CXXXII.—*The Solubility of the Nitrophenols and Other Isomeric Disubstitution Products of Benzene.*

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THE structure of the nitrophenols has for some time been a matter of dispute, and there are reasons for suspecting that the three compounds may not have analogous formulæ. It seemed possible that further evidence might be obtained on this question by an examination of their physical properties, and we have therefore examined their solubility, especially in water. If their structures are analogous, we should expect their solubility curves to show the same relations as those of other sets of ortho-, meta-, and para-isomerides. Very few aromatic compounds, however, have had their solubilities examined over any considerable range of temperature, and we were therefore led to investigate this property for other substances, in order to discover what is the normal influence of orientation on the solubility curves. The substances chosen for comparison must be sufficiently soluble to allow the curves to be followed from pure water up to pure substance; and they must have "unalterable" substituents, so that there should be no

question of the three isomerides having analogous constitutions. These requirements are fulfilled by the cresols and the toluic acids. They are all miscible with water below 200°, and there is no

FIG 1.

danger of the methyl group reacting with the other substituent, as the nitro-group may do with the hydroxyl in the nitrophenols.

We have therefore determined the complete solubility curves in water for the three cresols and the three toluic acids, and also for

the *m*- and *p*-nitrophenol; for *o*-nitrophenol this cannot be done, but we have followed the curves up to 200°.

We have further measured the solubility of the nitrophenols in toluene, so as to show the effect of using a non-associated solvent.

EXPERIMENTAL.

I. Solubility in Water.

The methods of measurement were essentially the same as those used to determine the solubility of aniline in solutions of its

FIG 2.

Percentage composition.

Toluic acids and water.

Ortho ○. Meta +. Para ×.

hydrochloride (Sidgwick, Pickford, and Wilsdon, T., 1911, 99, 1123). Weighed quantities of the components were heated, at lower temperatures in a flask, at higher temperatures in sealed tubes, until the contents became homogeneous and then slowly cooled, and the temperature observed at which separation took place. This gives good results when it is a liquid that separates out; when a solid is deposited, the flask or tube must be warmed very slowly, and the temperature taken at which the last traces are disappearing. The results are then less satisfactory, but, as will be seen, this affects only a small portion of the curves.

For the higher temperatures the heating took place in a glycerol bath, stirred by a motor. At lower temperatures a water-bath was used.

The thermometers used were standardised by comparison with a

FIG. 3.

platinum thermometer made by Mr. J. J. Manley, the resistance of which had been determined by him with great accuracy at 0°, 100°, and 444°. We wish to express our thanks to Mr. Manley for the instrument, and for his assistance in using it.

The cresols, the toluic acids, and the *o*- and *p*-nitrophenols were obtained from Kahlbaum. The first were purified by distillation, the fractions used distilling within half a degree; the toluic acids were recrystallised from water and alcohol, although the melting points were scarcely raised by this; the nitrophenols were purified in the first instance by distillation in a current of steam, and then by recrystallisation, the ortho from alcohol, and the para from water. Part of the *m*-nitrophenol was prepared from *m*-nitroaniline, and the rest obtained from Kahlbaum. It was twice recrystallised from water.

The solubilities are given in the following tables, *P* being the number of grams of substance in 100 grams of solution. An asterisk indicates that the solid phase is present. The results are plotted in Figs. 1, 2, and 3.

TABLE I.
Cresols and Water.

