July 11, 1932

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To The Committee on Graduate Study:

I submit herewith a thesis by Mr. Weldon Eugene Cate, "Molecular Organic Compounds of Ortho and Para Aminobenzoic Acids", and recommend that it be accepted for eighteen (18) quarter hours credit in fulfillment of the requirements for the degree of Master of Science in Education.

C. O. Buehler
Major Professor

At the request of the Committee on Graduate Study, I have read this thesis and recommend its acceptance.

Judson A. Robertson

Wm. J. Smith, Jr.

Accepted by the Committee

P. M. Horton
Chairman

MOLECULAR ORGANIC COMPOUNDS OF ORTHO AND PARA AMINOBENZOIC ACIDS

A THESIS

Submitted to the Graduate Committee
of
The University of Tennessee
in
Partial Fulfillment of the Requirements
for the Degree of
Master of Science in Education

WELDON E. CATE

August, 1932

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I wish to express my deepest appreciation to Dr. Calvin A. Buehler for his kindly criticism and guidance throughout this investigation. I also wish to acknowledge the cooperation and interest shown by Miss Mildred Gallaher while typing the manuscript.

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Chapter I

INTRODUCTION

The nature of the linkage between the components of molecular organic compounds is not clearly understood, although the existence of this type of compound has been known for many years. Since efforts to explain the structure of molecular compounds by the different theories of valence have met with only partial success, a series of investigations is being carried out in the Chemistry Laboratories of the University of Tennessee in an effort to formulate a theory by which the structure and properties of this interesting but perplexing type of compound may be explained.

The object of this investigation of the molecular organic compounds of the o- and p-aminobenzoic acids is to add to the data which is being collected in this laboratory with the hope that a sufficient amount of information will lead to a conclusive explanation of the linkage between the components of molecular compounds.

It is also thought that by determining the additive nature of o-aminobenzoic acid it will be possible to predict the possibility of a chelate ring structure which is characteristic of a large number of ortho disubstituted

benzene derivatives.

The procedure being followed in this investigation is much the same as that of preceding investigations which have been carried out in this laboratory on molecular organic compounds. The general procedure may be outlined as follows:

1. To make a survey of all available literature and collect data on all molecular organic compounds of the o- and p-aminobenzoic acids which have been prepared by other investigators.

2. To prepare molecular compounds of the o- and p-aminobenzoic acids with a number of amines, phenols, and hydrocarbons.

3. To determine the melting points, color, and neutral equivalents of the compounds prepared and check them against those found in the literature.

4. To determine by analysis the molecular ratios existing in the compounds prepared.

5. To consider the structure of these compounds and try to explain the nature of the linkage existing between the components.

Chapter II

HISTORICAL PART[1]

A number of molecular organic compounds of o- and p-aminobenzoic acid have been obtained by different investigators but no evidence was found in the literature searched of a thorough investigation of these compounds.

In 1908 Pawlewski[2] obtained a molecular compound of o-aminobenzoic acid with p-dimethylaminobenzaldehyde by grinding the two components together and moistening with alcohol. He later found that, if gently heated with aqueous alcohol or benzene, the amino acid and the aldehyde formed a yellow solution from which the molecular compound would crystallize as intensely red needles which melted at 180-182°. The ratio of the components in this compound was 1:1. Pawlewski suggested that this reaction with p-dimethylaminobenzaldehyde could be used to identify o-aminobenzoic acid.

In the same year Suida[3] obtained two molecular compounds of the ortho acid with picric acid. He found that by bringing hot concentrated solutions of the acids together they formed the compounds, $HOC_6H_2(NO_2)_3 \cdot H_2NC_6H_4CO_2H$ and $HOC_6H_2(NO_2)_3 \cdot 2H_2NC_6H_4CO_2H$. The former compound in

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1. Literature covered from 1841 to 1932.
2. Pawlewski, Ber., 41, 2353-2354 (1908).
3. Suida, Ber., 41, 1909 (1908).

which the ratio is 1:1 crystallized as long yellowish brown prisms. The compound which was formed by two molecules of the amino acid uniting with one of picric acid consisted of spherical aggregates of long light yellow needles which contained water of crystallization. When this compound was dehydrated it became orange colored. The investigator also obtained a second anhydrous modification of this compound which consisted of short deep red needles. The melting points of these compounds were not given.

While making a study of addition compounds of s-trinitrobenzene and arylamines in 1910, Sudborough and Beard[4] obtained an addition compound of o-aminobenzoic acid and trinitrobenzene which crystallized in orange-yellow needles and melted at 192-193°. p-Aminobenzoic acid also formed a molecular compound with trinitrobenzene which crystallized in deep orange colored needles and melted at 114-114.5°. The molecular ratio of the components in both of these compounds was 1:1. The investigators used chloroform, alcohol, benzene, ether, carbon disulphide and a number of other solvents but they did not state which solvent was used in the preparation of these two compounds. As alcohol was used in most of the other cases, it is probable that it was the one used to prepare the aminobenzoic acid compounds.

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4. Sudborough and Beard, J. Chem. Soc., 97, 786 (1910).

In 1912 Ostromisslenskii[5] obtained an addition compound by bringing together alcoholic solutions of o-aminobenzoic acid and 1,3,5-trinitrobenzene. The compound crystallized as long orange-yellow needles which melted at 186-187°.

Binz and Marx[6] in 1910 found that sodium formaldehydesulphoxylate, $HOCH_2OSONa$, would react with o-aminobenzoic acid to give a compound of the formula, $HO_2CC_6H_4NHCH_2OSOH \cdot NH_2C_6H_4CO_2H$, when the two were dissolved in methyl alcohol. In this particular case one molecule of the aminobenzoic acid reacted with the sodium formaldehydesulphoxylate to form sodium hydroxide and a second compound which united with another molecule of o-aminobenzoic acid to form a molecular organic compound. This compound crystallized from methyl alcohol as microscopic needles which melted at 143°. When treated with nitric acid it decomposed into salicylic acid and o-aminobenzoic acid was regenerated by the action of sodium thiosulphate and sodium hydroxide or of hydrogen peroxide and ammonia.

Eighteen years later a group of German investigators[7] prepared addition compounds with pentaphenylchromium hydroxide and o- and p-aminobenzoic acid which were much like the compound prepared by Binz and Marx in that one or more of the aminobenzoic acid molecules was disrupted to

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5. Ostromisslenskii, C. A., 6, 1288 (1912).
6. Binz and Marx, Ber., 41, 2344-2349 (1910).
7. Hein, Schwartzkopff, Hoyer, Klor, Eissner, and Clauss, Ber., 61, 730-753 (1928).

form an atomic compound with the pentaphenylchromium hydroxide. This compound then united with another molecule of aminobenzoic acid to form an addition compound. They found that when o-aminobenzoic acid and pentaphenylchromium hydroxide were dissolved in chloroform containing a few drops of methyl alcohol and heated very gently, one molecule of the aminobenzoic acid reacted with one molecule of the hydroxide to liberate water and form another compound. The compound formed reacted with a second molecule of o-aminobenzoic acid to form the addition compound of the formula $(C_6H_5)_5CrO_2CC_6H_4NH_2 \cdot HO_2CC_6H_4NH_2$. The molecular compound crystallized as red-orange colored prisms which melted at 141-142°. In a somewhat similar manner the p-aminobenzoic acid formed a tetraphenyl chromium salt of the formula, $3(C_6H_5)_4CrO_2CC_6H_4NH_2 \cdot 2HO_2CC_6H_4NH_2$, which melted at 141°.

Suchanke[8] studied the action of the three isomeric aminobenzoic acids on benzo-, tolu-, and p-xyloquinones and found that molecular compounds were formed in each case. He obtained these compounds by bringing together alcoholic solutions of the two components except in the cases of toluquinone and p-xyloquinone with o-aminobenzoic acid. In these two cases he used a mixture of ethyl alcohol and benzene as a solvent. One molecule of the quinones united with two molecules of the aminobenzoic acids

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8. Suchanke, C. A., 9, 913 (1915).

to form molecular compounds. Benzoquinone-di-p-aminobenzoic acid crystallized from ethyl alcohol in long ruby needles that melted at 380-381°. The corresponding compound with the ortho acid crystallized from ethyl alcohol in red monoclinic prisms with a melting point of 210°. Toluquinone-di-p-aminobenzoic acid was obtained from alcoholic solution as long dark red needles which melted at 176°. The ortho acid with toluquinone crystallized from a mixture of ethyl alcohol and benzene in red rhombic crystals which melted at 129°. p-Xyloquinone-di-o-aminobenzoic acid was also crystallized from a mixture of ethyl alcohol and benzene. The ruby colored monoclinic prisms melted at 107-108°. Although the article from which this data was taken stated that the para acid formed a red-colored molecular compound with p-xyloquinone, the melting point was not given.

In 1915 McMasters[9] obtained the neutral ammonium salts of the aminobenzoic acids by passing dry ammonia gas into a solution of the acids in ether. He also used a mixture of one volume of acetone and two volumes of ether as a solvent for the ortho acid. The ammonium o-aminobenzoate was obtained as a white amorphous powder when prepared in ether but in the acetone and ether mixture it formed fine white needles. The ammonium p-aminobenzoate precipitated as a white amorphous powder when ammonia was passed into a solution of the acid in ether. Analysis of these compounds

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9. McMasters, J. Am. Chem. Soc., 37, 2181 (1915).

showed the molecular ratio to be 1:1, but the melting points were not given.

While studying the constitution of proteins, Pfeiffer and Angern[10] prepared a number of addition compounds of glycine anhydride and sarcosine anhydride with amino acids. Two molecular compounds were obtained with o-aminobenzoic acid and one with the para acid. One molecule of glycine anhydride united with two of o-aminobenzoic acid to form an addition compound which melted at 183-184°. Sarcosine anhydride united with the ortho acid in the same ratio forming a compound with a melting point of 120-122°, while with p-aminobenzoic acid it united in the ratio of 1:1 to form an addition compound which melted at 140-143°.

The molecular organic compounds described in this chapter are conclusive proof that the additive nature of o- and p-aminobenzoic acid has been known for some time. The survey of the literature revealed the fact that most of these compounds were obtained by investigators while studying the properties of compounds other than the aminobenzoic acids.

Thirteen addition compounds of o-aminobenzoic acid and seven of p-aminobenzoic acid were described in the literature. This difference in the number of addition compounds formed by the two acids seems to be due to the fact that o-aminobenzoic or anthranilic acid is a more common compound than p-aminobenzoic acid and not because the

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10. Pfeiffer and Angern, C. A., 19, 2033 (1925).

ortho acid is more additive in its nature. In every case where both o- and p-aminobenzoic acid were used addition compounds were obtained with both acids.

Chapter III

EXPERIMENTAL PART

I. Preparation of First Components.

A. o-Aminobenzoic Acid

Most of the o-aminobenzoic acid used in this investigation was prepared in this laboratory by the method of Noyes[1].

Forty grams of finely powdered phthalic anhydride were added in small portions to 160 cc. of ammonia (sp. gr. 0.96). The mixture was cooled during the addition by shaking the flask under cold running water. When the anhydride had all been added and dissolved, the solution was filtered quickly and 128 cc. of hydrochloric acid (sp. gr. 1.112) was added to it. After thoroughly cooling, the phthalamidic acid which formed was filtered off and dried.

Ten and two tenths cubic centimeters of bromine were dissolved in 280 cc. of a ten per cent solution of sodium hydroxide. Thirty-three grams of phthalamidic acid were dissolved in 200 cc. of the sodium hydroxide solution and the sodium hypobromite was added to it in portions of about 20 cc. The mixture was kept cool during the addition by keeping the flask under running water. After all of the

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1. Noyes, "Organic Chemistry for the Laboratory", The Chemical Publishing Co., Easton, Pa., 1926, Fourth Edition Revised, pp. 235-236.

bromine solution had been added, the mixture was allowed to stand for half an hour. A little strong sodium acid sulfite solution was added to reduce the excess of sodium hypobromite. Seventy cubic centimeters of hydrochloric acid were added and the mixture was evaporated to about 200 cc. after which it was filtered and 80 cc. of thirty per cent acetic acid were added to the filtrate. After cooling, the anthranilic acid was filtered off and purified by recrystallizing from hot water. The forty-six grams of acid which were prepared by this method melted at 144°.

B. p-Aminobenzoic Acid

The greater amount of the p-aminobenzoic acid used in this investigation was prepared in this laboratory by Mr. F. Whitehead as follows[2]:

Twenty-five grams of p-nitrobenzoic acid and 76 grams of granular tin were placed in a one-liter three-necked flask fitted with a reflux condenser and a mechanical stirrer. The stirrer was started and 25 cc. of concentrated hydrochloric acid was added in small portions to prevent too violent a reaction. When all of the acid had been added, the mixture was gradually heated to about 100°, the temperature being maintained for one half hour. The solution was then filtered and the filtrate was evaporated until crystals began to form. Ammonium hydroxide was added until

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2. Kellner and Beilstein, A., 128, 164.(1863)

the solution was alkaline after which the precipitate of tin hydroxide was filtered off. The filtrate was next acidified with acetic acid to precipitate the p-aminobenzoic acid which was purified by recrystallization from hot water. The final product melted at 186-187°.

About twenty grams each of the two aminobenzoic acids used were purchased from the Research Laboratory of the Eastman Kodak Company, Rochester, New York.

II. Preparation of Organic Molecular Compounds.

A. Second Components

An attempt was made to prepare molecular compounds of o- and p-aminobenzoic acid with each of the following compounds:

1. Acetamide
2. p-Aminophenol
3. Ammonia
4. Aniline
5. Anthracene
6. Benzamide
7. Benzidine
8. Diethylamine
9. Dimethylaniline
10. Diphenyl
11. Fluorene
12. Methylaniline
13. Naphthalene

14. a-Naphthol
15. b-Naphthol
16. a-Naphthylamine
17. b-Naphthylamine
18. Phenol
19. o-Phenylenediamine
20. m-Phenylenediamine
21. p-Phenylenediamine
22. Pyridine
23. o-Toluidine
24. m-Toluidine
25. p-Toluidine
26. Triethylamine
27. Urea

As it was desired to obtain the molecular compounds in the purest form possible, these second components were repurified except in cases where the compound was chemically pure. In general purification was accomplished by either fractional distillation or recrystallization from a suitable solvent.

B. Methods of Preparation and Purification.

Three methods were used in the preparation and purification of the molecular compounds studied in this investigation.

1. Solution Method

Most of the compounds were prepared by the solution

method. This method was carried out by dissolving equivalent molecular quantities each in a suitable solvent and bringing the two hot concentrated solutions together. After the two solutions had been thoroughly mixed in a beaker, the mixture was poured upon a large watch glass to crystallize. When a part of the solid had crystallized out, the liquid was poured upon another watch glass and crystallization allowed to continue. This process was repeated a number of times, and in this way several fractions of crystals were obtained. The melting point of each fraction was determined and if a fraction, with a sharp melting point which did not correspond to that of either component, was found it was analyzed and the molecular ratio of the two components was determined. In some cases it was found possible to purify the compounds by recrystallizing them from the solvent. Absolute ethyl alcohol was used as a solvent in all cases where both components were solids except in the case of anthracene. Benzene was used in this case because anthracene is insoluble in alcohol.

The above procedure was modified in cases where the second components were liquids. If the second component was a liquid, the aminobenzoic acid was dissolved in a slight excess of the liquid component and the solution was cooled until the first component crystallized out either as a molecular compound or as the unchanged acid.

The compounds formed with ammonia and the aminobenzoic

acids were obtained by the same method used by McMasters[3]. The ammonium-o-aminobenzoate was prepared by passing dry ammonia gas into a solution of anthranilic acid in ether. The ammonium salt precipitated as a white amorphous solid. The neutral ammonium salt of p-aminobenzoic acid was obtained in the same way except that ethyl alcohol was used as a solvent. McMasters used ether as a solvent in both cases.

2. Fusion Method

The fusion method was used in two cases where compound formation was shown by concentration-freezing-point curves but efforts to isolate the compounds by the solution method failed.

The fusion method was carried out by mixing equimolecular quantities of the two components and fusing the mixture. The fused mass was cooled slowly and, when a part had solidified, the liquid portion was poured off into a warm beaker. After cooling until a part had solidified the excess liquid was poured off again. It was necessary to repeat this process several times in order to obtain pure compounds. This work was carried out over a hot plate to prevent the fused mixtures from cooling too rapidly.

The two compounds prepared by this method were diethylamine-p-aminobenzoic acid and triethylamine-o-aminobenzoic acid. It was found that these two compounds could be further purified by recrystallizing from absolute ethyl alcohol

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3. McMasters, J. Am. Chem. Soc., 37, 2181 (1915).

after they had been prepared by the fusion method.

3. Concentration-Freezing Point Curves

In cases where efforts to isolate a compound by the solution method failed, concentration-freezing-point curves were constructed to determine whether the two components formed a compound when fused together.

More than a century ago Blagden[4] showed that when one compound is dissolved in another the depression of the freezing point of the solvent is directly proportional to the concentration of the solution. This law is used in determining compound formation in a binary system by making concentration-freezing-point curves[5]. Two general types of curves were found in this investigation. In the first type of curve compound formation does not take place, and a curve of the type shown in Figure 1 is formed. This diagram is the curve for the binary system of o-aminobenzoic acid and acetamide. A study of the curve shows that as the percentage of acetamide is increased, the freezing point of the solvent is lowered until the eutectic point is reached. At this point the aminobenzoic acid and the acetamide exchange roles and the acetamide becomes the solvent and the acid the solute. After the eutectic point is reached, the freezing point of the mixture increases as the percentage of aminobenzoic acid decreases and the melting point of pure acetamide is approached.

When the two components form a stable compound possessing a congruent melting point, the curve takes the form

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4. Getman,"Outlines of Theoretical Chemistry", John Wiley and Sons, New York, 1928, fourth edition, p. 251.
5. Findlay, "The Phase Rule", Longmanns Green and Company, New York, 1931, seventh edition, p. 251.

shown in Figure 12. This graph represents the concentration-freezing point curve of o-aminobenzoic acid and triethylamine. Since the melting point of the compound formed is lowered by the presence of either of the two components, a eutectic point is formed with each component and the maxi-point on the center of the intervening curve is the freezing point of the molecular compound. In this curve the eutectic point between the molecular compound and triethylamine is not shown. This eutectic would be below —114°, the freezing point of triethylamine.

