CCCXXVIII.—*Equilibrium in the Binary Systems Cresols–Amines.*

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In this paper equilibrium diagrams are described which were obtained from thermal analysis of mixtures of *o*-, *m*-, or *p*-cresol, on the one hand, and dimethylaniline, *p*-toluidine, quinoline, piperidine, 1 : 5-naphthylenediamine, or carbamide, on the other. For every mixture the following data were determined : (1) the temperature of

complete melting of the crystallised mixture; (2) the complete cooling curve; (3) the duration of the eutectic crystallisation.

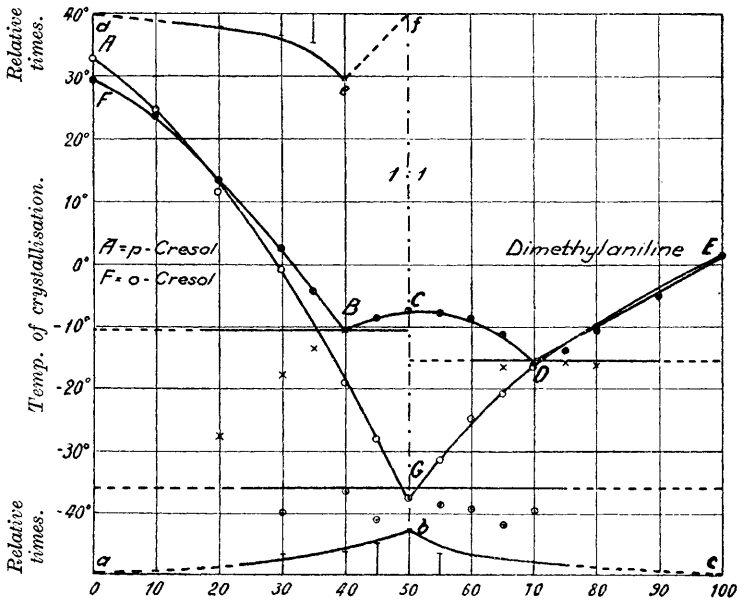
In the tables the temperature I is that of primary crystallisation, and II that of the eutectic (or final) crystallisation. The temperature III, when given, refers to complete melting of the mixture, and IV (for *o*-cresol and carbamide only) is the transition temperature.

TABLE I.

o-Cresol–Dimethylaniline (Fig. 1).

$C_6H_5{\cdot}NMe_2$, mols. %.	Temp. I.	Temp. II.	$C_6H_5{\cdot}NMe_2$, mols. %	Temp. I.	Temp. II.
0	29·5°	—	55	− 7·7°	—
10	23·8	—	60	− 8·5	—
20	13·5	−27·6°	65	−11·2	−16·2°
30	2·5	−17·7	70	—	−15·6
35	− 4·1	−13·5	75	−13·7	−16
40	—	−10·5	80	−10·7	−16·2
45	− 8·6	—	90	− 5	—
50	− 7·4	—	100	+ 1·6	—

FIG. 1.



Mols. % of dimethylaniline in { o-*cresol* + *dimethylaniline* · · · *and* × × × / p-*cresol* + *dimethylaniline* ○ ○ ○ *and* ⊙ ⊙ ⊙

o-*Cresol–Dimethylaniline.*—The diagram is composed of three parts and is characterised by two eutectic points with one open maximum at 50 mol.% of each component, showing the formation of

a definite *compound* of equimolecular composition, m. p. −6°. The two eutectics *B* and *D* correspond to 40 mols.% (at −9°) and 70 mols.% (at −14°) of dimethylaniline respectively. The triangle *def* shows the relative duration of crystallisation at and near the first eutectic point.

TABLE II.

p-Cresol–Dimethylaniline (Fig. 1).

$C_6H_5{\cdot}NMe_2$, mols. %.	Temp. I.	Temp. II.	$C_6H_5{\cdot}NMe_2$, mols.%	Temp. I.	Temp. II.
0	33°	—	55	−31·3°	−38·4°
10	24·6	—	60	−24·8	−39·3
20	11·7	—	65	−20·7	−41·7
30	− 0·8	−39·8°	70	−16·4	−39·4
40	−19	−36·2	80	−10·2	—
45	−28	−41	90	− 5	—
50	—	−37·2	100	+ 1·6	—

p-*Cresol–Dimethylaniline.*—Both the cooling curves and the temperatures of definite melting of the mixtures lead to the conclusion that *p*-cresol does not form a definite compound with dimethylaniline but only mechanically mixed crystals. The diagram is composed of two arms intersecting in the eutectic point (50 mols.% and −35°), the position of which is confirmed by the triangle *abc* for the duration of crystallisation.

