2. The Bernal hot wire technique has been further developed, by means of which the reality of existence of five of the six forms of sodium palmitate intermediate between crystal and liquid can be convincingly demonstrated. The transition temperatures have been determined within about three degrees.

3. Portions of the phase rule diagrams have been determined for five binary mixtures of anhydrous soaps (sodium palmitate–sodium stearate, sodium palmitate–sodium laurate, sodium palmitate–sodium behenate, sodium stearate–sodium laurate, and sodium stearate–sodium oleate).

4. From these diagrams the identity of some of the equivalent intermediate forms of different soaps has been established. These results for the saturated soaps are in entire agreement with the conclusions drawn on the basis of the relations between transition temperature and chain length. The form anhydrous neat soap, found in sodium stearate, is absent in sodium oleate. Neat soap is also absent from sodium behenate.

RECEIVED FEBRUARY 21, 1940

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, STANFORD UNIVERSITY]

Stable Phases Occurring between True Crystal and True Liquid for Single Pure Anhydrous Soaps

BY MARJORIE J. VOLD, MICHAEL MACOMBER AND ROBERT D. VOLD

A dilatometric and microscopic study has been made of the transition temperatures between successive stable forms for all the members of the homologous series of sodium salts of *n*-fatty acids containing an even number of carbon atoms from C_6 to C_{22}, and also for sodium cerotate (C_{26}), sodium oleate, and potassium stearate.

Previously reported values for the "melting points" of soaps have differed widely, sometimes by as much as 100° (see Table III), a condition which, as this work indicates, arises in part from the existence of liquid crystalline phases whose formation might have been inadvertently mistaken for melting to form isotropic liquid. The same difficulty has prevailed with regard to the supposed single transition from crystal to liquid crystal, different workers reporting values for different ones of the three to five such transitions whose existence is demonstrated in this paper.

The data obtained help to provide answers to some of the problems raised by the discovery that sodium palmitate passes through five states in the transformation from its ordinary crystal form into isotropic liquid.[1,2] Three of the most important of these are (1) the extent to which this behavior is general among substances of this type (soaps), (2) whether or not the number of intermediate forms is the same for all soaps, and (3) whether an equivalence or presumption of equivalence exists between individual phases in different soaps.

Experimental Technique and Materials.—The sodium palmitate, sodium oleate, sodium stearate and sodium laurate were from the same stocks used in phase rule studies reported from this Laboratory.[3,4,5] The caproic (C_6), caprylic (C_8), capric (C_{10}), and myristic (C_{14}) acids were Kahlbaum products. The behenic acid (C_{22}) was made for us by Mr. J. F. Carson by catalytic hydrogenation of Kahlbaum erucic acid. The stearic (for the potassium stearate) and cerotic acids were obtained from Eastman Kodak Co. and the arachidic acid from the British Drug Houses, Ltd. Most were used without further purification. The soaps were prepared by neutralizing a known weight of fatty acid with a standardized alcoholic solution of sodium hydroxide made from concentrated sodium drippings and boiled out alcohol. The solvent was evaporated and the soap dried to constant weight.

One of the five preparations of sodium cerotate was made by direct fusion of equivalent amounts of sodium metal and cerotic acid, heating until no further hydrogen was evolved, and another by fusion of cerotic acid with excess sodium, resulting in the presence of sodium carbonate as an impurity in the final product. All contained some apparently non-fusible material (up to 360°) in addition to a portion showing approximately the behavior predicted for sodium cerotate. The best specimen was that made by dissolving equivalent amounts of cerotic acid and of drippings from metallic sodium dissolved in alcohol, to form a clear solution in normal heptane, which was then evaporated to dryness.

Some experiments were also performed on a sodium oleate obtained from Merck; the oleic acid recovered from the soap had a mole weight of 288.5 (theoretical value, 282.2) and an iodine value of 93.4 (theoretical value 90). This soap gave results agreeing with those obtained on the much purer sample from British Drug Houses oleic acid,

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[1] R. D. Vold and M. J. Vold, THIS JOURNAL, **61**, 808 (1939).

[2] R. D. Vold, F. B. Rosevear and R. H. Ferguson, *Oil and Soap*, **XVI**, 48 (1939).

[3] R. D. Vold and M. J. Vold, THIS JOURNAL, **61**, 37 (1939).

[4] R. D. Vold, *J. Phys. Chem.*, **43**, 1213 (1939).

[5] J. W. McBain, R. D. Vold and M. Frick, *J. Phys. Chem.*, Dec. (1940).

prepared by the Lapworth method (molecular weight 284, iodine value 82.1) as to the number of transitions, but transition temperatures differed by 6–16°.

