[CONTRIBUTION FROM THE JARVIS CHEMICAL LABORATORY OF TRINITY COLLEGE]

Purification and Physical Properties of Organic Compounds. X. The Freezing Point Diagram for the System Acetanilide–Propionanilide[1]

BY EVALD L. SKAU AND LOUIS F. ROWE

In 1923 Hurd[2] isolated a white crystalline substance composed of propionanilide and acetanilide and concluded that in spite of the sharp melting point and apparent homogeneity of its long needle-like crystals it was not a compound but a mixture. Gilbert and Clarke[3] constructed the freezing point diagram of this binary system by a slightly modified Beckmann method and concluded that a compound crystallized from mixtures containing between 43 and 58 mole per cent. of propionanilide. Due to the unreliability of the Beckmann method for determining binary freezing points[4] it was thought desirable to reconstruct the diagram using a static method.

Materials.—Eastman Kodak Co. products were purified by repeated recrystallization from acetone. Their freezing points were determined by means of heating curves in an apparatus described elsewhere.[5] The curves showed that each still contained a trace of impurity.

Method.—The sample weighing from 1 to 3 g. was sealed in a glass tube (12 mm. diameter and 1 mm. wall thickness) extreme precautions being taken to avoid any overheating. The sample tube was fastened to the arm of an electric bell and vigorously agitated in a 2-liter water or glycerol bath. A 17-ohm nichrome filament wound around a Pyrex U-tube and connected to a lighting circuit through an 80-ohm Vitrohm rheostat controlled the temperature of the bath. A stream of bubbles released below the heater wires circulated the liquid. The temperature of the bath was measured by means of a carefully calibrated thermometer with 0.1° graduations. This type of thermostat was very easy to manipulate from one constant temperature to another and the temperatures in various parts of the bath differed by less than 0.1°.

The freezing point was determined by finding two temperatures, 0.2° or less apart, such that at the lower temperature a few crystals[6] persisted during thirty minutes of agitation and at the higher temperature the sample became completely liquid. The average of these two temperatures was taken as the freezing point of the sample after stem-emersion and calibration corrections had been made.

(1) From part of a thesis submitted by Louis F. Rowe in partial fulfillment of the requirements for a Master of Science Degree at Trinity College, 1933.

(2) Hurd, THIS JOURNAL, **45**, 3095 (1923).

(3) Gilbert and Clarke, *ibid.*, **49**, 2296 (1927).

(4) For an analysis of the magnitude of the errors involved see Skau and Saxton, *J. Phys. Chem.*, **37**, 183 (1933). See also Andrews, Kohman and Johnston, *ibid.*, **29**, 914 (1925); Skau, THIS JOURNAL, **52**, 945 (1930); *J. Phys. Chem.*, **39**, 761 (1935).

(5) Skau, *Proc. Am. Acad. Arts Sci.*, **67**, 551 (1933).

(6) Formed by bringing the very tip of the sample tube containing the liquid at that temperature above the surface and touching it with a cold object.

Results and Discussion

The results are given in Table I and are compared graphically in Fig. 1 with those previously obtained by the Beckmann method. Table I gives the equilibrium temperatures between the melt and the stable crystalline phases. For compositions up to and including 46.00% the crystalline phase is acetanilide (flakes), between 49.95

TABLE I

BINARY FREEZING POINT DATA FOR ACETANILIDE AND PROPIONANILIDE

Mole % of propionanilide	Equilibrium temp., °C.	Mole % of propionanilide	Equilibrium temp., °C.
0.00	114.1	51.48	79.8
10.31	107.9	51.68	79.6
22.76	100.5	51.79	79.6
30.19	95.1	53.40	80.0
39.25	87.9	54.86	80.1
39.30	87.7	56.57	81.35
41.15	86.5	56.95	81.6
41.82	86.0	57.09	82.0
45.00	83.55	60.83	85.0
46.00	82.4	67.16	88.7
49.95	79.4	79.97	96.5
50.77	79.4	90.19	101.6
50.95	79.5	100.00	105.6

