

Phase Diagrams of Binary Mixtures of Phenylenediamines and Dihydroxybenzenes

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Solid – liquid equilibria for o-phenylenediamine + resorcinol, m-phenylenediamine + pyrocatechol, + resorcinol and p-phenylenediamine + pyrocatechol, + resorcinol have been studied by the thaw-melt method. The types and melting temperatures of the complexes formed in these mixtures were ascertained from the phase diagrams.

Introduction

Solid – liquid equilibrium data of mixtures of phenylenediamines with naphthols, nitrophenols, phenol and hydroquinone have been reported earlier^{1–4}. In this paper we report corresponding data for mixtures of phenylenediamines with 1,2-dihydroxybenzene (pyrocatechol) and 1,3-dihydroxybenzene (resorcinol). The study of solid – liquid equilibria is one of the best tools to investigate the formation of complexes in condensed phase and provides information about the type and melting temperature of the complex.

Experimental

o-, m-, and p-Phenylenediamines were boiled with alcohol and activated charcoal, filtered while hot and repeatedly crystallized from alcohol. Pyrocatechol and resorcinol (B.D.H.) were fractionally crystallized from alcohol and distilled under vacuum. The purities of the samples were checked by determining the melting temperatures, which agreed to within 0.01 K with the corresponding values in the literature^{5, 6}.

Mixtures of various compositions were made in Rast tubes by weight. Each mixture was heated just above the melting temperature of the higher melting component in an oil bath, suddenly cooled in ice and ground. The procedure was repeated three to four times. The phase equilibria were studied by the thaw-melt method^{7, 8}. The heating and cooling rates were controlled to about 0.1 K min^{–1}. The temperatures were measured with a calibrated mercury-in-glass thermometer. The results are correct and reproducible to within 0.1 K. Checks by the method of thermal analysis⁹ gave the same results to within 0.1 K.

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Results and Discussion

The results are recorded in Table 1 and are plotted in Figs. 1 to 5. It is evident from the figures that the systems studied show congruent melting

Table 1. Solid – liquid equilibrium data of the mixtures.

<i>x</i>	Thaw temp. (T/K) – 273.15	Melting temp. (T/K) – 273.15	<i>x</i>	Thaw temp. (T/K) – 273.15	Melting temp. (T/K) – 273.15
<i>x</i> o-phenylenediamine + (1– <i>x</i>) resorcinol					
0.0000	—	110.0	0.5161	47.1	51.8
0.0612	48.5	104.4	0.5824	47.0	51.8
0.1386	48.4	98.6	0.6266	47.1	48.0
0.2129	48.5	88.4	0.6670	47.2	61.7
0.2876	48.6	75.6	0.7246	47.2	70.0
0.3394	48.5	64.8	0.8134	47.0	83.6
0.3886	48.5	52.4	0.9206	47.1	93.5
0.4198	48.4	49.2	0.0000	—	103.0
0.4872	48.5	51.6			
<i>x</i> m-phenylenediamine + (1– <i>x</i>) pyrocatechol					
0.0000	—	103.0	0.5416	41.4	66.7
0.1022	58.4	97.5	0.6431	41.4	66.5
0.1876	58.6	90.4	0.7388	41.5	66.0
0.2431	58.5	82.6	0.8149	41.5	50.6
0.3094	58.5	73.7	0.8782	41.4	44.3
0.4425	58.6	62.1	0.9431	41.5	48.9
0.5046	58.6	64.9	1.0000	—	63.8
<i>x</i> m-phenylenediamine + (1– <i>x</i>) resorcinol					
0.0000	—	110.0	0.4886	52.2	79.1
0.0871	52.0	101.0	0.5492	31.5	79.1
0.1436	52.2	90.4	0.6225	31.6	70.3
0.1879	52.1	81.6	0.7060	31.5	60.1
0.2446	52.0	70.2	0.7586	31.6	42.4
0.2791	52.0	59.2	0.8396	31.5	43.8
0.3241	52.1	63.1	0.9210	31.6	58.6
0.3876	52.1	70.0	1.0000	—	63.8
0.4346	52.2	78.5			
<i>x</i> p-phenylenediamine + (1– <i>x</i>) pyrocatechol					
0.0000	—	103.0	0.4775	100.4	108.4
0.0412	89.4	100.8	0.5836	100.3	102.5
0.0878	89.6	94.6	0.6516	100.3	105.4
0.1224	89.5	91.8	0.7324	100.4	111.3
0.1801	89.5	95.6	0.8176	100.3	119.6
0.2319	89.4	102.4	0.9234	100.4	129.8
0.2906	89.5	108.5	1.0000	—	140.0
0.3804	89.6	109.3			
<i>x</i> p-phenylenediamine + (1– <i>x</i>) resorcinol					
0.0000	—	110.0	0.5876	102.2	112.0
0.0596	94.7	102.9	0.6532	102.3	108.7
0.1206	94.8	97.3	0.7214	102.3	108.7
0.1877	94.8	97.6	0.8041	102.2	120.8
0.2532	94.7	104.2	0.8733	102.3	129.4
0.3448	94.8	109.9	0.9432	102.4	133.6
0.4295	94.7	113.2	1.0000	—	140.0
0.5104	102.3	118.5			



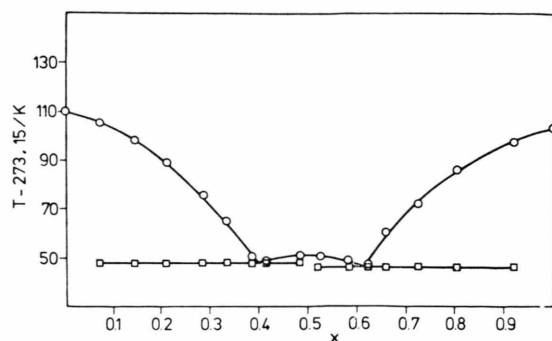


Fig. 1. Phase diagram of x o-phenylenediamine + $(1-x)$ resorcinol. ○○○ Melting temperature; □□□ thaw temperature.