Ortho-.		Meta-.		Para-.	
<i>P.</i>	Temp.	<i>P.</i>	Temp.	<i>P.</i>	Temp.
3.01	35.3°	2.24	— 0.2°	2.24	40.2°
3.22	50.2	2.36	+ 24.7	2.49	52.6
3.47	61.7	2.66	47.0	2.80	63.5
3.75	70.6	3.03	61.9	3.19	73.5
4.10	77.7	3.54	74.5	3.72	84.0
4.51	84.6	4.24	87.5	4.06	88.8
6.52	130.6	6.59	116.9	4.47	94.0
10.46	148.7	11.99	139.4	7.42	124.5
19.36	158.7	32.40	146.9	15.10	139.4
30.06	161.7	35.07	147.0	20.07	141.2
40.89	162.8	41.06	146.6	30.13	143.5
50.14	160.0	61.27	140.5	40.08	143.4
59.80	157.7	70.32	124.8	50.63	141.5
69.30	145.7	75.40	109.3	60.61	134.8
76.14	129.6	80.46	82.8	71.91	111.6
82.37	87.5	82.60	67.7	79.40	77.9
84.58	56.6	83.70	57.1	83.61	37.4
85.69	33.6	84.79	46.5	84.48	27.5
86.14	25.6	85.85	34.5	85.28	17.2
87.52	8.3*	87.05	20.3	86.86	8.7*
88.68	9.1*	87.58	13.2	87.90	9.2*
89.89	10.2*			90.09	10.8*
90.85	11.1*			94.68	17.1*
92.62	12.9*	Critical solution temp. 147.0°.		96.01	20.3*
94.08	15.3*			97.27	24.0*
97.46	22.3*			98.32	27.5*
99.01	26.9*			99.06	29.9*
100.00	29.9*			100.00	33.8*

Critical solution
temp. 162.8°.
Triple point 8.0°.
P = 87.0 and
about 2.5.

Critical solution
temp. 143.5°.
Triple point 8.7°.
P = 86.0 and
about 2.0.

Toluic Acids and Water.

Ortho-.		Meta-.		Para-.	
P.	Temp.	P.	Temp.	P.	Temp.
2.23	85.1*	1.53	89.8*	1.51	114.4*
3.66	109.1	3.13	118.6	2.96	133.7*
5.00	118.3	5.88	140.5	4.97	141.4*
6.99	130.4	9.96	153.3	10.08	150.9
10.20	143.7	29.94	162.2	20.27	157.9
20.23	156.5	40.11	162.1	30.14	159.1
31.47	160.2	50.10	160.7	40.57	158.5
39.92	161.2	60.15	157.7	50.38	158.0
48.63	160.2	71.17	145.1	60.55	152.6
60.16	154.6	79.57	129.6	79.68	145.1*
70.12	147.4	82.06	121.8	92.52	156.5*
84.64	119.8	86.67	105.9	100.00	176.8*
90.53	97.2	89.32	96.4		
91.98	93.7*	92.45	94.2*		
93.83	94.4*	96.93	101.9*		
95.95	96.0*	100.00	110.5*		
100.00	102.4*				
Critical solution temp. 161.2°.		Critical solution temp. 162.2°.		Critical solution temp. 159.1°.	
Triple point 93.5°.		Triple point 91.8°.		Triple point 142.0°.	
P=91.2 and 2.5.		P=90.5 and 1.6.		P=74.0 and 5.0.	

Nitrophenols and Water.

0.321	38.4*	3.03	40.4*	2.91	34.8*
0.346	42.8*	3.65	49.5	3.11	37.2*
0.376	47.5	4.66	61.1	3.34	40.4
0.455	59.4	5.42	67.1	3.93	47.7
0.513	65.7	7.64	79.1	4.30	51.2
0.589	72.8	9.47	85.1	5.33	59.1
0.690	80.3	10.94	88.5	6.99	67.8
0.833	88.9	13.92	93.2	8.28	72.6
1.343	109.9	18.85	97.1	10.61	79.3
3.03	151.8	21.55	98.0	13.70	84.4
5.04	169.5	29.10	98.5	17.53	87.9
9.90	196.5	35.13	98.5	21.58	90.2
...	...	38.84	98.6	26.16	91.3
90.68	196.5	40.94	98.7	30.41	92.3
95.14	163.4	43.12	98.5	33.19	92.8
98.48	91.7	48.12	97.9	36.46	92.6
98.73	82.9	53.95	94.5	40.45	92.0
99.24	59.3	57.19	91.9	45.40	91.3
99.51	43.6*	60.74	87.3	51.75	89.0
100.00	44.9*	63.47	82.6	60.16	80.2
Critical solution temp. above 200°.		67.38	72.7	72.10	40.4*
Triple point 43.5°.		71.56	55.8	74.18	41.9*
P=99.48 and 0.350.		75.89	42.3*	75.55	43.6*
		79.32	43.9*	77.95	46.7*
		89.90	62.0*	81.50	52.8*
		100.00	95.1*	85.47	63.1*
Critical solution temp. 98.7°.				88.38	70.9*
Triple point 41.5°.				91.14	79.9*
P=74.0 and 3.16.				94.37	91.5*
				98.21	106.0*
				100.00	113.8*
Critical solution temp. 92.8°.					
Triple point 39.6.					
P=71.2 and 3.26.					