The dilatometer measurements were made by the same technique described by Vold and Vold.[1] Duplicate runs were made in every case on at least two independent samples. Supplementary microscopic observations were made using the Leitz–Weygand hot stage[1] and also a development of the Bernal hot wire technique.[6] These observations were used particularly in the determination of temperatures of formation of isotropic liquid, which is accompanied by only a small volume change, in confirming the realty of other transitions in which the volume change is small, and in establishing the identity of equivalent phases in different soaps through their similarity in appearance.

The most conspicuous changes in appearance, viewed between crossed nicols, are shown in Fig. 1. On cooling from a temperature above its melting point this soap (sodium stearate) first separates multicolored batonnets which cohere to form a vividly colored mass which retains large areas of uniform shading ending in dark irregular seams where contact is established with similar areas differently oriented. This is neat soap. The next phase is still very bright, but the uniform areas are much smaller, and distinct "seams" between differently oriented areas are not visible. On heating, the transition from subneat soap to neat soap is not so pronounced as it is in these photographs, taken during cooling. The next three phases, superwaxy, waxy and subwaxy, all have the same grainy, stippled appearance. Curd fibers forming from subwaxy soap appear as dark lines forming a network throughout the sample.

In the second technique a thin film of soap pressed between cover slips is subjected to a temperature gradient by laying it across a heated wire. A photograph of the sequence of phases in sodium stearate is shown in Fig. 2, the lower strip being taken between crossed polaroids, the upper using the Mikropolychromar.

The Experimental Data

Curves of volume as a function of temperature appear in Fig. 3 for sodium caproate (C_6), caprylate (C_8), caprate (C_{10}), laurate (C_{12}), stearate (C_{18}), arachidate (C_{20}) and behenate (C_{22}). Values of temperatures of transition and of changes in specific volume for these soaps are given in Table I. Figure 3 was constructed by multiplying the observed dilatometer readings by empirical factors so that all could appear upon the same figure. The units of volume have no significance. The significant features of the curves are the temperatures at which discontinuous volume changes ("flats") occur; and these have been indicated by arrows. Each of the curves contains about half the data from a single typical run (except for sodium stearate where portions of two runs, neither of which covered the entire temperature range, have been pieced together). Readings between those plotted have been omitted for clarity.

TABLE I

TRANSITION TEMPERATURES OF SATURATED SODIUM SOAPS

Soap	Transition temperatures[a], °C.
NaC_6	172(0.0035), 207(0.012), 226[b](0.027), 350[b](*ca* .001)
NaC_8	75, 114(0.01), 188, 243(0.018), 347
NaC_{10}	85–100(?), 139(.015), 183(?), 247(0.017), 343
NaC_{12}	100(0.0025), 141(0.025), 182(0.011), 220[b](0.017), 255(0.0025), (244),[c] 336[b,f]
NaC_{14}	107,[b] 141,[b] 176,[c] 217,[b] 245,[b] 310[d](316[d,f])[g]
NaC_{16}[e]	117(0.0085), 135[b](.0148), 172,[e] 208[b](0.027), 253[b](0.0035), 295[b,d,f](0.0021)
NaC_{18}	90(.0069), 117(.0356), 132[b](.0144), 167,[b] 198, (205[c]), 257,[b] 288[b,d,f]
NaC_{20}	110, 131[b](0.013), 163,[b] 200[b](0.017), 262[b]
NaC_{22}	92,[b] 119[b](0.033), 158,[b] 202,[b] 264[b]

[a] Values determined dilatometrically. Values in parentheses are volume changes in cc. per gram of soap. [b] Confirmed by the hot wire technique. [c] Hot wire value. [d] Microscopic observation with Leitz–Weygand hot stage. [e] See ref. 1. [f] Visually determined melting point. [g] Melting point of an independent preparation of sodium myristate.

During the course of the work considerable trouble was caused by "settling," a decrease in volume that occurred on standing, an effect believed to be due to the collapsing of small vacuoles formed when the sample was cooled too rapidly after heating to a high temperature. This settling is particularly common as the hard cake of curd fiber phase softens at the first transition point. It is illustrated by the apparent volume decrease in the curve for sodium caproate (C_{10}) near 105°. On the other hand, the inflection near 188° for sodium caprylate, which seems to correspond to a negative volume change on heating, was reproducible, though experiments with more rigorously purified materials will be necessary to establish its reality.

In one instance it was possible to compare the results obtained with our preparation of sodium stearate with those from a specially purified sample given us by Thiessen and Stauff[7] and prepared in the same way as that used by them in their X-ray work on soaps. Comparison was made only of those transitions that are visible by the hot wire technique. The results are listed in Table II. On the whole the agreement appears satisfactory.

