saturated alcohol. Maximum solubility seems to be obtained with both the unsaturated and hydroxyl groups close to the center of a compact

molecule. The solubility also decreases with increasing molecular weight and temperature.

Successive Phases in the Transformation of Anhydrous Sodium Palmitate from Crystal to Liquid[1]

BY ROBERT D. VOLD AND MARJORIE J. VOLD

The purpose of this paper is to present the evidence for the existence of several new soap phases, to discuss the possibility that all are mesomorphic, and to indicate the nature of the extensions which these new phases make necessary in the technically important phase rule diagrams of systems of water and soap. Although the present work involves only anhydrous sodium palmitate, preliminary experiments on anhydrous sodium laurate, sodium stearate and sodium oleate (undertaken by Mr. Macomber) and on aqueous systems of sodium palmitate and sodium oleate show that also in these cases a larger number of phases exist in the concentrated systems than were previously suspected.

Simple crystals in which the binding forces are essentially isotropic melt at a single temperature, which provides a qualitative indication of the strength of the bonds. However, many more complex substances form crystals in which the binding forces are markedly anisotropic. Some of these compounds do not change directly from crystal to isotropic liquid, but instead pass through one or more distinct, stable intermediate phases, the liquid crystalline states.

Bernal and Crowfoot[2] have summarized the molecular characteristics favorable to liquid crystal formation: (1) the molecule must be anisometric, either rod-shaped or flat, lath-shaped; (2) it must contain not more than one highly polar group but may contain additional mildly polar groups such as —C—O—C— or —CH=N—. These authors also discuss the relation of the po-

sition of the active group in the molecule to the type of liquid crystal formed.

The alkali salts of the n-fatty acids (the soaps) conform to the general conditions summarized by Bernal and Crowfoot. Correspondingly, it has been long accepted that these substances undergo "double melting."[3,4] However, the temperatures that have been reported for the transition from crystalline curd fibers to liquid crystal, and from liquid crystal to isotropic liquid, vary widely. Visual and microscopic observations[3-5] of the temperature of liquid crystal formation have led to values in the neighborhood of 215–220° for the first melting point of sodium palmitate. However, McBain, Lazarus and Pitter[6] give 134° for this point, based partly on visual observations and partly on extrapolation of phase boundaries determined in the sodium palmitate–water system. They also noticed that incipient transition sometimes occurred at 114–121°. More recently Lawrence[7] has given the value 150–155° for this transition temperature. Visual and microscopic determinations of the temperature of formation of isotropic liquid from liquid crystal have led to the values 265°,[3] 291°[6,7] and 316°,[3] while a method based on apparent viscosity led to 259°.[7]

The measurements of specific volume as a function of temperature, reported in this paper, show that this galaxy of values arises from the existence of at least six phases of sodium palmitate between 70 and 320°, instead of the three heretofore recognized. Microscopic examination, together with

(1) This investigation was begun in collaboration with Dr. R. H. Ferguson and Dr. F. B. Rosevear in consultation with Dr. A. S. Richardson at the Procter and Gamble Company, Ivorydale, Ohio, primarily in connection with phase rule studies of soap–salt–water systems. A preliminary account of the discovery of two of the new soap phases, to be published in Oil and Soap, was presented at the Chicago meeting of the Oil Chemists' Association, October, 1938. The more thorough investigation discussed in this paper was carried out subsequently at Stanford University.

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

(3) D. Vorländer, Ber., 43, 3120 (1910).

(4) J. W. McBain, in Alexander's "Colloid Chemistry," Vol. 1, Chapter V, 1926.

(5) J. W. McBain and M. C. Field, J. Chem. Soc., 921 (1933).

(6) J. W. McBain, L. H. Lazarus and A. V. Pitter, Z. physik. Chem., A147, 87 (1930).

(7) A. S. C. Lawrence, Trans. Faraday Soc., 34, 660 (1938). The figures given in Table V of this author's paper purport to refer to sodium palmitate monohydrate. The inference is that the samples were prepared by drying the soap to constant weight at temperatures just above 100°. It has been shown, however,[20] that such a procedure results in essentially anhydrous soap.

inferences drawn from various supplementary observations, lead to the conclusion that the four consecutive intermediate phases may be liquid crystalline.

Materials and Procedure

The sodium palmitate used in these experiments was prepared specially by Kahlbaum for Professor J. W. McBain. The soap had an iodine value of zero, the theoretical molecular weight (by titration), and its hot alcohol solution was exactly neutral to phenolphthalein. Supplementary experiments on the transition temperatures of anhydrous soap mixtures have shown that small amounts (up to 2%) of homologous impurities cannot seriously impair the accuracy of the dilatometric measurements on the sodium palmitate.

The dilatometers used were similar to those described by McBain and Field.[8] About 0.8 g. of soap was weighed into a bulb of 3 cc. capacity, and dried to constant weight at 105°. The neck of the bulb was then sealed, and the soap melted to isotropic liquid. In this process considerable mechanically trapped air is expelled, and the soap solidifies to a compact cake which is more easily handled than the original fluffy powder. The bulb was then opened and sealed onto the short arm of a Pyrex capillary U-tube. The internal diameter of the capillary had been determined previously by weighing the mercury contained in a measured length, taken at several points along the tube. When the blowing is done through a trap filled with soda lime the water condensed in the soap during sealing is negligible. Air and residual water vapor were then removed by evacuation at 220° with an oil pump. The amount of water so removed was found to be not more than 0.3% of the weight of the soap. Nevertheless, its removal is of paramount importance.

If any water remains in the soap, steam forms in the dilatometer as soon as the temperature reaches such a point that the vapor pressure of water from the soap is greater than the external pressure due to the atmosphere plus the mercury column in the dilatometer. This formation of steam gives rise to a tremendous apparent expansion. Drying the soap to constant weight at 105° dehydrates it within 0.5%.[9] If no further dehydration is accomplished, formation of steam begins near 200°, accompanying the change from waxy to subneat soap. From the observed "volume increase" one can calculate that an amount of water equal to about 0.3% of the weight of the soap is expelled. At the transition to neat soap, 253° in dry sodium palmitate, most of the expelled steam is reabsorbed. In drying the soap prior to a dilatometric run, advantage is taken of the relatively high vapor pressure of water from subneat soap, and the drying is carried out in the temperature region of stability of this phase.[10]

(8) J. W. McBain and M. C. Field, J. Phys. Chem., **37**, 675 (1933).

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

(10) A. R. Ubbelohde [Proc. Roy. Soc. (London), **A167**, 136 (1938)] has noticed a somewhat similar effect with pentaerythritol which had not been freed completely from traces of moisture. It may be that spurious expansion due to traces of moisture is responsible for Lawrence's (ref. 7) conclusion that the density of sodium laurate varies from 0.5 at high temperatures to 1.9 at 15°. Direct measurement at ordinary temperatures has always led to values in the neighborhood of unity (sodium stearate, 1.033, ref. 13; sodium oleate, 1.018, E. Heymann, Trans. Faraday Soc., **34**, 689 (1938)).

