

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT OF MCGILL UNIVERSITY.]

**THE COMPOUNDS OF PHENOL AND THE CRESOLS WITH PYRIDINE.**

BY W. H. HATCHER<sup>1</sup> AND F. W. SKIRROW.  
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The extraction of phenol and pyridine from the coal-tar oils of the tar distillery is effected by first agitating the oil with a sufficient excess of sodium hydroxide solution, separating the sodium phenate solution from the oil, and then extracting the pyridine by means of a solution of sulfuric acid which is sufficiently dilute to avoid sulfonation of the hydrocarbons present. Some years ago one of us, while engaged in a technical study of the phenol in the tar oils, desired to reverse the above order of washing in some experimental work. No definite information seemed to be available as to the extent to which the bases could be extracted first, the reverse being the universal practice. It was found that pyridine could not be washed out efficiently by sulfuric acid without first removing the phenol, although no difficulty is experienced in extracting the phenol while the pyridine is still present.

Lunge<sup>2</sup> stated that the tar oils do not contain the bases in the free state, but that the latter must first be isolated by an alkaline treatment.

Lunge<sup>3</sup> quotes Spilker<sup>4</sup> to the effect that "the pyridines in coal tar must be presumed to be loosely combined with phenols and that it must be very difficult to extract them completely without having first destroyed those loose compounds by the action of stronger alkalies which take hold of the phenols." No comment is made on the fact that the phenols also are in loose union with the bases, and that difficulty might be experienced in getting a complete extraction of the former.

The following experiments, which were carried out some years ago by one of us, confirmed this result as far as the crude phenolic bodies and bases are concerned. A sample of light oil was taken which contained 24% of crude phenols and 5% of crude bases; one portion of this oil was washed with 1.6 theoretical sodium hydroxide solution of 1.08 sp. gr., and was then further extracted with 1.9 theoretical sulfuric acid of 1.28 sp. gr. Another similar portion was extracted using the extracting solutions in the reverse order.

TABLE I.

Expt.	Oil taken.	Contained.		NaOH used.	H <sub>2</sub> SO <sub>4</sub> used.	Phenol extr.	Pyridine extracted.	Phenol extr.
		Crude phenol.	Crude pyridine.					
1.....	2 liters	480 cc.	100 cc.	4000 cc.	240 cc.	480 cc.	100 cc.	..
2.....	2 liters	480 cc.	100 cc.	4000 cc.	240 cc.	..	23 cc.	480 cc.

<sup>1</sup> The experimental work of this paper was presented by W. H. Hatcher in partial fulfillment of the requirements for the degree of M.Sc. at McGill University.

<sup>2</sup> "Coal Tar and Ammonia," Ed. 1900.

<sup>3</sup> "Coal Tar and Ammonia," Ed. 1916.

<sup>4</sup> "Kokerei und Teerproducte der Steinkohle."

Thus the crude phenols in the oil phase appear able to compete successfully with the sulfuric acid in the aqueous phase for the pyridine, while the bases do not seem able to compete with the sodium hydroxide for the phenols. The dissociation constants of phenol as an acid and of pyridine as a base are well known and have been determined by standard methods with the following results:<sup>1</sup>

$$K_{\text{Ph}} = 1.3 \times 10^{-10}; \quad K_{\text{Pyr.}} = 23.0 \times 10^{-10}, \text{ both at } 25^\circ.$$

The crude phenols, however, include a large number of bodies of widely differing acid strength, and the crude pyridine also contains many bodies of differing basic strength, and it seemed desirable to investigate similar cases with only single chemical individuals present. Experiments were therefore carried out with solutions of pure phenols and pure pyridine in benzene.

#### Purification of Materials.

**Phenol.**—C. P. Phenol was fractionated six times through a six-bulb pear still head, the fractions being collected in a receiver closed with a calcium chloride tube to prevent access of moisture. A fraction was collected which distilled completely between  $184.8^\circ$  and  $184.9^\circ$ .

**Pyridine.**—A large sample of pyridine of very good quality was specially prepared for the authors by Messrs. Hardman and Holden, Ltd., of Manchester, England, to whom the authors take this opportunity of expressing their indebtedness. This sample was allowed to stand for some time over sticks of potassium hydroxide, and was then fractionated through a four-foot column packed with short pieces of glass tube; after four such fractionations the greater bulk of the material was obtained in a fraction distilling completely between  $115.5^\circ$  and  $115.6^\circ$ .

**Benzene.**—The benzene was dehydrated over sodium and then fractionated through the above column, coming over within  $0.1^\circ$ . In carrying out the washing experiments with pure phenol and pyridine the solubility of these substances in the aqueous layer was such that it was not possible to estimate the amount extracted by liberating and measuring the volume of phenol or of pyridine; the amounts of phenol and of pyridine extracted were therefore determined by titration.

**Estimation of Phenol.**—This was determined by conversion into tri-iodo phenol by the method of Messinger and Vortmann,<sup>2</sup> which is described in detail by Skirrow.<sup>3</sup> In this method a definite excess of sodium hydroxide is added and then an excess of standard iodine, at a temperature of  $60^\circ$ . After standing 20–30 minutes, the cooled mixture is acidified and the excess iodine determined.

<sup>1</sup> J. Walker, *Z. physik. Chem.*, 32, 137 (1900). Constam, White, *Am. Chem. J.*, 29, 1 (1903).

<sup>2</sup> *Ber.*, 22, 2313 (1889).

<sup>3</sup> *J. Soc. Chem. Ind.*, 27, 58 (1908).

Trial experiments were carried out with varying and known amounts of phenol, and also with known amounts of phenol in the presence of varying amounts of pyridine.

TABLE II.

Wt. phenol in 100 cc. of solution.	Mol pyridine added per mol phenol.	% phenol found.
0.200 gram .....	None	100.0
0.100 gram .....	None	100.6
0.200 gram .....	1/2	100.2
0.200 gram .....	2	100.2
0.100 gram .....	1/2	100.4
0.100 gram .....	2	100.4

Thus the method gives fairly accurate results with varying concentrations of phenol, and the presence of pyridine in even large amounts is without effect. The phenol solutions, if stronger than the above, should be proportionally diluted before titration.

**Estimation of Pyridine.**—The titration of pyridine with standard sulfuric acid has been proposed using ferric chloride as indicator,<sup>1</sup> and also using Patent Blue V. N.<sup>2</sup> These methods did not seem entirely convenient. Quite satisfactory results were, however, obtained by the use of methyl violet as an indicator; and this method could be worked in either direction, titrating pyridine with sulfuric acid or, running the pyridine into excess sulfuric acid and titrating back with sodium hydroxide.

TABLE III.

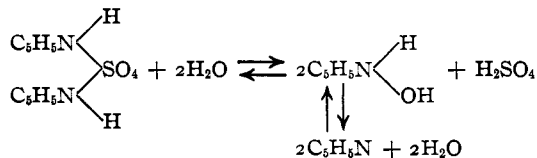
Wt. pyridine taken in 100 cc. solution.	Molecular ratio of phenol added.	Percentages pyridine found
4.67 grams.....	None	100.0
1.40 grams.....	None	99.85
0.09 grams.....	None	100.0
1.40 grams.....	1/2 equivalent	100.0
1.40 grams.....	2 equivalents	99.9

Thus the method can be used with varying concentrations of pyridine and the presence of phenol is without effect on the result.

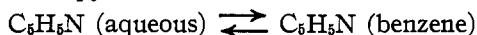
**Washing Experiments.**—(1) Extraction of pyridine from benzene solution by means of sulfuric acid.

In this case the following equilibria are involved:

(A) Hydrolysis of pyridine sulfate which may be formulated thus:



(B) Distribution of pyridine between two solvents:



<sup>1</sup> Schulze, *Ber.*, 20, 3391 (1887).

<sup>2</sup> Milbauer and Stanck, *Z. anal. Chem.*, 43, 205 (1904).

Owing to the weakness of pyridine as a base the hydrolysis is pronounced, and in order to effect complete extraction a considerable excess of sulfuric acid is needed. The minimum amount of sulfuric acid was determined under the conditions of experiment as follows:

The strength of acid used was 9.63 *N*. Five grams of pyridine were taken in each experiment, were dissolved in benzene, and made up to 100 cc. This was vigorously shaken in a separating funnel with the sulfuric acid for five minutes, and the total amount of aqueous layer separated. The benzene layer was then drained out and the funnel washed with water, the washings being added to the acid liquid and the whole made up to a known volume. An aliquot portion of this solution was treated in a distilling flask with excess sodium hydroxide and distilled into 1 *N* sulfuric acid, of which the excess was titrated back with 1 *N* sodium hydroxide, using methyl violet as indicator.

5 g. of pyridine theoretically equal 3.10 g. sulfuric acid.

TABLE IV.  
Pyridine Only.

Volume H <sub>2</sub> SO <sub>4</sub> .	Wt. H <sub>2</sub> SO <sub>4</sub> .	Wt. pyridine extracted.	% total pyridine.
7 cc.	3.31	4.6485	92.97
8 cc.	3.784	4.944	98.88
9 cc.	4.257	4.990	99.80
10 cc.	4.730	4.996	99.92
12 cc.	5.670	4.990	99.80

Thus 9 cc. of acid are necessary for complete extraction and this equals 4.257 g. sulfuric acid, or about 1.38 times the theoretical. No commensurate improvement is obtained by taking more acid than this.

In the following experiments 5 g. of pyridine were taken in each case, were dissolved in benzene, and made up to 100 cc. with or without the addition of phenol; 9 cc. of sulfuric acid were taken in each case, and the extractions conducted as before, phenol being estimated in the pyridine sulfate layer for control purposes.

TABLE V.  
Pyridine in Presence of Phenol.

No.	G. phenol added.	Mol phenol to 1 mol pyridine.	Wt. pyridine extracted.	% total pyridine.	Wt. phenol extracted.	% total phenol.
1.....	0	0	4.990	99.80	...	...
2.....	2.975	1/2	4.993	99.85	0.905	30.45
3.....	5.95	1	4.830	96.60	2.198	36.94
4.....	11.90	2	2.9675	59.35	2.199	18.48
4a <sup>1</sup> .....	11.90	2	2.845	56.90	2.185	18.35
5.....	17.85	3	1.7189	34.38	0.596	3.34
5a <sup>2</sup> .....	17.85	3	1.740	34.80	0.654	3.66
6.....	24.00	4	1.279	25.58	0.438	1.81
6a <sup>2</sup> .....	24.00	4	1.273	25.46	0.555	2.31

<sup>1</sup> In this the solution was made up to 200 cc. with benzene.

<sup>2</sup> In these experiments the solutions were shaken for thirty minutes instead of for five minutes as with the rest.

The above figures show that the presence of phenol in the benzene layer has a very striking effect on the extraction of pyridine from benzene by means of sulfuric acid, and that this effect increases rapidly with increasing amounts of phenol present. The percentage extraction in No. 6 above, in which the amounts roughly correspond to those in the experiment quoted on light oil is of the same order as in the latter experiment.

The behavior of the phenol is somewhat paradoxical, as increasing the concentration of phenol in the benzene layer causes the concentration of phenol in the aqueous phase to diminish. This must obviously be due to a change in the limiting solubility in the aqueous layer, which would thus shift the distribution in favor of the benzene. To check this point the solubility of phenol was determined in the sulfuric acid solution and also in the sulfuric acid after partial neutralization with pyridine. The phenol, as before, was determined by titration after saturating the solution in question with crystals of phenol.

TABLE VI.  
Solubility of Phenol.

Solution.	Equivalent pyridine added.	G. phenol in 10 cc.
9.63 <i>N</i> H <sub>2</sub> SO <sub>4</sub> .....	None	0.204 = A
9.63 <i>N</i> H <sub>2</sub> SO <sub>4</sub> .....	1/4	1.77 = 8.7 A
9.63 <i>N</i> H <sub>2</sub> SO <sub>4</sub> .....	1/2	6.15 = 30 A
9.63 <i>N</i> H <sub>2</sub> SO <sub>4</sub> .....	1	10.08 <sup>1</sup> = 50 A

Thus the solubility of phenol in the aqueous acid layer increases very largely as the acid is more and more neutralized by pyridine, and this explains the large amount of phenol removed from the benzene in Expts. 1, 2 and 3, above (Table V); but as the pyridine is more and more held back in the benzene by phenol, the aqueous solution becomes also a much poorer solvent for phenol.

(2) Extraction of phenol from benzene by sodium hydroxide. Strength of sodium hydroxide solution used was 7.56%, free from carbonate.

In these experiments 5.59 g. of phenol were in each case dissolved in benzene and made up to 100 cc. The smallest amount of sodium hydroxide necessary to extract this phenol completely was first determined. The benzene solution was shaken for five minutes with the sodium hydroxide and then separated, and the aqueous layer completely removed as in the case of pyridine.

TABLE VII.  
Phenol Only.

Vol. NaOH.	Wt. NaOH.	Wt. phenol extracted.	% total phenol.
35 cc.	2.64 g.	5.840 g.	98.15
38 cc.	2.867 g.	5.904 g.	99.23
39 cc.	2.94 g.	5.989 g.	99.15
40 cc.	3.02 g.	5.950 g.	100.00
	5.95 g. phenol =	2.53 g. NaOH.	
	40 cc. NaOH =	3.02 g. NaOH = 1.19 theoretical.	

<sup>1</sup> Still unsaturated with phenol.

TABLE VIII.

## Phenol in Presence of Pyridine.

5.95 g. phenol + stated amount of pyridine, dissolved in benzene, diluted to 100 cc. and washed with 40 cc. NaOH.

Wt. pyridine added.	Mol pyridine to 1 mol phenol.	Wt. phenol extracted.	% total phenol.	Wt. pyridine in aqueous phase.	% total pyridine.
None	None	5.950 g.	100.0	None	None
1.25 g.	0.25	5.955 g.	100.0	0.271	21.70
2.50 g.	0.50	5.930 g.	99.70	0.429	17.15
5.00 g.	1	5.910 g.	99.44	0.743	14.86
10.00 g.	2	5.780 g.	97.14	1.454	14.54
20.00 g.	4	5.685 g.	95.55	4.260	21.30

It will be seen that in this case the presence of pyridine in the benzene does slightly diminish the extraction of phenol, but to a far less extent than is the case with the influence of phenol on the extraction of pyridine; and when four molecules of pyridine are present to every molecule of phenol, the percentage extraction is only diminished by about 4.5%. Further, the pyridine distributes itself roughly in the same proportion throughout between the benzene and the aqueous layer.

