[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Liquid Crystalline, Waxy, and Crystalline Phases in Binary Mixtures of Pure Anhydrous Soaps

BY MARJORIE J. VOLD

This investigation of the phase rule behavior of binary mixtures of anhydrous soaps (sodium laurate–sodium palmitate, sodium laurate–sodium stearate, sodium palmitate–sodium stearate, sodium palmitate–sodium behenate, and sodium oleate–sodium stearate) was undertaken to determine the extent to which each of the many stable phases of a single soap will dissolve those of another pure soap. Each has from four to six transition temperatures in addition to the one at which ordinary isotropic liquid forms. Study of the solubility relations among the various phases can give qualitative information about their internal rigidity and regularity of structure since the crystal forms may have only a slight tendency to form mixed crystals while, on the other hand, liquid crystals tend, like liquids, toward having much less restricted solvent properties.

In cases where the two soaps are almost completely miscible, and corresponding transitions are connected by smooth curves of the solidus–liquidus type a definite correlation can be established between their mesomorphic forms.

For the determination of the temperatures at which phase changes occur, a "hot wire" technique suggested for this problem by J. D. Bernal was employed. The illuminating device known as the Mikropolychromar[1] was found to provide more contrast between some phases than do crossed polaroid pieces. The microscopic studies were supplemented by macroscopic visual observations of one gram samples, and by dilatometric studies.

Materials.[2]—The sodium palmitate used is a Kahlbaum product made specially for J. W. McBain, and is the same as that used by McBain, Vold and Jameson.[3] Sodium laurate and sodium stearate were prepared by neutralization of hot alcoholic solutions of lauric acid (Eastman Kodak Co.) and stearic acid (Kahlbaum) with sodium ethylate. Sodium behenate was prepared in the same way from an acid obtained by catalytic hydrogenation of erucic acid (Kahlbaum). The sodium oleate was a Merck product which probably contains appreciable amounts of lineoleate or higher molecular weight unsaturated soaps as well as some laurate and myristate.

Experimental Procedure.—Samples were prepared by weighing out the required amounts of soap previously dried to constant weight at 105°, mixing and homogenizing them by melting them together in sealed tubes and agitating them thoroughly in the liquid state. Four methods were employed in the determination of the temperatures of phase change, from which the phase rule diagrams are drawn. The temperature at which liquid crystal first forms from isotropic liquid, T_i, was determined by visual observation of a one gram sample sealed in a small glass tube and hung in a small electric furnace equipped with Pyrex windows as previously described.[4] An extensive dilatometric and microscopic study of the mixtures of sodium laurate and sodium palmitate was carried out in the manner described[5] for anhydrous sodium palmitate. Most of the experimental results, however, were obtained by means of the "hot wire" technique for the microscopic determination of transition temperatures. All determinations of temperature by visual or microscopic methods, and also by the dilatometric technique were carried out in duplicate or triplicate on different portions of the same sample, previously made up and homogenized as described above. Duplicate samples of the same composition were also made up in a few cases. Results with these samples showed that random errors arising from possible non-uniformity of the original materials, weighing errors, failure to obtain adequate homogenization, etc., are not important. One typical duplicate result is included in Tables III and IV (50.0 mole per cent.).

The hot wire apparatus is shown in Fig. 1. A no. 28 chromel A wire (A), replaced as necessary, is stretched across a hole 1.5 cm. in diameter cut in a 5 × 5 cm. "Transite" base. The wire is kept in place by means of the grooves in the heads of screws BB′ and is kept taut by means of a steel spring S. It is heated to any desired temperature by application of an electric current at terminals TT′. Samples for observation are prepared in the form of thin films (0.1–0.2 mm. thick) mounted between two cover glasses, and placed directly over the wire. The edges of the cover glass rest on the glass supports GG′ which are of the same height above the transite base as is the wire. Under these conditions the temperature at any point in the sample decreases nearly linearly with the distance from that point to the wire.

At a transition temperature the difference in microscopic appearance between the two phases gives rise to a sharp boundary parallel to the wire. Five such boundaries are visible in the photograph shown in Fig. 2. The distance between the edge of the wire and any given boundary is determined by shifting the entire apparatus, mounted on the mechanical stage of the microscope, until the boundary is just at the intersection of a pair of cross hairs, located

---

[1] Obtained from Carl Zeiss, Inc., San Francisco.

[2] The author is indebted to R. D. Vold and M. E. L. McBain for the preparation of these soaps.

[3] J. W. McBain, R. D. Vold and W. T. Jameson, THIS JOURNAL, **61**, 30 (1939).

[4] J. W. McBain, G. C. Brock, R. D. Vold and M. J. Vold, *ibid.*, **60**, 1870 (1938).