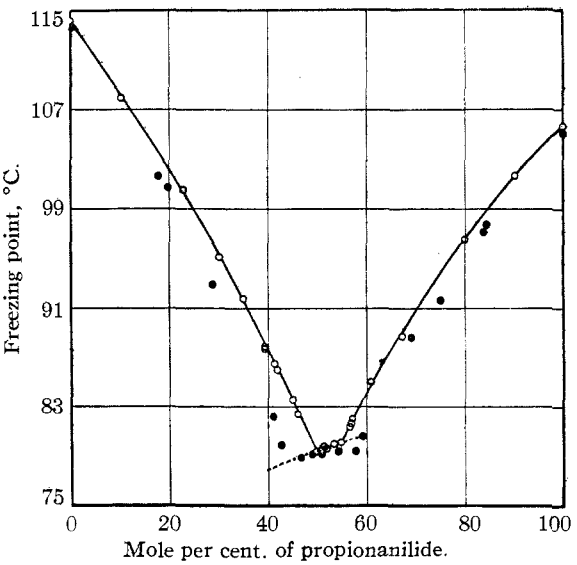

Fig. 1.—Binary freezing point diagram of the system acetanilide–propionanilide: ○, static method; ●, previous authors by Beckmann method; - - - -, unstable equilibrium.

and 54.86% it is compound (needles), and between 56.57 and 100% it is propionanilide (granules).

The results bear out the fact that the Beckmann method, giving values as it does from 0.5 to 5° too low, is not suitable for determining binary freezing points. It is found that the needle-shaped crystals of the compound are in stable equilibrium with liquid mixtures between about 49.5 and 55 mole per cent. of propionanilide instead of between about 43 and 58 mole per cent. as previously accepted. The 49.5 per cent. composition, freezing at 79.4°, is a eutectic between the compound and acetanilide; and the 55 per cent. point, at 80.1°, is an incongruent melting point for the compound.

An interesting fact was noted in regard to the behavior of mixtures between about 42 and 57 mole per cent. propionanilide but outside the compound region. When the tip of the sample tube containing the supercooled liquid was brought above the surface of the bath and touched with a cool object, needle-shaped crystals were formed. These seemed always to melt rapidly when agitated in the bath unless the temperature was below about 79.5° on the acetanilide side and about 80.2 to 80.5° on the propionanilide side. If the temperature was so regulated that the needles persisted, the liquid became turbid in a few minutes and very soon the characteristic flake-like crystals of acetanilide (or the granular crystals of propionanilide in the case of compositions above 55 per cent.) formed as the needles disappeared. These flakes (or granules) did not then disappear until the melting point represented for this composition in the diagram was reached. It was never found possible to cause the flakes of acetanilide to crystallize out spontaneously even by continued agitation at temperatures between the full line and the dotted line in the figure. This behavior makes it seem probable that Gilbert and Clarke were dealing with the unstable solid phase at either end of the compound region and illustrates an additional source of error involved in the Beckmann method.

The determination of the exact composition of the compound was hindered by the great difficulty of isolating it in a pure state but our results indicate that it is perhaps composed of two moles of propionanilide and one mole of acetanilide. A small crop of the needle-shaped crystals was crystallized from a mixture containing 55 mole per cent. of propionanilide and separated by means of a centrifugal filtration tube.[7] Due to the fact that the temperature range over which the compound forms is so small (0.7°) these crystals were undoubtedly contaminated with a very considerable amount of the eutectic mixture of about 49.5 per cent. composition. Their melting point was 80.2° and after being kept just below this temperature for a few minutes, granular propionanilide crystals formed which did not dissolve until 81.3° had been reached, corresponding to a composition of 56.5 mole per cent. of propionanilide. This also corroborates the fact that the compound has an incongruent melting point.

Grateful acknowledgment is made for grants from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences and from Curtis H. Veeder, of Hartford, which have made this investigation possible.

Summary

The binary freezing point diagram for the acetanilide–propionanilide system has been reconstructed by means of an accurate static method; the Beckmann method for binary freezing point determinations has again been shown to be unreliable. The system shows compound formation with incongruent melting. The compound tends to crystallize out in unstable equilibrium from liquid mixtures near the compound region.

HARTFORD, CONN. RECEIVED JULY 24, 1935

(7) Skau and Rowe, *J. Ind. Eng. Chem., Anal. Ed.*, **3**, 147 (1931)