

method in rats proved to be identical. An explanation for this was found in the ability of the rat to convert neovitamin A to vitamin A.

5. Catalytic interconversion of the anthra-

quinone carboxylate esters of the two vitamins was accomplished *in vitro* by the action of iodine in benzene solution.

ROCHESTER 13, NEW YORK RECEIVED AUGUST 28, 1946

[CONTRIBUTION FROM THE PROCTER AND GAMBLE CO.]

The Phase Nature of Beta Sodium Palmitate

BY R. H. FERGUSON, F. B. ROSEVEAR AND H. NORDSIECK

Introduction

In an earlier paper¹ evidence was presented to show that solid sodium soaps could be described in terms of four distinct crystalline structures, each identifiable with the aid of one or two carefully selected X-ray short spacings. At the same time² certain minor variations were recognized among patterns of the beta structure, depending upon whether "anhydrous" palmitate, hydrous palmitate or commercial soap was involved. Similar minor effects in the omega structure were noted in a companion paper,³ and the variations in beta palmitate were localized in the narrow composition range below about 3% water.

In the present contribution, which extends the earlier X-ray evidence and supplements it with vapor pressure and microscopic results, it is shown that the foregoing spacing variations in beta sodium palmitate are not indicative of new phases, but arise from the existence of a continuous beta solid solution phase which, at room temperature, extends from almost anhydrous soap to about 2.5% water.

The four phase concept outlined in references 1 and 3, while not intended to rule out possible additional phases, is nevertheless regarded by some as an oversimplification. In this connection certain of the above variations in X-ray patterns have recently been rediscovered and used, along with other variations of comparable magnitude, as evidence for the existence of definite soap hydrates. This brings to ten the number of proposed crystalline phases in the sodium soaps.^{4,5}

In showing that two, and possibly three, of these phases are simply members of one solid solution series, our evidence, while confined to the beta structure, suggests that a similar close relationship may exist among other patterns bearing marked resemblance to each other.

Experimental

A. Materials and Methods.—The sodium palmitate used in this work is characterized in reference 1. With the

(1) R. H. Ferguson, F. B. Rosevear and R. C. Stillman, *Ind. Eng. Chem.*, **35**, 1005-1012 (1943).

(2) Note *b* in Table II and note *a* in Table V of ref. 1.

(3) R. H. Ferguson, *Oil & Soap*, **21**, 6-9 (1944).

(4) M. J. Buerger, L. B. Smith, F. V. Ryer and J. E. Spike, Jr., *Proc. Nat. Acad. Sci. U. S.*, **31**, 226-233 (1945).

(5) K. W. Gardiner, M. J. Buerger and L. B. Smith, *J. Phys. Chem.*, **49**, 417-428 (1945).

exception of a few points below 2.2% water, specifically noted below, all experimental points were obtained on soap crystallized by cooling homogeneous melt, usually neat soap, from above the "Tc" curve.

For samples below about 5% moisture, the starting material was prepared as follows: 20-g. samples of 20-25% water content were held in sealed glass tubes at 100° with occasional shaking until homogeneous. After spontaneous cooling (100 to 30° in thirty to sixty minutes), the contents of each tube were ground, given a preliminary drying in air of not less than 30% humidity, stored several days in closed jars to equalize moisture, and then analyzed to ensure a moisture content of at least 3%. The X-ray spacings of each batch were identical with those of the original soap crystallized from melt.

For points above 5% moisture, portions of the crystallized melt were placed directly in the vapor pressure tubes.

Per cent. moisture was determined from the loss in weight resulting from one hour of holding at 150°. Values are reproducible to $\pm 0.2\%$.

Further experimental details are given in connection with the corresponding results.

B. X-Ray Results.—Figure 1 presents graphically, for a series of hydrous sodium palmitate samples, the four strongest short spacings as a function of per cent. water. It is evident that from about 2.5% water up to at least 95% water, the spacings are constant at about 2.77, 3.16, 3.90 and 4.29 Å., whereas below 2.5% water each of the four varies continuously, the smaller spacing increasing to about 2.84 Å. and the three larger spacings decreasing to about 3.07, 3.75 and 4.17 Å., respectively, at 0.2% water. Attention has been focused on the three smaller spacings since the fourth spacing is complex and less closely measurable; it is included because it shows the same type of behavior as the other three.

