droxyazo compounds described by Hewitt and Pope.[1] This led to the belief that it might be the sulphate of benzeneazochlorphenol. Water was poured over it, the mixture heated slightly and filtered. The resulting compound was found to be benzeneazoorthochlorphenol. The sulphuric acid in the water was determined.

Calculated for $C_{12}H_9N_2ClO.H_2SO_4$: H_2SO_4, 30.09.
Found: H_2SO_4, 29.65.

The formation of this compound is undoubtedly due to the saponification of the hydrazone at first formed, the resulting oxyazo compound then combining with the sulphuric acid originally present in the hydrazine sulphate to form the corresponding sulphate. While the hydrochlorides of a number of the hydroxyazo compounds have been prepared, so far as I know, this is the first sulphate to be described. Other quinones gave similar results, so that this method of preparation would seem to be a general one for the preparation of the sulphates of the hydroxyazo compounds.

COLUMBUS, OHIO.

STUDIES IN NITRATION. II.[2]—MELTING POINT CURVES OF BINARY MIXTURES OF ORTHO- META- AND PARANITRANILINES: A NEW METHOD FOR DETERMINING THE COMPOSITION OF SUCH MIXTURES.

BY J. BISHOP TINGLE AND H. F. ROELKER.

Received March 5, 1908.

During the last academic year the senior author, in conjunction with Dr. F. C. Blanck, carried out a somewhat extensive investigation of the nitration of *N*-substituted aniline derivatives. In the course of this work, the results of which have been awaiting publication, in the *American Chemical Journal* since the middle of August, 1907, the need was frequently felt for a simple, expeditious method for the determination of the composition of mixtures of the isomeric nitranilines. Moreover, for our purpose, it was necessary that the method should be applicable to relatively small quantities of material. The only processes of which we have been able to find descriptions in the literature consist of recrystallizations, accompanied, in some cases, by conversion of one or more of the nitranilines into some simple derivative. Apart from the question of their accuracy, such methods did not appeal to us because they certainly involve a considerable amount of labor, and probably demand for their successful operation a relatively large quantity of material.

Besides their differences in solubility, the nitranilines vary somewhat in color, in their strength as bases, and, quite widely, in their melting-

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[1] *Ber.*, **30**, 1624.

[2] Bishop Tingle and Blanck, *Am. Chem. J.*, **36**, 605 (1906).

points. The color of the compounds, especially in dilute solutions, appeared to be too nearly alike for our purpose, and a determination of the partition of acid between the isomers involves too much trouble, consequently we decided to investigate the curves produced by plotting the melting points of binary mixtures of the nitranilines against the composition. In this connection we should like to mention that A. F. Holleman has been for some time engaged with the investigation of the influence of water on the course of nitration of benzene, acetanilide, etc., and he has also studied the influence of substitution in the benzene nucleus.[1] In the course of a paper with C. H. Sluiter[2] he gives a brief tabular statement of the melting points of a few mixtures of *p*-nitracetanilide and dinitracetanilide. In another communication, with which we were not acquainted until after our own work was in progress, he speaks of "perhaps being able to determine the composition of binary mixtures of aromatic nitro compounds by reading off from a curve the depression in the melting point of A caused by the addition of varying quantities of B." As will be seen from the contents of our paper, such a mode of procedure is inapplicable to mixtures of the nitranilines and is essentially different from the plan which we have adopted. Holleman also describes briefly and without working details, a "method of extraction," which is applicable to the determination of the composition of ternary mixtures in general.[3]

Experimental.

Materials.—The nitranilines were obtained from Kahlbaum, they melted at 71°, 114° and 147°, the temperatures given in the literature for the *o*-, *m*- and *p*-compounds, respectively. Before use they were recrystallized from 95 per cent. alcohol, in such a way that half of the substance employed remained in the mother liquor. This treatment produced no change in the melting point.

The alcohol employed in the experiments described below was the ordinary commercial 95 per cent. It was filtered before use.

Preparation of Mixtures.—A weighed quantity of each nitraniline was dissolved separately in alcohol, at the ordinary temperature; the solutions contained about 2 per cent. of ortho- and metanitraniline, respectively, but in the case of the para derivative the concentration was only about 1 per cent. The quantities of each solution required to produce a mixture of the composition desired were run out from a burette and the alcohol evaporated on the water bath. In some cases the evaporation was allowed to take place at the ordinary temperature. The residue was then placed in a desiccator on filter paper, allowed to remain

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[1] *Ber.*, **39**, 1715 (1906).

[2] *Rec. trav. chim.*, **26**, 208 (1906).