After drying was complete the soap was alternately melted to isotropic liquid and cooled under vacuum until further repetition of the process evolved practically no air. Mercury was then introduced into the evacuated dilatometer through a three-way stopcock attached to the dilatometer, the oil pump and a mercury reservoir. The mercury level in the dilatometer capillary was adjusted to an arbitrary zero by sucking out the excess through a finer capillary. The mercury reservoir was weighed before and after the filling operation to determine the weight of mercury in the dilatometer in order to correct the observed readings for its expansion.

Heating was accomplished in a small furnace made from two concentric cans, insulated with asbestos paper. Twenty feet of no. 24 Chromel A wire served as the heating unit, the current being controlled by a Variac transformer. The line voltage was usually sufficiently constant to maintain constant temperature within one degree for several hours even without manual control. The insulation at the top of the furnace prevented the dilatometer and thermometer stems from heating appreciably above room temperature. The height of the mercury above the arbitrary zero was read by means of a steel rule, graduated in half millimeters. Readings were in general reproducible within 0.2 mm.

After the dilatometer had been assembled, the soap was heated rapidly to 310° and held there a few minutes until a comparison sample, sealed in a glass tube and hung in the furnace close to the dilatometer, had melted completely. This procedure tends to collapse small vacuoles that may have formed. Experience has shown that the correct procedure to be followed to ensure that the starting material at room temperature is actually curd fiber phase must be worked out separately for each soap. In the case of sodium palmitate, reversion to curd fibers occurs in a few hours at about 100°, but may require ten days at room temperature.

During a run the temperature was raised in steps of two degrees and held constant at each temperature for ten minutes, unless previous runs had shown that reproducible readings could be obtained in less time in any particular temperature region. The temperature was held nearly constant for much longer periods, up to seventy-two hours, in the neighborhood of transitions or suspected transitions, unless previous experience had shown the transition to be complete in less time.

Samples for microscopic observation were sealed in small flattened Pyrex capillary tubes, conveniently drawn from 5-mm. tubing. For high temperature work the rapidity of oxidation of soap by air makes the use of slides and ordinary cover glasses wholly unsatisfactory. In these experiments relatively thick soap samples (about 0.5 mm.) were used in order to preclude the possibility of spurious effects due to induced orientation of the liquid crystalline phases by the glass.

Observations were made using a Leitz polarizing microscope, equipped with a Weygand Hot Stage. Temperature gradients in the interior of this hot stage are very large, especially at high temperatures. Consequently, the temperature of the soap under observation was determined by means of a thermocouple, one junction of which was bound to the sample tube in the field of view

of the microscope, the other junction being bound to the bulb of a lagged, calibrated, mercury-in-glass thermometer hung in a small furnace similar to that used with the dilatometer. The auxiliary furnace was kept at very nearly the same temperature as the hot stage, any small difference being read by a calibrated milliammeter.

All the thermometers employed in this work were compared under conditions of use with the same secondary standard, a mercury-in-glass thermometer graduated in degrees from -10 to $+360°$. In general, the use of calculated stem corrections at high temperatures was unsatisfactory because of the difficulty in defining and measuring an average stem temperature. This secondary standard was compared with a thermometer calibrated by the Bureau of Standards, and also with an accurate copper-constantan thermocouple kindly lent us by Mr. W. D. Kennedy working with Professor G. S. Parks. In addition, a few microscopic determinations of the melting points of crystalline benzoic acid, anthracene, phenolphthalein and sodium nitrate were made to check the accuracy of the calibration. We believe these calibrations establish the temperature scale to within $3°$.

Photomicrographs were taken with polarized light and crossed Nicols on Kodak XX panchromatic film packs in a Zeiss Phoku camera. The over-all magnification, determined by photographing a Zeiss objektmikrometer, was 166 fold. Plates III, IV, V and VI show the appearance of essentially the same field of view at different temperatures.
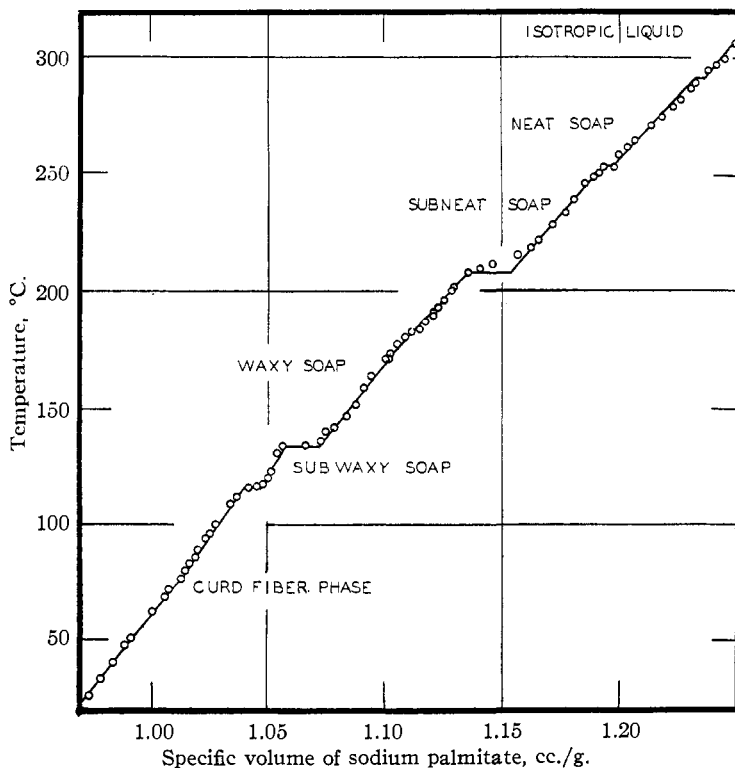
Results

