New Allotropic Forms of Anhydrous Sodium Palmitate

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Abstract

Two new phases in anhydrous sodium palmitate have been demonstrated. On heating, the crystalline curd phase transforms not directly to liquid crystalline neat soap, as previously believed, but (near 125° C.) to "waxy soap." At 195°, a softer "sub-neat" phase appears. The familiar phases, neat soap and isotropic liquid nigre do not appear until 255° and 297° respectively. All of these phases have a stable range of existence, the transitions being reversible on cooling. *Photomicrographs* of each phase, and a typical dilatometer curve with data illustrate the nature of the evidence.

GENERAL DISCUSSION

THE purpose of this communication is to announce the discovery of two new allotropic modifications of anhydrous sodium palmitate. These new forms of soap exist only at elevated temperatures in the sodium palmitate system, and can be observed either when the solid anhydrous soap is heated, or in reverse order, when the melted soap is cooled. While the new phases exist also in systems of soap and water, the limits of temperature and composition have not yet been determined with sufficient accuracy to report them.

Since 1910, when Vorländer (2) first described the phenomenon, it has been commonly accepted that soap undergoes "double melting." Important additions have been made to the concept of double melting by McBain and coworkers (4), (5), (6). They have pointed out that at very high temperatures anhydrous soap exists as a true liquid, which is essentially continuous with the nigre phase of the binary system of soap and water. They have also indicated the existence of anhydrous soap as a liquid crystalline phase, identified with ordinary neat soap of the soap kettle.

In the table immediately following are summarized the diverse melting points attributed to anhydrous sodium palmitate by the principal authorities.

Observer	1st M. P.	2nd M. P.
Krafft (3)	—	270° C.
Vorländer (2)	220°	265°
	215°	316°
McBain (4)	220°	316°
McBain, Lazarus and Pitter (5)	134°	290°
McBain and Field (6)	216°	316°
International Critical Tables (7)	220°	265°
Lawrence (8)	150°	291°
	155°	259°

It will be observed that Vorländer gives two values for the first melting point, as well as two for the second melting point. No explanation is made for these double figures, which apparently by some random method of selection, are widely quoted and used even today.

Reflected in this group of values is the unquestioned difficulty in making a really accurate determination of the transition temperatures of anhydrous soap by ordinary melting point methods. Except for the highest temperature transition, the changes are difficult to detect, if visual observation alone is relied on. This difficulty is increased by decomposition which occurs in open melting point tubes. In the earlier work too much reliance was perhaps placed on visual methods, although several investigators have used polarized light. In the present work we have made extensive use of the polarizing microscope and have supplemented visual observation with measurement of the change in volume which occurs in the system with change in temperature. A dilatometer has been used for these measurements, which form the basis for drawing the curve shown in Figure 1.

The melting of anhydrous soap, according to the earlier experiments of Vorländer (2) and McBain (4), has been considered to take place as follows. The soap at low temperatures exists in solid, crystalline form which at a temperature of about 220° melts or transforms to a liquid crystalline phase. The latter has been held by McBain to be continuous with neat soap of the soap kettle. Upon further heating to about 265° (or 316°) the liquid crystalline phase has been supposed to melt or transform to a true liquid, considered to be a continuous extension of ordinary solutions formed by dissolving soap in water. The nigres of the soap kettle are, on this view, an extension of essentially the same phase into the three component soap, water, electrolyte system.

Lawrence (8) in a recent paper has introduced some new conceptions, among which there is the denial that a genuine liquid crystalline phase exists in the sodium soaps. He prefers to consider that soaps exist at low temperatures in a "hard, fully crystalline" state which at higher temperatures transforms to a "soft crystalline" state and then to a "very viscous liquid" and finally to an "isotropic liquid of low viscosity."

The present work makes it clear that the foregoing does not give a complete, accurate description of the melting behavior of anhydrous soap. Specifically, at least three (and possibly four) distinct phases instead of one have been found to exist between the solid (curd) phase and the isotropic liquid phase representing complete melting. The evidence, based on volume-temperature relations of the soap when heated in a dilatometer and on the striking changes which are observed when the soap is examined between crossed nicols on the microscope hot stage, is presented graphically in Figure 1. This figure contains the generalized dilatometric curve and photomicrographs representing each form of soap. No attempt has been made in the chart to give detailed numerical results nor the different forms of curve obtained with different heating rates, etc., but the temperatures of the various transitions are given and the relative volume changes at each transition are plotted to scale.

