrum of several portions of air dried 2-nitroso-1-naphthol-4-sulfonic acid were determined. The potassium bromide pellet press was out of commission at the time and hence it was necessary to use a nujol mull.

Air dried 2-nitroso-1-naphthol-4-sulfonic acid was sent to a commercial laboratory (Weiler and Strauss, Oxford) for elemental analysis.

5. Results

The values of the melting points obtained, along with literature values and references, are given in Table 2.

Upon drying the air dried 2-nitroso-1-naphthol-4-sulfonic acid to constant weight at 110° over a period of 15 hours, samples of 0.8345, 0.7934 and 0.9306 g. lost 0.1628, 0.1550 and 0.1830 g., respectively. Respective values of 19.51,

Table 2. Melting points

Substance	Experimental value	Literature value	Reference
2,4-dinitro-1-naphthol	138	138, 138.5	15, 34b
2-nitroso-1-naphthol-4-sulfonic acid (air dried)	240-245 d.		
p-tolyl-ammonium chloride	243	243	34a
p-tolyl-ammonium 1-naphthol-4-sulfonate	196	196	29, 34b

19.54 and 19.67 per cent were obtained. The average value of 19.57 agreed with the value of 19.44 obtained by Witt and Kaufmann (62), but is low compared to 19.94 for 3½ molecules of water. During the process of drying, the organic substance changed in color from a golden-yellow to an orange-brown, with the brown color being predominate upon the surface of the material and indicating possible decomposition.

Nitrogen determinations upon this material that had been dried to constant weight at 110° gave values of 5.27, 5.40, 5.31 and 5.38 per cent N, with an average value of 5.34 per cent N. Nitrogen determinations upon the air dried material, but calculated for 19.57 per cent loss on drying at 110°, gave values of 5.24 and 5.37 per cent N, with an average value of 5.31 per cent N. An average of 5.33 per cent N was obtained for the six determinations. Witt and Kaufmann (62) obtained 5.39. Comparison of the results of the determinations in this work with the results obtained by Witt and Kaufmann clearly indicated that this is the same substance with which Witt and Kaufmann worked. These same results, however, indicated that since the theoretical value for the per cent N in anhydrous 2-nitroso-1-naphthol-4-sulfonic acid is 5.53 that neither the material in this work nor the material of Witt and Kaufmann that was dried to constant weight at 110° was the anhydrous material.

The results of a titration with standard base of the material (0.6745 g.) that had been dried to constant weight at 110° verified this. The sodium hydroxide solution used in the titration was 0.09868 N (average of 6 values with standard deviation of 0.64 parts per thousand gave 0.09702 for the standard hydrochloric acid). The titration curve, given as Figure 7, had two distinct breaks showing that the acid was dibasic. The first end-point, the second end-point and the difference between the first end-point and the second end-point gave values of 263.4, 263.8 and 264.2, respectively, for the molecular weight. The average value of 263.8 deviated by only 1.6 from the theoretical value of 262.2 for a hydrate containing one-half molecule of water of hydration, and showed that the air dried 2-nitroso-1-naphthol-4-sulfonic acid occurs as a tetrahydrate. The first break was that of a strong acid, while the second one was for a weak acid with $pK_{a2} = 6.36$.

The presence of one-half of a molecule of water of hydration in the material dried to constant weight at 110°, lowered the theoretical value for the per cent N to 5.32 which agreed very well with the average value of 5.33 obtained experimentally. Comparison of the analytical results obtained by Witt and Kaufmann (62) with theoretical values calculated on the basis of this partial hydration showed closer agreement in all cases.

Attempts to prepare anhydrous 2-nitroso-1-naphthol-4-sulfonic acid by drying at 110° failed. The material ap-

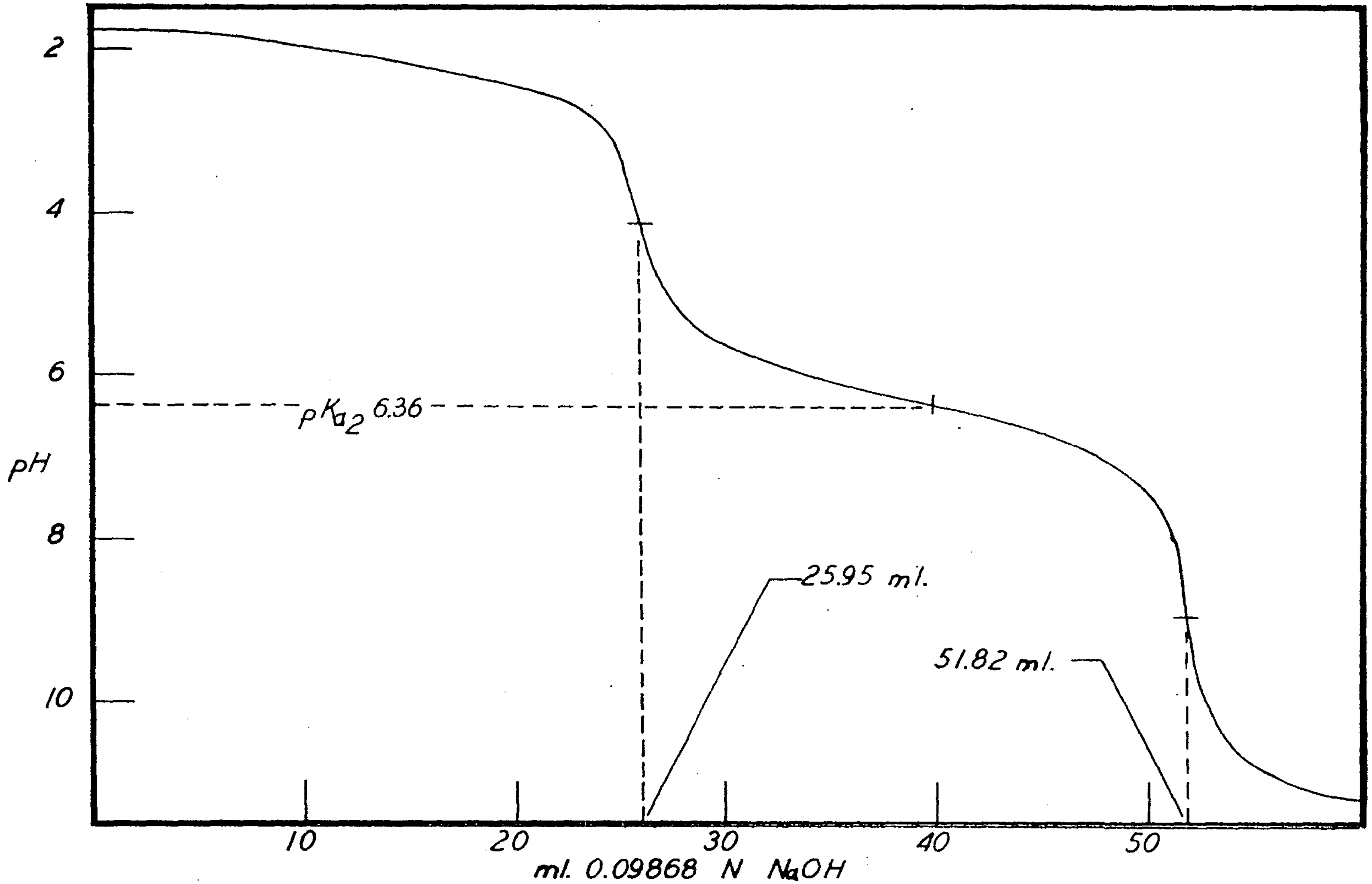


FIGURE 7. TITRATION WITH BASE OF 2-NITROSO-1-NAPHTHOL-4-SULFONIC ACID DRIED AT 110°

preciably decomposed if the drying proceeded over a period of time longer than about 18 hours. Over a 3 day period, the material became very brown in color and lost about 25 per cent of its weight. When the drying was done in a vacuum oven under low pressures obtained from the use of an aspirator, the results were similar. Titration of this dried brown colored material with standard base, yielded a titration curve of shape similar to the curve obtained above in Figure 7, but the position of the end-points showed that both of the acid functional groups on the organic substance had been partially decomposed. Both end-points occurred early, yielding high values for the equivalent weight and showing that decomposition had taken place. A larger volume of titrant was used between the start of the titration and the first end-point than was used between the first end-point and the second end-point. Thus the -OH group was decomposed to a greater extent than the $-SO_3H$ group. A value of 6.35 was determined for pK_{a2} from this titration.

Anhydrous 2-nitroso-1-naphthol-4-sulfonic acid was obtained by drying the air-dried substance over anhydrous magnesium perchlorate in an aspirator evacuated vacuum desiccator. A 1.2520 g. sample of the air dried 2-nitroso-1-naphthol-4-sulfonic acid lost 0.2747 g. in 2 and ½ months and another 0.0012 g. in 3 more months, for a total of 0.2759 g. This was a weight loss of 22.04 per cent. Theoretically the tetrahydrate to 2-nitroso-1-naphthol-4-sulfonic acid contains 22.15 per cent water. During this period of drying lasting more than 5 months, the organic material changed from its characteristic golden-yellow color to a beautiful orange-red without a trace of brown. Apparently no decomposition took place during the drying.

The titration curve obtained while following the titration of a portion (0.9495 g.) of this nearly anhydrous 2-nitroso-1-naphthol-4-sulfonic acid with standard base was found to be very similar in shape to the one in Figure 7. The sodium hydroxide solution was 0.1209 N (average of 6 values with a standard deviation of 1.4 parts per thousand; gave 0.09712 for the standard hydrochloric acid). The first end-point, 30.76 ml., the second end-point, 61.62 ml. and the difference between the first end-point and the second end-point gave values of 255.3, 254.5 and 254.9, respectively, for the molecular weight. The average value was 254.9. When this value was multiplied by the factor (100.00 - 22.15)/(100.00 - 22.04) to account for the incomplete drying, a corrected value of 254.5 was found, which varied from the theoretical value of 253.23 by only 5.1 parts per thousand. From the titration curve, $pKa_2 = 6.37$.

More evidence for the existence of the air dried form of 2-nitroso-1-naphthol-4-sulfonic acid as the tetrahydrate was found through the titration of the air dried material (0.8814 g.) with sodium hydroxide. The same 0.1209 N solution was used again. The titration curve of the tetrahydrate was characterized by two well defined breaks as is shown in Figure 8. The first end-point (22.32 ml.), the second end-point (44.78 ml.) and the difference between the first end-point and the second end-point gave values of 32.6, 324.6 and 325.6, respectively, for the molecular weight of the air dried material. The theoretical value for the tetrahydrate is 325.3. Thus, the average experimental value, 325.6, varied by only 0.9 parts per thousand from the theoretical value. From this titration curve, $pKa_2 = 6.24$. An attempt to repeat this titration in the presence of enough potassium chloride to maintain a 0.100 M solution failed when the potassium salt of 2-nitroso-1-naphthol-4-sulfonic acid was found to be insoluble in the solution.

Titration of the air dried 2-nitroso-1-naphthol-4-sulfonic acid with titanium(III) chloride left little doubt but that the air dried material existed as the tetrahydrate. The titanium(III) solution used was 0.03291 N, while the iron(III) perchlorate solution used was 0.04007 N. Potassium thiocyanate was used as the indicator. Direct titration of a sample of the air dried material, 0.1419 g., with the titanium solution, using the disappearance of the color of the nitroso compound as the end-point, required 52.97 ml. titanium(III) chloride. Indirect titration of a sample of the air dried

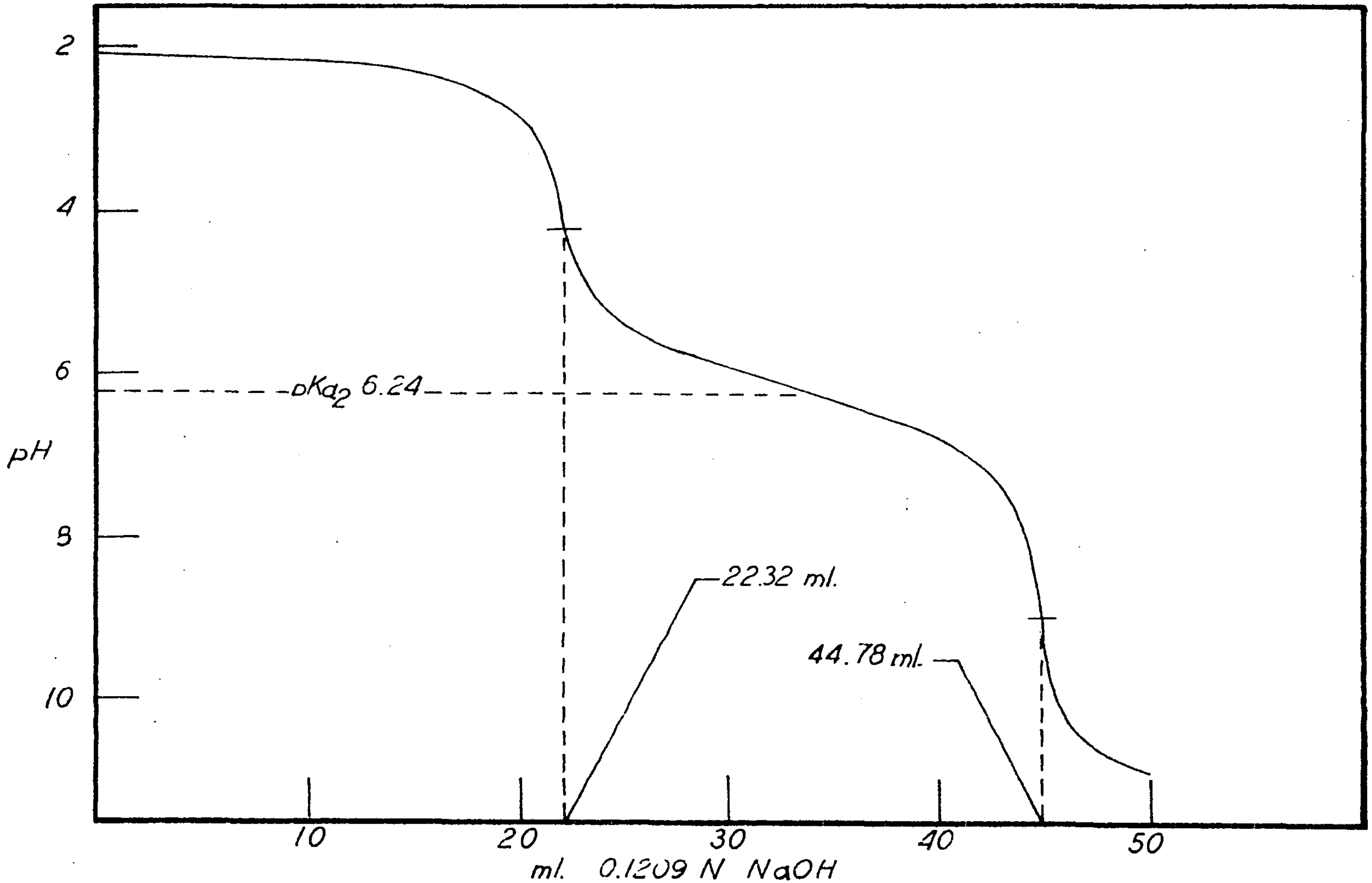


FIGURE 8. TITRATION WITH BASE OF 2-NITROSO-1-NAPHTHOL-4-SULFONIC ACID (AIR DRIED)

material, 0.1379 g., by the addition of excess titanium(III) chloride solution, 51.77 ml. total, and titration of the excess with the iron(III) perchlorate solution to the thiocyanate end-point, required 1.35 ml. iron(III) perchlorate. Assuming the air dried material to be the tetrahydrate with a molecular weight of 325.3, values for the per cent purity of the material were calculated to be 99.91 and 100.48, respectively. The average value, 100.2, deviated from the possible 100.0, by an error of only 2 parts per thousand.

The ultraviolet and the visible absorption spectra of 2-nitroso-1-naphthol-4-sulfonic acid and its disodium salt are given in Figure 9 and Figure 10, respectively. The solutions used to determine the spectra contained 1.703 mg. 2-nitroso-1-naphthol-4-sulfonic acid tetrahydrate/50 ml. (1.047×10^{-4} M). The disodium salt, the basic form, was prepared in solution by the addition of 3.00 ml. 0.1209 N NaOH (standardization results were given above) before the solution was diluted to a volume of 50.00 ml. The spectra were determined against deionized water blanks in matched 1.000 cm. silica cells. The wavelengths of maximum absorption and the molar absorptivities at those wavelengths are given in Table 3.