[3] *Rep. Congres. chim. Pharm. Liege.*, p. 283, July, 1905.

about 24 hours and the melting-point determined. Fresh solutions were made up each day as required.

Orthonitraniline is very slightly volatile at the ordinary temperature and, like the other isomers, vaporizes somewhat with boiling alcohol. The magnitude of the error introduced in this manner cannot be very great, because mixtures of similar composition, prepared by evaporating the alcohol at the two temperatures mentioned, always showed the same melting point. Moreover, mixtures which had been wrapped in filter paper and exposed to the air showed no change in their melting point after several months. As will be seen from the tables, the composition of the mixtures which we employed varied by intervals of 2 per cent.

During the course of this work we had reason to suspect the accuracy of the statements made in the literature regarding the solubility of the nitranilines and we therefore made the following determinations. Separate portions of the three isomers were mixed with quantities of alcohol insufficient for complete solution, and the liquids were maintained for about 30 minutes, at 40°, in a thermostat. The clear solutions were then decanted and allowed to cool slowly to 15°. After remaining for a time at this temperature, in contact with the crystals which had separated, 10 cc. of each clear liquid was withdrawn by means of a pipette, the solutions allowed to evaporate at the ordinary temperature, and the residue dried in a desiccator. At 15°, 10 cc. of the respective solutions, in 95 per cent. alcohol, contain 1.5845 grams of ortho-, 0.4960 gram of meta- and 0.4030 gram of paranitraniline, respectively.

TABLE I.—MELTING POINT OF MIXTURES OF ORTHO- AND METANITRANILINES.

Per cent. of ortho.	M. p.	Per cent. of ortho.	M. p.	Per cent. of ortho.	M. p.	Per cent. of ortho.	M. p.	Per cent. of ortho.	M. p.
98	68.7°	78	55.3°	58	56.6°	38	57.5°	18	107.0°*
96	68.0°	76	55.0°	56	56.7°	36	60.2°	16	108.0°*
94	67.0°	74	54.8°	54	56.8°	34	58.2°	14	109.0°*
92	63.0°	72	54.6°	52	56.8°	32	57.8°	12	110.0°*
90	61.0°	70	54.0°	50	57.0°	30	57.2°	10	111.0°*
88	60.6°	68	55.4°	48	57.3°	28	64.0°	8	108.0°*
86	58.0°	66	55.6°	46	57.6°	26	70.4°	6	109.0°*
84	57.3°	64	55.7°	44	58.0°	24	80.0°	4	111.5°*
82	55.5°	62	55.8°	42	58.6°	22	87.8°	2	112.0°*
80	55.4°	60	56.5°	40	59.2°	20	104.0°		

The *melting points* were determined in the ordinary manner; the thermometer employed was a "standard" one, capable of being read to 0.1°. The temperature of the bath was usually raised rather rapidly until it was within 25° of the melting point of the substance under examination, after which the increase was about 8° per minute. No difficulty was experienced in obtaining constant results, even when the conditions were somewhat varied. In certain cases, which are duly noted, it was found to be desirable to determine the temperature at which the substance gave *clear globules* on the sides of the melting point tubes, because for the mixtures mentioned this was much more definite than the point at which the material melted completely and collected at the bottom of the capillary. This procedure does not affect the use of the curves for quantitative purposes.

The temperatures marked * are those at which the substances melted completely (see above). These mixtures, containing from 20 to 2 per cent. of orthonitraniline, became clear and globular at temperatures higher than those required to produce the same effect in the case of specimens containing a higher proportion of ortho compound; consequently this change of standard does not invalidate the use, for analytical purposes, of the curve given below. In Fig. 1, the data contained in the above table are plotted in the form of a curve.