The triple points were determined graphically.

To show more clearly the relative solubilities of the several compounds at lower temperatures, the values obtained by interpolation on the curves for a series of "round" temperatures are given in table II.

TABLE II.
Solubilities in Water.

Temp.	Cresols.			Toluic acids.			Nitrophenols.		
	Ortho-.	Meta-.	Para-.	Ortho-.	Meta-.	Para-.	Ortho-.	Meta-.	Para-.
40°	3.08	2.51	2.26	—	—	—	0.330*	3.02*	3.28
50	3.22	2.72	2.43	—	—	—	0.388	3.68	4.22
60	3.40	2.98	2.69	—	—	—	0.463	4.54	5.53
70	3.74	3.35	3.03	—	—	—	0.560	5.80	7.50
80	4.22	3.80	3.52	2.03*	1.16*	—	0.685	7.90	10.85
90	4.80	4.43	4.16	2.42*	1.54*	—	0.856	11.69	21.2
100	5.30	5.47	5.10	2.97	1.98	1.16*	1.078	∞	∞
110	5.80	5.96	5.50	3.71	2.52	1.36*	1.37	—	—
120	6.22	7.00	6.58	5.10	3.24	1.75*	1.59	—	—
130	6.70	8.86	9.00	6.93	4.30	2.50*	1.91	—	—
140	7.67	12.3	15.9	9.25	5.77	4.30*	2.32	—	—
150	11.1	∞	∞	13.7	8.40	9.33	2.90	—	—
160	23.7	—	—	30.0	19.4	∞	3.75	—	—
Critical solution temp....	162.8	147.0	143.5	161.1	162.2	159.1	> 200	98.7	92.8
Melting point...	29.9	[4°] ¹	33.8	102.4	110.5	176.8	44.9	95.1	113.8

¹ According to Stadel, *Ber.*, 1885, 18, 3443.

Discussion of Results.

The results obtained with the cresols and the toluic acids are so similar that they may be taken to illustrate the normal behaviour of position-isomerides; and this normal behaviour may therefore be discussed first, the question of its bearing on the nitrophenols being left until later.

It is evident that when we are dealing with the liquid state, the influence of orientation on the solubility is very small. Both with the cresols and with the toluic acids the three curves run very close to one another, and the critical solution temperatures never differ by more than 20°, and usually lie much nearer than this. The solid-liquid equilibrium, on the other hand, is very greatly affected by the position of the substituent groups. The melting points differ in one case by 30°, and in the other by more than 70°. The depression caused by the presence of water—the interval between the melting point and the triple point—is correspondingly variable. But it is to be noticed that this difference vanishes when the solid disappears. Thus *p*-toluic acid, with a melting point some 70°

and a triple point about 50° higher than the *o*- and *m*-isomerides, has very much the same solubility at its triple point as the other two acids at that temperature. Speaking generally, we may say for any set of normal position-isomerides that the liquid-liquid curves run close together, and the only considerable differences are in the points at which the solid-liquid curves branch off from them.

This result is to be expected. The anomalous differences in physical properties caused by small differences in the structure of similar substances are confined—or very nearly so—to those phenomena in which the solid state is concerned (see Biach, *Zeitsch. physikal. Chem.*, 1904, 50, 43). They are found in the melting points and solubilities of the solids, but scarcely if at all in the boiling points, or, as our results indicate, in the liquid-liquid curves. This is illustrated by the acids of the acetic series, where the melting points alternately rise and fall, as the series is ascended, whilst the boiling points rise steadily. Again, among the aromatic compounds it is well known that position-isomerides differ far more in melting than in boiling points. The reason, no doubt, is that small differences in structure, which do not seriously affect the properties of the liquid, may have a considerable influence on the readiness with which the molecules can be packed together into the crystalline form. The para-compounds, as we might expect from their greater symmetry, assume the crystalline state more easily than the ortho and meta; and hence their melting points are higher, and their solubilities as a rule are less.