All the soaps except sodium caprylate (C_8) and

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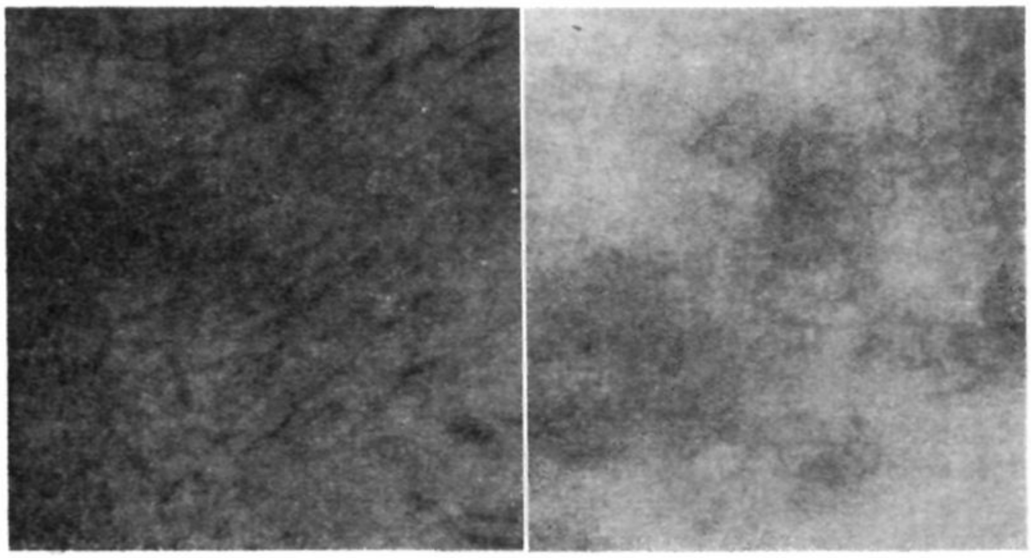
(6) M. J. Vold, THIS JOURNAL, **63**, 160 (1941).

(7) P. A. Thiessen and J. Stauff, *Z. physik. Chem.*, **A176**, 397 (1936).

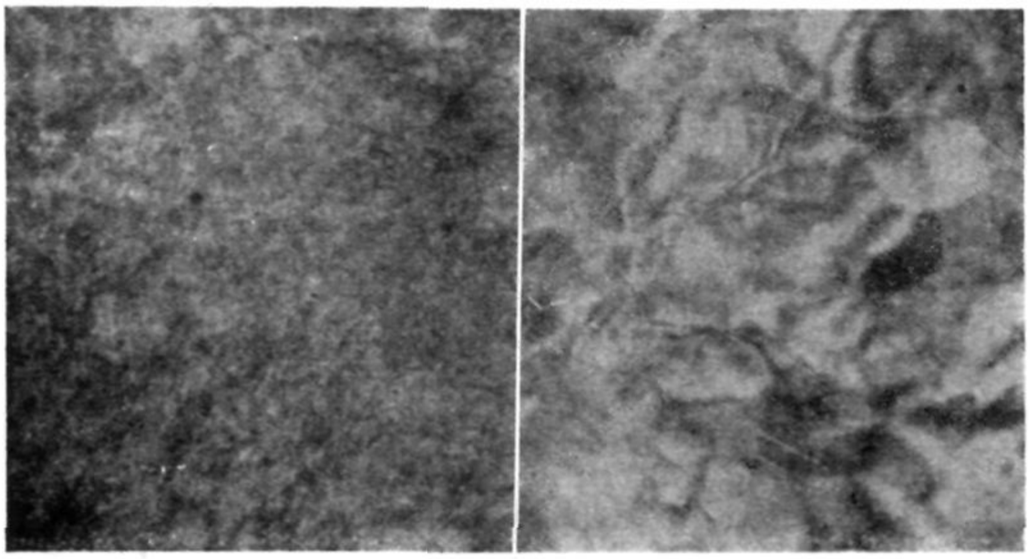
TABLE II

TRANSITION TEMPERATURE OF SODIUM STEARATE

Transition temperature, °C.	Sample and method Vold's dilatometric	 Vold's hot wire	 Thiessen and Stauff's hot wire
Crystal–waxy	132	130	130
Waxy–superwaxy	167	166	169
Superwaxy–subneat	198	205	206
Subneat–neat	257	260	258



a. Curd fibers forming in waxy soap (90°). b. Waxy soap (140°).



c. Subneat soap (215°). d. Neat soap (265°).

Fig 1.—Characteristic microscopic appearance of various phases of sodium stearate (crossed nicols, × 200).

sodium caprate (C_{10}) were also examined using the hot wire microscopic technique. In general, values for the temperatures of transition previously obtained by dilatometer studies were confirmed. Points for which this check has been obtained are marked ^{b} in Table I. There are two instances of disagreement: for sodium stearate near 200° and for sodium laurate near 250°. We have no explanation of these discrepancies.

