Disintegrated wheat starch was extracted in a rubber type Soxhlet extractor with 80% dioxane–water solution (constant boiling mixture). After one and two week periods the starch was dried and analyzed for "fat by hydrolysis" and phosphorus. The results were as follows: fat 0.015 and 0.000%, respectively; phosphorus, 0.004 and 0.003%, respectively.

Summary

Extraction of raw and disintegrated wheat starch with methanol removes most of the fat and phosphorus. Extraction of disintegrated wheat starch with 80% dioxane–water solution (constant boiling mixture) removes all the fat but not all the phosphorus. This shows that a small amount of the phosphorus is present not as a phospholipid, but possibly linked in some way with the starch. The extracted starch is more nearly free of phosphorus than any starch previously reported in the literature.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

The Binary System Stearonitrile–Palmitonitrile

BY EVERETT J. HOFFMAN, C. W. HOERR AND A. W. RALSTON

Binary systems of long-chain compounds have been the subject of numerous investigations. The saturated acids have received the most attention,[1] while binary systems involving the ethyl and methyl esters,[2-5] the alcohols[2,3,6] the alkyl iodides,[7] the amides and related compounds,[5] and also the hydrocarbons[6,7] have been studied. These investigations have been rendered rather complex by the existence of various polymorphic forms, and in many instances complete phase diagrams have not been obtained.

Smith[2] found two forms of ethyl stearate and ethyl palmitate although he was unable to obtain the high melting form for compositions very far removed from the pure components, the lower-melting modifications forming a continuous series of solid solutions without minimum or maximum. The portions of the curve obtained for the high melting form indicated that they were part of a system with a minimum melting point. Mumford and Phillips[4] obtained similar results for the systems ethyl myristate–ethyl palmitate and ethyl laurate–ethyl myristate. With decreasing molecular weight of the components, larger portions of the upper curve (high melting modification) and smaller portions of the lower curve (low freezing modification) were found until, for the system ethyl decoate–ethyl laurate, only the melting curve for the higher modification was shown. In this case, the minimum melting point is definitely indicated. Guy and Smith[5] showed that methy, palmitate and methyl stearate are polymorphousl yielding transparent (metastable) and opaque crystals. In mixtures, the transparent form is stabilized. The evidence for compound formation was inconclusive according to these authors. Smith[2] showed that the system hexadecyl alcohol–octadecyl alcohol forms a continuous series of solid solutions with a minimum.

Investigation of the system octadecyl iodide–hexadecyl iodide[7] showed that some change took place in the crystals soon after formation although there was no evidence of polymorphism in the cooling curves. Except near the extreme compositions, the mixtures crystallized slowly, and it was difficult to obtain concordant values of the freezing points. The amides and anilides of palmitic and stearic acids[5] yield mixed melting point curves similar to the curves for the corresponding acids, although there is less depression of the melting point. An equimolecular compound is formed in each case.

Phillips and Mumford[8] found no evidence of polymorphism in pure hexadecane, but Smith[7] showed that about 5% of octadecane is required to stabilize the metastable (transparent) form. This is similar to the result obtained for the system ethyl palmitate–ethyl stearate.[2] A mixture containing 2 mole per cent. of octadecane cools to 16.11°, and the temperature remains constant while the transparent form separates. These crystals can be kept for several minutes, but if they are pressed with a thermometer (or stirred), they immediately become opaque, and the temperature rises 1.2°. The transparent form can be kept for several hours if the composition is near that of the minimum freezing mixture (5.3 mole per cent. octadecane). Meyer and Reid[9] made similar observations in their study of octadecyl acetate. This behavior was also observed in the present investigation in the vicinity of the minimum freezing composition.

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(1) W. Heintz, *Pogg. Ann.*, **92**, 588 (1854); L. E. O. de Visser, *Rec. trav. chim.*, **17**, 182, 346 (1898); E. Carlinfanti and M. Levi-Malvano, *Gazz. chim. ital.*, **39**, II, 353 (1909); G. T. Morgan and A. R. Bowen, *J. Soc. Chem. Ind.*, **43**, 346T (1924); N. N. Efremow, *Ann. inst. polytech. Oural*, **6**, 155 (1927); R. L. Shriner, J. M. Fulton and D. Burks, Jr., THIS JOURNAL, **55**, 1494 (1933); R. N. Wenzel, *Ind. Eng. Chem., Anal. Ed.*, **6**, 1 (1934); R. Ashton, R. Robinson and J. C. Smith, *J. Chem. Soc.*, 283 (1936); J. C. Smith, *ibid.*, 625 (1936); H. A. Schuette and H. A. Vogel, *Oil and Soap*, **17**, 155 (1940); H. A. Schuette, R. N. Christenson and H. A. Vogel, *ibid.*, **20**, 263 (1943).

