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An X-Ray Study of the Stepwise Melting of Anhydrous Sodium Palmitate*

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X-ray powder patterns on anhydrous sodium palmitate show that the five phases already known to occur between crystal and isotropic melt can be grouped into two basic structures. Both structures are liquid crystalline, i.e., crystalline in the direction of the long spacing and liquid-like laterally. Between the lower temperature "waxy" structure, which includes the previously known subwaxy, waxy, and superwaxy phases, and the higher temperature "neat" structure, which includes subneat and neat, there is a pronounced break in the curve of long spacing *vs.* temperature; in addition, the three waxy phases exhibit two diffuse short spacing rings, whereas the neat phases exhibit only one. These pattern differences lead to the interpretation that the waxy phases contain structural restraints on molecular position and motion not present in the neat phases.

I. INTRODUCTION

THE present paper describes an x-ray study of the progressive melting behavior of anhydrous sodium palmitate. Previously, six phase transitions have been reported to occur in anhydrous sodium palmitate between the crystalline state and isotropic melt. The present study was carried out more to investigate the structure of these high temperature phases than to check previous transition temperatures. The data to be presented show that, as the soap is heated, it transforms from the fully crystalline state to the isotropic liquid state, or "nigre," by way of two intermediate basic structures, one of which embraces the three waxy phases (subwaxy, waxy, and superwaxy) and the other the two neat phases (neat and subneat).

For background, Table I lists chronologically the transition temperatures obtained by various recent investigators and the experimental methods used. Vold, Rosevear, and Ferguson,¹ who discuss the work prior to 1939, report the determination of four transition temperatures found by the dilatometer and polarizing microscope. These results are corroborated, with slight differences in transition temperatures, by Vold and Vold² who, in addition, resolved the waxy phase into two phases, subwaxy and waxy. These same

investigators³ later discovered with the dilatometer and the hot wire microscope technique of Bernal⁴ the waxy-superwaxy transition at 172°C, bringing the total of waxy phases to three. Chesley⁵ examined the melting behavior of anhydrous sodium palmitate by taking x-ray patterns from room temperature up to 300°C and listed all of the previously described transitions, except the waxy-superwaxy one at 172°C. Finally, R. D. Vold⁶ applied a differential calorimeter technique to the problem and found all of the transitions except the waxy-superwaxy one at 172°C. Thus, the phase sequence on heating is crystal, subwaxy, waxy, superwaxy, subneat, neat, and, finally, isotropic liquid or nigre above 295°C.

II. X-RAY EVIDENCE ON THE HIGH TEMPERATURE PHASES

In Fig. 1 are reproduced illustrative x-ray powder patterns of each of the phases formed as anhydrous sodium palmitate is heated to the temperatures indicated in the figure. Exact reproduction of the patterns in such a figure is difficult, so that most of the details are dealt with graphically in Fig. 2. Nevertheless, certain features should be noted: (a) The long spacing rings are grouped near the center of the pattern and the short spacing rings farther out. (b) There are

* Presented at the meeting of the American Society for X-ray and Electron Diffraction, December 5, 1946, Pittsburgh, Pennsylvania.

¹ R. D. Vold, F. B. Rosevear, and R. H. Ferguson, *Oil and Soap* 16, 48 (1939).

² M. J. Vold and R. D. Vold, *J. Am. Chem. Soc.* 61, 808 (1939).

³ R. D. Vold, *Soap and Sanitary Chemicals* (June, 1940); M. J. Vold, *J. Am. Chem. Soc.* 63, 160 (1941).

⁴ J. D. Bernal and D. Crowfoot, *Trans. Faraday Soc.* 29, 1032 (1933).

⁵ F. G. Chesley, M. S. Thesis, M.I.T. (1940); *J. Chem. Phys.* 8, 643 (1940).

⁶ R. D. Vold, *J. Am. Chem. Soc.* 63, 2915 (1941).