Despite the very large number of transitions, it cannot yet be stated with assurance that the list is complete. The reality of those reported can be demonstrated convincingly in the particular preparations studied. Furthermore, a plot of transition temperatures against the number of carbon atoms in the molecule resolves itself into a series of smooth curves so that it seems probable that none of the transitions is caused by impurities. Only a very few points are disconnected from these curves, whose existence and properties constitute the chief experimental result of this work. The order of magnitude of the uncertainty in individual transition temperatures may well be as high as three degrees.

The Classification of Transitions

The values obtained for the transition temperatures and melting points have been plotted against the number of carbon atoms in the molecule in Fig. 4 for the nine soaps forming a homologous series. Smooth curves have been drawn through points which are presumed equivalent on the basis of visual and microscopic appearance, relative volume change, and regular variation in transition temperature with chain length.

The transition from superwaxy soap to subneat soap is one of the easiest to identify in the case of single soaps. It is marked uniformly by the largest volume change, and is accompanied by a pronounced increase in translucence and decrease in rigidity. It is the one most frequently reported in work of previous authors as the single transition from crystal to liquid crystal. It is marked by a change in microscopic appearance between crossed nicols from a stippled structure to a coarser and also more highly iridescent structure (b and c of Fig. 1). This transition is also easily identified in the hot wire technique using either crossed polaroids or the Mikropolychromar (see Fig. 2). The outer phase (lower temperature range of existence), superwaxy soap, is only slightly doubly refracting when pressed out between glass plates and is so transparent as to be predominantly the color of the transmitted light. Subneat soap, on the other hand, is highly doubly refracting and, with the Mikropolychromar, shows the color of the scattered light. Finally, without exception, this same transition has been identified for the whole series from C_{12} to C_{22}, and the curve of transition temperature against chain length is fairly smooth.

Four members of the soap series, C_{12} to C_{18}, have an additional transition point between the temperature of formation of subneat soap from superwaxy soap just discussed, and the melting point to ordinary liquid. This transition is accompanied by only a slight volume change, but there is a pronounced increase in transparency and fluidity, so that the transition has previously often been wrongly reported as the melting point. The change is visible, but is conspicuous only with the hot wire technique. The neat soap intermediate between subneat soap and liquid over this range of chain length, rapidly orients itself between glass plates to simulate an isotropic appearance.

The curve of transition temperature against chain length has in this instance a positive slope, and consequently intersects both the curve for change from superwaxy soap to subneat soap and that for formation of isotropic liquid, thus dividing the soaps into three groups. For those of intermediate chain length, subneat soap changes to neat soap, and neat soap melts to isotropic liquid. At longer chain lengths subneat soap goes over in one step at a single temperature to isotropic liquid, while at shorter chain lengths, subneat soap is not formed at all. Direct extrapolation gives C_6 and C_{22} as the intersection points. However, the indicated change in phase sequence occurs before the curves actually intersect, at a value of the chain length where they are less than about twenty degrees apart.

For example, from the curves, sodium arachidate, C_{20}, would be expected to form neat soap at 264° and melt to isotropic liquid at 278°. Actually both transitions occur at the first temperature, which although it lies on the same curve as do changes from subneat to neat soap for other soaps actually involves direct transformation from subneat soap to isotropic liquid. In similar fashion, at the other terminus of the curve for the neat–subneat change, the temperature range of existence of subneat soap is predicted to be eight degrees for C_8 and thirteen degrees for C_{10}, whereas in fact this phase apparently does not exist for either soap. In these cases the volume change accompanying the formation of neat soap is large, as is the case for the formation of subneat soap, rather than small as in cases of formation of neat soap from subneat, giving support to the hypothesis that two transitions that occur separately at higher chain length are here occurring at one temperature.