TABLE III.

o-Cresol–*p*-Toluidine (Fig. 2).

$C_7H_7{\cdot}NH_2$, mols. %.	Temp. I.	Temp. II.	$C_7H_7{\cdot}NH_2$, mols. %.	Temp. I.	Temp. II.	$C_7H_7{\cdot}NH_2$, mols. %.	Temp. I.	Temp. II.
0	30·3°	—	30	21·4°	12·9°	75	—	24·8°
10	23	—	40	32·8	—	80	31°	25·6
15	19·2	14°	50	38	—	90	37·3	22·5
20	—	14	60	34	22·2	100	43·5	—
25	17·6	13·8	70	26·5	24·5			

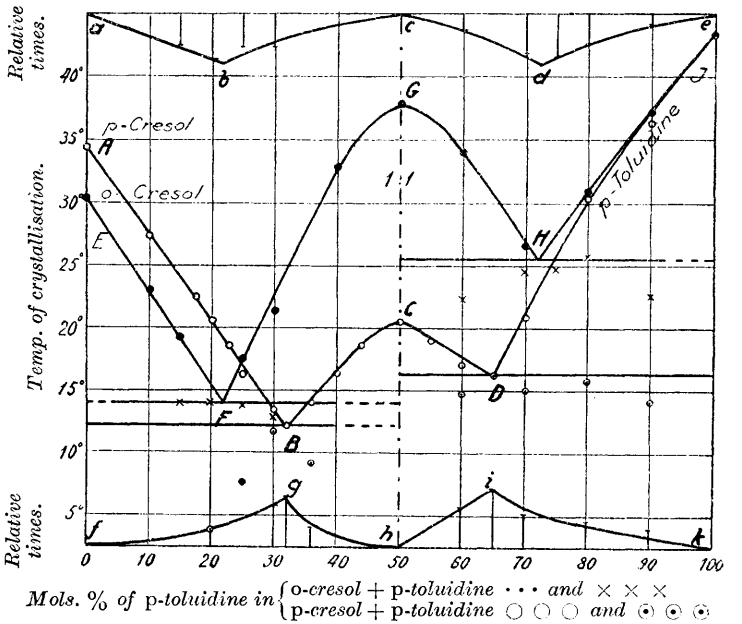
TABLE IV.

p-Cresol–*p*-Toluidine (Fig. 2).

$C_7H_7{\cdot}NH_2$, mols. %.	Temp. I.	Temp. II.	$C_7H_7{\cdot}NH_2$, mols. %.	Temp. I.	Temp. II.	$C_7H_7{\cdot}NH_2$, mols. %.	Temp. I.	Temp. II.
0	34·4°	—	32	—	12·1°	60	17·1°	14·8°
10	27·3	—	36	14°	9·1	65	—	16·4
17·5	22·5	—	40	16·4	—	70	20·9	15
20	20·6	3·8°	44	18·6	—	80	30·4	15·8
23	18·6	—	50	20·5	—	90	37·4	14·1
25	16·3	7·6	55	19·1	—	100	43·5	—
30	**13·4**	**11·7**						

o-*Cresol*–p-*Toluidine* *and* p-*Cresol*–p-*Toluidine*.—These two systems give very similar diagrams, each consisting of three sections and two eutectic points with one open maximum between them which corresponds to 50 mols.% of each component. Hence each pair forms an equimolecular *compound* of m. p.'s 38° and 20·5°, respectively, melting being without decomposition in each case. In the system *o*-cresol–*p*-toluidine the eutectic points are at 22 and 72 mols.% of *p*-toluidine, and 14° and 25·6°, and in the other system at 32 and 65 mols.% and 12·1° and 16·4°. The duration of eutectic

FIG. 2.



crystallisation of different mixtures (triangles *abc*, *cde*, *fgh*, *hik*) confirms the position of the eutectic points.