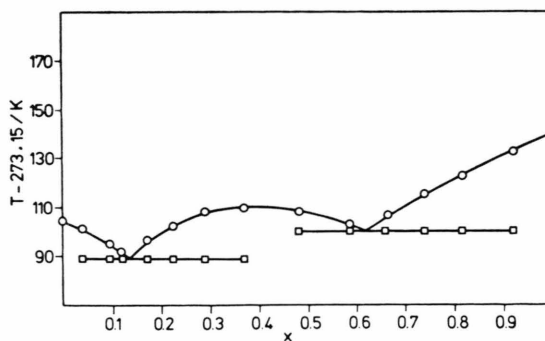


Fig. 4. Phase diagram of x p-phenylenediamine + $(1-x)$ pyrocatechol. ○○○ Melting temperature; □□□ thaw temperature.

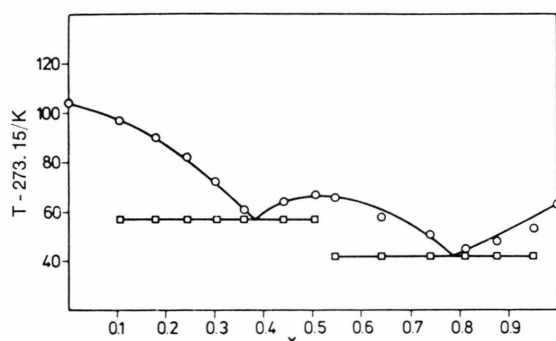


Fig. 2. Phase diagram of x m-phenylenediamine + $(1-x)$ pyrocatechol. ○○○ Melting temperature; □□□ thaw temperature.

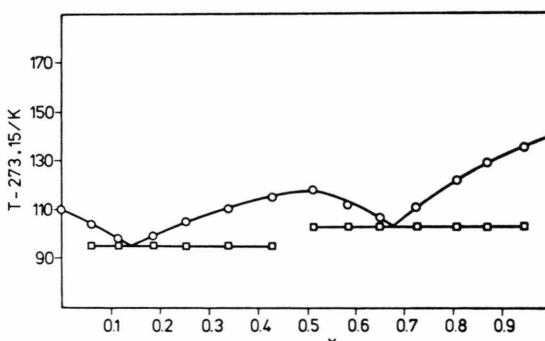


Fig. 5. Phase diagram of x p-phenylenediamine + $(1-x)$ resorcinol. ○○○ Melting temperature; □□□ thaw temperature.

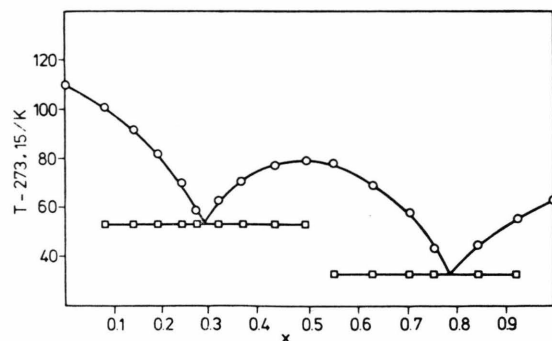


Fig. 3. Phase diagram of x m-phenylenediamine + $(1-x)$ resorcinol. ○○○ Melting temperature; □□□ thaw temperature.

temperatures indicating the formation of complexes. The formulae of the complexes and the melting temperatures are reported in Table 2.

The heat of fusion of the addition compound $A_{\nu_1}B_{\nu_2}$ formed between the species A and B can be estimated from the freezing curve between the two

eutectic temperatures from the relation

$$\frac{1}{T} = -\frac{R}{\Delta_f h} \ln(x_A)^{\nu_1}(x_B)^{\nu_2} + \frac{R}{\Delta_f h} \ln(x_A)_c^{\nu_1}(x_B)_c^{\nu_2} + \frac{1}{T_c} \dots \quad (1)$$

where $\Delta_f h$ is the heat of fusion of the addition compound, T_c its melting temperature and $x_{A,B}$ and $(x_{A,B})_c$ the mole fractions of the species A, B at the temperatures T and T_c . ν_1 and ν_2 are the integers. The plots of $1/T - 1/T_c$ against $-\ln(x_A)^{\nu_1}(x_B)^{\nu_2}$ showed large deviations from linearity, indicating

Table 2. Melting temperatures and formula of the complexes.

System	Type of complex	Melting temp./K
o-phenylenediamine+resorcinol	1-1	324.95
m-phenylenediamine+pyrocatechol	1-1	339.85
m-phenylenediamine+resorcinol	1-1	352.25
p-phenylenediamine+pyrocatechol	1-2	382.45
p-phenylenediamine+resorcinol	1-1	391.65

that these mixtures are far from being ideally associated, and that the heats of fusion of the complexes can not be determined by this method. The formation of complexes in the solid phases of these mixtures is presumably due to hydrogen bonding between the NO_2 -groups of the diamines and the OH-groups of the dihydroxybenzenes.

The NH_2 -groups being farthest away from each other in p-phenylenediamine, this molecule appears to be able to form a 1 – 2 complex with pyrocate-

chol. This is not the case with resorcinol, probably because its more distant OH-groups, as compared to pyrocatechol, interact with both NH_2 -groups of p-phenylenediamine.

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