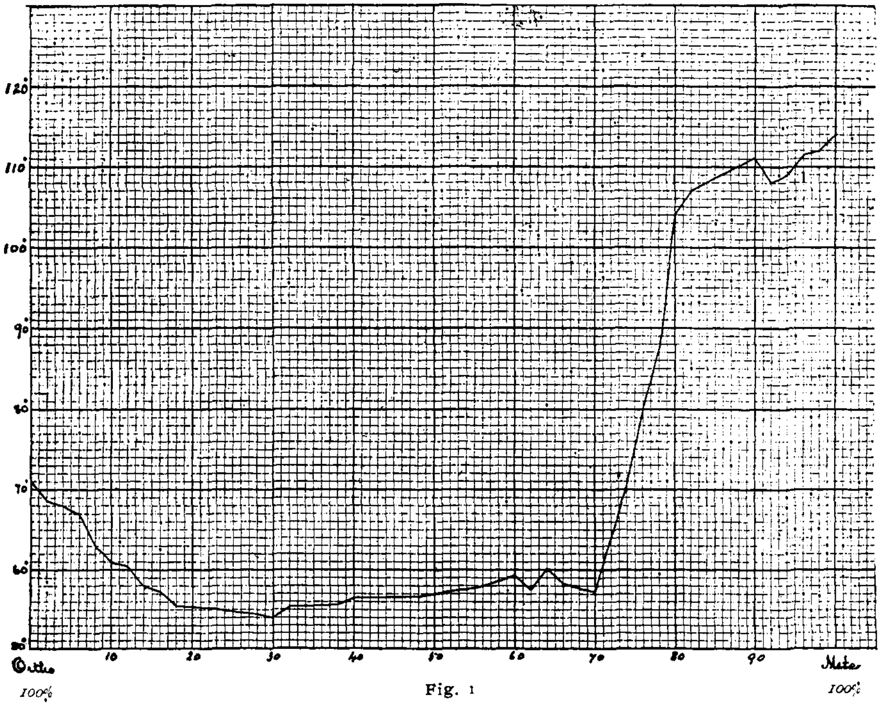

Fig. 1

In Table II are given the melting points of mixtures of meta- and paranitraniline.

The mixtures marked * became clear and globular (*vide* Table I) at the temperatures given, but did not melt completely. In a few cases the melting-point was not sharp, therefore we determined the limits of temperature within which the substance liquefied and give the mean value

TABLE II—MELTING POINTS OF MIXTURES OF META- AND PARANITRANILINE.

Per cent. of meta.	M. p.	Per cent. of meta.	M. p.	Per cent. of meta.	M. p.	Per cent. of meta.	M. p.	Per cent. of meta.	M. p.
98	111.5°	78	105.0°	58	91.5°	38	108.0°†	18	130.5°†
96	110.5°	76	104.5°	56	91.0°	36	111.5°†	16	135.5°†
94	111.0°	74	101.0°	54	90.5°	34	107.0°	14	136.5°
92	110.0°	72	102.0°	52	85.0°*	32	112.5°†	12	138.0°
90	107.5°	70	100.0°	50	93.0°	30	118.5°	10	140.0°
88	106 0°	68	99.0°	48	91.5°	28	123.0°†	8	142.0°
86	104.5°	66	91.0°	46	91.0	26	125.3°†	6	143.0°
84	110.5°	64	92.0°	44	98.8°†	24	122.0°	4	145.0°
82	107.0°	62	94.0°	42	95.5°	22	128.0°†	2	146.0°†
80	106.0°	60	93.5°	40	104.8°†	20	127.0°		

in the table; these figures are marked †. So far as we have been able to test the question, we have found these temperature limits to be constant. The 30 per cent. mixture was almost, but not completely, melted at 118.5°, whereas that containing 46 per cent. of meta derivative behaved exactly like a pure compound. The data in Table II are reproduced in the curve Fig. 2.

Mixtures of ortho- and paranitraniline melt in a highly irregular manner and the curve prepared from our data is quite unsuited for analytical