TABLE I. Phase transitions on heating anhydrous sodium palmitate.

Reference	Vold, Rosevear, and Ferguson (1939) ^a	Vold and Vold (1939) ^b	R. D. Vold (1940) M. J. Vold (1941) ^c	Chesley (1940) ^d	R. D. Vold (1941) ^e
Method	Dilatometer and microscope	Dilatometer and microscope	Dilatometer and microscope hot wire	X-ray	Calorimeter
Phase	Transition temperatures, °C				
Crystal	125	117	117	117	114
Subwaxy	—	135	135	138	135
Waxy	—	—	172	—	—
Superwaxy	195	208	208	205	209
Subneat	255	253	253	257	237
Neat	297	292	295	290	292
Nigre					

^a See reference 1.^b See reference 2.^c See reference 3.^d See reference 5.^e See reference 6.

several sharp short spacing rings up to 110°C; at the higher temperatures, any short spacings are diffuse. (c) The patterns of the three waxy phases (subwaxy, waxy, and superwaxy) are similar. (d) The patterns of the two neat phases (neat and subneat) are similar. (e) The long spacing rings of all the phases except nigre are sharp.

Figure 2 shows diagrammatically the dependence of x-ray pattern on temperature as anhydrous sodium palmitate is heated. The transition temperatures (Table I) are indicated by the vertical lines. These data, coupled with certain features displayed in Fig. 1, lead to the following description of the various phases.

The Crystalline Region

In the present work the starting material was omega phase, which is the crystalline phase obtained on cooling the anhydrous soap from the subwaxy or higher regions to room temperature. Below 117°C the soap remains essentially crystalline, as shown by the several sharp diffractions in Fig. 1. The relatively slight change in the long spacing and the strongest short spacing between 25°C and 110°C indicates that omega phase persists, any differences in these and other spacings being possibly the result of Thiessen's⁷ genotypical effect, or of Chesley's⁸ change at 67°, or

⁷ P. A. Thiessen and Eva Ehrlich, *Zeits. f. physik. Chemie* **A165**, 453, 464 (1933).

of simple thermal expansion. Since, on the basis of the evidence in Figs. 1 and 2, there can be no doubt as to the existence of a discontinuity near 120°, and since the details of behavior in the crystalline region are not the concern of this paper, the pairs of points at 25° and 110° are deemed sufficient.

The Waxy Phases

On the basis of the x-ray evidence, the subwaxy, waxy, and superwaxy phases appear to fall into one inclusive structural group. Specifically, all three phases exhibit sharp long spacing rings and two diffuse short spacing halos. In addition, the long spacings of all three phases lie on the same curve for spacing *versus* temperature; the short spacings, though diffuse, likewise appear to fall on continuous curves. The above curve for long spacing *versus* temperature and the presence of two diffuse short spacings serve to distinguish the waxy structure from the crystalline phase, which exhibits several sharp, short spacing rings and long spacing curve which is discontinuous with that of the waxy structure, and from the neat structure, which exhibits only a single, diffuse, short spacing ring and a separate curve for long spacing *versus* temperature. An additional distinction between the waxy and crystalline structures is furnished by the intensity sequence of the long spacing rings (Fig. 1); these rings in the case of the waxy phases show a progressive decrease in intensity with order, while the crystal phase exhibits long spacing rings with odd orders strong.

By way of interpretation, the waxy structure can be described as liquid crystalline, i.e., crystalline in the long spacing direction because the long spacings are sharp, and liquid or amorphous laterally because the short spacings, at 2.9 and 4.8Å, are diffuse. The halo at 4.8Å probably represents the average lateral separation of the hydrocarbon chains in a loose hexagonal packing, and the halo at 2.9Å indicates an additional structural restriction such as an average common orientation of the dipolar end groups of the soap molecules. This restriction of molecular motion may account for the stiffness of the waxy phases.