Table I at the end of the paper gives a cross-section of actual numerical data on which Figure 1 is based. The newly reported temperatures of the transitions vary in accuracy. At any temperature, the thermostat can be held within 0.5°; the thermometer has been corrected by comparison under conditions of use with a Bureau of Standards thermometer. The transition points are correct to ± 3° at 297°, ± 2° at 255°, and ± 1° at 195°. All are perfectly reproducible in the sense that they can be obtained time after time (within the above limits) both on heating and cooling. The curd-waxy transition is plotted in Figure 1 at 125°, the mean between the volume changes at 117 ± 1° and 136 ± 1°, as a plot of the results in Table I will show. The results for the transition at 125°, indicate the distinct possibility of two adjacent transitions rather than one. However until further investigation is completed, the curve is drawn as if one transition alone occurred at the midpoint, 125°.

The presence of small quantities of water in the soap causes profound changes not only in transition temperatures, but in the form of the temperature-volume curve itself, as will be noted below. Extraordinary precautions have been taken in the present work to insure dryness of the soap. The dilatometer used was designed with a special lip so that the capillary could be sealed to the bulb without entrance of water from the blast lamp flame. In addition all samples were evacuated in the dilatometer at temperatures above 200° C., before filling the capillary with mercury previous to making runs.

Very little can be seen either visually or microscopically upon heating sodium palmitate in its usual granular or powdery form, until it has been once converted into neat soap or preferably nigre. The photomicrographs shown in this paper were obtained on a thin, transparent layer obtained by melting the soap with minimum decomposition between two cover glasses, then cooling slowly through the neat-nigre transition point so that relatively large "liquid crystals" were formed. "Visual" observations were made on compact plugs of soap formed by solidification of the melt.

Phase Equilibria in Anhydrous Sodium Palmitate.

From an inspection of Figure 1, it will be clear that anhydrous NaP is capable of forming at least five different allotropic modifications:

1. Curd Phase
2. Waxy Soap
3. Sub-neat Soap
4. Neat Soap
5. Nigre

We have named the phases in conformity with the names assigned to phase areas in the hydrous system, which are believed to be continuous with the analogous anhydrous areas.

Phases 2 and 3 have never been reported previously as distinct phases, and are notably not met with in sodium palmitate systems at concentrations involved in soap boiling practice, although the evidence is not complete on this score. The new phase 2 has been named "waxy soap" in harmony with its most pronounced characteristic, and phase 3 has been called tentatively "sub-neat soap," since it occurs immediately below neat soap and is the phase which melts or transforms into neat soap when heated.

1. The Curd Phase-Waxy Phase Transition.

At temperatures below about 125° C. anhydrous NaP exists in the solid, crystalline form, which is identical with the curd phase described by Vold and Ferguson (10) at 90° C., and in general is similar in type to the curd soap of the soap kettle. The curd phase is a hard, brittle, opaque solid (9), which, when examined between crossed nicols has the crystalline appearance shown in the photomicrograph at the bottom of Fig. 1. If scraped