[5] R. D. Vold and M. J. Vold, *ibid.*, **61**, 808 (1939).

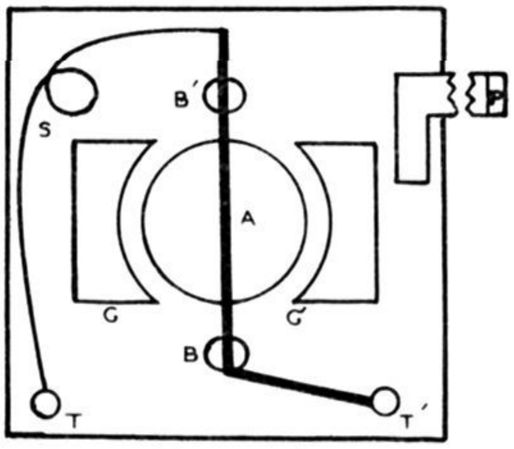


Fig. 1.—The hot wire apparatus.

in the focal plane of the microscope eyepiece, and measuring the displacement with an auxiliary Gaertner traveling microscope focused on a fine scratch on the extension (P) of the apparatus. Displacements can be measured to 0.01 mm., corresponding, with the gradient employed, to about 0.5°.

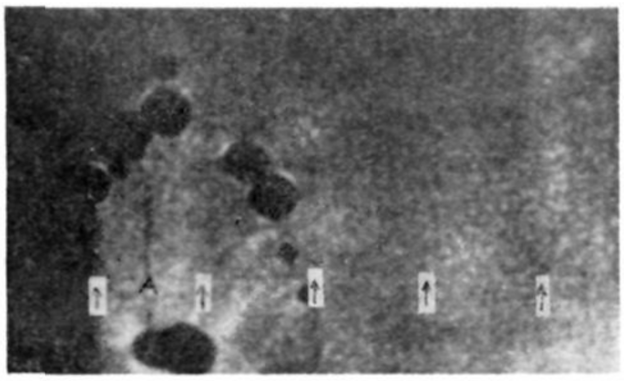


Fig. 2.—Film of sodium palmitate subject to a temperature gradient of 40°/mm. (crossed polaroids, × 20). Arrows show the positions of transitions. Point A is not a transition but arises from orientation of the neat soap which begins at A and gradually spreads.

Temperature can be measured either by calibrating the wire so that the temperature gradient is known as a function of the current through it, or by mounting a comparison substance (sodium palmitate) on the same cover slip with the sample being studied. The first named procedure is replete with opportunities for error and was employed only in the beginning to explore the possibilities of the method. Room temperature remained constant during the day at about 23° to within one degree (in an interior "cubby-hole" with neither windows nor outside walls). The current in the wire was kept constant within 0.02 amp. by hand manipulation, and the assembly was shielded from chance drafts by a double cardboard shield on three sides, only the side toward the operator being open. Under these circumstances the same temperature corresponds to a given distance from the wire within about 3°. The calibration changes with time, due to surface oxidation of the wire. A platinum wire was employed at first, and for this the calibration was independent of time for a few days, but the wire develops thin spots when heated under tension, resulting in boundaries no longer regular and parallel to the wire.

It is more satisfactory to mount a comparison substance (sodium palmitate whose transition temperatures had been previously determined in this Laboratory,[5] and further checked by the calibrated wire modification of the hot wire technique) on the same cover glass with the soap to be studied, measure the positions of the boundaries for both, plot the positions obtained for the comparison substance against the known transition temperatures, and determine the temperatures for the unknown under investigation by interpolation. In this way errors due to variation in external conditions are eliminated. There remain the possibilities of error due to the transverse temperature gradient in films differing in thickness or being wedge-shaped. That errors due to the two films differing in thickness are small is shown by the fact that duplicate experiments on independently prepared films generally gave the same results within 3°. Films which are wedge-shaped in the direction of the wire give boundaries which are not parallel to the wire and all such films are discarded. In a few instances the uniformity of films which did give parallel boundaries was checked by reexamination of the sample placed at right angles to its original position on the wire, and finding that the new boundaries were also parallel to the wire.

While the hot wire method has not been made precise in this work, careful refinement of apparatus and technique probably could yield values good to within 0.5°. The over-all reproducibility of a given result, including errors of temperature and composition was about 3°. It is probably not desirable, however, to attach significance to deviations of less than 5° from curves of transition temperature *versus* composition. About one hundred hot wire experiments are reported here. Eighty-eight per cent. of the values deviate from the smooth curves of Figs. 4, 5, 7, 8 and 9 by not over 3° and 99% by not over 5°.

