CVIII.—*Influence of Position on the Solubility and Volatility of the Mono- and Di-nitrophenols.*

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THE mononitrophenols have been shown to be highly abnormal as regards their solubility in water, the ortho-compound being far less soluble than the other two. In the following paper, the solubilities of five of the six dinitrophenols in water and benzene are described, and also their volatility in steam, together with that of the mononitro-compounds and picric acid; and the interpretation of the results is discussed.

EXPERIMENTAL.

Preparation of Materials.

In indicating the structure of the isomerides, the hydroxyl group is always taken to occupy position 1.

o- and *p*-Nitrophenol.—Ordinary pure laboratory specimens were further purified by steam distillation and recrystallisation.

m-Nitrophenol.—This was made by the usual method of diazotising *m*-nitroaniline (Bantlin, *Ber.*, 1868, **11**, 2100; Holleman and Wilhelmy, *Rec. trav. chim.*, 1902, **21**, 432). Various efforts were made to diminish the bulk of the solution during the decomposition of the diazo-compound, while avoiding excessive resinification. The use of copper sulphate as a catalyst was found to be disadvantageous. The process finally adopted was as follows:

Fourteen grams of *m*-nitroaniline were dissolved in 200 c.c. of water containing 35 c.c. of concentrated sulphuric acid. The solution was filtered and cooled in ice, when the sulphate separated as a pink paste. The concentrated nitrite solution was added slowly with stirring, and the sulphate dissolved. The cold filtered

solution was then added very slowly to a boiling solution of 40 c.c. of concentrated sulphuric acid in 500—600 c.c. of water and the solution boiled until nitrogen ceased to be evolved and the liquid became clear. It was then allowed to cool somewhat, in order to permit the resin to settle, filtered, cooled, and extracted with ether. The crude product, after evaporation of the ether, was recrystallised from hydrochloric acid (yield 9—10 grams). In this way, the bulk of the liquid is reduced to about a quarter of that used by Holleman and Wilhelmy for the same weight of *m*-nitroaniline.

Dinitrophenols : 1 : 2 : 4- and 1 : 2 : 6-.—Prepared by nitration of *o*-nitrophenol, and purified and separated as described by Holleman and Wilhelmy (*loc. cit.*).

Melting points : 1 : 2 : 4-, 112.9°; 1 : 2 : 6-, 62.2°.

1 : 3 : 4-, 1 : 3 : 6-, and 1 : 3 : 2-.—These were all made by the nitration of *m*-nitrophenol, by the method described by Holleman and Wilhelmy, but this was modified in some respects.

The 1 : 3 : 6- is easily removed by making use of its relatively small solubility in cold alcohol; the other two can be separated by crystallisation from benzene. Holleman and Wilhelmy recommend that the benzene solution should be left overnight, but we find that in this case the 1 : 3 : 4- comes down contaminated with 1 : 3 : 2-, whereas if the benzene solution is rapidly cooled, and the crystals are filtered off at once, they are nearly pure. The method finally used was to dissolve the product from 20 grams of *m*-nitrophenol (after removing the 1 : 3 : 6- with alcohol, and drying) in 100 c.c. of benzene containing a little light petroleum (b. p. 60—80°). The solution was boiled for half an hour to let the resin collect, filtered, and cooled rapidly with stirring. The 1 : 3 : 4- (7 grams) which came out was filtered off at once, and the filtrate deposited during thirty-six hours 6 grams of 1 : 3 : 2-, mixed with some 1 : 3 : 4-. The 1 : 3 : 4- was recrystallised from benzene in the same way, and gave 4—5 grams of pure product, melting at 134.7°; while the 1 : 3 : 2-, after two recrystallisations from hot water (with rapid cooling and immediate filtration), gave 3 grams, melting at 145.1°.

The benzene had been freed from thiophen by treatment with sulphuric acid, and frozen out seven times.

Determination of Solubilities.

These were carried out in the usual manner, by enclosing weighed quantities of the components in tubes, which were then sealed and the temperature determined at which the liquid separated into two layers, or the last crystals disappeared. The thermometer

had been compared with a standard instrument, and the readings were corrected, when necessary, for the exposed stem.

FIG. 1.

Solubilities of nitrophenols and dinitrophenols in water.