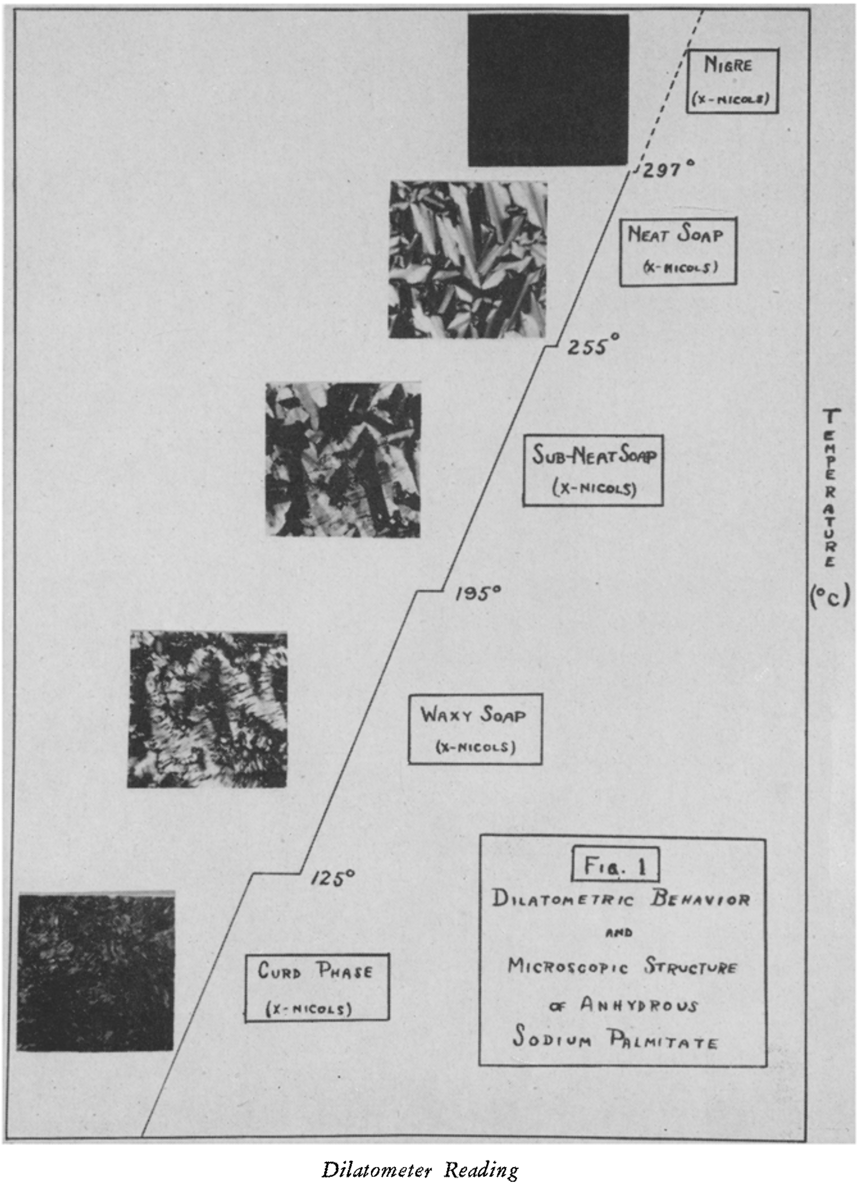

Fig. 1

Dilatometric Behavior and Microscopic Structure of Anhydrous Sodium Palmitate with a knife, it yields a granular powder.

Upon reaching a temperature of about 125° the soap undergoes a phase transition. This transition is accompanied by a marked decrease in density(increase in volume) and by a change in the visual and microscopic appearance of the sample. Visually the soap becomes waxy and more translucent, although still very turbid. Instead of yielding powdery fragments when scraped with a knife, it now yields wax-like ribbons or shreds, which are rubber-like and nonbrittle as compared with curd phase. A very slight plasticity can also be noted around air bubbles in microscopic specimens on the hot stage, and any microscopic fissures* in the solid soap have a tendency to heat together to give a more homogeneous mass, which is waxy.

As the temperature is raised, phase 2 becomes more plastic and, at about 180°, is noticeably deformed by pressing the cover glass over a microscopic specimen with a blunt point.

Under the microscope, phase 2 has the curved structure shown in the second photomicrograph in Figure 1, as compared with the more grainy appearance of phase 1. The change from phase 1 to phase 2 is characterized also by an increase in brightness as observed between crossed nicols on the microscope hot stage.

There are slight but definite divergences in the dilatometer curve at 166° and 177°. The latter corresponds exactly to a change in anhydrous NaL and may indicate its presence in the palmitate.

2. The Waxy Phase-Sub-Neat Transition.

When the temperature of the soap in the dilatometer reaches 195°, another transition occurs which involves a change in specific volume about half that at the lower transition. Sub-neat phase which forms here is "sticky" as compared with waxy phase, but in gross visual appearance the two phases are quite similar. Between crossed nicols on the microscope hot stage, however, the transition is readily observed, the "plaid" structure shown in the photomicrograph being a highly distinguishing characteristic of sub-neat phase. A very definite change under the microscope is always obtained at this transition point, and it is especially notable when the transition is passed by way of cooling rather than heating.

Existing just below neat soap, this phase (phase 3) is tentatively termed sub-neat soap. The evidence indicates that sub-neat soap is a liquid crystalline phase, although like waxy phase, X-ray technique will probably be required to settle its nature more precisely.