The equilibrium curve for anhydrous sodium

palmitate is shown in Fig. 1, where volume is plotted against temperature. The points are those of Table I, and were all obtained on heating. The same curve has been reproduced, for the most part, on cooling, although the behavior in the neighborhood of the transition from waxy soap to subneat soap ($208°$) and from subwaxy to waxy soap ($135°$) is a bit unusual as will be discussed later. The data of Table I are a representative cross section of those obtained, which are too voluminous to be given in full. Column 1 gives the temperature, column 2 the observed dilatometer readings and column 3 the specific volume of the soap. Specific volumes were calculated by the equation

$$V_s = V_s^0 + \frac{1}{W} [(r - r_0) \delta + V_B \alpha_B (t - t_0) - (V_{Hg}^0 - (r - r_0) \delta) \alpha_{Hg} (t - t_0)]$$

where V_s and V_s^0 are the volumes occupied by the soap at temperatures t and t_0, r and r_0 the dilatometer readings at t and t_0, V_B^0 the volume of the Pyrex glass bulb at t_0, α_B its coefficient of expansion, V_{Hg}^0 the mercury content of the dilatometer bulb at t_0, α_{Hg} the coefficient of expansion of mercury, δ the factor converting dilatometer readings from mm. to cc., and W the weight of the soap sample. r and t are measured directly, V_{Hg}^0, W, δ and r_0 are obtained at the beginning of each experiment. The expansion of the dilatometer bulb, α_B, was calculated from the work of Jones and Jelen,[11] and that of mercury, α_{Hg}, was taken from "I. C. T."[12] The volume of the soap at room temperature is obtained from its weight and the density, 1.032, calculated from the X-ray measurements of Thiessen and Stauff[13] on their monoclinic β-sodium palmitate, which the work of Thiessen and Spychalski[14] shows is probably identical with our crystalline curd fiber phase.

The temperatures at which phase changes occur and the volume changes at the transitions are summarized in Table II. The mean thermal ex-

Fig. 1.—Dilatometric behavior of sodium palmitate.

(11) G. Jones and F. C. Jelen, THIS JOURNAL, 57, 2532 (1935).

(12) "International Critical Tables." Vol. I, 1926, p. 102.

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

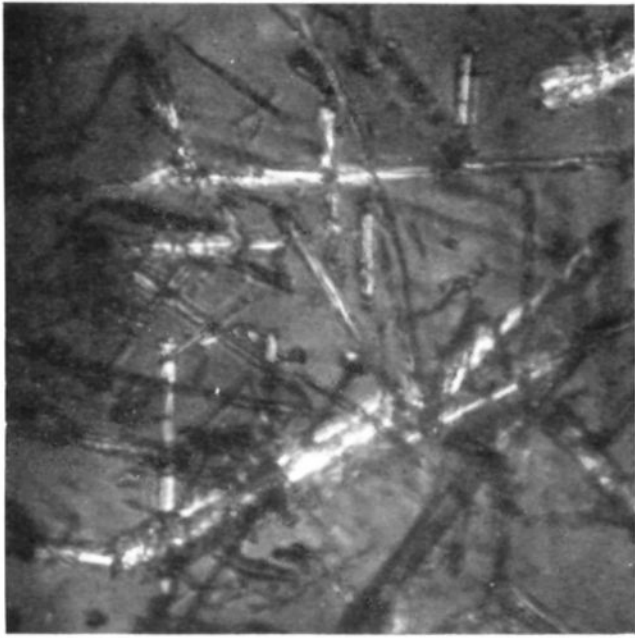(14) P. A. Thiessen and R. Spychalski, ibid., A156, 435 (1931).

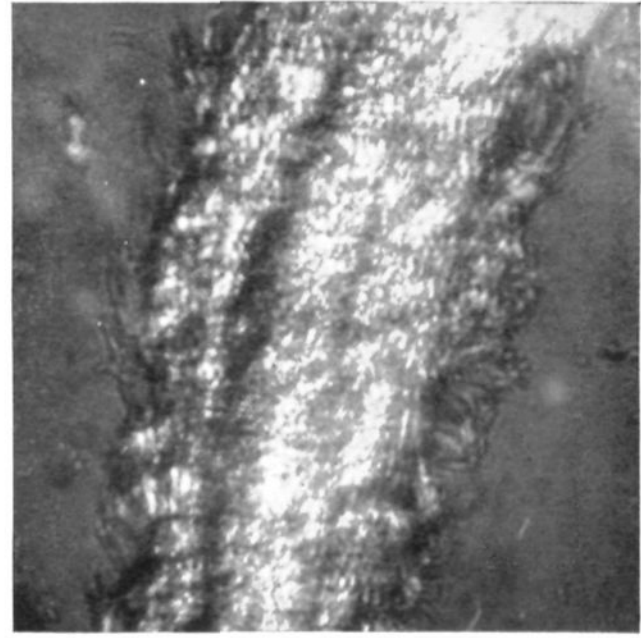Plate I.—Fully developed curd fibers at 98°.

Plate II.—Typical appearance of curd fiber phase at 96°.

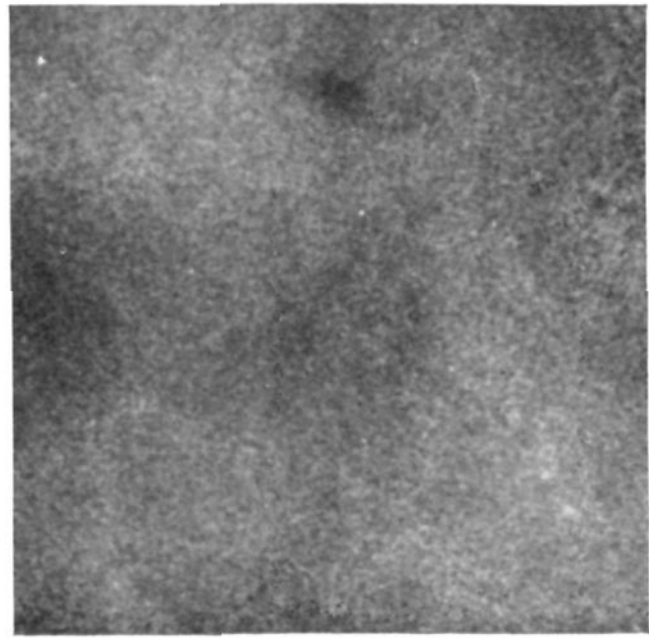Plate III.—Well developed fibers forming in curd fiber phase at 104°.
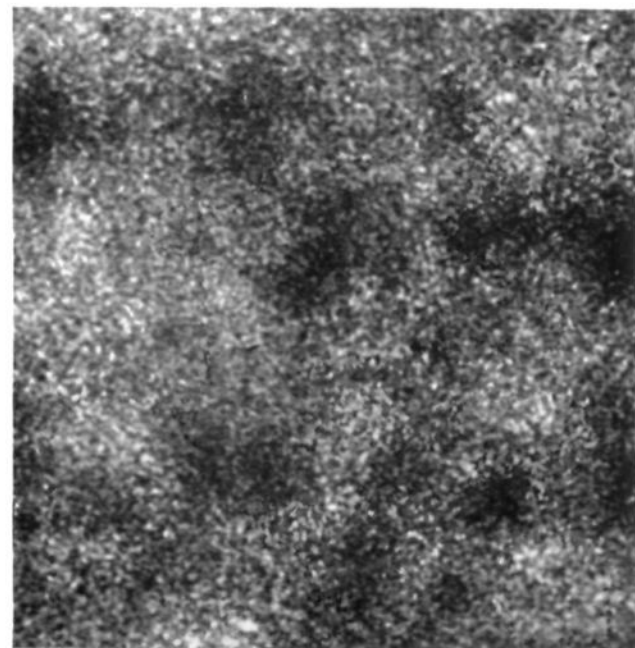