It seems difficult to explain the selective decomposition of the "loose compounds" of the phenol and base in benzene solution by sodium hydroxide in preference to sulfuric acid on any assumption of equilibrium merely based on hydrolysis of the respective salts in water solutions, and consequent distribution of the free base or phenol between the aqueous and the benzene layer. So it seemed desirable to subject the condition of the materials in the non-aqueous phase to a closer study.

## Compounds of Phenol and Pyridine.

**Freezing Point Curves.**—The results in this section were obtained by one of us some two years ago, but owing to the pressure of other work the research could not be proceeded with at the time. In the meantime, in a very comprehensive study of various properties of binary mixtures, Bramley<sup>1</sup> has worked out by the same method the compounds between pyridine and phenol, *o*-, *m*- and *p*-cresol with practically identical results, so that it will not be necessary to do more than quote the figures obtained.

In this work a weighed quantity of pyridine was placed in a small test tube provided with a stirring device and a small pentane thermometer. The whole apparatus could be weighed to control the weight of pyridine. The maximum freezing point of this was taken when in contact with an infinitesimal amount of solid, and then the freezing points were determined after addition of successive weighed amounts of pure phenol or cresol, as the case might be. The chief precaution taken was to avoid too great supercooling or a large amount of crystals would form, causing alteration of the composition of the solution in contact at equilibrium.

<sup>1</sup> *J. Chem. Soc.*, 109, 469 (1916).

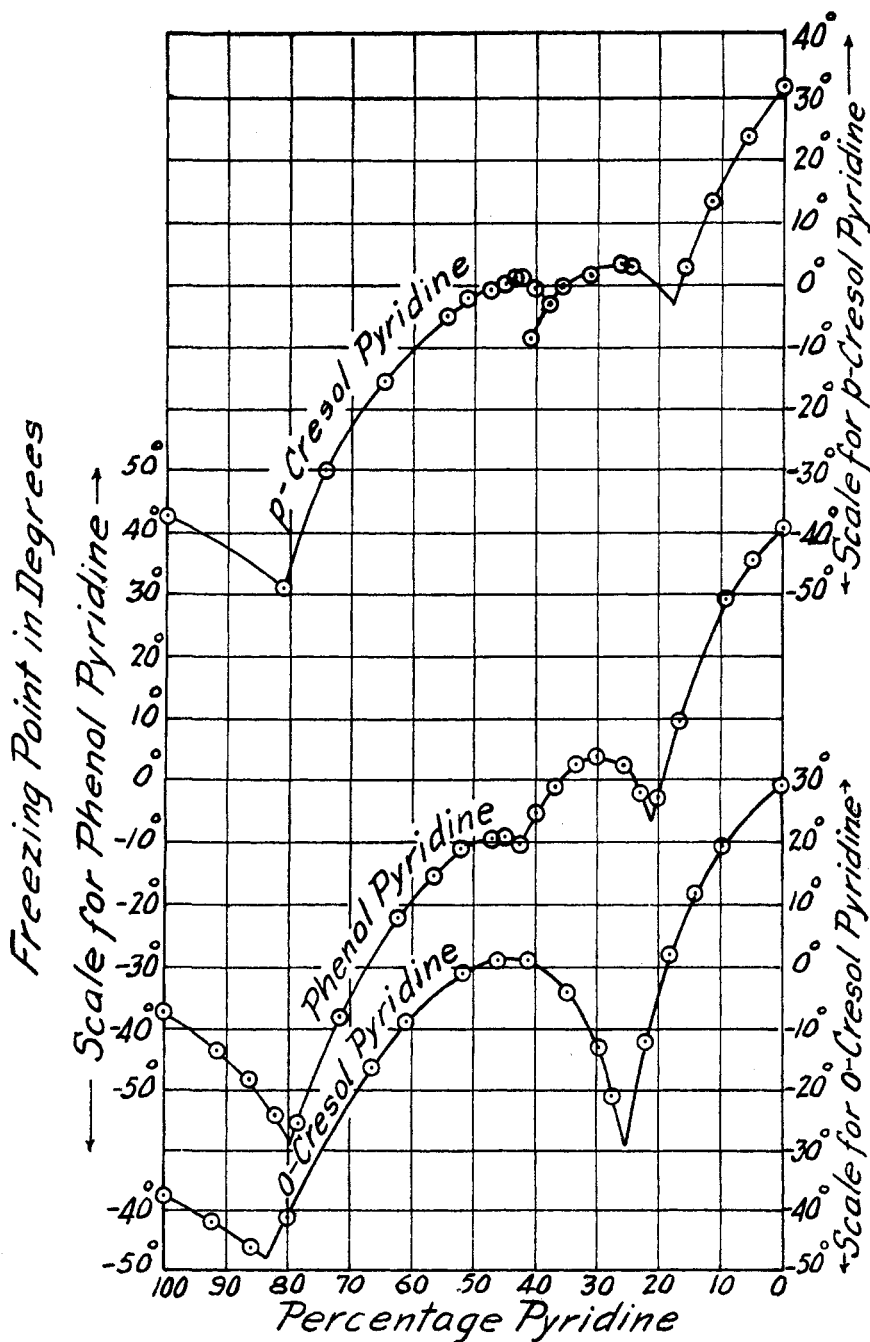


FIG. 1

By approaching the equilibrium slowly and repeatedly from opposite sides, it was possible to correct for the lag of the pentane thermometer and also to prevent excessive supercooling.

TABLE IX.

Pyridine and phenol.		<i>o</i> -Cresol and pyridine.		<i>p</i> -Cresol and pyridine.	
% pyridine.	M. p.	% pyridine.	M. p.	% pyridine.	M. p.
100	-37.5°	100	-37.5°	100	-37.5°
91.37	-43.5	92.35	-41.5	80.92	-49.0
86.28	-48.0	86.1	-46.0	74.22	-30.0
82.05	-54.0	80.17	-41.0	64.65	-15.5
78.8	-55.5	66.63	-16.0	54.63	-5.0
71.45	-38.0	60.89	-9.0	50.8	-2.0
62.29	-22.0	51.73	-1.0	47.72	-0.5
56.63	-15.5	45.86	+1.0	45.02	+0.5
51.9	-11.0	41.13	+1.0	42.16	+1.5
47.09	-9.5	34.66	-4.0	40.74	-8.5
44.87	-9.0	29.85	-13.0	40.06	-0.5
42.39	-10.3	27.43	-21.0	37.9	-3.0
39.86	-5.3	21.85	-12.0	35.75	0.0
36.85	-1.0	18.23	+2.2	31.16	+2.0
33.7	+2.5	14.03	+11.5	26.28	+3.5
30.2	+3.8	9.53	+19.4	24.38	+3.3
25.5	+2.5	0.00	+29.4	15.48	+3.0
22.58	-2.0	..	..	11.64	+13.5
20.13	-2.7	..	..	6.03	+24.0
16.4	+9.5	..	..	0.00	+32.0
9.07	+29.3	..	..	..	..
4.76	+35.6	..	..	..	..
0.00	+40.8	..	..	..	..

From the curves in Fig. 1, it is seen that the following compounds are formed at any rate in the neighborhood of 0°:

Phenol and pyridine— $C_6H_5OH.C_5H_5N$ ;  $(C_6H_5OH)_2.C_5H_5N$ .

*o*-Cresol and pyridine— $C_7H_7OH.C_5H_5N$ .

*p*-Cresol and pyridine— $C_7H_7OH.C_5H_5N$ ;  $(C_7H_7OH)_2.C_5H_5N$ .

From Bramley's figures it will be seen that it is impossible to decide whether any compound is formed between *m*-cresol and pyridine or not, and the figures unfortunately do not extend far enough to exclude the possibility of the formation of the 2 : 1 compound,  $(C_7H_7OH)_2.C_5H_5N$ .

#### The Dissociation of the Compound $C_6H_5OH.C_5H_5N$ in Benzene Solution.

The determination of the apparent molecular weight of a molecular compound such as the above, by the freezing point or boiling point method, might be expected to give information as to the extent to which the compound is formed in solution.

Walden<sup>1</sup> has studied the "solvolytic power" of different solvents on a large number of binary compounds; the results of this work are unfortu-

<sup>1</sup> *Bull. Acad. Sci. Petrograd*, 1914, 1161; 1915, 1, 509; *C. A.* 10, 2348 (1916).



nately only available to the writers in abstract. Turner and English<sup>1</sup> in a paper on the connection between molecular association and chemical combination, determined the molecular weight, by the cryoscopic method, of phenol and of  $\alpha$ -naphthylamine, and also of an equimolecular mixture of the two; and from the deviation in the depressions by the latter from the sum of the depressions by the constituents attempted to calculate the extent of combination, making certain assumptions as to the molecular associations of the constituents.

The fact that phenol and, to a lesser extent, pyridine are associated in benzene and that this association of each will by no means be uninfluenced by the presence of the other, renders the method of uncertain value at the best. The apparent molecular weight of phenol in benzene varies from 144 to 252 ( $C_6H_5OH = 94.08$ ) at concentrations ranging from 0.3 to 36 g. of phenol per 100 g. benzene.<sup>2</sup>

In the sequel attempts have been made to calculate the true dissociation of the pyridine phenate into its constituents after making allowance for the subsequent association of those constituents themselves.

The depression of freezing point of phenol, pyridine and equimolecular mixtures of the two was measured over a range of concentrations in benzene and in naphthalene, and also the depressions caused by *o*-cresol, pyridine, and equimolecular mixtures of the two in both solvents. As noted in the preceding, two compounds are formed by phenol and pyridine, while only one compound is given by *o*-cresol and pyridine, and consequently in the latter case one source of possible complication would be eliminated.

Freezing point curves of mixtures of each solute with each of the two

TABLE X.  
Freezing Points of Phenol-Benzene Mixtures.

Wt. phenol.	Wt. benzene.	Mol % phenol.	M. p.
3.410 g.	0.00 g.	100.0	+39.4°
3.410	0.458	86.2	+30.0
3.410	0.840	77.2	+23.6
3.410	1.208	70.0	+18.4
3.410	2.022	58.3	+11.0
3.410	2.808	50.2	+ 4.9
3.410	3.640	43.7	+ 0.6
3.410	4.446	39.0	- 3.6
1.816	2.547	37.3	- 5.4
1.816	2.864	34.5	- 4.4
1.816	3.494	30.2	- 3.0
1.816	4.395	25.6	- 1.8
0.893	3.228	18.7	0.0
0.893	5.365	12.1	+ 1.65
0.00	All	0.0	+ 5.1

<sup>1</sup> *J. Chem. Soc.*, 105, 1795 (1914).

<sup>2</sup> Beckmann, *Z. physik. Chem.*, 2, 715 (1888); Auwers, *Ibid.*, 12, 689 (1893).

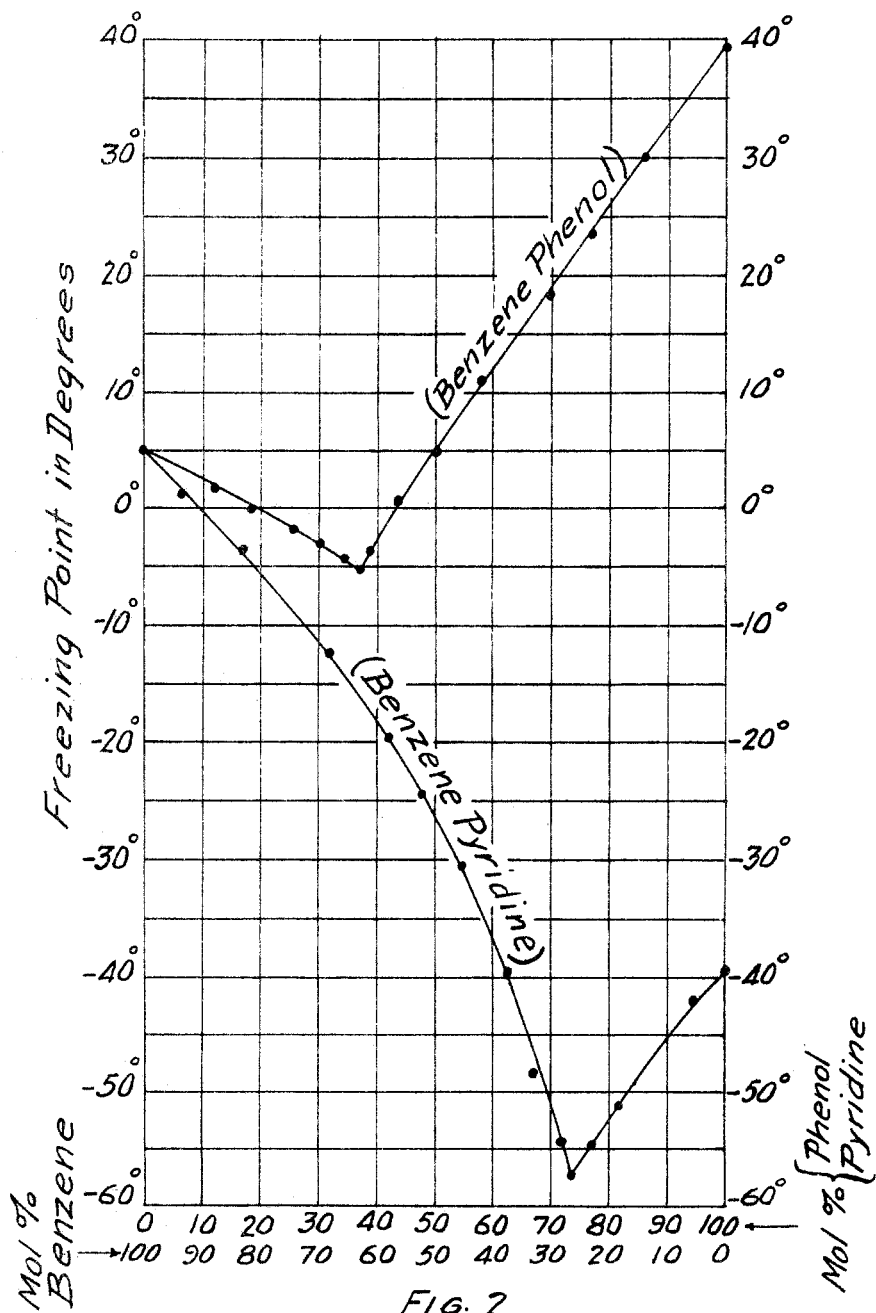


FIG. 2

solvents were first determined in order to ascertain whether any complication might be expected from combination with the solvent.