The data for the concentration-freezing-point curves was obtained by placing 0.01 mol of the pure aminobenzoic acid in a pyrex test tube and adding enough of the second component to make a molar mixture of ninety per cent aminobenzoic acid and ten per cent of the second component. The test tube was then immersed in a sulfuric acid bath and the mixture was heated until it melted. The solution was constantly stirred with a thermometer and slowly cooled until a solid phase began to form. The temperature at this point was recorded as the freezing point. Another weighed portion of the second component was added and the freezing point taken in the same way. This process was repeated until a series of freezing points were obtained for mixtures of different molecular percentages ranging from pure aminobenzoic acid to the pure second component. In cases where the second component was a liquid, it was added from a burette.

The freezing points were taken close enough together to give a smooth curve and thus eliminate the danger of missing a break in the curve if one should occur. The test tube was not removed from the acid bath but was allowed to cool slowly with the acid surrounding it. This prevented supercooling and gave more accurate results. It was found impossible to eliminate all supercooling, but in most cases the temperature of the supercooled liquid would rise to the true freezing point as soon as the solid phase began to appear. The thermometer was watched closely during this rise in temperature, and the highest reading was recorded as the freezing point. When the freezing point was lower than the room temperature, the test tube was removed from the bath and cooled in cold water, an ice bath, or solid carbon dioxide and ether, depending upon the temperature of the freezing point. The tables and graphs shown on the following pages give the results of all the concentration-freezing-point curves studied in this investigation.

Table 1

Concentration-Freezing Point Data of the Binary Solution of o-Aminobenzoic Acid and Acetamide

o-Aminobenzoic Acid		Acetamide		Freezing Point
Grams	Mol Per Cent	Grams	Mol Per Cent	
1.3706	100	0,0000	00.	144.0
1.3706	90	0.0656	10	134.0
1.3706	80	0.1476	20	123.5
1.3706	70	0.2530	30	109.5
1.3706	60	0.3936	40	93.0
1.3706	55	0.4831	45	84.0
1.3706	50	0.5905	50	70.0
1.3706	45	0.7216	55	59.5
1.3706	40	0.8857	60	43.0
1.3706	35	1.0966	65	29.5
1.3706	30	1.3777	70	45.0
1.3706	20	2.3618	80	61.3
1.3706	10	5.3141	90	71.0
0.0000	00	2.0000	100	78.0

Figure 1.

Freezing-Point Curve for o-Aminobenzoic Acid and Acetamide

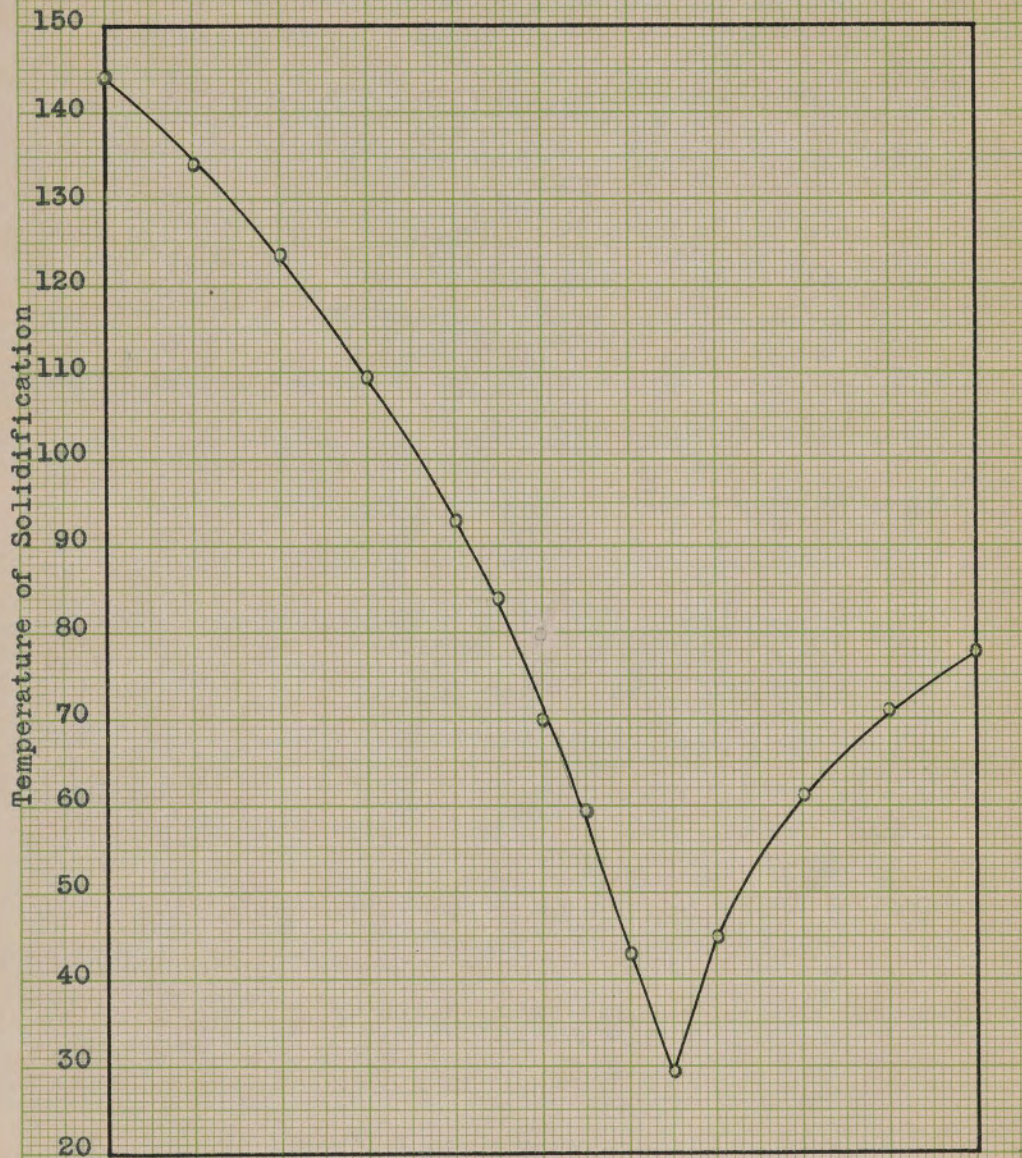

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Table 2

Concentration-Freezing Point Data of the Binary Solution of o-Aminobenzoic Acid and Aniline

o-Aminobenzoic Acid		Aniline		Freezing
Grams	Mol Per Cent	Grams	Mol Per Cent	Point
1.3706	100	0.0000	00	144.0
1.3706	90	0.1032	10	136.0
1.3706	80	0.2323	20	127.0
1.3706	70	0.3982	30	119.0
1.3706	60	0.6194	40	110.0
1.3706	55	0.7602	45	105.0
1.3706	50	0.9292	50	98.5
1.3706	45	1.1357	55	93.0
1.3706	40	1.3932	60	85.0
1.3706	35	1.7257	65	78.0
1.3706	30	2.1682	70	67.0
1.3706	25	2.7877	75	56.5
1.3706	20	3.7170	80	43.0
1.3706	15	5.2657	85	18.0
1.3706	10	8.3633	90	-10.0

Figure 2.

Freezing-Point Curve for o-Aminobenzoic Acid and Aniline

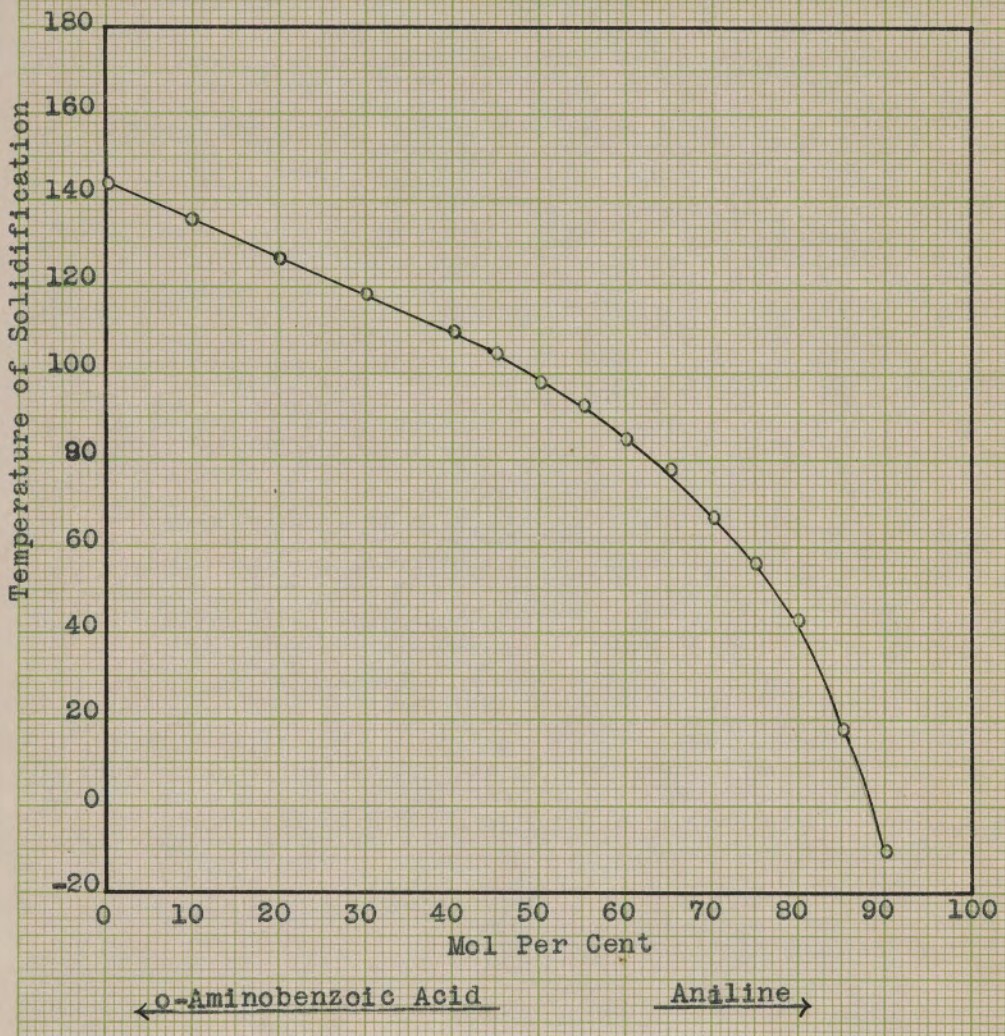

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Table 3

Concentration-Freezing Point Data of the Binary Solution of o-Aminobenzoic Acid and Dimethylaniline

o-Aminobenzoic Acid		Dimethylaniline		Freezing Point
Grams	Mol Per Cent	Grams	Mol Per Cent	
1.3706	100	0.0000	00	144.0
1.3706	90	0.1345	10	135.0
1.3706	80	0.3027	20	126.5
1.3706	70	0.5189	30	118.0
1.3706	60	0.8072	40	110.0
1.3706	55	0.9907	45	105.5
1.3706	50	1.2109	50	100.5
1.3706	45	1.4799	55	98.0
1.3706	40	1.8163	60	92.5
1.3706	35	2.2488	65	86.0
1.3706	30	2.8254	70	81.0
1.3706	25	3.6327	75	68.5
1.3706	20	4.8437	80	57.0
1.3706	15	6.8618	85	38.0
1.3706	10	10.8983	90	1.5
0.0000	00	4.0000	100	2.0

Figure 3

Freezing-Point Curve for o-Aminobenzoic Acid and Dimethylaniline

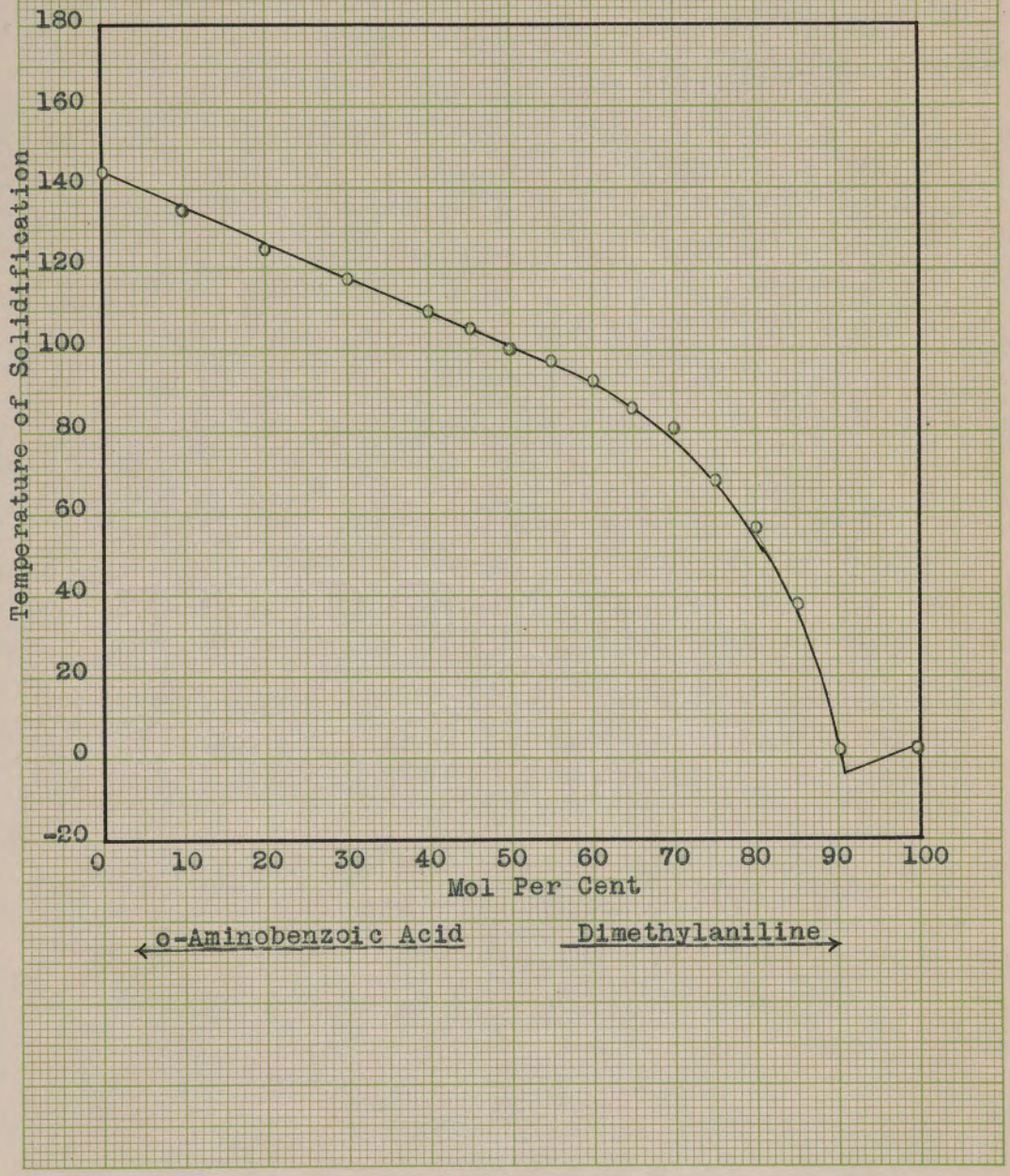

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Table 4

Concentration-Freezing-Point Data of the Binary Solution of o-Aminobenzoic Acid and Methylaniline

o-Aminobenzoic Acid		Methylaniline		Freezing Point
Grams	Mol Per Cent	Grams	Mol Per Cent	
1.3706	100	0.0000	00	144.0
1.3706	90	0.1189	10	136.5
1.3706	80	0.2676	20	127.0
1.3706	70	0.4588	30	119.0
1.3706	60	0.7127	40	111.0
1.3706	55	0.8759	45	105.0
1.3706	50	1.0707	50	100.5
1.3706	45	1.3084	55	94.5
1.3706	40	1.6058	60	87.0
1.3706	35	1.9882	65	81.0
1.3706	30	2.4279	70	75.0
1.3706	25	3.2117	75	65.0
1.3706	20	4.2823	80	48.0
1.3706	15	6.0666	85	19.0
1.3706	10	9.6351	90	12.0

Figure 4.