(2) J. C. Smith, *J. Chem. Soc.*, 802 (1931).

(3) P. C. Carey and J. C. Smith, *ibid.*, 635 (1933).

(4) J. W. C. Phillips and S. A. Mumford, *Rec. trav. chim.*, **52**, 175, 181 (1933).

(5) J. B. Guy and J. C. Smith, *J. Chem. Soc.*, 615 (1939).

(6) P. C. Carey and J. C. Smith, *ibid.*, 1348 (1933).

(7) J. C. Smith, *ibid.*, 737 (1932).

(8) J. W. C. Phillips and S. A. Mumford, *ibid.*, 1735 (1931).

(9) J. D. Meyer and E. E. Reid, THIS JOURNAL, **55**, 1574 (1933).

Ferguson and Lutton[10] pointed out that, in general, transformations from one form to another are slowed up when an impurity is present. The impurity may be another member of the same homologous series. This observation has been substantiated by several of the cases cited above.

Experimental

Preparation of Materials: Palmitonitrile.—Neo Fat 1-56 (Armour and Co., Chicago, Illinois) was distilled *in vacuo*, and approximately the middle 60% was retained. The distilled acid was then crystallized from acetone (10% solute) at *ca.* 5°. The acid (crude palmitic) was again distilled *in vacuo*, and a small forerun and residue were discarded (weight of distillate was 45.5% of starting material). This distilled acid was redistilled *in vacuo* through a Stedman Packed Column; eight fractions were collected. The four middle fractions (f. p. 62.18, 62.40, 62.34, 62.12°) were combined (yield 20.2%, based on starting material).

The palmitic acid was converted to palmitonitrile.[11] The crude nitrile was washed repeatedly with hot water to remove any soap present, and it was then dried over anhydrous potassium carbonate (at *ca.* 105°) prior to filtration through more potassium carbonate (anhydrous). The palmitonitrile was then distilled *in vacuo*, and a small forerun was discarded. The remainder of the palmitonitrile was distilled *in vacuo* through the Stedman Packed Column; six fractions were taken. Fractions 4 and 5 (f. p. (cor.) 31.51°) were combined: yield (based on wt. of pure acid) was 57%; (based on wt. of starting material) was 14.1%.

Stearonitrile.—Stearonitrile (N-180 prepared from Neo Fat 1-60, Armour and Co., Chicago, Illinois) was distilled *in vacuo*, and the first 25% of the distillate was discarded. The remainder of the distillate was crystallized twelve times from ethanol (Formula 3A, 10% solutions) at *ca.* 5°. The nitrile was distilled *in vacuo* after the fourth, eighth and twelfth crystallizations. The nitrile was then distilled through a Stedman Packed Column; five fractions were taken. Fractions 2, 3 and 4 (f. p. (cor.) 41.24°) were combined.

Experimental Procedure.—Mixtures of palmitonitrile and stearonitrile were prepared by combining precisely weighed portions of the two components. These samples were melted to ensure thorough mixing.

Heating curves and cooling curves were run on all mixtures and on the two pure nitriles. For these experiments a sample was placed in an air-jacketed test-tube in a water-bath. A thermometer (760 mm., graduated in 0.1° intervals, calibrated) was immersed in the sample to a depth of about 10 mm. above the top of the bulb. A nichrome wire stirrer was provided to stir the molten sample. On cooling, the sample was stirred vigorously until just shortly after crystals appeared. On heating, the stirrer was moved gently after melting started, but no stirring was attempted until all large portions of solid were broken up. Temperature readings were taken at one-minute intervals during both heating and cooling experiments. The rate of heating or of cooling the water-bath was adjusted so that it was practically constant (*ca.* 0.3° per min.).