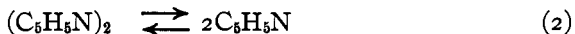
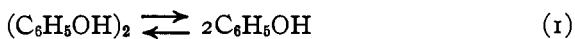
TABLE XI.  
Freezing Point of Pyridine-benzene Mixtures.

Wt. pyridine.	Wt. benzene.	Mol % pyridine.	M. p.
3.934 g.	0.00 g.	100.0	-39.4°
3.934	0.215	94.8	-42.2
3.934	0.881	81.5	-51.3
3.934	1.156	77.2	-54.8
3.934	1.526	71.9	-54.4
3.934	1.894	67.2	-48.4
3.934	2.320	62.6	-39.7
3.934	3.231	54.7	-30.6
1.973	2.130	47.8	-24.4
1.973	2.703	41.9	-19.7
1.973	4.187	31.8	-12.4
0.673	3.620	17.0	- 3.6
0.276	3.620	6.7	+ 1.1
0.00	All	0.0	+ 5.1

#### Assumptions Made and Method of Calculation.

The molecular weight of phenol in benzene reaches a value just double the normal one at a concentration of approximately 7.05%. It seems a fairly reasonable assumption that, in the polymerization process at concentrations well below this, the major part of the molecules will be either single or double; while in the case of pyridine the molecular weight does not nearly reach the double value within the above range of concentration. Here also we may assume that we are dealing mainly with single and double molecules.

The dominant equilibria will thus be:



No attempts have been made to go as high as this concentration. If now we have an equimolecular mixture of phenol and pyridine in benzene solution, we should have in addition the following equilibrium:



The single molecules of phenol and pyridine then polymerize according to Equations 1 and 2.

Equilibrium 1:

Suppose C is the concentration of phenol taken (mols  $\times 10^{-2}$  per 100 g. benzene),

M the apparent molecular weight from freezing point data,

$\mu$  the true molecular weight as single molecules,

S the percentage of actual molecules present which are single,

and  $\alpha_1$  the fraction of the possible number of double molecules which are dissociated;

then the percentage of actual molecules present which are double =  $100 - S$ .

And since  $M$  is the average molecular weight of these

$$S = \frac{(2\mu - M) 100}{\mu}$$

$$\text{But the ratio } \frac{\text{No. of double molecules present}}{\text{No. of single molecules present}} = \frac{1 - \alpha_1}{2\alpha_1} = \frac{100 - S}{S}$$

$$\begin{aligned} \therefore \alpha_1 &= \frac{S}{200 - S} \\ &= \frac{2\mu - M}{M} \end{aligned}$$

$\alpha_1$  was thus calculated for a series of different values of  $C_1$ , and, as will be shown later, the curve obtained by plotting  $\alpha_1$  against  $C_1$  was in practically every case a straight line. The relation between  $\alpha_1$  and  $C_1$  was obtained by substituting the coördinates of two points into the equation of a straight line,

$$\alpha_1 = a + b.C,$$

and finding the constants  $a$  and  $b$ .

Similarly for pyridine the relation between  $\alpha_2$  and  $C_2$  was found to be linear, and a similar equation was obtained connecting the two.

If now we take Equilibrium (3) and write  $\beta$  for the percentage of the compound dissociated under actual conditions at any initial concentration expressed as centigram molecules of compound in 100 g. of benzene  $C'$ , then the actual concentration of the compound =  $C'(1 - \beta)$ , the total concentration of the phenol =  $C'.\beta$  as single concentrating, or  $C'.\beta/2$  as double molecules, the actual concentration of double molecules of phenol =  $C'.\beta/2.(1 - \alpha_1)$  and the actual concentration of single molecules of phenol =  $2C'.\beta/2.\alpha_1$ . And the total concentration of both kinds of phenol molecules =  $C'.\beta/2.(1 + \alpha_1)$ . Similarly the total molecules of both kinds of pyridine molecules =  $C'.\beta/2.(1 + \alpha_2)$ .

So that the sum of the molecules of compound, and of single and double molecules of phenol and pyridine present

$$\begin{aligned} &= C'(1 - \beta) + C'.\beta/2.(1 + \alpha_1) + C'.\beta/2.(1 + \alpha_2) \\ &= C' + C'.\beta/2.(\alpha_1 + \alpha_2). \end{aligned}$$

$\alpha_1$  and  $\alpha_2$  are related to  $C'.\beta$  by the equations

$$\begin{aligned} \alpha_1 &= a + b.C'.\beta \\ \alpha_2 &= c + d.C'.\beta, \end{aligned}$$

in which the numerical values of the Constants  $a$ ,  $b$ ,  $c$  and  $d$  have been already found.

By equating this calculated value for the number of molecules present to that actually obtained by the depression of the freezing point of benzene

by the equimolecular mixture, an approximate value for  $\beta$  has been determined.

The dissociation of associated compounds like phenol does not appear to follow the Mass Action Law.<sup>1</sup> All attempts to get a constant for the dissociation of the associated molecules or of the compounds formed in the present paper were attended with negative results.

The freezing point depression of benzene by means of varying concentrations of phenol was determined in an apparatus of the Beckmann type, the solution being electro-magnetically stirred. The freezing bath was a suitable mixture of ice and water.

When the freezing point of benzene had been accurately determined, weighed pellets of phenol (made by cooling molten phenol in  $\frac{1}{4}$ " glass tubing and breaking off) were introduced into the freezing tube by a side tube, all recognized precautions being carefully observed, and the supercooling averaging  $0.25^\circ$ . Each set of points was confirmed by duplicate determination over the same range; both sets were usually found to lie exactly on the same curve.<sup>2</sup>

The constants used were: Benzene 5000, Naphthalene 7000. For similar results see Beckmann<sup>3</sup> and Turner and English.<sup>4</sup>

TABLE XII.  
Freezing Point Depressions of Phenol in Benzene.  
 $\mu = 94.08$ .

No.	Wt phenol in 100 grams benzene.	Mols $\times 10^{-3}$ phenol in 100 g. benzene.	$\Delta_0^\circ$	M.	$\alpha_1$	$\alpha_1$ calcu- lated from equations.
1.....	0.4894 g.	0.520 g.	0.158	154.8	0.215	0.215
2.....	0.8670	0.922	0.277	156.5	0.202	0.202
3.....	1.463	1.555	0.460	159.1	0.183	0.182
4.....	2.065	2.195	0.639	161.5	0.165	0.162
5.....	2.655	2.822	0.909	164.3	0.145	0.142
6.....	3.434	3.650	1.014	169.3	0.111	0.115
7.....	4.329	4.601	1.249	173.4	0.085	0.085
8.....	4.870	5.176	1.377	176.8	0.064	0.066
9.....	5.650	6.005	1.558	181.3	0.038	0.040

$$\alpha_1 = 0.2313 - 0.0318 C_1.$$

The last column is included in this instance to show that this method of interpolating the value of  $\alpha_1$  gives satisfactory results; the agreement in all subsequent cases was found to be equally satisfactory, except in one case which is mentioned later.<sup>5</sup>

The depression of the freezing point of benzene caused by pyridine of varying concentrations was determined in a similar manner to that em-

<sup>1</sup> Cf. Auwers and Orton, *Z. physik. Chem.*, 21, 35 (1896); Turner, "Molecular Association," p. 35.

<sup>2</sup> Vid., Fig. 4.

<sup>3</sup> *Z. physik. Chem.*, 2, 715 (1888).

<sup>4</sup> *J. Chem. Soc.*, [2] 106, 1795 (1914).

<sup>5</sup> Vid., Fig. 3.

ployed for phenol, the pyridine being added, drop by drop, from a weighing pipet closed at the end by a rubber bulb to regulate the flow of liquid. This form of delivery was used whenever it was necessary to give accurate weights of liquid solute.

TABLE XIII.  
Freezing Point Depressions of Pyridine in Benzene.

No.	$\mu = 79.075.$		$\Delta_0^\circ.$	M.	$\alpha_2.$
	Wt. pyridine in 100 g. benzene.	Mols $\times 10^{-2}$ pyridine in 100 g. benzene.			
1.....	0.1865 g.	0.236	0.103	90.55	0.747
2.....	0.3730	0.472	0.204	91.20	0.734
3.....	0.6116	0.773	0.333	91.85	0.722
4.....	0.8702	1.101	0.477	91.22	0.734
5.....	1.516	1.917	0.818	92.66	0.707
6.....	2.266	2.865	1.227	92.32	0.713
7.....	2.961	3.744	1.606	92.19	0.715
8.....	3.538	4.474	1.906	92.81	0.704
9.....	4.102	5.187	2.197	93.35	0.694
10.....	4.826	6.103	2.578	93.61	0.689

$$\alpha_2 = 0.7378 - 0.0080 C_2.^1$$

Calculation of  $\beta$ :

$$\text{Total number of molecules present} = C' + C'\beta/2(\alpha_1 + \alpha_2).$$

$$\alpha_1 = 0.2313 - 0.0318 C'\beta.$$

$$\alpha_2 = 0.7378 - 0.0080 C'\beta.$$

Hence total number of molecules present =  $C' + C'\beta/2 (0.9691 - 0.0398 C'\beta)$ ,

$$= C' + 0.4845 C'\beta - 0.0199 (C'\beta)^2.$$

$\beta$  is then evaluated by equating to the number of centigram molecules as indicated by the freezing point depression  $\Delta_0/0.500$  for that concentration.

TABLE XIV.  
Freezing Point Depressions of Pyridine-phenate in Benzene.

No.	Wt. com- pound in 100 g. benzene.	Mols $\times 10^{-2}$ compound in 100 g. benzene.	$\Delta_0^\circ.$	$\Delta_0/0.500.$	$\beta.$
1.....	0.1358 g.	0.078	0.058	0.116	0.990
2.....	0.2865	0.165	0.115	0.230	0.804
3.....	0.4275	0.247	0.168	0.336	0.753
4.....	0.6194	0.358	0.225	0.450	0.547
5.....	1.023	0.590	0.361	0.722	0.470
6.....	1.622	0.936	0.546	1.092	0.352
7.....	2.400	1.387	0.771	1.542	0.236
8.....	3.455	1.995	1.078	2.156	0.169
9.....	4.106	2.371	1.256	2.512	0.126
10.....	5.093	2.942	1.529	3.058	0.082
11.....	5.610	3.240	1.671	3.342	0.068
12.....	6.582	3.802	1.919	3.838	0.018
13.....	8.011	4.628	2.296	4.592	—0.017
14.....	9.044	5.225	2.552	5.104	—0.048

<sup>1</sup> Vid., Fig. 3.

Similar experiments were carried out with *o*-cresol; in this case only one compound with pyridine exists, so that complications due to the possible presence of a second compound do not arise. Further, the acidity of *o*-cresol is weaker than that of phenol, according to Boyd,<sup>1</sup> who gives the values

$$\begin{aligned} \text{Phenol, } & 1.15 \times 10^{-10}; \\ \text{\textit{o}-Cresol, } & 0.63 \times 10^{-10}. \end{aligned}$$

This would lead one to expect a greater dissociation of the pyridine *o*-cresolate in benzene than is the case with pyridine phenate, provided the dissociation constant in aqueous solution has any significance for the behavior in non-aqueous solutions.

TABLE XV.  
Freezing Point Depressions of Ortho-cresol in Benzene.

No.	Wt. <i>o</i> -cresol in 100 g. benzene.	$\mu = 108.10.$		$\Delta_0$ , °.	M.	$\alpha_3$ .
		Mols $\times 10^{-2}$ <i>o</i> -cresol in 100 g. of benzene.				
1.....	0.2704 g.	0.250	0.136	99.42	1.174	
2.....	0.8114	0.751	0.388	104.6	1.067	
3.....	1.232	1.140	0.573	107.5	1.011	
4.....	1.804	1.669	0.818	110.3	0.960	
5.....	2.507	2.319	1.100	114.0	0.896	
6.....	3.028	2.802	1.307	115.9	0.865	
7.....	4.267	3.948	1.761	121.2	0.784	
8.....	5.017	4.640	2.015	124.5	0.736	
9.....	5.782	5.350	2.269	127.5	0.696	

$\alpha_3 = 1.090 - 0.0776 C_3$  (neglecting the first two points).

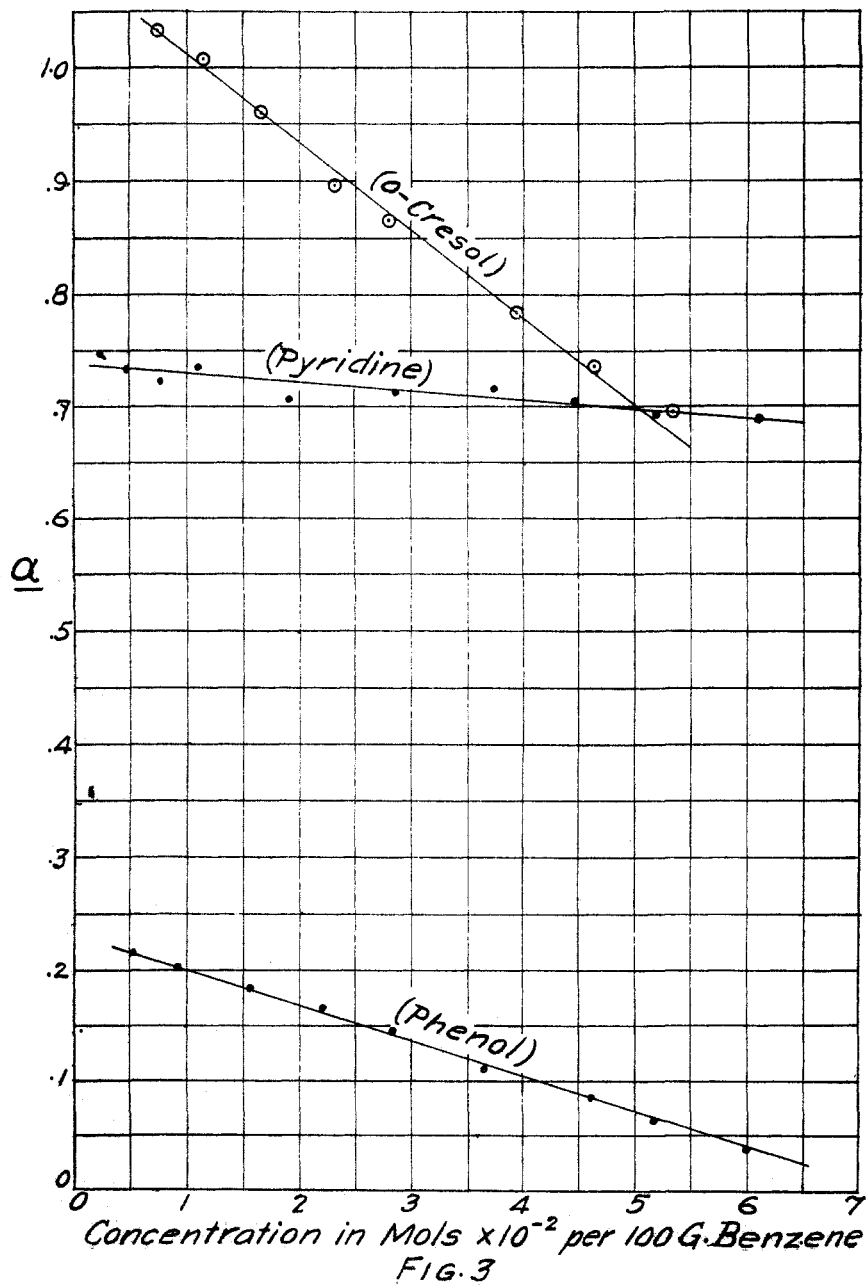
TABLE XVI.  
Freezing Point Depressions of Pyridine *o*-Cresolate in Benzene.