Although *o*-cresol melts at a lower temperature (30·3°) than *p*-cresol (34·4°), yet in the equimolecular compounds with *p*-toluidine there is a difference of 18·5° in the reverse direction. If it be assumed that a greater change in physical properties corresponds to a deeper change in the chemical nature and to greater stability of a newly-formed compound, then it follows that the *o*-cresol compound is more stable than its isomeride.

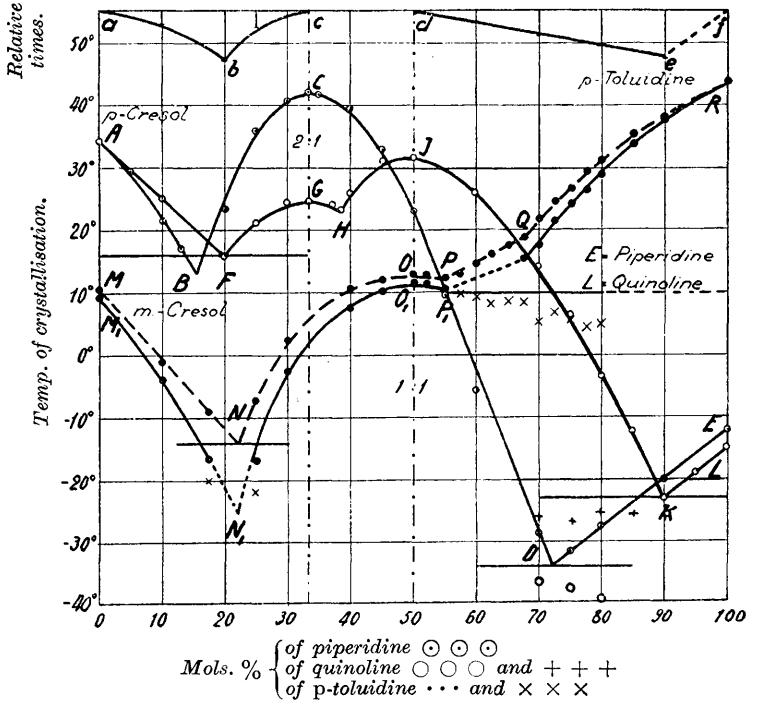
m-*Cresol*–p-*Toluidine*.—In this system the temperature of primary crystallisation is given as well as the temperature of melting of the last crystals. The first curve is shown by a continuous and the

TABLE V.

m-Cresol–*p*-Toluidine (Fig. 3).

$C_7H_7\cdot NH_2$, mols. %.	Temp. I.	Temp. II.	Temp. III.	$C_7H_7\cdot NH_2$, mols. %.	Temp. I.	Temp. II.	Temp. III.
0	+ 9·4°	—	10·4°	62·5	—	8·2°	16°
10	− 3·9	—	− 1·0	65	—	8·6	17·4
17·5	−16·4	−20°	− 9	67·5	15·5°	8·5	18·9
25	−16·7	−21·7	− 7·3	70	17·5	5·2	21·7
30	− 2·5	—	+ 2·5	72·5	21·5	6·9	24·7
40	+ 7·7	—	10·6	75	24	5·8	26·7
45	10·1	—	12	77·5	26·2	4·4	29·3
50	11·8	—	12·9	80	28·6	5	31
52	11·5	—	12·9	85	33·7	—	35·1
55	10·7	—	12·2	90	37·2	—	38
57·5	—	9·7	13·0	100	43·5	—	—
60	—	9·1	14·8				

FIG. 3.