Several compositions were investigated by another method. Samples were sealed in small glass tubes which were placed directly in the water-bath. For this test, the temperature of the water-bath was maintained constant or else was varied very slowly depending on the purpose of the particular experiment. Visual, as well as thermal, observations were made during the course of the various experiments.

A third method of investigation employed was the slow cooling of a sample immersed directly in the water-bath, until crystallization commenced, followed immediately by the addition of a small amount of heat to melt the crystals. This method aided in the establishment of the freezing curve and eliminated the possibility of any questions in regard to supercooling.

A modified type of cooling curve was also employed. For these experiments the sample was placed in the air-jacketed test-tube in the water-bath which was maintained at a temperature approximately one degree below that at which crystallization would commence as determined from previous experiments. The rate of cooling was so slow that supercooling was practically eliminated. The temperature of crystallization would remain constant until transformation to the higher melting form began. It would then rise to the higher melting point. During this portion of the experiment, the temperature of the water-bath was allowed to rise slowly in order to minimize any heat loss. However, care was taken to maintain the temperature of the water-bath at least a half degree below that of the sample.

Some samples were chilled rapidly by plunging them into an acetone–Dry Ice-bath, and they were then warmed while observations were made over a limited temperature range (usually *ca.* 10°). For this purpose the temperature of the water-bath was set slightly above the upper limit of the temperature range being investigated. This is similar to the method of Clarkson and Malkin.[12]

Examination of several samples (particularly in the range 10–50 mole per cent. stearonitrile) was made by means of a polarizing microscope.

For certain critical concentrations for which the thermal data were inconclusive, recourse was taken to an entirely different method. This consisted in establishing the solubility curve for the particular forms in acetone and in cyclohexane, followed by extrapolation of the curve to the pure solute. This gives the melting point of the particular form.

Results

The system stearonitrile–palmitonitrile is shown in Fig. 1. Point A represents the freezing point of palmitonitrile, and point B is the freezing point of stearonitrile. The curves AC, CD and DB represent the temperatures at which crystals first appear on cooling samples of the various compositions. These crystals are extremely fine and transparent. If they are warmed immediately, they will melt to form an isotropic solution at the same temperature at which they first appeared. This form will be referred to as the lower-melting or α-form. As the temperature is lowered, solidification continues, becoming complete at temperatures represented by the curves AH, HCJ, FG, GB. On cooling, temperature arrests are obtained at points corresponding to the curves AC, CD, DB, HCJ and DFG.

The diagram for the α-modification shows the formation of a compound with a meritectic or incongruent melting point. The point C (26.3 mole per cent. stearonitrile) at 14.78° is the eutectic. The curve CD is the equilibrium curve for the compound with a submerged maximum at E (apparently corresponding to $C_{17}H_{35}CN\cdot C_{15}H_{31}CN$). The melting point and composition of the compound can be obtained only by inference from the general shape and direction of curve DE, because at D the compound breaks down into stearonitrile and liquid

$$[C_{17}H_{35}CN\cdot C_{15}H_{31}CN] \rightleftarrows C_{17}H_{35}CN + \text{liquid}$$

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(10) R. H. Ferguson and E. S. Lutton, *Chem. Rev.*, **29**, 355 (1941).

(11) A. W. Ralston, H. J. Harwood and W. O. Pool, THIS JOURNAL, **59**, 986 (1937).

(12) C. E. Clarkson and T. Malkin, *J. Chem. Soc.*, 666 (1934).