Figure 3 shows a portion of a "double film," consisting of sodium palmitate and a mixture of sodium palmitate with

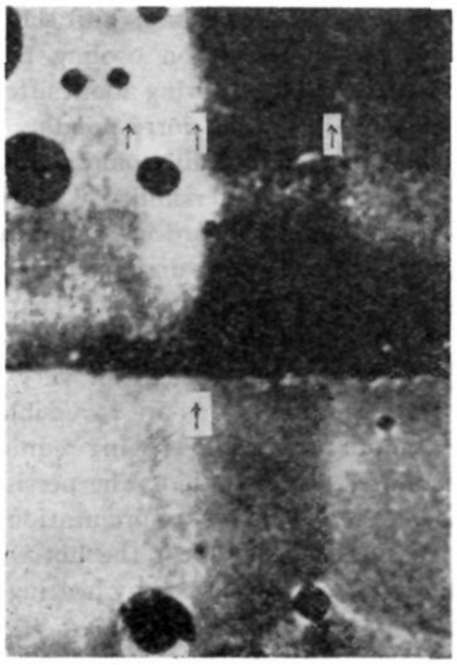


Fig. 3.—Double film: upper soap—mixture of sodium laurate (29.0 mole %) and sodium palmitate (71 mole %); lower soap—sodium palmitate. Arrows show transitions. Phases (left to right) for top, subneat, mixture, superwaxy and waxy; for bottom, subneat, superwaxy and waxy. At the bottom of the upper film, some mixing of the two has occurred.

29.0 mole per cent. sodium laurate. The preparation of such a sample requires considerable practice. About 10 mg. of the higher melting soap is placed on one-half of a cover glass and melted over a small gas flame (the size of a pinhead). A half cover glass is laid on over the still soft lump, and the soap is then remelted. It flows out in a uniform sheet just to the edge of the top cover glass. Any excess that escapes can be scraped off with a razor. Next, about 10 mg. of the second soap is placed on the other half of the first cover glass, melted, covered, and remelted. The difficulty comes in getting the two films to spread evenly, but without mixing along the adjacent parallel edges of their separate covers. Sometimes a glass fiber was employed as a spacer to keep the two films apart.

Mikropolychromar.—The successful application of the hot wire technique depends upon the contrast in microscopic appearance between the different phases being sufficiently great to produce recognizable boundaries at the transition points. Observation with the sample between crossed polaroids is satisfactory, but the device known as the *mikropolychromar* sometimes renders the contrast much more striking. The sample is illuminated simultaneously with light of two colors, one directly transmitted, and the other shining on the sample so obliquely that only light scattered by the sample itself enters the microscope objective (as in ordinary dark field illumination). The result is that the different soap phases appear as bands of varying hue, depending on the proportion of scattered and transmitted light making up the image.

Attainment of Equilibrium.—Each of the transitions has its own characteristic behavior with regard to the speed of attainment of equilibrium. The melting point (formation of isotropic liquid) and the formation of neat soap from subneat are rapidly reversible, and the corresponding boundaries move back and forth in response to changes in the heating current. The same is true of the boundary between subwaxy and waxy soap, but the re-establishment of its original position on cooling from a higher temperature is quite slow, requiring about fifteen to twenty minutes in a thin film. The corresponding change in a 1-g. sample has been found dilatometrically to require several days for complete reversibility. The change from subwaxy to curd fiber phase proceeds rapidly on cooling once nuclei are formed, but undercooling is common. Both boundaries involving superwaxy soap (*i. e.*, the waxy–superwaxy and superwaxy–subneat transitions) persist after the sample has cooled, for very long periods (months). That the transitions are reversible was shown dilatometrically, only a few hours being required on either heating or cooling a 1-g. sample. The persistence of the boundaries is believed to be due to orientation on the glass cover slip. Because of this effect the hot wire assembly was always brought to a given state by heating in quantitative experiments.

Results

A New Transition in Sodium Palmitate.—As a test of the hot wire technique, the transition temperatures of sodium palmitate[5] (except for that to isotropic liquid) were redetermined, using the melting points of *p*-toluidine, benzoic acid, *p*-acet-toluide, benzanilide, anthracene and phenolphthalein to calibrate the wire at a constant current. The genotypic point (62.5°) and the transition from curd fibers to subwaxy soap (117°) are not distinguishable by this procedure. The boundaries between subwaxy and waxy soap (135°), the transition to subneat soap at 208°, the transition to neat soap at 253° and that to isotropic liquid at 295°[6] were all present. In addition, a further boundary was observed at 172 ± 2°. This boundary is clearly visible in Fig. 2, and again in Fig. 3. This transition is accompanied by only a small volume change, and was at first passed over in our dilatometric investigation of sodium palmitate, though the presence of an irregularity in the curve near 180° was noted. The new phase has been named "superwaxy" soap.

