[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, COLLEGE OF ENGINEERING, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Systems (I) Diphenyl–Diphenylamine, (II) Diphenyl–Benzophenone and (III) Benzophenone–Diphenylamine[1]

BY H. HOWARD LEE AND J. C. WARNER

This investigation was undertaken for the purpose of determining the freezing point–composition diagrams for the binary systems (I) diphenyl–diphenylamine, (II) diphenyl–benzophenone and (III) benzophenone–diphenylamine. The system benzophenone–diphenylamine was investigated by Giua and Cherchi[2] but their results are evidently in error over a considerable range of composition and we have consequently reinvestigated the entire system. Each of the three compounds contains two phenyl groups. Diphenyl is non-polar but benzophenone and diphenylamine possess electric moments of considerable magnitude. It was therefore considered of interest to compare actual solubilities to ideal solubilities in these systems.

Materials.—The chemicals were Eastman's "Highest Purity" grade. The diphenyl was purified by crystallization from alcohol, washing with ether and drying in an oven at 100°. The diphenylamine and benzophenone were distilled under reduced pressure. In each case recrystallization or redistillation was continued until no further change in melting point was observed. The melting points of the compounds used in the investigation are compared to the "International Critical Tables" values in Table I.

TABLE I

	Melting point, °C. Our material	I. C. T.	Heat of fusion,[3] g. cal./mole
Diphenyl	69.0	69.0	4020
Diphenylamine	52.8	53.0	4260
Benzophenone	47.7	48.5	4290

The agreement in melting points is good except for benzophenone. It seems certain that the "I. C. T." melting point for benzophenone is in error since any number of recrystallizations or redistillations failed to yield a product of melting point higher than 47.7°. Furthermore, none of the seven reported investigations on binary systems with benzophenone[4] as one constituent shows a melting point for pure benzophenone above 47.7°.

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[1] This paper is based on a thesis submitted by H. Howard Lee to the Graduate Committee of the Carnegie Institute of Technology in partial fulfilment of the requirements for the degree of Master of Science.

[2] Giua and Cherchi, *Gazz. chim. ital.*, **49**, II, 264 (1919).

[3] "International Critical Tables," Vol. V, p. 134.

[4] "International Critical Tables," Vol. IV.

Temperatures were measured with 100° thermometers graduated in tenths of a degree. They were compared to a thermometer of the same type which had been calibrated by the Bureau of Standards. Correction for emergent stem was always made when the correction was equal to, or greater than, the experimental error.

Experimental

Weighed samples in test-tubes (15 mm. diameter) were placed in larger test-tubes which were immersed in a water-bath. The melt was allowed to cool with the bath, the temperature difference between the bath and the sample ranging between a few tenths of a degree and several degrees depending upon the particular sample and the temperature at which observations were made. The samples were well agitated during cooling by a glass stirrer which encircled the thermometer stem. When undercooling occurred, the cooling curves were projected back to intersect with the liquid cooling curve to obtain a more accurate primary crystallization temperature. With some samples, particularly those containing high percentages of benzophenone or diphenylamine, undercooling was very marked in spite of vigorous agitation and inoculation. In such cases, the results obtained from cooling curves were checked by thermostating samples to determine the temperature at which the solid phase disappeared.

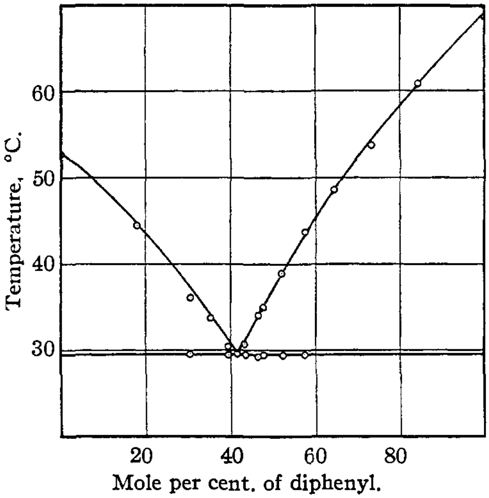

Fig. 1.—Diphenyl–diphenylamine.

(I) **Diphenyl–Diphenylamine.**—The freezing point–composition diagram for this system is shown in Fig. 1. The diagram is based upon the data in Table II.

A sample having the eutectic composition (41.7 mole per cent. diphenyl) indicated by the intersection of the liquidus curves solidified at 29.6°. This is in good agreement with the average final solidification temperature of 29.5°. Assuming ideal solution behavior and constant heats of fusion (see Table I), the calculated eutectic temperature is 26.5° and the eutectic composition is 43.8 mole per cent. diphenyl. The solubility of each constituent in the other is therefore less than the ideal solubility. This should be expected since one component is polar and the other non-polar.

Primary crystals of diphenyl which were separated from the liquid above the eutectic temperature melted sharply at 68.8°. Similarly obtained crystals of diphenylamine melted sharply at 52.8°. Hence there is no appreciable solubility of the constituents in each other in the solid state.