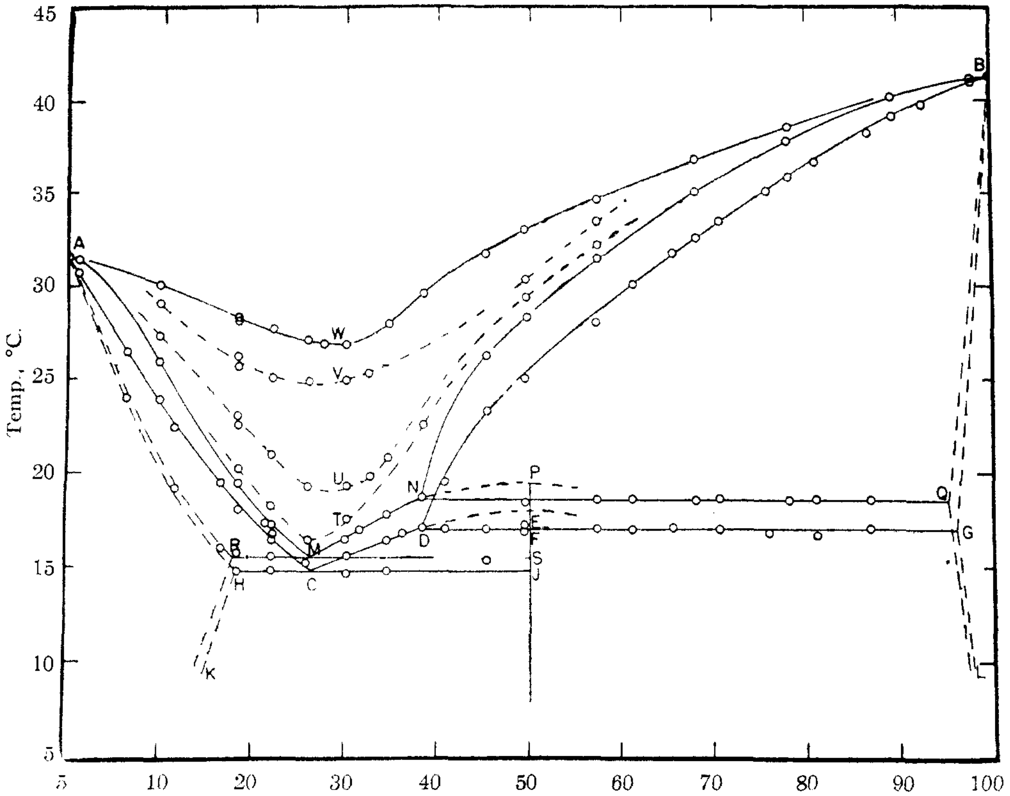

Fig. 1.—The system stearonitrile–palmitonitrile.

This meritectic reaction proceeds at the constant temperature of the meritectic line DG.

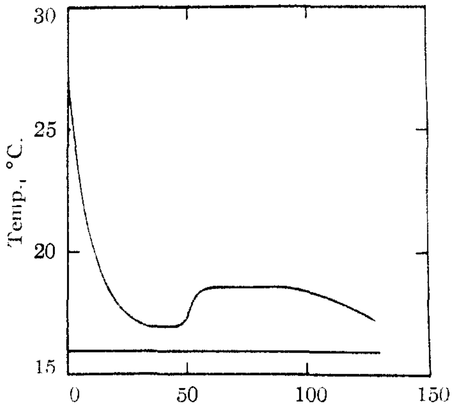

Fig. 2.—Cooling curve showing melting points of α- and β-forms for a mixture containing 38.35 mole per cent. stearonitrile.

The temperature of the eutectic is indicated by the isothermal line HCJ. There is evidence of some mutual solubility of the two components in the solid phase as indicated by the lines AHK and BGL. This system is quite similar to that obtained by Smith in a study of octadecyl and hexadecyl iodides.[7]

Figure 2 shows the result obtained when the modified type of cooling curve (see "Experimental Procedure") is run. This curve is for a sample containing 38.35 mole per cent. stearonitrile and is typical of the curves obtained for other compositions. The temperature remains constant during the crystallization of the α-form and then rises to the freezing point of the higher-melting or β-form during the transformation. The isothermal line about a degree below the temperature of the freezing point of the α-form represents the temperature of the water-bath. The β-modification is a white, opaque, crystalline solid. This behavior in other systems has been cited above[8,9] and is typical of compounds or mixtures possessing two melting points.[13] The freezing points thus obtained for the β-form are represented by the curves AM, MN, NB. The β-system is similar to the α-system in all respects. Most of the behavior of the solid β-form has been deduced from heating curves which show no evidence of the existence of the α-form.