It can be seen from Figure 9, that the maximum absorption of the free acid at 261 millimicrons was partially retained in the spectrum of the disodium salt as a shoulder at 262

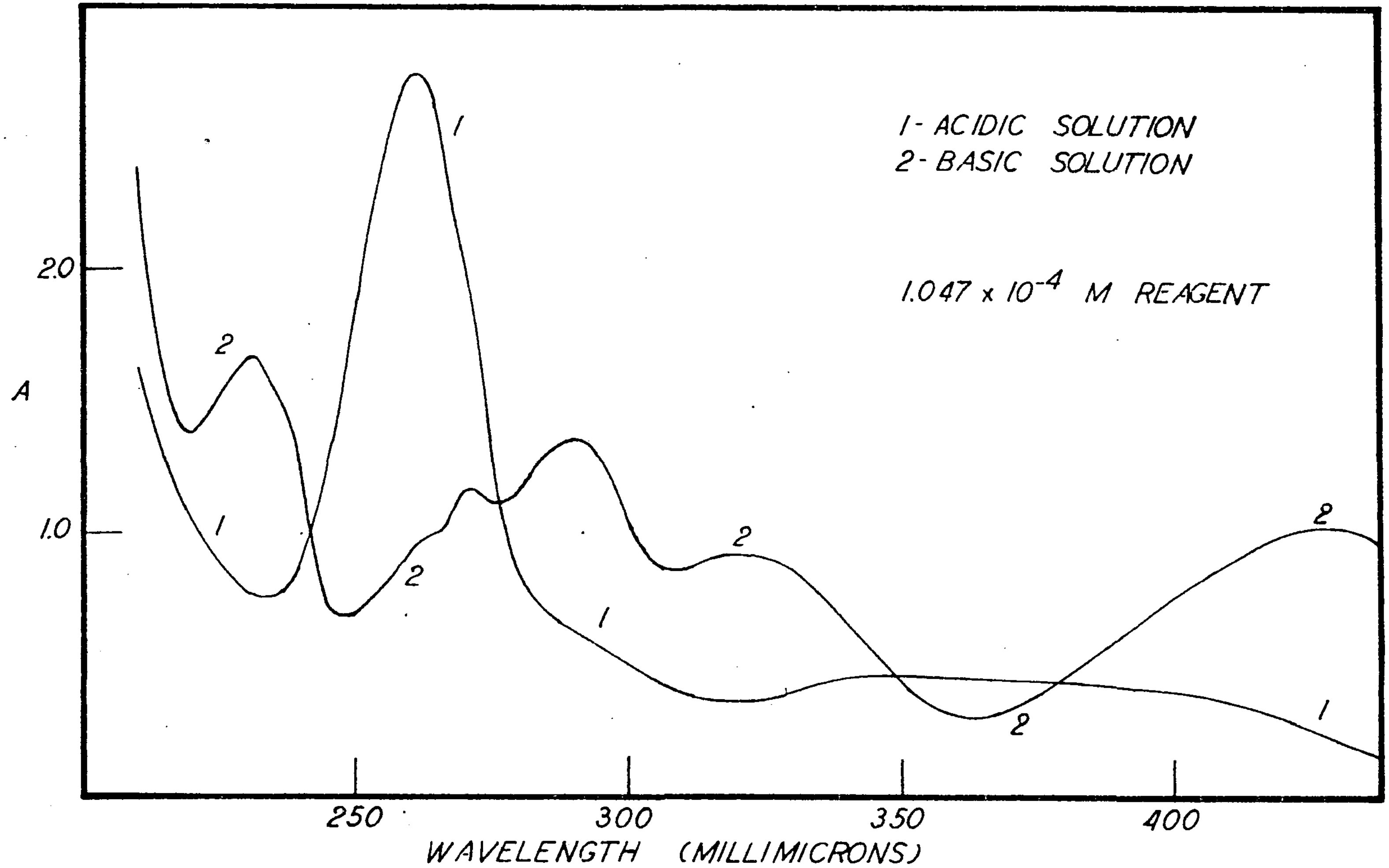


FIGURE 9. ULTRAVIOLET ABSORPTION SPECTRA OF 2-NITROSO-1-NAPHTHOL-4-SULFONIC ACID

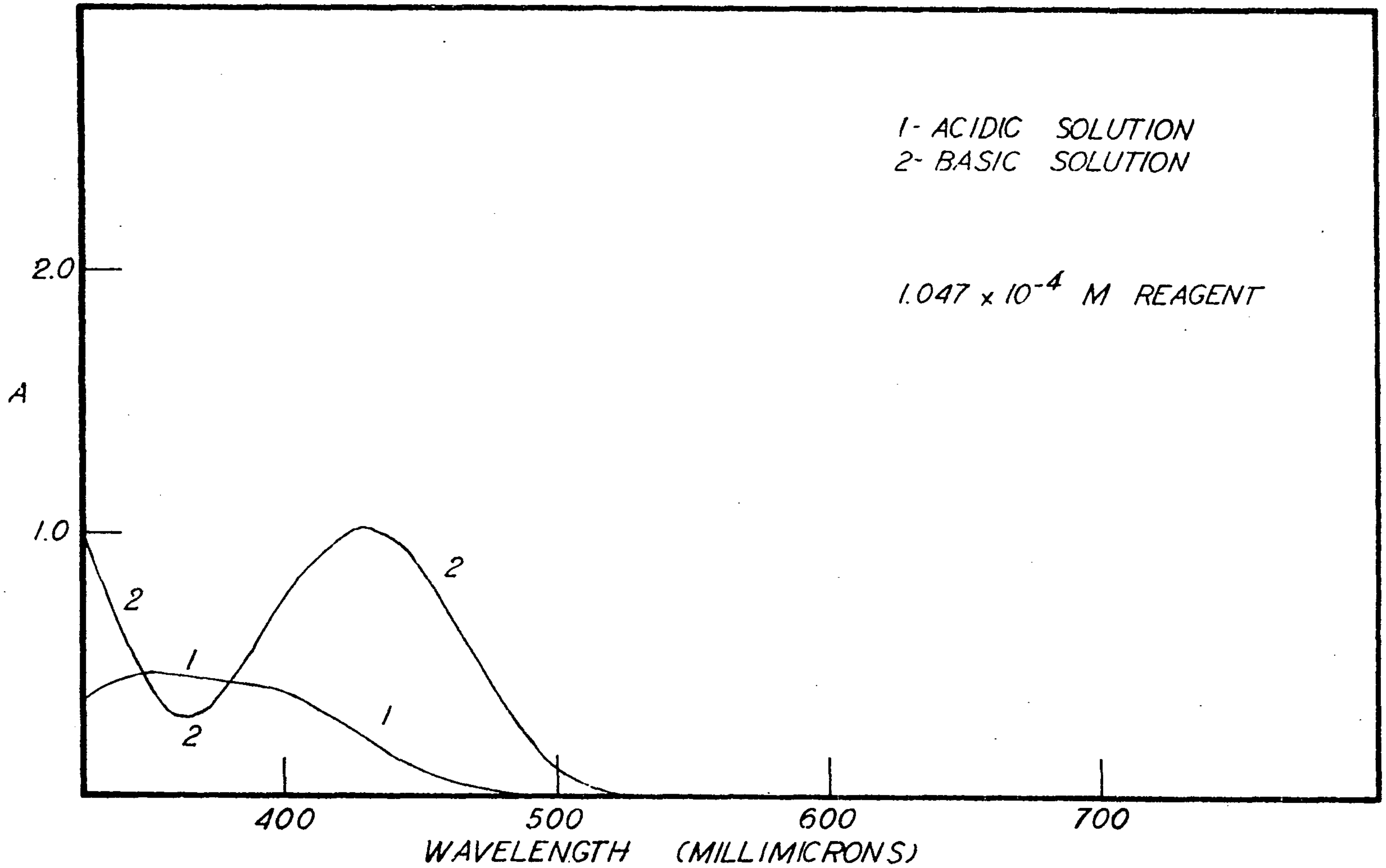


FIGURE 10. VISIBLE ABSORPTION SPECTRA OF 2-NITROSO-1-NAPHTHOL-4-SULFONIC ACID

Table 3. Absorption maxima in the spectra of 2-nitroso-1-naphthol-4-sulfonic acid

Free acid		Disodium salt	
Wavelength (millimicrons)	Molar absorptivity	Wavelength (millimicrons)	Molar absorptivity
261	26390	232	16050
347	4451	271	11200
		292	12950
		322	8885
		430	9866

millimicrons. This shoulder was evident in all spectra that were run of the disodium salt.

The values of the molar absorptivities given in Table 3 were obtained from Beer's Law plots. The spectra in Figure 9 and in Figure 10, were only several of the twenty-five spectra used to prepare the plots, in order to accurately measure the molar absorptivities. The values reported in Table 3 were considered accurate to 4 significant figures, since all measurements were made to that accuracy. The extent to which Beer's Law was obeyed at some of the wavelengths will be shown graphically in a following section of this dissertation.

The infrared spectrum of 2-nitroso-1-naphthol-4-sulfonic acid tetrahydrate was determined by using a nujol mull. It was necessary to compress only the wavelength scale of the original graph in order to obtain the spectrum as shown in

Figure 11.

The bands in Figure 11 at 3.4, 3.5, 6.9 and 7.3 microns are well known bands that can readily be assigned to nujol, a hydrocarbon mixture. The shorter wavelength bands can be considered to be due to the stretching of the C-H bonds, while the longer wavelength bands can be considered to be due to the bending of the C-H bonds. Similarly, the wide band at 2.9-3.3 microns has long been known to arise when water was present.

Colthup (19) has indicated that the band due to N=O stretching in nitroso compounds appeared at 7.1-7.6 microns. A band at 7.5 microns is evident in Figure 11. Colthup also assigned bands at 8.0-8.7, 9.3-9.9, and 14.3-16.7 microns to the sulfonic acid group. Bands are present in Figure 11 at 8.2, 8.5, 9.2, 9.4, 14.6 and 15.4 microns. Bellamy (2) made similar assignments for the sulfonic acid group.

Both Bellamy (2) and Colthup (19) assigned weak bands in the 6.1-6.7 micron region to aromatic carbon systems and to the -C=C- bond in particular. Bellamy indicated quite definitely that these bands were often undetected because of a stronger band due to water. Two weak bands are present in Figure 11, at 6.1 and 6.3 microns, while a much stronger band is present at 6.0 microns.

Colthup (19) assigned bands at 12.8-13.3 microns to 1-substituted naphthalene and bands at 11.6-12.5 and 13.1-13.9 microns to 2-substituted naphthalene. Bands are present

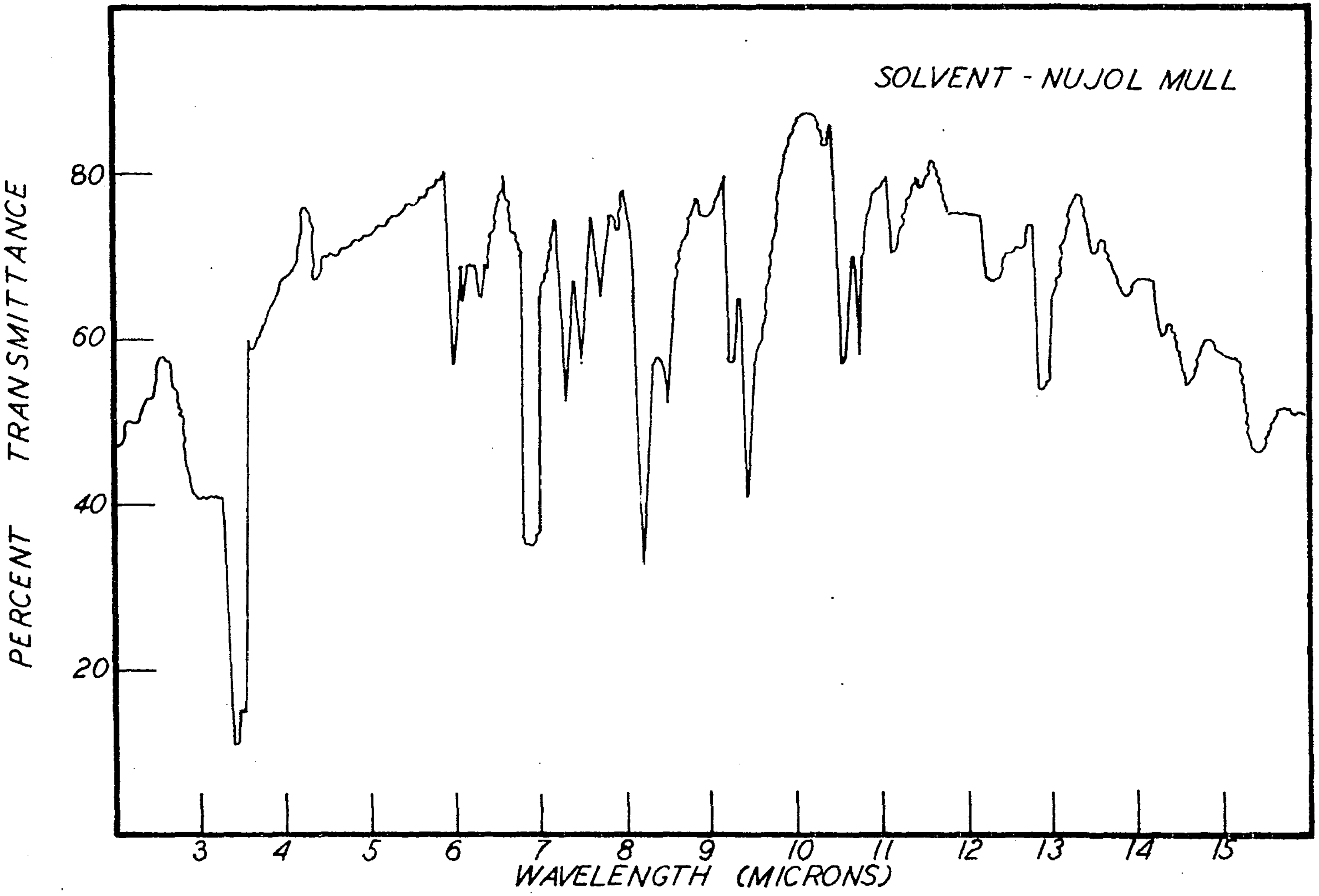


FIGURE 11. INFRARED SPECTRUM OF 2-NITROSO-1-NAPHTHOL-4-SULFONIC ACID TETRAHYDRATE

at 12.3, 12.6, 12.9, 13.5 and 13.9 microns, in Figure 11.

The results of the elemental analysis by the commercial laboratory gave further evidence for the existence of air dried 2-nitroso-1-naphthol-4-sulfonic acid as the tetrahydrate. Values of 37.37 for carbon and 4.69 for hydrogen were obtained. The tetrahydrate has theoretical values of 36.39 for carbon and 4.65 for hydrogen.

C. Determination of pKa_2

1. Method of approach

An accurate measurement of the ionization constant of an acid requires accurate control of temperature, ionic strength and purity of the reagents. The temperature is readily controlled by a good constant temperature bath. Similarly the purity of reagents can be affirmed by analytical methods. However, the control of ionic strength is difficult in the usual potentiometric titration used for the measurement of acid ionization constants. In addition, the ionization of the untitrated acid is neglected, which yields low results for the determination of the value of an ionization constant. Hence, it was decided to use a spectrophotometric method in this work.

A rapid search of the literature yielded no suitable monobasic acid or monoacidic base (1), except hydroxylamine, that had been used in a buffer system at pH 6.3, the approximate value of the pKa_2 of 2-nitroso-1-naphthol-4-sulfonic acid. Hydroxylamine was eliminated as a possibility for use in a buffer because it might oximate the quinone-oxime tautomer.

It was felt that a highly halogenated phenol might be a suitable acid. 2,4,6-Trichlorophenol was chosen for several reasons. It was appreciably water soluble. It had been studied more extensively than others. Last, but not least, the acid ionization constant would probably be of the correct order. Literature values varied from 1.1×10^{-7} (32) to 3.16×10^{-6} (48), with many values falling in between (40, 54, 55).

As was to be expected, the literature revealed that an acid-base indicator was no available for titration of 2,4,6-trichlorophenol, or a buffer mixture of it and its salt, with standard base. A suitable indicator, a methylated derivative of phenolphthalein, was prepared.

Then, using standard spectrophotometric methods, the acid ionization constant of 2,4,6-trichlorophenol was determined using a hydroxylamine-hydroxylammonium chloride buffer system. In turn, the second acid ionization constant of 2-nitroso-1-naphthol-4-sulfonic acid was determined using 2,4,6-trichlorophenol and its sodium salt as the buffer system. All measurements were made in aqueous solution, at constant ionic strength and at constant temperature.

2. Reagents

Many of the reagents previously described in this dissertation were used in this portion of the study.

The 2,4,6-trichlorophenol used was Eastman Kodak "white label" grade, catalog #1469.

The slightly impure, commercial 2,4,6-trichlorophenol was purified by sublimation. The sublimed material was both dried and stored over anhydrous magnesium perchlorate.

The thymolphthalein used was borrowed as a 1 per cent ethanol solution from the sophomore quantitative analysis laboratory.

The 2,3-dimethylphenol used was obtained from the K and K Laboratories, Inc., Long Island City 1, New York. It was from lot #10437. The material was sublimed for purification. The melting point, 74°, and the boiling point, 213°, agreed identically with those in the literature (33).

Reagent grade stannic chloride (anhydrous), sodium bicarbonate, sodium carbonate, hydroxylammonium chloride, silver nitrate, potassium dihydrogen phosphate, disodium hydrogen phosphate (anhydrous powder), and sodium tetraborate decahydrate were used.