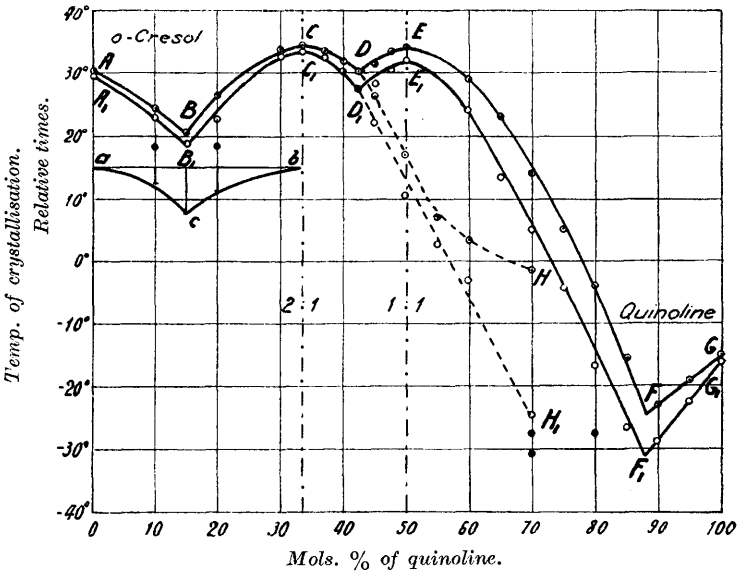
second by a broken line (Fig. 3); the two are almost parallel, but the upper curve (complete melting) gives more definite results than the other because in the ranges 17·5—25 and 55—67·5 mols.% of *p*-toluidine it has not been possible to determine the temperature of the primary crystallisation, owing to the slowness of crystallisation

TABLE VI.

o-Cresol–Quinoline (Fig. 4).

C_9H_7N, mols. %.	Temp. I.	Temp. II.	Temp. III.	C_9H_7N, mols. %.	Temp. I.	Temp. II.	Temp. III.
0	29·5°	—	30·3°	50	32°	—	34·2°
10	23	18·6°	24·4	55	2·8	—	7
15	18·7	18·7	20·7	60	− 3	—	+ 3·5
20	22·8	18·5	26·6	60	+24·1	—	+29
30	32·8	—	34	65	+13·5	—	23
33·3	33·5	—	34·5	70	−24·5	−30·7°	− 1·2
37	32·5	—	33·7	70	+ 5	−27·4	+14
40	30·1	—	32	75	− 4·3	—	+ 5
42·5	—	27·2	30·5	80	−16·7	−27·7	− 4
45	22	—	26·4	85	−26·4	—	−15·5
45	28·3	—	31·7	90	−28·7	—	−22·8
47·5	30·7	—	33·4	95	−22·3	—	−19
50	10·5	—	17	100	−16	—	−15

FIG. 4.



and to the proximity to the eutectic point. The positions of the eutectic points N_1 and P_1 can therefore be determined only approximately, but the eutectic point N lies at 22 mols.% of *p*-toluidine and −14°, and P at 56 mols.% and 12°. The maximum at O corresponds to an equimolecular *compound*.

There appears to be a break in the curve at 67 mols.% of *p*-toluidine, and on the cooling curves there is a slight change of

direction, corresponding to a heat effect, at 72·5—80%; no significance can be attached to these, however.

o-*Cresol–Quinoline.*—For this system the cooling curve, ($A_1B_1C_1D_1E_1F_1G_1$) and the temperatures of complete melting of crystalline mixtures (curve *ABCDEFG*) have been determined (see Fig. 4). These curves are very similar, but in places they are separated by 12°.

The diagram is composed of four sections giving two open maxima at *C* and *E*, corresponding to *compounds* $C_9H_7N,2C_7H_7{\cdot}OH$ (m. p. 34·5°) and $C_9H_7N,C_7H_7{\cdot}OH$ (m. p. 34·2°). Two eutectics are at 15 and 88 mols.% of quinoline and 20° and −24° respectively.

The lines *DH* and D_1H_1 represent a metastable state of the ternary and not of the binary compound, for (1) they are continuations of the curves *CD* and C_1D_1, and (2) every temperature of crystallisation of the mixture along the curve D_1H_1 corresponds to a temperature along the curve *DH*, where the whole mixture is in a liquid state, whereas the crystals of the binary compound melt only at temperature shown by the curve *DEF*.

TABLE VII.

p-Cresol–Quinoline (Fig. 3).