Characteristic Appearance of the Different Phases.—Examined by means of the hot wire technique between crossed polaroids, isotropic liquid appears completely dark. The phase first separating from it as the temperature is lowered, neat soap, appears bright at first, but becomes rapidly oriented between the glass cover slips to simulate isotropic behavior. This orientation is just starting at point A in Fig. 2. Curiously, it begins first at about 270°, near the center of the neat field. The next, subneat soap, appears very bright and remains so. The next, superwaxy soap, appears much darker but is still doubly refracting. The next, waxy soap, is brighter than superwaxy soap, but darker (*i. e.*, less doubly refracting) than subwaxy soap or curd. Curd fiber phase and subwaxy soap have such similar appearance that no boundary appears between them by the hot wire technique. All of the anisotropic phases, including neat soap, have the stippled grainy structure visible in the photographs of Figs. 2 and 3.

When the crossed polaroids are replaced by the mikropolychromar, the phases show progressively more of the color of the transmitted light as the temperature is raised, up to the point where subneat soap forms. This phase is predominantly the color of the scattered light. Neat soap shows less scattered and more transmitted light and, finally, isotropic liquid shows only the color of the transmitted light.

This behavior is in striking contrast with the

---

(6) This change in our reported value of the melting point of sodium palmitate from 292 to 295° results from a recalibration of our temperature scale in this region. Values for other transition temperatures remain unchanged.

TABLE I

TRANSITION TEMPERATURES FOR MIXTURES OF SODIUM PALMITATE AND SODIUM STEARATE

Phase change	Composition, mole % NaP					Technique employed
	0	25.2	49.9	74.3	100	
Formation of subwaxy soap	117	...	...	...	117	Dilatometer
Formation of waxy soap	132	126	126	...	135	Hot wire × polaroids
Waxy–superwaxy	167	164	166	172	172	
Superwaxy–subneat	203	202	206	207	208	
Subneat–neat	257	253	253	253	253	
Neat–isotropic	288	289	293	295	295	Visual obsn.

results obtained by the procedure in which the temperature of the whole sample is raised uniformly. Under these circumstances isotropic liquid, the two "neat" soap phases together, the three "waxy" phases together, and curd fibers are clearly differentiated, but the difference between subneat and neat soap is slight (except for highly oriented neat soap prepared by slow cooling of isotropic liquid) and that between subwaxy and waxy, and between waxy and superwaxy is invisible. The explanation of this behavior is to be found in the fact that the hot wire procedure takes full advantage of all the points of contrast including relative transparency and magnitude of the double refraction as well as intrinsic structural differences. It is easier to see the difference between two phases placed side by side than to detect a change in the whole sample from one to the other.

Since all of the phase changes reported can be made conspicuous by one technique or another, there is no doubt of their reality. However, it is possible that some may remain undiscovered.

The System Sodium Palmitate–Sodium Stearate.—Results of observations on three mixtures of sodium palmitate and sodium stearate, together with transition temperatures for the two pure soaps (reported elsewhere[5,7]) are listed in Table I.

There is no evidence that sodium palmitate and sodium stearate are not completely miscible at all temperatures above the transition to waxy soap. Corresponding transitions are connected by smooth curves. The boundaries appear to be single, which would mean that change from one phase to another occurs without appreciable fractionation of the two soaps. In a two-component system in general, such transitions would be connected by a pair of curves of the solidus–liquidus type between which the system would exist as two phases, both of different composition from the sample as a whole.

The addition of sodium palmitate to sodium stearate at first lowers the temperature at which waxy soap is formed. When the proportion of sodium palmitate is 74.3 mole per cent., no sharp boundary appears, but instead the film exhibits a gradual change from the curd to waxy appearance over a range of temperature whose limits cannot be determined by the hot wire method. This negative observation shows that the phase changes occur over so wide a temperature region that no sharp contrast in appearance develops at any single temperature, and is an indication that extensive fractionation occurs in this portion of the composition and temperature range.

The System Sodium Palmitate–Sodium Behenate.—Transition temperatures of mixtures of sodium palmitate and sodium behenate are recorded in Table II and plotted on a phase rule diagram in Fig. 5.

TABLE II

TRANSITION TEMPERATURES OF MIXTURES OF SODIUM PALMITATE AND SODIUM BEHENATE

Composition mole % NaBe	Phase change				
	Neat–isotropic	Sub-neat–neat	Super-waxy–sub-neat	Formation of waxy on heating	Superwaxy-waxy
13.8	...	254	204	*ca.* 128	*ca.* 170
33.0	287	256	203	....	*ca.* 163
57.4	275	258	205	*ca.* 120	....
82.7	272	257	200	125	....