Table I supplements Fig. 1 by presenting data for the entire pattern at each of several representative moisture contents in and beyond the range of pattern variability. Study of this table shows that, except for the four reflections plotted in Fig. 1, the rest of the spacings are practically constant. It is especially noteworthy that the long spacing is constant even in the moisture range where the short spacings of Fig. 1 vary continuously.

X-Ray patterns were obtained by techniques previously described,^{1,6} all samples being sealed in thin-walled Pyrex capillaries. Estimated accuracy of short spacings is about ± 0.02 Å., of long spacings ± 0.5 Å. Most of the data of Fig. 1 were obtained at 5 cm. sample-to-film distance, but

(6) R. H. Ferguson and H. Nordsieck, *Ind. Eng. Chem.*, **36**, 748-752 (1944).

TABLE I

POWDER PATTERN DATA OF SEVERAL REPRESENTATIVE BETA SODIUM PALMITATE SAMPLES															
% Moisture Order	0.23		0.64		1.50		2.28		3.36		33.5		74.4		
	<i>i</i>	<i>d/n</i>	<i>I</i>	<i>d/n</i>	<i>I</i>	<i>d/n</i>	<i>I</i>	<i>d/n</i>	<i>I</i>	<i>d/n</i>	<i>I</i>	<i>d/n</i>	<i>I</i>	<i>d/n</i>	
Long Spacings, Å.	2	S	21.3	S	21.3	S	21.3	M	21.3	M	21.0	M	20.5	M	20.5
	3	VS	13.9	VS	14.2	VS	13.9	S	14.1	S	14.0	S	13.9	S	14.0
	4	W	10.6	W	10.6	W	10.6	VW	10.6	VW	10.5	VW	10.3	VW	10.4
	5	M	8.48	M	8.45	M	8.48	M	8.45	M	8.50	W	8.36	M	8.40
<i>c</i> sin β		42.3		42.5		42.3		42.3		42.2		41.8		41.8	
Short Spacings, Å.		VS	4.15	S	4.22	VS	4.26	S	4.30	S	4.30	S	4.27	S	4.30
		S	3.75	MS	3.77	S	3.85	S	3.89	S	3.91	S	3.90	S	3.90
		VW	3.23	VVW	3.23	VW	3.23
		M	3.07	VM	3.08	M	3.13	W	3.16	W	3.17	W	3.17	W	3.16
		M	2.85	WM	2.82	M	2.82	M	2.78	WM	2.77	M	2.77	M	2.77
		W	2.63	VW	2.66	W	2.63	VW	2.63
		W	2.48	VW	2.51	W	2.48	VW	2.48
		M	2.35	W	2.39	W	2.34	W	2.34	VW	2.36	VW	2.35
		VVW	1.88	VVW	1.94	VVW	1.95
		VVW	1.79	VW	1.77	VVW	1.78

the reality of the continuous spacing variability over the range 0.2 to 2.5% was verified at representative moisture contents by patterns at 10 cm. in which the resolution is adequate to ensure that the variations encountered in this composition range do not represent the progressive replacement of fixed spacings characteristic of 2.5% water by fixed spacings typical of 0.2% water. Because the X-ray data are based on powder patterns which cannot at present be indexed, the actual atomic planes which contribute to each of the variable powder pattern rings remain unidentified. Consequently, no statement will be attempted as to the position of the structural water in the beta soaps.

Below about 5% moisture, X-ray samples were taken directly from the soap equilibrated in vapor pressure tubes. Above 5% moisture X-ray patterns were obtained from enough vapor pressure samples to show that no change in pattern had occurred during vapor equilibration, but the majority of X-ray data in this range were obtained directly on the melt-crystallized soap.