Plate IV.—Subwaxy soap at 118°.
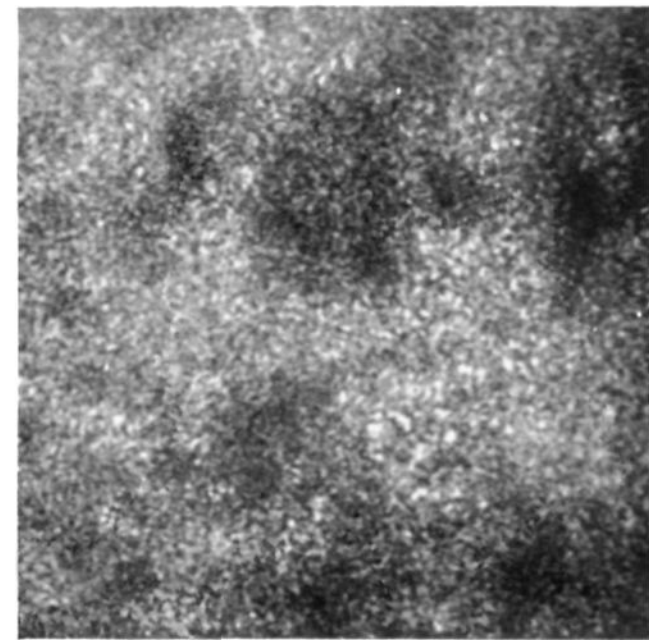

Plate V.—Waxy soap at 159°.

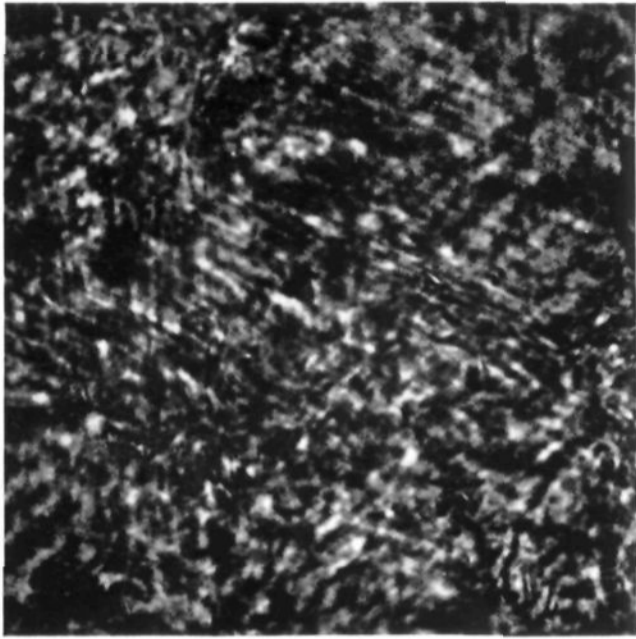Plate VI.—Waxy soap at 198°.

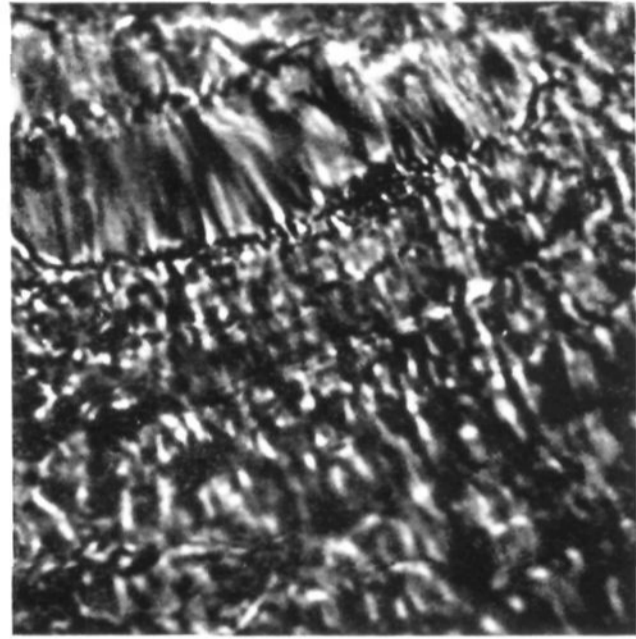Plate VII.—Subneat soap at 220°.

Plate VIII.—Neat soap at 263°.

Plate IX.—Neat soap separating from isotropic
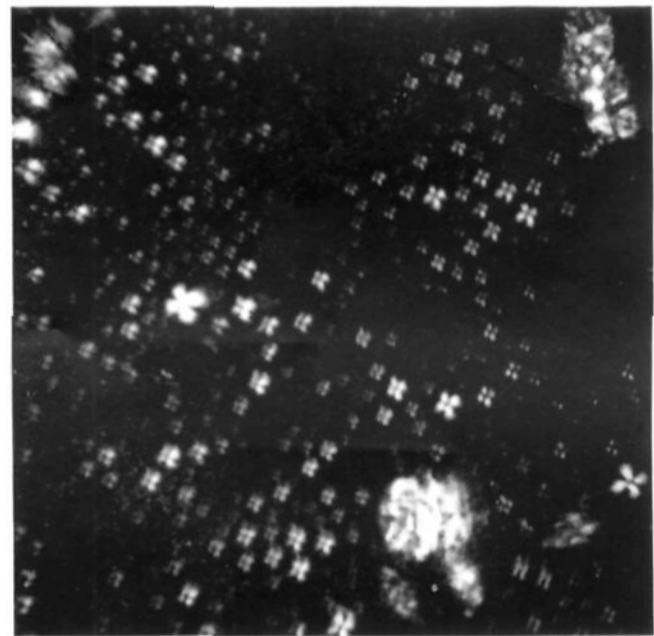liquid at 292°.

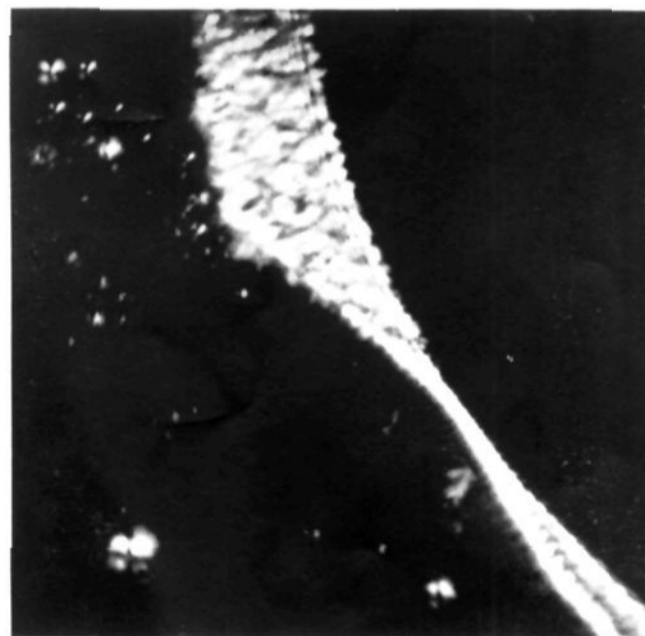Plate X.—Neat soap separating from isotropic
liquid at 292°.