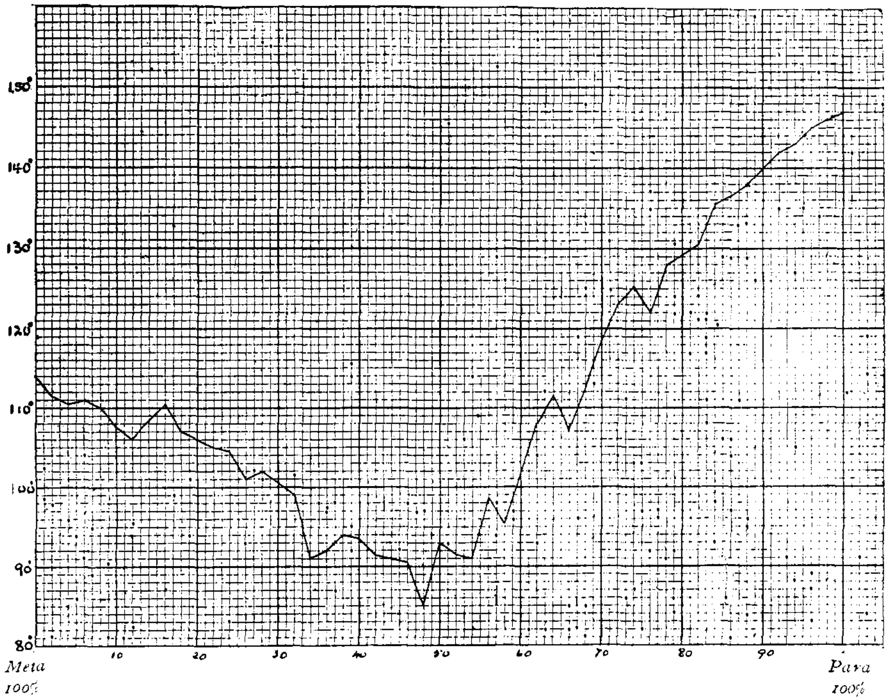

Fig. 2

purposes. At first we were inclined to refer this irregularity to the presence of moisture, but this is hardly probable because the pure constituents, after exposure to air, exhibit the correct melting points quite sharply; moreover, all our mixtures were treated in exactly the same manner, so that the disturbing factor should have affected each one to an equal extent. In order to make certain of this point, however, some of the mixtures were dried with very special care, but no alteration was apparent in their melting points. It may be added that of the mixtures showing the more pronounced irregularities, various specimens were prepared at different times, but the results were unchanged. The mixtures which exhibit the most marked breaks in the curve (containing 58–68 per cent. of ortho compound) do not contain the constituents in any simple molecular ratio.

At present we have no explanation to offer of the reason for the irregularities in question. It may be that they have a casual connection with the well-known simultaneous production of ortho and para disubstituted benzene derivatives and they are decidedly reminiscent of the alternate rise and fall shown in the melting point of the aliphatic monobasic acids. We are at present investigating this question more fully.

Application of the Melting Points for Analytical Purposes.

An inspection of the curves for the ortho- meta- and meta-para-mixtures shows that the direct determination of the melting point would be sufficient, within some regions of temperature, to demonstrate the composition of a substance containing either of these constituents in unknown proportion. Within a greater range of temperature, however, there are at least two mixtures of widely differing composition which have identical melting points. In such cases the determination is made as follows: Assuming that the material under examination consists of ortho- and metanitraniline, a portion of it is mixed with an approximately equal quantity of, say, pure metanitraniline, and the melting points of this mixture and of the original material are determined simultaneously, on the same thermometer. If the original material melts at a higher temperature than it does after the addition of metanitraniline, its composition is indicated by a point on the left side of the curve, otherwise by the corresponding position on the right-hand branch. If pure *orthonitraniline* is used for mixing, these relationships will be, of course, reversed. In the case of the meta-para-curve the addition of pure *paranitraniline* will *lower* the melting points of a mixture whose composition is situated to the left of the eutectic point, whereas the remaining possible mixtures, to the right of it, will have their melting points *raised* by the addition of the pure para compound. Admixture with pure *metanitraniline* will, necessarily, reverse these relations.

It will be obvious that the *quantity* of pure isomer which is added is of no particular importance; we have found it convenient to take an amount approximately equal to that of the material under examination.

The method has been tested by the junior author, who received a number of mixtures, the composition of each of which was unknown to him. His results were accurate to 2 per cent. and in some cases agreed even more closely.

In dealing with ternary mixtures it is advisable to crystallize them fractionally from alcohol once or twice. In this manner we have found that we could obtain two portions, one containing substantially all the orthonitraniline together with some meta-, while the other portion consisted of the meta- and paraisomers. We have made a few experiments on the separation of ortho- and paranitraniline by crystallization. So far as we can judge, the separation can be made quantitatively. The mixture is weighed and treated with just sufficient boiling alcohol (95 per cent.) to dissolve it. When cool, the volume is measured. The paranitraniline which deposits is collected and to its weight is added that of the quantity dissolved in the filtrate; the sum of these, subtracted from the weight of the original material, represents the orthonitraniline.

Summary.

1. Curves have been constructed showing the relationship between the melting points and the composition of the three binary mixtures of the isomeric nitranilines.

2. In the case of the mixtures of ortho- and meta- and of meta- and paranitraniline, these curves are comparatively regular; they fall to the eutectic point and then rise to the melting point of the pure compound.

3. The curve representing the relationship between the melting point and composition of mixtures of ortho- and paranitraniline is highly irregular. At present it is impossible to give a satisfactory explanation of this phenomenon.

4. The curves mentioned above can be used to determine the composition of mixtures of otho- and meta- and of meta- and paranitraniline, respectively, by a simple and expeditious method which requires only a minimal quantity of material. The results are usually accurate within two per cent.

McMaster University,
Toronto, Canada.
December, 1907.

SOME DERIVATIVES OF 1,3-DIMETHYL-2,6-DINITROBENZENE-4-SULPHONIC ACID.

By W. J. Karslake and W. J. Morgan.

Received March 10, 1908.

The initial material used was the potassium salt of 1,3-dimethyl-2,6-dinitrobenzene-4-sulphonic acid, which was prepared as follows:[1] 800

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[1] Claus and Schmidt, *B.* **19**, 1424.