CCCXXVI.—*The Solubility of the Phenylenediamines and of their Monoacetyl Derivatives.*

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The boiling points of the phenylenediamines (ortho 252°, meta 287°, para 267°) not only differ widely, but are in an unusual order, the para-compound coming between the other two, and much nearer to the ortho. This peculiarity, which is found also among other amino-derivatives, but nowhere else (Sidgwick, T., 1920, **117**, 395), led us to measure the solubility of these substances, and of their acetyl derivatives, in water and benzene.

Preparation of Materials.

o-*Phenylenediamine.* Made by the reduction of *o*-nitroaniline with cast-iron turnings and 2 per cent. calcium chloride solution, a method suggested to us by Prof. T. S. Moore, to whom we wish to express our thanks. The hydrochloride was recrystallised from water, and the free base twice recrystallised from chloroform in the absence of air; m. p. 103·8°. The meta-diamine was twice recrystallised from alcohol; m. p. 62·8°. The para-diamine was made by the reduction of *p*-nitroaniline or better of *p*-nitroacetanilide with iron and calcium chloride. The hydrochloride was recrystallised from water, and the free base twice from alcohol; m. p. 139·7°.

Monoacetyl-diamines. Ortho: twice recrystallised from water; m. p. 144·8°. Meta: made by the action of acetic acid on the

diamine (Wallach and Schulze, *Ber.*, 1882, **15**, 3020); twice recrystallised from water; m. p. 279°. Para: by the reduction of *p*-nitroacetanilide with iron and acetic acid (Nietzki, *Ber.*, 1884, **17**, 343) or calcium chloride (Moore). The brown product was boiled with animal charcoal and twice recrystallised from water. Colourless; m. p. 160·5°.

FIG. 1.

Solubility of the phenylenediamines.
Full lines: in water.
Dotted lines: in benzene.

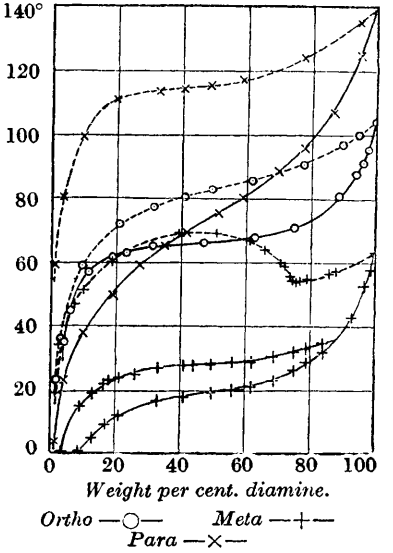
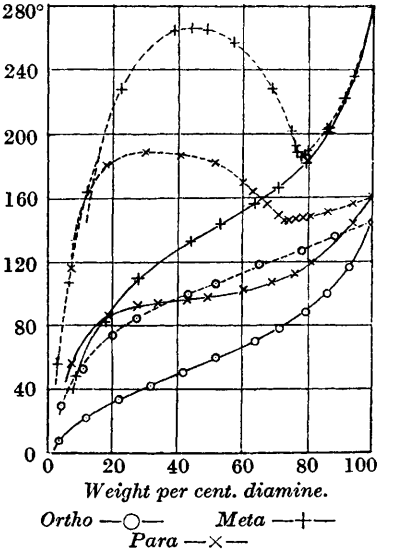


FIG. 2.

Solubility of the monoacetylphenylenediamines.
Full lines: in water.
Dotted lines: in benzene.



Determination of Solubility.

This was measured synthetically in corked or sealed bulbs, the point being observed at which the liquid became cloudy on cooling, or, when the solid phase was present, at which the last crystals disappeared on slow warming.

m-Phenylenediamine was found to be dimorphic. The two forms are enantiotropic, with a transition point at 36°; this was determined from the solubility curves, and also by special experiments with a dilatometer. The α-form (stable above 36°) consists of brown needles, the β- (stable below 36°) of mauve plates. The colour is no doubt due to traces of decomposition products, but the difference is easily recognised. The α-form appears to be the usual one at the ordinary temperature; the first point obtained

TABLE I.

Solubility of the Phenylenediamines in Water and Benzene.

Solubility in water.

Ortho.		Meta.			Para.	
Weight per cent.	Temp.	Weight per cent.	Temp. β-Form.	Temp. α-Form.	Weight per cent.	Temp.
		3·27	0·3°	—	1·08	3·6°
4·05	35·1°	8·71	—	0·3°	3·70	23·7
5·85	45·8	9·22	14·3	—	9·85	37·8
11·86	56·3	12·64	18·3	4·6	18·75	49·9
18·72	61·3	17·16	22·0	9·3	27·22	59·2
23·43	62·8	19·05	23·1	—	34·43	64·6
31·55	64·2	21·21	24·1	11·7	41·75	69·2
46·81	66·1	26·17	25·1	—	51·80	75·5
62·53	67·7	32·83	26·3	16·1	59·02	80·3
74·74	71·3	40·62	27·1	17·3	70·03	88·5
88·36	80·8	43·77	27·1	—	78·10	95·9
93·83	88·1	49·83	27·9	18·7	86·63	107·0
96·15	91·7	56·51	29·0	19·9	95·04	125·1
97·72	95·5	61·94	29·1	20·8	100·0	139·7
100·0	103·8	69·63	30·2	22·7		
		75·52	31·5	26·0		
		79·15	32·8	28·7		
		83·83	34·4	32·6		
		92·32	—	43·5		
		96·81	—	53·6		
		98·40	—	57·6		
		100·0	—	62·8		

Transition point 36°.