Freezing-Point Curve for o-Aminobenzoic Acid and Methylaniline

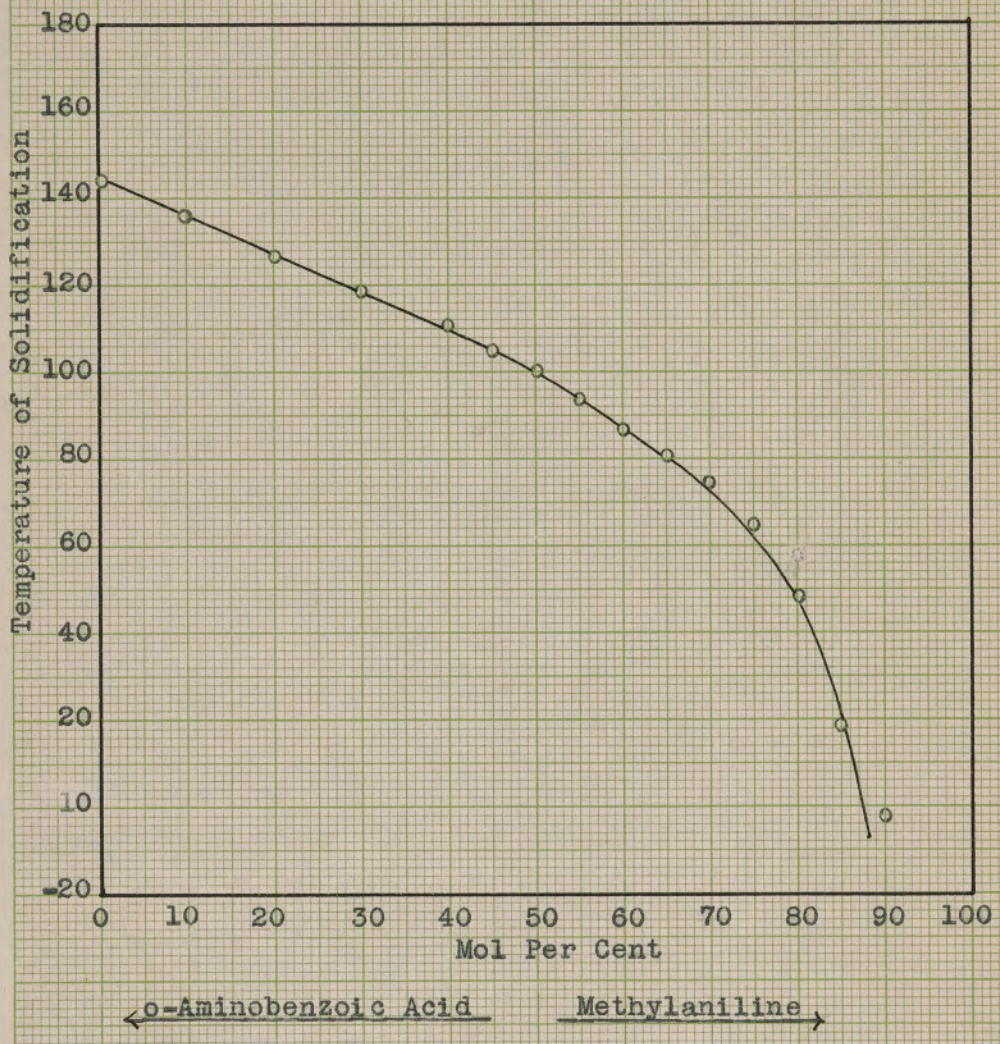

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Table 5

Concentration-Freezing-Point Data of the Binary Solution of o-Aminobenzoic Acid and a-Naphthylamine

o-Aminobenzoic Acid		a-Naphthylamine		Freezing Point
Grams	Mol Per Cent	Grams	Mol Per Cent	
1.3706	100	0.0000	00	144.0
1.3706	90	0.1584	10	134.0
1.3706	80	0.3562	20	127.0
1.3706	70	0.6108	30	119.0
1.3706	60	0.9800	40	109.0
1.3706	50	1.4308	50	98.5
1.3706	40	2.1378	60	81.0
1.3706	30	3.3250	70	57.5
1.3706	25	4.2757	75	47.0
1.3706	20	5.7016	80	34.0
1.3706	15	8.0767	85	38.5
1.3706	10	12.8286	90	42.0
0.0000	00	2.0000	100	50.0

Figure 5

Freezing-Point Curve for o-Aminobenzoic Acid and a-Naphthylamine

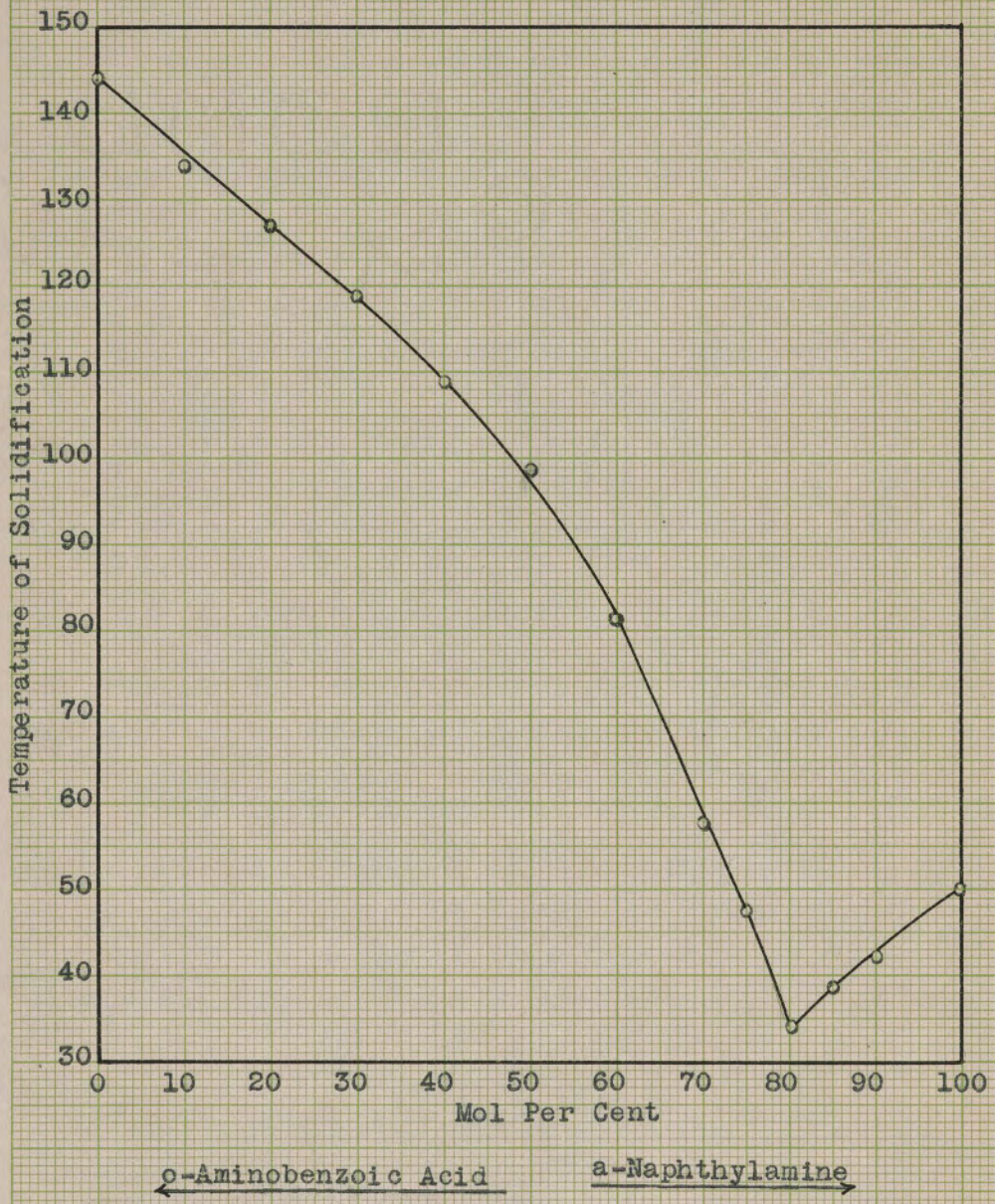

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Table 6

Concentration-Freezing-Point Data on the Binary Solution of o-Aminobenzoic Acid and o-Phenylenediamine

o-Aminobenzoic Acid		o-Phenylenediamine		Freezing Point
Grams	Mol Per Cent	Grams	Mol Per Cent	
1.3706	100	0.0000	00	144.0
1.3706	90	0.1201	10	134.0
1.3706	80	0.2702	20	121.5
1.3706	70	0.4632	30	111.5
1.3706	60	0.7205	40	97.0
1.3706	50	1.0808	50	85.0
1.3706	40	1.6211	60	72.0
1.3706	35	2.6070	65	82.5
1.3706	30	2.5216	70	88.0
1.3706	25	3.2422	75	93.0
1.3706	20	4.3229	80	96.0
1.3706	10	9.7265	90	99.0
0.0000	00	2.0000	100	101.0

Figure 6.

Freezing-Point Curve for o-Aminobenzoic Acid and o-Phenylenediamine

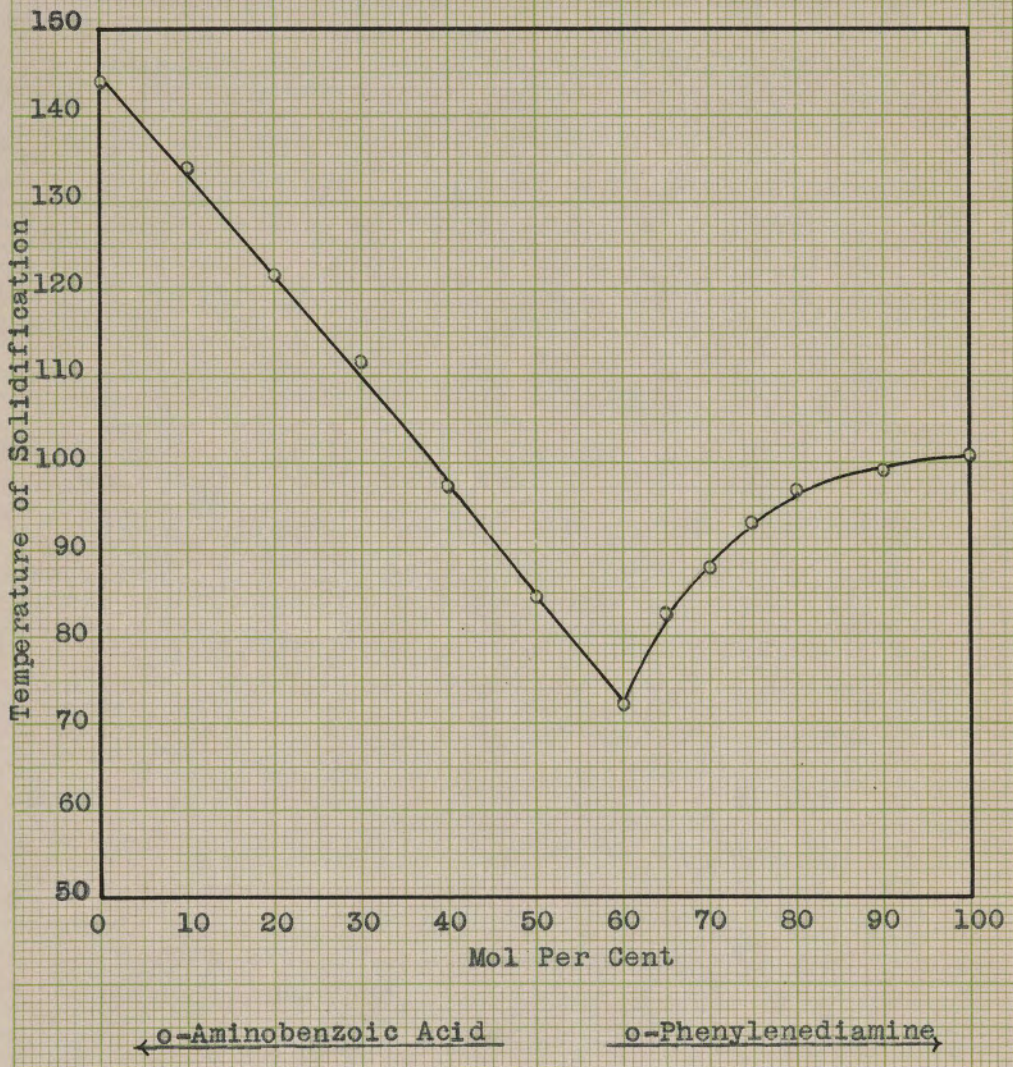

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Table 7

Concentration-Freezing-Point Data on the Binary Solution of o-Aminobenzoic Acid and m-Phenylenediamine

o-Aminobenzoic Acid		m-Phenylenediamine		Freezing Point
Grams	Mol Per Cent	Grams	Mol Per Cent	
1.3706	100	0.0000	00	144.0
1.3706	90	0.1201	10	132.5
1.3706	80	0.2702	20	121.5
1.3706	70	0.4632	30	110.0
1.3706	60	0.7205	40	96.5
1.3706	50	1.0808	50	83.0
1.3706	40	1.6211	60	69.0
1.3706	35	2.0070	65	52.0
1.3706	30	2.5216	70	31.0
1.3706	25	3.2422	75	38.0
1.3706	20	4.3229	80	47.0
1.3706	10	9.7265	90	56.0
0.0000	00	2.0000	100	63.0

Figure 7

Freezing-Point Curve for o-Aminobenzoic Acid and m-Phenylenediamine

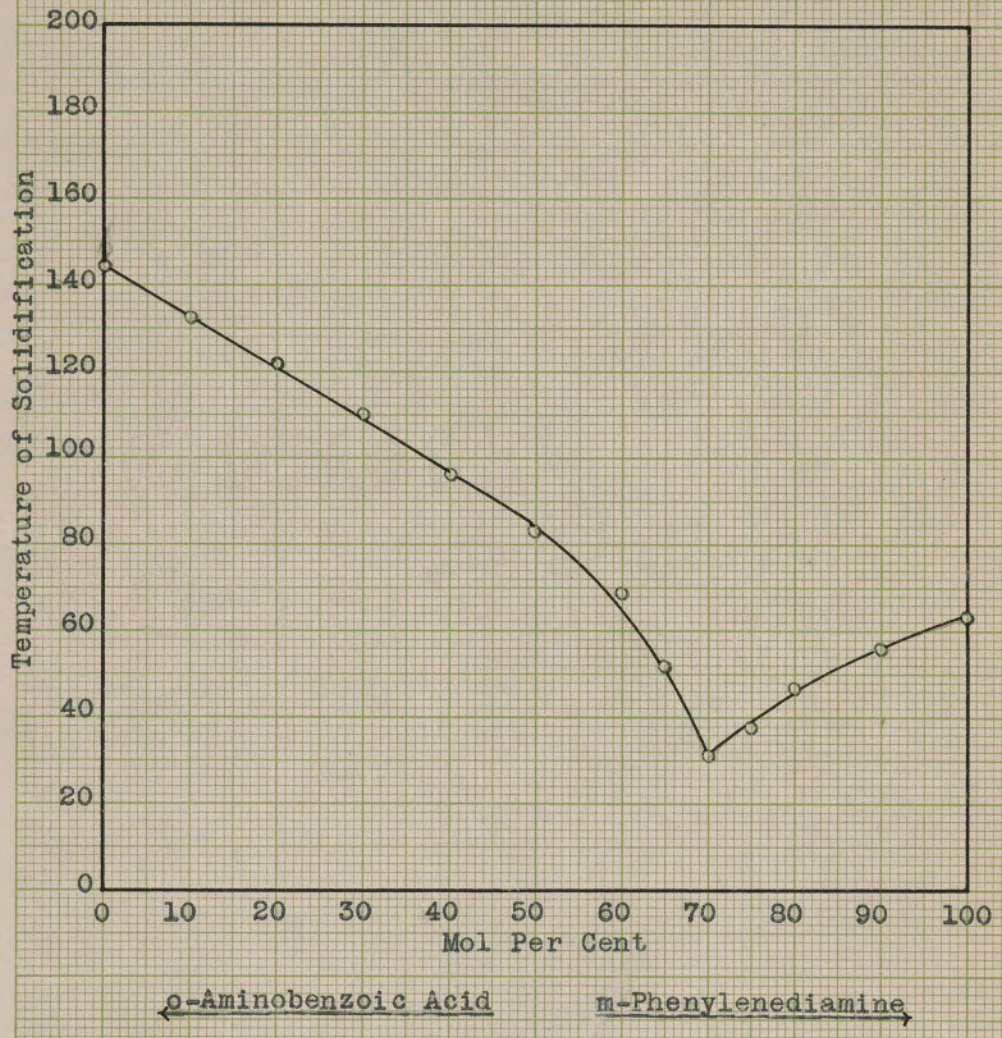

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Table 8

Concentration-Freezing-Point Data of the Binary Solution of o-Aminobenzoic Acid and Pyridine

o-Aminobenzoic Acid		Pyridine		Freezing Point
Grams	Mol Per Cent	Grams	Mol Per Cent	
1.3706	100	0.0000	00	144.0
1.3706	90	0.0878	10	134.0
1.3706	80	0.1976	20	129.0
1.3706	70	0.3387	30	105.0
1.3706	60	0.5269	40	82.0
1.3706	55	0.6467	45	60.0
1.3706	50	0.7905	50	34.0
1.3706	45	0.9660	55	- 1.0
1.3706	40	1.1856	60	-10.0
1.3706	35	1.4679	65	-20.0
1.3706	30	1.8443	70	-40.0

Figure 8

Freezing-Point Curve for o-Aminobenzoic Acid and Pyridine

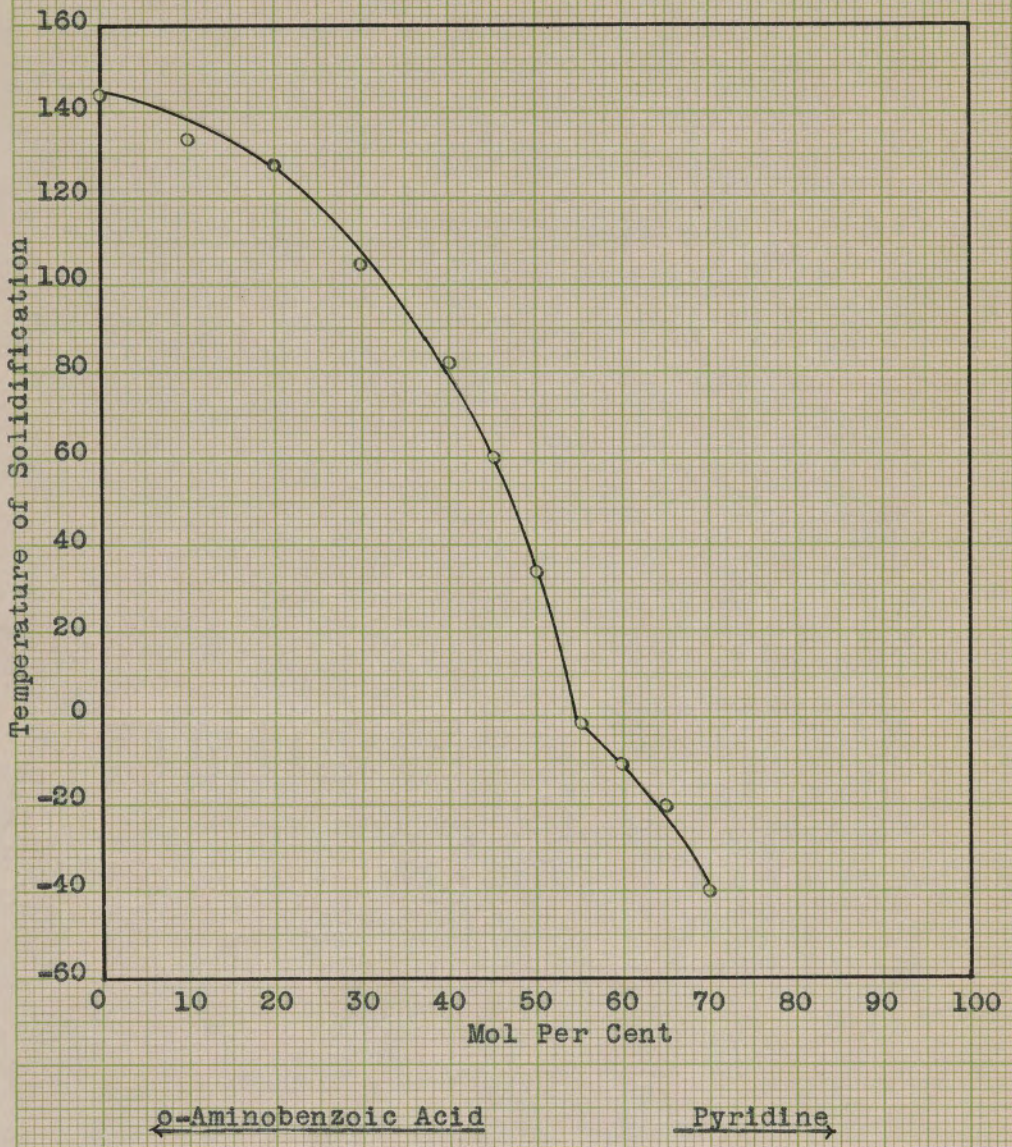

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Table 9

Concentration-Freezing-Point Data of the Binary Solution of o-Aminobenzoic Acid and o-Toluidine

o-Aminobenzoic Acid		o-Toluidine		Freezing Point
Grams	Mol Per Cent	Grams	Mol Per Cent	
1.3706	100	0.0000	00	144.0
1.3706	90	0.1189	10	135.0
1.3706	80	0.2677	20	126.5
1.3706	70	0.4589	30	120.0
1.3706	60	0,7138	40	111.0
1.3706	50	1.0708	50	99.5
1.3706	45	1.3086	55	90.5
1.3706	40	1.6056	60	81.0
1.3706	35	1.9884	65	72.0
1.3706	30	2.4983	70	62.5
1.3706	25	3.2121	75	41.0
1.3706	20	4.2828	80	17.0
1.3706	15	6.0673	85	- 9.0