C. Vapor Pressure Results.—In Fig. 2 is shown the dependence of vapor pressure on water content at 27 ± 0.3°. From 0.2 to 2.5% water,

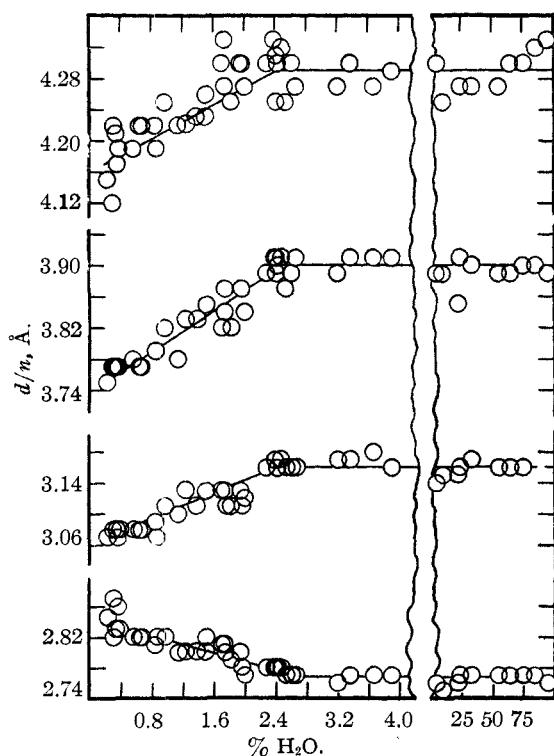


Fig. 1.—Variation of certain interplanar short spacings with water content in beta sodium palmitate.

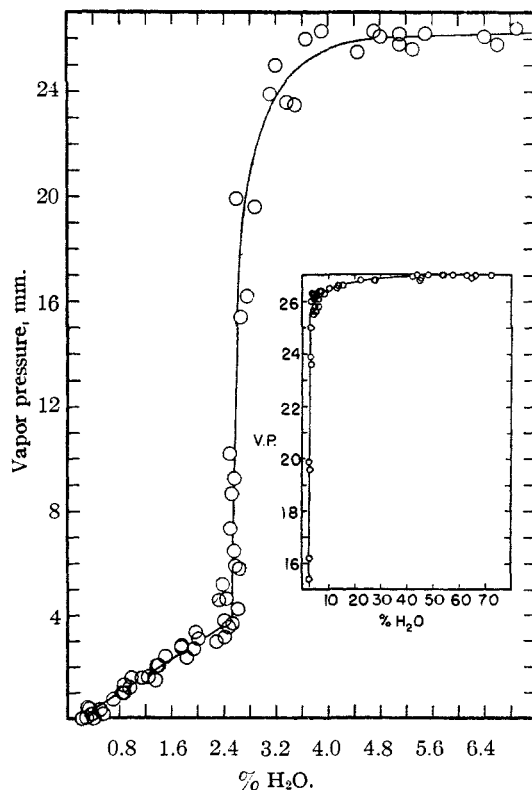


Fig. 2.—Dependence of vapor pressure upon water content in beta sodium palmitate, 27°.