Solubility in benzene.

Ortho.		Meta.		Para.	
Weight per cent.	Temp.	Weight per cent.	Temp.	Weight per cent.	Temp.
1·72	22·2°	1·02	19·0°	1·20	59·1°
3·13	36·0	2·84	34·1	3·25	79·9
9·35	58·4	7·43	46·8	9·67	98·5
21·06	72·1	9·75	50·7	20·14	110·6
31·43	76·9	19·36	59·8 L	33·32	112·9
40·95	80·0	39·04	69·0 L	41·04	113·9
49·47	82·5	50·91	68·8 L	49·10	115·2
62·05	85·6	61·60	66·5 L	59·12	117·1
77·94	91·1	65·91	64·2 L	77·86	124·0
90·04	96·8	71·04	60·0 L	94·75	135·5
95·12	100·1	72·14	58·8 L	100·0	139·7
100·0	103·8	74·56	55·5 L		
		74·84	54·7 L		
		75·33	53·9		
		76·84	54·1		
		78·57	54·2		
		79·31	54·7		
		85·85	56·3		
		88·64	57·2		
		100·0	62·8		

Crit. soln. temp. 69·0°.

Triple point.

75·0 53·8°

TABLE II.

Solubility of Monoacetylphenylenediamines.

Solubility in water.

Ortho.		Meta.		Para.	
Weight per cent.	Temp.	Weight per cent.	Temp.	Weight per cent.	Temp.
3·40	7·2°	9·05	48·7°	6·50	56·8°
12·05	22·0	18·12	82·9	18·63	86·3
22·32	33·5	28·20	110·1	27·63	92·1
31·95	42·1	44·13	132·9	34·27	93·7
41·64	50·4	53·34	144·2	42·82	96·5
51·73	59·1	63·56	156·3	49·10	98·6
64·10	69·9	71·10	167·0	60·15	103·2
71·72	78·2	79·34	181·9	69·35	107·1
79·22	88·1	86·73	204·4	76·50	112·6
85·80	99·0	94·15	235·8	81·74	119·2
93·23	115·4	100·0	279·0	94·13	144·0
100·0	144·8			100·0	160·5

Solubility in benzene.

Ortho.		Meta.		Para.	
Weight per cent.	Temp.	Weight per cent.	Temp.	Weight per cent.	Temp.
4·13	29·9°	3·13	56·5°	7·15	116·2°
11·21	53·6	6·72	107·1	17·36	180·8 L
20·24	73·5	12·24	163·2	30·12	187·8 L
27·36	84·2	22·75	228·5 L	41·23	186·3 L
35·27	92·4	39·10	263·4 L	51·70	181·3 L
43·04	99·8	44·31	265·5 L	59·95	170·0 L
51·50	106·7	49·23	265·1 L	63·07	163·5 L
65·12	117·8	57·03	257·6 L	67·66	155·9 L
77·76	127·5	68·90	227·8 L	71·05	150·1 L
88·05	135·2	74·65	201·9 L	72·71	147·1 L
100·0	144·8	76·17	193·4 L	73·90	146·8 L
		76·86	188·4 L	74·62	147·3
		77·55	185·4	75·42	147·7
		78·61	187·1	76·85	148·2
		80·12	190·0	78·41	148·7
		85·50	203·1	80·70	149·8
		91·06	221·9	86·14	152·0
		100·0	279·0	93·82	156·8
				100·0	160·5
		Crit. sol. temp. 266°.		Crit. sol. temp. 188°.	
		Triple point.		Triple point.	
		77·5	184·9°	74·0	146·8°

with a tube lay always on the α-curve; but if the tube was frozen with ice and salt, and the solubility redetermined, it gave a point on the β- (stable) curve.

Measurements with the *o*- and *p*-diamines at temperatures above 80° were difficult on account of the darkening of the liquid, which was not wholly prevented by filling the tubes with hydrogen. No such difficulty occurred with the acetyl derivatives, for which very

high temperatures could be reached by the use of specially thick sealed bulbs, the observer being protected by a plate-glass screen.

The results are given in Tables I and II, and plotted on Figs. 1 and 2, the concentrations being expressed in grams of amine to 100 grams of solution. Two-liquid points are marked L, and metastable points with an asterisk.

The nominal heats of solution, given in Table III, are calculated by means of the usual formula $Q = \log_e \frac{S}{S^1} \cdot \frac{RT_1T}{T - T_1}$. Since none of these compounds forms two liquid layers with water, the heats of solution were calculated for the water curves as well as for those in benzene. The values obtained for water are not comparable with those in benzene, on account of the uncertainty as to the molecular weight of the water, which was assumed to be 18, but is no doubt larger than this, and is affected both by the concentration and by the temperature. But they are comparable with one another, and enable us to form an approximate idea of the relative miscibility of the different isomerides with water. The values in benzene have also been calculated for those substances which do not form two liquid layers with this solvent; when this occurs, the nominal heat of course becomes infinite.