No.	Wt. com- pound in 100 g. benzene.	Mols $\times 10^{-2}$ compound in 100 g. of benzene.	$\Delta_0$ , °.	$\Delta_0/0.500$ .	$\beta$ .
2.....	1.108	0.592	0.435	0.870	0.515
3.....	1.800	0.962	0.668	1.336	0.430
4.....	2.541	1.358	0.903	1.806	0.366
5.....	3.596	1.922	1.213	2.426	0.292
6.....	4.846	2.589	1.567	3.134	0.235
7.....	6.340	3.388	1.968	3.936	0.188
8.....	7.872	4.207	2.368	4.736	0.145
9.....	9.552	5.104	2.780	5.560	0.099
10.....	11.470	6.125	3.241	6.482	0.064

It will be noted that *o*-cresol in very dilute benzene solution has an apparent molecular weight actually smaller than corresponds to the formula. Auwers has observed a similar behavior in the case of *p*-cresol in benzene.<sup>2</sup>

<sup>1</sup> *J. Chem. Soc.*, 107, 1538 (1915).

<sup>2</sup> *Z. physik. Chem.*, 12, 689 (1892).





Possibly this may be due to combination with the solvent. This point will be further investigated when more material is available.

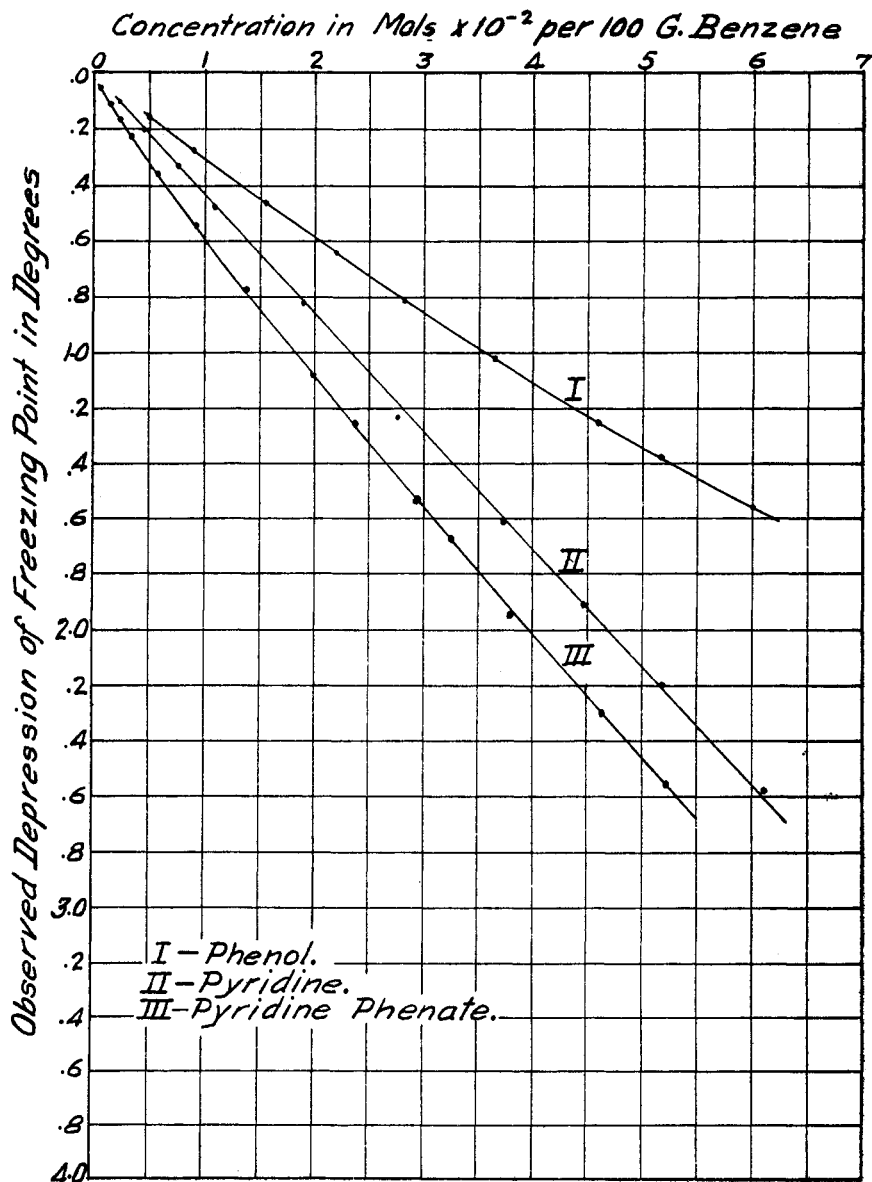


FIG. 4

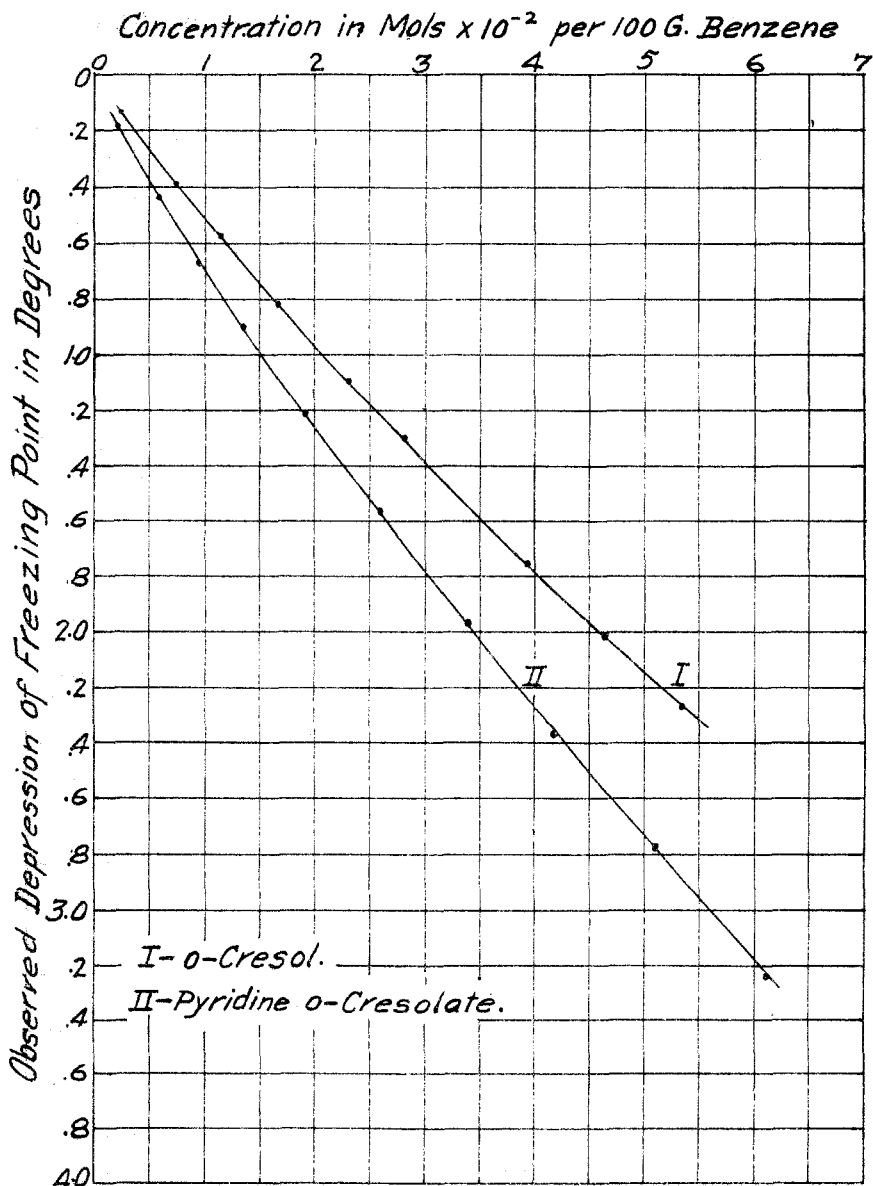


FIG. 5

Pyridine *o*-Cresolate in Benzene.—

$$\alpha_3 = 1.090 = 0.0776 C'.\beta \quad \dots \quad \text{for } o\text{-cresol}$$

$$\alpha_2 = 0.7378 - 0.0080 C'.\beta \quad \dots \quad \text{for pyridine.}$$

$$\text{Total number of molecules present} = C' + C'.\beta/2.(\alpha_3 + \alpha_2)$$

$$= C' + 0.9139 C'.\beta - 0.0428 C'^2.\beta^2.$$

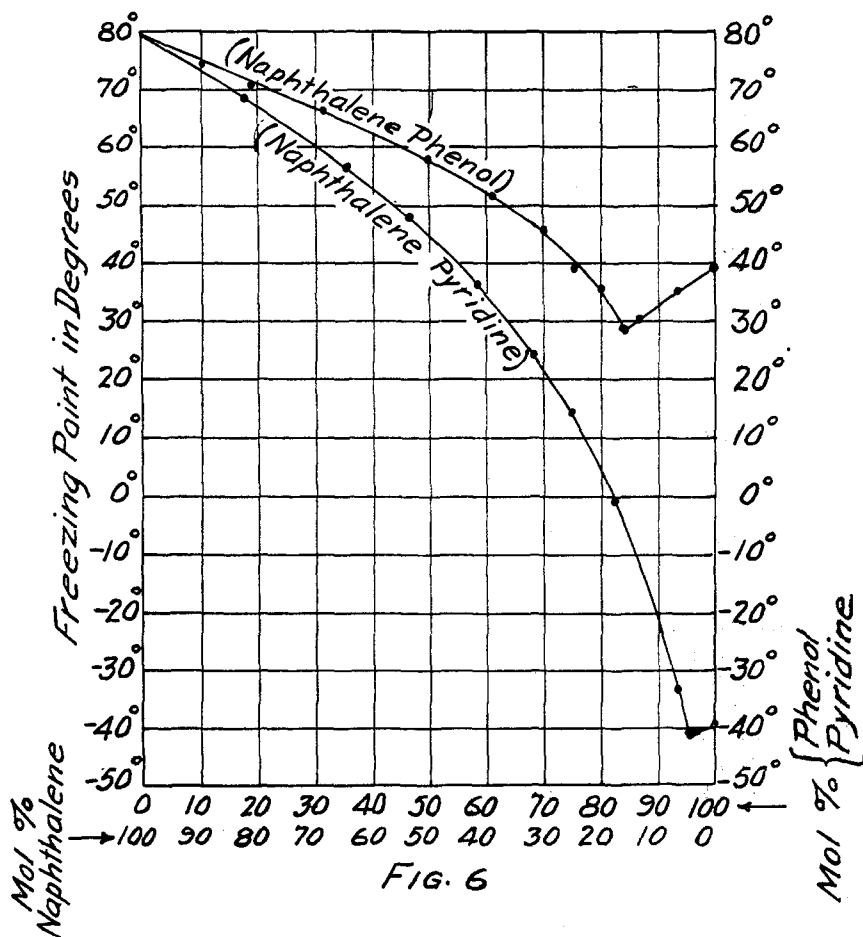


FIG. 6

## Naphthalene as Solvent.

A similar series of determinations was carried out in naphthalene to compare the dissociation of pyridine phenate and of pyridine *o*-cresolate in benzene with the dissociation in naphthalene. According to Auwers,<sup>1</sup> the molecular association of phenol in naphthalene is very much less pronounced than in benzene; so that one would expect any uncertainties in the foregoing method of calculation of  $\beta$  to be also less in this solvent. The molecular association of *o*-cresol in naphthalene is also comparatively small according to Auwers.<sup>2</sup>

As before, a freezing point curve of phenol-naphthalene mixtures and of pyridine-naphthalene mixtures was found, and, as will be seen, no evidence whatever of compound formation was shown. In the case of

<sup>1</sup> *Z. physik. Chem.*, 18, 595 (1895); 21, 337 (1896):

<sup>2</sup> *Loc. cit.*

*o*-cresol, the supply was too small to allow of similar freezing-point curves being found with either benzene or naphthalene; it is hoped to rectify this omission when further supplies can be obtained.

TABLE XVII.  
Freezing Point of Phenol-naphthalene Mixtures.

Wt. phenol.	Wt. naphthalene.	Mol % phenol.	F. P.
3.996 g.	0.00 g.	100.0	+39.4°
3.996	0.385	93.3	35.1
3.996	0.852	86.5	30.2
3.996	1.058	83.8	28.7
3.996	1.363	80.0	35.4
3.996	1.763	75.5	39.3
3.996	2.335	70.0	45.6
2.236	1.937	61.1	51.6
2.236	3.074	49.8	58.0
1.522	4.455	31.7	66.2
0.360	2.078	19.1	70.9
0.224	2.585	10.6	74.4
0.00	All	0.0	79.4

TABLE XVIII.  
Freezing Point of Pyridine-naphthalene Mixtures.