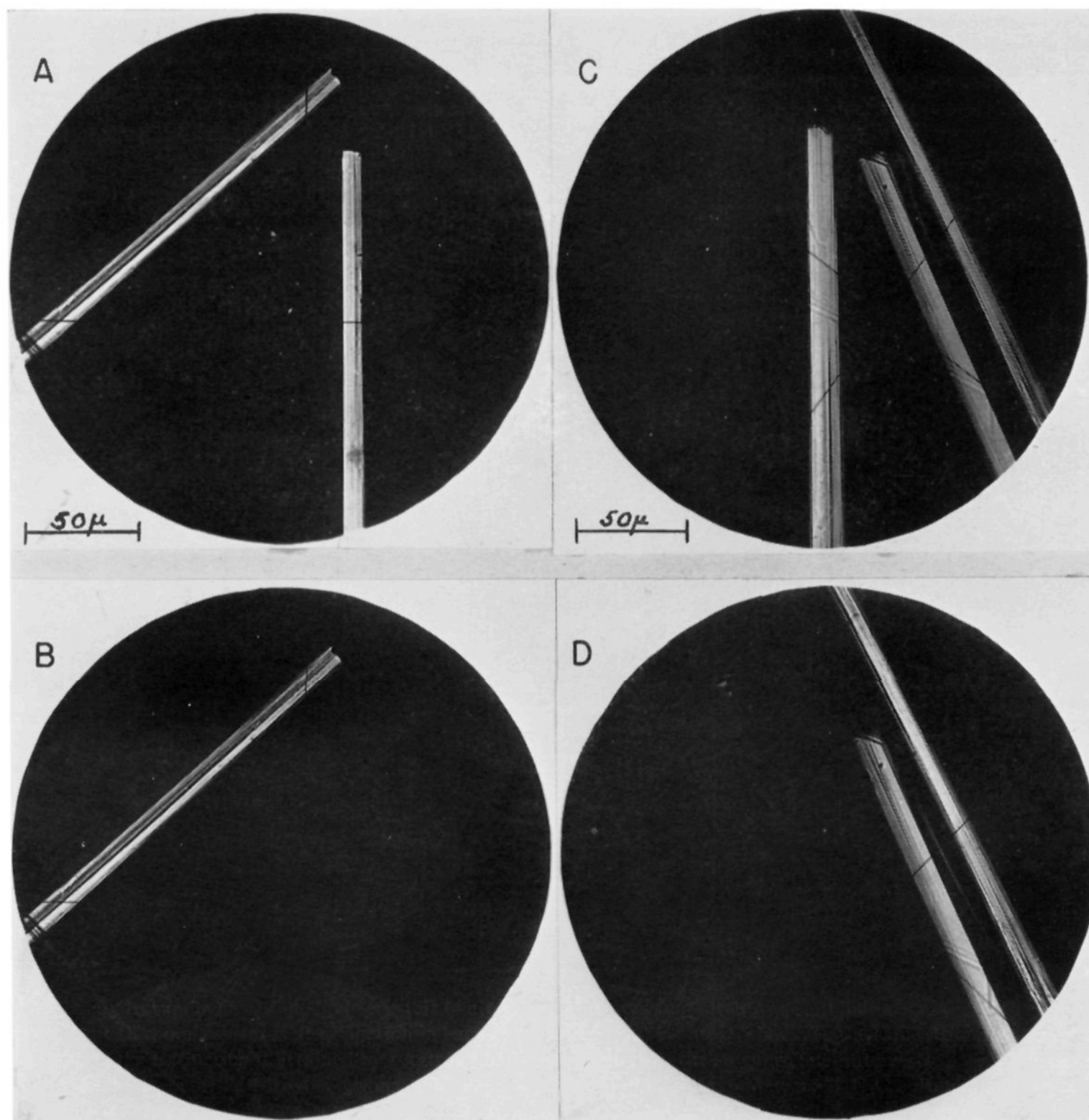


Fig. 3.—Dehydration behavior of single crystals of alpha and beta sodium palmitate: (All pictures taken with crossed nicols. Except that one crystal is at extinction in each of pictures B, D, F and H, these are the same fields respectively as A, C, E and G. Extinction is attained by rotating the nicols rather than the stage, to facilitate vertical comparison of pictures.) A and B, beta: air-dried single crystals separated from fiber bundle; about 2.5% H₂O. Refractive indices: lengthwise 1.514, crosswise 1.492; C and D, beta: (another field) dehydrated to 0.2% water over concentrated sulfuric acid. Complete extinction of centered crystal indicates no discontinuous change brought about by decrease in water-content. Refractive indices: lengthwise 1.522, crosswise 1.500. Contrast D with H; E and F, alpha: air-dried only. To illustrate completeness of extinction before dehydration; G and H, originally a single alpha crystal of the type shown in E and F, but dehydrated over concentrated sulfuric acid. Resulting polycrystalline pseudomorph proves occurrence of a discontinuous phase change.