Figure 9

Freezing-Point Curve for o-Aminobenzoic Acid and o-Toluidine

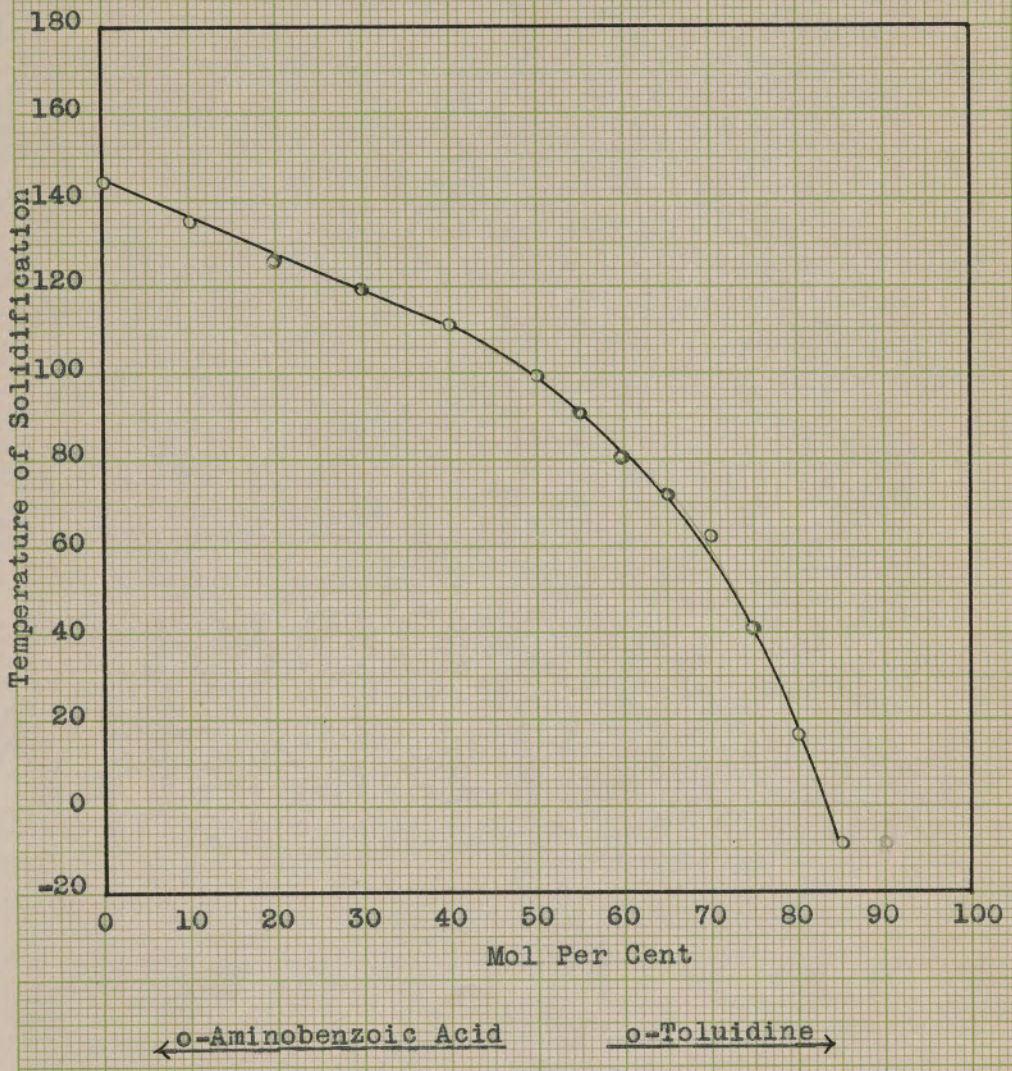

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Table 10

Concentration-Freezing-Point Data of the Binary Solution of o-Aminobenzoic Acid and m-Toluidine

o-Aminobenzoic Acid		m-Toluidine		Freezing Point
Grams	Mol Per Cent	Grams	Mol Per Cent	
1.3706	100	0.0000	00	144.0
1.3706	90	0.1189	10	135.0
1.3706	80	0.2677	20	126.0
1.3706	70	0.4589	30	119.0
1.3706	60	0.7138	40	109.0
1.3706	50	1.0708	50	98.0
1.3706	45	1.3086	55	91.0
1.3706	40	1.6056	60	83.0
1.3706	35	1.9884	65	74.0
1.3706	30	2.4983	70	65.0
1.3706	25	3.2121	75	45.0
1.3706	20	4.2828	80	19.5
1.3706	15	6.0673	85	-10.0

Figure 10

Freezing-Point Curve for o-Aminobenzoic Acid and m-Toluidine

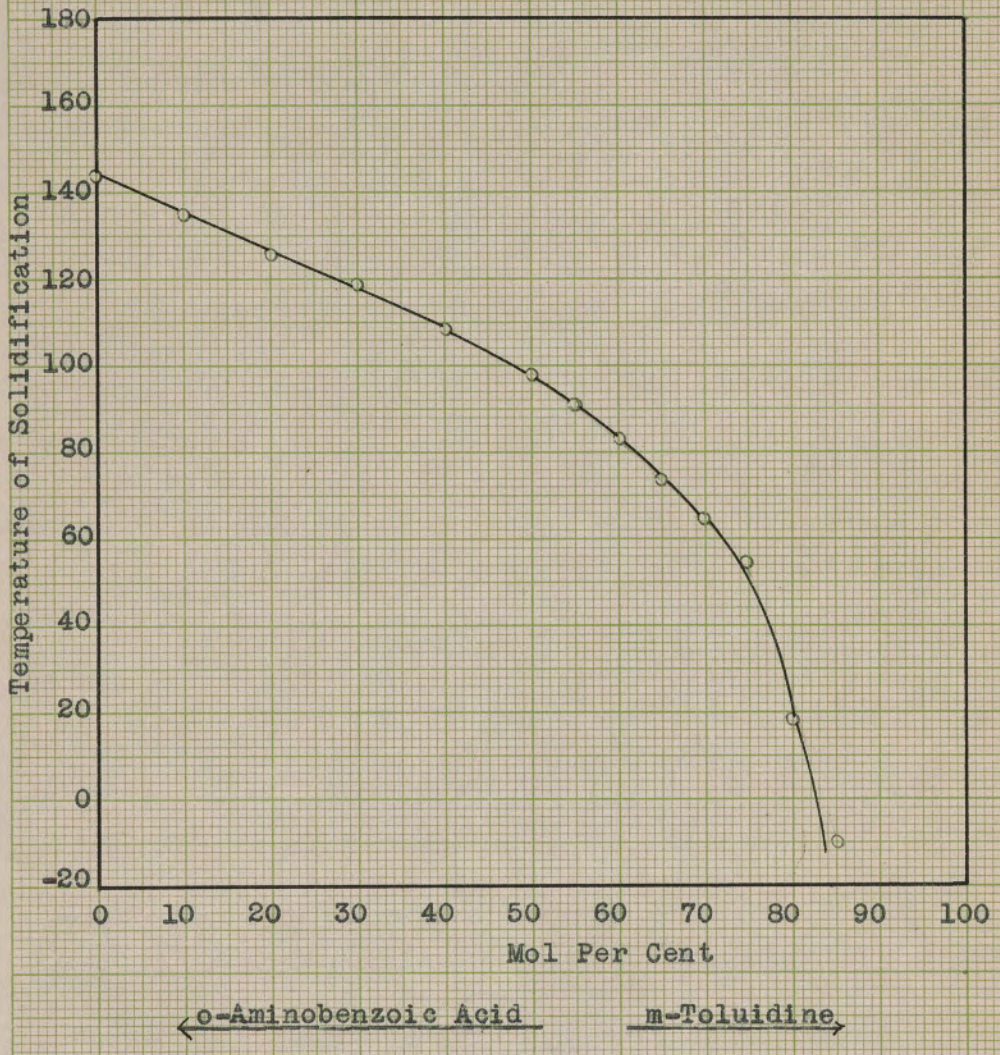

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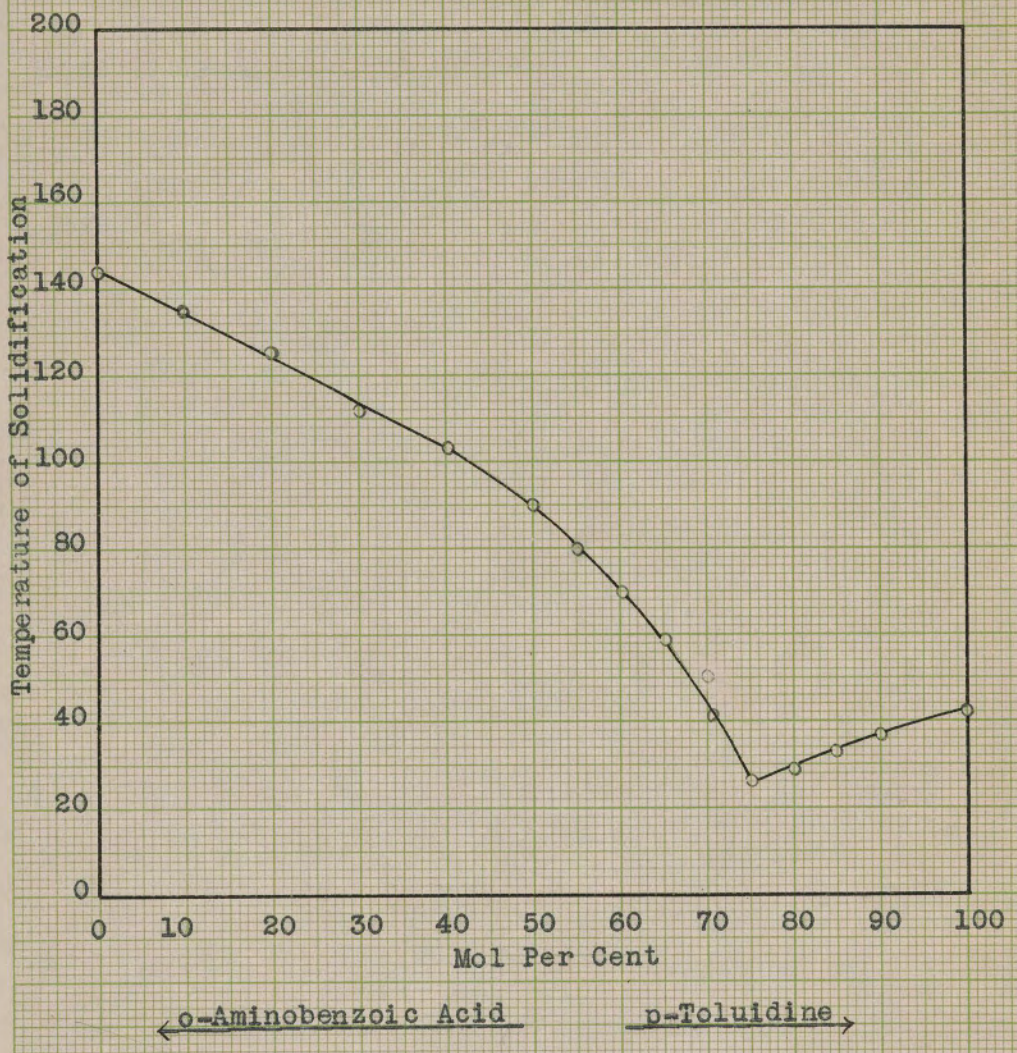
Table 11

Concentration-Freezing-Point Data of the Binary Solution of o-Aminobenzoic Acid and p-Toluidine

o-Aminobenzoic Acid		p-Toluidine		Freezing Point
Grams	Mol Per Cent	Grams	Mol Per Cent	
1.3706	100	0.0000	00	144.0
1.3706	90	0.1189	10	135.0
1.3706	80	0.2677	20	125.0
1.3706	70	0.4589	30	112.0
1.3706	60	0.7138	40	103.0
1.3706	50	1.0708	50	90.5
1.3706	45	1.3086	55	80.0
1.3706	40	1.6056	60	70.0
1.3706	35	1.9884	65	59.5
1.3706	30	2.4983	70	40.0
1.3706	25	3.2121	75	26.0
1.3706	20	4.2828	80	29.0
1.3706	15	6.0673	85	33.0
1.3706	10	9.6364	90	37.0
0.0000	00	2.0000	100	42.0

Figure 11

Freezing-Point Curve for o-Aminobenzoic Acid and p-Toluidine



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Triethylamine and o-aminobenzoic acid were the first compounds studied which showed compound formation. The data and results are given in Table 12 and Figure 12. The third and fourth freezing points in this curve were hard to determine because of supercooling, but after the first eutectic point was reached at 11° and the molecular compound became the solvent this difficulty ceased. The curve rose to a maximum of 90° after the first eutectic was passed and then fell off rapidly. Due to the low freezing point of triethylamine the second eutectic point was not reached. The maximum point on the curve was reached when the mixture was composed of fifty per cent of each component. This showed that the two components combined at a ratio of 1:1. This same ratio was also shown by an analysis of the compound.

Table 12

Concentration-Freezing-Point Data of the Binary Solution of o-Aminobenzoic Acid and Triethylamine

o-Aminobenzoic Acid		Triethylamine		Freezing Point
Grams	Mol Per Cent	Grams	Mol Per Cent	
1.3706	100	0.0000	00	144.0
1.3706	90	0.1124	10	133.0
1.3706	80	0.2528	20	105.0
1.3706	70	0.4334	30	12.0
1.3706	60	0.6741	40	60.0
1.3706	55	0.8273	45	88.0
1.3706	50	1.0112	50	90.0
1.3706	45	1.2359	55	89.0
1.3706	40	1.5168	60	80.0
1.3706	30	2.3595	70	60.0
1.3706	20	4.0449	80	38.0
1.3706	10	9.1011	90	8.5

Figure 12

Freezing-Point Curve for o-Aminobenzoic Acid and Triethylamine

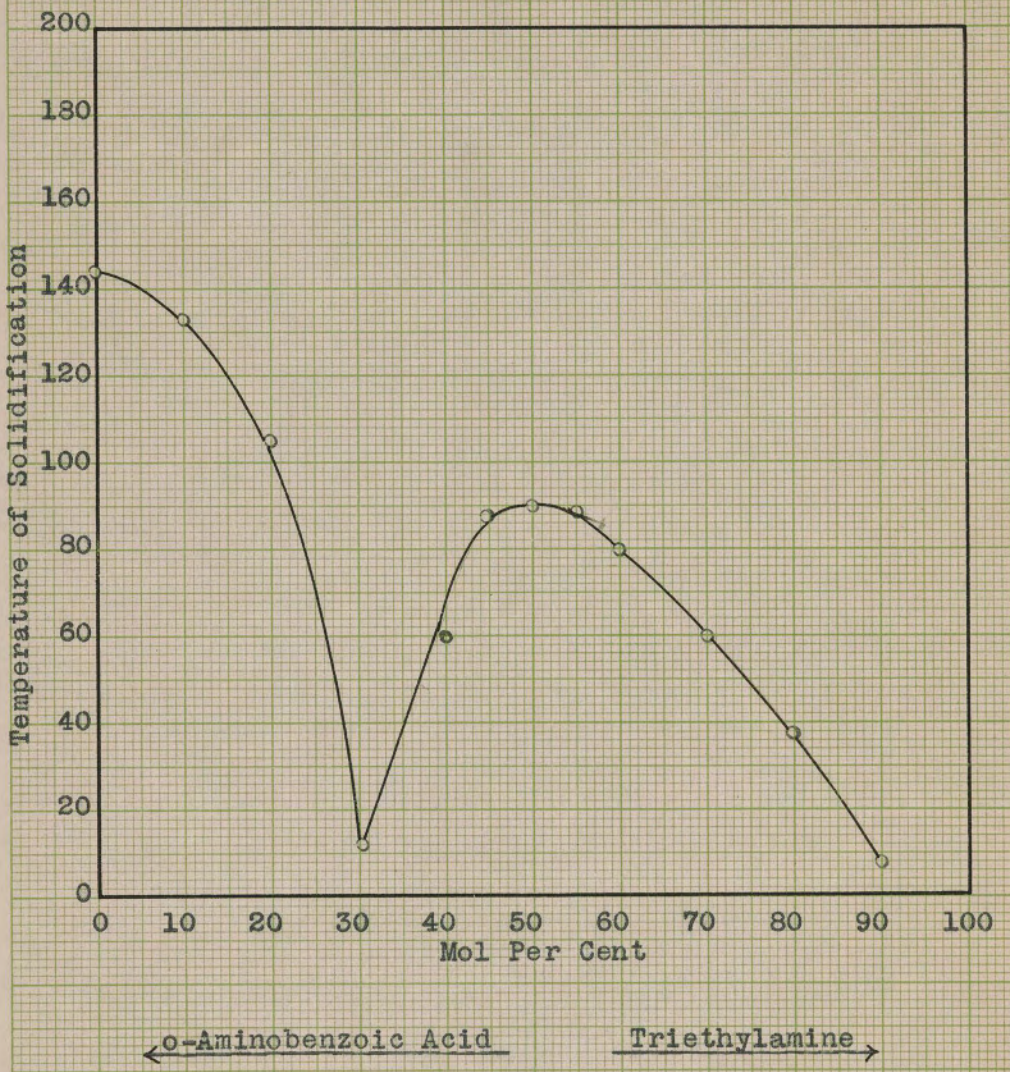

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Table 13

Concentration-Freezing-Point Data of the Binary Solution of p-Aminobenzoic Acid and Acetamide

p-Aminobenzoic Acid		Acetamide		Freezing Point
Grams	Mol Per Cent	Grams	Mol Per Cent	
1.3706	100	0.0000	00	187.5
1.3706	90	0.0656	10	165.0
1.3706	80	0.1476	20	148.0
1.3706	70	0.2530	30	122.5
1.3706	65	0.3179	35	109.7
1.3706	60	0.3936	40	99.0
1.3706	50	0.5905	50	75.0
1.3706	45	0.7216	55	65.0
1.3706	40	0.8857	60	52.0
1.3706	35	1.0966	65	25.0
1.3706	30	1.3777	70	41.0
1.3706	25	1.7714	75	50.0
1.3706	20	2.3618	80	59.2
1.3706	10	5.3141	90	69.0
0.0000	00	2.0000	100	78.0