Wt. pyridine.	Wt. naphthalene.	Mol % pyridine.	F. P.
3.026 g.	0.00 g.	100.0	-39.4°
3.026	0.158	97.1	-40.6
3.026	0.338	93.5	-33.2
4.334	1.489	82.5	-1.0
2.778	1.489	75.1	+14.2
1.994	1.489	68.5	24.0
1.288	1.489	58.4	36.4
1.192	2.214	46.6	47.9
0.757	2.214	35.6	56.6
0.299	2.214	17.9	68.7
0.00	All	0.0	+79.4

TABLE XIX.  
Freezing Point Depressions of Phenol in Naphthalene.<sup>1</sup>

No.	Wt. phenol in 100 g. naphthalene.	Mols $\times 10^{-3}$ phenol in 100 g. naphthalene.	$\Delta_0$ °.	$\mu = 94.08.$	
				M.	$\alpha_1.$
1.....	0.4671 g.	0.496	0.328	99.7	0.887
2.....	0.8354	0.888	0.581	100.7	0.868
3.....	1.591	1.690	1.084	102.7	0.832
4.....	2.047	2.177	1.377	104.1	0.807
5.....	2.546	2.707	1.690	105.4	0.785
6.....	3.142	3.339	2.049	107.3	0.754
7.....	3.859	4.102	2.463	109.6	0.717
8.....	4.615	4.906	2.893	111.6	0.686
9.....	4.908	5.217	3.041	112.7	0.670
10.....	5.891	6.262	3.565	115.7	0.626

$$\alpha_1 = 0.9052 - 0.0451 C_1.$$

<sup>1</sup> Auwers, *Z. physik. Chem.*, 18, 599 (1895); 21, 345 (1896).

TABLE XX.  
 Freezing Point Depressions of Pyridine in Naphthalene.

No.	Wt. pyridine in 100 g. naphthalene.	$\mu = 79.075$ .			
		Mols $\times 10^{-2}$ pyridine in 100 g. naphthalene.	$\Delta_0$ °.	M.	$\alpha_1$ .
1.....	0.3267 g.	0.413	0.264	86.62	0.826
2.....	0.4398	0.556	0.355	86.76	0.823
3.....	0.7852	0.993	0.625	87.90	0.800
4.....	1.326	1.677	1.059	87.64	0.805
5.....	1.766	2.235	1.404	88.08	0.796
6.....	2.177	2.753	1.733	87.94	0.798
7.....	2.596	3.284	2.056	88.39	0.789
8.....	3.169	4.007	2.497	88.84	0.780
9.....	3.891	4.921	3.039	89.69	0.763
10.....	4.519	5.715	3.516	89.97	0.758

$\alpha_2 = 0.8317 - 0.0139 C_2$ .

**Pyridine Phenate in Naphthalene:**

$$\alpha_1 = 0.9052 - 0.0451 C'.\beta.$$

$$\alpha_2 = 0.8317 - 0.0139 C'.\beta.$$

$$\begin{aligned} \text{Total number of molecules present} &= C' + C'.\beta/2.(\alpha_1 + \alpha_2). \\ &= C' + 0.8684 C'.\beta - 0.0295 C'^2.\beta^2. \end{aligned}$$

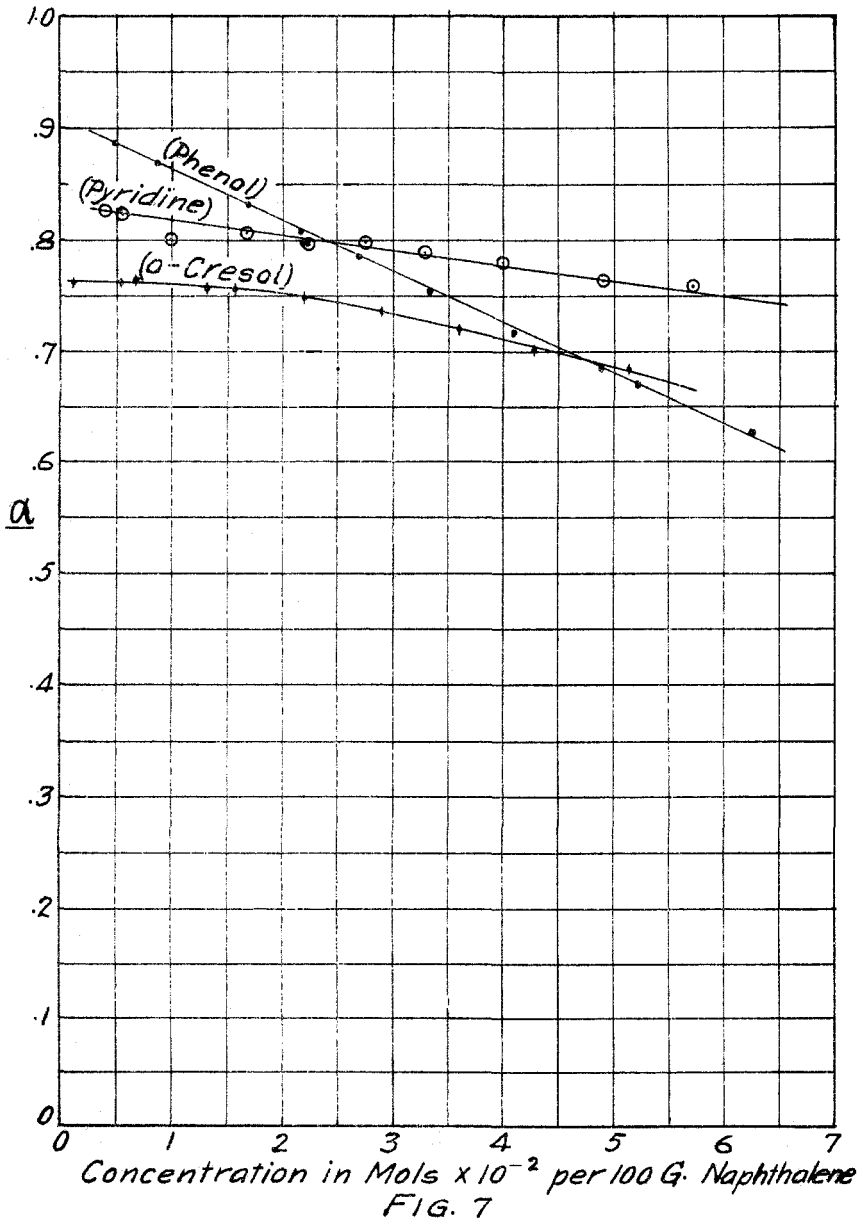
 TABLE XXI.  
 Freezing Point Depressions of Pyridine-phenate in Naphthalene.

No.	Wt. compound in 100 g. naphthalene.	$\mu = 108.10$ .			
		Mols $\times 10^{-2}$ compound in 100 g. naphthalene.	$\Delta_0$ °.	$\Delta_0/0.700$ .	$\beta$ .
1.....	0.3148 g.	0.182	0.217	0.310	0.811
2.....	0.5323	0.307	0.348	0.497	0.710
3.....	0.8861	0.512	0.565	0.807	0.664
4.....	1.531	0.884	0.965	1.380	0.645
5.....	2.359	1.363	1.391	1.987	0.527
6.....	2.767	1.598	1.611	2.301	0.506
7.....	3.514	2.030	1.983	2.833	0.455
8.....	4.107	2.372	2.270	3.243	0.423
9.....	4.767	2.754	2.553	3.647	0.374
10.....	5.650	3.266	2.964	4.234	0.341
11.....	6.934	4.005	3.508	5.011	0.289

 TABLE XXII.  
 Freezing Point Depressions of *o*-Cresol in Naphthalene.<sup>1</sup>

No.	Wt. <i>o</i> -cresol in 100 g. naphthalene.	$\mu = 108.10$ .			
		Mols $\times 10^{-2}$ <i>o</i> -cresol in 100 g. naphthalene.	$\Delta_0$ °.	M.	$\alpha_1$ .
1.....	0.1209 g.	0.112	0.069	122.7	0.762
2.....	0.5893	0.545	0.336	122.8	0.761
3.....	0.7386	0.683	0.422	122.6	0.763
4.....	1.425	1.318	0.810	123.1	0.756
5.....	1.691	1.565	0.962	123.1	0.756
6.....	2.384	2.206	1.350	123.7	0.748
7.....	3.132	2.897	1.760	124.6	0.735
8.....	3.899	3.608	2.171	125.7	0.720
9.....	4.635	4.288	2.554	127.1	0.701
10.....	5.551	5.136	3.026	128.4	0.684

<sup>1</sup> Vid. Auwers, *Z. physik. Chem.*, 18, 599 (1895).



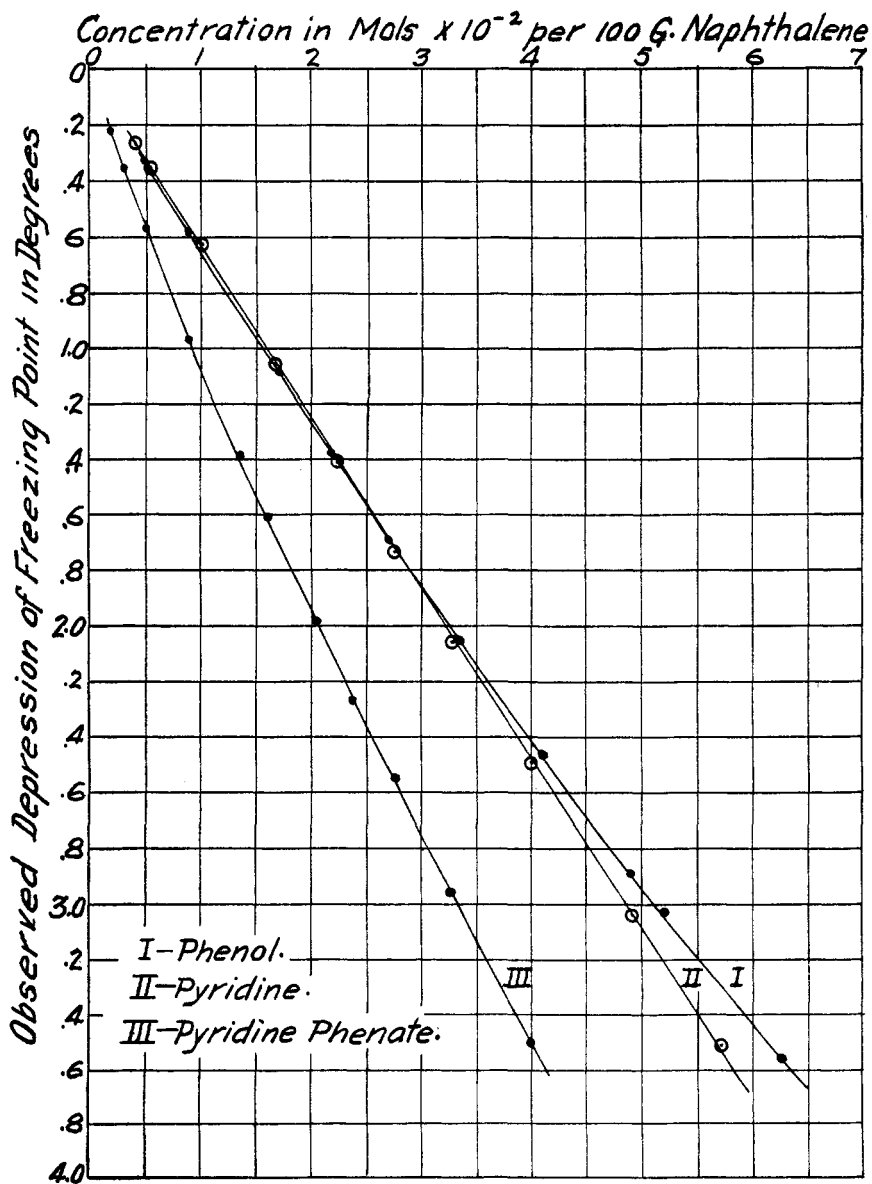


FIG. 8

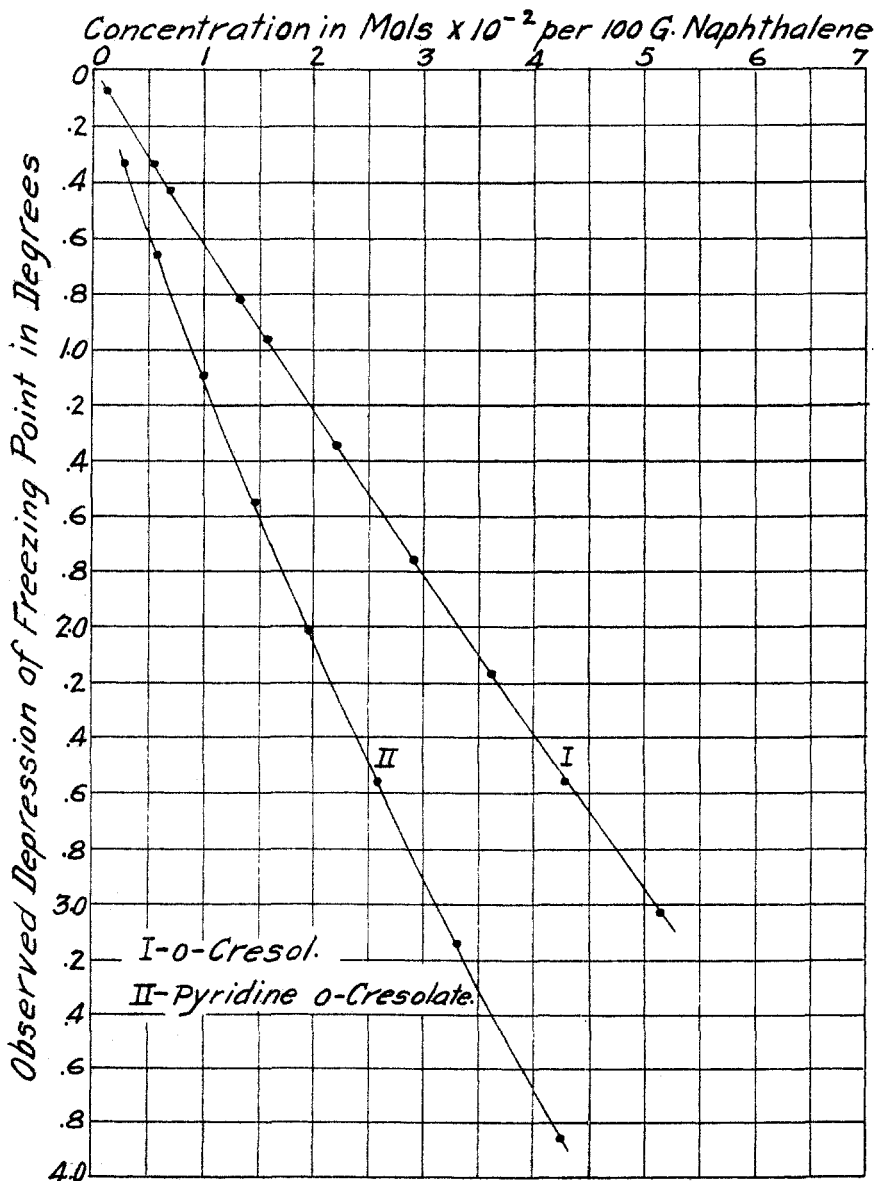


FIG. 9

The apparent molecular weight of *o*-cresol in naphthalene is in no case less than the formula weight, in contrast to the behavior in benzene.

