at this stage, and as a result the corresponding benzyl-benzoic acids were the only compounds isolated and identified.

5. *o*-Phthalaldehydic acid was condensed with phenol, anisole and *p*-bromo-anisole to give the corresponding substituted phthalides.

6. In the condensation of opianic acid with phenol, anisole, *o*-cresol and *m*-cresol, by-products were formed. These were found to be derivatives of *bis*-phthalidyl phenol, formed by the condensation of two molecules of opianic acid with one of the phenol or phenol derivatives. By varying the conditions these could frequently be made the main product of reaction.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

A STUDY OF THE SYSTEM: ACETANILIDE–PROPIONANILIDE

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Incidental to a study of ketenes, Hurd[1] reports that fractional crystallization of mixtures of acetanilide and propionanilide yields a crystalline material melting sharply at 79.0–79.5°, but states that it is not a definite compound. The behavior would seem to indicate either that the material is a compound or a solid solution, and it was thought by the writers that a study of the freezing-point curves of mixtures of the two substances might furnish additional confirmation of his conclusions.

Experimental

Materials.—Propionanilide was prepared by refluxing redistilled aniline with propionic acid (Eastman Kodak Company). It was recrystallized from alcohol and carbon tetrachloride and melted at 105.0° (corr.).

The acetanilide (Merck) was recrystallized from alcohol, acetone and carbon tetrachloride and froze at 113.6° (corr.).

It was found early in the investigation that very small traces of water had a large effect on the freezing point, though not so much on the customary capillary tube melting point, so the materials were preserved at all times in a vacuum desiccator over sulfuric acid.

Manipulation.—Mixtures of approximately 10 g. each were made up by weight in a large stoppered test-tube, fused and then placed in a Dewar flask filled with hot water. A stirrer and an accurately calibrated thermometer were inserted and the temperature noted while the system cooled. The points at which the first solid phase separated out were obtained with ease and accuracy as there was always a small amount of supercooling, with the resultant rise of temperature. Where the per cent. of either component was large, the system was almost solid at the tem-

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[1] Hurd, THIS JOURNAL, 45, 3095 (1923).

perature at which the second solid phase appeared and it was difficult to obtain equilibrium conditions and also contact of the mixture with the thermometer. Stirring, such as was permitted by the state of the mixture, aided. Without it the lower points of inflection on the curves fell many degrees too low. No difficulty was experienced with the middle range portions. All temperatures were corrected for emergent stem.

Results

The freezing points of various mixtures are given in Table I and the results are plotted graphically in Fig. 1.

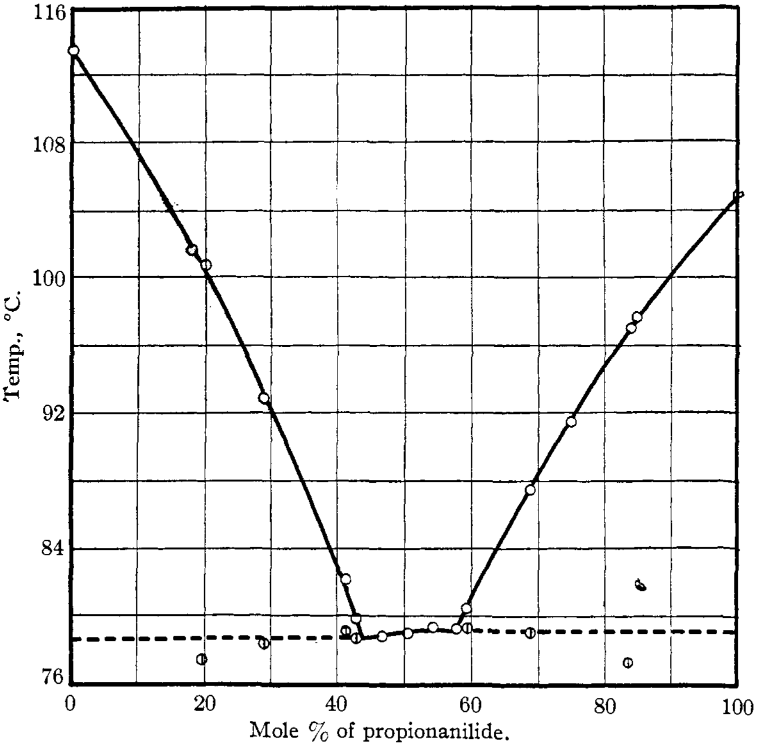

Fig. 1.—Freezing-point composition curves for the system: acetanilide-propionanilide. ○ Freezing points of mixtures. ⦶ Temp. of eutectic halting point.