The 2,2',5,5'-tetramethylphenolphthalein was prepared by a published method (53). Both the 2,5-dimethylphenol (m.p. 76°) and the o-phthalic anhydride used (m.p. 132°) were shelf chemicals of unknown sources. The stannic chloride was removed from the raw product by extracting the product from an ice cold hydrochloric acid solution with diethyl ether. The material was recrystallized from tetraline and also from ethyl alcohol-water solutions. The experimental value of the melting point, 285.5-7°, agreed with the highest of the ones reported in the literature, 276° (53) and 286-7° (26).

The dichlorofluorescein used was borrowed as a 0.1 per cent solution from the sophomore quantitative analysis laboratory.

The hydroxylammonium chloride, $NH_2OH \cdot HCl$, was purified by recrystallization from dilute aqueous hydrochloric acid solutions. After the material had been washed with ethanol and dried for 30 minutes at 110°, it was stored over anhydrous magnesium perchlorate.

A 0.1 M silver nitrate solution was prepared by dissolving the solid, 17.0 g., in water and diluting the resulting solution to a volume of one liter with deionized water.

The 0.1000 M potassium chloride solution was prepared in large quantities. Several samples of dried potassium chloride, 7.456 g., were each dissolved in separate portions of deionized water. The resulting solutions were diluted to volumes of 1 liter and were then combined in a large polyethylene bottle.

A saturated solution of potassium chloride was prepared by dissolving the solid in hot deionized water. Enough was dissolved so that upon cooling, some of the material crystallized from the solution.

The strong base, anion exchange resin, Amberlite IRA-410 was used. The particular portion of resin had been cycled numerous times between the Cl^- and OH^- forms. In this work it was used in the OH^- form. A 100 ml. buret was used to hold the resin.

A solution of 0.100 M potassium hydroxide in 0.1000 M potassium chloride was prepared. A sample of previously dried potassium chloride, 7.4555 g., was dissolved in deionized water. The solution was then passed into the ion exchange column containing the Amberlite IRA-410 ion exchange resin in the OH^- form. The eluate was caught in a 1 liter volumetric flask as soon as it was faintly basic. The column was thoroughly washed with several small portions of deionized water. Then a portion of the dried potassium chloride, 7.6568 g., was added to the flask. The resulting solution was diluted to volume and made homogeneous. Using this solution as the titrant, a sample of dried potassium hydrogen phthalate, 0.8897 g., was titrated to the phenolphthalein end-point, 43.82 ml. being required. The solution was found to be 0.09942 N in KOH.

The stock solution of 2,4,6-trichlorophenol used in this study to determine the extent to which 2,4,6-trichlorophenol obeyed Beer's Law was prepared as follows: The purified 2,4,6-

trichlorophenol, 0.2148 g. = 1.09 moles, was suspended in 0.1000 M potassium chloride solution and then dissolved by the addition of 31.0 ml. (3.10 mmoles) of 0.100 M potassium hydroxide (in 0.1000 M potassium chloride). The resulting solution was diluted to a volume of 1 liter using 0.1000 M potassium chloride. The solution was 0.0020 M in potassium hydroxide.

A National Bureau of Standards standard buffer solution for pH 6.86 was prepared as described in the literature (1). Potassium dihydrogen phosphate, 3.4023 g., and disodium hydrogen phosphate, 3.5505 g., were dissolved in deionized water. The resulting solution was diluted to a volume of 1 liter with more deionized water. The phosphate salts had previously been dried at 115° for 4 hours and had been stored over anhydrous magnesium perchlorate. This solution, 0.02500 M KH_2PO_4 and 0.02500 M Na_2HPO_4, has been defined to have a pH_s 6.86 at 25°. This buffer solution was stored such that its temperature remained near 25°.

A National Bureau of Standards standard buffer solution for pH 9.18 was prepared as described in the literature (1). Sodium tetraborate decahydrate, 3.8144 g., was dissolved in deionized water and the resulting solution was diluted to a volume of 1 liter with more deionized water. This 0.01000 M $Na_2B_4O_7 \cdot 10H_2O$ solution has been defined to have a pH_s 9.18 at 25°. This buffer solution was stored such that its temperature stayed near 25°.

The buffer solution of hydroxylammonium chloride was prepared following the practice of Bates (1). Purified hydroxylammonium chloride, 3.4753 g., and potassium chloride, 3.7280 g., were dissolved in deionized water and the resulting solution was diluted to a volume of 1 liter with deionized water. The resulting solution was 0.05000 M in both KCl and $NH_2OH \cdot HCl$ and had an ionic strength of 0.1000.

Each of the stock solutions of 2,4,6-trichlorophenol used in the determination of the pK_a of 2,4,6-trichlorophenol was prepared to be 0.1000 M in potassium chloride. The weighed, purified 2,4,6-trichlorophenol was dissolved in a measured volume of 0.100 M potassium hydroxide (in 0.1000 M potassium chloride), using a very slight excess. Separately, a weighed amount of potassium chloride (dried at 110°) was dissolved in deionized water. The two solutions were combined and the resulting solution was diluted to a volume of 1 liter with deionized water. The weight of 2,4,6-trichlorophenol, the volume of 0.100 M potassium hydroxide, and the weight of potassium chloride used, respectively, for each of the solutions prepared follow: for the study at 312 mμ., 0.3871 g., 20.00 ml., and 7.3069 g.; for the study at 286.5 mμ., 0.8294 g., ml., and 7.1425 g.; for the study at 246 mμ., 0.2106 g., 11.00 ml., and 7.3733 g.

The buffer solution of 2,4,6-trichlorophenol was prepared following the practice of Bates (1). Sublimed, dried 2,4,6-trichlorophenol, 3.8499 g., was dissolved in 200.0 ml. of 0.100 M potassium hydroxide (in 0.1000 M potassium chloride) and solid potassium chloride, 0.7455 g., was added to the mixture. After the solid had dissolved, the solution was diluted to a volume of 500 ml. with deionized water. The resulting solution was 0.04000 M in potassium 2,4,6-trichlorophenolate and 0.06000 M in potassium chloride and had an ionic strength of 0.1000.

The stock solution of 2-nitroso-1-naphthol-4-sulfonic acid used in this study to determine the extent to which 2-nitroso-1-naphthol-4-sulfonic acid obeyed Beer's Law was prepared by dissolving 2-nitroso-1-naphthol-4-sulfonic acid tetrahydrate, 0.1703 g., in deionized water and diluting the resulting solution to 1 liter using deionized water.

A solution that was 0.1000 M in both potassium chloride and hydrochloric acid was prepared. A portion of potassium chloride, 14.9113 g., which had been dried at 110°, was dissolved in deionized water. To this solution was then added 16.7 ml. of concentrated (37%) hydrochloric acid, after which the solution was diluted to a volume of 2 liters. Titration of an aliquot proved that the solution was more than 0.1000 M in hydrochloric acid. It was diluted a calculated amount with 0.1000 M potassium chloride. A 50.00 ml. aliquot of this solution, titrated with 0.12092 N sodium hydroxide (average of 6 values with standard deviation = 1.4 parts per thousand, gave 0.09712 for N hydrochloric acid) to the phenolphthalein end-point, required 41.32 ml. of the base. The solution was calculated to be 0.09994 M in hydrochloric acid.

The stock solution of 2-nitroso-1-naphthol-4-sulfonic acid used in the determination of pK_{a2} by following the spectra at 362 mμ. was prepared by dissolving the tetrahydrate of the nitroso compound, 0.6761 g., and previously dried potassium chloride, 7.3725 g., in water and diluting the resulting solution to a volume of 1 liter with deionized water. This solution had an ionic strength of 0.100.

A similar stock solution was prepared for the study at 428 mμ. This solution was prepared from 2-nitroso-1-naphthol-4-sulfonic acid tetrahydrate, 0.3072 g., and previously dried potassium chloride, 7.4563 g. This solution also had an ionic strength of 0.100.

3. Equipment

Much of the equipment used has been previously described in this dissertation.

Special emphasis was placed upon the cleaning of the volumetric flasks. After the usual cleaning procedure, described earlier, the volumetric flasks were rinsed with distilled water, by inverting them over a glass tube through which the distilled water was cascaded.

The constant temperature bath used was a Sargent bath, Catalog Number S-84805. The bath could be regulated to control to within 0.01°. The bath was used without the cooling coil. It was maintained at 25.0°, throughout these studies. Water was used in the 16 in. diameter jar. The temperature of the room was partially controlled and there was no difficulty in controlling the temperature of the bath. Room temperature did not vary far from 25°.

The solutions were held in the constant temperature bath in the flasks in which they were prepared. Portions of the solutions were transferred to 30 x 80 mm. weighing bottles, that had the ground surface on the outside of the main body of the bottle, previous to the time when pH measurements were made. The weighing bottles rested on individual racks that were in turn attached to the side of the water bath.

A sleeve type saturated calomel electrode was used as a reference electrode in conjunction with the Beckman Model G pH meter. The saturated potassium chloride solution was replaced every time a new series of measurements was begun.

No particular effort was made to use a glass electrode that would be effected only slightly by sodium ion at high pH. The glass electrode used however was required to meet the following test. After the pair of electrodes was thoroughly rinsed with deionized water, and the pH meter was "on" for 30 minutes, the pH meter was standardized with the N.B.S.

phosphate buffer at pH 6.86. This was done by immersing the pair of electrodes in about 20 ml. of the pH 6.86 buffer, and then adjusting the "zero". The solution was discarded and the beaker was refilled, without rinsing either the pair of electrodes or the beaker. The "zero" was adjusted if necessary. The electrodes were then immersed in another portion of the same buffer, which had been equilibrated in the constant temperature bath. As soon as equilibrium was reached, in a minute or so, a final adjustment was made on the zero.

The pair of electrodes was removed from the previous solution, sprayed with deionized water, immersed in two portions of deionized water, and finally wiped free of excess liquid with a Kleenex. The pair of electrodes was then immersed in a 20 ml. portion of the pH 4.01 buffer and the pH recorded as "trial 1". Without rinsing the pair of electrodes was immersed in another portion, the pH was measured and recorded as "trial 2". The pair of electrodes was then immersed in a third portion of the pH 4.01 buffer, which had been equilibrated in the constant temperature bath, the pH measured and recorded as "trial 3".

The pH of the borate buffer was similarly measured. The pair of electrodes was rinsed, wiped free of excess liquid, and the pH of three portions of the pH 9.18 buffer was carefully measured, the last measurement carefully made at constant temperature.

The measured pH of the pH 4.01 buffer and the measured pH of the pH 9.18 buffer had to agree within 0.01 unit of the standard value in order for the glass electrode to be satisfactory.

4. Experimental procedure

Most of the analytical methods used have previously been described.

The feasibility of 2,4,6-trichlorophenol for use as a weak acid-alkali salt buffer was first proven. The commercially available material was titrated potentiometrically with standard base.

In order to show that sublimation was a suitable means of purifying the commercially available 2,4,6-trichlorophenol, the dried, sublimed material was titrated potentiometrically with standard base.

Attempts to locate a suitable visual acid-base indicator for the titration of 2,4,6-trichlorophenol with standard base were at first not very fruitful. Samples were dissolved in 100 ml. of 50% ethyl alcohol, indicator added and the solutions titrated. Additional water was added, such that the total volume was about 300 ml. at the end-point. Phenolphthalein, thymolphthalein and 2,2',5,5'-tetramethylphenolphthalein were unsuitable, even when the solvent was varied from 100% water to 100% alcohol. The solvent had almost no effect upon the calculated results. Results, as % purity, were low for the former indicator and high for the latter indicator, although not quite as high as for thymolphthalein. It was then decided to prepare 2,2',3,3'-tetramethylphenolphthalein (3,3-bis-(4-hydroxy-2,3-xylyl)phthalide). The International Critical Tables indicated that it had a color change from colorless to blue at pH of about 9.0. A reference (22) was listed. A look at the paper revealed nothing more than was already mentioned, except that its preparation was given in an Austrian Patent (21). The patent gave nothing that aided in the preparation. A search of the literature revealed no other mentions of 2,2',3,3'-tetramethylphenolphthalein.

The preparation of 2,2',3,3'-tetramethylphenolphthalein: A mixture of 2,3-dimethylphenol, 6.11 g. = 0.050 mole, and o-phthalic anhydride, 3.7 g. = 0.025 mole, was treated in a 100 ml. round bottomed flask with anhydrous stannic chloride. The mixture was refluxed for 5 hours. A red colored solution and a dark solid formed during this process. The ice cold mixture was extracted with many small portions of an ice cold mixture of 1:1 hydrochloric acid and diethyl ether. The polymeric by-product was filtered from the liquids before they were separated, the product remaining in the ether. The ether layer was extracted three times with each of the following solvents: dilute hydrochloric acid, water, dilute sodium bicarbonate and finally dilute sodium bicarbonate-sodium carbonate with pH 9. The latter solution was used until the aqueous layer remained nearly colorless. It was necessary to repeat the filtration of the polymeric by-product from the solutions from time to time. The indicator was then extracted into a dilute sodium hydroxide solution, to separate it from colored neutral organic material. The sodium hydroxide extract was acidified with hydrochloric acid and the indicator extracted back into diethyl ether. The ether solution was allowed to evaporate to dryness. The unreacted 2,3-dimethylphenol was sublimed from the brown solid and identified by its melting point (74°). The brown solid remaining was recrystallized from carbon tetrachloride and from ethanol-water mixture. A tan product, 1 g., resulted that melted about 275°, but which was probably slightly impure.

A portion of the tan 2,2',3,3'-tetramethylphenolphthalein dissolved in ethanol, yielding a 0.1% solution. This solution was used to supply the indicator for the following titrations.

The suitability of 2,2',3,3'-tetramethylphenolphthalein as an indicator for the titration of 2,4,6-trichlorophenol was studied in two different experiments. The first experiment that was run, involved a straight forward titration of samples of sublimed 2,4,6-trichlorophenol with standard base. A sample was dissolved in 50 ml. of ethanol and an equal volume of water was added. Several drops of the above mentioned indicator solution were added and the titration was begun. As soon as it was possible to add it, without precipitating the phenol, 100 additional ml. of water was added. The approach of the end-point was very evident as is the case with phenolphthalein. A permanent faint blue was taken as the end-point.

The second portion of the study involved a potentiometric titration of 2,4,6-trichlorophenol with standard base, but in the presence of the indicator. The titration described in the previous paragraph was followed with a pH meter.

Since the assay of $NH_2OH \cdot HCl$ in reagent grade hydroxylammonium chloride was given as a minimum of 97%, it was first purified and then its chloride content was determined. The familiar adsorption indicator method was used. Samples of potassium chloride (dried at 110°), which was used as the primary standard, or the purified hydroxylammonium chloride were weighed and dissolved in deionized water. Dichlorofluorescein indicator solution, 10 drops, was added to each and the resulting solutions were titrated with the 0.1 M silver nitrate to a deep-pink end-point. A consistent blank was obtained, after a little practice.

The ultraviolet and visible absorption spectra of 2,4,6-trichlorophenol and its alkali metal salt were determined in aqueous solutions. The spectra were determined for both dilute and concentrated solutions. For the latter spectra, the useful wavelength range was determined over which a buffer solution of 2,4,6-trichlorophenol would function. The spectra were also determined in the presence of 0.1000 M potassium chloride.

The ultraviolet and visible absorption spectra of hydroxylammonium chloride in aqueous solution were also determined. Then, the spectra of solutions containing both hydroxylammonium chloride and 2,4,6-trichlorophenol, or its alkali metal salt, were determined.

The ultraviolet absorption spectrum of 2,4,6-trichlorophenol has been reported in the literature twice. In 1913, the spectra of the material in both the vapor phase and in solution, were reported (50). However, in this paper no relationship was given between the maxima and the wavelength. The second paper (16), was published in 1952, and reported the spectrum of an ethyl alcohol solution. One maximum was reported, which occurred at 2941 A with = 2900. The spectrum of 2,4,6-trichlorophenol in absolute alcohol was determined, to see if the reported spectrum could be duplicated.

It has long been known that phenols such as 2,4,6-trichlorophenol can be readily oxidized to quinones (43, 44). Partial oxidation results in polymer formation. The corresponding triiodophenol has been shown to undergo this same type of decomposition forming a red, polymeric, oxidized product (63) in a basic solution. A red impurity was found in the commercial 2,4,6-trichlorophenol used in this work. This then raised the question concerning the stability of basic solutions of 2,4,6-trichlorophenol. To test the stability of such solutions, one was prepared and its spectrum was determined numerous times over the following weeks.

One of the earliest papers, if not the first, to consider the determination of acid ionization constants through the utilization of the absorbance of the solutions appeared in 1926 (52). The authors, Stenstrom and Goldsmith, pointed out the fact that utilization of the method required that the colored species obeyed Beer's Law. In order to determine if 2,4,6-trichlorophenol and its potassium salt obeyed Beer's Law the spectra of two series of solutions, an acid series and a basic series, of various concentrations were measured. A plot of the data obtained then indicated the extent to which the system obeyed Beer's Law.

After the conditions had been determined under which 2,4,6-trichlorophenol and its potassium salt obeyed Beer's Law, the determination of the pKa of the phenol was done under the same set of conditions. Three independent measurements of the pKa were made. Each of the measurements was followed at a different wavelength and, of course, using different concentrations of the phenol. In all other aspects the three determinations were identical. They were made at an ionic strength of 0.1000 and at a constant temperature of 25.0°.