The results are given in tables I and II, and plotted on Figs. 1 and 2. In Fig. 1 the solubilities of the three mononitrophenols in water are added (dotted lines) for comparison, the values being

taken from Sidgwick, Spurrell, and Davies (T., 1915, 107, 1202). The concentrations are expressed as grams of nitrophenol in 100 grams of solution. An asterisk indicates that the solid phase was present.

TABLE I.
Solubilities of Dinitrophenols in Water.

1 : 2 : 3-		1 : 2 : 4-		1 : 2 : 5-		1 : 2 : 6-		1 : 3 : 4-	
Sol ^y .	Temp.	Sol ^y .	Temp.	Sol ^y .	Temp.	Sol ^y .	Temp.	Sol ^y .	Temp.
100·0	145·1°*	100·0	112·9°*	100·0	105·6°*	100·0	62·2°*	100·0	134·7°*
89·85	112·3°*	99·02	108·1°*	98·48	100·0°*	99·11	59·5°*	89·48	84·5°*
74·32	96·0°*	"	100·5	97·50	98·0°*	98·42	84·5	74·91	53·0°*
60·44	116·7	98·24	117·6	"	92·4	97·80	102·6	"	48·0
52·15	120·4	97·70	121·7	96·72	113·5	95·96	138·3	70·23	73·8
35·13	122·2	97·14	131·2	94·51	146·4	93·44	158·0	55·40	101·6
20·83	120·1	93·35	156·0	91·73	172·2	—	—	36·65	105·2
10·90	108·2	86·36	187·7	—	—	12·26	192·5	23·28	104·6
6·74	94·5	—	—	12·24	194·5	3·97	147·9	12·79	97·5
		12·98	182·5	5·69	162·1	3·24	139·7	6·05	82·0
		8·99	170·5	3·91	146·4	1·87	117·6		
		3·81	137·7	2·97	135·8	1·00	89·5		
		2·98	126·1	2·33	124·7	0·703	71·1		
		1·95	109·6						
Crit. sol. temp.	122·5°	> 200°		> 200°		> 200°		105·2°	
Triple pt.	95·0	104·2		97·5		59·2		52·5°	

TABLE II.
Solubilities in Benzene (Solid phase always present).

1 : 2 : 3-		1 : 2 : 4-		1 : 2 : 5-		1 : 2 : 6-		1 : 3 : 4-	
Sol ^y .	Temp.	Sol ^y .	Temp.	Sol ^y .	Temp.	Sol ^y .	Temp.	Sol ^y .	Temp.
100·0	145·1°	100·0	112·9°	100·0	105·6°	100·0	62·2°	100·0	134·7°
91·57	134·9	93·61	105·6	92·90	98·5	92·85	55·0	86·64	122·6
69·05	118·6	86·59	99·5	82·44	88·6	86·87	50·0	73·10	116·1
38·66	102·5	79·00	93·9	72·97	82·4	78·52	44·5	60·49	113·0
25·30	93·8	69·52	87·2	54·78	71·4	60·17	34·0	56·86	112·1
12·77	78·7	62·77	83·7	48·91	67·9	43·36	25·5	41·65	109·1
		52·36	77·1	33·81	57·0			27·27	106·5
		34·60	65·0	24·22	48·5			6·54	89·2
		21·01	51·0	13·96	33·5				

Measurement of the Heat of Fusion from the Freezing-point Constant.

These constants were determined in the usual Beckmann apparatus in a glycerine bath; benzil, *p*-dibromobenzene, and anthraquinone were used as solutes. Owing to the difficulty of inducing crystallisation in the nitrophenols, it was found necessary to cool until a considerable amount of solid had separated, and then to raise the temperature slowly until only a trace of crystals remained.

The 1 : 2 : 3-dinitrophenol, when fused, slowly darkened, and its

melting point fell continuously, so that no results could be obtained.

The results are tabulated below, E being the cryoscopic constant, and Q the heat of fusion in kgr.-cals. per gram-molecule.