C_9H_7N, mols. %	Temp. III.	Temp. II.	C_9H_7N, mols. %	Temp. III.	Temp. II.	C_9H_7N, mols. %	Temp. III.	Temp. II.
0	34·4°	—	38·5	23·2°	—	75	6·3°	−27·2°
10	25·0	6·7°	40	26	—	80	− 3·3	−24·8
20	16	—	45	31	—	85	−12·3	−25·4
25	21·2	4	50	31·8	—	90	−23	−26
30	24·4	—	60	26	—	95	−19	—
33·3	24·5	—	70	14	−25·6°	100	−15	—
37	24·2	—						

p-*Cresol–Quinoline.*—The diagram of this system is very similar to that of the system *o*-cresol–quinoline, showing two open maxima corresponding to the *compounds* $C_9H_7N,C_7H_7{\cdot}OH$ and $C_9H_7N,2C_7H_7{\cdot}OH$ of m. p. 31·8° and 24·5° respectively. Two well-defined eutectic points are at 20 and 90 mols.% of quinoline and 16° and −23°, respectively; these have been confirmed by the duration of crystallisation (triangles *abc* and *def*). The minimum at 38·5 mols.% may not be a true eutectic, for it has not yet been ascertained whether a series of solid solutions is formed.

Comparison of the diagrams for the systems *o*-cresol–quinoline and *p*-cresol–quinoline shows that the curves of the first system are higher than those of the second, almost throughout. Both cresols therefore behave towards quinoline just as towards *p*-toluidine except that with quinoline they form not one but two definite compounds.

TABLE VIII.

p-Cresol–Piperidine (Fig. 3).

$C_5H_{11}N$, mols. %.	Temp. III.	$C_5H_{11}N$, mols. %.	Temp. III.	Temp. II.
0	34·4°			
5	29·5	45	33°	—
10	21·5	50	23	—
13	17·0	55	9·7	—
20	23·5	60	− 5·6	—
25	36	70	−28·6	−36·7°
30	40·9	75	−31·7	−37·7
33·3	42·1	80	−27·5	−39·5
35	41·9	90	−20	—
40	39·5	100	−12	—

p-*Cresol–Piperidine.*—The diagram consists of three sections showing two eutectic points and one open maximum, which corresponds to the *compound* $C_5H_{11}N,2C_7H_7{\cdot}OH$, m. p. 42·1°. The eutectics are at 15·5 and 72 mols.% of piperidine (14° and −34°, respectively), the former having been determined by interpolation because within 13—20 mols.% and 60—70 mols.% of piperidine we were unable to make the mixtures crystallise. It is noteworthy that the above compound does not correspond to piperidine as mono-acid base and to *p*-cresol as monobasic phenol.

TABLE IX.

p-Cresol–1 : 5-Naphthylenediamine (Fig. 5).

$C_{10}H_6(NH_2)_2$, mols. %.	Temp. I.	Temp. II.	$C_{10}H_6(NH_2)_2$, mols. %.	Temp. I.	Temp. II.
0	33°	—	37	119·2°	118°
5	31·6	—	40	125	116·5
10	—	29°	45	128·2	116·1
13	106	28·7	50	136·5	111
15	109	—	60	145	107·8
15·8	110	13·5	70	154·6	86·7
20	114·2	—	80	164·1	—
25	116·9	—	90	170·5	—
33·3	118	—	100	189	—

p-*Cresol*–1 : 5-*Naphthylenediamine.*—From naphthylenediamines as diacid bases one might have expected the formation of compounds with *p*-cresol of the type $C_{10}H_6(NH_2)_2,2C_7H_7{\cdot}OH$, and this is actually found.