Into each of several 100 ml. volumetric flasks was pipeted a 25.00 ml. aliquot of the stock solution of potassium 2,4,6-trichlorophenolate and a 10.00 ml. aliquot of the hydroxylammonium chloride-potassium chloride buffer mixture. Either 0.0971 M hydrochloric acid or 0.100 M potassium hydroxide (in 0.1000 M potassium chloride) was then added to adjust the pH. Deionized water was also added to a strongly basic solution to control the ionic strength at 0.1000. Each solution was then diluted to volume, made homogeneous by shaking, and finally placed in the constant temperature bath.

Because of the instability of hydroxylamine in a basic solution, particularly with respect to its disproportionation into nitrogen and ammonia (46), it was necessary to use the prepared solutions as soon as they had reached constant temperature. After the zero line was adjusted on the spectrophotometer, a flask was removed from the constant temperature bath and was taken to the instrument. A portion was transferred to the thoroughly rinsed absorption cell and the spectrum run over the desired, short, wavelength range. A time of about 110 seconds was required to prepare the cell and run the spectrum. The flask was returned to the constant temperature bath and the next flask was taken. As a maximum the flask was out of the bath for only 8-9 minutes and most of this time the flask was at 25° since the temperature of the room containing the spectrophotometer varied from 74-78°F.

The measurement of the pH of the solution was done simultaneously with the determination of the spectra, following in every detail the procedure outlined previously for the measurement of the pH of one of the N.B.S. buffer solutions. At the time the solution was removed from the constant temperature bath, a portion was placed in a capped weighing bottle and returned to the bath. Another portion was placed in a small beaker and the pair of electrodes inserted into it. The spectrum was then run, and the solution that still remained in the flask was used to adjust the pH meter a second time before the pH of the solution in the weighing bottle was measured. Less than 10 minutes elapsed between the time the spectrum was run and the pH was accurately determined. The pH did not change during a further period of ten minutes.

The extent to which 2-nitroso-1-naphthol-4-sulfonic acid obeyed Beer's Law was determined. This study, however, was not done at constant ionic strength. From a stock solution, a series of solutions containing various known amounts of the nitroso compound was prepared and the spectrum of each solution was then determined. Similarly a second series was prepared, base added to each, and the spectrum of each was then determined. The change of absorbance with concentration was then graphed, and showed the extent to which the system obeyed Beer's Law.

After the conditions had been determined, under which 2-nitroso-1-naphthol-4-sulfonic acid and its dipotassium salt obeyed Beer's Law, the pKa_2 of the nitroso compound was measured. It was determined by following data obtained at the two useful wavelengths. The use of 2,4,6-trichlorophenol as a buffer prevented the full use of the ultraviolet region of the spectrum. Two independent measurements were made, each at a different wavelength, and each one using different concentrations of the nitroso compound. In all other aspects the two determinations were identical. They were made at an ionic strength of 0.1000 and at a constant temperature of 25.0°.

Into each of several 100 ml. volumetric flasks was pipeted a 25.00 ml. aliquot of the stock solution of 2-nitroso-1-naphthol-4-sulfonic acid and a 10.00 ml. aliquot of the 2,4,6-trichlorophenol-potassium chloride buffer mixture. Each flask was then nearly filled to the mark with 0.1000 M potassium chloride. To each flask was then added a measured portion of 0.1000 M hydrochloric acid (in 0.1000 M potassium chloride) or 0.100 M potassium hydroxide (in 0.1000 M potassium chloride) and a volume of deionized water. Since 2,4,6-trichlorophenol would precipitate from a strongly acid solution at the concentration used here, two other solutions were prepared containing 25.00 ml. of the solution of the nitroso compound (but no buffer) and several ml. of 0.0971 N hydrochloric acid. The flask was diluted to volume with 0.1000 M potassium chloride, made homogeneous by shaking, and finally placed in the constant temperature bath.

The spectrum of each of the solutions was run and the pH of each was measured as described above for the similar experiments on 2,4,6-trichlorophenol. However, the measurements were not made simultaneously. After all of the spectra had been determined, then all of the pH measurements were made.

5. Results

The titration of the commercially available 2,4,6-trichlorophenol proved the feasibility of its use in a buffer system of the necessary pH of about 6.2 for the determination of pKa_2 of 2-nitroso-1-naphthol-4-sulfonic acid. The purchased material, 0.9112 g., was titrated with standard, 0.1209 N NaOH (average of 6 values with standard deviation 1.4 parts per thousand; gave 0.09712 for N of the HCl). The sample completely dissolved before the end-point. The end-point, 38.39 ml., yielded an experimental value of 196.3 for the equivalent weight, compared to a theoretical value of 197.46, and showed the presence of impurities. The mid-point of the titration indicated the pKa of 2,4,6-trichlorophenol to be in the order of 6.25. The solution remained colorless to the eye during the titration.

The data obtained from the potentiometric titration of sublimed 2,4,6-trichlorophenol with standard base indicated its purity. A 50 per cent ethyl alcohol solution was used as the solvent in order to keep the halogenated phenol in solution. The sample, 1.0366 g., required 43.35 ml. of 0.1209 N NaOH (same as above). The experimental value, 197.7 ± 0.2, and the theoretical value, 197.5, obtained for the equivalent weight were in complete agreement.

The 2,2',3,3'-tetramethylphenolphthalein was obtained as a tan material in a very low yield (about 15 per cent). A study of various other conditions for the preparation can probably improve this yield. The relatively pure material dissolved readily in alcohol to give a pale yellow solution, which upon the addition of excess base became a pure, intense blue in color. The color change, that occurred under the conditions necessary for the titration of an acid with a base, was colorless to blue. The very dilute solution of the acid form was without any visible color.

The first six titrations of 2,4,6-trichlorophenol with standard base run, using 2,2',3,3'-tetramethylphenolphthalein as the indicator, are summarized in Table 4. The sodium hydroxide solution used was 0.12002 ± 0.00005 N (average of 8 values, with standard deviation of 0.45 parts per thousand). Results of such excellent agreement leave little doubt of the ease with which the end-points were detectable.

Table 4. Titrations of 2,4,6-trichlorophenol with standard base: 2,2',3,3'-tetramethylphenolphthalein as the indicator

Trial number	Weight 2,4,6-trichlorophenol g.	Base added ml.	Found 2,4,6-trichlorophenol %	Average and standard deviation
1	1.1587	48.93	100.07	
2	1.0013	42.29	100.09	100.12
3	0.7975	33.74	100.26	$\sigma = 0.09$
4	1.1059	46.76	100.29	or
5	1.1336	47.84	100.01	0.9 p.p.t.
6	0.9171	38.75	100.13	

The six titrations were run in a time span of about 30 minutes.

The accuracy of such titrations, using 2,2',3,3'-tetramethylphenolphthalein as the indicator was measured with the use of a potentiometric titration of 2,4,6-trichlorophenol in the presence of the indicator. The titration curve, which is very similar in all details to the ones mentioned earlier, was determined as shown in Figure 12. The break at the end-point, upon the addition of 0.10 ml. of the standard base, was slightly greater than 0.4 pH. The color change occurred during the addition of the first portion of this aliquot. The visual end-point thus agreed closely with the experimentally determined equivalence point. The latter value, 34.23 ml., gave a recovery or purity of 100.08 per cent, which was in good agreement with the average value of 100.12 ± 0.09 found

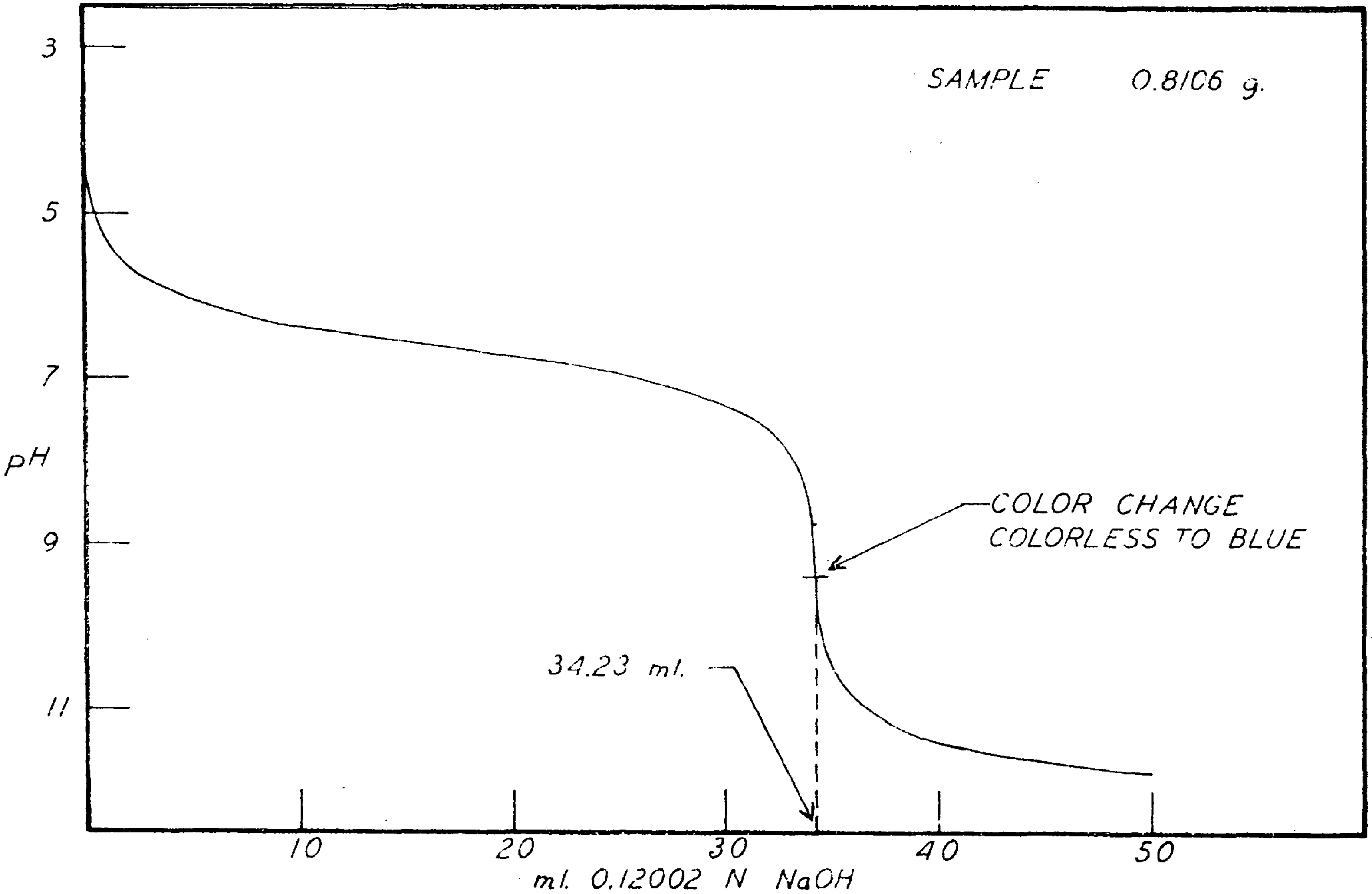


FIGURE 12. TITRATION WITH BASE OF 2,4,6-TRICHLOROPHENOL IN THE PRESENCE OF 2,2',3,3'-TETRAMETHYLPHENOLPHTHALEIN

by titration with the visual indicator.

The question arose, of course, as to whether or not a change in solvent from pure water to a high concentration of ethanol would change the results. The changes, if any, that arose during the use of phenolphthalein, thymolphthalein or 2,2',5,5'-tetramethylphenolphthalein were less than the experimental error in each case. Thus, if the ionization of the halogenated phenol and the indicator were effected at all near the end-point, by a change in solvent, the effects were of the same order and in the same direction. 2,2',3,3'-Tetramethylphenolphthalein would be expected to act similarly.

The results of the determination of chloride in hydroxylammonium chloride were obtained as given in Table 5. The results spoke for themselves and left little doubt of the "assay" of the purified hydroxylammonium chloride. Only this purified and analyzed material was used in the studies that followed.

The ultraviolet absorption spectra in aqueous solution of 2,4,6-trichlorophenol and its potassium salt were obtained as recorded in Figure 13. There was no absorption in the visible region. Curves 2 and 4 were obtained on 1.75×10^{-4} M solutions. The solution of the acid form contained a slight excess of hydrochloric acid, while the solution of the basic form contained a slight excess of potassium hydroxide. The free phenol was found to have two absorption maxima of nearly

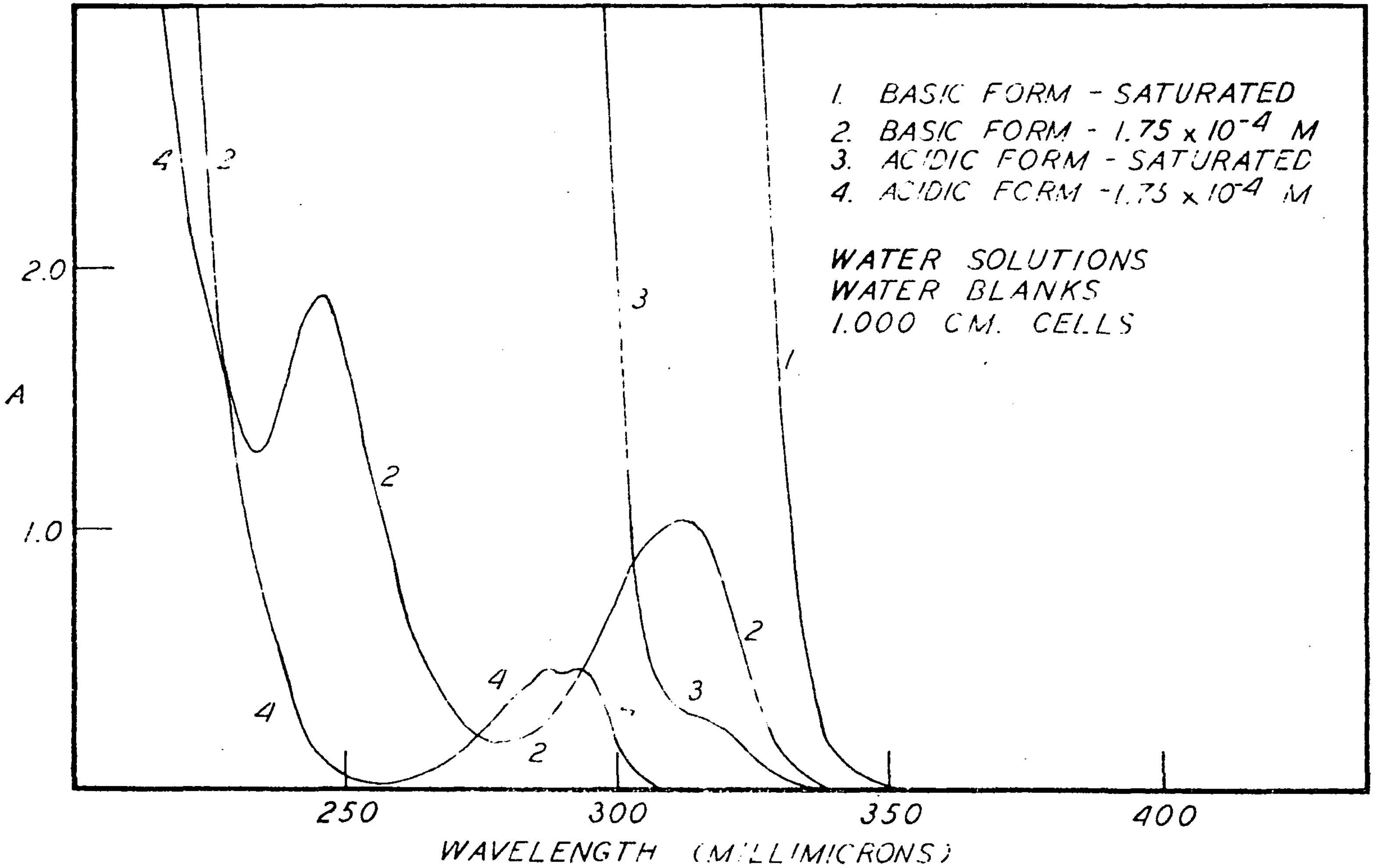


FIGURE 13. ULTRAVIOLET ABSORPTION SPECTRA OF 2,4,6-TRICHLOROPHENOL

Table 5. The determination of chloride in hydroxylammonium chloride

Trial number	Taken $NH_2OH \cdot HCl$ g.	Taken KCl g.	$AgNO_3$ ml.	Found $AgNO_3$ N	Average and standard deviation
1		0.3490	46.43	0.1008	
2		0.3410	45.37	0.1008	0.1009
3		0.3569	47.22	0.1014	$\sigma = 0.00023$
4		0.3615	48.18	0.1007	or
5		0.3420	45.15	0.1007	2.3 p.p.t.
6		0.3528	46.88	0.1009	
				Found $NH_2OH \cdot HCl$ %	
7	0.3177		45.40	100.2	100.15
8	0.3303		46.97	99.7	$\sigma = 0.30$
9	0.3201		45.81	100.4	or
10	0.3480		49.80	100.3	3.0 p.p.t.

equal intensity at 286.5 and 293 mμ., and a much stronger maximum just out of the range of the spectrophotometer on the short wavelength side. The basic form of the phenol, the potassium salt, also had two maxima, one at 246 mμ. and the other at 312 mμ., the former being the most intense. A third maximum was present at about 200 mμ., but its exact position was in doubt, because of its location near the limit of the spectrophotometer.