Plate XI.—Neat soap separating at the edge of a
bubble in isotropic liquid at 292°.

TABLE I

REPRESENTATIVE DILATOMETRIC DATA

The first and second series of points are taken from runs on different samples of sodium palmitate.

Temp., °C.	Dil. reading, mm.	Sp. vol. cc./g.	Temp., °C.	Dil. reading, mm.	Sp. vol. cc./g.
20.0	0.0	0.97000	171.6	149.3	1.1000
26.6	5.5	.97356	173.9	151.0	1.1020
33.3	11.5	.97818	177.9	154.0	1.1052
40.1	18.5	.98382	180.7	157.2	1.1089
48.0	25.8	.98927	183.2	159.6	1.1112
50.9	28.6	.99136	187.3	164.0	1.1168
62.3	41.0	1.00205	191.4	167.1	1.1202
68.4	46.6	1.00560	193.7	168.7	1.1216
72.2	49.5	1.00727	196.5	170.8	1.1249
76.8	55.0	1.01250	200.4	172.9	1.1277
79.9	56.9	1.01400	202.6	174.5	1.1288
83.2	60.0	1.0163	208.8	179.5	1.1346
86.2	62.8	1.0186	210.9	184.0	1.1395
89.1	64.5	1.0194	212.5	189.9	1.1451
94.3	69.4	1.0231	215.9	198.0	1.1556
96.0	71.8	1.0254	219.0	203.4	1.1620
100.5	74.8	1.0271	222.2	206.1	1.1649
109.2	83.9	1.0344	229.1	211.1	1.1708
112.3	86.7	1.0363	233.9	215.0	1.1765
115.8	90.9	1.0409	239.7	219.2	1.1805
116.9	93.9	1.0443	246.3	223.8	1.1850
117.5	95.0	1.0457	249.2	226.0	1.1880
117.8	95.9	1.0464	251.7	229.0	1.1910
120.2	99.1	1.0496	253.9	230.6	1.1930
123.3	101.0	1.0506	253.9	232.2	1.1960
125.7	103.7	1.0508	259.0	236.0	1.1992
131.4	106.2	1.0534	261.9	239.5	1.2030
134.4	112.4	1.0590	264.9	242.2	1.2060
134.4	116.7	1.0650	271.3	248.1	1.2130
136.7	122.7	1.0720	279.3	256.3	1.2221
140.3	125.6	1.0740	284.8	260.1	1.2175
142.3	129.0	1.0772	282.5	258.4	1.2260
147.8	134.9	1.0832	284.8	260.8	1.2275
151.9	139.3	1.0870	287.0	262.8	1.2300
159.5	145.0	1.0905	289.2	265.3	1.2318
164.1	149.0	1.0938	294.7	269.5	1.2375
171.3	157.5	1.1016	297.6	272.0	1.2410
179.8	168.5	1.1122	300.7	275.0	1.2429
184.4	172.0	1.1147	304.9	275.5	1.2435
190.0	178.1	1.1202	307.1	277.1	1.2480

pansions of each phase are presented in Table III. In both these tables the indicated uncertainties in the values are the mean deviations be-

TABLE II

TRANSITIONS OF ANHYDROUS SODIUM PALMITATE

Phase change	Temp., °C.	Vol. incr. cc./g.
Curd fibers–subwaxy soap	117	0.0085 ± 0.004
Subwaxy soap–waxy soap	135	.0148 ± .004
Waxy soap–subneat soap	208	.027 ± .002
Subneat soap–neat soap	253	.0035
Neat soap–isotropic liquid	292	.0021

tween results on different samples. However, the uncertainty as to whether air has been removed completely from a given sample makes the absolute accuracy of the tabulated values of the expansion coefficients doubtful.

TABLE III

MEAN COEFFICIENTS OF THERMAL EXPANSION

Phase	$10^4\alpha$ (deg. $^{-1}$)
Curd fibers	4.6 ± 2.3
Subwaxy soap	8.0 ± 2.3
Waxy soap	8.6 ± 1.0
Subneat soap	6.0 ± 0.8
Neat soap	9.2 ± 1.0
Isotropic liquid	...

The transitions occurring at 117, 135 and 208° are accompanied by large volume changes and consequently are detected readily with the dilatometer. Although changes in visual appearance can be noticed it is almost impossible to determine the temperatures of change by inspection.

As ordinarily prepared, curd fiber phase, the stable phase at room temperature, appears as a white granular powder. Crystallized from aqueous neat soap and subsequently dried, these fibers appear as fiber bundles, even under the highest magnification.[15] At no time have we seen any trace of definite crystal faces, although X-ray evidence[13,14] indicates that these fibers have three-dimensional crystal regularity. The characteristic appearance of this phase is shown in Plates I, II and III.

Waxy soap, stable between 135 and 208°, can be distinguished readily from curd fibers. It is considerably more translucent and individual structural units, either fibers or crystals, are no longer visible. In the polarizing microscope between crossed nicols this phase has a characteristic somewhat grainy, predominantly golden, slightly irridescent appearance. The gross structure can be seen in Plates V and VI. Subwaxy soap, stable between 117 and 135°, closely resembles waxy soap and cannot be distinguished from it by visual inspection. Neither have we found any apparent difference in microscopic appearance (compare Plates IV and V). Nevertheless, the magnitude and reversibility of the volume changes accompanying its formation and disappearance prove its existence as a separate phase.

Subneat soap, stable between 208 and 253°, is visibly different from the waxy soap from which

(15) R. D. Vold and R. H. Ferguson, THIS JOURNAL, **60,** 2066 (1938).

it forms, and from the neat soap to which it melts; but the difference is of degree rather than kind. It has a very pale lemon color rather than white, and is more plastic than waxy soap. The grained structure visible in the polarizing microscope is much coarser, polarization colors of the most varied hues are brilliant, small cracks heal, and bubbles have a limited mobility. A photomicrograph of this phase is shown in Plate VII.