It should be noted here that a startling increase in volume is obtained in the dilatometer at this transition if a little water is present in the sample. The great expansion apparently is due to formation of water vapor coincident with the transformation of waxy phase to sub-neat phase. This vapor is reabsorbed when neat soap forms on further heating to just below 255°. The dilatometer curve thus shows a large expansion followed by a large contraction when the phase changes take place in the slightly wet soap. These facts doubtless account for some of the anomalous expansion obtained by Lawrence (8).

3. The Sub-Neat Phase-Neat Phase Transition.

At a temperature of 255° C., sub-neat soap melts or transforms into neat soap. A small but definite increase in volume again occurs. Microscopically, between crossed nicols, the 255° transition is easily observed. The familiar conic structure of neat soap appears, and is at once distinguishable from the "plaid" structure of sub-neat phase. Visually the change is attended with a marked lowering of viscosity, and the system now has the characteristic molten, translucent appearance of neat soap.

All the evidence taken together seems convincing that the phase formed at 255° is neat soap, and that it is continuous and identical in phase nature with the neat soap of the soap kettle.

4. The Neat Phase-Nigre Phase Transition.

Upon heating the anhydrous neat soap to 297° C. (determined microscopically) the turbid anisotropic phase (neat soap) melts sharply and characteristically to a thin, mobile, isotropic liquid which is practically clear and exhibits a meniscus. This liquid, in form, character and appearance is continuous with and identical in type with ordinary soap solutions in the hydrous system and with the nigres of the soap kettle.

The change in volume at this transition or complete melting point is small and since the temperature is very high the dilatometric curve is difficult to establish accurately. However on the microscope hot stage the transition is sharply defined by the areas of isotropic (black between crossed nicols) nigre which form beside the anisotropic (visible structure between crossed nicols) neat soap as the latter melts. The gross change is also easily observed visually. The photomicrographs at the top of figure 1 indicate the striking contrast in appearance at the transition as observed microscopically.

CONCLUSION

At least five allotropic forms are exhibited by anhydrous sodium palmitate. Three have been previously described, although frequently incorrectly as to melting temperatures and relationships. These three are curd phase, neat soap and nigre. They are identical in type and continuous in composition with phases of the same name encountered in soap boiling practice.

Two new allotropic forms, waxy soap and sub-neat soap, have not been described previously, and the evidence indicates that they probably are not continuous with or similar to any form of soap existing at kettle concentrations or temperatures in hydrous NaP systems. For example, at 90° C. neither phase was observed in a hydrous system of NaP-H_2O or NaP-NaCl-H_2O (10). It is possible of course that these phases may exist in other hydrous soaps.

The transition point for curd-neat at 134° given by McBain (5) is believed to be our curd phase-waxy soap transition. The upper limit of our inflection is about 135° and this represents the temperature of the last disappearance of curd fiber as measured by McBain over relatively short periods of time. The value 125° represents the mean inflection of the temperature-volume curves and as pointed out may actually refer to two separate transitions. The new phase into which the last curd fiber melts is not, however, neat soap as believed by McBain, but is phase 2 or waxy soap. Neat soap does not come into existence for another 130° C. of temperature rise.

It is also possible that the transitions reported at 265-70° by previous investigators (2), (3) were in

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*These fissures always form when molten soap is cooled through the 125° transition and are evidence of the pronounced contraction which takes place.

reality our sub-neat to neat transition, although it seems hardly likely that earlier workers failed to distinguish between melting to form liquid crystalline neat soap on the one hand and melting to form isotropic nigre on the other.

ACKNOWLEDGMENT

The authors are very heavily indebted to Dr. A. S. Richardson of this laboratory, under whose direction the work was initiated and carried out. His assistance is also gratefully acknowledged in the interpretation and presentation of the experimental results, upon which this paper is based.

Table I.
Dilatometric Data for Sodium Palmitate.