Curves 1 and 3 in Figure 13 were obtained on nearly saturated solutions of 2,4,6-trichlorophenol. Light absorption of the basic form began at 350 mμ., while the acid form started to absorb at 340 mμ. The useful region for absorption studies using 2,4,6-trichlorophenol as a buffer was thus found to be above 350 mμ., but extending all the way through the visible region of the spectrum.

The presence of hydroxylammonium chloride, as a 1 per cent solution, had no effect on the ultraviolet absorption spectra of 2,4,6-trichlorophenol and its sodium salt, except where the light absorption by the amine occurred below 240 mμ. This absorption was very slight, but indicated that hydroxylammonium chloride-hydroxylamine buffers can be used only above 240 mμ. The presence of potassium chloride in 0.1000 M concentration had no effect upon the spectra of hydroxylamine, hydroxylammonium chloride, 2,4,6-trichlorophenol and the sodium salt of the latter.

When absolute ethanol was used as the solvent, spectra similar to the ones reported in Figure 13 were obtained for the halogenated phenol. However, all of the maxima were shifted slightly to longer wavelengths and were more intense, when compared to those of aqueous solutions. For 2,4,6-trichlorophenol, maxima occurred at 290 and 297 mμ., with nearly equal molar absorptivities of 2.7 x 10^3. The maximum at 297 mμ., was less intense than the one at 290 mμ. by less than 1 part per hundred. The three maxima in the spectrum of the potassium salt of 2,4,6-trichlorophenol occurred at 319, 249 and 222 mμ. The latter two peaks were very intense. The molar absorptivity at 319 mμ. was found to be 5.4 x 10^3. As was to be expected, the solvent had some effect upon the absorption spectra, but the similarity of the spectra has shown similar species to be present in the two solvents, water and ethyl alcohol.

The solution used to measure the extent of the stability of basic aqueous solutions of 2,4,6-trichlorophenol contained 0.0722 g. of the free phenol per liter, and an excess of potassium hydroxide. The spectrum of the solution was run 5 times over a 7 week period, the duration of the study. The shape of the spectrum did not change during this time. The molar absorptivity at the absorption maximum at 312 mμ. was constant at 4.78 x 10^3, within the limits of the accuracy of reading the absorbance values. The potassium salt of 2,4,6-trichlorophenol was thus seen to be stable in basic aqueous solutions for at least 7 weeks.

The composition of the solutions used to determine the extent to which aqueous solutions of 2,4,6-trichlorophenol and its potassium salt obeyed Beer's Law are reported in Table 6. When the solutions were prepared, various portions of the stock solution of 2,4,6-trichlorophenol, 0.2158 g./liter, were placed in separate 50 ml. volumetric flasks. To the flasks

Table 6. Composition of the solutions used to determine Beer's Law data for 2,4,6-trichlorophenol

Free phenol			Potassium salt	
Solution number	Stock solution ml.	HCl ml.	Solution number	Stock solution ml.
1	48.00	2.00	11	24.00
2	45.00	2.00	12	21.50
3	40.00	2.00	13	18.00
4	35.00	2.00	14	15.50
5	30.00	2.00	15	13.00
6	25.00	1.00	16	10.50
7	20.00	1.00	17	8.00
8	15.00	1.00	18	6.00
9	10.00	1.00	19	4.00
10	5.00	1.00	20	2.00

indicated, 0.09702 N hydrochloric acid was added and then all of the flasks were diluted to volume with 0.1000 M potassium chloride. The absorption spectra of the solutions were then determined against a 0.1000 M potassium chloride solution as a blank.

Beer's Law plots prepared from the spectra of the solutions described in Table 6, were obtained as shown in Figure 14. At this concentration range, both 2,4,6-trichlorophenol and its potassium salt were found to obey Beer's Law at the 4 absorption maxima of their spectra, 246, 287, 293 and 312

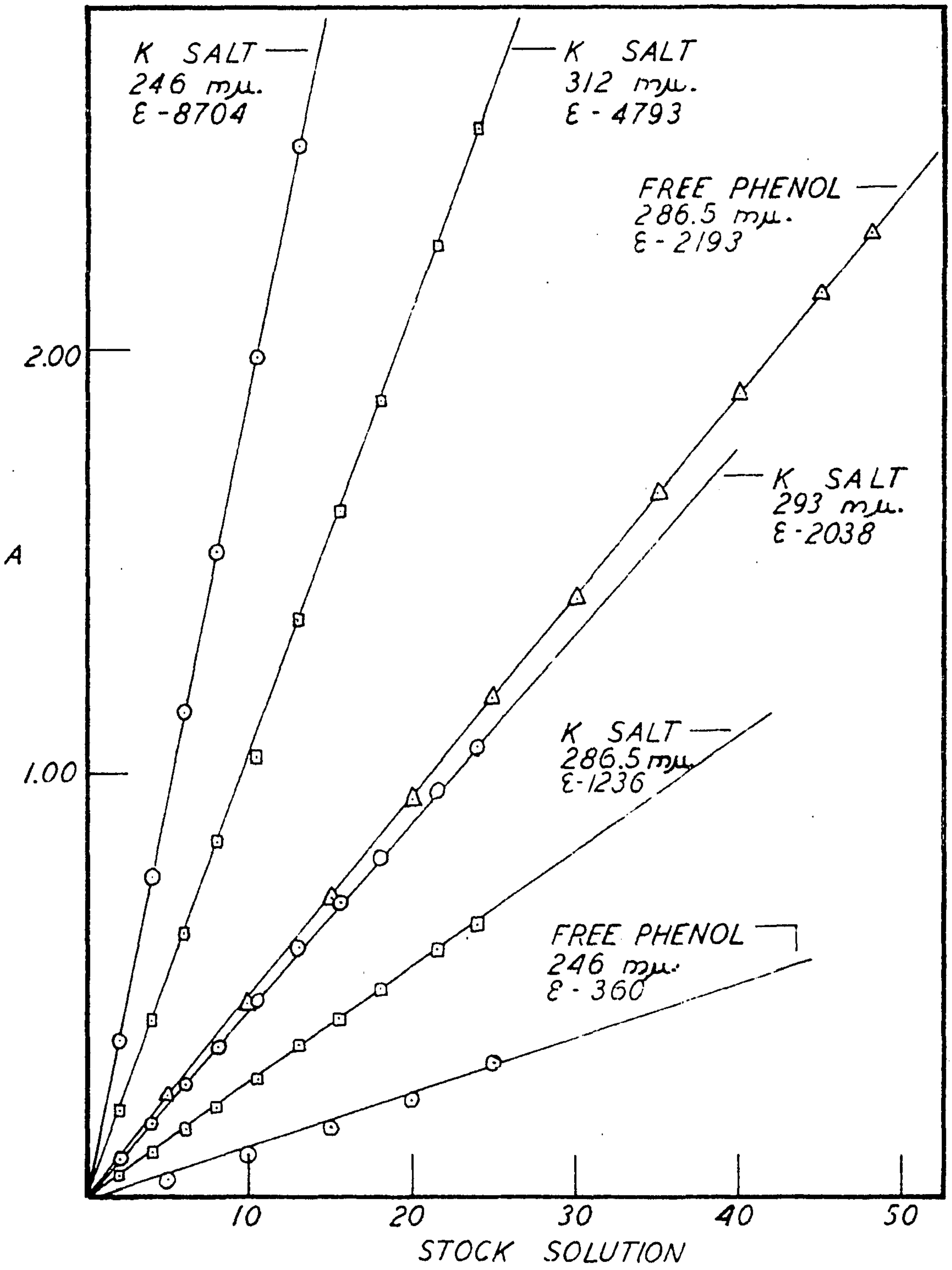


FIGURE 14. BEER'S LAW PLOTS FOR 2,4,6-TRICHLOROPHENOL AND ITS POTASSIUM SALT

mμ. At the concentration used, 2,4,6-trichlorophenol absorbed almost no light at 312 mμ., and hence no attempt was made to make a plot at that wavelength. Also, because of the large slope of the spectrum of 2,4,6-trichlorophenol at 246 mμ., the data for the phenol were scattered, but left little doubt but that it obeyed Beer's Law. At 293 mμ., the Beer's Law plot for the free phenol was found to be almost identical with the one at 287 mμ. The slope was slightly less, yielding $\varepsilon = 2170$. All of the ε values given were calculated from the slopes of the corresponding lines.

Careful examination of the spectra in Figure 13 indicated that the light absorption of both 2,4,6-trichlorophenol and its potassium salt was nearly identical in the region of 294 mμ. This was verified from the presentation in Figure 14. The molar absorptivities at 293 mμ. were very similar, 2170 and 2038, respectively, and indicated that this absorption maximum was unsuitable for the studies to follow.

Data, further describing the solutions and their properties used to determine the pK_a of 2,4,6-trichlorophenol, were obtained for the studies at 312, 286.5 and 246 mμ. as shown in Tables 7, 8 and 9, respectively. In addition to 0.1000 M potassium chloride, the blanks contained only the buffer solution.

Not all of the solutions described, however, yielded data that could be used. Solution 10 gave definite evidence

Table 7. Data for the determination at 312 mμ. of the pK_a of 2,4,6-trichlorophenol

Solution number	0.0971 N HCl ml.	0.100 N KOH ml.	H_2O ml.	A at 312 mμ.	pH Trial 1	pH Trial 2	pH Trial 3
1	5.00			0.005	2.38	2.38	2.38
2	2.00			0.005	2.63		2.65
3		1.00		0.008	3.28	3.23	3.30
4		1.50		0.011	3.56	3.54	3.54
5		2.00		0.038	4.16	4.17	4.18
6		2.50		0.262	5.10	5.08	5.09
7		3.00		0.580	5.52	5.52	5.54
8		3.50		0.985	5.90	5.90	5.91
9		4.00		1.423	6.21	6.21	6.22
10		6.00	1.00	2.350	7.57	7.51	7.57
11		8.00	3.00	2.345	10.84	10.85	10.84
12				Blank			
13		3.25		0.837	5.75	5.74	5.74
14		3.75		1.235	6.07	6.07	6.07
15		4.25		1.655	6.42	6.42	6.42
16		4.50		1.865	6.64	6.63	6.63
17		4.75		2.075	6.97	6.94	6.94

Table 8. Data for the determination at 286.5 mµ. of the pK_a of 2,4,6-trichlorophenol

Solution number	0.0971 N HCl ml.	0.100 N KOH ml.	H_2O ml.	A at 286.5 mµ.	pH Trial 1	pH Trial 2	pH Trial 3
18	5.00			2.297	2.43	2.43	2.43
19	2.00			2.295	2.73	2.73	2.73
20		1.00		2.285	3.58	3.58	3.59
21		1.50		2.265	4.33	4.33	4.30
22		2.00		2.175	5.17	5.18	5.15
23		2.25		2.080	5.51	5.54	5.50
24		2.50		2.025	5.58	5.64	5.63
25		2.75		1.950	5.70	5.72	5.73
26		3.00		1.892	5.87	5.87	5.87
27		3.25		1.800	6.02	6.02	6.03
28		3.50		1.730	6.13	6.14	6.14
29		3.75		1.655	6.27	6.28	6.28
30		4.00		1.582	6.40	6.41	6.41
31		4.50		1.430	6.80	6.82	6.83
32		6.00	1.00	1.315	10.64	10.64	10.65
33		8.00	3.00	1.320	11.20	11.22	11.23
34				Blank			

Table 9. Data for the determination at 246 mμ of the pK_a of 2,4,6-trichlorophenol

Solution number	0.0971 N HCl ml.	0.100 N KOH ml.	H_2O ml.	A at 246 mμ.	pH Trial 1	pH Trial 2	pH Trial 3
35	5.00			0.010	2.42	2.40	2.37
36	2.00			0.025	2.79	2.77	2.73
37		1.50		0.458	5.47	5.47	5.45
38		2.00		0.790	5.82	5.80	5.80
39		2.25		0.895	5.89	5.89	5.88
40		2.50		0.972	5.97	5.96	5.95
41		2.70		1.012	5.98	5.98	5.98
42		3.05		1.225	6.17	6.14	6.17
43		3.25		1.335	6.24	6.24	6.24
44		3.50		1.455	6.37	6.37	6.37
45		3.75		1.575	6.48	6.48	6.48
46		4.00		1.695	6.61	6.61	6.61
47		4.50		1.940	6.90	6.89	6.89
48		6.00	1.00	2.265	10.66	10.60	10.68
49		8.00	3.00	2.320	11.22	11.20	11.27
50				Blank			
51		2.00	2.00	2.160	11.02		11.10

of the decomposition of hydroxylamine in a basic solution as indicated by its unexpectedly low pH. Solution 48, as well as solution 49, yielded evidence that pointed in the same direction, an unexpectedly high absorption of ultraviolet light of short wavelength. In fact a maximum did not occur at the expected position, 246 mμ., but occurred at a slightly shorter wavelength. Although the decomposition was not great enough to effect the pH, the products of the decomposition absorbed light strongly in the region of the study. The spectrum of solution 51, which was prepared without the buffer, was of the expected shape and intensity. The random variation of pH values between the 3 trials run on each solution, indicated the necessity of careful cleansing practices while measuring the pH values of a series of solutions. The value recorded for trial 3 was a corrected one if the calibration of the pH meter was found to be incorrect. When the data were graphed to determine the numerical value of pKa of 2,4,6-trichlorophenol, only the trial 3 pH values were used.

The spectra of the solutions described above varied with pH, as shown for the 3 wavelengths followed, 312, 286.5 and 246 mμ., in Figures 15, 16, and 17, respectively. The complete data are shown plotted in the small insert in each graph, while only the most important region is shown on a large scale. Well defined linear regions were found to exist within the pH range of 5.0 to 7.0 as is shown in each of the figures.

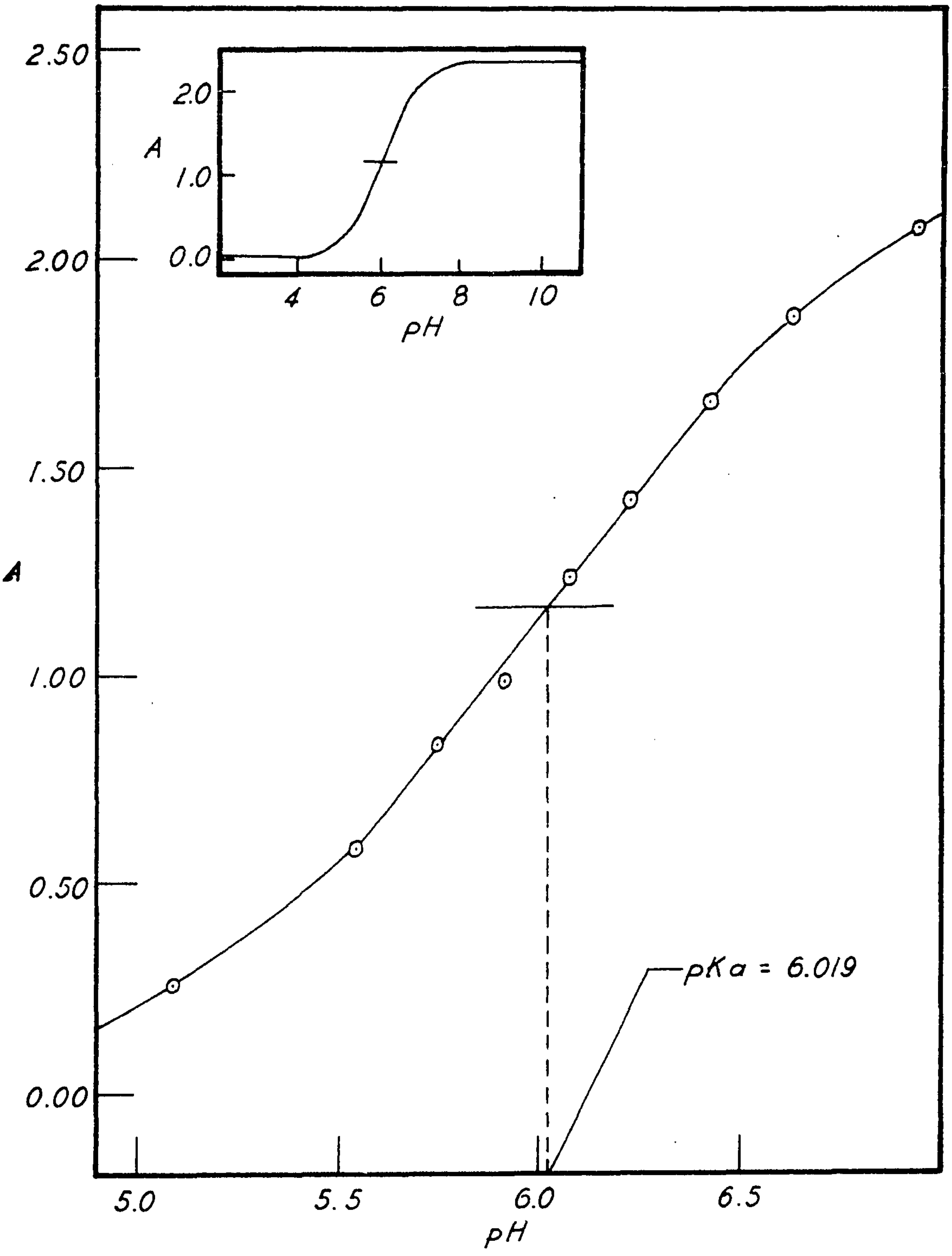


FIGURE 15. EVALUATION OF THE pKa OF 2,4,6-TRICHLOROPHENOL FROM MEASUREMENTS AT 312 mμ.