The two curves bounding the field of existence of neat soap intersect at the melting point of sodium behenate. The temperatures of transition from superwaxy soap to subneat soap for sodium palmitate and sodium behenate are joined by a single smooth curve. Thus it is possible to pass continuously from subneat sodium palmitate to subneat sodium behenate, and from superwaxy sodium palmitate to superwaxy sodium behenate. The use of the names subneat and superwaxy as indicating a definite type of mesomorphic form or a definite position in the sequence of phases existing for these substances between true crystal and

---

(7) M. J. Vold, M. Macomber and R. D. Vold, THIS JOURNAL, **63**, 168 (1940).

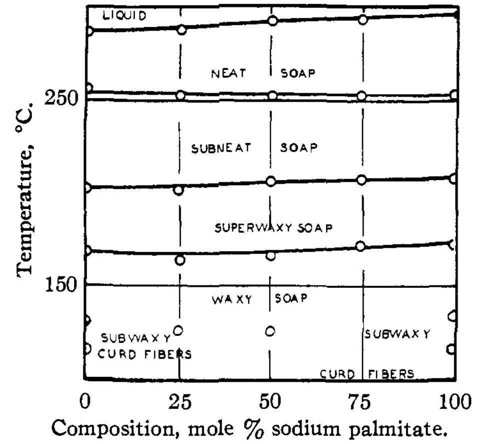


Fig. 4.—Phase rule diagram for sodium palmitate and sodium stearate.

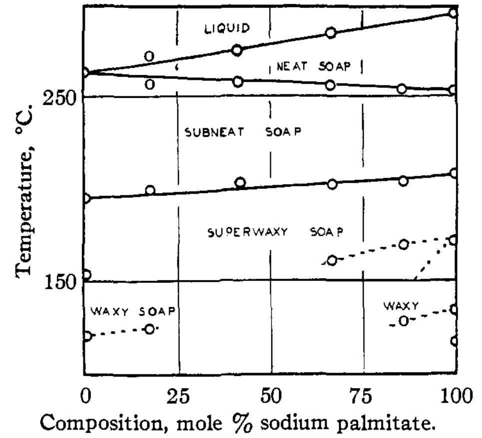


Fig. 5.—Phase rule diagram for sodium palmitate and sodium behenate.

true liquid to describe certain phases of sodium palmitate and sodium behenate is thus fully justified despite the fact that the phases occur in a different numerical position counting downward from isotropic liquid.

However, it is not possible, on the basis of these results, to decide whether or not the next lower or waxy forms of the two soaps can be considered similar, because, except in a relatively short region near the palmitate axis of Fig. 8, the phase changes occur over a range of temperature wide enough to prevent boundary formation in the hot wire technique. There is no evidence that the waxy forms are *not* similar; they may well be similar but not entirely miscible owing to the disparity in chain length. The waxy forms of sodium palmitate and sodium stearate (see Fig. 4) appear to be identical.

The System Sodium Palmitate–Sodium Laurate.—The temperatures at which mixtures of sodium palmitate and sodium laurate first form a liquid crystalline phase from isotropic liquid were determined by visual observation of 1-g. samples, and confirmed by microscopic observation in the Leitz–Weygand hot stage (uniform, continuously variable temperature) between crossed nicols. The formation of liquid crystal seems complete in a temperature interval of not over 2°. These data are recorded in Table III.

TABLE III

TEMPERATURES OF THE TRANSITION OF ISOTROPIC LIQUID TO NEAT SOAP FOR THE SYSTEM SODIUM LAURATE–SODIUM PALMITATE

Composition, Mole % NaL	T_i	Composition, Mole% NaL	T_i
100.0	336	50.0	312
94.8	334	50.0	310
86.8	329	37.5	307
74.7	324	25.2	308
61.8	320	15.4	305
57.5	313	5.1	301
		0.0	295

The curve appears to have an S-shape, which, if real, provides an unusual type of "solidus–liquidus" pair, in which the two curves (too close together to separate experimentally) have a common point of tangency, not at a minimum or maximum but at a point of inflection. However, the data could be represented almost equally well by a straight line running from the melting point of sodium laurate to that of sodium palmitate.

The temperatures at which sharp boundaries form in films subjected to a uniform temperature gradient (hot wire technique) are recorded in Table IV. Values for samples containing more than 60 mole per cent. sodium laurate, other than of the temperature of the neat-subneat transition (column 2) are subject to considerable uncertainty owing to the extensive cracks which form spontaneously in the prepared films and obscure the boundaries. Curves of volume against temperature were obtained for six mixtures. These curves[8] are given in Fig. 6. The temperatures of phase change derived from them are summarized in Table V.