TABLE II

Mole per cent. diphenyl	Initial cryst. temp., °C.	Final solidification temp., °C.
0.0	52.8	52.8
18.0	44.5	
30.5	36.0	29.6
35.4	33.6	
39.7	30.3	29.5
41.7 E	29.6	29.6
43.5	30.8	29.6
46.7	34.1	29.3
47.8	35.0	29.5
52.3	39.0	29.5
57.5	43.7	29.4
64.6	48.6	
73.2	53.7	
84.5	60.9	
100.0	69.0	69.0

TABLE III

Mole per cent. diphenyl	Initial cryst. temp., °C.	Final solidification temp., °C.
0.0	47.7	47.7
22.8	35.0	
30.7	30.3	24.9
37.2	25.9	
39.3 E	25.2	25.2
42.5	28.0	25.0
47.0	32.3	25.4
54.2	38.5	25.2
63.8	46.1	
78.0	56.2	
100.0	69.0	69.0

(II) **Diphenyl–Benzophenone.**—The freezing point–composition diagram for this system, constructed from the data given in Table III, is shown in Fig. 2.

This system also shows a simple eutectic. According to the intersection of the liquidus curves, the eutectic composition is 39.3 mole per cent. diphenyl and the eutectic temperature is 25.2°. A sample of this composition solidified at 25.2°. The average of the four final solidification temperatures in Table III is 25.1°. Using the method described under the previous system, we have shown that there is no appreciable solubility of the constituents in each other in the solid state. Assuming ideal solution behavior, we calculate that the eutectic composition should be 41.3 mole per cent. diphenyl and the eutectic temperature should be 23.5°. Here again, due to one constituent being polar and the other non-polar, solubilities are lower than ideal.

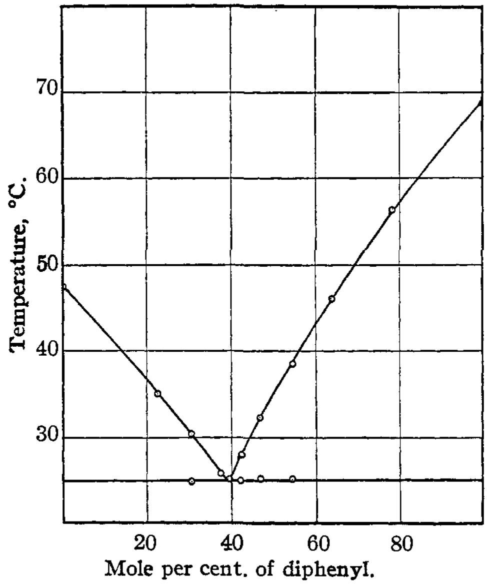

Fig. 2.—Diphenyl–benzophenone.

(III) **Benzophenone–Diphenylamine.**—The unbroken freezing point–composition curve in Fig. 3 is constructed from our data given in Table

IV and the broken curve from our data in Table V. The dots in the figure represent points reported by Giua and Cherchi.[2] The curve shows a compound with equimolecular quantities of diphenylamine and benzophenone and two eutectics; one at 30 mole per cent. benzophenone and at 34.1°; the other at 74.5 mole per cent. benzophenone and at 31.9°. Due to the marked interaction between these polar compounds, solubilities are much higher than ideal. There is definite evidence that there are two forms of the compound. If a sample consisting of the compound composition is melted and then solidified in an ice–salt bath, crystals of the metastable compound are obtained. These crystals melt sharply at 30.8°. When this melt is agitated, it solidifies completely, yielding crystals which melt sharply at 40.2°. Although the transition temperature has not been determined, it is definitely below room temperature. A sample of the metastable solid

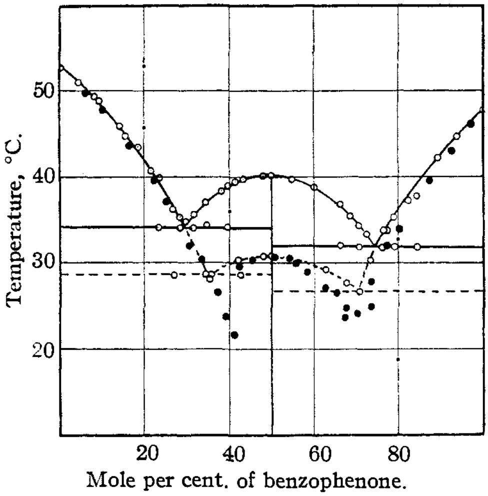

Fig. 3.—Benzophenone–diphenylamine.