The curve connecting  $\alpha_3$  and  $C_3$  is not a straight line, but it was found that the values were given fairly closely by the following empirical equation:

$$\alpha_3 = 0.7606 + 0.000955 C_3 - 0.003054 C_3^2$$



TABLE XXIII.

 Freezing Point Depressions of Pyridine *o*-Cresolate in Naphthalene.

$$\alpha_3 = 0.7606 + 0.000955C'\beta - 0.003054 (C'\beta)^2.$$

$$\alpha_2 = 0.8317 - 0.0139 C'\beta.$$

$$\text{Total number of molecules} = C' + C'\beta/2.(\alpha_2 + \alpha_3).$$

No.	Wt. compound in 100 g. naphthalene.	Mols $\times 10^{-3}$ com- pound in 100 g. naphthalene.	$\Delta_0^\circ$ .	$\Delta_0/0.700$ .	$\beta$ .
1.....	0.5206 g.	0.278	0.331	0.473	0.881
2.....	1.066	0.570	0.661	0.944	0.825
3.....	1.862	0.995	1.095	1.564	0.714
4.....	2.740	1.464	1.556	2.223	0.656
5.....	3.663	1.957	2.013	2.876	0.593
6.....	4.842	2.587	2.559	3.656	0.526
7.....	6.160	3.292	3.136	4.480	0.459
8.....	7.925	4.235	3.861	5.516	0.385

In this case the equation obtained is a cubic in  $\beta$  but a close approximation is obtained by neglecting the cube term which is small and solving the quadratic equation thus obtained.

In Fig. 10 are given the curves obtained by plotting the value of  $\beta$  against concentration for the compounds phenol-pyridine and *o*-cresol-pyridine in benzene, and for the compounds phenol-pyridine and *o*-cresol-pyridine in naphthalene. It will be seen that the dissociation of the *o*-cresol-pyridine compound is considerably greater than the dissociation of the phenol-pyridine compound in either solvent. Further, the dissociation of both compounds in naphthalene is greater than that in benzene. In this connection it must be remembered that in benzene the dissociation is measured at the freezing point of the benzene solutions, while in naphthalene it is measured at the freezing point of the naphthalene solutions. The effect of increase of temperature would undoubtedly be to increase dissociation. No attempt has been made in the present work to ascertain the effect of temperature.

In the papers of Walden<sup>1</sup> on "Solvolysis" it was shown that naphthalene exercised a greater "solvolytic" effect than benzene at the same temperatures and concentrations. He examined the effect on a number of binary salts using the boiling point method for benzene and the freezing point method for naphthalene, and, as the boiling point of benzene lies very near the freezing point of naphthalene, the effect of temperature is to a large extent eliminated. The boiling point method could obviously not be used in the present work with pyridine, owing to the simultaneous evaporation of the solute. An apparent exception to this generalization is found in the present paper in the dissociation of *o*-cresol alone in benzene and in naphthalene; the apparent molecular weight in benzene at low concentrations is actually less than the formula weight, while in naphthalene it is higher than the formula weight at all concentrations. It is possible

<sup>1</sup> *Loc. cit.*

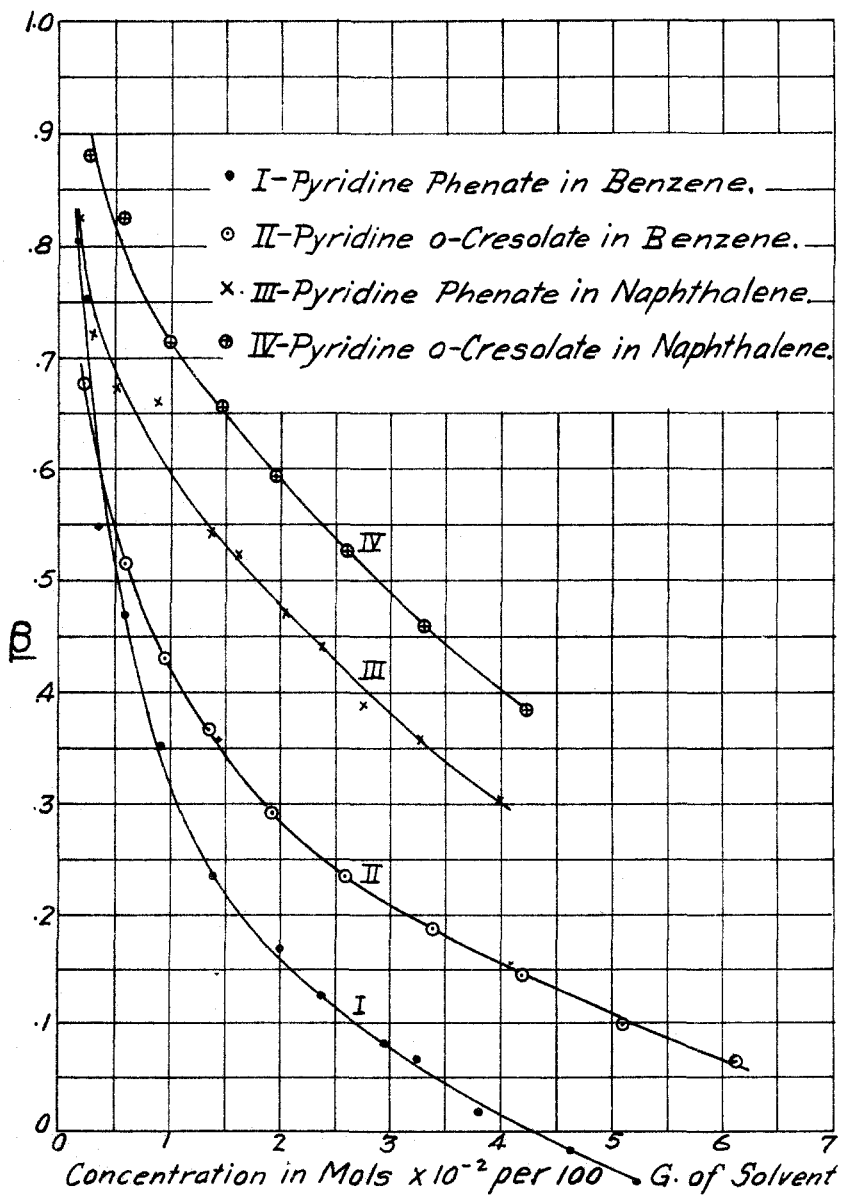


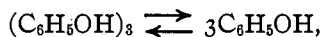
FIG. 10

that this may be explained, at least partially, by combination with the solvent,<sup>1</sup> but this point must for the present be left in abeyance.

It will be seen that the compounds are very considerably dissociated in dilute solutions in all cases, but that the dissociation decreases with increasing concentration. From the curve for  $\beta$  for pyridine phenate in benzene, it is apparent that the value of  $\beta$  would become zero at a concentration of only about  $4.3 \text{ mols} \times 10^{-2}$  per 100 g. solvent. This is probably due to polymerizations of the compound itself which increases with increasing concentration.

The assumption on which the calculation of the values of  $\beta$  was founded, was that the compound in each case was in equilibrium with single molecules of the individual constituents, and that these single molecules were in turn in equilibrium with their polymerized forms which were assumed to be double molecules at the concentrations dealt with. The only case in which this latter assumption was strained was that involving phenol in benzene solution, as this associated further than the double molecule above a concentration of 7%. This association does not quite reach the state of triple molecules even at the highest concentrations investigated, *i. e.*, about 36%.<sup>2</sup>

In the following the assumption has been made that the polymerization takes place exclusively according to the scheme



at all concentrations, and the value for  $\beta$  has been recalculated, assuming as before that the pyridine equilibrium involves only single and double molecules.

(1) Phenol only.

Let  $\gamma$  = the fraction of triple molecules dissociated;

S = the percentage of single molecules;

C<sub>1</sub> = the concentration of phenol taken (as single molecules);

M = the apparent molecular weight.

$$\text{Then the ratio } \frac{\text{No. of triple molecules}}{\text{No. of single molecules}} = \frac{1 - \gamma}{3\gamma} = \frac{100 - S}{S},$$

$$\text{whence } \gamma = \frac{S}{300 - 2S}.$$

$$\text{But } S = \frac{(282.24 - M)100}{188.16}.$$

$$\therefore \gamma = \frac{282.24 - M}{2M}.$$

<sup>1</sup> Cf. Turner and Bissett, *J. Chem. Soc.*, 105, 1777 (1914).

<sup>2</sup> Beckmann, *Z. physik. Chem.*, 2, 715 (1888).

TABLE XXIV.

No.	Mols $\times 10^{-3}$ phenol in 100 g. benzene.	M.	$\gamma$ .
1.....	0.520	154.8	0.411
2.....	0.922	156.5	0.402
3.....	1.555	159.1	0.387
4.....	2.195	161.5	0.374
5.....	2.822	164.3	0.359
6.....	3.650	169.3	0.333
7.....	4.601	173.4	0.314
8.....	5.176	176.8	0.298
9.....	6.005	181.3	0.278

These values of  $\gamma$  when plotted against the concentration lie exactly on a straight line, the values being from two to three times as large as the corresponding values for  $\alpha_1$ . The connection between  $C_1$  and  $\gamma$  is expressed by the equation

$$\gamma = 0.4241 - 0.0243 C_1.$$

### (2) Pyridine-phenate.

If  $\beta$  = the fraction of the compound dissociated at equilibrium,

$C'$  = initial concentration of the double compound,

then the total concentration of free phenol =  $C'.\beta$  as single molecules,  
=  $C'.\beta/3$  as triple molecules.

The actual concentration of triple molecules at equilibrium

$$= C'.\beta/3.(1 - \gamma).$$

The actual concentration of single molecules at equilibrium

$$= 3C'.\beta/3.\gamma.$$

Total molecules of both kinds of phenol =  $C'.\beta/3.(1 + 2\gamma)$ .

Total molecules of pyridine as before =  $C'.\beta/2.(1 + \alpha_2)$ .

Total molecules of compound, phenol, and pyridine present

$$= C'(1 - \beta) + C'.\beta/3.(1 + 2\gamma) + C'.\beta/2.(1 + \alpha_2),$$

$$= C' + C'.\beta.(2/3.\gamma + \alpha_2/2 - 1/6).$$

But, by experiment,

$$\gamma = 0.4241 - 0.0243 C'.\beta$$

and

$$\alpha_2 = 0.7378 - 0.0080 C'.\beta.$$

Whence the total number of molecules

$$= C' + C'.\beta (0.4850 - 0.0202 C'.\beta),$$

$$= C' + 0.4850 C'.\beta - 0.0292 C'^2.\beta^2.$$

This is then equated to  $\Delta_0/0.500$  and  $\beta$  calculated.

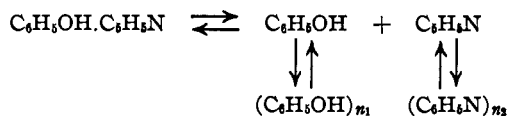
In the following table  $\beta_D$  is the value previously obtained (Table XIV), assuming that phenol associates to double molecules, while  $\beta_T$  is the value now calculated assuming that phenol associates solely to triple molecules.

TABLE XXV.

No.	C'.	$\Delta_s/0.500.$	$\beta_D.$	$\beta_{\pi}.$
1.....	0.078	0.166	0.990	0.989
2.....	0.165	0.230	0.804	0.805
3.....	0.247	0.336	0.753	0.744
4.....	0.358	0.450	0.547	0.532
5.....	0.590	0.722	0.470	0.461
6.....	0.936	1.092	0.352	0.342
7.....	1.387	1.542	0.236	0.230
8.....	1.995	2.156	0.169	0.166
9.....	2.371	2.512	0.126	0.123
10.....	2.942	3.058	0.082	0.081
11.....	3.240	3.342	0.068	0.065
12.....	3.802	3.838	0.018	0.019

It will be seen from Table XXV that the value of  $\beta$  is practically independent of the particular scheme according to which the phenol is assumed to associate. The following considerations will show that this rather remarkable result is quite general.

Stating the equilibria in general terms,



(1) Considering the equilibrium  $(\text{C}_6\text{H}_5\text{OH})_{n_1} \rightleftharpoons n_1\text{C}_6\text{H}_5\text{OH}$ :

Let C = the concentration of the phenol as single mol.

$C/n_1$  = total amount phenol as polymerized mol.

$\alpha_1$  = fraction of total associated mols which are dissociated;

$\mu_1$  = true molecular weight as single mols;

$M_1$  = observed molecular weight.

Then the actual concentration of polymerized mols =  $C/n_1 (1 - \alpha_1)$ ;

actual concentration of single mols =  $C/n_1 \times n_1\alpha_1$ .

But as  $M_1$  is the average molecular weight of these

$$M_1 = \frac{C/n_1 (1 - \alpha_1)n_1\mu_1 + C/n_1 \times n_1\alpha_1 \times \mu_1}{C/n_1 (1 - \alpha_1 + n_1\alpha_1)},$$

whence

$$\alpha_1 = \frac{n_1\mu_1 - M_1}{(n_1 - 1)M_1}$$

for any concentration of C. Similarly, if  $\alpha_2$ , etc., be the corresponding values for the same concentrations of pyridine,

$$\alpha_2 = \frac{n_2\mu_2 - M_2}{(n_2 - 1)M_2}$$

(2) Considering the equilibrium  $\text{C}_6\text{H}_5\text{OHC}_5\text{H}_5\text{N} \rightleftharpoons \text{C}_6\text{H}_5\text{OH} + \text{C}_5\text{H}_5\text{N}$ :

Let C' = the initial concentration of the compound;

$\beta$  = the fraction of this dissociated at equilibrium.

Then the total concentration of liberated phenol =  $C'\beta$  as single mol;  
 the total concentration of liberated phenol =  $C'\beta/n_1$  as assoc. mol;  
 and the total concentration of pyridine =  $C'\beta/n_2$  as assoc. mol.