Temperature (° C.)	Reading* (mm.)	
	Heating	Cooling
90	—72.0	
95	—61.5	
100	—50.5	
105	—38.5	
110	—28.0	
115	—18.5	(+10.0 to —8.5)
116	—16.0	
117	—12.5	+24.0
119	(+21.5 to +29.0)	
120	45.0	
122	50.5	
125	57.5	
130	67.5	
132	73.5	
134	81.0	
135	86.0	(124.0 to 113.5)
136	(90.0 to 101.0)	125.5
140		136.0
150		156.0
152		159.5
156.5	168.0	
160	175.0	
162	178.5	178.5
164		183.0
165		(190.0 to 186.0)
166		(191.5)
167	188.0	
168	(190.5)	199.5
170		204.5
172	208.0	
174	213.0	
176	215.5	(223)
177.5	(220.0 to 222.5)	
178		228.5
180	232.0	232.5
182	236.5	
184	240.7	
185		243.0
186	245.0	
188	249.0	
190	253.5	
192	257.0	
193		(292.0)
194.5	261.5	
195	263.0	
196	(265.0 to 269.0)	
197	(307.0 to 309.0)	315.5
200		322.5
202	326.0	
204	331.0	
206	335.5	
208	340.5	
210	345.5	346.5
211		348.5
212	350.0	
214	355.0	
215		359.0
216	360.0	360.5
217	362.5	
218	365.5	
220	369.5	370.5
225	380.5	
230	391.0	391.5
234.5	402.5	
239.5	413.0	412.0
242		417.5
245	426.5	
249		434.5
251	439.0	439.5
253	444.5	445.0
254.5	449.0 to (450.5)	
255.5	459.0	459.5
257.5	464.0	464.0
261.5	474.0	
266.5	488.5	
272	501.5	501.5
277	515.5	
282.5		530.0
286	540.0	
288		545.5
291.5	554.0	552.5
293.5	559.5	558.5
294.5		562.0
295.5		570.5
297		574.0
299	580.0	580.5
304.5	593.5	

* The dilatometer readings represent the distance of the mercury meniscus from a fixed reference point. These readings are directly proportional to the volume of the soap and could be converted to a volume basis by using capillary calibration, and corrections for the mercury, the dilatomer volume, etc.
( ) represents points in a state of adjustment to the stable equilibrium curve.

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(2) Ber. **43**, 3120 (1910) Vorländer

(3) Ber. **32**, 1598 (1899) Krafft

(4) Alexander's Coll. Chem. Vol. I, Chapter by McBain (1926)

(5) Z. physik Chem. A147, 92-110 (1930)

(6) J. Chem. Soc. p. 921 (1933) McBain & Field

(7) International Critical Tables (1929) Vol. V., p. 449.

(8) A.S.C.Lawrence Trans. Farad. Soc. 34, 660, (1938). The figures given in Table V refer to sodium palmitate monohydrate. If the samples were prepared, as would be inferred, by drying the soap to constant weight at temperatures just above 100° C., anhydrous soap would result.

(9) See Thiessen & Stauff. Z. phys. Chem. A176, 397 (1936), (and previous papers). These authors believe that certain "genotypical" transformations occur within the solid soap at temperatures well below 100° C. Our experience indicates that these changes are relatively small compared with the phase changes discussed herein.

(10) J. Am. Chem. Soc. Sept. 1938 p. 2066 Vold & Ferguson.

LECITHIN-Its Manufacture and Use in the Fat and Oil Industry

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Abstract

Lecithin, produced economically and on a commercial scale from soybeans, has been on the market in this country only since 1929. The lecithin and associated phosphatides are extracted with a petroleum solvent and separated mechanically from the mass of oil. Special grades may be prepared by subjecting to further solvent purification and fractional crystalization.

In the fat and oil industry the properties of lecithin are used to inhibit rancidification and to modify interfacial tension relationships. Quantities used range from .01% to 1.0%. Various applications are noted as in oleomargarine, shortenings, confections, coatings and icings, vitamin oils and for industrial purposes.

WHILE lecithin was first prepared many years ago from egg yolk and brain substance, its development from a laboratory curiosity and costly pharmaceutical into an industrially useful commodity, available in quantity, is of recent date. And this transition waited upon recognition of the natural connection between lecithin and the production of edible oils[1], for essentially lecithin is a close relative of ordinary oils and fats. Indeed, lecithin is a tri-glyceride except for substitution of one of the fatty acid radicals by phosphoric acid combined with a nitrogen containing base[2].

For years the term "lecithin" was used inclusively. The broader term is "phosphatide" and from a strictly technical standpoint lecithin is that alcohol soluble phosphatide containing the base choline. However, commercial lecithins have always consisted of mixtures of phosphatides[3], especially lecithin and cephalin (alcohol insoluble, with amino-ethyl alcohol as the base) along with a carrier of oil and are still generally referred to in the trade as "lecithin." The commercial product may or may not contain an appreciable proportion of carbohydrate. The fatty acid radicals vary depending, for example, on the species of bean and the environment so that phosphatides from American grown beans will differ slightly from those of Manchurian origin. There is always one unsaturated fatty acid radical, however, which appears to