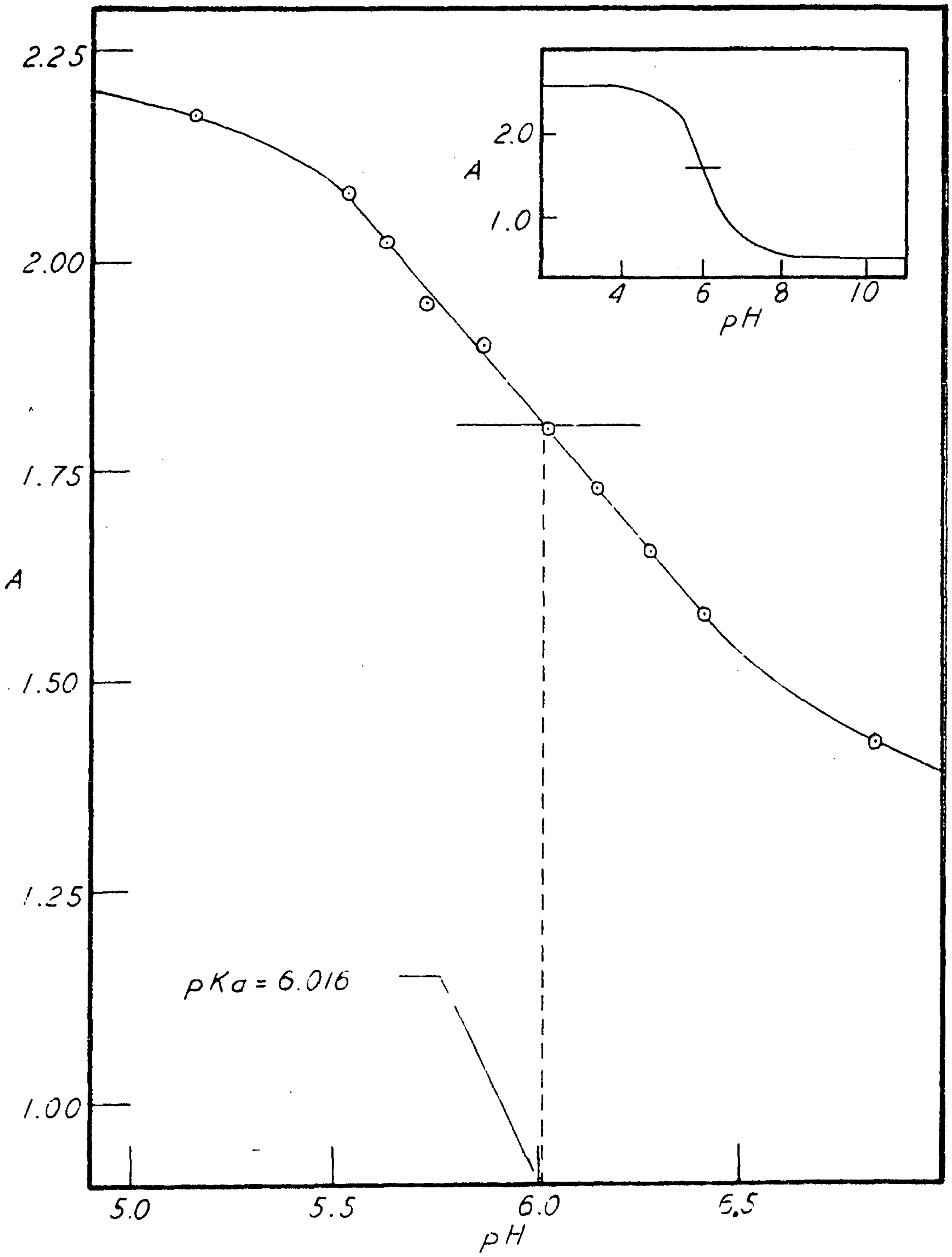


FIGURE 16. EVALUATION OF THE pKa OF 2,4,6-TRICHLOROPHENOL FROM MEASUREMENTS AT 286.5 mμ

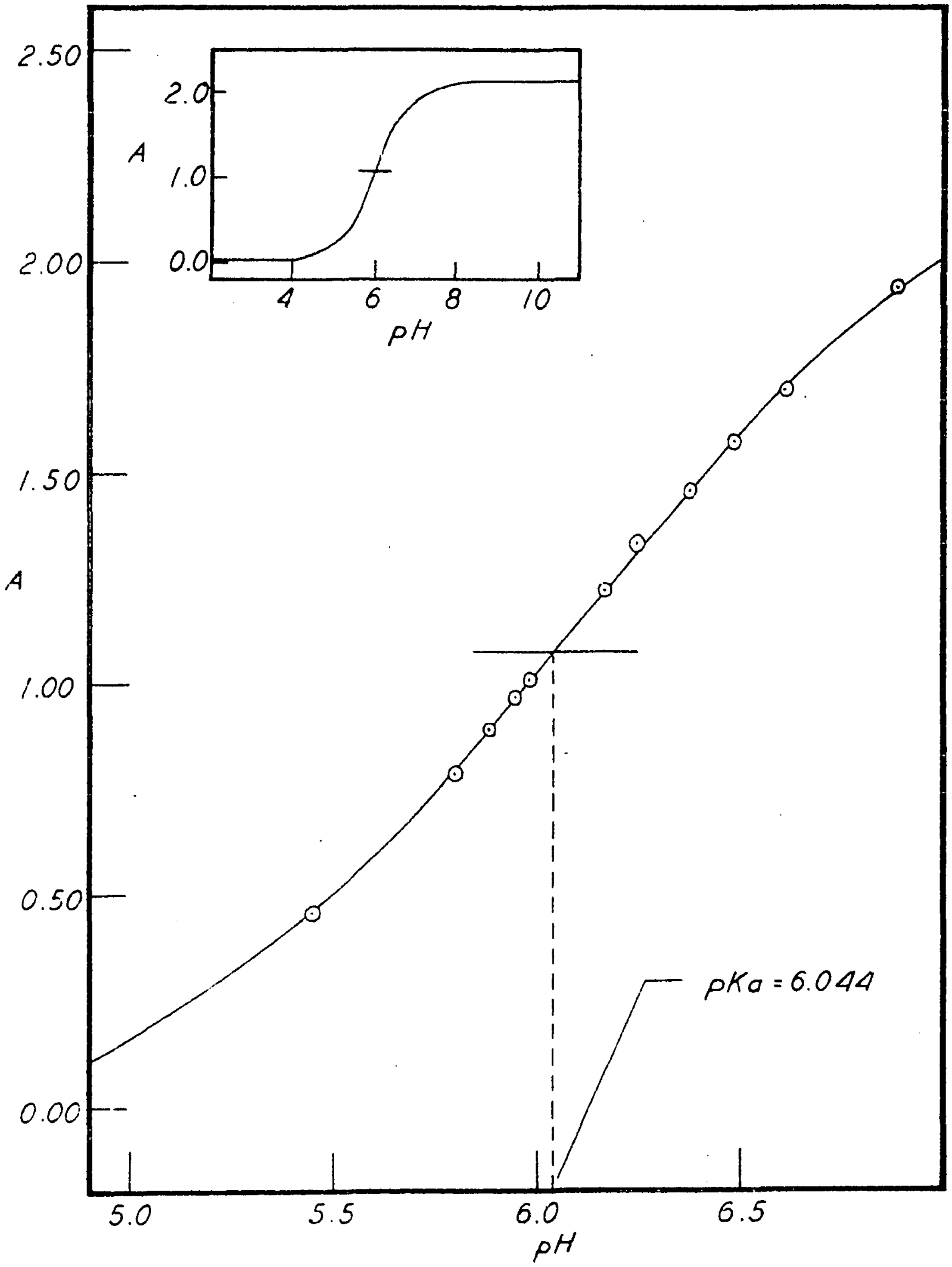


FIGURE 17. EVALUATION OF THE pKa OF 2,4,6-TRICHLOROPHENOL FROM MEASUREMENTS AT 246 mμ

Thus, the pH values at which equal concentrations of 2,4,6-trichlorophenol and its potassium salt were present were readily determined by the intersection of two straight lines. The points of intersection were calculated through the use of similar triangles, to relieve some of the human error in observing the points of intersection of non-perpendicular lines.

At 312, 286.5 and 246 $m\mu$., values of 6.019, 6.016 and 6.044, respectively, were obtained for the pK_a of 2,4,6-trichlorophenol at 25.0° and an ionic strength of 0.1000. An average value of 6.026, with a standard deviation of 0.015, was calculated. Using the average value, the numerical value of the constant was then found to be 9.42×10^{-7}, which fell within the range of values, 1.1×10^{-7} to 3.2×10^{-6}, reported in the literature (32, 40, 48, 54, 55). The standard deviation indicated that there was about 3 per cent error in the experimental value of the ionization constant found in this work. It, of course, must be noted that some of the literature values were reported for conditions of temperature and ionic strength different from 25.0° and 0.100, but none of the differences were great enough to explain the differences in values.

The important data obtained in the study concerning the extent to which 2-nitroso-1-naphthol-4-sulfonic acid and its disodium salt obeyed Beer's Law are predominantly reported in Table 10. When the solutions were prepared, various portions of the stock solution of 2-nitroso-1-naphthol-4-sulfonic acid, 0.1703 g. of the tetrahydrate per liter, were transferred to 50 ml. volumetric flasks. After 0.1209 N sodium hydroxide (average of 6 values with standard deviation of 1.4 parts per thousand) was added to the flasks indicated, all of the solutions were diluted to volume with deionized water. The absorption spectra of the solutions were measured against a deionized water blank.

Not all of the data obtained is reported in Table 10. The data for the other absorption maxima, and the other wavelength used in the experiments to follow, are reported graphically in Figure 18. Beer's Law was obeyed at all wavelengths. The ϵ values reported in Figure 18, as well as those mentioned earlier in Table 3, were calculated from the slopes of the lines.

An absorption minimum at 362 mμ. was one wavelength chosen for the following experiments, in preference to 347 mμ., since the broad band in the spectrum of 2-nitroso-1-naphthol-4-sulfonic acid extended from 347 mμ. to a point above 362 mμ. (see Figures 9 and 10). Also, 347 mμ. was at the lower wavelength limit for use of 2,4,6-trichlorophenol as a buffer in spectrophotometric work. The absorption maximum at 430 mμ. was the only other useful wavelength and it was also used to determine the pKa_2 of 2-nitroso-1-naphthol-

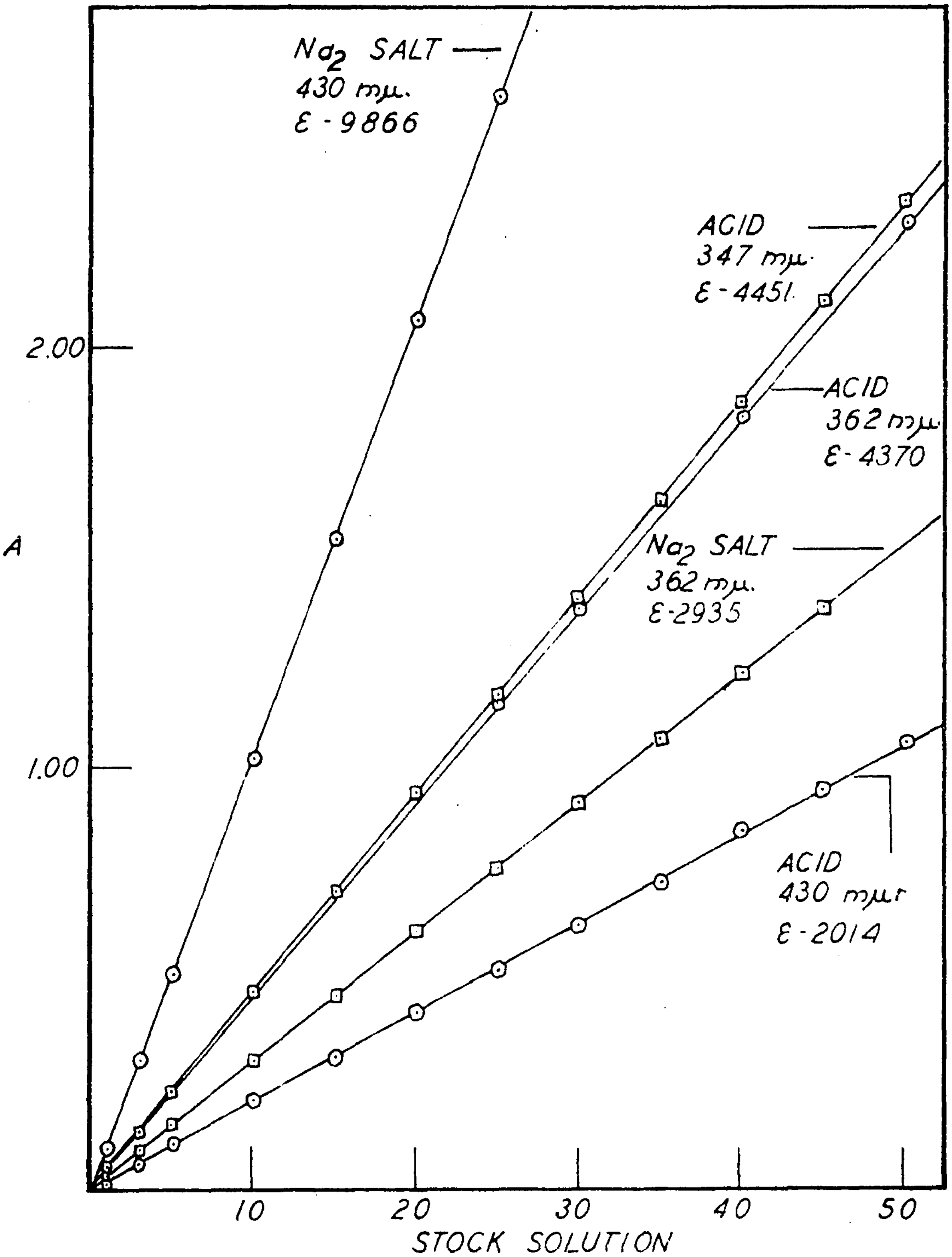


FIGURE 18. BEER'S LAW PLOT FOR 2-NITROSO-1-NAPHTHOL-4-SULFONIC ACID

Table 10. Data used to determine the extent to which 2-nitroso-1-naphthol-4-sulfonic acid obeyed Beer's Law

Solution number	Stock solution ml.	0.1209 N NaOH ml.	A at 261 mμ.	A at 232 mμ.	A at 271 mμ.	A at 292 mμ.	A at 322 mμ.
1	45.00	3.00					
2	40.00	3.00					
3	35.00	3.00					3.250
4	30.00	3.00					2.795
5	25.00	3.00			2.925	3.390	2.320
6	20.00	3.00		3.38	2.340	2.700	1.860
7	15.00	3.00		2.550	1.755	2.035	1.400
8	10.00	3.00		1.685	1.160	1.345	0.925
9	5.00	3.00		0.845	0.580	0.675	0.463
10	3.00	3.00		0.493	0.340	0.398	0.275
11	1.00	3.00		0.160	0.110	0.130	0.090
12	1.00		0.258				
13	3.00		0.810				
14	5.00		1.360				
15	10.00		2.74				
16	15.00						
17	20.00						
18	25.00						
19	30.00						
20	35.00						
21	40.00						

Table 10. (Continued)

Solution number	Stock solution ml.
22	45.00
23	50.00

4-sulfonic acid.

Data, further describing the solutions and their properties used to determine the pKa_2 of 2-nitroso-1-naphthol-4-sulfonic acid, were obtained for the studies at 362 and 430 mμ. as shown in Tables 11 and 12, respectively. The blanks contained only 0.1000 M potassium chloride. Solution 15 contained the buffer, but no nitroso compound.

Not all of the solutions described, however, yielded data that could be used. Solutions 1 through 5 developed precipitates of the halogenated phenol. Solutions 17 through 20 were therefore prepared containing none of the buffer. Solution 21 also developed a small amount of precipitate, but it was decanted from the solid and used anyway.