The construction of a definitive phase rule diagram on the basis of these results has not been possible. The curves of Fig. 7 (other than the top curve previously discussed) serve only to connect corresponding points. Their phase rule significance is not yet clear. Wherever the boundaries

---

[8] Some of these curves were determined for the author by Mr. Wm. Nye and Mr. C. E. Schwerdt.

TABLE IV

TEMPERATURES OF PHASE CHANGE FOR THE SYSTEM: SODIUM LAURATE–SODIUM PALMITATE DETERMINED USING THE HOT WIRE TECHNIQUE (BOTH WITH CROSSED POLAROIDS AND WITH MIKROPOLYCHROMAR)

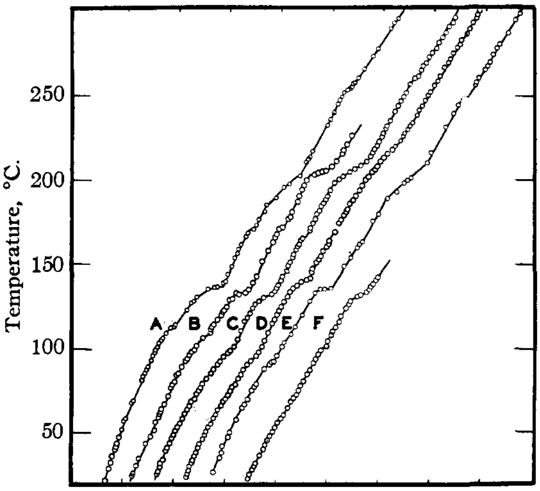
Composition mole% NaL	Subneat soap to neat soap	Superwaxy soap to subneat soap T_1	T_2	Waxy to superwaxy soap
100	244	220	[a]	182
86.8	249	213?	184?	169?
80.0	249	214?	184?	163?
74.7	247	...	...	171?
61.8	247	214?	186?	165?
57.5	241	224	192	165
50.0	246	221	193	169
50.0	246	218	197	171
37.5	249	214	192	164
29.0	253	[a]	196	169
25.2	253	[a]	201	167
15.4	257	[a]	204	171
5.1	253	[a]	207	170
0.0	253	208	208	172

[a] Boundary absent.

TABLE V

REGIONS OF PHASE CHANGE IN MIXTURES OF NaP AND NaL AS DETERMINED BY INSPECTION OF DILATOMETER CURVES

	Nature of Change				
Composition mole% NaL	Formation of subwaxy soap	Formation of waxy soap	Waxy soap-superwaxy soap	Superwaxy-subneat soap	Subneat-neat soap
5.1	113	132–137	171	203	252
15.4	109	131–134	172	205	...
25.0	100	127–132	167	201–211	260?
37.5	96	136–145	...	198–222	?
50.0	92	135	164?	192–211	Present
74.7	101	125–132	...		...

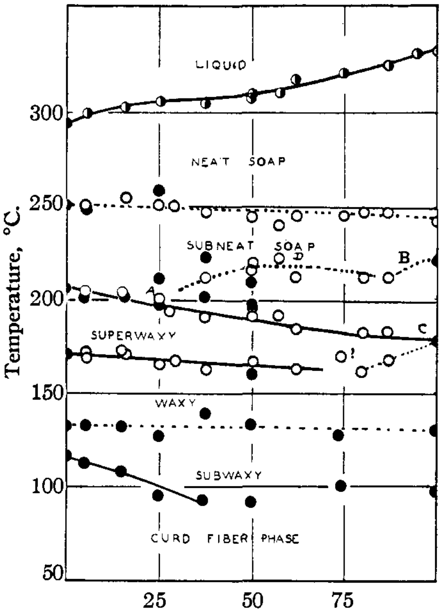


Specific volume in arbitrary units.

Fig. 6.—Dilatometric behavior of mixtures of sodium palmitate and sodium laurate: mole per cent. of sodium laurate: A, 5.1; B, 15.4; C, 25.0; D, 37.5; E, 50.0; F, 74.7.

between phases are sharp, it seems that the separation (on a temperature scale) of "solidus–liquidus" curves must be small, and if the curves are smooth, it is reasonable to suppose that miscibility is complete in both upper and lower phases.