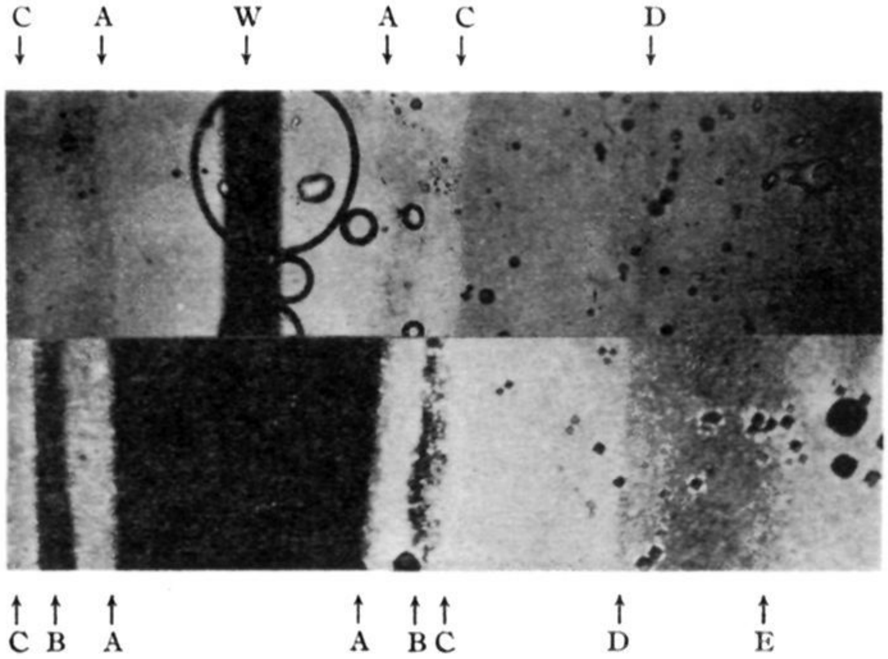


Fig. 2.—Photomicrographs of sodium stearate by the hot-wire technique. Five of the six phases of sodium stearate appear successively as the temperature falls from about 350° near the wire (W) to about 140° at the right-hand edge of the photograph. A, boundary between isotropic liquid and neat soap; C, boundary between neat soap and subneat soap; D, boundary between subneat soap and superwaxy soap; E, boundary between superwaxy soap and waxy soap. The upper photograph was taken with the Micropolychromar, the lower, showing an adjacent portion of the same field of view, with crossed polaroids. Magnification is about 20 fold. At B the neat soap has begun to become oriented, simulating the appearance of isotropic liquid.

The temperatures of formation of isotropic liquid do not lie upon a smooth curve. Furthermore the discrepancies seem far too large to be accounted for by assumed impurities in the materials. The three most important possible contaminants are water, free fatty acid, and adjacent homologous soaps. Work on the transition temperatures of binary mixtures[6] has shown that the presence of up to 10% of homologous soaps would be entirely inadequate to account for the deviations observed. Moreover, in several instances

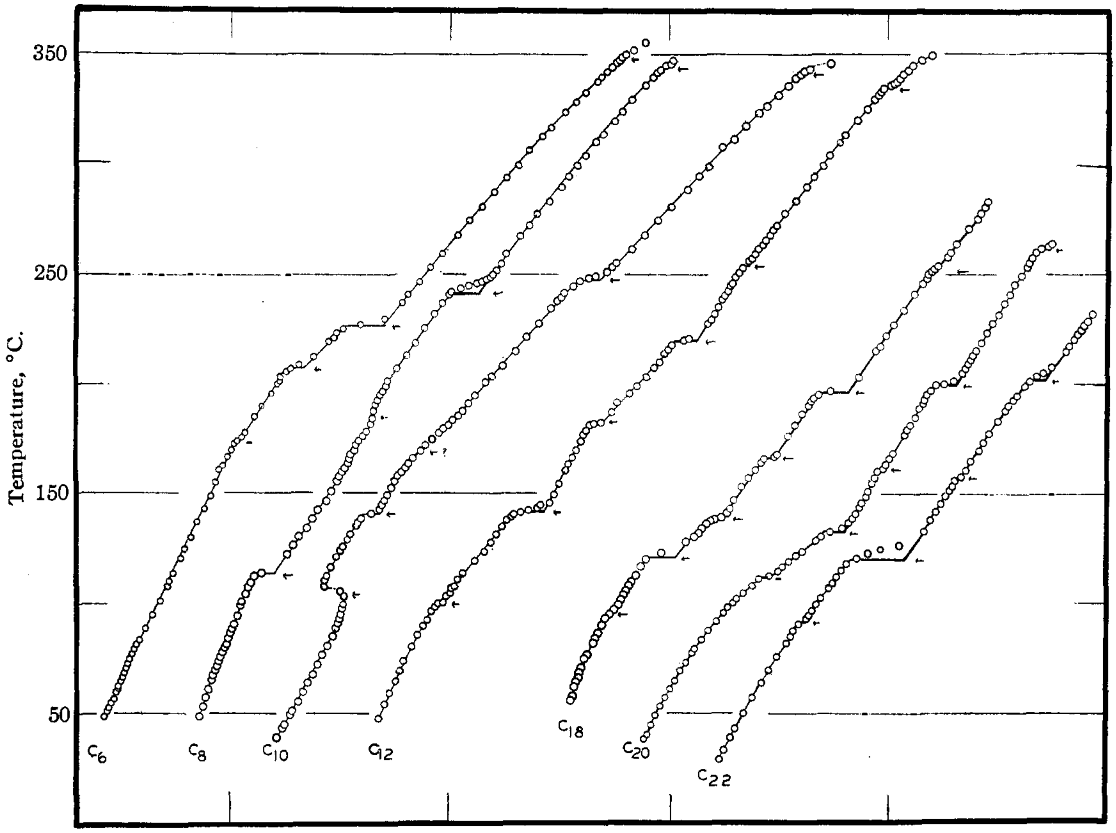


Fig. 3.—Dilatometer curves for saturated sodium soaps (arrows indicate transitions).

entirely independent preparations gave identical results.