It is also to be noticed that the solubility curves for these substances frequently cut one another. Thus with the cresols, the order of the critical solution temperatures is the exact opposite of what we should expect from the solubilities at 40° . Again, with the toluic acids, the ratio of the solubilities at 100° is roughly 3:2:1, which would not lead us to anticipate that at higher temperatures the curves would lie so near together. It is evident that the measurement of the solubility at a few temperatures, especially where it is small, may be very misleading, and that if any conclusions are to be drawn from it, the whole course of the curves should be investigated.

It appears, then, that a mere difference in orientation among di-derivatives of benzene does not produce any marked change in the solubility of the substances in the liquid state. The melting points and the solid-liquid curves may differ to any extent, but the liquid-liquid curves will be very similar.

When we come to the nitrophenols we see that the meta- and para-compounds follow this general rule, and their behaviour is perfectly normal. The two curves run very near together, and

their critical-solution temperatures are within 7° of one another. The behaviour of *o*-nitrophenol is, however, entirely different. Its solubility is never more than about one-tenth of that of the other two compounds. At a temperature at which they are miscible with water in all proportions, not more than 1 per cent. of the ortho-compound will dissolve. Even 100° above this, its solubility is under 10 per cent. Its critical-solution temperature could not be determined, partly from the difficulty of working with water under so high a pressure, and partly because even at 200° there were very obvious signs of decomposition and blackening; but it is clearly very high, well above 200° . Yet on general grounds we should expect the ortho- to be more soluble than the para-compound.

The anomaly is the more remarkable since the vapour pressure of ortho- is far higher than that of para-nitrophenol. This difference has been generally overlooked, since the boiling point of *p*-nitrophenol is not recorded, as it decomposes below that temperature. We are examining the vapour pressures of these substances, and preliminary experiments have shown that whilst the ortho-compound boils at 214° , the para-, from observations at lower pressures, would boil at about 295° ; and that the vapour pressure of the para, in the neighbourhood of 100° , is only about one-seventieth of that of the ortho. This great difference is in itself enough to show that the two compounds do not behave as a normal pair of position-isomerides. It also emphasises the anomaly of the solubilities, since we should expect the substance with the higher vapour pressure to be the more readily soluble. In fact, if we assume that at the ordinary temperature ortho-nitrophenol is one-tenth as soluble as para, and has seventy times the vapour pressure, it follows that the partition-coefficient between the vapour and the aqueous solution is seven hundred times as great for the former as for the latter.

These facts show clearly that whilst meta- and para-nitrophenol exhibit the normal relations of position-isomerides, the ortho-compound in its physical behaviour is entirely different. We cannot avoid the conclusion that this is due to some difference in structure. With substances like the cresols and the toluic acids there can be no question of the orientation affecting the structure, since the methyl group cannot, so far as we know, react with the hydroxyl or the carboxyl. With the nitrophenols, however, such interaction undoubtedly takes place, as is shown by the change of colour in the formation of salts. The discovery by Hantzsch and Gorke (*Ber.*, 1906, **39**, 1093) of a series of red ethers isomeric with the colourless nitroanisoles is a conclusive proof that the change of colour is associated with a change of structure. From the fact

that *p*-nitrophenol is colourless, whilst the ortho-compound is yellow, but much paler than its salts, Hantzsch concludes that the ortho-compound is a solid solution of a small quantity of the coloured *aci*-form in the neutral, and that the deepening of the colour when alkali is added to the aqueous solution is due to the conversion of the whole of the nitro-compound present into a salt of this *aci*-form. We do not propose to discuss this question in detail at present, or to criticise the formulæ which have been

FIG. 4.

suggested for the *aci*-forms; but one or two considerations may be pointed out. Firstly, the enormous difference in solubility between the ortho- and the meta- or para-compounds can hardly be due to the presence in the former of a small quantity of a second modification, but rather suggests that the whole or nearly the whole of the ortho-compound has a different structure from the meta and para. Secondly, if this different structure is that of a more strongly acidic substance, it is remarkable that the solubility should be

diminished; we should expect it to be increased. Thirdly, the argument from colour must be used with caution. No doubt all three nitrophenols give strongly coloured salts, either yellow or red; but there are great differences in the intensity of the colour, which is enormously greater in the ortho-series than in the meta, and less again in the para.