Dinitro-phenol.	Solute.	Per cent. Solute.	Depr ⁿ .	E .	
1 : 2 : 4-	Benzil	0.255	0.120°	98.7	Mean E : 94.9
		1.523	0.662	91.0	$Q = 5.73$
1 : 2 : 5-	Dibromobenzene	0.667	0.230	81.4	Mean E : 83.2
		1.610	0.580	85.0	$Q = 6.29$
1 : 2 : 6-	,,	0.639	0.255	94.1	Mean E : 93.1
		0.769	0.300	92.1	$Q = 4.41$
1 : 3 : 4-	Anthraquinone	1.296	0.655	105.2	Mean E : 100.4
		1.416	0.650	95.5	$Q = 6.05$

Volatility in Steam.

These measurements were carried out in the apparatus and under the conditions already described by one of us (Sidgwick, T., 1920, **117**, 389). The distillate was analysed by the method of Knecht and Hibbert (*Ber.*, 1903, **36**, 1549), by reduction with titanous chloride,* the excess of which was estimated with iron alum, using potassium thiocyanate as indicator. The method was tested with solutions of nitrophenols of known strength, and found to give satisfactory results, the error not exceeding one or two per cent.

The composition of the distillate was found to become constant after about an hour's distillation : thus, with 1 : 2 : 3-dinitrophenol, four successive portions of distillate required respectively 20.48, 20.36, 20.48, and 20.17 c.c. of titanous chloride solution per 100 c.c.

The volatility was measured not only of the dinitrophenols but also of the mononitro-compounds and of picric acid. The compounds all liquefied under water at 100° except 1 : 2 : 4-dinitrophenol and picric acid. *m*- and *p*-Nitrophenol are completely miscible with water at 100°; with these compounds the percentage composition of the liquid in the distilling flask was determined, and is given in brackets in the column headed "solubility" in the table below. In this table the first column gives the elevation of the boiling point of the liquid; the second the weight per cent. of nitrophenol in the distillate; the third the pressure of nitrophenol in the vapour (in hundredths of a mm.); the fourth the solubility in water at 100°; the fifth the partition coefficient (concentration in vapour divided by concentration in liquid). The sixth and seventh give

* *p*-Nitrophenol is remarkable for the extreme slowness with which it is reduced by titanous chloride.

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the relative values of the vapour pressure and the partition coefficient, those for *p*-nitrophenol being taken as unity.

Substance.	<i>dt.</i>	Wt. per cent. in dist.	V.p. in mm. $\times 100$.	Solv.	Parti- tion.	Relative v.p.	Relative Part ⁿ .
Nitrophenol <i>o</i> -	—	2.79	283.0	1.08	1570	160	6280
<i>m</i> -	0.25°	0.0596	5.87	(47.7)	0.733	3.32	3.07
<i>p</i> -	0.24	0.0180	1.77	(42.3)	0.250	1	1
Dinitro-phenol							
1 : 2 : 3-	0.12	0.0736	5.48	7.8	5.6	3.10	22
1 : 2 : 4.*	—	0.306	22.8	1.5	120	12.9	480
1 : 2 : 5-	0.06	0.599	44.8	1.4	250	25.3	1010
1 : 2 : 6-	—	0.147	11.0	1.3	67	6.20	270
1 : 3 : 4-	0.34	0.00139	0.103	15	0.054	0.0582	0.218
Picric acid *	0.40	0.00417	0.249	6.33	0.388	0.441	1.55

* Solid under water at 100°.

Corrected Vapour Pressures for Pure Liquids.

From these values we can calculate the vapour pressures of the pure liquids by the methods described in the preceding paper, the ratio of the vapour pressures of liquid and solid being given by the equation

$$2.3026 \log \frac{p}{p_1} = \frac{1000W}{R} \times \left(\frac{1}{T} - \frac{1}{T_0} \right).$$

When the substance is solid during the distillation, the value of this ratio at 100° is taken as the correction factor; when it is liquid, the value at the triple point. The heats of fusion employed are the following: for *o*-nitrophenol, 4.295 (Bogojawlenski, *Chem. Centr.*, 1905, II, 945; *Schriften d. Dorpater Naturfor. Ges.*, 1904, **13**, 1); the value of 3.72 given by Brunner (*Ber.*, 1894, **27**, 2102) is undoubtedly too low; for *m*- and *p*-nitrophenol, the values obtained by extrapolation from the heats of solution (see below) in toluene (Sidgwick, Spurrell, and Davies, *loc. cit.*) and in trichloroacetic acid (Kendall, *J. Amer. Chem. Soc.*, 1916, **38**, 1309), which agree well with one another; for 1 : 2 : 3-dinitrophenol, the extrapolated value from the heats of solution in benzene; for the other four dinitrophenols, those obtained from the cryoscopic experiments already described. These values are given in Table III (p. 1010). For picric acid there are no satisfactory data; but since the heat of fusion of *o*-nitrophenol is 4.30, of 1 : 2 : 4-dinitrophenol 5.73, and of the 1 : 2 : 6-isomeride 4.71, we may probably assume without serious error (as the correction is only small) that the heat of fusion of picric acid is 5; and the correction has been calculated on this basis. A difficulty arises with *m*- and *p*-nitrophenol from the fact that they are miscible with water in all