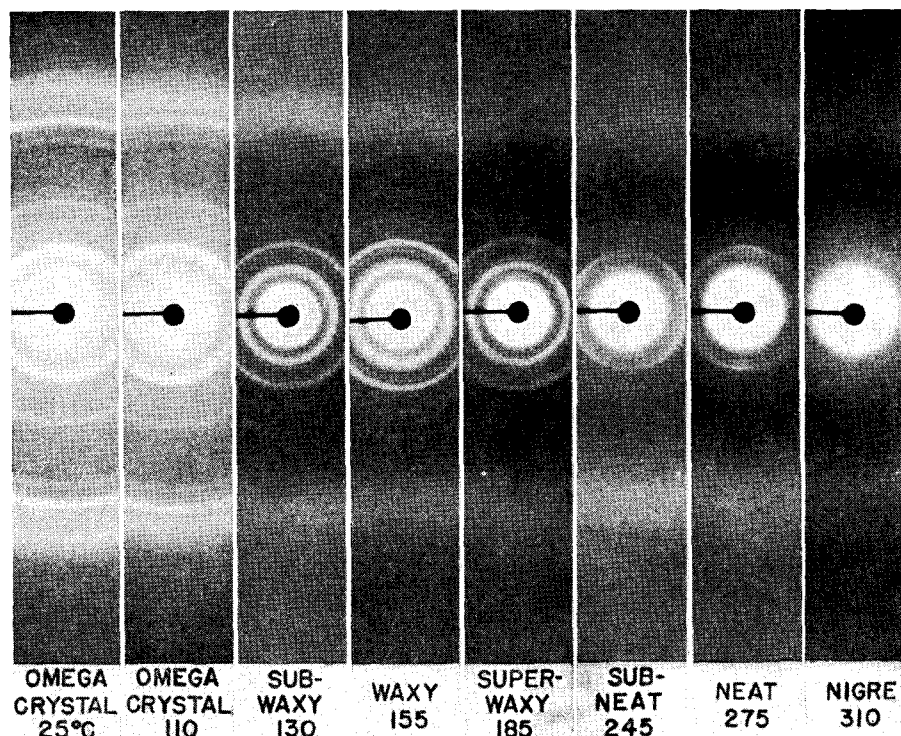


FIG. 1. X-ray patterns of the high temperature phases of anhydrous sodium palmitate.

The Neat Phases

As in the waxy phases, the subneat and neat phases appear to belong to an inclusive basic structure, to judge by the x-ray evidence. Both phases share a common curve for long spacing *versus* temperature.** Furthermore, both show only a single, diffuse, short spacing ring, the 2.9 Å ring of the waxy phases having disappeared in the transition to subneat.

The distinction of the neat structure from the adjacent waxy structure is discussed in the preceding section. The distinction between the neat and the nigre phases is less clear cut on the basis

** In connection with the long spacings of the neat phases, several anomalous long spacings of weaker intensity and fewer orders than the main long spacing have been observed. These are plotted as filled circles in Fig. 2. No really satisfactory explanation for these spacings is known. It is thought that they might arise from planes of Miller indices other than 00 ℓ . Regardless of the origin of these weaker, anomalous long spacings, the experimental fact of the discontinuities in long spacing at the waxy-neat and neat-nigre transitions remains real. For the time being we have limited the interpretations in this paper to a consideration of the more intense, continuously variable, long spacing of the neat phases, as indicated by the straight line through the neat region in Fig. 2.

of x-ray pattern alone, although there seems to be a definite discontinuity in long spacing. The chief pattern difference lies in the character of the long spacing diffractions (Fig. 1); the neat phases exhibit three or four relatively sharp orders of the long spacing, whereas the nigre phase exhibits only two rather diffuse long spacing orders. This information and the microscopic observation that neat is anisotropic while nigre is isotropic, plus the great difference in fluidity (neat being relatively viscous while nigre is a mobile liquid), all contribute to the distinction of the neat phases from nigre.