A sample of sodium palmitate of entirely different origin[1] gave transition temperatures essentially identical with those reported here, except for the change from waxy to subneat soap, which occurred at 197° rather than 208°. Only one sample of the present stock behaved similarly in the dilatometer ($t = 193°$). The discrepancy cannot be due to the presence of moisture since microscopic determination of the transition on a sample which had been dried only by heating to constant weight at 105° gave a value within one degree of the dilatometric value of 208° for a completely dried sample. Nevertheless, there is a slight but reproducible change in microscopic appearance at 195° on heating, preceding the very pronounced change to subneat soap. It may be seen by careful comparison of Plates V and VI. It should be kept in mind, however, that the change in appearance is not much more pronounced than many which have been observed with one and the same phase at different temperatures.

There is a further complication at about 180°, where the dilatometer curve is not entirely smooth, but has a slight irregularity. At all other temperatures mentioned in this work either there is a considerable volume change or else a very pronounced change in microscopic appearance. Neither of these criteria is fulfilled in the present instance. Further work by some other method may be necessary to determine definitely whether some phase change occurs at about this temperature.

The change from subneat to neat soap at 253° results in only a small change in volume but is also marked dilatometrically by a considerable change in the slope of the volume–temperature curve. The formation of neat from subneat soap in bulk samples is accompanied by loss of mechanical rigidity and the development of a characteristic turbid bubbly appearance. The most characteristic change microscopically is the development of the focal conic structures character-

istic of smectic liquid crystals.[16] Plate VIII shows the characteristic appearance of neat soap. Plates IX, X and XI show neat soap in equilibrium with isotropic liquid and display many of the optical forms characteristic of smectic liquid crystals.[17]

The transition from neat soap to isotropic liquid at 292° is detectable dilatometrically from the difference in the slope of the volume–temperature curve and from a small change in volume. In this instance, however, the change in volume is so small that other methods were relied on to give the exact transition temperature. This transition is detected easily in bulk samples by the development of a meniscus and the free movement of bubbles through the molten material. Microscopically it is very striking since the brilliantly colored neat soap disappears, leaving the field of view between crossed nicols dark.

Discussion

The results of this investigation provide definite evidence for the existence of six allotropic modifications of anhydrous sodium palmitate. The transition point for curd–neat given by McBain[6] as 121 or 134° appears to correspond to the present transitions from curd fiber phase to subwaxy soap at 117° and from subwaxy to waxy soap at 135°. The values reported by McBain were based on visual determinations of the temperature of final disappearance of curd fibers. It seems all the more likely that the phase change at 134° (point E of Fig. 1 of McBain's paper) refers to the transition from subwaxy to waxy soap since subwaxy soap is itself so opaque that it might readily be mistaken for curd if its presence were not suspected.

It is also possible that the transitions reported at 265–270° by previous investigators[3,18] were in reality our subneat to neat soap transition.

Lawrence's observations[7] also may be correlated with the results described in the present paper. Presumably his "hard fully crystalline" state corresponds to curd fiber phase, and his "soft crystalline" state to either subwaxy or waxy soap, while his "isotropic liquid of low viscosity" is obviously identical with our isotropic liquid. It is not at all clear to which phase his "very

(16) Lawrence's statement that these structures are not found in sodium soaps[7] is possibly due to the fact that he may have looked for them around 220°, where the transition to neat soap had previously been supposed to occur, rather than at the higher temperature.

(17) A. S. C. Lawrence, J. Roy. Microscop. Soc., 58, 30 (1938).

(18) Krafft, Ber., 32, 1598 (1899).

viscous liquid" refers. It seems likely, since his determinations of this state are based only on observation of viscosity changes, that it may not always refer to the same phase, or indeed to any change of phase.

In the case of sodium palmitate, Lawrence reports transitions at 150–155, 259 and 291°. Both 259 and 291° are referred to as T_1, the temperature at which the molten substance no longer drops from the thermometer. The transition at 150°, T_2, is regarded as the temperature at which the substance becomes hard crystalline solid, and was determined as the point above which the soap flowed under pressure and adhered to the glass when rubbed against the side of the tube. In view of our results it appears that Lawrence's change at 150° probably corresponds to the transition from subwaxy to waxy soap (135°), his change at 259° to the transition from subneat to neat soap (253°) and his change at 291° to the transition from neat soap to isotropic liquid (292°). When one considers his experimental method with regard to the characteristics of the various transitions described earlier in this paper, it is not surprising that the agreement between the two sets of values is not very close.

Thiessen and co-workers[19] have found two sodium palmitate phases not so far considered in the present paper. The first of these is a rhombic crystalline modification with a structure similar to that of the odd-numbered n-hydrocarbons. In the case of the soaps, and also the fatty acids, this form is metastable with respect to a monoclinic form, which can be identified in the case of the soaps as curd fiber phase.

Their second transition, at 63°, the "genotypic" effect, is accompanied by only a slight alteration in mechanical structure. Only minute inflections occur in their dilatometer curves and total cooling curves, although an ingenious differential method showed the change very clearly. The X-ray work of Thiessen and Spychalski[14] shows that, despite the absence of gross external manifestation, this change is a very fundamental one; one of the characteristic reflections gradually becomes diffuse over a range of temperature and finally disappears. Since this change occurs for each soap at the melting point of the corresponding fatty acid, these authors conclude that it corresponds to the same change that brings about

genuine melting in the case of the acids. The genotypic transformation may, then, be regarded as the first stage in the step-wise disintegration of the soap lattice.

Our own dilatometric curves also show a very slight inflection at 65° which might be ascribed to the genotypic transformation.

Possible Effects of the New Phases on Aqueous Systems.—The formation of subwaxy soap from a phase which we shall for the present continue to call curd fibers, despite the fact that it is known to differ from the curd fibers that are stable at room temperature, is accompanied by a considerable increase in volume. This phase when found in the aqueous system[9,20] was originally designated "waxy" prior to definite establishment of the transition at 135°. However, it now seems preferable to reserve this name for the second of these two phases (that stable between 135 and 208°), which it most aptly describes, referring to the phase existing between 117 and 135° as "subwaxy."

That the genotypic transformation is of possible practical importance is attested by the fact that it affords a reasonable explanation for the existence of the Krafft point, i. e., the temperature at which the solubility of soap in water increases enormously. This tremendous rise in the temperature coefficient of solubility of sodium soaps in water occurs at about the melting point of the corresponding fatty acid. Attempts have been made to explain this effect on the basis of some change in the properties of the soap solution[21] but on this view the correspondence between the Krafft point and the melting point of the fatty acid has to be regarded as coincidence. It seems more likely that the inflection in the solubility curve arises from a transition in the equilibrium solid phase, which itself occurs at about the melting point of the fatty acid.

While it is apparent that the existence of this large number of hitherto unrecognized soap phases makes necessary a considerable extension of the previous phase rule work, this point is deserving of special emphasis with regard to the formation of the waxy phases because of their possible importance in the technology of soaps. These phases are not found at kettle temperatures in systems of pure sodium palmitate and water.[15]

(19) P. A. Thiessen and Ehrlich, Z. physik. Chem., **A165**, 453 (1933). Cf. also ref. 13.