The spectra of the solutions varied with pH, as shown in Figures 19 and 20 for the 2 wavelengths followed, 362 and 430 mμ., respectively. The complete data are shown plotted in the small insert in each graph, while only the most important region is shown on a large scale. Well defined linear regions were found to exist within the pH range of 5.5

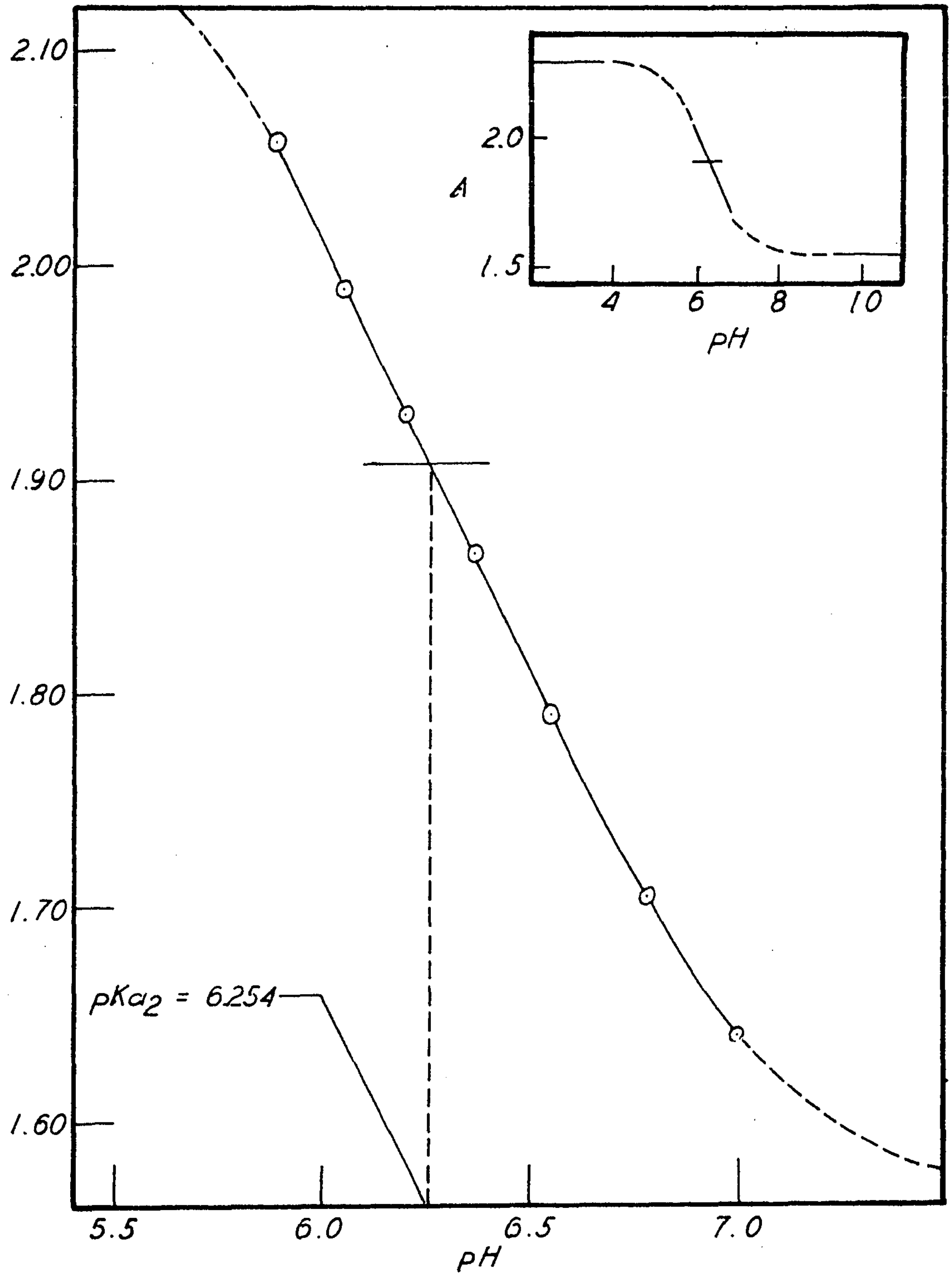


FIGURE 19. EVALUATION OF THE pKa_2 OF 2-NITROSO-1-NAPHTHOL-4-SULFONIC ACID FROM DATA AT 362 mμ.

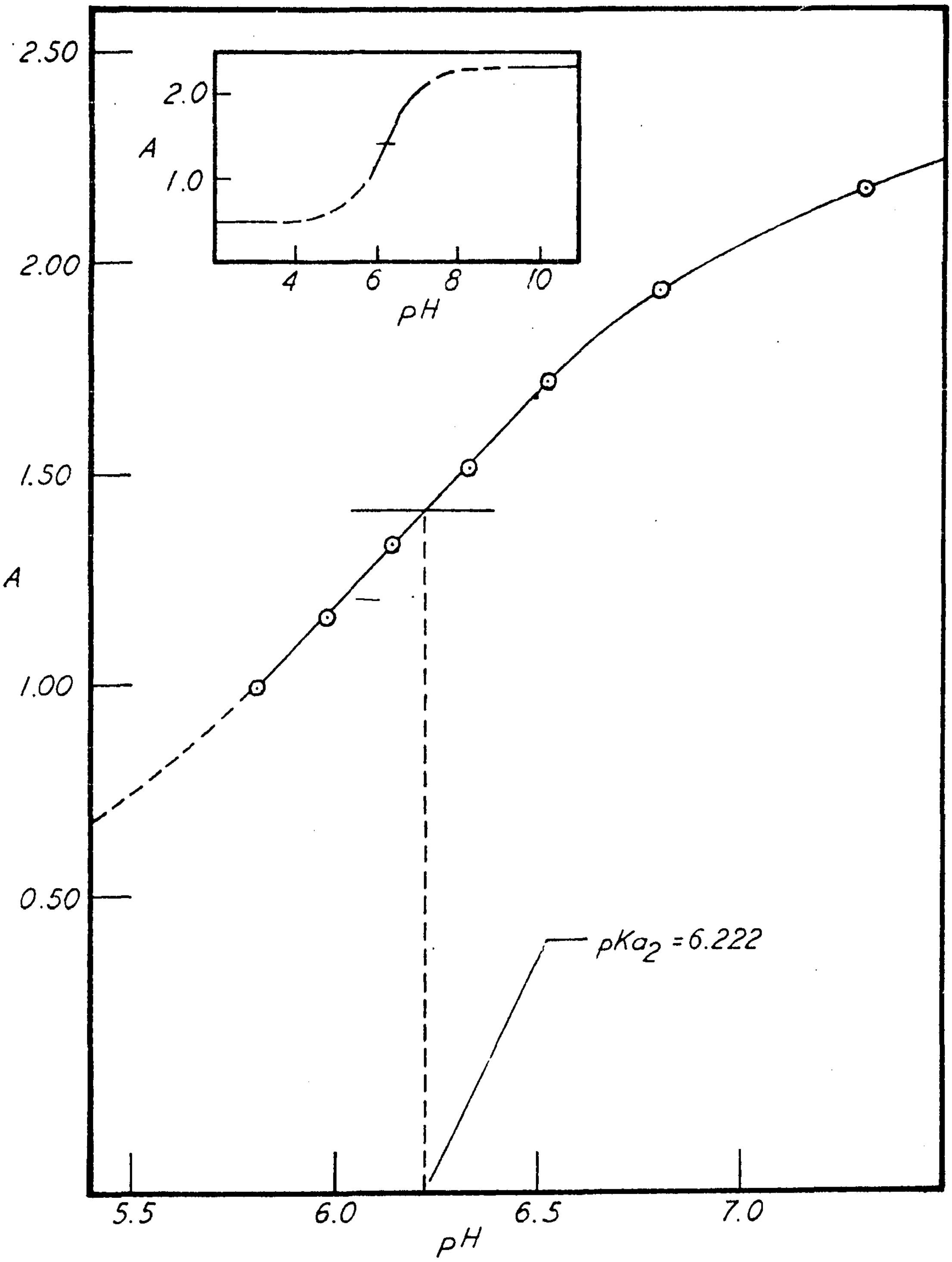


FIGURE 20. EVALUATION OF THE pKa_2 OF 2-NITROSO-1-NAPHTHOL-4-SULFONIC ACID FROM DATA AT 430 mμ.

Table 11. Data for the determination at 362 mμ. of the pKa_2 of 2-nitroso-1-naphthol-4-sulfonic acid

Solution number	0.0971 N HCl ml.	0.1000 N HCl ml.	0.100 N KOH ml.	H_2O ml.	A at 362 mμ.	pH Trial 1	pH Trial 2	pH Trial 3
1		7.45		4.00		Precipitate formed		
2		5.45		2.00		Precipitate formed		
3		3.00				Precipitate formed		
4		2.60				Precipitate formed		
5		2.20				Precipitate formed		
6		1.80			2.058	5.89	5.90	5.89
7		1.40			1.988	6.03	6.04	6.05
8		1.00			1.930	6.20	6.22	6.20
9		0.60			1.865	6.37	6.39	6.37
10		0.20			1.790	6.54	6.56	6.55
11			0.20		1.705	6.78	6.79	6.78
12			0.50		1.640	7.00	7.00	7.00
13			2.00	1.50	1.530	10.79	10.78	10.76
14			5.00	0.50	1.530	11.42	11.43	11.43
15					0.000			
16					Blank			
17	5.00				2.285	2.40	2.40	2.38
18	2.00				2.287	2.73	2.72	2.72

Table 12. Data for the determination at 430 mμ. of the pKa_2 of 2-nitroso-1-naphthol-4-sulfonic acid

Solution number	0.0971 N HCl ml.	0.1000 N HCl ml.	0.100 N KOH ml.	H_2O ml.	A at 430 mμ.	pH Trial 1	pH Trial 2	pH Trial 3
19	5.00				0.489	2.39	2.39	2.39
20	2.00				0.495	2.74	2.73	2.73
21		2.20			0.996	5.82	5.83	5.81
22		1.80			1.165	5.99	6.01	5.98
23		1.40			1.335	6.14	6.14	6.14
24		1.00			1.515	6.33	6.34	6.33
25		0.60			1.720	6.52	6.53	6.52
26		0.20			1.933	6.83	6.83	6.80
27			0.20	0.20	2.175	7.30	7.30	7.30
28			0.50		2.317	9.27	9.19	9.21
29			2.00	1.50	2.335	11.01	10.99	11.01
30			5.00	4.50	2.335	11.46	11.48	11.49
31					Blank			

to 7.0 as shown in the figures. Thus, the pH values at which equal concentrations of the 2-nitroso-1-naphthol-4-sulfonate anion and its potassium salt were present were readily determined by the intersection of straight lines. As before, the points of intersection were calculated by using similar triangles.

At 362 and 430μm . values of 6.254 and 6.222, respectively, were obtained for the pKa_2 of 2-nitroso-1-naphthol-4-sulfonic acid. An average value of 6.238 was calculated for the pKa_2, which yielded $Ka_2 = 5.78 \times 10^{-7}$. When the average deviation of 0.016 for the pKa_2 was considered to be indicative of the uncertainty in the measurement, an uncertainty 3.6 per cent was calculated for Ka_2. Thus $Ka_2 = (5.78 \pm 0.21) \times 10^{-7}$, at 25.00° in a solution with an ionic strength of 0.100. The value for Ka_2 reported by the Russians (56, 57) of 8.2×10^{-7} is of the same order. Nothing can be said concerning the latter value, except that it was reported.

D. The Reaction with Cobalt(II)

1. Method of approach

In as much as the reaction between cobalt(II) and 2-nitroso-1-naphthol-4-sulfonic acid has already been studied (61) with respect to addition of reagents, optimum conditions of pH and interfering ions, now that pure reagent has been prepared, the stoichiometry of the reaction can be determined.

Job's method of continuous variations (39, 60), the desirable method for reactions with large formation constants, was used to determine the stoichiometry. The formation constant of the complex had to be large, since only a slight excess of reagent is necessary to cause the complex to obey Beer's Law. The studies were done at a constant ionic strength of 0.100 and at 25.0°.

2. Reagents

Most of the reagents used have been described in earlier sections.

The sodium perchlorate used was reagent grade (G. Frederick Smith Chemical Company) and contained 13.22 per cent moisture as determined by loss on drying. The apparent molecular weight was therefore 141.1.

A 0.1000 M solution of sodium perchlorate was prepared by dissolving the solid, 28.2272 g., in deionized water and diluting the resulting solution to a volume of 2 liters with more deionized water.

Portions of 2-nitroso-1-naphthol-4-sulfonic acid tetrahydrate, 0.3253 g., and sodium perchlorate, 14.1111 g., were dissolved in deionized water. The resulting solution was diluted to a volume of 1 liter with deionized water and was then 0.001000 M in 2-nitroso-1-naphthol-4-sulfonic acid and 0.1000 M in sodium perchlorate.

The anhydrous cobalt(II) sulfate used was iron and nickel free. Its preparation was previously described (24).

A standard cobalt(II) sulfate solution was prepared by dissolving portions of the anhydrous solid, 0.1550 g., and sodium perchlorate, 14.1120 g., in deionized water. The resulting solution was diluted to a volume of 1 liter with more deionized water and was then 0.1000 M in sodium perchlorate and 0.001000 M in cobalt(II) sulfate.

A phosphate buffer solution was prepared by dissolving dried disodium hydrogen phosphate, 7.0998 g., in deionized water and then adding enough 0.0971 N hydrochloric acid to adjust the pH to 8.0. The solution was diluted to a volume of 1 liter and was 0.0500 M in disodium hydrogen phosphate.

3. Equipment

All of the equipment used has been previously described in earlier sections.

4. Procedure

The choice of pH for the continuous variations study was very critical. If the study was made at pH 7.0, the pH used by Wise and Brandt (61), an appreciable amount of the naphthol hydrogen would remain unionized. On the other hand, if the pH of the solutions used was too high cobalt hydroxide would precipitate. A pH high enough to ionize completely the second acid hydrogen of 2-nitroso-1-naphthol-4-sulfonic acid and yet not high enough to precipitate cobalt hydroxide was desirable.

Although the cobalt complex was found to be stable by Wise and Brandt in the presence of an excess of reagent between pH 6 and pH 10, its stability with respect to pH was not known in the presence of excess cobalt. The effect of pH upon the formation of the complex in the presence of excess cobalt was first determined.

A series of solutions was prepared by transferring 10.00 ml. portions of 0.001000 M cobalt(II) sulfate (in 0.1000 M sodium perchlorate) and 10.00 ml. portions of 0.001000 M 2-nitroso-1-naphthol-4-sulfonic acid (in 0.1000 M sodium perchlorate) into each of several beakers. Each solution was diluted to about 70 ml. with 0.1000 M sodium perchlorate and then using the pH meter the pH was adjusted to a desired value with 0.0971 N hydrochloric acid or 0.1209 N sodium hydroxide (average of 6 values with a standard deviation of 1.4 parts per thousand). The solution was transferred to a 100 ml. volumetric flask, diluted to volume with 0.1000 M sodium perchlorate, made homogeneous, and its spectrum determined. The pH of each was redetermined. The highest pH at which cobalt hydroxide did not precipitate was chosen for the continuous variations study.

For the continuous variations study, another series of solutions was prepared by transferring into each of several beakers measured portions of both 0.001000 M cobalt(II) sulfate (in 0.1000 M sodium perchlorate) and 0.001000 M 2-nitroso-1-naphthol-4-sulfonic acid (in 0.1000 M sodium perchlorate). A volume, 10.00 ml., of the 0.0500 M disodium hydrogen phosphate buffer was added to each. Enough 0.1000 M sodium perchlorate was added to bring the volumes to about 70 ml. each. Using the pH meter, the pH was adjusted to 8.0 ± 0.05 with 0.1209 N sodium hydroxide (same as above).

Each solution was then transferred to a 100 ml. volumetric flask, diluted to volume with 0.1000 M sodium perchlorate, made homogeneous, and placed in the constant temperature bath at 25.0°. The visible spectrum of every solution was determined as previously described for the other studies at constant temperature. The pH was then determined again on several of the solutions.

The ultraviolet spectrum of one of the solutions containing an excess of cobalt(II) sulfate over 2-nitroso-1-naphthol-4-sulfonic acid was determined in order to evaluate the spectrum of the cobalt complex.

5. Results

The effect of pH upon the formation of the complex in the presence of excess cobalt(II) was readily determined. Part of the data is summarized in Table 13. Spectral data at other wavelengths varied in identical manners and were not included. From the data in Table 13 it was apparent that the complex formed at a pH 5.1 or above. Solutions number 40, 41 and 42 gave evidence that precipitation of cobalt hydroxide occurred between pH 8.1 and 8.7 and that it was very appreciable above pH 8.7. A pH 8.0 was chosen for the continuous variations study to follow. At pH 8.00, the naphthol hydrogen of 2-nitroso-1-naphthol-4-sulfonic acid was calculated to be 98.3 per cent ionized.

Table 13. The data used to determine the effect of pH upon the formation of the cobalt complex in the presence of excess cobalt

Solution number	pH before dilution	pH after running spectra	A at 500 mμ.	A at 370 mμ.
32	3.1	4.0	0.010	0.430
33	3.2	3.9	0.339	0.917
34	3.6	4.2	0.384	0.990
35	4.3	5.1	0.423	1.055
36	5.0	5.4	0.423	1.055
37	5.7	6.0	0.423	1.055
38	7.1	6.5	0.423	1.055
39	8.8	7.3	0.423	1.055
40	10.4	9.9	0.450	1.070
41	8.6	8.1	0.423	1.060
42	9.15	8.7	0.440	1.075

Table 13 also yielded other information of importance. The solutions were not stable with respect to pH between the time preceding dilution to volume until after the spectra were read. Obviously, in order to have meaningful results in a continuous variations study, the pH would have to be controlled. Since orthophosphate does not interfere with the formation of the complex (61), a 0.00500 M phosphate buffer was used.