Structurally the neat phases can be described as crystalline in the long spacing direction, and liquid or amorphous laterally. This description characterizes the smectic state and is in accord with the microscopic identification of anhydrous neat soap as smectic by means of the distinctive batonnets and focal conic texture. As in the waxy phases, the diffuse halo at 4.9 Å probably represents the average interchain distance in a loose hexagonally packed structure. However, since the neat phases exhibit only one short spacing

halo, the chains in the neat structure may be either rotating or in states of frozen rotation. This suggests a possible difference between the subneat and neat phases on the basis of frozen rotation in subneat and actual rotation in the less viscous neat.

The above structural descriptions of the waxy and the neat structures would account on a molecular basis for the greater fluidity of the neat phases over the waxy phases.

The Nigre Phase

The nigre pattern has already been described and discussed. Nigre is an isotropic liquid, and the long spacing diffractions which it exhibits probably arise from short range, one-dimensional order within particles or micelles too small to be detected with the light microscope. As in neat, the single diffuse short spacing ring probably arises from the lateral separation of the molecules.

Relation to Data from Other Methods

The x-ray data and structural interpretations just presented, while by no means invalidating the first-order transitions previously detected by dilatometer, microscope, and calorimeter, suggest that there is one basic waxy structure which em-

braces the three waxy phases and, similarly, that there is one basic neat structure which includes subneat and neat. This raises the question as to why the subwaxy-waxy, the waxy-superwaxy, and the subneat-neat discontinuities are not evident in the curves for x-ray spacing *versus* temperature. An explanation consistent with both x-ray and other evidence is that the phases within each basic structure are actually different and related by a first-order transition, as shown by the dilatometric and other discontinuities, but possess structures which lead to identical x-ray patterns. An example of such a situation is the frozen and free rotation postulated above for the subneat and neat phases. Alternatively, there is a real but relatively slight pattern difference which the present x-ray technique cannot detect. However, even if breaks should be revealed within the basic waxy and neat regions by more precise x-ray technique, they can be only minor compared with the break between these two regions.

III. CORRELATION WITH PREVIOUS X-RAY DATA

The data of Chesley⁵ have been indicated in Table I. He reported all of the transition temperatures, except the waxy to superwaxy one, on