It is at once apparent that the full sequence of phases for sodium laurate does not correspond to that for sodium palmitate. The isotropic liquid phases of the two are mutually miscible, and the same is true of the neat soap phases. According to the diagram (Fig. 7, curve next to top) the subneat soap phases are also continuous. However, in this case doubt is cast on the results by the wide deviation of experimental points from the smooth curve. Dilatometer curve C (25 mole % NaL) has this point at 260°, a full 10° above the smoothed curve, while it is missing from curve D (hot wire value, 249) and a small, troublesome "wiggle" occurs at about 280°. This transition is being investigated further.



Composition, mole per cent. sodium laurate.

Fig. 7.—Phase rule diagram of sodium palmitate and sodium laurate: ◑, visual observation; ●, dilatometric values; ○, hot wire results.

Experimentally, the boundary between superwaxy soap (NaP type) and subneat soap remains sharp and single in systems containing up to about 25 mole per cent. NaL. As the sodium laurate increases this boundary spreads out into a bright band (see Fig. 3) whose sharp edges trace out the curves AC and ADB of Fig. 7. The dilatometric work indicates that this band may be a temperature range over which transition occurs from superwaxy to subneat soap, but the quantitative agreement is poor. That this region (BAC) may be heterogeneous and not consist of a single phase throughout is further indicated by the fact that the upper curve is not continuous but has a fairly distinct maximum, and a possible break near B. The same kind of behavior is more clearly demonstrated with sodium laurate and sodium stearate in Fig. 8. If this suggested form for the curves is correct, it is apparent that some additional phase boundaries must exist in region BAC that were not experimentally detected by any of the methods thus far employed. The superwaxy-subneat transition of sodium palmitate is connected by a smooth curve to the "waxy"-"superwaxy" (NaL type) transition of sodium laurate.

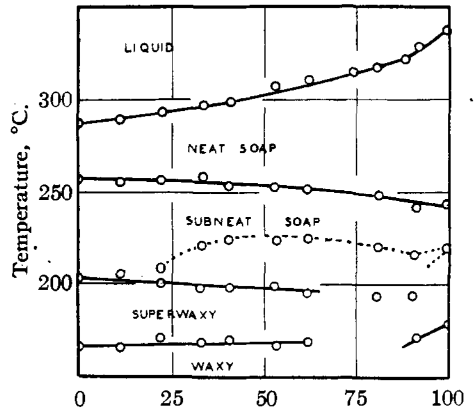


Fig. 8.—Phase rule diagram for sodium laurate and sodium stearate.

The boundary between waxy and superwaxy sodium palmitate persists essentially unchanged as sodium laurate is added up to 60 mole per cent., whereupon it simply disappears, though there is some indication of a boundary of a different appearance with a position quite different from the former smooth curve in samples containing up to 87 mole per cent. sodium laurate.

Unambiguous interpretation of all these results is not yet possible. It is also not yet possible to deduce the relations between the "waxy" and "subwaxy" forms of these two soaps.

The temperature at which the formation of subwaxy soap is complete is lowered considerably as sodium laurate is added to sodium palmitate. Dilatometer curves C and D (25.2 and 37.5 mole per cent. NaL) show a minute wiggle, not reported in Table IV, at 70–75°, which may mean that a eutectic exists somewhere in this temperature region, indicating limited miscibility of the two soaps in the curd fiber phase (crystalline phase), but some more sensitive experimental method will have to be developed before this hypothesis can be tested.

The System Sodium Laurate–Sodium Stearate.—The transition temperatures of mixtures of sodium stearate and sodium laurate, determined microscopically and by visual observations on one-gram samples, are recorded in Table VI. The behavior above 150° is represented on a phase rule diagram in Fig. 8.

TABLE VI

TRANSITION TEMPERATURES OF MIXTURES OF SODIUM STEARATE AND SODIUM LAURATE

Composition mole% NaL	Visual "T_i" neat-isotropic	Hot wire results				
		Neat–subneat	Subneat–superwaxy T_1	Subneat–superwaxy T_2	Superwaxy–waxy	Waxy–curd
11.1	289	255	...	205	166	126
22.1	293	255	209	201	171	...
33.5	296	259	222	198	169	114?
40.5	298	253	224	199	170	...
53.3	307	253	224	199	167	116–130
62.1	311	252	224	195	169	115–132
74.3	315	...	...	...	...	...
80.6	317	249	220	192	...	...
88.3	322	...	...	...	...	...
91.8	329	243	218	194	171	147?

The diagram has much in common with that for sodium palmitate and sodium laurate, as might be expected from the fact that the neat, subneat, superwaxy and waxy forms of sodium palmitate and sodium stearate are in perfect correspondence.