Figure 13

Freezing-Point Curve for p-Aminobenzoic Acid and Acetamide

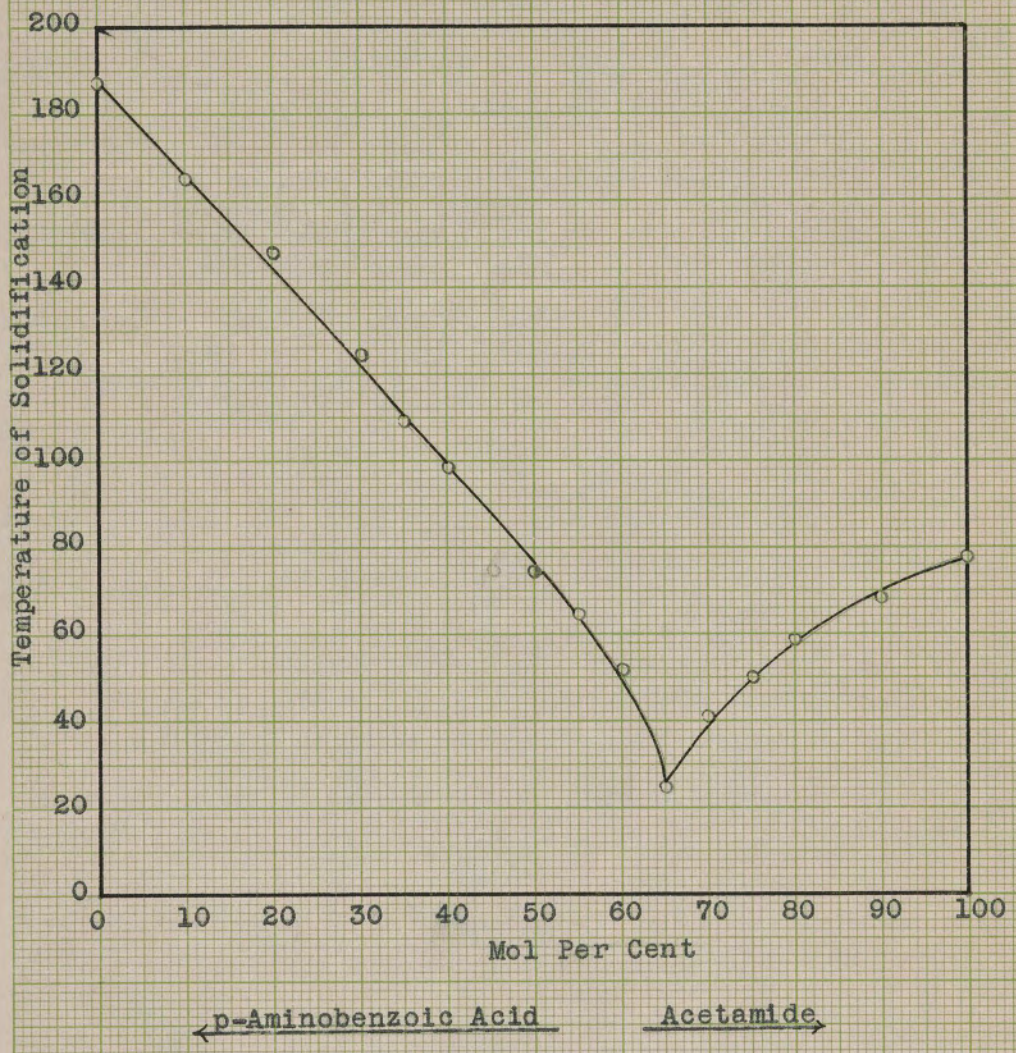

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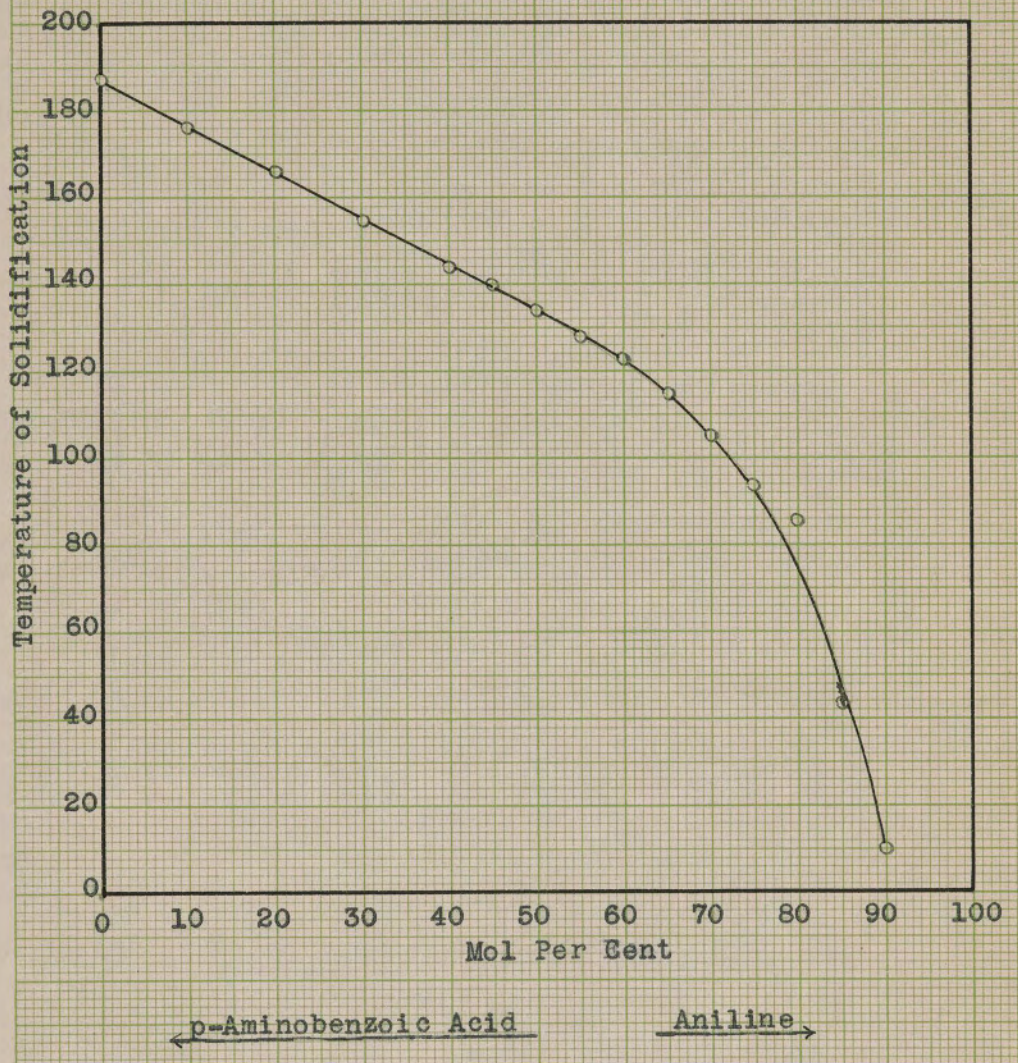
Table 14

Concentration-Freezing-Point Data of the Binary Solution of p-Aminobenzoic Acid and Aniline

p-Aminobenzoic Acid		Aniline		Freezing Point
Grams	Mol Per Cent	Grams	Mol Per Cent	
1.3706	100	0.0000	00	187.5
1.3706	90	0.1032	10	176.5
1.3706	80	0.2323	20	166.0
1.3706	70	0.3982	30	155.0
1.3706	60	0.6194	40	144.5
1.3706	55	0.7602	45	140.0
1.3706	50	0.9292	50	134.5
1.3706	45	1.1357	55	128.5
1.3706	40	1.3932	60	123.0
1.3706	35	1.7257	65	115.0
1.3706	30	2.1682	70	105.0
1.3706	25	2.7877	75	94.0
1.3706	20	3.7170	80	76.0
1.3706	15	5.2657	85	43.0
1.3706	10	8.3633	90	10.0

Figure 14

Freezing-Point Curve for p-Aminobenzoic Acid and Aniline



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Diethylamine and p-aminobenzoic acid were the second and last compounds to give a concentration-freezing point curve showing compound formation. This curve is shown in Figure 15 and the data is given in the corresponding table. This curve was difficult to run due to the high melting point of the amino acid and the low boiling point of diethylamine. This difficulty was overcome by cooling the mixture below the boiling point of diethylamine before each addition of the second component. When the maximum freezing point between the two eutectics was reached, it was found impossible to pass this point by the addition of more diethylamine. This was due to the fact that compound formation was no longer taking place and the excess diethylamine evaporated. The curve was completed by adding enough of the second component to lower the freezing point to less than the boiling point of diethylamine. This explains why no data is given for points between the diethylamine concentrations of fifty-five and eighty-five per cent. Both the freezing point curve and analysis showed the components of this compound to be combined in a ratio of 1:1.

Table 15

Concentration-Freezing-Point Data of the Binary Solution of p-Aminobenzoic Acid and Diethylamine

p-Aminobenzoic Acid		Diethylamine		Freezing Point
Grams	Mol Per Cent	Grams	Mol Per Cent	
1.3706	100	0.0000	00	187.8
1.3706	90	0.0812	10	168.0
1.3706	80	0.1828	20	140.0
1.3706	75	0.2438	25	115.0
1.3706	70	0.3132	30	129.0
1.3706	60	0.4872	40	148.0
1.3706	55	0.5980	45	159.0
1.3706	50	0.7310	50	160.0
1.3706	45	0.8933	55	158.0
1.3706	40	1.0963	60	---
1.3706	30	1.7055	70	---
1.3706	20	2.9237	80	---
1.3706	15	4.1420	85	39.5
1.3706	10	6.5785	90	10.0

Figure 15.

Freezing-Point Curve for p-Aminobenzoic Acid and Diethylamine

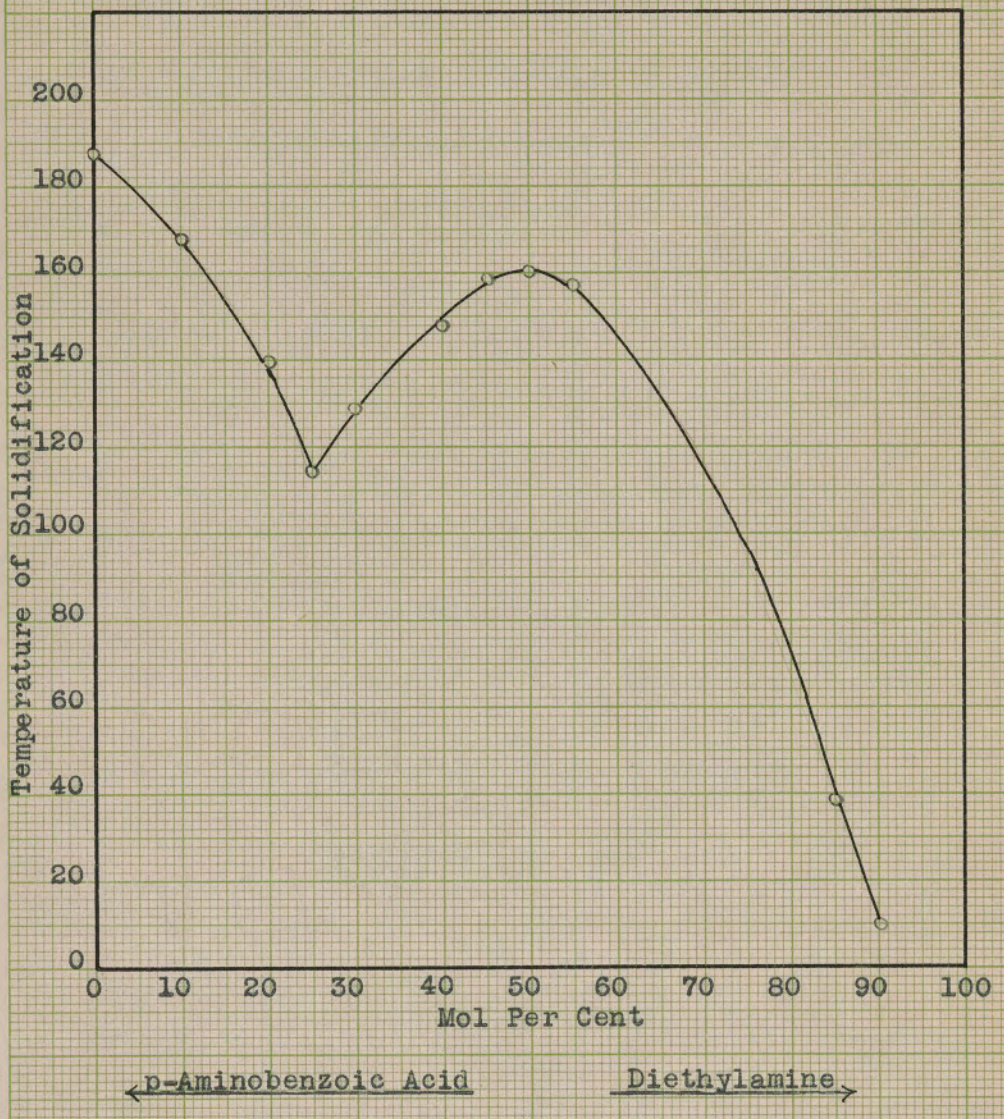

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Table 16

Concentration-Freezing-Point Data of the Binary Solution of p-Aminobenzoic Acid and Dimethylaniline

p-Aminobenzoic Acid		Dimethylaniline		Freezing
Grams	Mol Per Cent	Grams	Mol Per Cent	Point
1.3706	100	0.0000	00	187.5
1.3706	90	0.1345	10	177.5
1.3706	80	0.3027	20	167.0
1.3706	70	0.5189	30	160.0
1.3706	60	0.8072	40	153.5
1.3706	55	0.9907	45	150.5
1.3706	50	1.2109	50	146.5
1.3706	45	1.4799	55	143.0
1.3706	40	1.8163	60	140.0
1.3706	35	2.2488	65	137.0
1.3706	30	2.8254	70	133.0
1.3706	25	3.6327	75	128.0
1.3706	20	4.8437	80	121.0
1.3706	15	6.8618	85	104.0
1.3706	10	10.8983	90	81.0
1.3706	5	24.0075	95	0.5
0.0000	0	4.0000	100	2.0

Figure 16

Freezing-Point Curve for p-Aminobenzoic Acid and Dimethylaniline

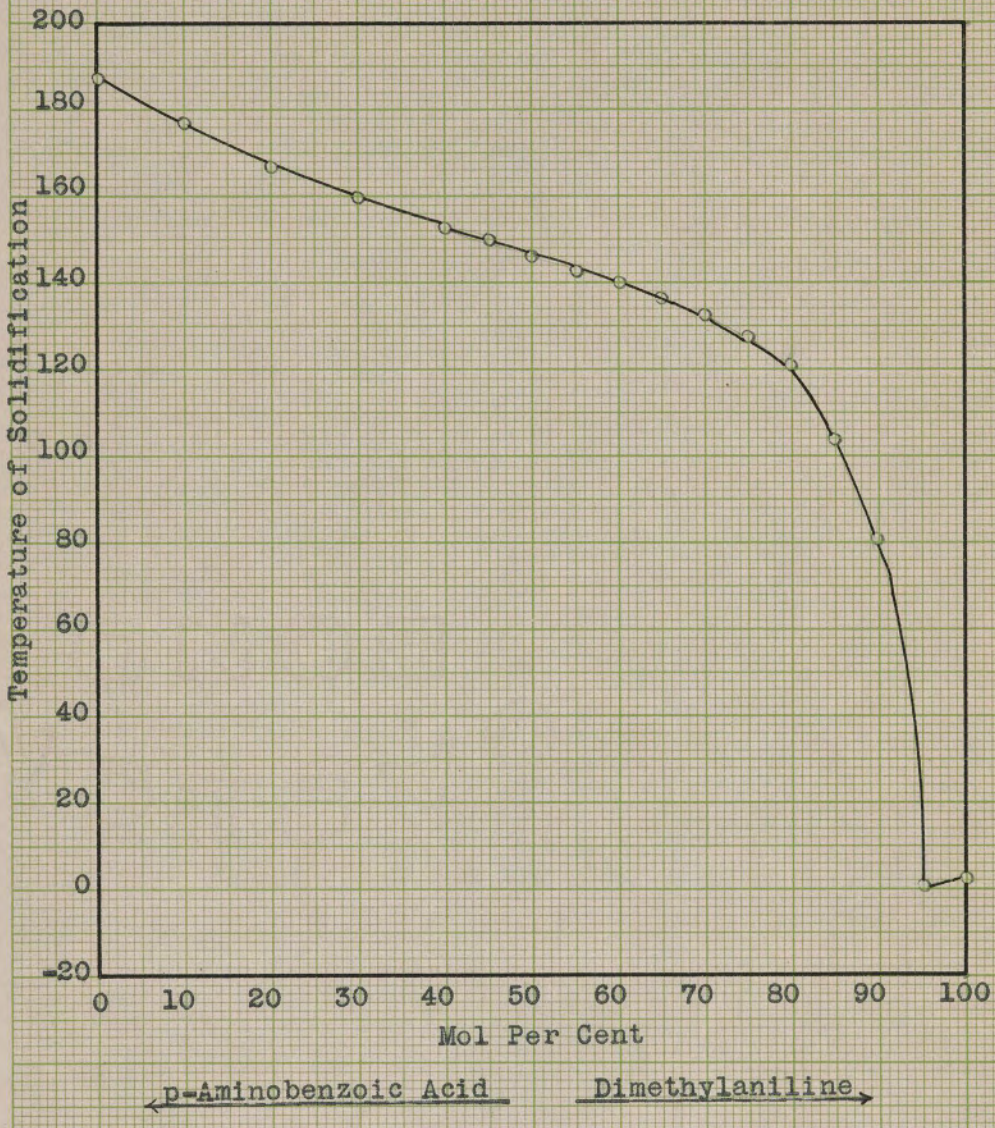

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Table 17

Concentration-Freezing-Point Data of the Binary Solution of p-Aminobenzoi c Acid and Methylaniline

p-Aminobenzoic Acid		Methylaniline		Freezing Point
Grams	Mol Per Cent	Grams	Mol Per Cent	
1.3706	100	0.0000	00	187.5
1.3706	90	0.1189	10	176.0
1.3706	80	0.2676	20	165.5
1.3706	70	0.4588	30	156.0
1.3706	60	0.7127	40	147.0
1.3706	55	0.8759	45	144.0
1.3706	50	1.0705	50	139.0
1.3706	45	1.3084	55	135.0
1.3706	40	1.6058	60	131.0
1.3706	35	1.9882	65	126.5
1.3706	30	2.4279	70	121.5
1.3706	25	3.2117	75	115.0
1.3706	20	4.2823	80	100.5
1.3706	15	6.0666	85	90.0
1.3706	10	9.6351	90	73.0

