

171. *Solid-Liquid Equilibria in the System Nitrobenzene-*m*-Dinitrobenzene.*

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TEMPERATURES of solid-liquid equilibria in the system nitrobenzene-*m*-dinitrobenzene have been reported in a previous communication (Hammick, Andrew, and Hampson, J., 1932, 171). The results there recorded were the temperatures, reproducible to within $\pm 0.3-0.4^\circ$, at which small traces of solid phase, of known composition, were just in equilibrium with liquid phases of known composition. Lehmstedt (*Ber.*, 1932, 65, 1218) declares, however, that these data are unreliable and that the conclusion drawn from them as to the composition of the molecular compound $C_6H_5 \cdot NO_2, C_6H_4(NO_2)_2$ is incorrect. In view of the fact that many solubility data in two-component systems have been obtained by the method employed by Hammick, Andrew, and Hampson, and that important conclusions as to molecular composition have been drawn from such data, we feel that it is necessary to point out that Lehmstedt's statement is unsupported by experimental evidence. He refers to van der Linden (*Helv. Chim. Acta*, 1932, 15, 592), who, however, merely shows that in three-component systems solubility determinations made by "melting point" methods are often unreliable owing to doubt as to the composition of the solid phase. We therefore maintain that the synthetic method for finding temperatures of solid-liquid equilibria in two-component systems gives results that mean precisely what they say within the limits set by the reproducibility of the equilibrium temperatures, as indicated above.

In order to remove any doubt as to the reproducibility of results obtained by the synthetic method in the particular system under discussion, we have redetermined solubilities of *m*-dinitrobenzene in nitrobenzene, using the procedure already described (*loc. cit.*). Our results are given below, where $T = \text{temp. of solid-liquid equilibrium for liquid phase of composition } x$, in mols. % of *m*-dinitrobenzene.

T	13.1°	17.8°	22.0°	22.8°	23.9°	25.7°	30.4°	35.0°	40.0°	66.0°
x	13.6	18.72	24.75	25.58	28.10	30.22	34.36	37.67	41.28	65.6

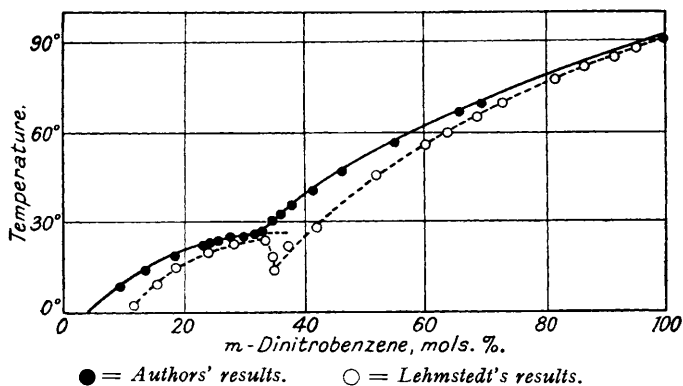
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The above data, together with those obtained by Hammick, Andrew, and Hampson, give the upper curve (with black dots) in the fig., in which Lehmstedt's results are also shown (open circles). In order to avoid confusing the curve, the whole of our available data is not shown as points.

It will be observed that the results of the present investigation and of the earlier work lie very well on the same curves, whereas Lehmstedt's results give curves entirely different in character. Our curves show an incongruent m. p. at about 25° , $x = 33\%$. The composition of the solid phases in equilibrium at room temp. has been found by two methods. *m*-Dinitrobenzene was recrystallised from $\text{Ph}\cdot\text{NO}_2$, the solid phase being removed by filtration and rapidly dried by rubbing on porous tile. A portion of the solid was then enclosed in a bulb tube, and the temp. at which the last trace of cryst. solid phase was just in equil. with the liquid was found in the usual way. From the temp.-compn. curve the compn. of the solid phase was found to be 49.3 mols. % of $\text{C}_6\text{H}_4(\text{NO}_2)_2$.

A second portion of the solid phase in equil. at room temp. was analysed [Found : N, 14.57. $\text{C}_6\text{H}_5\cdot\text{NO}_2, \text{C}_6\text{H}_4(\text{NO}_2)_2$ requires N, 14.43%. $2\text{C}_6\text{H}_5\cdot\text{NO}_2, \text{C}_6\text{H}_4(\text{NO}_2)_2$ requires N, 13.52%].



These results support our view that the compound in the system is $\text{C}_6\text{H}_5\cdot\text{NO}_2, \text{C}_6\text{H}_4(\text{NO}_2)_2$. It cannot, of course, be claimed that no PhNO_2 was lost by vaporisation during drying on the porous tile. Nevertheless, the low v. p. of PhNO_2 itself at room temp. enables us to conclude that such loss must be very small.

Lehmstedt interprets his results as evidence for $2\text{C}_6\text{H}_5\cdot\text{NO}_2, \text{C}_6\text{H}_4(\text{NO}_2)_2$. His data were obtained, however, by cooling homogeneous mixtures of the two components, and it is not clear from his account whether separation of the solid phase was detected by the "thermal arrest" method or by observation of the crystal shower. In either case, and particularly in the former, corrections for supercooling must be applied even in systems less prone to supercooling than the one under discussion (cf. van der Linden, *loc. cit.*). In our experience, the presence of traces of solid phase, as in Lehmstedt's experiments, is quite ineffective in preventing considerable supercooling unless the rate of cooling is very slow indeed. We would suggest, therefore, that the difference between our results and Lehmstedt's is due to progressive supercooling in his experiments as the system proceeds from pure dinitrobenzene to about 33 mols. %. A new phase, much nearer in composition to the liquid phase than dinitrobenzene, here making its appearance, supercooling is likely to become suddenly less and, as we proceed towards the pure nitrobenzene end of the diagram, to increase again. The only conclusion we would therefore be prepared to draw from Lehmstedt's curve is that at the hump with an almost vertical side at the liquidus composition of about 33 mols. % of dinitrobenzene a new phase makes its appearance. The conclusion that the summit of the hump represents a true congruent m. p. is difficult to accept in the face of our results in which supercooling is not in question and in view of the obvious possibility of supercooling in Lehmstedt's experiments.