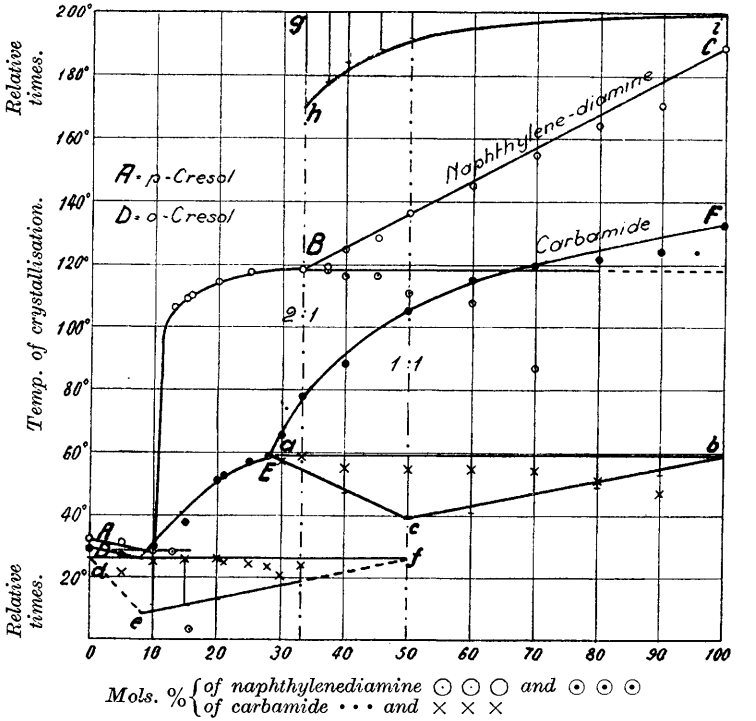
The diagram is composed of three sections and is characterised by one eutectic point at 10 mols.% of naphthylenediamine and 29° and by one transition point at 33 mols.% of naphthylenediamine and 118°. For the determination of the composition of the compound the duration of crystallisation at the transition temperature was studied (triangle *ghi*), and showed a maximum at 33·3 mols.% of naphthylenediamine.

TABLE X.

o-Cresol–Carbamide (Fig. 5).

$CO(NH_2)_2$, mols. %.	Temp. I.	Temp. II.	Temp. IV.	$CO(NH_2)_2$, mols. %.	Temp. I.	Temp. II.	Temp. IV.
0	29·5°	—	—	33·3	78°	24°	58·3°
5	27·4	21·2°	—	40	88·2	—	55
10	29·9	25·1	—	50	105	—	55
15	38	25·9	—	60	115	—	55
20	51·7	26·1	—	70	120	—	54
21	53	25·1	—	80	122	—	51·3
25	57·2	24·4	—	90	124·5	—	47
28	59	22·6	59°	100	133	—	—
30	66	20·5	56·9				

FIG. 5.



o-Cresol–Carbamide.—According to Philip (J., 1903, **83**, 814) and Kremann and Rodinois (*Monatsh.*, 1906, **27**, 138), 1 mol. of carbamide forms compounds with 2 mols. of phenol, and with 1 mol. of each cresol (Kremann, *ibid.*, 1907, **28**, 1125), but Kremann studied only

the temperature of first crystallisation and not that of definite crystallisation of the mixtures. He determined the composition of the compounds by analysis. We have now investigated complete cooling curves of all mixtures, and have confirmed Kremann's results.

The diagram of this system consists of three sections and is characterised by a eutectic point at 8 mols.% of carbamide and 26°, and by a transition point at 28 mols.% of carbamide and 59°, corresponding to the dissociation of the compound $C_7H_7{\cdot}OH,CO(NH_2)_2$ into its components. The composition was determined by the duration of crystallisation at the temperature of formation (triangle *abc*) and at the eutectic temperature (triangle *def*). The maximum duration is shown for the equimolecular mixture.

Summary.

The diagrams of ten binary systems have been constructed for the cresols with certain bases, and the existence of the following compounds has been demonstrated :

$C_6H_5{\cdot}NMe_2$,*o*-$C_6H_4Me{\cdot}OH$	C_9H_7N,*o*-$C_6H_4Me{\cdot}OH$	$C_5H_{11}N$,2*p*-$C_6H_4Me{\cdot}OH$
p-$C_6H_4Me{\cdot}NH_2$,*o*-$C_6H_4Me{\cdot}OH$	C_9H_7N,2*o*-$C_6H_4Me{\cdot}OH$	1 : 5-$C_{10}H_6(NH_2)_2$,2*p*-$C_6H_4Me{\cdot}OH$
p-$C_6H_4Me{\cdot}NH_2$,*m*-$C_6H_4Me{\cdot}OH$	C_9H_7N,*p*-$C_6H_4Me{\cdot}OH$	$CO(NH_2)_2$,*o*-$C_6H_4Me{\cdot}OH$
p-$C_6H_4Me{\cdot}NH_2$,*p*-$C_6H_4Me{\cdot}OH$	C_9H_7N,2*p*-$C_6H_4Me{\cdot}OH$	

All except the last melt without decomposition.

Dimethylaniline and *p*-cresol form only mechanical mixtures.

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