Figure 17

Freezing-Point Curve for p-Aminobenzoic Acid and Methylaniline

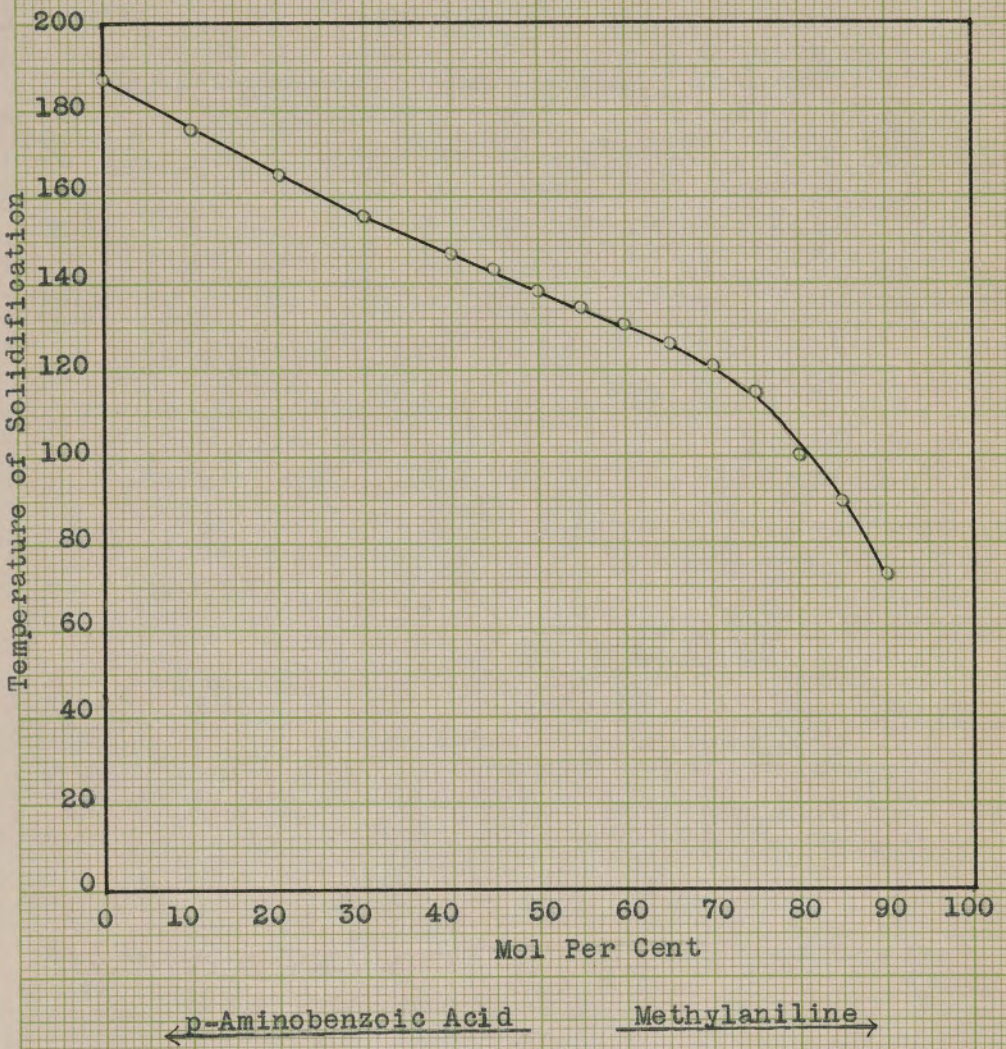

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Table 18

Concentration-Freezing-Point Data of The Binary Solution of p-Aminobenzoic Acid and a-Naphthylamine

p-Aminobenzoic Acid		a-Naphthylamine		Freezing Point
Grams	Mol Per Cent	Grams	Mol Per Cent	
1.3706	100	0.0000	00	187.5
1.3706	90	0.1584	10	176.0
1.3706	80	0.3562	20	168.0
1.3706	70	0.6108	30	156.5
1.3706	60	0.9800	40	145.0
1.3706	50	1.4308	50	134.5
1.3706	40	2.1378	60	119.5
1.3706	30	3.3250	70	109.5
1.3706	25	4.2757	75	99.0
1.3706	20	5.7016	80	83.0
1.3706	15	8.0767	85	63.0
1.3706	10	12.8286	90	41.0
0.0000	00	2.0000	100	50.0

Figure 18

Freezing-Point Curve for p-Aminobenzoic Acid and a-Naphthylamine

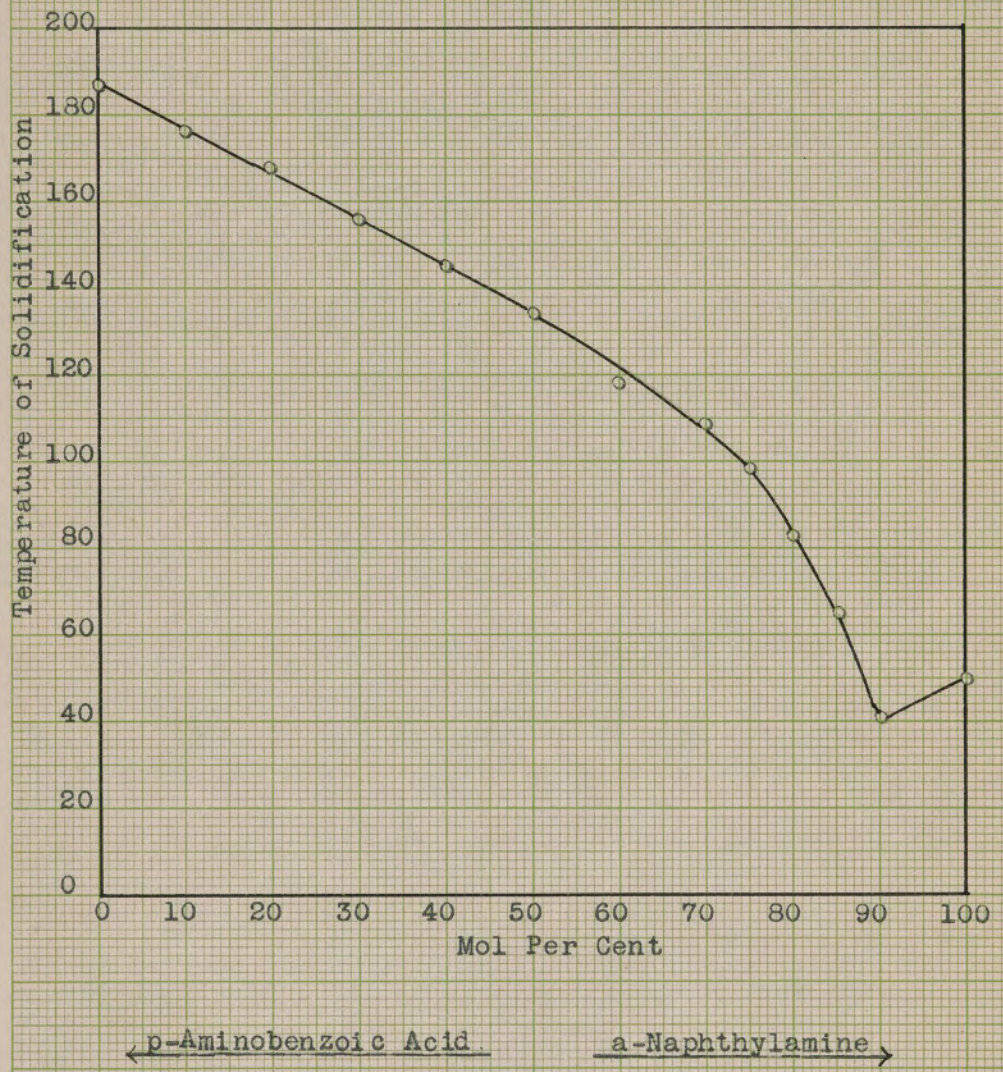

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Table 19

Concentration-Freezing-Point Data of the Binary Solution of p-Aminobenzoic Acid and o-Phenylenediamine

p-Aminobenzoic Acid		o-Phenylenediamine		Freezing Point
Grams	Mol Per Cent	Grams	Mol Per Cent	
1.3706	100	0.0000	00	187.5
1.3706	90	0.1201	10	170.5
1.3706	80	0.2702	20	157.0
1.3706	70	0.4632	30	144.0
1.3706	60	0.7205	40	131.5
1.3706	50	1.0808	50	111.5
1.3706	40	1.6211	60	88.0
1.3706	35	2.0070	65	76.0
1.3706	30	2.5216	70	85.0
1.3706	25	3.2422	75	89.0
1.3706	20	4.3229	80	92.0
1.3706	10	9.7265	90	96.0
0.0000	00	2.0000	100	101.0

Figure 19

Freezing-Point Curve for p-Aminobenzoic Acid and o-Phenylenediamine

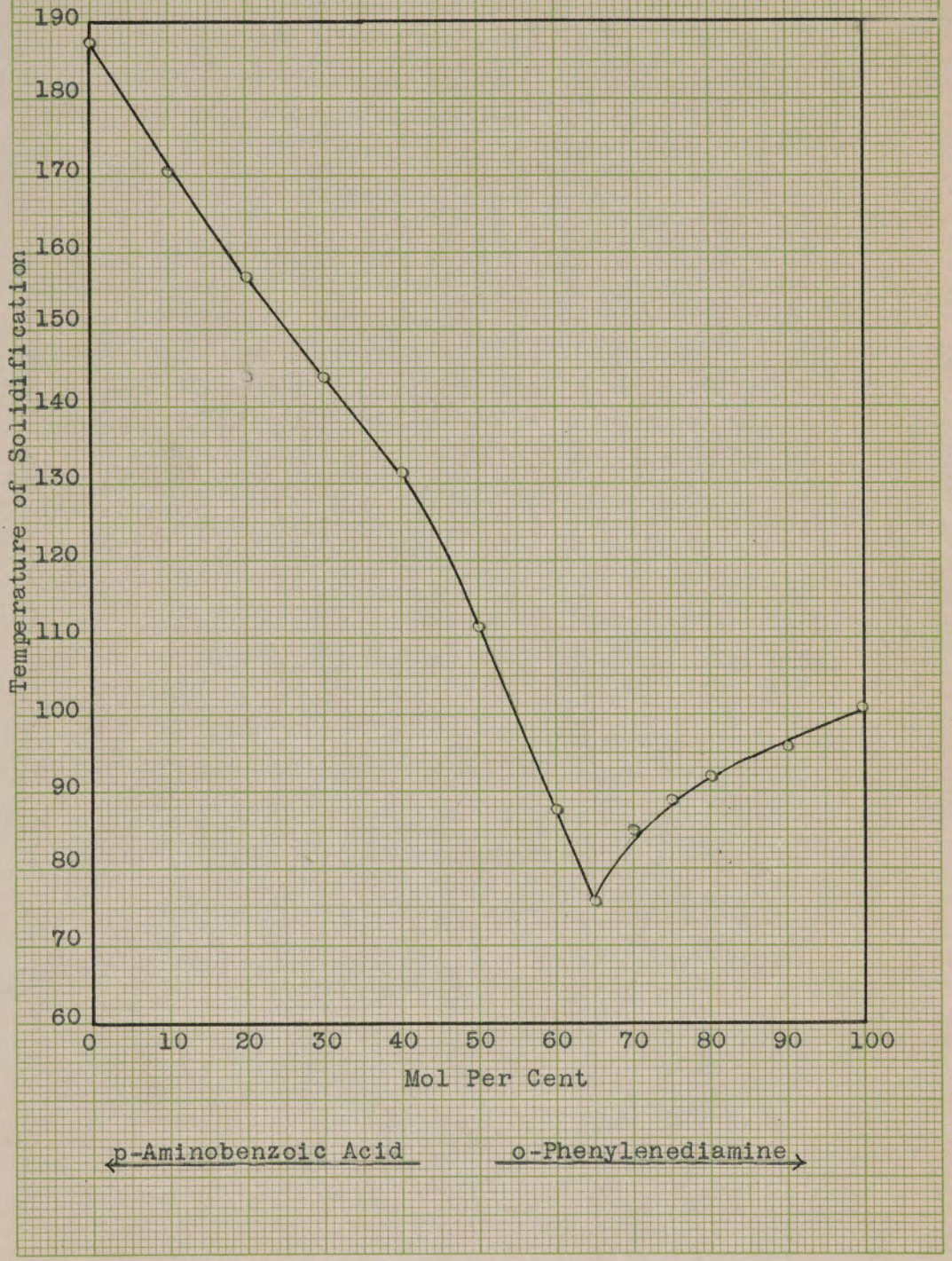

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Table 20

Concentration-Freezing-Point Data of the Binary Solution of p-Aminobenzoic Acid and m-Phenylene-diamine

p-Aminobenzoic Acid		m-Phenylendiamine		Freezing
Grams	Mol Per Cent	Grams	Mol Per Cent	Point
1.3706	100	0.0000	00	187.5
1.3706	90	0.1201	10	170.0
1.3706	80	0.2702	20	158.0
1.3706	70	0.4632	30	145.0
1.3706	60	0.7205	40	132.0
1.3706	50	1.0808	50	118.0
1.3706	40	1.6211	60	100.0
1.3706	35	2.0070	65	86.0
1.3706	30	2.5216	70	70.0
1.3706	25	3.2422	75	42.0
1.3706	20	4.3229	80	43.0
1.3706	10	9.7265	90	53.5
0.0000	00	2.0000	100	63.0

Figure 20

Freezing-Point Curve for p-Aminobenzoic Acid and m-Phenylenediamine

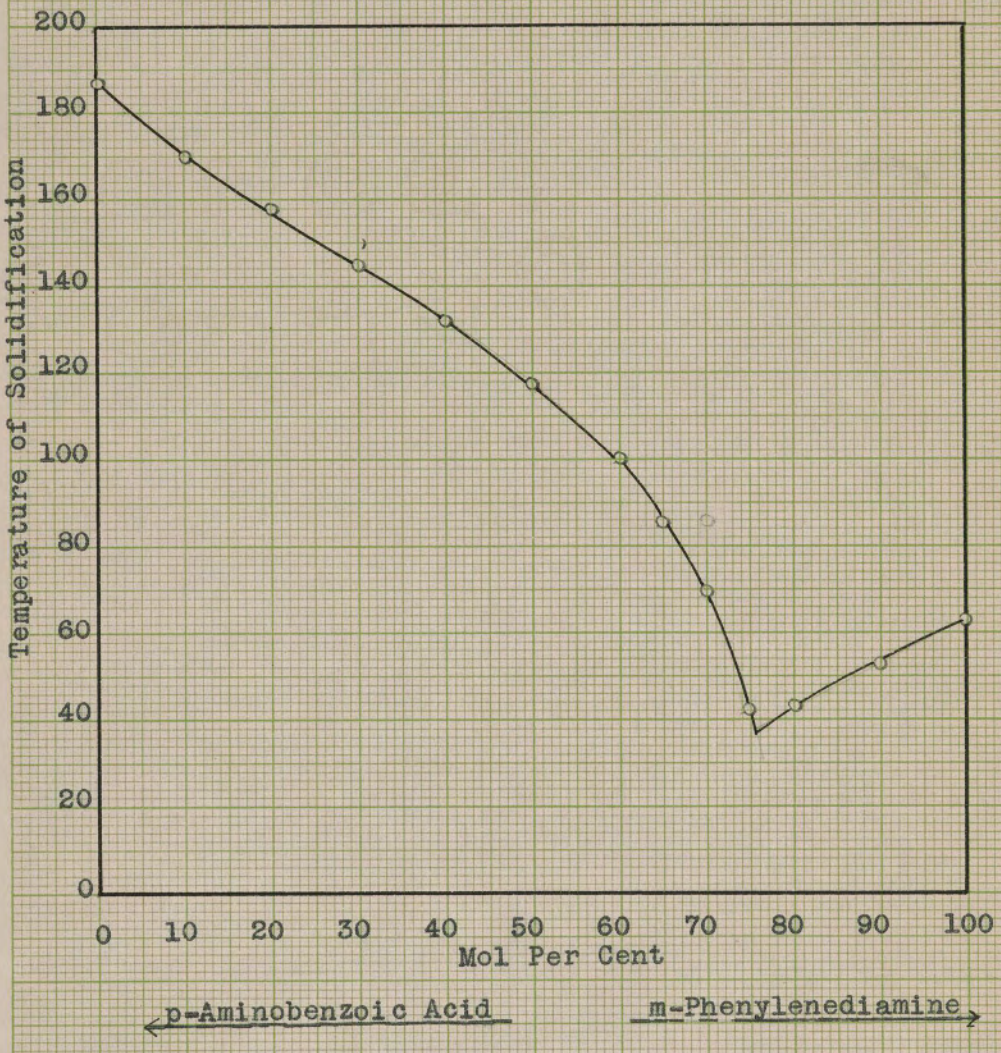

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Table 21

Concentration-Freezing-Point Data of the Binary Solution of p-Aminobenzoic Acid and Pyridine

p-Aminobenzoic Acid		Pyridine		Freezing Point
Grams	Mol Per Cent	Grams	Mol Per Cent	
1.3706	100	0.0000	00	187.5
1.3706	90	0.0878	10	176.0
1.3706	80	0.1976	20	163.0
1.3706	70	6.3387	30	148.0
1.3706	60	0.5269	40	129.0
1.3706	55	0.6467	45	115.0
1.3706	50	0.7905	50	100.5
1.3706	45	0.9660	55	82.0
1.3706	40	1.1856	60	60.0
1.3706	35	1.4678	65	48.5
1.3706	30	1.8443	70	39.0
1.3706	25	2.3712	75	27.0
1.3706	20	3.1617	80	10.5
1.3706	15	4.4790	85	-10.0