Table IV

Mole per cent. benzophenone	Initial cryst. temp., °C.	Final solidification temp., °C.	Disappearance of solid, °C.	Mole per cent. benzophenone	Initial cryst. temp., °C.	Final solidification temp., °C.	Disappearance of solid, °C.
0.0	52.8	52.8		48.2			40.1
4.7			51.0	50.0 Compd.			40.2
8.5	49.3			54.5	39.7		40.0
9.3			49.0	60.0			38.7
14.0			46.0	66.5		32.2	37.0
15.5	44.8			68.4			35.4
18.8			43.5	70.5	34.5	31.8	34.4
21.7	40.8			72.2			33.5
23.5	38.9	34.1	40.0	74.5 E		31.9	
27.0	36.3			76.2	34.0	31.8	34.1
28.5	35.5	34.1	35.0	77.6	34.0		
30.0 E	34.1	34.1		79.0	35.4	32.0	35.5
31.7		34.1	35.6	82.4	37.3		
34.8		34.3	37.2	84.1	37.6	31.7	37.5
38.2			38.3	89.4	42.1		42.4
39.8		34.2	39.1	94.7			45.0
41.2			39.5	100.0	47.7	47.7	
43.2			39.7				

TABLE V

METASTABLE COMPOUND

Mole per cent. benzophenone	Initial cryst. temp., °C.	Final solidification temp., °C.
27.0	36.3	28.6
34.8 E′	28.6	28.6
35.8		28.6
42.6	30.5	28.6
48.2	30.8	
50.0 (M.S. Compd.)	30.88	30.88
62.8	29.4	
67.8	27.8	
70.5 E′(?)		26.6
73.6	30.2	

compound was largely converted into stable solid in fifteen hours at room temperature.

In general, on cooling melts containing from 31 to 74 mole per cent. of benzophenone, initial crystallization temperatures which fall on the metastable curve will be obtained unless the samples are carefully inoculated with crystals of the stable compound. Due to the marked tendency of the compound and of benzophenone to undercool, most of the points on the unbroken curve (Fig. 3) were obtained by thermostating samples for eight to twelve hours to determine the temperature at which the last of the solid phase disappeared. However, a number of points were checked by carefully determining the temperature of initial and final crystallization.

Up to 30 mole per cent. and in the range above 75 mole per cent. benzophenone, the data reported by Giua and Cherchi, based entirely on cooling curves, are in fair agreement with ours. In the region 30 to 75 mole per cent. benzophenone, their curve is somewhat similar to our metastable curve, but most of their points are too low, evidently due to undercooling. It is very difficult to obtain reliable data in the vicinity of the eutectic between metastable compound and benzophenone. This eutectic temperature may be in error by as much as 2 or 3°.

Summary

1. The freezing point–composition diagram for the system diphenyl–diphenylamine shows a simple eutectic at 41.7 mole per cent. diphenyl. The eutectic temperature is 29.5°.

2. In the diphenyl–benzophenone system, there is likewise a simple eutectic at 39.3 mole per cent. diphenyl with a eutectic temperature of 25.2°.

3. Diphenylamine forms an equimolecular compound with benzophenone. The stable compound has a melting point of 40.2°. The eutectic between compound and diphenylamine occurs at 30.0 mole per cent. benzophenone and at 34.1°. The eutectic between compound and benzo-

phenone occurs at 74.5 mole per cent. benzophenone and at 31.9°. Evidence is presented for the existence of a metastable form of the compound with a melting point of 30.8°.

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The Kinetics of the Thermal Decomposition of Trichloromethyl Chloroformate

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Trichloromethyl chloroformate gas is known to decompose at 300° to give two molecules of phosgene[1] as shown by the equation

$$ClCOOCCl_3 = 2COCl_2 \qquad (1)$$

The liquid can be decomposed at room temperature by the addition of various metallic chlorides such as aluminum chloride,[1,2] in which case, however, the reaction is

$$ClCOOCCl_3 = CO_2 + CCl_4 \qquad (2)$$

The rate of the thermal decomposition in the gas phase has been studied by us between 260 and 310° and in the pressure range 4 to 17 mm. with the intention of providing further data on unimolecular reactions.

Preparation of the Compound.—The method of preparation was similar to that of other investigators,[1,2] namely, the photochemical chlorination of methyl formate. A 100-cc. portion of methyl formate was placed in an all-glass apparatus provided with a reflux condenser cooled with ice and salt to prevent loss of the very volatile methyl formate. The flask containing the methyl formate was illuminated by a 500-watt lamp placed just above it. To avoid explosions illumination was commenced before the slow stream of "tank" chlorine was passed in. The temperature was kept at about 30° during the initial stages of the reaction. As the chlorination progressed the chlorine was passed in more rapidly and the temperature was gradually increased until finally it reached about 90°. Chlorination was complete after thirty hours.

A portion of the product was distilled under reduced pressure in a small all-glass apparatus provided with a fractionating column and condenser. The middle fraction of a sample, which boiled between 50.0 and 50.1° under 48 mm. pressure, was collected in a bulb containing calcium chloride. This supply was frozen with a carbon dioxide–ether mixture, sealed onto a high-vacuum line, pumped off and allowed to diffuse over into a second bulb immersed in carbon dioxide–ether, after which the original container was sealed off. The sample (A in Fig. 1) could be partially evaporated into the 500-cc. bulb B, frozen back into A and any non-condensed gas pumped off. Repetition of this process ensured the elimination of dissolved gas.

Apparatus and Experimental Method.—A diagram of the apparatus is shown in Fig. 1. C_1, C_2 and C_3 are stopcocks specially designed to handle corrosive gases; these

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[1] Hentschel, *J. prakt. Chem.*, [2] **36,** 99, 209, 305, 468 (1887).

[2] Grignard, Rivat and Urbain, *Ann. chim.*, 9 [13], 229 (1920).