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

(21) R. C. Murray and G. S. Hartley, Trans. Faraday Soc., **31**, 183 (1935).

However, one of them does exist at 90° in the sodium laurate–water system,[9] and experiments under way on mixed anhydrous systems of sodium palmitate and sodium laurate show that it can exist even as an equilibrium phase at much lower temperatures. In many systems it is quite likely that curd fiber phase is not formed directly from neat soap on cooling as has always been supposed. It is even possible that some commercial mixtures may remain in the subwaxy or waxy state for long periods, forming genuine curd fibers, wholly or partially, only on aging if at all.

Reversibility of the Various Transitions.—In the formation of a true crystal from a liquid the phenomenon of undercooling, or suspended transformation, is quite common. With anhydrous sodium palmitate, genuine undercooling occurs only with respect to the formation of curd fiber phase from subwaxy soap. Mechanical jarring of

Fig. 2.—Non-equilibrium behavior at the transition involving subneat and waxy soap. The dotted line is the equilibrium curve: □, cooling at 10° per hour; ○, heating at 20° per hour.

Fig. 3.—Non-equilibrium behavior at the transition involving waxy and subwaxy soap. The dotted line is the equilibrium curve: □, cooling at 10° per hour; ○, heating at 30° per hour.

the undercooled material can initiate the transition which then proceeds rapidly. If the temperature is lowered below 117° while some curd fibers still remain in the system no undercooling occurs.

The highest rate of cooling at which it was certain from the agreement of results obtained on heating and cooling that the dilatometer and thermometer were at the same temperature was 2° per minute. At this rate, both the change from isotropic liquid to neat soap and from neat soap to subneat soap occur on cooling at identically the same temperature as on heating.

The behavior at the two remaining transitions, from subneat to waxy soap (208°) and from waxy soap to subwaxy soap (135°), as the temperature is lowered, is entirely different alike from ordinary undercooling and from rapid reversibility. These transitions can be made to occur at any temperature up to 20° below the value obtained reproducibly on heating. They also can be made to occur in several steps within this temperature range, or loops as in Figs. 2 and 3 can be obtained, with suitable manipulation of the rate of cooling. This behavior is quite similar to that of ethyl stearate as reported by Baker and Smyth.[22]

These observations can be interpreted in terms of the concepts that (1) the transition at the temperature found on heating is truly reversible, and (2) the rate of reversal of the transformation on cooling is slow in the neighborhood of the transition point, but increases rapidly as the temperature is lowered. Figure 4 shows the average rate of change from subneat to waxy soap under varying conditions. Uniform cooling results in volume–temperature curves having the same shape as the curve of rate of transformation *versus* temperature. If heating is commenced before reversal is complete loops similar to those of Figs. 2 and 3 are realized. The rate of transformation of subwaxy soap on heating is also slow, so that the loop can have a finite width above as well as below the transition temperature. Since the change from subneat to waxy soap is apparently rapidly and reproducibly accomplished at the same temperature (208°) on heating or cooling in very small samples, as judged by microscopic appearance, we are inclined to adopt this point of view.

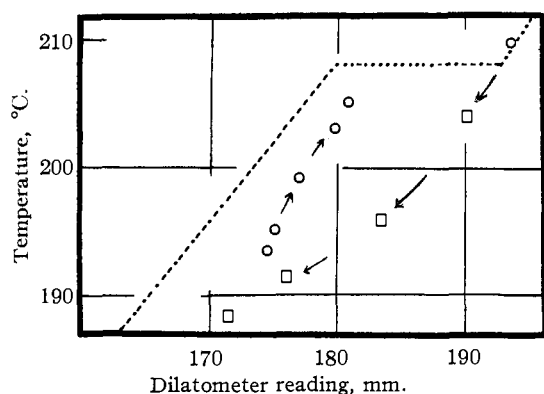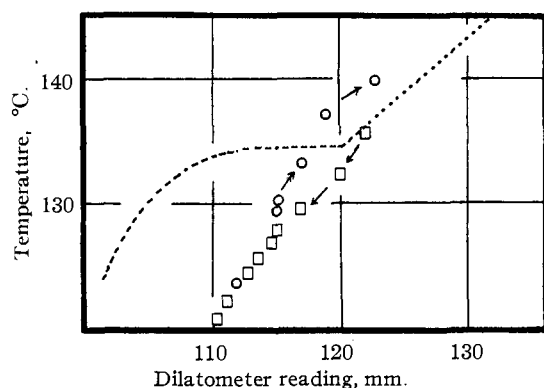However, if the rate of transformation is actually zero in the region just below the transition

(22) W. O. Baker and C. P. Smyth, THIS JOURNAL, **60**, 1229 (1938).

temperature observed on heating, as would be indicated by the dotted line in Fig. 4, some other explanation would be necessary. It would tend to show that in the region between 193 and 208° either subneat or waxy soap could be made to persist indefinitely; both 193 and 208° would have to be recognized as transition temperatures, the lower realizable only on cooling, the upper only on heating.[23]

Internal Nature of the Different Soap Phases. —Insofar as the magnitude of the volume increase on transition affords a qualitative measure of the extent of the internal rearrangement taking place, it is apparent that curd fiber phase, subwaxy soap, waxy soap and subneat soap are all quite different from each other, while the structural changes in going from subneat soap to neat soap and finally to isotropic liquid are much smaller. The thermal expansion per degree also bears out the supposition that there is an extensive change when curd fibers transform to subwaxy soap. The thermal expansions of subwaxy and waxy soap are nearly the same, in harmony with other similarities of these two phases. Curiously, the coefficient of thermal expansion of subneat soap is smaller than that of either waxy soap or neat soap. This indication of stronger bonding forces is in accord with the fact that water seems to be less soluble in this phase than in either waxy or neat soap. That the thermal expansions of the successive phases increase progressively with rising temperature (except for subneat soap) suggests a progressive loosening of the structure which, eventually, culminates in melting to isotropic liquid.

There is a close similarity in appearance between subneat soap and the α-modification of the fatty acid esters described by Malkin[24] and by Baker and Smyth.[22] The X-ray evidence of Malkin shows that this form (of the esters) may be regarded as mesomorphic since one of the side spacings characteristic of the crystal has disappeared. It is probably identical with what K. Hermann[25] has called the "ordered smectic" state.