proportions at 100°, so that the solutions distilled were necessarily unsaturated, and their vapour pressure correspondingly lowered. It is impossible to make any definite allowance for this; but owing to the flatness of the vapour-pressure curves in the neighbourhood of the two-liquid area (which is in both cases within 10° of the

point of observation), the error is not likely to be large. The corrected values of the vapour pressures are given in the table on p. 1009.

Discussion of Results.

Solubilities in Water.

The curves (Fig. 1) show a marked similarity to those of the mononitrophenols, which are given in dotted lines on the diagram.

The behaviour of *o*-nitrophenol is closely followed by that of the 1:2:4-, 1:2:5-, and 1:2:6-dinitro-compounds. In all these the solubilities are very small, and the critical solution temperature is somewhere above 200°. On the other hand, the *m*- and *p*-nitrophenol curves resemble that of the 1:3:4-dinitrophenol, the only isomeride examined in which no ortho-position is occupied. That

FIG. 3.

Nominal heats of solution of mono- and di-nitrophenols in benzene.

Nitrophenols :

Ortho -- ○ --

Meta -- + --

Para -- × --

Dinitrophenols :

1:2:3 — △ —

1:2:4 — + —

1:2:5 — ⊕ —

1:2:6 — ○ —

1:3:4 — × —

is, the influence of the ortho-nitro-group in diminishing the solubility prevails, and to nearly the same extent, whether the second nitro-group is in positions 4, 5, or 6; whereas if there is no ortho-nitro-group, the solubility is much greater. A remarkable anomaly is offered by the 1:2:3-compound. Although the ortho-meta-derivative which has the two nitro-groups on opposite sides of the ring (1:2:5) is scarcely more soluble than the di-ortho- or the

ortho-para-, the other ortho-meta-derivative (1 : 2 : 3), in which they are on the same side, is nearly as soluble in water as the meta-para-isomeride. This anomaly is repeated in the volatility and in the heat of solution in benzene. The peculiarity is so far unexplained. We do not even know whether it depends on the chemical nature of the adjacent group, or merely on its steric effect. This can only be determined by examining such compounds as the nitrocresols. It is to be noticed that the hydroxytoluic acid ($\text{CO}_2\text{H} : \text{OH} : \text{CH}_3 = 1 : 2 : 3$) (see preceding paper) shows no corresponding anomaly; it in no way differs from the other isomerides in which the carboxyl and hydroxyl groups are next to one another.

Nominal Heats of Solution.

The nominal heats of solution in benzene have been calculated by the methods described in the preceding paper. The values for the mononitrophenols have been added, from the solubility data of Bogojawlenski, Boguljubow and Winogradow (*Chem. Centr.*, 1907, I, 1738; *Schriften d. Dorpater Naturfor. Ges.*, 1907, 15, 216). The results are given in Table III and Fig. 3, the heats being expressed in kgr.-cals. per gram-mol. The general results for all these compounds are briefly summarised in the following table, which gives the vapour pressure at 100° (observed and corrected), the critical solution temperatures in water, and the increase of the heat of solution in benzene.