Then assuming each of these associated as if alone in the solvent, we have:

$$\begin{aligned} \text{Actual concentration of the compound} &= C'(\text{I} - \beta); \\ \text{Actual concentration of unassociated phenol} &= C'\beta/n_1.(n_1\alpha_1); \\ \text{Actual concentration of associated phenol} &= C'\beta/n_1.(1 - \alpha_1); \\ \text{Actual concentration of unassociated pyridine} &= C'\beta/n_2.(n_2\alpha_2); \\ \text{Actual concentration of associated pyridine} &= C'\beta/n_2.(1 - \alpha_2); \end{aligned}$$

and hence the total number of solute molecules

$$\begin{aligned} &= C'(\text{I} - \beta) + C'\beta/n_1(\text{I} - \alpha_1 + n_1\alpha_1) + C'\beta/n_2(\text{I} - \alpha_2 + n_2\alpha_2); \\ &= C'(\text{I} - \beta) + C'\beta/n_1\{\text{I} + \alpha_1(n_1 - 1)\} + C'\beta/n_2\{\text{I} + \alpha_2(n_2 - 1)\}; \end{aligned}$$

and substituting the corresponding values of  $\alpha_1$  and  $\alpha_2$  in this expression we get:

$$\begin{aligned} \text{Total number of solute molecules} \\ = C'(\text{I} - \beta) + \frac{C'\beta}{n_1} \left\{ \text{I} + \frac{(n_1\mu_1 - M_1)(n_1 - 1)}{M_1(n_1 - 1)} \right\} + \\ \frac{C'\beta}{n_2} \left\{ \text{I} + \frac{(n_2\mu_2 - M_2)(n_2 - 1)}{M_2(n_2 - 1)} \right\} \end{aligned}$$

$$\text{which reduces to} \quad = C' + C'\beta \left( \frac{\mu_1}{M_1} + \frac{\mu_2}{M_2} - 1 \right)$$

and is independent of  $n_1$  and  $n_2$ .

Here  $M_1$ ,  $\alpha_1$ ,  $M_2$ ,  $\alpha_2$  are corresponding values for the concentration  $C'\beta$  of free phenol and free pyridine, respectively.

Obviously,  $\mu_1/M_1$  is itself dependent on  $n_1$  for if  $n_1 = 1$  then  $M_1 = \mu_1$ .

$$\text{Actually} \quad \frac{\mu_1}{M_1} = \frac{1 + (n_1 - 1)\alpha_1}{n_1}.$$

#### Alternative Assumptions.

In the preceding work it has been assumed that the chief equilibrium involved is the dissociation of the compound into its simple constituents, followed by the association of those simple constituents in a similar manner to that in which they would associate if alone in the solvent at the same concentration as the liberated constituent, and it has been shown that the mode of association of the constituents is without effect on the value of  $\beta$ . In the following considerations, limiting assumptions are made which would lead to a minimum and to a maximum value, respectively, in the value of  $\beta$ .

(A) Let us assume that the compound dissociates in solution but that no association of the constituents follows: This would furnish a lower limit for  $\beta$ .

Let  $C$  = the initial concentration of the compound;

$\beta$  = the fraction of the molecules dissociated at equilibrium.

Then the final concentration of the compound =  $C(1 - \beta)$ ;

the concentration of the particular phenol =  $C\beta$ ;

the concentration of the pyridine =  $C\beta$ ;

the total number of solute mols =  $N$  =  $C(1 + \beta)$ ;

whence

$$\beta = N - C/C.$$

The values so obtained for a series of points in each case studied are given in the summarized Table XXVI.

(B) In this case it is assumed that the compound itself is associating as well as the single constituents.

In the case of pyridine phenate in benzene this is obviously true as the value of  $\beta$  previously obtained falls to zero at a concentration of only about 4 centigram mols of compound in 100 grams of benzene, while at higher concentrations the apparent value of  $\beta$  becomes negative.

This effect will increase with increasing concentration as the dissociation of the compound is depressed.

At first sight this case seems hopeless of giving any information but by again resorting to fairly legitimate assumptions it has been found possible to arrive at tentative higher limit figures. These assumptions are:

(1) That the compound itself associates in the solvent in the same manner and to the same extent that the phenol in it would do if alone in the solvent.

(2) That the compound associates in the solvent to the same extent that the pyridine in it would do if alone in the solvent. The case of pyridine phenate in benzene will be worked out in detail and in the other cases the equations deduced will alone be given.

The mode of association is in all cases taken to be to double mols:

Let  $C$  = the concentration of the compound taken.

If this were totally dissociated it would give us  $C$  mols of phenol as single molecules. If this phenol associates as if alone in the solvent, then the actual concentration of double mol of phenol would be

$$C/2 (1 - \alpha_1).$$

Assumption (1) would thus lead us to the relation

No. of mols of "double compound" + No. of mols of double phenol =  $C/2 (1 - \alpha_1)$ .

Now let  $x$  = fraction of total potential double compound which is dissociated at equilibrium; then

Actual concentration of double compound =  $C/2 (1 - x)$ ;

Total concentration of single compound =  $C/2 \times 2n = Cx = C'$ ;

Therefore the total no. of mols of phenol (as single mols) =  $Cx\beta$ ;

Hence the actual number of double phenol mols =  $Cx\beta/2 (1 - \alpha_1)$ .

Hence, applying Condition 1,

$$C/2 (1 - x) + Cx\beta/2 (1 - \alpha_1) = C/2 (1 - \alpha_1);$$

$$\text{whence } x = \frac{\alpha_1}{1 + \alpha_1\beta - \beta} \text{ and } C' = Cx = \frac{C\alpha_1}{1 + \alpha_1\beta - \beta}$$

But by earlier experiments,  $\alpha_1 = 0.2313 - 0.0318 C'\beta$ .

Substituting this value and simplifying we get Equation a:

$$C' + (0.0318 C - 0.7687)C'\beta - 0.0318 (C'\beta)^2 = 0.2313 C.$$

Further, this total concentration  $C'$  of single molecules of compound will furnish a total number of molecules =  $C' + C'\beta/2 (\alpha_1 + \alpha_2)$ , as shown in the earlier part of this paper.

Hence, the actual number of double molecules of the compound must be the difference between this number and the total number of molecules found by Experiment N, *i. e.*, the number of mols of double compound

$$= N - C' - C'\beta/2 (\alpha_1 + \alpha_2).$$

Further, the number of mols of double phenol =  $C'\beta/2 (1 - \alpha_1)$ .

And by experiment

$$\alpha_1 = 0.2313 - 0.0318 C'\beta.$$

$$\alpha_2 = 0.7378 - 0.008 C'\beta.$$

Again equating the sum of the double mols of compound and of phenol to  $C/2 (1 - \alpha_1)$ , and substituting the values of  $\alpha_1$  and  $\alpha_2$ , we obtain Equation b

$$C' + (0.1002 + 0.0159 C) C'\beta - 0.0358 (C'\beta)^2 = N - 0.3843 C.$$

From Equations a and b, by eliminating the squared term, we obtain a relation between  $C'$  and  $\beta$ , and substituting in the original equations, we obtain the four values of  $\beta$ .

This operation must be carried out separately, for each point on the curve after first substituting the numerical values of  $C$  and of  $N$ . No difficulty is found in selecting the appropriate root as usually two are imaginary and only one lies between zero and unity, between which limits  $\beta$  must lie.

Assumption 2 is calculated in an analogous manner. In this case the assumption is represented by the relationship

No. of mols of double compound + No. of mols of double pyridine =  $C/2 (1 - \alpha_2)$ , thus  $x = \frac{\alpha_2}{1 + \alpha_2\beta - \beta}$  and the two final equations are

$$(a) C' + (0.008 C - 0.2622) C'\beta - 0.008 (C'\beta)^2 = 0.7378 C;$$

$$(b) C' + (0.3534 + 0.004 C) C'\beta - 0.0239 (C'\beta)^2 = N - 0.1311 C.$$

The following are the equations for the other cases dealt with:



**Pyridine-phenate in Naphthalene.**—Compound associated as phenol.

$$(a) C' + (0.0451 C - 0.0948) C'\beta - 0.0451 (C'\beta)^2 = 0.9052 C;$$

$$(b) C' + (0.8210 + 0.02255 C) C'\beta - 0.05205 (C'\beta)^2 = N - 0.0474 C.$$

Compound associated as pyridine:

$$(a) C' + (0.0139 C - 0.1683) C'\beta - 0.0139 (C'\beta)^2 = 0.8317 C;$$

$$(b) C' + (0.7843 + 0.00695 C) C'\beta - 0.03645 (C'\beta)^2 = N - 0.08415 C.$$

**Pyridine *o*-Cresylate in Benzene.**—Compound associated as *o*-cresol.

$$(a) C' + (0.0900 + 0.0776 C) C'\beta - 0.0776 (C'\beta)^2 = 1.0900 C;$$

$$(b) C' + (0.9588 + 0.0388 C) C'\beta - 0.0816 (C'\beta)^2 = N + 0.0450 C.$$

Compound associated as pyridine:

$$(a) C' + (0.0080 C - 0.2622) C'\beta - 0.0080 (C'\beta)^2 = 0.7378 C;$$

$$(b) C' + (0.7828 + 0.0040 C) C'\beta - 0.0468 (C'\beta)^2 = N - 0.1311 C.$$

**Pyridine *o*-Cresylate in Naphthalene.**—Compound associated as *o*-cresol.

In this case, as before mentioned, the curve connecting  $\alpha_1$  with the concentration of the *o*-cresol alone in naphthalene is not a straight line, the relationship being fairly represented by the equation

$$\alpha_1 = 0.7606 + 0.000955 C'\beta - 0.003054 (C'\beta)^2.$$

Using this value of  $\alpha_1$ , two cubic equations resulted.

$$(a) C' - (0.2394 + 0.000955 C) C'\beta + (0.000955 + 0.003054 C)(C'\beta)^2 - 0.003054 (C'\beta)^3 = 0.7606 C;$$

$$(b) C' + (0.6764 - 0.0004775 C) C'\beta + (0.001527 C - 0.005995)(C'\beta)^2 - 0.003054 (C'\beta)^3 = N - 0.1197 C.$$

These equations happen to be capable of an easy solution.

**Pyridine *o*-Cresylate in Naphthalene.**—Compound associated as pyridine.

$$(a) C' + (0.0139 C - 0.1683) C'\beta - 0.0139 (C'\beta)^2 = 0.8317 C;$$

$$(b) C' + (0.7119 + 0.00695 C) C'\beta - 0.01342 (C'\beta)^2 - 0.001527 (C'\beta)^3 = N - 0.08415 C.$$

A rigid solution of these two equations is extremely cumbersome but an approximate solution may be easily obtained by neglecting the cube term in Equation *b* and solving the simultaneous quadratic equations so obtained. This would not introduce serious error as the cube term is small. The figures given in the table were obtained in this way. The results obtained in this way for a series of points in each set are given in Table XXVI. The numbers in the first column refer to the points given in the earlier tables. The third column contains the values of  $\beta$  taken from the earlier tables for comparison. The fourth column gives the lower limit figures, assuming no association of any kind occurs, while the fifth and sixth columns contain the figures obtained on Assumptions 1 and 2, respectively, as to the simultaneous association of both compound and constituents.

TABLE XXVI.

	No.	Concentration.	Previous value.	No. assoc.	$\beta$ .	
					Comp. assoc. as	
					Phenol	Pyridine.
Pyridine-phenate in benzene.....	2	0.1654	0.804	0.391	0.974	0.899
	6	0.9364	0.352	0.166	0.896	0.569
	8	1.995	0.169	0.081	0.866	0.428
	11	3.240	0.068	0.039	0.855	0.343
	13	4.628	—0.017	0.009	0.851	0.269
Pyridine-phenate in naphthalene....	1	0.1819	0.824	0.704	0.842	0.855
	5	1.363	0.542	0.458	0.608	0.634
	8	2.372	0.438	0.367	0.525	0.550
	11	4.005	0.302	0.251	0.408	0.427
Pyridine <i>o</i> -cresylate in benzene.....					as <i>o</i> -cresol.	
	1	0.2293	0.677	0.622	0.669	0.786
	3	0.9618	0.430	0.389	0.402	0.586
	6	2.589	0.235	0.211	0.208	0.421
	9	5.104	0.099	0.089	0.078	0.285
Pyridine <i>o</i> -cresylate in naphthalene..	1	0.2782	0.881	0.700	0.950	0.910
	5	1.957	0.604	0.469	0.725	0.650
	8	4.235	0.410	0.303	0.546	0.526

It will be seen from Figs. 11–14 that the limits vary very widely in the case of pyridine phenate in benzene, but that the limits are much narrower in each of the other cases. It must be remarked, however, that in Fig. 11, Curve 1, is undoubtedly considerably too low, as it presupposes no association of any kind taking place. The compound, however, does associate as evidenced by the negative values for  $\beta$  in Curve 2. On the other hand, there is strong reason to suppose that Curve 4 is much too high. It is unlikely that the values for  $\beta$  in benzene will be as high as the values for the same compound in naphthalene (see Fig. 12), as naphthalene has been shown generally to have higher solvolytic power than benzene at the same temperature. (Walden, *Loc. cit.*) In these experiments the temperature is higher in the case of naphthalene than in the case of benzene, which would still more accentuate the solvolytic power of the naphthalene. Further, it has been generally observed that substances are more associated in benzene than they are in pyridine as a solvent and hence it seems probable that the free phenol (and consequently also the compound) would be less associated in presence of free pyridine than it would be in presence of benzene only.