We have not yet fully investigated the isotropic liquid nor the neat soap phases to see whether a difference can be found in either adequate to account for the break in the melting point curve that seems to occur between C_{12} and C_{16}.

The absence of steam formation in the dilatometer even above 350° demonstrates the absence of appreciable amounts of water. The presence of more than a trace of fatty acid seems unlikely since the soaps were made up neutral and preserved out of contact with moisture and carbon dioxide.

The curve for the transition of waxy soap to superwaxy soap appears uniform over the entire range of chain length with a maximum at C_{10}. However, in the range from C_{14} to C_{22} the general appearance of each of these two phases is the same from soap to soap, while from C_6 to C_{12} the properties seem quite different. Both phases are somewhat translucent, superwaxy soap showing almost entirely the color of the transmitted light with the Mikropolychromar, and waxy soap showing only slightly more of the scattered light. Using the hot wire technique both are nearly dark between crossed polaroids. The two phases are soft, but not fluid, and entrapped air bubbles frequently retain irregular shapes. Both can be undercooled extensively. The phase changes found dilatometrically for C_6, C_8 and C_{10} in this same range of temperature are not visible by any of the three microscopic techniques yet employed. These may be unrelated since the corresponding volume changes are quite different, and it does not seem justifiable to extend the smooth curve below C_{14}. The position of sodium laurate with regard to this change is ambiguous. While it lies on the same side of the apparent maximum as do C_{14} to C_{22}, the corresponding volume change is much larger than for the others, and the microscopic appearance (hot wire) of the phase is different. Since a similarity is implied between phases of the same assigned name (if used without special reservation) from one soap to the next, the name superwaxy soap is provisionally retained only for soaps above C_{12}.

The curve for transitions from waxy soap to the phase next lower in the sequence seems fairly regular from C_{10} to C_{22}. However, the properties of the transition at which this phase is formed from crystalline curd fibers do not vary in a regular manner over the whole range of chain length. There is consequently no basis for supposing that the phase confined between these two curves has the same structure for all soaps. The name *subwaxy soap* given this form of sodium palmitate has been shown applicable also to sodium stearate,[6] and is restricted to these two, pending further investigation. The temperature below which any one of these soaps exists as curd fibers is given by this series of points from C_{12} to C_{22}, but in the case of C_6 the visual appearance remains fibrous up to considerably higher temperatures (*ca.* 120°).

For sodium palmitate the two transitions, one from crystal to subwaxy soap and the second from subwaxy soap to waxy soap are only seventeen degrees apart. This is the shortest temperature range of stability of one of these intermediate phases we have yet observed. In fact the two transitions do not always occur independently, sometimes yielding instead a single transition (observed dilatometrically) at about 125°. This behavior is at present under further investigation in this Laboratory.

Two transitions (for C_8 and for C_{18}) occur below the tentative curd fiber-subwaxy line.[7a] These do not appear to belong to characteristic changes occurring in all members of the series of soaps.

P. A. Thiessen and co-workers[8,9] discovered the existence of a transition occurring in soaps of a monoclinic crystal form at the melting point of the corresponding fatty acid. This transition was accompanied by a minute inflection in the curve of specific volume versus temperature.

In the case of C_{16} a small inflection of our dilatometric curves, occurring near the proper temperature can be interpreted as confirming the existence of this transition.

A few experiments were performed on several preparations of sodium cerotate. In no case was a really isotropic liquid obtained on melting. Formation of a liquid containing a large number of faintly anisotropic patches occurred at about 245°. Three intermediate phases, possibly subneat, superwaxy and waxy, were observed by the hot wire technique.

Previously reported values for the melting points of soaps of the even homologous series are summarized in Table III. The discrepancies vary from 8° to 133°. Figure 5 shows these values superposed on the curves of Fig. 4. It is apparent that the transition from neat soap to subneat soap frequently has been reported as the melting point. Even allowing for this source of confusion, the results are badly scattered. Of special interest is the series of values of the melting points reported by Vorländer which follow along the upper segment of our melting point curve, without showing the break we find between C_{12} and C_{14}. (This point is under further investigation.)