Compound.	Nitrophenols.			Dinitrophenols.					Picric Acid.
	Ortho.	Meta.	Para.	1 : 2 : 3.	1 : 2 : 4.	1 : 2 : 5.	1 : 2 : 6.	1 : 3 : 4.	
Vap. press. at 100° in mm. × 100 ...	Obs. 283 Corr. 292	5·87 19·6	1·77 8·28	5·48 12·8	22·8 29·4	44·8 50·6	11·0 11·7	0·103 0·664	0·249 0·364
Crit. sol. temp. in water	v. high	98·7°	92·8°	122·5°	v. high	v. high	v. high	105·2°	
Increase of <i>Q</i> in benzene	2·2	18·7	26·4	12·1	4·9	4·0	5·1	46·4	

It will be seen that in each group the three properties—a high vapour pressure, a small solubility (high critical solution temperature) in water, and a large solubility (small rise in *Q*) in benzene—go together. *o*-Nitrophenol and, with one marked exception, all the dinitrophenols which have at least one ortho-position occupied have these characteristics, and the occupation of a second ortho-position does not greatly increase them, whilst those compounds (*m*- and *p*-nitrophenol, and 1 : 3 : 4-dinitrophenol) in which neither ortho-position is occupied have low vapour pressures, are much more soluble in water, and show a much larger increase of the heat of solution in benzene. The one exception, the anomalous 1 : 2 : 3-dinitrophenol, is intermediate in all these properties between these two groups.

TABLE III.

Nominal Heats of Solution in Benzene (Molecular, in kgr.-cals.).

Mean mol. per cent.	Mononitrophenols.			
	Ortho-.	Meta-.	Para-.	
95	4.56	7.82	5.73	
85	5.17	8.86	6.70	
75	5.44	9.85	8.82	
65	6.09	12.20	10.20	
55	6.29	14.63	14.69	
45	6.30	18.62	22.45	
35	6.75	21.60	26.46	
25	5.68	26.54	32.10	
17.5	—	22.92	25.58	
12.5	—	16.62	18.62	
7.5	—	12.90	15.81	
Mol. heat of fusion	4.295	5.20	5.05	

Mean mol. per cent.	Dinitrophenols.				
	1 : 2 : 3-.	1 : 2 : 4-.	1 : 2 : 5-.	1 : 2 : 6-.	1 : 3 : 4-.
95	6.19	6.09	6.36	5.08	7.54
85	7.90	6.88	6.91	5.64	9.24
75	—	7.66	7.47	6.22	10.26
65	10.09	8.73	8.41	7.40	12.52
55	11.40	9.64	8.76	8.04	18.44
45	12.59	10.23	9.66	8.58	33.42
35	14.18	10.98	10.39	9.54	37.04
27.5	—	—	—	10.00	—
25	16.56	10.82	10.39	—	53.94
17.5	18.33	10.54	10.42	—	43.71
12.5	16.78	8.77	9.59	—	30.33
Mol. heat of fusion	5.20	5.70	6.29	4.41	6.05

The solubilities of mononitrophenols have been measured in various other solvents : in aniline, urea, and picric acid (Kremann and Rodinis, *Sitzungsber. K. Akad. Wien*, 1905, **117**, 1237), in naphthalene (Kremann, *ibid.*, 1904, **116**, 865), in toluene, bromobenzene, and ethylene dibromide (Sidgwick, Spurrell, and Davies, *loc. cit.*), and in trichloroacetic acid (Kendall, *J. Amer. Chem. Soc.*, 1916, **38**, 1309); in some of these solvents the meta-compound was not examined. The solubility of 1 : 2 : 4-dinitrophenol has been measured by Kremann in aniline (*Sitzungsber. K. Akad. Wien*, 1906, **118**, 427) and in naphthalene (*ibid.*, 1904, **116**, 865), and by Kremann and Hofmeier in phenanthrene (*ibid.*, 1910, **122**, 121). We have calculated the heats of solution in all solvents in which the curve could be carried far enough. The increase in the heat is :

Solvent.	Toluene.	Naphth- alene.	Bromo- benzene.	Ethylene dibromide.	Trichloro- acetic acid.	Aniline.	Phenan- threne.
Ortho-	2.9	(0.8)	1.4	(1.0)	0.2	0.4	—
Meta-	39.4	—	—	—	0.1	—3.0	—
Para-	32.1	8.6	20.3	11.6	0.0	—2.4	—
1 : 2 : 4-	—	(0.2)	—	—	—	—1.9	—1.3

(Where the values are in brackets, the solubilities do not extend beyond 75 molecules per cent.).