Cooling and heating curves for pure stearo- and palmitonitrile exhibit no evidence of polymorphism since, in each case, there is only a single arrest in the cooling curve occurring at the freezing point. Likewise, in the heating curves, there is

[13] A. A. Morton, "Laboratory Technique in Organic Chemistry," 1st ed., 2nd imp., McGraw-Hill Book Company, Inc., New York, N. Y., 1938, p. 42.

only one arrest, and melting is completed at the same temperature at which freezing occurs within the limits of experimental precision. The addition of either component to the other permits the realization of both forms. This fact has been demonstrated for compositions of approximately 99 mole per cent. of either of the nitriles. This behavior is identical with that observed by Smith[6,7] in his study of hydrocarbon systems, and is apparently a common phenomenon in systems of aliphatic compounds of high molecular weight.[14]

When the β-form melts it does not form an isotropic liquid immediately but goes through a series of mesomorphic states as represented by the transition curves T, U and V, finally becoming clear along curve W. Samples in this concentration range were examined by means of a polarizing microscope and gave no evidence of any crystalline structure at temperatures above the curves AM, MN, NB. Curve W was obtained readily on visual observation. There was evidence for curves T, U and V from thermal data, but the changes in direction of the curves were insufficient to establish definitely the location of these transitions. This was accomplished by determining the solubility in acetone and in cyclohexane of several samples at various concentrations of solute and extrapolating to the pure solute. Points obtained in this manner have been used in conjunction with the thermal data in the establishment of curves T, U and V. Solubility measurements of this sort on the pure nitriles indicated the existence of only one form since in both cases extrapolation of all solution temperatures gave only one melting point for each.

A mixture of stearonitrile and palmitonitrile of any composition whatsoever, if initially heated to a temperature above curve W, will remain entirely an isotropic liquid for an indefinite period on cooling so long as the temperature does not fall below the corresponding point on the α-liquidus (AC, CD, DB). Likewise, if a sample has been cooled and allowed to transform to the β-modification, it may be warmed but will not become an isotropic liquid below the corresponding temperature on curve W. Samples in the composition range 10–80 mole per cent. stearonitrile in sealed glass tubes have exhibited the above described behavior when held at the proper temperatures in a water-bath over a period of ten days.

Summary

1. The investigation of the system stearonitrile–palmitonitrile shows that mixtures of these compounds exhibit dimorphism, although no such behavior was observed in the case of the pure components.

2. The α-form shows the formation of a compound containing one mole of each component, with a meritectic or incongruent melting point.

3. The α-form can be obtained only by cooling a molten mixture of the nitriles.

4. The β-form, which can be obtained only by transition from the α-form, exhibits the same type of system as the α-form.

5. The α-form melts to form an isotropic liquid whereas the β-form passes through a series of mesomorphic states before producing an isotropic liquid.

CHICAGO, ILLINOIS RECEIVED DECEMBER 1, 1944

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[14] Unpublished observations in this Laboratory.

[CONTRIBUTION FROM GENERAL ELECTRIC RESEARCH LABORATORY]

The Vapor Phase Alkylation and Hydrogenation of Chlorosilanes

BY DALLAS T. HURD

In 1919 Stock and Somieski[1] reported the methylation of monochlorosilane and dichlorosilane to methylsilane and dimethylsilane, respectively, by the reaction of the chlorosilanes with zinc dimethyl at room temperature. Attempts in this Laboratory to apply this reaction to the methylation of silicon tetrachloride and dimethyldichlorosilane have been made using aluminum trimethyl and mercury dimethyl as well as zinc dimethyl. Although temperatures as high as 150° have been employed, such attempts have been without success. The mixtures have stood for over four months with no indication of any reaction.

It recently has been found possible to effect the alkylation of silicon tetrachloride and various organochlorosilanes by passing the vapors of a chlorosilane together with an alkyl halide over finely divided aluminum, zinc or other reactive metal at elevated temperatures, 300–500°. A reaction occurs under these conditions with replacement of part or all of the chlorine on the chlorosilane by alkyl groups.

In addition it has been found that the reaction of a chlorosilane with hydrogen gas or with hydrogen chloride under similar conditions results in the removal of chlorine and the formation of Si–H bonds. The halogen involved in these reactions is removed as a chloride of the particular metal used. Although aluminum and zinc have so far been found to be the most suitable reactive metals, others may possibly be of use.

Experimental

Apparatus.—The reactions were generally carried out in vertical Pyrex tubes 3″ in diameter and 24″ long, although

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[1] A. Stock and C. Somieski, *Ber.*, **52**, 695 (1919).