TABLE III.

Nominal Heats of Solution in Water (in kgr.-cals.).

Mean mols. per cent.	Diamines.				Acetyl-diamines.		
	Ortho.	Meta (α).	Meta (β).	Para.	Ortho.	Meta.	Para.
95	3·64	2·55	—	5·85	5·13	6·96	7·79
85	6·28	4·17	—	6·35	5·04	6·92	8·23
75	8·69	4·52	—	5·22	4·23	7·22	9·38
65	9·82	7·45	—	6·66	5·01	6·95	9·57
55	7·51	5·79	—	6·50	5·88	6·33	9·88
45	10·69	8·23	14·0	8·85	6·12	6·86	9·10
35	33·8	10·3	26·6	8·01	6·30	6·36	8·91
25	31·3	17·5	36·9	10·4	8·29	6·52	10·4
15	92·8	22·8	36·5	11·1	5·39	6·24	12·6
7·5	52·2	28·5	60·8	11·0	9·48	6·02	30·1

Nominal Heats of Solution in Benzene.

Mean mols. per cent.	Diamines.			Acetyl-diamine.
	Ortho.	Meta.	Para.	Ortho.
95	5·63	5·83	5·08	7·52
85	6·93	8·50	7·93	8·56
75	10·1	14·3	9·61	9·10
65	12·1	Inf.	12·6	7·90
55	17·2		18·5	8·75
45	22·4		30·5	8·29
35	23·0		61·4	9·64
25	22·4		85·5	8·87
15	10·3		20·3	6·44
7·5	—		18·1	7·57

Discussion of Results.

The results show that these substances are not only abnormal, but have marked peculiarities of their own. Their behaviour in benzene can be compared by means of the critical solution temperatures, which can be observed directly for three of the compounds (*m*-diamine, *m*- and *p*-acetyldiamine) and for the other three can be calculated approximately by the rule of Flaschner and Rankin (*Sitzungsber. K. Akad. Wiss. Wien*, 1909, **118**, IIb, 695). This rule states that the slope of the S–L solubility curve (increase in weight per cent. solute for 1° rise of temperature) at 40 per cent. solute, multiplied by the difference in degrees between the S–L and the L–L curves at this concentration, is equal to a constant, the value of which for benzene was found (Sidgwick and Ewbank, T., 1921, **119**, 991) to be 190. In water, the increase of Q, the nominal heat of solution, affords a method of comparison. The values so obtained are as follows (calculated critical solution temperatures are enclosed in brackets):

Diamines.

	Ortho.	Meta.	Para.
Crit. sol. temp. in benzene	(18°)	69°	(91°)
Increase of Q in water	89·1	α 25·9 β 58·2	5·2
Boiling point (760 mm.)	252°	287°	267°

Acetyl-diamines.

	Ortho.	Meta.	Para.
Crit. sol. temp. in benzene	(−20°)	266°	188°
Increase of Q in water	5·7	0	22·3

The usual behaviour of abnormal isomerides is that in benzene the ortho is the most miscible (lowest crit. sol. temp. and smallest increase in Q) and the para the least miscible, the meta coming near the para: and that in water these relations are reversed. The peculiarities of these amino-compounds are of two kinds, (1) the exceptional position of the meta-series and (2) the anomalous behaviour of the acetyl compounds in water. Disregarding the latter for the moment, the relation of ortho to para is what we should expect; the ortho-series is the more volatile, the more soluble in benzene, and the less soluble in water. The meta-diamine is exceptional in that its solubility in benzene and in water comes nearer to that of the ortho than is usual; its volatility also, instead of being greater than that of the para, is less. The meta-acetyl-diamine is less soluble in benzene than the para, whereas we should expect it to be more so. The behaviour of the acetyl derivatives in water

is wholly anomalous; instead of getting the order of solubilities $o \ll m < p$, we get $p \ll o < m$.

The fact that the para-diamine is more volatile than the meta is to be noticed. It has already been pointed out (Sidgwick, *loc. cit.*) that this behaviour is confined to compounds in which at least one substituent is an amino- or substituted amino-group, the only observed cases being those in which the substituents are CH_3, $N(CH_3)_2$; CH_3, $N(C_2H_5)_2$; CH_3O, NH_2; Cl, $N(CH_3)_2$; $N(CH_3)_2$, $N(CH_3)_2$; and NH_2 with NH_2, $NH{\cdot}CH_3$, $NH{\cdot}C_2H_5$, $N(CH_3)_2$, and $N(C_2H_5)_2$.

The phenylenediamines are the most basic compounds which have had their solubilities examined from this point of view, and this may well be the cause of some of their peculiarities. The remarkable behaviour of the diamines and their acetyl derivatives in water is no doubt connected with the power of the amino-groups to form stable hydrates. This would not, however, explain their behaviour in benzene, or their anomalous volatility, which seem to point to association in the pure liquid.

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