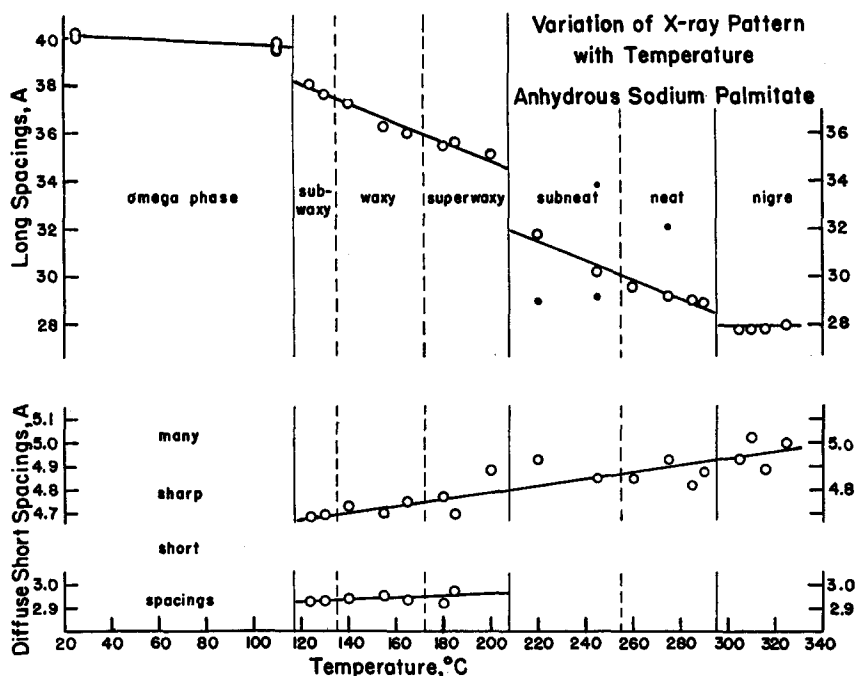
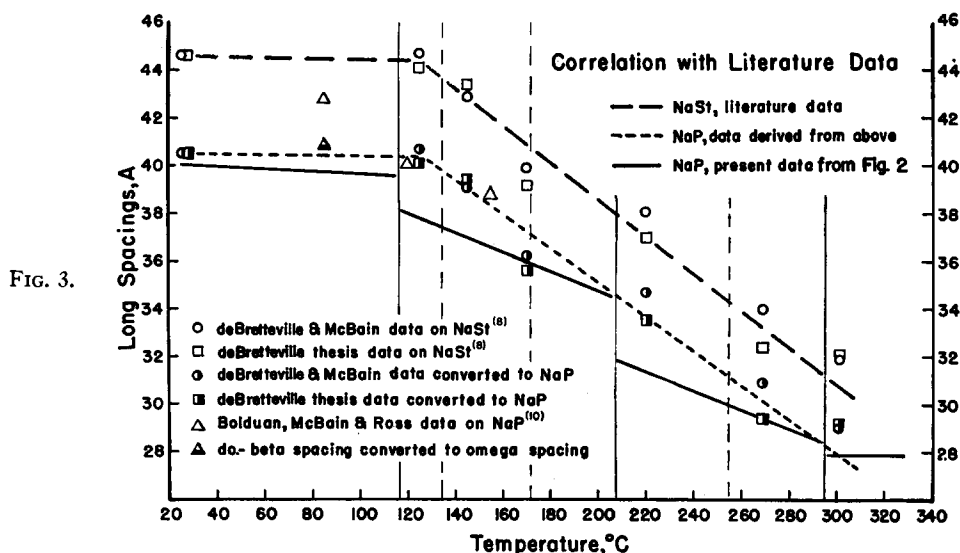


FIG. 2.



the basis of changes in x-ray pattern. The x-ray data of the present paper indicate that the transitions among the waxy phases and between the neat phases are accompanied by a continuous x-ray pattern variation, and therefore the x-ray method cannot be used to determine these transition temperatures. Unfortunately, there are not enough detailed x-ray data in either Chesley's publication or his thesis to make possible a comparison of his data with ours.

DeBretteville and McBain⁸ presented x-ray data on the high temperature phases of anhydrous sodium stearate which can be compared with the present data on palmitate. To begin with, deBretteville and McBain did not find the differences in short spacing between the waxy phases and the neat phases which have just been presented. In fact, they concluded that the subwaxy and waxy phases were definitely crystalline and that the superwaxy phase more nearly resembled the neat phases. Neither of these conclusions is in accord with the data just presented.

A comparison of their long spacing data for anhydrous sodium stearate and the present data on palmitate is shown in Fig. 3. This figure is similar to Fig. 2 except that it shows long spacing data only. The solid lines are the data of this paper, reproduced from Fig. 2, and the dashed curve represents the data of deBretteville and

McBain on sodium stearate. The half-filled squares and circles represent the sodium stearate data scaled down to sodium palmitate by assuming each long spacing quoted to equal $c \sin \beta$ and substituting 44.6 Å, the experimentally determined c length of the sodium palmitate double molecule, instead of 51.4 Å, the c value for sodium stearate.⁹ These derived data, through which the dotted curve has been drawn, should be directly comparable with the present data except for differences in transition temperatures between palmitate and stearate.

