CCXCIII.—*A Case of Apparently Isothermal "Mixed Melting Points."*

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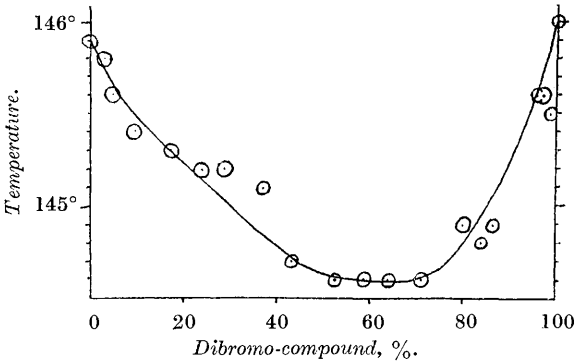
IN a previous communication (Waters, J., 1929, 2111) it was recorded that "the m. p. of this substance [3-bromo-5-iodo-4-aminobenzophenone] was not depressed after its admixture in various proportions with 3:5-dibromo-4-aminobenzophenone," the m.p. of each substance



being given as 148°. In view of the rarity of this phenomenon and of the general use of "mixed m. p.'s" for confirming identity of organic compounds, the system has been investigated further.

The two components were prepared in large quantities as previously described (*loc. cit.*), both the final products and the 3-iodo-4-aminobenzophenone being carefully purified by repeated crystallisation from benzene, alcohol, and acetone.

The freezing points of mixtures of various compositions were determined by observing the cooling curves of quantities up to 10 g. which were allowed to cool in test-tubes separated by an air-jacket from a bath of hot glycerol. An Anschütz thermometer was used, and was compared directly with one calibrated by the N.P.L. The correction for the exposed stem was found to be about 0·6° by immersion in a glycerol-bath. In no case was more than one arrest observed, and in each case determinations were made in duplicate,

values identical to 0·1° being obtained. The results are shown in the graph.

The revised m. p.'s of the pure substances, *viz.*, 3 : 5-dibromo-4-aminobenzophenone 146·0° (compare Clarke and Esselen, *J. Amer. Chem. Soc.*, 1911, **33**, 1135, who previously gave this value), and 3-bromo-5-iodo-4-aminobenzophenone 145·9°, can be regarded as more accurate than the value of 148° previously given.

Freezing points (corrected).

(*B* = % of dibromo-compound.)

B.	F. p.	*B.*	F. p.	*B.*	F. p.	*B.*	F. p.	*B.*	F. p.
100	146·0°	84·0	144·8°	59·2	144·6°	28·5	145·2°	4·2	145·6°
98·8	145·5	80·1	144·9	52·7	144·6	23·9	145·2	2·8	145·8
97·5	145·6	70·8	144·6	42·6	144·7	17·3	145·3	0·9	145·8
96·0	145·6	64·3	144·6	37·3	145·1	9·7	145·4	0·0	145·9
86·5	144·9								

Melting points, determined by heating in capillary tubes attached to a thermometer graduated in $\frac{1}{2}$°, in a glycerol-bath, gave by visual observation, m. p. 146·1° (corr.) for both pure substances, and a maximum depression for mixtures of $\frac{1}{2}$°.

Melting points determined in a similar manner, but with an Anschütz thermometer reading to 0·1°, a lens being used for observation of the first sign of melting, showed a maximum depression of 1°.

These results are insufficient to establish the exact nature of the phase diagram, on account of the relatively large experimental error in the m. p. determinations and the difficulty of correlating them with the f. p. measurements with a certainty of 0·1°. A probable explanation is the formation of a continuous series of mixed crystals, especially as bromo- and iodo-derivatives are frequently isomorphous. The present results, however, confirm the earlier observation that the system is almost unique, in that, without special precautions such as are seldom necessary in organic chemistry, both the pure components would appear to have the same m. p., and that the depression of m. p. on mixing them would be regarded as negligible.

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[*Received, July 10th*, 1931.]