Figure 21

Freezing-Point Curve for p-Aminobenzoic Acid and Pyridine

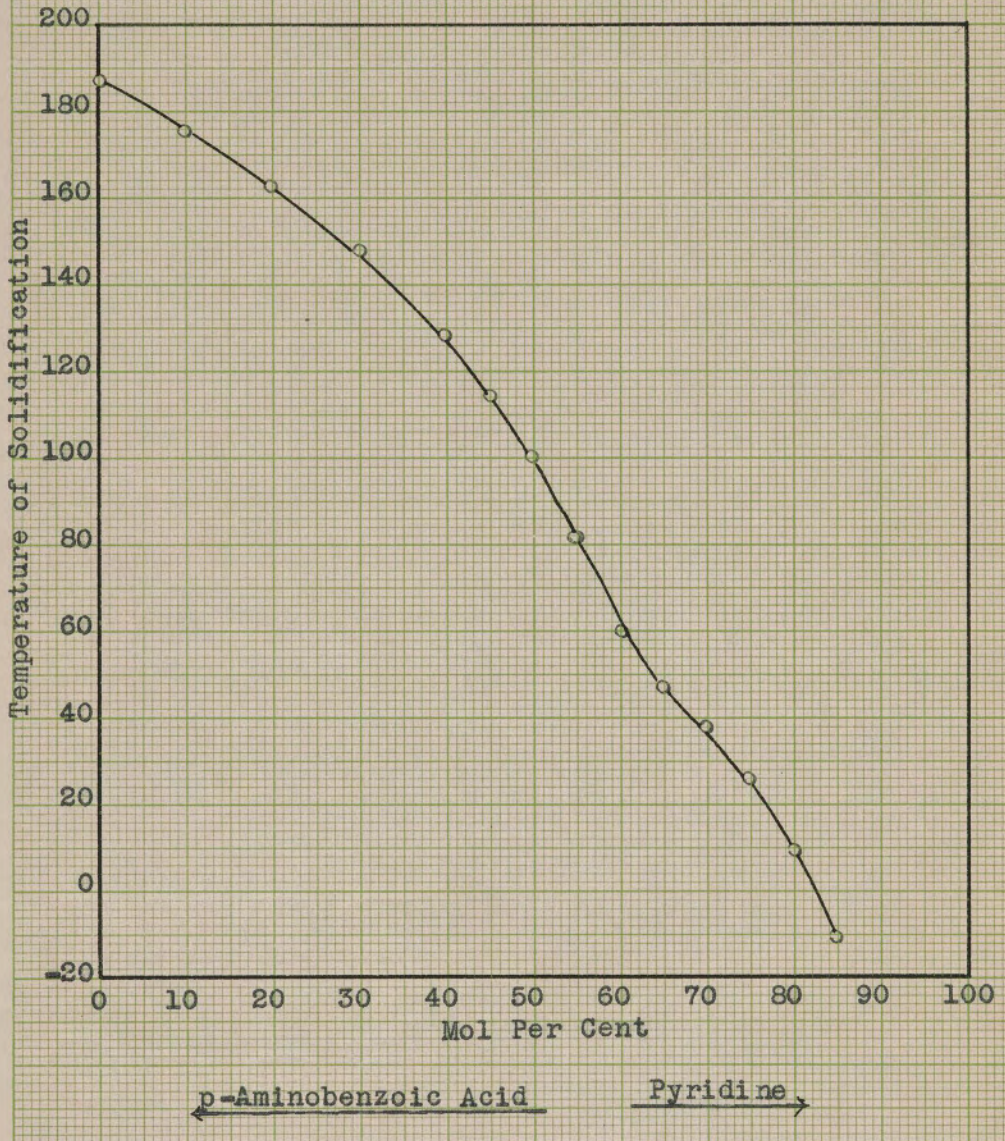

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Table 22

Concentration-Freezing-Point Data of the Binary Solution of p-Aminobenzoic Acid and o-Toluidine

p-Aminobenzoic Acid		o-Toluidine		Freezing Point
Grams	Mol Per Cent	Grams	Mol Per Cent	
1.3706	100	0.0000	00	187.5
1.3706	90	0.1189	10	176.0
1.3706	80	0.2677	20	165.0
1.3706	70	0.4589	30	151.5
1.3706	60	0.7138	40	144.0
1.3706	50	1.0708	50	130.0
1.3706	45	1.3086	55	125.0
1.3706	40	1.6056	60	118.0
1.3706	35	1.9884	65	110.0
1.3706	30	2.4983	70	103.5
1.3706	25	3.2121	75	95.0
1.3706	20	4.2828	80	84.0
1.3706	15	6.0673	85	60.0
1.3706	10	9.6364	90	7.5

Figure 22

Freezing-Point Curve for p-Aminobenzoic Acid and o-Toluidine

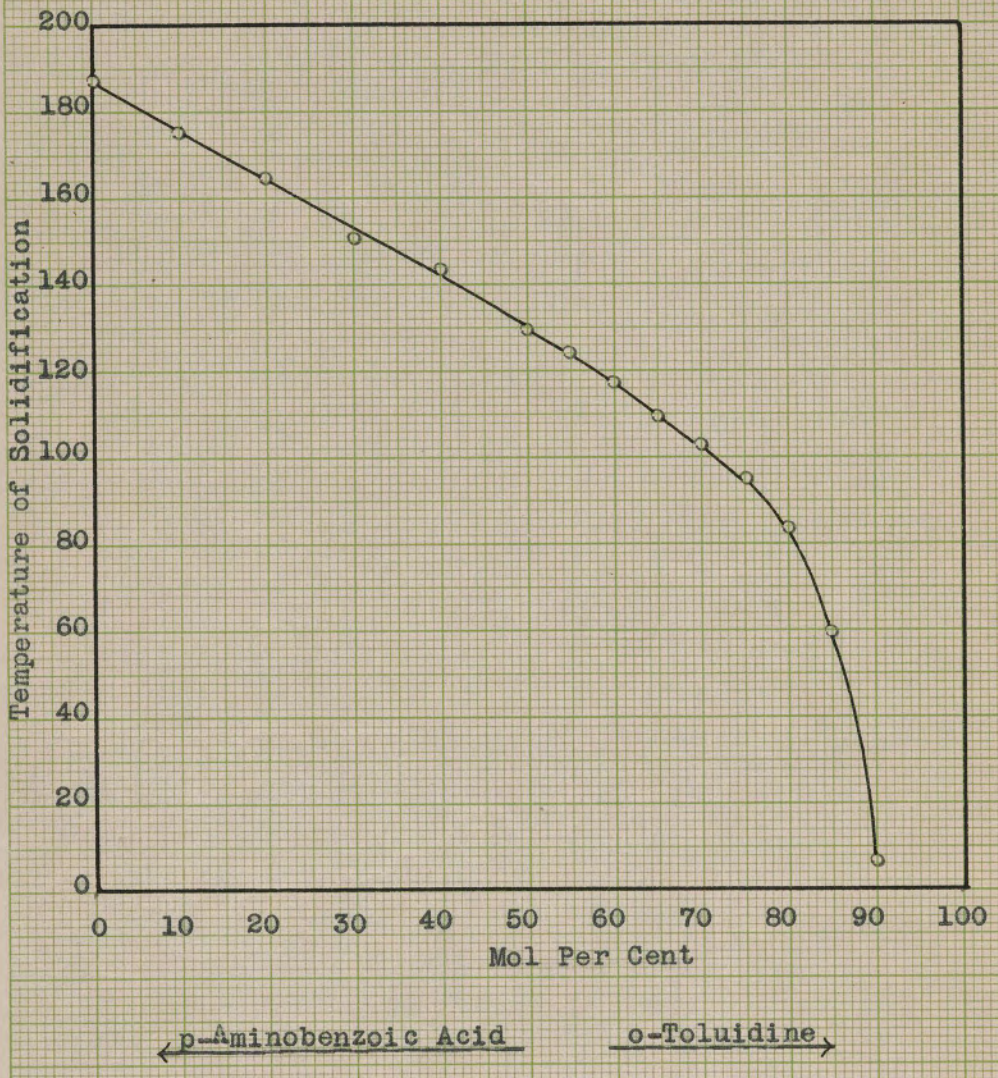

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Table 23

Concentration-Freezing-Point Data of the Binary Solution of p-Aminobenzoic Acid and m-Toluidine

p-Aminobenzoic Acid		m-Toluidine		Freezing Point
Grams	Mol Per Cent	Grams	Mol Per Cent	
1.3706	100	0.0000	00	187.5
1.3706	90	0.1189	10	175.0
1.3706	80	0.2677	20	165.5
1.3706	70	0.4589	30	154.5
1.3706	60	0.7138	40	145.0
1.3706	50	1.0708	50	134.0
1.3706	45	1.3086	55	128.0
1.3706	40	1.6056	60	121.0
1.3706	35	1.9884	65	113.0
1.3706	30	2.4983	70	105.0
1.3706	20	4.2828	80	80.0
1.3706	15	6.0673	85	52.0
1.3706	10	9.6364	90	- 2.0

Figure 23

Freezing-Point Curve for p-Aminobenzoic Acid and m-Toluidine

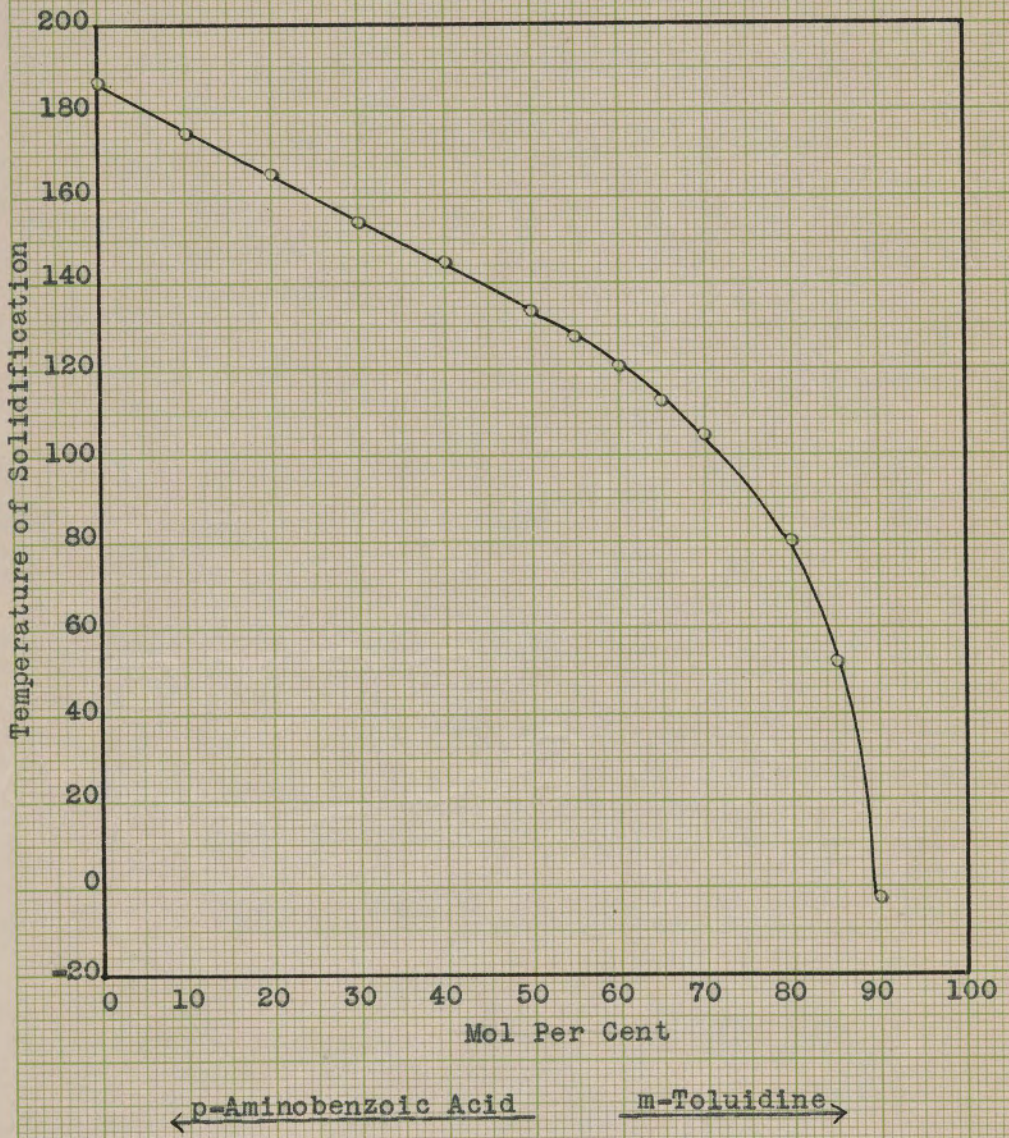

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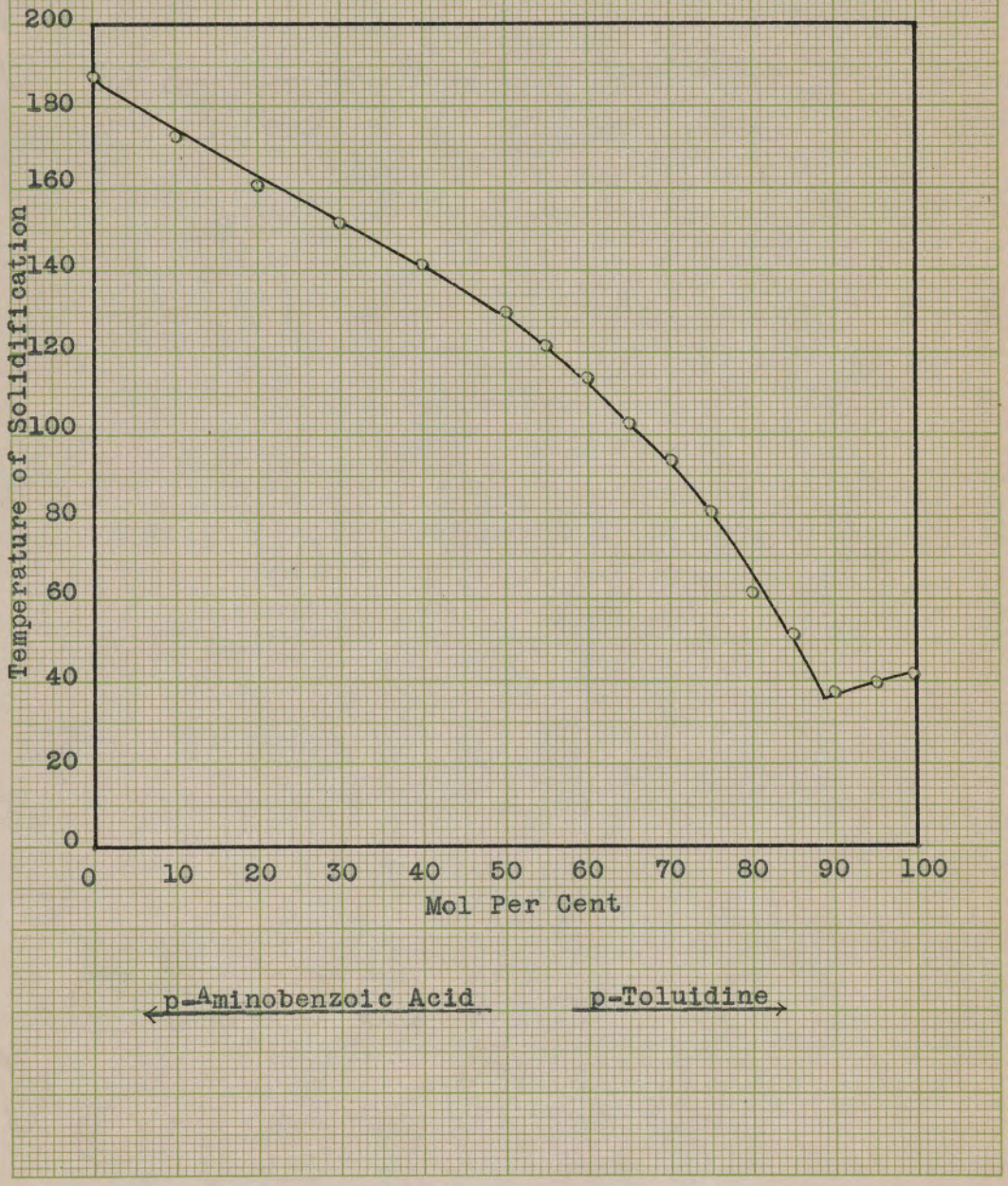
Table 24

Concentration-Freezing-Point Data of the Binary Solution of p-Aminobenzoic Acid and p-Toluidine

p-Aminobenzoic Acid		p-Toluidine		Freezing Point
Grams	Mol Per Cent	Grams	Mol Per Cent	
1.3706	100	0.0000	00	187.5
1.3706	90	0.1189	10	173.0
1.3706	80	0.2677	20	161.5
1.3706	70	0.4589	30	152.0
1.3706	60	0.7138	40	141.0
1.3706	50	1.0708	50	130.5
1.3706	45	1.3086	55	122.0
1.3706	40	1.6056	60	114.0
1.3706	35	1.9884	65	103.0
1.3706	30	2.4983	70	94.0
1.3706	25	3.2121	75	81.0
1.3706	20	4.2828	80	62.0
1.3706	15	6.0673	85	52.0
1.3706	10	9.6364	90	38.0
1.3706	5	20.3435	95	40.0
0.0000	0	2.0000	100	42.0

Figure 24

Freezing-Point Curve for p-Aminobenzoic Acid and p-Toluidine



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III. Determination of Physical Properties.

Since it is a known fact that the physical properties of a compound are determined largely by its structure, the melting point, neutral equivalent and molecular ratio of the components for each of the compounds were determined with the hope that these properties would be of value in explaining their structure.

A. Determination of Melting Points

The melting points of the molecular organic compounds were determined by the capillary tube method described by Mulliken[6]. The apparatus used in determining the melting points was made by suspending in a 250 cc. short-necked flask a test tube just long enough to hang by its rim on the mouth of the flask and reach within one centimeter of the bottom of the flask. The flask filled about two-thirds full of sulfuric acid served as an outer bath for the test tube which was also filled with acid to the same level as the acid in the flask. This double bath arrangement made it possible to control the temperature of the acid in the test tube which surrounded the thermometer and sample. A small crystal of potassium nitrate was added to the acid to prevent it from turning dark. The sample to be melted was placed in a small capillary tube which was made to adhere by surface tension

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6. Mulliken, "The Identification of Pure Organic Compounds", John Wiley and Sons, New York, 1904, Vol. 1, p. 218.

to a thermometer which had been dipped in sulfuric acid. The capillary tube was then placed parallel to the thermometer so that the sample was exactly even with the thermometer bulb. At this point the thermometer and capillary tube were immersed in the acid bath and enough heat was applied to raise the temperature at the rate of about six degrees per minute. The temperature at which the first drop of liquid was observed clinging to the side of the capillary tube was recorded as the melting point.