Discussion

The completed freezing-point-composition curve of the system offers strong evidence of the formation of a compound of the two substances. The central portion is very flat, indicating that the compound is practically completely dissociated in the liquid state. In fact the temperatures along the middle branch of the curve are so close together that the maximum (if any) representing the exact freezing point of the compound cannot

TABLE I

FREEZING POINTS OF MIXTURES OF ACETANILIDE AND PROPIONANILIDE

Mole % of propionanilide	Freezing point, °C.	Temp. of eutectic, °C.
0.0	113.6	..
17.75	101.6	74.2
19.76	100.7	77.5
28.70	92.9	78.4
41.00	82.2	79.2
42.76	79.9	78.8
46.65	78.9	..
50.51	79.1	..
50.93	79.2	..
54.13	79.4	..
48.94	79.1	..
57.85	79.4	..
59.10	80.6	79.4
69.02	88.6	79.2
75.00	91.6	..
83.75	97.1	77.1
84.33	97.7	..
100.00	105.0	..

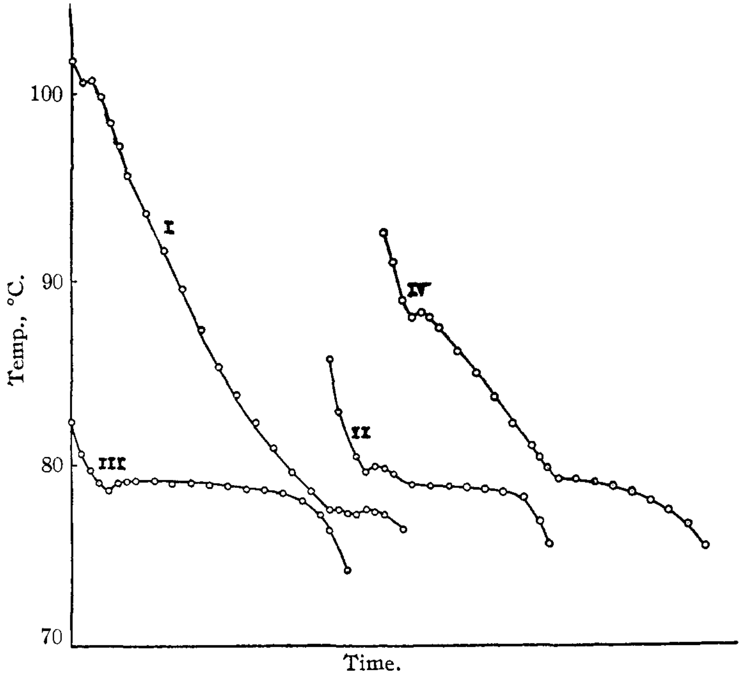

Fig. 2.—Cooling curves. System: acetanilide-propionanilide. Mole % of propionanilide: I, 19.76; II, 42.76; III, 50.51; IV, 69.02. (Curve I made with air cooling.)

be determined accurately. These same temperatures 79.1–79.4°, however, coincide definitely with the melting point reported by Hurd,[1] 79.0–79.5°. From a consideration of the combustion analysis (and other data apparently not included in his article) Hurd concludes that the constant melting substance is a mixture or a solid solution, and the freezing point curve might almost be drawn on that basis, since the central portion is so flat. Consideration of the individual cooling curves (Fig. 2), however, each having two definite breaks, many times with supercooling in each, indicates clearly that in our work we are not dealing with a solid solution but with a compound which forms eutectic mixtures with the pure components. The lower break on each curve occurs within limits of the experimental technique, at the same temperature.

A study of the curves obtained by plotting "eutectic halting time" against composition leads to the conclusion, further, that the system forms no solid solutions, the solid phases consisting of the pure components and the compound.

Summary

1. The freezing-point curves of the system acetanilide-propionanilide have been determined.

2. The presence of a compound, almost completely dissociated in the liquid state, is indicated. The central portion of the curve is so flat that the composition of the compound cannot be determined with certainty.

3. The melting point of the compound is 79.2–79.4°.

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HALOGENATED TERTIARY AMINES

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A considerable number of halogenated amines are reported in the literature but as a general rule their properties have not been studied in detail. Gabriel[1] has prepared chloro-ethylamine and bromo-ethylamine and has shown that they undergo internal condensations very easily. Knorr[2] and his students have prepared a few derivatives of the type $XCH_2CH_2NR_2$ and $XCH_2CH_2CH_2NR_2$ and have studied their tendency toward ring formation. The first type forms six-membered piperazine rings and the second type forms eight-membered rings containing two nitrogen atoms. The delta halogenated butylamines have

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[1] (a) Gabriel, *Ber.*, **21**, 567, 574 (1888); (b) **22**, 1140 (1889).

[2] (a) Knorr, *Ber.*, **37**, 3511 (1904); (b) Knorr and Roth, *Ber.*, **39**, 1424 (1906); (c) Hörlein and Kneisel, *Ber.*, **39**, 1429 (1906).