In Figs. 12, 13 and 14 it is seen that the possible values of  $\beta$  lie in much narrower limits, while the above considerations also apply to a smaller extent. It is further seen by comparing Figs. 13 and 14 that the values of  $\beta$  for pyridine orthocresylate are on all assumptions much lower in benzene than in naphthalene. It is, of course, impossible to assign definite values to these opposing tendencies, but sufficient evidence has been

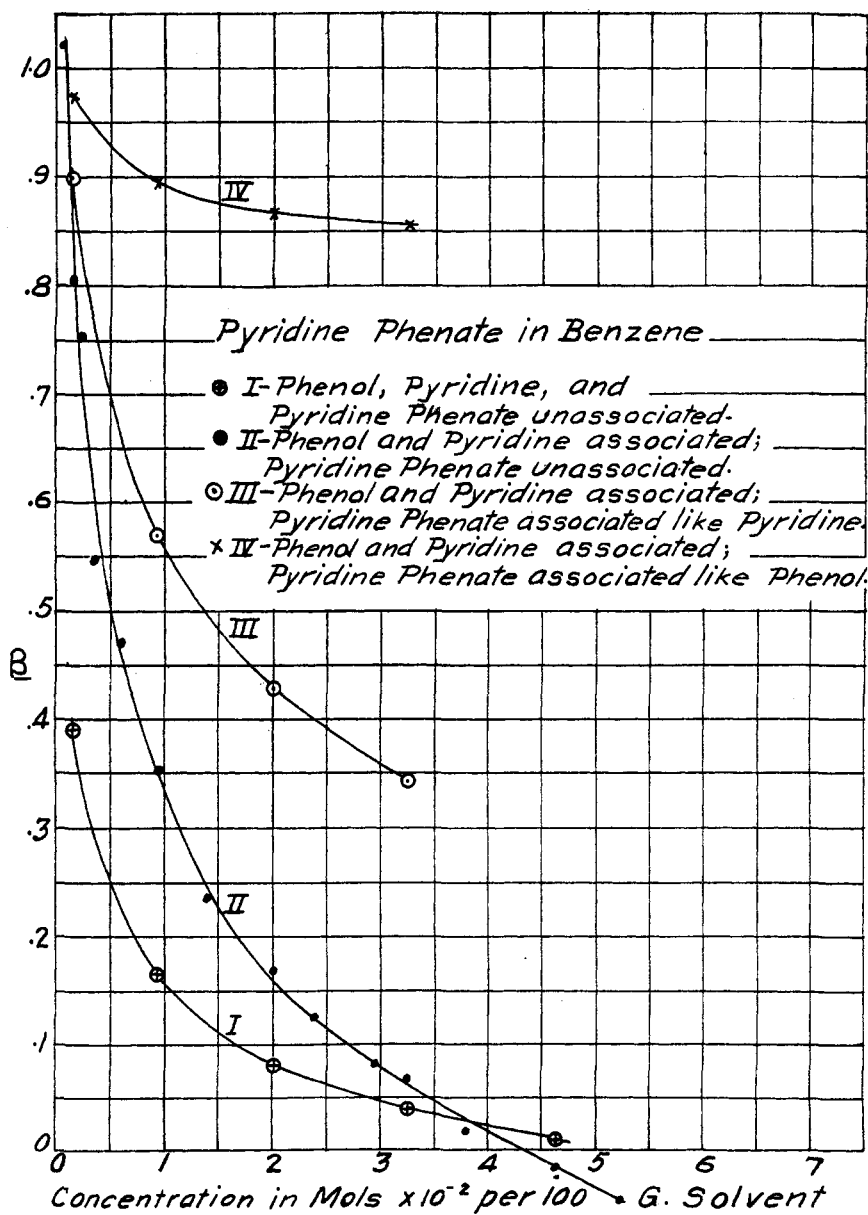
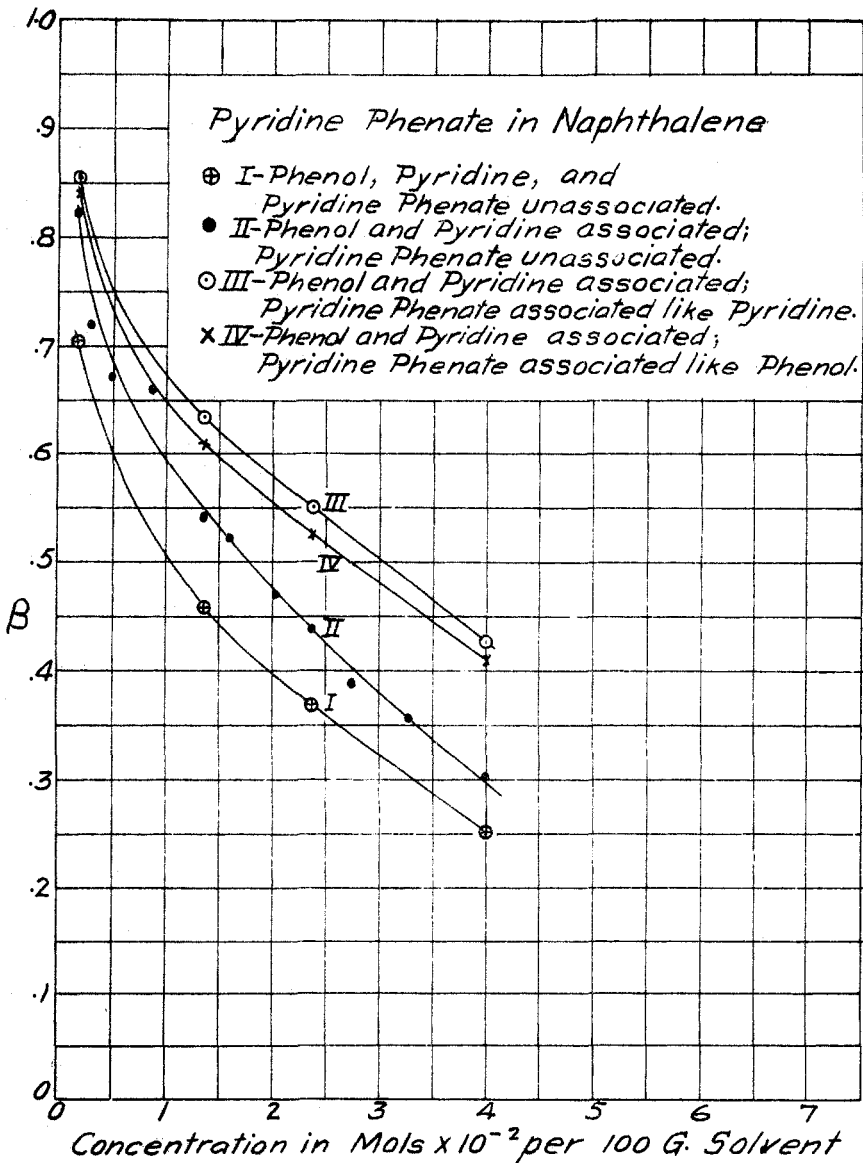
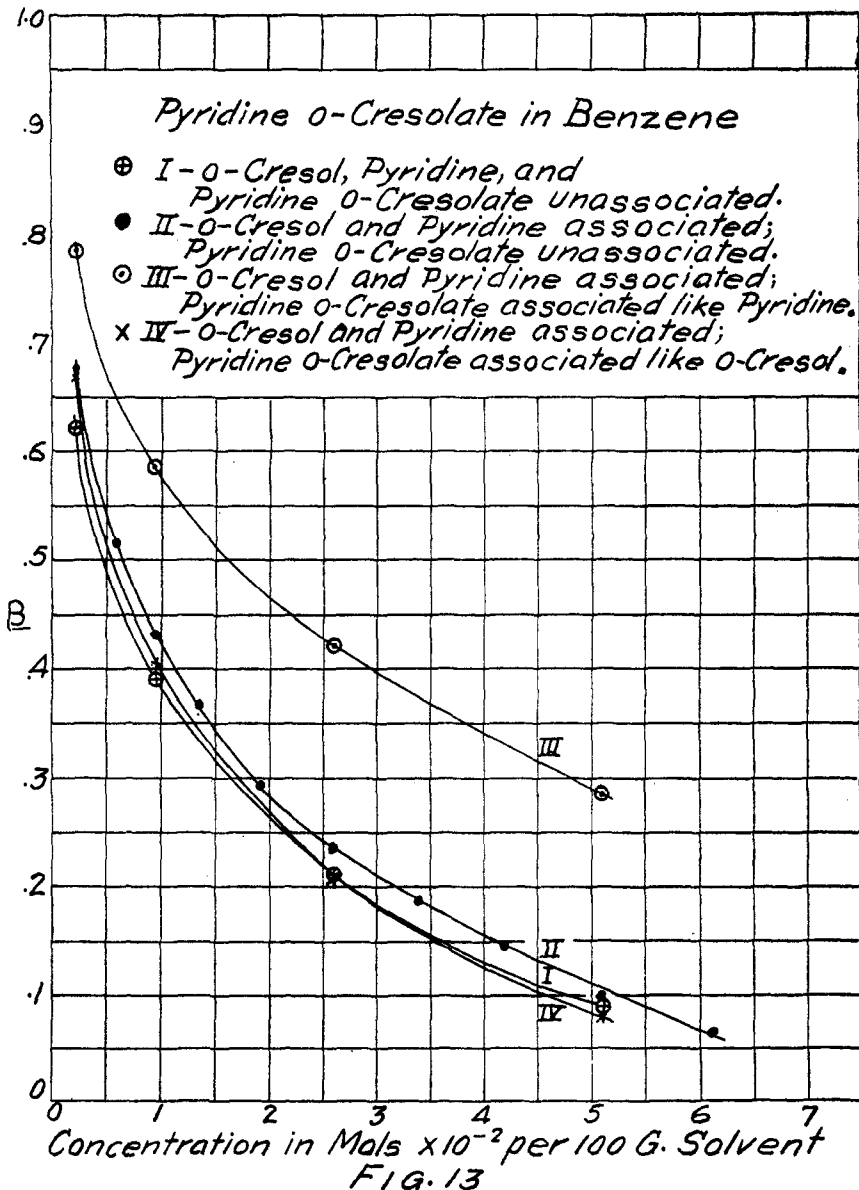


FIG. 11





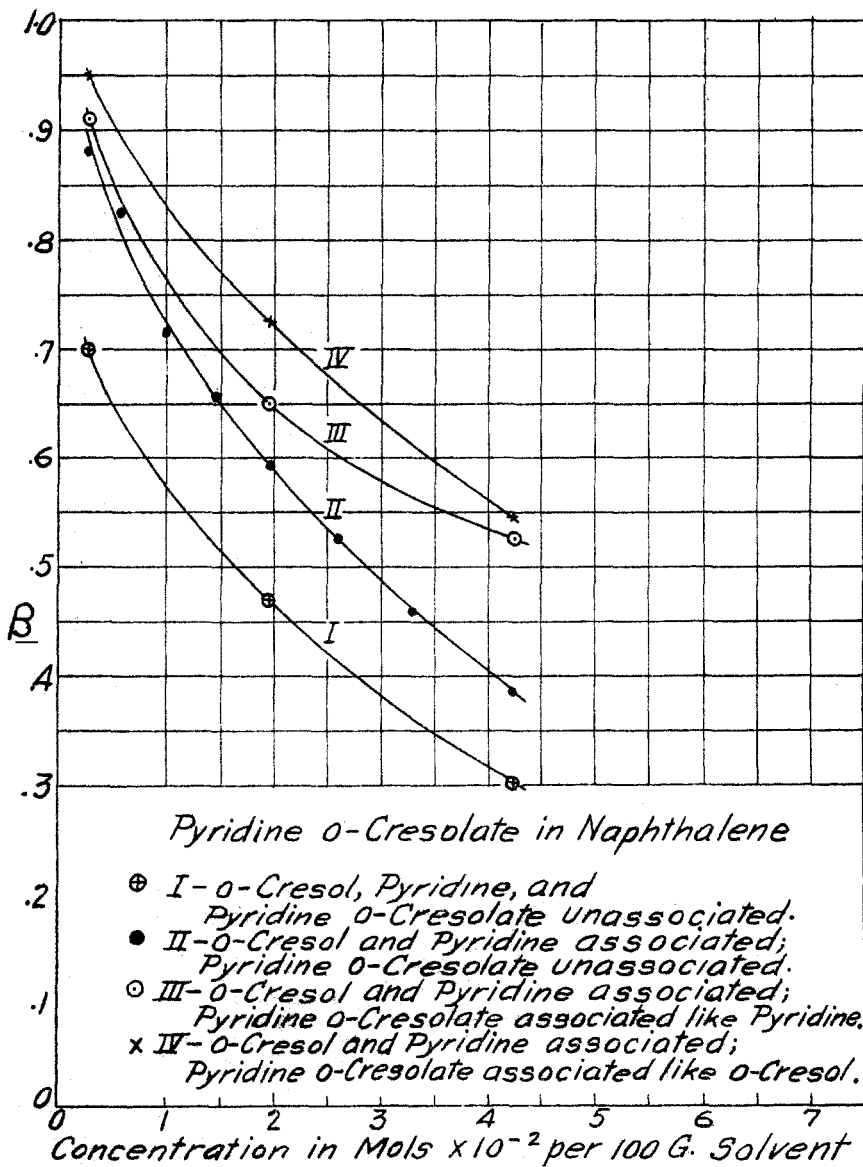


FIG. 14

brought forward to show that there is undoubtedly a considerable dissociation and that this dissociation increases rapidly with increasing dilution.

This work is being continued and extended, and further discussion of the foregoing results and of their bearing on the question of the behavior of these solutions towards aqueous alkali and acid is reserved for a subsequent communication.

#### Summary.

(1) Attention is drawn to the fact, known empirically by the tar distiller, that the crude phenols must be extracted from the coal-tar oils by means of sodium hydroxide before the pyridine can be economically extracted by sulfuric acid.

(2) It is shown that pure phenol can be extracted practically completely from benzene in presence of equimolecular amount of pyridine by an amount of sodium hydroxide which would be just sufficient to extract the same amount of phenol from the benzene in absence of the pyridine; and that if the pyridine be increased so that four molecules of pyridine are present for one molecule of phenol the percentage extraction of phenol is only reduced by less than 5%.

(3) When equimolecular amounts of phenol and pyridine dissolved in benzene are extracted by dilute sulfuric acid, the percentage extraction of pyridine is almost as great as though the phenol were absent; but if excess of phenol is added so that four molecules of phenol are present for one molecule of pyridine, the percentage extraction of the pyridine is reduced by about 75%.

(4) The difficulty of explaining this behavior on any assumption of hydrolysis and distribution equilibria is pointed out.

(5) The compounds formed by pyridine with phenol, ortho- and *p*-cresol were studied by means of freezing-point curves and results were obtained in confirmation of the results of Bramley, which were published after that section of the work was completed.

(6) A preliminary investigation of the dissociation of the compounds of pyridine with phenol and with *o*-cresol in benzene solution and in naphthalene solution is made by the cryoscopic method, the pyridine and the phenol or cresol being present in equimolecular amounts, and it is shown that the compounds are in all cases considerably dissociated, and that the dissociation increases rapidly with increasing dilution. Attempts have been made to calculate upper and lower limits for this dissociation, taking into account the simultaneous association of the compound and its separate constituents.