All melting points were determined with a thermometer calibrated by the Bureau of Standards and both stem correction and absolute correction for the thermometer were made on the readings obtained. The stem correction was made by using the general formula, Stem correction = Kxn(T-t), where K is the differential expansion coefficient of mercury in the particular kind of glass of which the thermometer is made, n the number of degrees emergent from the bath, T the temperature of the bath, and t the mean temperature of the emergent stem. In this particular case K was equal to 0.00016.

The absolute corrections were obtained from a graph made by plotting the corrections given in a table prepared by the Bureau of Standards against the corresponding temperature.

B. Neutral Equivalents.

Since the neutral equivalent of an acid is equal to the molecular weight divided by the number of replacable

Table 25

Physical Properties of the Molecular Compounds of o-Aminobenzoic Acid

Second Component	Color	Melting Point Corrected	Neutral Equivalent Observed		Neutral Equivalent Calculated
p-Aminophenol	White	124.0	250.61	249.87	246.12
Ammonia	White	137.4	267.89	266.08	154.09
Anthracene	White	182.5	362.32	365.63	315.14
Benzamide	White	85.6	270.27	268.45	258.12
Benzidine	Gray	81.7	286.12	285.71	229.11
Diethylamine	White	108.0	1818.18	1848.21	210.16
b-Naphthol	Gray	99.5	259.99	258.96	281.12
b-Naphthylamine	White	99.7	869.56	869.56	280.14
p-Phenylenediamine	Purple	97.4	244.08	243.90	245.14
Triethylamine	White	95.6	556.56	557.08	238.19
Urea	White	95.6-96.7	177.18	177.20	177.09

Table 26

Physical Properties of the Molecular Compounds of p-Aminobenzoic Acid

Second Component	Color	Melting Point Corrected	Neutral Equivalent Observed		Neutral Equivalent Calculated
p-Aminophenol	White	144.1	151.07	150.12	246.12
Ammonia	White	57.43	277.77	276.24	154.09
Benzamide	Light yellow	102.0	261.43	260.74	258.12
Benzidine	Gray	82.0	315.74	312.50	229.11
Diethylamine	White	170.2	1666.66	1639.34	210.16
b-Naphthol	Gray	107.5	257.08	257.92	281.12
b-Naphthylamine	White	101.2	649.35	645.15	280.14
p-Phenylenediamine	Purple	109.8	249.37	248.75	245.14
Triethylamine	White	123.7-125.2	555.55	552.48	238.19
Urea	Light yellow	144.1	176.99	176.91	177.09

hydrogen atoms, this property was determined and checked against the molecular ratios of the compounds as determined by analysis. The neutral equivalents were determined by dissolving a 0.2 gram sample of the compound in seventy-five cubic centimeters of water, heating the solution to boiling and titrating the hot solution with tenth normal sodium hydroxide. The neutral equivalent was calculated from the expression,

$$\text{Neutral equivalent} = \frac{\text{Weight of Sample x 1000}}{\text{cc. of Normal Alkali}}.$$

Phenolphthalein was used as an indicator in titrating all of the compounds except the two molecular compounds of p-phenylenediamine. These two compounds acted as their own indicators, giving a purple color in acid solution and a deep red in alkali.

The neutral equivalents obtained for the compounds did not check with the calculated values except in a few cases. This was doubtless due to interference from the amino groups which was extremely great in the case of aliphatic amines.

The melting points and neutral equivalents of all the organic molecular compounds isolated are given in Tables 25 and 26. The ammonium salts of o- and p-aminobenzoic acid are the only compounds prepared which were found described in literature.

C. Analysis of the Molecular Compounds.

The percentage of nitrogen in all of the molecular compounds was determined by a modification of the Kjeldahl[7]

7. Noyes, "Organic Chemistry", The Chemical Publishing Company, Easton, Pa., Fourth Edition, Revised (1920), p. 18.

method which was carried out as follows:

A 0.3 to 0.5 gram sample was placed in a 500 cc. Kjeldahl flask and to this was added 10 grams of potassium sulphate, 0.5 gram copper sulphate and 25 cc. of sulfuric acid. The contents of the flask were refluxed gently until a clear blue or green color was obtained. This usually required about two hours. The acid solution was then cooled and 160 cc. of twenty per cent sodium hydroxide was added. The first half was added slowly and thoroughly mixed with the contents of the flask. The last half of the alkali was added by gently pouring it down the side of the flask so that it did not mix with the solution in the flask but formed a layer on top of it. This prevented ammonia from being given off. About a tenth of a gram of powdered zinc was added to prevent the contents of the flask from bumping and the ammonia was distilled off into a measured amount of standard acid. After all of the ammonia had distilled off the excess acid was titrated with tenth normal sodium hydroxide solution. The percentage nitrogen was calculated from the following formula,

$$\text{Percentage nitrogen} = \frac{\text{cc. acid} \times N \times 0.014 \times 100}{\text{Weight of sample}},$$

where cc. of acid is the number of cc. of standard acid that was equivalent to the ammonia distilled off, N is the normality of the acid, and 0.014 the milliequivalent weight of nitrogen.

The percentages of nitrogen found in the compounds together with the molecular ratios of the components are given in Tables 27 and 28.

Table 27

Analytical Results on the Molecular Compounds of o-Amino-benzoic Acid

Second Components	Per Cent Nitrogen Found		Per Cent Nitrogen Calculated	Molecular Ratio of Acid to Second Component
p-Aminophenol	11.42	11.51	11.37	1:1
Ammonia	18.19	18.20	18.17	1:1
Anthracene	4.43	4.36	4.44	1:1
Benzamide	10.91	11.03	10.84	1:1
Benzidine	12.28	12.31	12.22	2:1
Diethylamine	13.34	13.39	13.32	1:1
b-Naphthol	5.01	5.06	4.98	1:1
b-Naphthylamine	9.92	9.87	9.99	1:1
p-Phenylenediamine	17.16	17.28	17.13	1:1
Triethylamine	11.79	11.81	11.75	1:1
Urea	18.49	18.52	18.44	3:2

Table 28

Analytical Results on the Molecular Compounds of p-Amino-benzoic Acid

Second Components	Per Cent Nitrogen Found		Per Cent Nitrogen Calculated	Molecular Ratio of Acid to Second Component
p-Aminophenol	11.36	11.41	11.37	1:1
Ammonia	18.14	18.21	18.17	1:1
Benzamide	10.93	11.01	10.84	1:1
Benzidine	12.36	12.23	12.22	2:1
Diethylamine	13.35	13.40	13.32	1:1
b-Naphthol	5.02	4.89	4.98	1:1
b-Nahpthylamine	9.98	10.02	9.99	1:1
p-Phenylenediamine	17.26	17.32	17.13	1:1
Triethylamine	11.76	11.87	11.75	1:1
Urea	18.35	18.41	18.44	3:2

CHAPTER IV

THEORETICAL DISCUSSION

I. Theories of Valence.

The theory of principal valence, of subsidiary valence, and the electronic theory have been used with more or less success in explaining the structure of organic molecular compounds.

A. Theory of Principal Valence.

Kendall[1] pointed out that an additive reaction takes place between two compounds which differed greatly in acidic strength. He explained this by assuming the acidic properties of the weaker acid were suppressed and basic properties introduced in the characteristic carbonyl group. He illustrated this reaction with the following equation:

$$R-\underset{\underset{OH}{|}}{C}=O + HX \rightleftharpoons R-\underset{\underset{OH}{|}}{C}=O\begin{matrix}X\\H\end{matrix}.$$

In reactions of this type he assumed that the oxygen in the weaker acid or compound of lower acidity changed its valence from two to four and united with the ions of

---

1. Kendall and Carpenter, J. Am. Chem. Soc., 36, 2498 (1914)

the stronger acid.

Although this theory has been used successfully in explaining the linkage in certain types of organic molecular compounds its use is limited by the fact that it is applicable to certain types only.

B. Subsidiary Valence.

In 1893 Werner[2] advanced the theory of subsidiary valence to explain the structure of certain types of complex or molecular inorganic compounds which could not be explained by the older theories of valence. This theory explained the fact that two apparently saturated molecules could unite to form a stable compound by assuming that after the normal valence of a molecule had been satisfied it could unite with other molecules due to a residual affinity or subsidiary valence.

According to Werner certain atoms could attach to themselves, by non-ionized links, a definite number of other atoms, radicals, or even whole molecules. The maximum number of groups which could be attached to an atom by non-ionized links, was either four or six, and was called the coordination number. The molecule might contain other atoms or groups in addition to those which made up the coordination number, but such groups were less closely attached. Coordinatively unsaturated molecules, in which the maximum coordination number was not reached,

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2. Werner, Z. Anorg. Chem., 3, 267 (1893)

were possible.

This theory was applied to organic as well as inorganic compounds[3], but with only partial success. The merits of this theory were offset by the indefiniteness of residual affinity and the real significance of Werner's coordinate links was not understood until they were later explained in terms of electrons.

C. The Electronic Theory.

The first workable explanation of chemical combination in terms of electrons was made by Lewis[4] and based upon the octet theory of the atom. According to this theory the most stable atom is one which has a complete outside octet of eight electrons, and an atom with an incomplete outer octet tends to complete this by taking up electrons from other atoms or two atoms may share electrons and thus contribute to the stability of both. According to this theory chemical combination may take place by the transference of electrons from one atom to another or by the sharing of pairs of electrons between the atoms. These two types of combination are known respectively as electrovalency and covalency and the valence is represented by the number of electrons transfered or the number of pairs shared.

The electronic theory has been developed to a considerable extent since Lewis first published his explanation

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3. Werner, Ber., 42, 4324 (1909).
4. Lewis, J. Am. Chem. Soc., 38, 762-785 (1916).

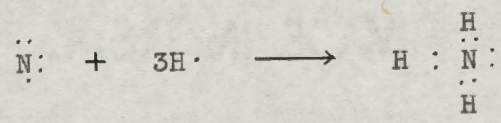
of it in 1916.

Although recent investigations in physics have shattered the theory of a static atom, the electronic theory of valence is more applicable today than ever before.

Sidgwick[5] gives the following classification of electronic types of linkages:

> (1) Polar or ionized linkages: due to the transference of electrons from one atom to another (electrovalency).
>
> (2) Non-polar, non-ionizable (covalent) linkages: due to the sharing of electrons, two to each link, between the atoms. These can arise in two ways:
>
> a. One electron contributed by each atom: normal covalencies: limited in number (like electrovalencies) by the periodic group of the atom.
>
> b. Both electrons contributed by the same atom: co-ordinate covalencies; when these are formed the numerical value of the covalency is no longer dependent on the periodic group to which the atom belongs.

The normal covalent type of linkage is illustrated in the union of hydrogen with nitrogen to form ammonia.



In this reaction each hydrogen atom unites with the nitrogen atom by sharing a pair of electrons in a normal covalent linkage, and in each case one electron is furnished

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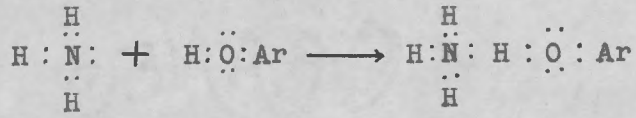
5. Sidgwick, "The Electronic Theory of Valence", Oxford University Press, London, 1929, p. 61.

by the hydrogen and one by the nitrogen. Three normal covalences are the maximum number that can be formed by nitrogen since this gives it the full valency group of eight. Three pairs of the eight electrons are shared with hydrogen, leaving two unshared electrons to form a so-called "lone pair".

The existence of a lone pair gives rise to the coordinate covalent type of linkage in which both electrons are contributed by the same atom. This type of linkage may be shown by the combination of ammonia with a phenol



In a coordinate link the atom which furnishes the two electrons is called the donor and the one which receives a share in them is known as the acceptor. In the above example nitrogen is the donor and the phenolic hydrogen the acceptor.

In cases where a single molecule contains two atoms which are capable of acting as acceptor and donor a coordinate linkage may take place and thus form a ring structure which is known as a chelate ring. This is especially true in the case of ortho disubstituted benzene derivatives.

The nitrogen atom in the amino group of o-aminobenzoic acid possesses a lone pair of electrons and the hydrogen atom in the carboxyl group is capable of acting as an acceptor. Since this acid meets the theoretical requirements

for forming a chelate ring, a study was made of its properties to find any evidence for the actual existence of a ring structure.

The additive nature was the first property to be considered since recent evidence seems to prove that a chelated ortho disubstituted benzene derivative is less additive in nature than its meta and para isomers. This is brought out by an investigation by Buehler, Alexander and Stratton on the o-, m-, and p-nitrophenols[6]. In the case of the nitrophenols it was found that the ortho compound which had a chelate ring structure formed only one molecular organic compound while the m- and p-nitrophenols were very additive in nature.

However in this investigation the additive property of o-aminobenzoic acid was found to be as great if not greater than that of its para isomer. Thus the first link in the evidence indicated that a chelate ring was not present in the o-aminobenzoic acid molecule.

The solubility of the acid was checked since chelation makes the solubility greater in unassociated solvents and less in associated. It was found that o-aminobenzoic acid was less soluble in water than its para isomer and more soluble in benzene. Since water is an associated solvent and benzene is nonassociated, solubilities seemed to indicate a chelate ring structure. However both acids were only sparingly soluble in both

---

6. Buehler, Alexander, and Stratton, J. Am. Chem. Soc., 53, 4094 (1931).

solvents and it is doubtful if the solubility of the anthranilic acid was great enough to indicate a chelated structure.

Sidgwick and Callow[7] while studying the abnormal properties of ortho benzene derivatives which were chelated, found that the amino compounds did not show evidence of a chelate ring. They claimed that this was due to the fact that nitrogen has a stronger tendency than oxygen to form a positive ion and for this reason it has a weaker tendency to coordinate with hydrogen.

The properties studied of o-aminobenzoic acid seemed to indicate that it does not have a chelated structure but it would be necessary to make a more thorough investigation before coming to a conclusive answer.

II. Probable Structure of the Organic Molecular Compounds of o- and p-Aminobenzoic Acid.

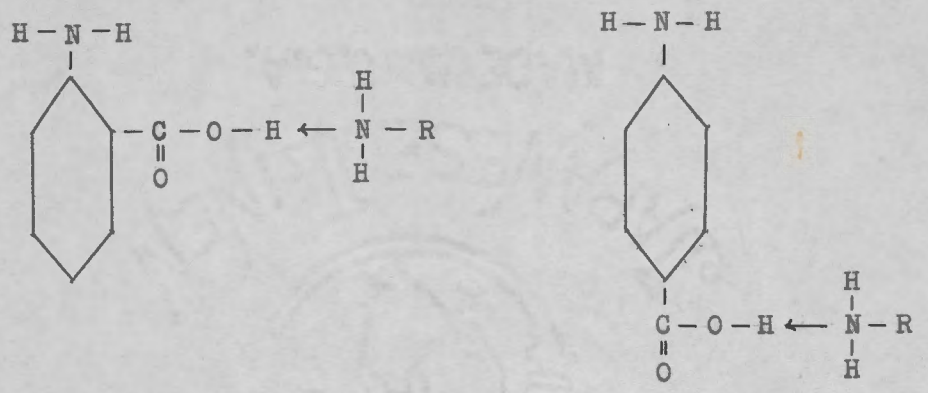
There are two atoms in the aminobenzoic acids capable of forming coordinate covalent linkages. The nitrogen in the amino group possessed a lone pair of electrons and is therefore capable of assuming the role of a donor while the hydrogen in the carboxyl group may act as an acceptor.

In cases where the second component was an amine the most likely point of addition was between the nitrogen atom in the amino group of the second component and the

---

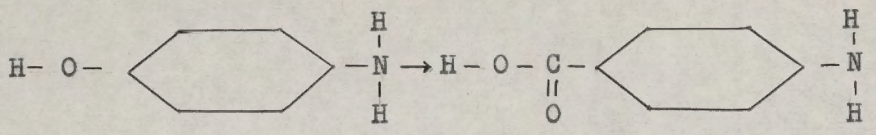
7. Sidgwick and Callow, J. Chem. Soc., 125, 527 (1924).

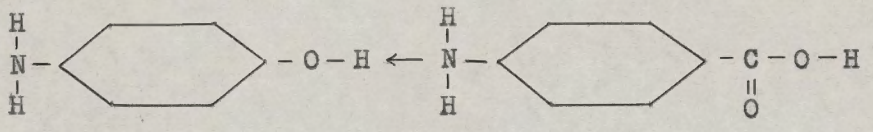
hydrogen atom in the carboxyl group of the acid. The probable structure of the molecular compounds formed by the aminobenzoic acid with amines would then be as follows:



The arrow in the formulas shown above represents a coordinate linkage and points to the atom which acts as the acceptor. In these compounds the nitrogen atom of the amino group in the second component is the donor and the hydrogen in the carboxyl group of the acid is the acceptor.

There are two possible points of coordinate linkage in the compounds formed with p-aminophenol. The linkage could take place between the nitrogen of the aminophenol and the hydrogen of the carboxyl group as it does with amines or the nitrogen atom in the amino group of the acid could act as a donor and combine with the phenolic hydrogen atom which is capable of acting as an acceptor. The two possibilities are shown in the following formulas of p-aminobenzoic acid-p-aminophenol.





Sufficient evidence was not obtained from the properties of the compounds formed with p-aminophenol to justify a choice between the two formulas.

The most logical structure of the compounds formed by the aminobenzoic acids with b-naphthol would be a coordinate linkage between the nitrogen atom of the aminobenzoic acid molecule and the phenolic hydrogen of the b-naphthol. The same type of linkage is probably present in o-aminobenzoic acid-anthracene, with a hydrogen in the hydrocarbon molecule acting as the acceptor.

The compounds formed with urea are exceptional cases in that the molecular ratio of the components is 3:2 and the nature of the linkages between the components could not be determined.

CHAPTER V

SUMMARY

I. A historical treatment has been given of the work of previous investigators on the molecular compounds of o- and p-aminobenzoic acid.

II. Eleven organic molecular compounds of o-aminobenzoic acid and ten of p-aminobenzoic acid were isolated, and their molecular ratios, neutral equivalents, melting points, and color were observed and recorded. None of the compounds isolated have been described in literature except the two neutral ammonium salts.

III. In cases where compound formation was expected but attempts to isolate the compound failed, concentration-freezing-point curves were constructed; a total of twenty-four of these curves was completed.

IV. The properties of o-aminobenzoic acid were studied and evidence for the chelate ring structure was missing.

V. An electronic formula for the organic molecular compounds of o- and p-aminobenzoic acid was proposed.

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