TABLE III

PREVIOUSLY REPORTED VALUES FOR SODIUM SOAPS

Soap	Liquid crystal formation	Melting point, °C.
NaC_2		324[h]
NaC_4	210,[a] 220[a]	250,[a] 310[a]
NaC_6	225[a]	350,[a] 225–235[e]
NaC_8	225,[a] 217[g]	355,[a] 222–230,[e] 344[g]
NaC_{10}	220[a]	318[a]
NaC_{12}	220[a], 226[c], 200[g]	310,[a] 310,[c] 242–244,[f] 255–260,[d] 324[g]
NaC_{14}	240,[a] 203[g]	330,[a] 250,[d] 299[g]
NaC_{16}	215,[a] 220,[a] 115–120,[b] 134,[b] 150–155[g]	265,[a] 316,[a] 290,[b] 258–267,[e] 270,[f] *ca.* 270,[d] 259,[g] 291[g]
NaC_{18}	220,[a] 225,[a] 162[g]	305,[a] 255–272,[e] *ca.* 260,[d] 270[g]
NaC_{26}	116[g]	360[g] (our value, 219°)

[a] D. Vorländer, *Ber.*, **43**, 3132 (1910); [b] McBain, Lazarus and Pitter, *Z. physik. Chem.*, **A147**, 87 (1930); [c] McBain, Brock, Vold and Vold, THIS JOURNAL, **60**, 1870 (1938); [d] Krafft, *Ber.*, **32**, 1596 (1899); [e] N. Godbole and K. Joshi, *Allgem. Oel u. Fett-Ztg.*, **27**, 77 (1930); [f] H. A. R. Kauffel, Dissert. Hanover, 1936; [g] A. S. C. Lawrence, *Trans. Faraday Soc.*, **34**, 660 (1938); [h] "International Critical Tables," vol. I, p. 151.

Discussion

The curves of Fig. 5 contain the answers to the principal problems discussed at the beginning of the paper. First, the behavior found for sodium palmitate,[1] in which melting occurs in several separate steps with stable intermediate forms, is found for the entire sequence of sodium soaps at least from C_6 to C_{26}. However, the number of intermediate forms is not always the same from soap to soap. Over the range of chain length from C_{22} to C_{14}, and possibly including some of the forms of C_{12}, the regularity of the curves of transition temperature versus chain length, together

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[7a] A similar transition has now been found, both dilatometrically and calorimetrically for sodium myristate (C_{14}) at 80°.

[8] P. A. Thiessen and E. Ehrlich, *Z. physik. Chem.*, **A165**, 453 (1933).

[9] P. A. Thiessen and E. Ehrlich, *ibid.*, **B19**, 299 (1932).

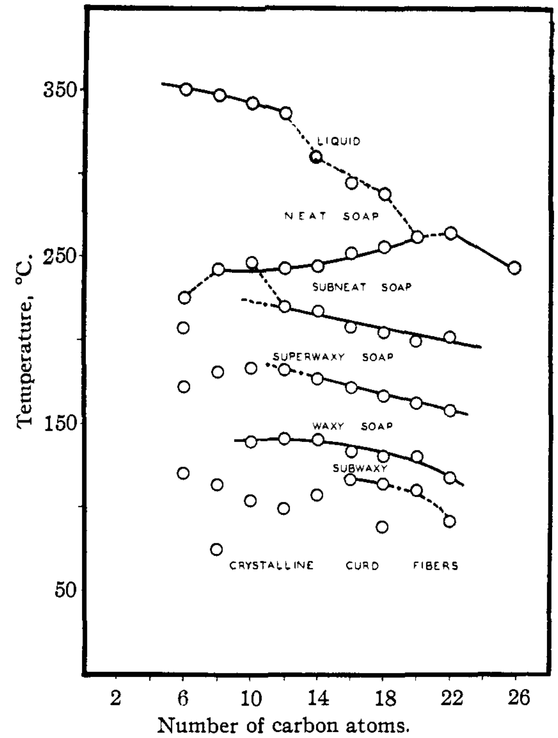

Fig. 4.—Transition temperatures of n-sodium soaps of even number of carbon atoms.

with similarities in volume change and visual and microscopic appearance, strongly suggest that for the different soaps the phases assigned the same name will be found to have a similar molecular arrangement.

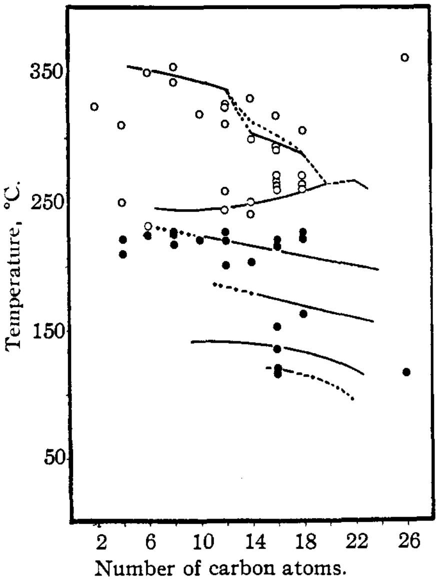

Fig. 5.—Previously reported transition temperatures for n-sodium soaps: ●, crystal to liquid crystal; O, melting point.