At any rate, our experiments seem to show conclusively that there must be some difference of structure beyond the mere orientation between ortho-nitrophenol and its meta- and para-isomerides.

II. Solubility in Organic Solvents.

We hoped to be able to find some non-associated organic solvent with which the nitrophenols would form two liquid layers; but we were unable to do so. We have, however, measured the solubilities of the solid substances in toluene, and with less accuracy in bromobenzene and ethylene dibromide. The results with toluene are given in table III, and plotted in Fig. 4.

TABLE III.

Nitrophenols and Toluene.

Ortho-.		Meta-.		Para-.	
P.	Temp.	P.	Temp.	P.	Temp.
27.01	— 0.6	4.63	39.6	5.60	62.4
35.73	+ 6.9	6.00	45.8	6.54	66.3
43.06	12.5	7.03	48.9	9.99	72.2
52.77	18.5	9.11	54.0	14.22	77.1
59.15	22.3	11.28	58.0	22.41	82.6
66.84	26.1	16.44	64.8	26.4	84.5
74.53	30.0	20.26	67.7	34.67	87.7
81.98	33.7	33.16	71.5	44.45	90.0
85.88	35.8	46.93	74.5	49.96	91.0
90.48	38.5	57.71	75.7	61.50	93.8
93.21	40.1	70.50	78.5	68.69	95.8
95.43	41.6	79.57	82.3	79.80	100.2
97.87	43.3	91.43	88.8	89.98	105.4
100.00	44.9	100.00	95.1	100.00	113.8

It is evident that the whole position of these curves is dominated by the melting points of the pure compounds, and the anomalous behaviour of the ortho-compound does not appear at all. The inflexion of the curves, which is perceptible with the ortho-compound, and very marked with the other two, indicates an approach to the condition where two liquid layers are formed.

From the initial rate of fall of the melting point of the nitrophenol on adding toluene (determined graphically), we can calcu-

late the freezing-point constant, and also the heat of fusion of the nitrophenol. The values obtained are:

	Lowering of freezing point by 1 per cent. toluene.	Freezing point constant.	Heat of fusion.
Ortho-	0.82°	75	28
Meta-	0.85°	78	34
Para-.....	0.93°	86	34

Using these values, we can calculate from the depression of the freezing point by water the association factor of water in nitrophenol solution. We thus find:

Ortho :	association factor of water at 45°,	3.2
Meta :	„ „ „	95°, 1.21
Para :	„ „ „	114°, 1.22

The value in *o*-nitrophenol is very rough, owing to the sparing solubility of water in this substance; but it is natural that the association factor should be greater at the lower temperature.

The measurements of solubility in bromobenzene and ethylene dibromide were made with less accuracy; but the results are worth recording, if only to show the remarkably small difference in solubilities in these very different solvents. The values given in the following table are obtained by interpolation on the curves. The corresponding values in toluene are added for the sake of comparison.

TABLE IV.

Nitrophenols in Organic Solvents.

Temp.	<i>o</i> -Nitrophenol in			Temp.	<i>p</i> -Nitrophenol in		
	Toluene.	C ₆ H ₅ Br.	C ₂ H ₄ Br ₂ .		Toluene.	C ₆ H ₅ Br.	C ₂ H ₄ Br ₂ .
15°	46.9	—	40.0	70°	18.5	—	31.0
20	55.2	48.8	47.8	80	28.1	32.7	52.0
25	64.6	57.7	56.8	90	54.4	59.7	73.2
30	74.6	67.2	67.2	100	79.6	80.6	88.5
35	84.5	78.3	79.0	110	96.3	96.3	98.0
40	93.1	89.7	90.6				

The investigation is being extended to other similar substances, and the vapour pressures are also being measured.

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