It will be seen that the long spacing data on sodium stearate cannot be grouped into separate straight lines for the three waxy phases and the two neat phases. There is need for more data on anhydrous sodium stearate because a minimum of two patterns is required for each phase to test the continuity or discontinuity of the long spacing variation. There is qualitative agreement with our data as regards the break at 117°C, which is the crystal-to-subwaxy transition, and at 170 and 270°C in the waxy and neat regions respectively. In the absence of further experimental data, the discrepancies at other temperatures may be accounted for by lack of complete conversion in their samples or by the differences between palmitate and stearate.

⁸ Alexander deBretteville, Jr. and J. W. McBain, deBretteville Ph.D. Thesis, Stanford University (1941); J. Chem. Phys. 11, 426 (1943).

⁹ R. H. Ferguson and H. Nordsieck, Ind. Eng. Chem. 36, 748 (1944).

Bolduan, McBain, and Ross¹⁰ published x-ray fiber patterns of Na palmitate as supercurd at 85°C, subwaxy at 120°C, and waxy at 155°C. Their long spacing data also appear in Fig. 3. The point at 85°C probably corresponds to beta-phase because a correction for the known difference (42.1–40.2Å)⁹ in long spacing between beta- and omega-phases brings their value into fair agreement with ours. Incidentally, the existence of beta-phase at 85°C probably requires that the sample be partly hydrated. This is in keeping with the fact that the samples used by Bolduan, McBain, and Ross were fibers grown in a hydrous system.

Their subwaxy long spacing at 120°C indicates that the sample was incompletely converted and therefore contained some crystal. This interpretation is supported by the fact that Bolduan, McBain, and Ross found "definite crystallinity" at 120°C, contrary to the findings of this paper. Incomplete conversion is a real danger here because it takes about 2 hours for crystal to convert completely to subwaxy at 120°C even in a small, capillary x-ray sample. The discrepancy in long spacing at 155°C, together with the existence once more of "definite crystallinity," may again be the result of incomplete conversion.

IV. MATERIALS AND METHODS

The sodium palmitate used in this work was made by saponification of palmitic acid (Eastman Kodak Company) with reagent grade sodium hydroxide in alcohol solution followed by oven drying to constant weight at 150°C. This treatment results in omega-phase at room temperature. The palmitic acid had an acid value of 215.5 and saponification value of 216.2 from which the

¹⁰ O. E. A. Bolduan, J. W. McBain, and S. Ross, J. Phys. Chem. **47**, 528 (1943).

molecular weight is calculated to be 259.2 compared with the molecular weight of pure palmitic acid of 256.4.

X-ray patterns were recorded on flat film at 10 cm from the sample, using copper K_α radiation. By this technique the accuracy of the long spacing measurements is, on the average, $\pm 0.5\text{\AA}$ for the various orders of a given spacing; the short spacings, even though diffuse, are accurate within $\pm 0.1\text{\AA}$ (estimated). The sample was enclosed in a Pyrex glass capillary about 1 mm in diameter with a wall thickness of about 0.05 mm and heated in a small furnace attached to the catcher part of the x-ray collimating system. The heating furnace consists of a copper block, $1\frac{1}{4} \times \frac{1}{2} \times \frac{1}{8}$ ", suitably wound with Nichrome resistance wire and insulated with mica and asbestos. The sample capillary is placed inside a longitudinal tunnel through the block, and the x-ray beam traverses the sample at right angles to the tunnel. Temperature is maintained by supplying electrical power to the resistance winding. Water cooling of the film is not necessary by this technique because the film is 10 cm from the sample. The sample temperature is measured by means of an iron-constantan thermocouple inside the block. No great precision in temperature was attempted, so that temperatures are accurate to about ± 2 or 3°C . The time necessary for the sample to attain phase equilibrium differs for the various phases at the various temperatures so that, for each pattern reported here, a sufficient preheating time was used before x-raying to insure that the pattern would undergo no more change at each temperature. The preheating times were determined by recording successive x-ray patterns at $2\frac{1}{2}$ cm, after the sample attained temperature, until no further change in pattern was observed.