Part of the data obtained during the continuous variations study is given in Table 14. In order that a wavelength was

Table 14. Data related to the continuous variations study of the reaction of cobalt(II) with 2-nitroso-1-naphthol-4-sulfonic acid

Solution number	0.001 M reagent ml.	0.001 M Co(II) ml.	A at 365 mμ.	A at 490 mμ.	A at 525 mμ.	A at 565 mμ.	A at 600 mμ.
43	40.00	0.00	1.210	0.845	0.057	0.037	0.020
44	36.00	4.00	2.015	1.005	0.550	0.390	0.143
45	32.00	8.00	2.775	1.175	1.020	0.720	0.265
46	28.00	12.00	2.880	1.150	1.120	0.780	0.280
47	24.00	16.00	2.470	0.995	0.965	0.680	0.255
48	20.00	20.00	2.070	0.835	0.810	0.575	0.213
49	16.00	24.00	1.670	0.673	0.650	0.465	0.170
50	12.00	28.00	1.290	0.520	0.505	0.362	0.137
51	8.00	32.00	0.885	0.360	0.345	0.252	0.097
52	4.00	36.00	0.500	0.200	0.185	0.140	0.060
53	0.00	40.00	Precipitate formed				
54	39.00	1.00	1.420	0.890	0.185	0.128	0.052
55	38.00	2.00	1.610	0.930	0.310	0.220	0.090
56	37.00	3.00	1.820	0.975	0.432	0.305	0.120
57	0.00	40.00	0.060	0.020	0.015	0.012	0.015
58	0.00	0.00	Blank	Blank	Blank	Blank	Blank

chosen for the preparation of a Job's Plot, it had to give a maximum change in absorbance from one solution to the next and it also had to be in such a position that the slope of the spectral curve at the point was near zero. Data for other wavelengths were not considered.

Figure 21 contains the Job's Plots prepared from the data reported in Table 14. In the preparation of the plots the reaction

$$Co^{+2} + n\ R^{-2} \rightleftharpoons CoR_n^{2-2n} \qquad (5)$$

was considered, where R^{-2} was used as a symbol for the completely neutralized 2-nitroso-1-naphthol-4-sulfonic acid. Thus the fraction, x, of 2-nitroso-1-naphthol-4-sulfonic acid in the system was related to n by the relationship

$$n = \frac{x}{1 - x} \qquad (6)$$

at the particular x where the absorbance difference, ΔA, was a maximum. The curves in Figure 21 indicated that $x = 0.75$ and $n = 3$.

Equation 5 thus became

$$Co^{+2} + 3\ R^{-2} \rightleftharpoons CoR_3^{-4} \qquad (7)$$

for which the formation constant was written:

$$K_f = \frac{[CoR_3^{-4}]}{[Co^{+2}][R^{-2}]^3} . \qquad (8)$$

Using the method so beautifully described by Diehl and Lindstrom (25), K_f was evaluated from the Job's Plots shown in Figure 21. The fraction of the complex dissociated, d, was determined. Then

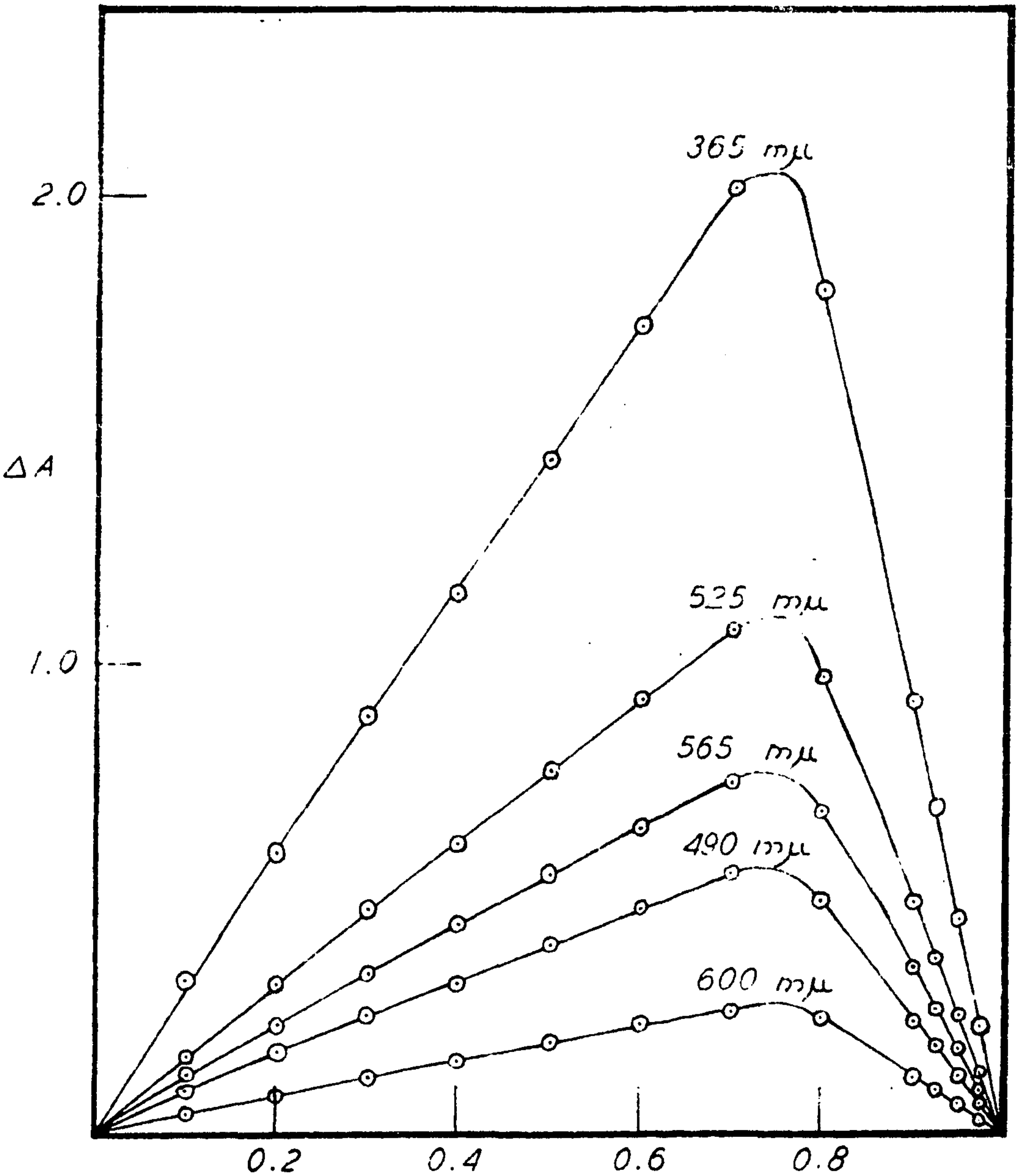


FIGURE 21. JOB'S PLOTS FOR THE REACTION OF COBALT (II) WITH 2-NITROSO-1-NAPHTHOL-4-SULFONIC ACID

$$\left[\mathrm{Co}^{+2} \right] = d\ C_1 , \tag{9}$$

$$\left[\mathrm{R}^{-2} \right] = 3 \left[\mathrm{Co}^{+2} \right] = 3\ d\ C_1 , \tag{10}$$

and

$$\left[\mathrm{CoR}_3^{-4} \right] = (1 - d)\ C_1 \tag{11}$$

where C_1 was the maximum concentration of the complex that could exist in the solution for which $x = 0.75$, if the reaction as shown by Equation 7 was quantitative.

Combining Equations 8, 9, 10 and 11, yielded

$$K_f = \frac{(1 - d)}{27\ d^4\ C_1{}^3} \tag{12}$$

which could be used to evaluate K_f if d̲ was known.

The fraction of the complex dissociated, d̲, was determined from the Job's Plots shown in Figure 21. Each of the linear portions of a plot was extended until the extensions intersected. This pair of intersecting lines represented the plot that would have been obtained if the reaction shown by Equation 7 was quantitative. The value of d̲ was determined by dividing the distance between the point of intersection of the two lines and the experimentally determined maximum by the distance between the point of intersection of the two lines and the x̲ axis. Values of d̲ of 0.081, 0.075, 0.084, 0.101 and 0.094 were obtained at 365, 490, 525, 565 and 600 m ., respectively. The average value obtained for d̲ was 0.087 with a standard deviation of 0.0104. In nine out of ten times the true average d̲ would thus fall within 0.087 ± 0.011.

Using d = 0.087 ± 0.011, the log K_f was found to be 14.77 ± 0.21 at 25.0° and an ionic strength of 0.1000. The value obtained was of the same order as that obtained for the copper(II) and nickel(II) complexes (56, 57).

The spectrum of the cobalt(II) complex of 2-nitroso-1-naphthol-4-sulfonic acid was determined on solution number 51 and is reported in Figure 22. Sharp maxima occurred at 246, 306 and 368 mμ. A broad maximum occurred between 490 and 525 mμ., with a shoulder at 565 mμ. Another maximum was indicated just below 210 mμ., beyond the lower limit of the spectrophotometer.

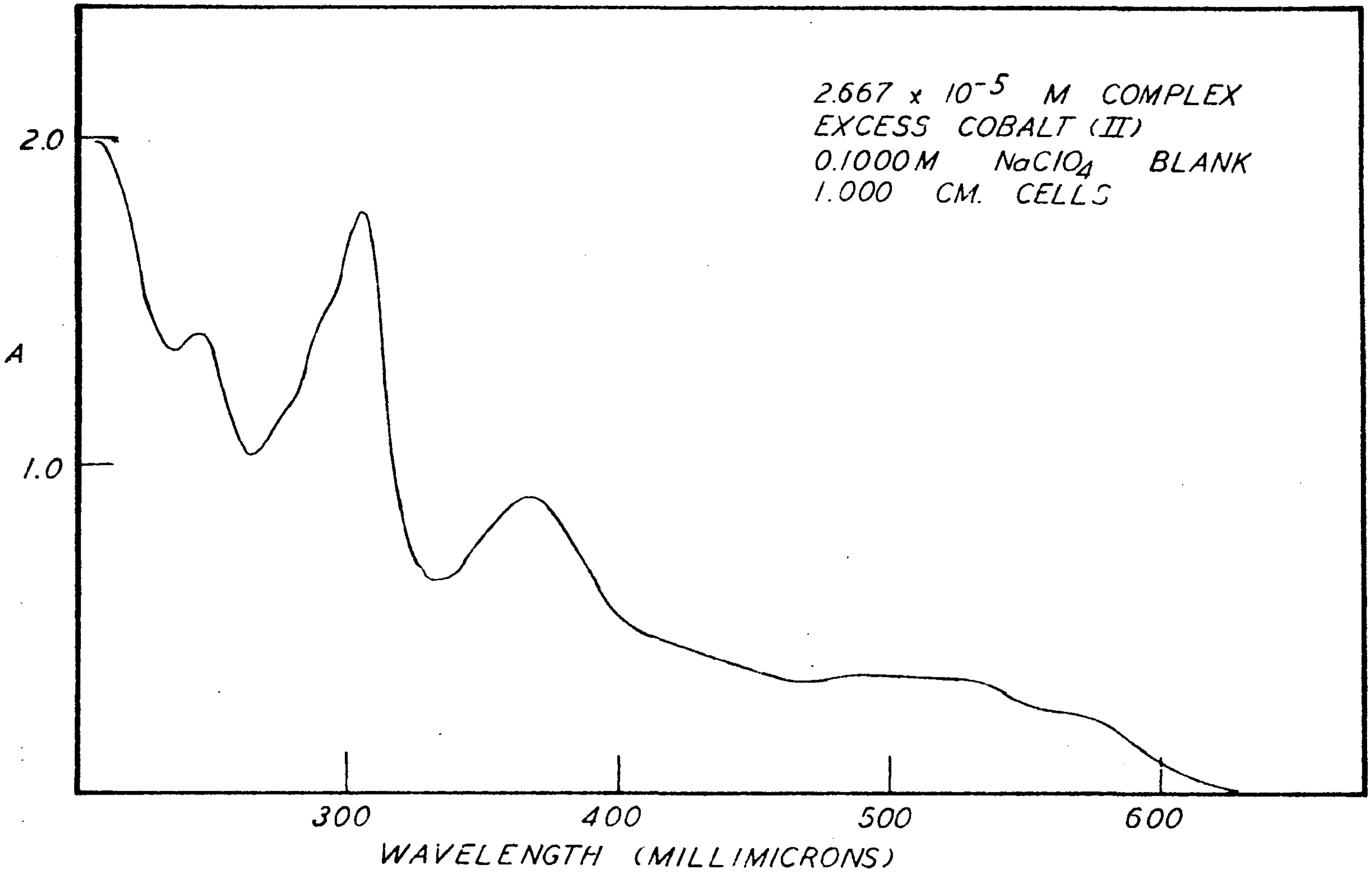


FIGURE 22. ABSORPTION SPECTRUM OF THE COBALT(II) COMPLEX OF 2-NITROSO-1-NAPHTHOL-4-SULFONIC ACID

IV. SUMMARY AND CONCLUSIONS

2-Nitroso-1-naphthol-4-sulfonic acid was prepared by the method of Witt and Kaufmann (62). A great deal of difficulty arose in the purification of the material, particularly with respect to removal of a red colored species. A new method of preparation was devised that changed the method of Witt and Kaufmann in two ways. The starting material, 1-naphthol-4-sulfonic acid, was purified by recrystallizing its p-tolylammonium salt from dilute hydrochloric acid followed by removal of the amine by extraction of a basic, aqueous solution of the salt with diethyl ether. The second change occurred during purification of the product. In addition to recrystallization from hydrochloric acid solution, recrystallization from anhydrous 1:1 acetone-benzene was utilized. During the latter recrystallizations, moisture from the atmosphere was absorbed by the solution to precipitate the pure solid as a hydrate. The product was the same from either method of recrystallization, and was in a very pure form.

The work of Witt and Kaufmann (62) indicated that the air dried 2-nitroso-1-naphthol-4-sulfonic acid lost 3 1/2 molecules of water of hydration upon drying at 115°. Elemental analysis of the residue led them to believe the air dried acid was the 3 1/2 hydrate. The loss of moisture corresponding to 3 1/2 molecules of water, when dried at 115°, was confirmed, but further heating at the same temperature indicated decomposition and further loss in weight. The neutralization equivalent and elemental analysis of the air dried material indicated that it was actually a tetrahydrate. This was verified by preparing the anhydrous solid by drying the air dried material for several months, at room temperature, over anhydrous magnesium perchlorate. The infrared and visible-ultraviolet absorption spectra of 2-nitroso-1-naphthol-4-sulfonic acid were used to further characterize it.

The second ionization constant of 2-nitroso-1-naphthol-4-sulfonic acid was determined at 25.0° and at an ionic strength of 0.1000. A spectrophotometric measurement was used to follow the ionization. Difficulty arose in finding a suitable monobasic acid or monoacidic base to use in a buffer system. Hydroxylamine, the only one available that would buffer in the correct pH range, was discarded because of the possibility of its reaction with the quinone-oxime tautomer of the sulfonic acid. 2,4,6-Trichlorophenol was considered as a possibility, investigated thoroughly, and was then used along with one of its alkali metal salts, in the buffer system. The pKa_2 of 2-nitroso-1-naphthol-4-sulfonic acid was found to be 6.24 at 25.0° and at an ionic strength of 0.1000.

The 2,4,6-trichlorophenol was purified by sublimation and its purity determined. Its spectra indicated that it did not absorb light above 350 $m\mu$, and could therefore be used above that wavelength as a buffer in spectrophotometric work. The optimum pH for its use as a buffer, its pK_a, was determined spectrophotometrically at 25.0° and at an ionic strength of 0.1000 using hydroxylamine and its hydrochloride salt as the buffer. The pK_a was found to be 6.03 at 25.0°. 2,4,6-Trichlorophenol was found to be useful in a buffer system above pH 5.8.

A method was not available for rapidly determining 2,4,6-trichlorophenol either in the presence of its alkali salts or inert impurities. An acid-base indicator was prepared that could be utilized in titrations of the phenol with standard base. The indicator, 3,3-bis-(4-hydroxy-2,3-xylyl)-phthalide, with a sharp colorless to blue color change, was utilized for rapid, accurate titrations of 2,4,6-trichlorophenol.

The reaction between cobalt(II) and 2-nitroso-1-naphthol-4-sulfonic acid was examined through the method of continuous variations. The complex formed was characterized in part by its absorption spectrum. It was found to contain 3 organic ligands per cobalt atom. The formation constant, K_f, of the reaction between cobalt(II) and the completely ionized 2-nitroso-1-naphthol-4-sulfonic acid was evaluated. The log K_f was found to be 14.77 ± 0.21 at 25.0° and an ionic strength of 0.100.

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VI. ACKNOWLEDGMENT

The author wishes to express his gratitude to Dr. Harvey Diehl for setting an example that a young chemist should strive to follow. Mere words can not express the thankfulness of the author for the path that lit the way when the going was the roughest. This work would have never been completed without the early guidance and tolerance of Dr. Diehl.