Toluene, bromobenzene, and ethylene dibromide are very similar to benzene in their solvent action. Trichloroacetic acid is remarkable for the extraordinary constancy of the heat values, which are practically unaffected by concentration with any of the three isomerides. In aniline, *o*-nitrophenol gives constant values, whilst those of the *m*- and *p*-nitrophenols fall rapidly, the solubility being abnormally high. This is no doubt connected with the fact that these two form stable compounds with aniline, which the ortho-derivative does not. A similar fall in the *Q* values occurs with 1 : 2 : 4-dinitrophenol in phenanthrene, where again a compound is formed. An analogous fall, which may be due to the same cause, was observed in the heat of solution of the hydroxybenzoic acids in ethyl and butyl alcohols.

It is known that the chlorophenols show differences in vapour pressure (as indicated by the boiling points) comparable with those of the nitrophenols. In order to discover whether this abnormality extended to the solubility in water, some measurements were made with *o*- and *p*-chlorophenol in water. It was found that their critical solution temperatures differ widely (although not so much as those of the nitrophenols), and in the usual direction. The values are :

Position.	Ortho-.	Meta-.	Para-.
Boiling point	175°	214°	217°
Crit. sol. temp. in water	186°	—	125°

This is exactly parallel to the behaviour of the nitrophenols; the ortho-compound has by far the lowest vapour pressure, the para- the highest, and the meta- comes very near the para-; and the ortho- is much less soluble in water than the para-. This is of some interest, since it has been shown that the introduction of a chlorine atom into benzoic acid does not lead to any serious abnormality of behaviour.

In view of the possible suggestion that these abnormalities are due to association, the experiments of Hewitt and Winnill on the surface tensions of the substituted phenols (T., 1907, 91, 441) are of interest. They calculated from their results the following values of the association factor; the figures in brackets after each value give the temperature range over which the measurements were taken :

	Ortho-.	Meta-.	Para-.
Cresols.....	1.12 (40-67°)	1.48 (19-57°)	1.62 (46-74°)
	1.06 (67-100°)	1.33 (57-100°)	1.26 (74-100°)
Nitrophenols	0.84 (53-79°)	1.48 (116-147°)	1.25 (130-163°)
Chlorophenols ...	1.0 (13-45°)	1.49 (33-79°)	1.22 (52-72°)
	1.0 (45-73°)	1.11 (78-139°)	1.08 (72-100°)

It will be seen that the cresols, which in our sense are quite normal give as much indication of association in the meta- and

para-compounds as the nitrophenols, and much more than the chlorophenols; and the degree of association (which practically never reaches 50 per cent.) seems quite insufficient to account for the enormous difference in solubility and vapour pressure.

There is an obvious connexion between our results and those of Auwers (*Zeitsch. physikal. Chem.*, 1893, **12**, 689; 1895, **18**, 599; 1897, **23**, 449; 1899, **30**, 300; Auwers and Orton, *ibid.*, 1896, **21**, 337) on the depression of the freezing point of solvents such as benzene or naphthalene by isomeric aromatic derivatives. Speaking generally, Auwers finds that among what we have called abnormal groups the ortho-compound gives a normal lowering of the freezing point, whilst with the meta- and para- the lowering is less than we should expect. This is commonly expressed by saying that the molecular weights (calculated on the usual formula) for the ortho-compounds are normal, while the isomerides are associated. We might, however, equally well say that if we assume the molecular weights of the solute in the latter case to be normal, the calculated heats of solution of the solvent are abnormally high. So in our experiments, when on our assumption of normal molecular weights the heats of solution are high, we might have taken the heats to be normal, in which case the molecular weight of the benzene would have been calculated to be very high. The two results are really parts of the same phenomenon. The lowering of the freezing point is a measure of the fall of the partial pressure of the component which freezes out. In such a system as, say, benzene and *p*-nitrophenol, our results show that the vapour pressure of the nitrophenol is less lowered by the addition of benzene than the mixture law requires. Auwer's results show that this is true also of the effect of the solute on the vapour pressure of the benzene. Both results are necessary in a system which is near the temperature at which it separates into two layers. In such cases the isothermal vapour-pressure curve has the same general form for each component: starting from the pure component, it falls less rapidly than we should expect, becomes nearly flat (horizontal if separation occurs) towards the centre of the diagram, and then falls very steeply towards the end. The relation is symmetrical with respect to the two components, and cannot be taken by itself as evidence that the nitrophenol is associated, any more than that the benzene is associated. What it does show is that the two liquids are not far removed from the temperature of imperfect miscibility.

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