The System Sodium Oleate–Sodium Stearate.—Transition temperatures of mixtures of sodium oleate and sodium stearate are recorded in Table VII and plotted on a phase rule diagram in Fig. 9. The diagram is similar to that of sodium behenate and sodium palmitate in the region investigated, except that correspondence between the superwaxy phases cannot be established on the basis of the available data.

TABLE VII

TRANSITION TEMPERATURES OF MIXTURES OF SODIUM OLEATE AND SODIUM STEARATE

Composition wt.% NaOl	Phase change		
	Neat soap–isotropic liquid	Subneat soap–neat soap	Superwaxy–subneat soap
91.5	271	257	207
73.6	278	252	193
49.0	285	254	194
23.6	288	256	201

The sample of sodium oleate used (Merck), despite a relatively satisfactory iodine number, has a molecular weight indicative of the presence of appreciable quantities of higher fatty acids. The first three transition points, 257, 212 and 185°, are considerably higher than the values 241, 201 and 178° obtained by Vold,[9] and by Vold, Macomber and Vold[7] for a much more nearly pure sodium oleate prepared from oleic acid obtained from the British Drug Houses, Ltd., made by Lapworth's method.

Discussion

The results obtained suffice for the construction of phase rule diagrams of varying degrees of completeness for five pairs of sodium soaps. The derivation of these diagrams (Figs. 5–9) from the experimental results already has been discussed.

These diagrams help to establish the identity of equivalent phases of the single soaps, on the principle that two condensed phases will be considered equivalent if it is possible to pass from one to the other by continuous alteration of temperature and composition without crossing a phase boundary.

On this basis, the first liquid crystalline phase formed on cooling from isotropic liquid is the same, neat soap,[10] for sodium laurate, sodium palmitate and sodium stearate. However, inspection of the diagram for the system of sodium palmitate and sodium behenate shows that the two curves defining the region of existence of this phase in the mixtures intersect at the melting point of sodium behenate. Apparently there are (at least) two distinct steps in the transformation of subneat soap to isotropic liquid. In sodium laurate, sodium palmitate and sodium stearate they occur at different temperatures giving rise to the existence of an intermediate form (neat soap) stable over a temperature range varying from 113° for sodium laurate to 31° for sodium stearate, while in sodium behenate the same transformation occurs at a single temperature which can therefore be regarded, in a limited sense, as a double melting point.

All of these instances of the equivalence of phases of the same assigned name are in accord with the conclusions of Vold, Macomber and Vold,[7] drawn on the basis of the variation in transition temperatures with chain length.

These authors also studied the transition temperatures of anhydrous sodium oleate. This work also provided the first positive correlation between the forms of sodium oleate and the saturated soaps. According to Fig. 9 the liquid crystalline form first separating from isotropic liquid sodium oleate is equivalent to the subneat form of the saturated soaps.

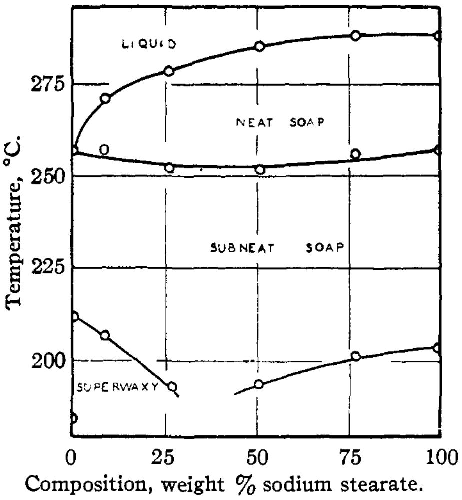


Fig. 9.—Phase rule diagram for sodium stearate and sodium oleate.

The second liquid crystalline form, subneat soap, is on the same basis fully equivalent for sodium palmitate, sodium stearate, sodium behenate and, possibly, sodium laurate. Equivalence of the superwaxy phases has been established for sodium palmitate, stearate and behenate and of the waxy phases for sodium palmitate and stearate. The "superwaxy" form and "waxy" form of sodium laurate do not seem to be the same as those of sodium palmitate and should not be called by the same name without the addition of some such reservation as "superwaxy soap (NaL type)."

Acknowledgment.—The author wishes to thank Drs. J. W. McBain and R. D. Vold for their valuable advice and assistance throughout the course of this investigation.

Summary

1. The following forms of a single pure anhydrous sodium salt of a *n*-fatty acid can occur between room temperature and the melted liquid: crystalline (of which there is more than one kind), subwaxy, waxy, superwaxy, subneat, neat, and ordinary liquid. All those mentioned are stable phases, most or all of which occur successively on warming. The superwaxy phase has not been described previously.

---

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

[10] Not to be confused with the aqueous phase containing about 70% soap originally called by this name in industrial practice.

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,

---

(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).