X-ray work on the anhydrous soaps under controlled conditions, which has been begun, probably will provide valuable information concerning the degree of internal regularity of these phases. Neat soap is certainly a smectic liquid crystal;

Fig. 4.—Rate of transformation from subneat to waxy soap: O, one-half gram soap sample; □, one-gram sample; △, 0.8-gram soap sample.

subneat soap is quite possibly an "ordered smectic" state. The remaining phases intermediate between curd fibers and subneat soap are probably all mesomorphic, since curd fiber phase itself cannot be considered fully crystalline above the genotypic transformation. Sodium palmitate then provides an example of a substance in which the various lattice forces are so anisotropic and so different in magnitude that melting from crystal to liquid occurs in six or more separate discontinuous steps.

The authors wish to express their appreciation to Professor J. W. McBain for many helpful discussions during the course of this work.

Summary

1. Dilatometric and microscopic evidence shows that anhydrous sodium palmitate has at least five successive phase changes between 70 and 300°. The corresponding phases are curd fibers (up to 117°), subwaxy soap (117–135°), waxy soap (135–208°), subneat soap (208–253°), neat soap (253–292°) and isotropic liquid (above 292°).

2. One or more of these phases may be formed during the process of soap manufacture, and may persist in some mixtures for long periods of time at room temperature.

(23) A. Smits and G. J. Muller, Z. physik. Chem., **B36**, 146 (1937).
(24) T. Malkin, Trans. Faraday Soc., **29**, 977 (1933).
(25) K. Hermann, Z. Krist., **92**, 49 (1935).

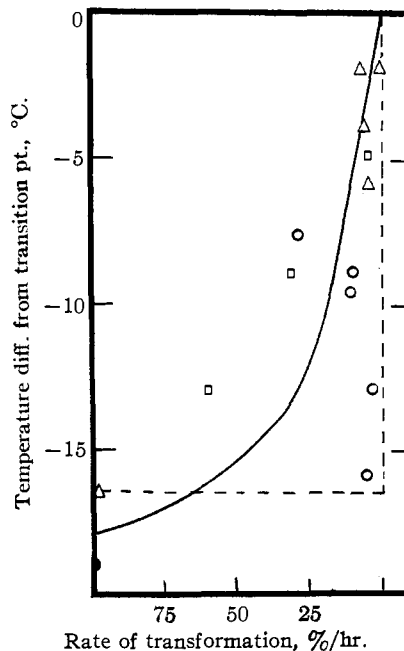3. These transitions may all be regarded as successive stages of melting, the phases intermediate between crystal and liquid being of a

mesomorphic nature.

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Fluorenones and Diphenic Acids. VI.[1] Ring Cleavage of 2-Chloro-, 2-Hydroxy-, 2-Amino- and 2-Sulfofluorenones with Potassium Hydroxide in Diphenyl Ether

BY ERNEST H. HUNTRESS AND MARGARET K. SEIKEL[2]

In connection with studies of the action of concentrated sulfuric acid upon substituted diphenic acids which has for some time[3] been in progress in this Laboratory the use of alkali as a means of fission of the ketonic linkage of substituted fluorenones has been examined. Since the preparation of o-phenylbenzoic acid by potassium hydroxide fusion of fluorenone[4] affords excellent yields and since alkali fusion of unsymmetrical ketones recently has been shown to proceed smoothly in certain other cases,[5] we have examined this process to determine whether the conditions could be so modified that fission of the fluorenone ring would occur without (serious) action on nuclear substituents. The demonstrated necessity (see Experimental Part) of absolutely avoiding reducing solvents compelled us to try inert materials even though the alkali was thus merely suspended, and after some attempts with biphenyl we discovered that the desired ketonic cleavage could be effected by using potassium hydroxide in diphenyl ether at about 180°. A large excess (e. g., ca. 15 mols.) of fused potassium hydroxide vigorously stirred at 180–200° with fluorenone dissolved in diphenyl ether gave a quantitative yield of o-phenylbenzoic acid of excellent purity. The present paper reports the results obtained with several fluorenones substituted in the 2-position.

(1) Presented at the Rochester meeting of the American Chemical Society, September, 1937.

(2) From a dissertation submitted by Miss Seikel to the Faculty of the Massachusetts Institute of Technology, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1938.

(3) Previous papers: (a) I, Huntress, Hershberg and Cliff, THIS JOURNAL, **53**, 2720–2724 (1931); (b) II, Huntress and Cliff, ibid., **54**, 826–828 (1932); (c) III, Huntress and Cliff, ibid., **55**, 2559–2567 (1933); (d) IV, Huntress, Cliff and Atkinson, ibid., **55**, 4262–4271 (1933); (e) V, Huntress and Atkinson, ibid., **58**, 1514–1518 (1936).

(4) Fittig and Ostermayer, Ann., **166**, 374 (1873).

(5) Bachmann, THIS JOURNAL, **57**, 737–738 (1935).

2-Chlorofluorenone (I).—Upon heating this compound with potassium hydroxide in diphenyl ether a nearly quantitative yield of 4'-chlorobiphenyl-2-carboxylic acid (V) was obtained. The identity of this acid was attested in several ways.
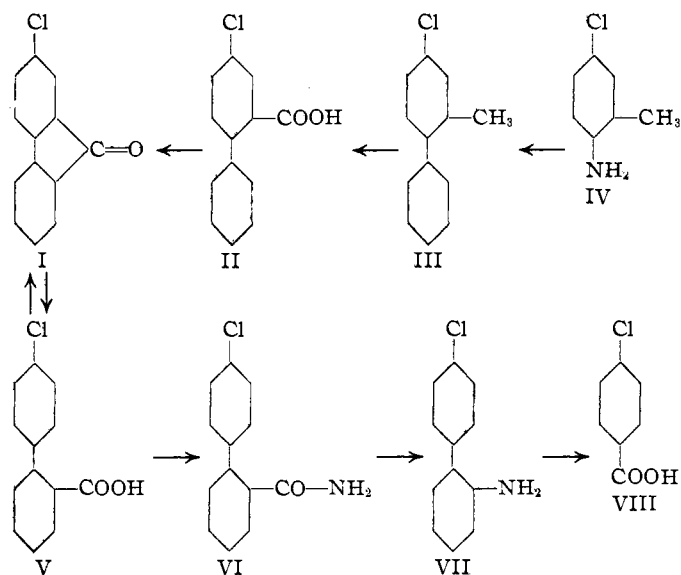
First, upon treatment with concentrated sulfuric acid it was reconverted to the original 2-chlorofluorenone. Second, the cleavage acid (V) was converted with phosphorus pentachloride to the corresponding acid chloride (not isolated) and thence with ammonia (in benzene) to the corresponding 2-(4'-chlorophenyl)benzamide (VI) which was then degraded by application of the Hofmann reaction to the corresponding amine, viz., 4'-chloro-2-aminobiphenyl (VII). The acetyl derivative of this amine melted in accordance with the recorded value and the amine itself on oxidation with alkaline potassium permanganate gave p-chlorobenzoic acid (VIII). This formation of p-chlorobenzoic acid is consistent only with that formulation (V) of the two conceivable