In some instances, this equivalence has been confirmed by showing that it is possible to pass from a given phase of one soap to the corresponding phase of another by continuous changes in temperature and composition without crossing any phase boundaries.[6]

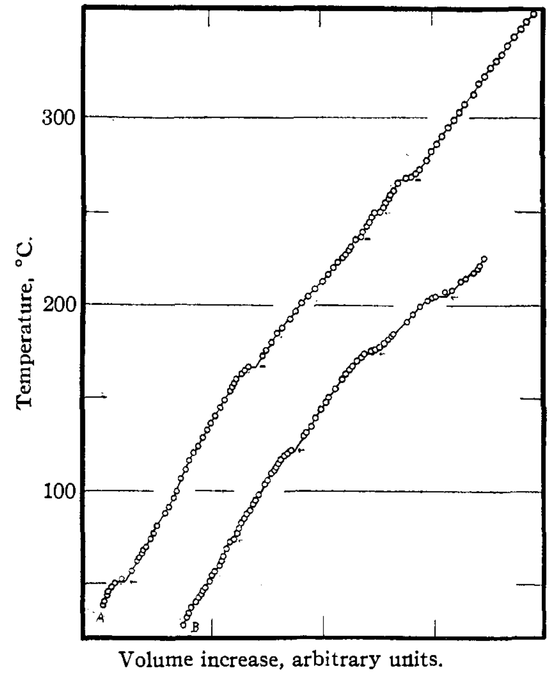

Fig. 6.—Dilatometer curves for potassium stearate (A) and sodium oleate (B).

Bernal and Crowfoot[10] have given a discussion of the states of aggregation in which they point out that the factors favoring the formation of mesomorphic forms are geometrical anisotropy of the molecule and the existence in it of a moderate but not large difference in polar character between different atomic groupings. As the soaps either decrease or increase in length of chain, both these two conditions, fulfilled by NaC_{14}, NaC_{16} and NaC_{18}, disappear gradually. As the chain length decreases, most of the curves appear to break off abruptly, a phenomenon apparent for some transitions at C_{10}, others not until C_6 or perhaps judging from Vorländer's work[11] even C_4. On the side of increasing chain length the curves appear to be converging, possibly toward the value of 117°, the limiting melting point for many homologous series of compounds containing paraffin chains.[12] It might be predicted that a soap

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

(11) D. Vorländer, Table V, reference *a*.

(12) J. Timmermans, *Bull. soc. chim. belg.*, **28**, 392 (1919).

of sufficiently long chain length would melt directly in one step from crystal to liquid at the "genotypic" point.

The fact, that this sequence of phases exists for the saturated sodium soaps but not for the corresponding acids, immediately raises the question as to whether it exists for soaps with different cations. If our interpretation is correct that the sequence represents a stepwise melting process, it would be surprising if it were peculiar to sodium soaps. Exploratory experiments show that a similar, but probably not identical, sequence exists also for potassium stearate (Table IV, B).

TABLE IV

TRANSITION TEMPERATURES AND VOLUME CHANGES FOR ADDITIONAL SOAPS

A. Sodium Oleate

Samples	Unclassified			Super-waxy-subneat	Formation of liquid
Sample 1, 1st runs	68	115	169	200	241[b]
Relative vol. changes	V. s.	Med.	Med.	Large	..
Sample 1, runs after 6 mo.	..	122	178	202	..
Sample 2, runs after 6 mo.	..	123	178	..	..
Sodium oleate, Merck	[c]	[c]	185[a]	212[a]	249[b] 257[a]

[a] Hot wire result. [b] Visual observations. [c] Microscopically present.

B. Potassium Stearate

Transition temp.	Volume change, cc./g. soap
51	0.006
162	.0095
235	.003
249	.0047
265[b]	.012
353[a]	?

[a] Formation of isotropic liquid. [b] Resembles neat soap formation.

A similar sequence exists for sodium oleate. The relation between the phases of sodium oleate and sodium stearate has not been completely established, except that on the basis of the volume change the liquid crystal formed at *ca.* 200° seems more closely related to subneat soap than to neat soap, an inference confirmed by work on mixtures of the two soaps[6] (Table IV, A).

Acknowledgment.—The authors wish to express their appreciation to Dr. M. E. Laing McBain for preparing and testing most of the samples of soaps, and also to Dr. J. W. McBain for his continued interest and for presenting the results of this investigation at the 99th meeting of the American Chemical Society.

Summary

The following stable phases can occur in successive ranges of temperature above that for a crystalline soap and below that for true liquid: subwaxy, waxy, superwaxy, subneat and neat.

The transition temperatures of sodium salts of the even members of the homologous series of fatty acids have been determined for all these phases from C$_6$ to C$_{22}$, using three experimental methods. Values previously reported for the "melting points" of these compounds by various authors in the past often relate to a transition sometimes as much as one hundred degrees lower. In two instances curves of transition temperature against length of carbon chain run together, giving rise to a change in the number of stable phases intervening between the normal crystalline form and isotropic liquid.

STANFORD UNIVERSITY, CALIFORNIA

RECEIVED MARCH 27, 1940