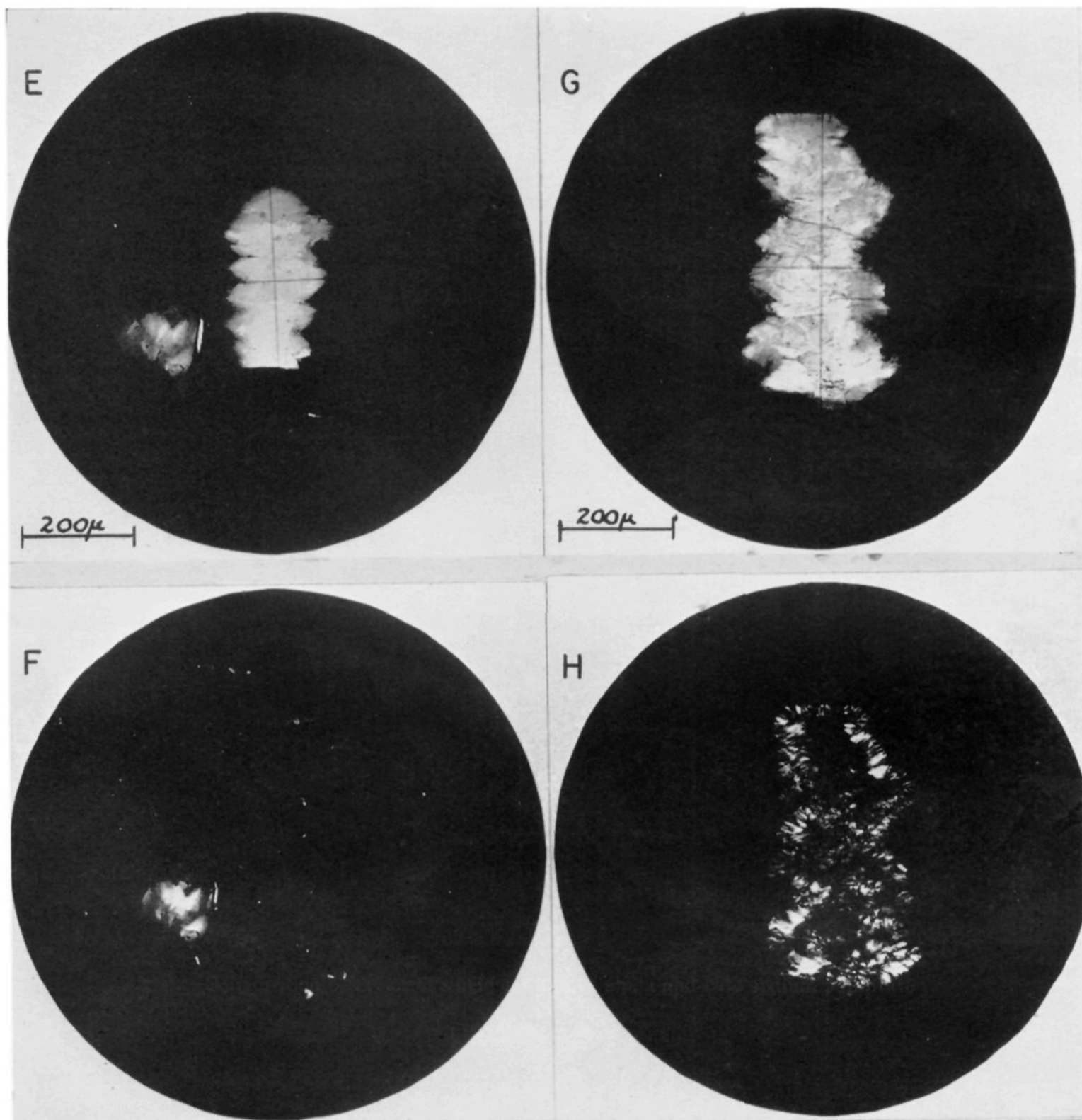


Fig. 3.—Dehydration behavior of single crystals of alpha and beta sodium palmitate.

corresponding closely to the range over which the X-ray spacings of Fig. 1 vary, the vapor pressure increases continuously from practically zero to about 4 mm., where an abrupt break occurs. Beyond this the curve rises very steeply at first, the vapor pressure exceeding 90% of saturation by 3.5% water, but gradually rounds off. The absence of a strict "flat" at constant vapor pressure (see inset in Fig. 2), except possibly at considerably higher moisture contents, will be discussed presently.

The vapor pressure data were obtained by an isopiestic method based on that used by Vold and Ferguson.⁷ To compensate for the lower vapor diffusion rate at room temperature, a shorter, wider path than in the tubes used by Vold and Ferguson at higher temperatures was employed. The tubes were sealed off under vacuum.

Equilibration time was usually ten weeks, though for some samples equilibrium was attained in one to two weeks, judging by results on samples held for the longer period. After equilibration the tubes were opened, X-ray samples of the soap taken, the soap analyzed for moisture, and the acid analyzed by titration with standard alkali solution. Sulfuric acid concentrations were converted to vapor pressures in mm. of mercury using the combined experimental data of Collins,⁸ Regnault⁹ and Sorel.¹⁰

Dehydration was satisfactory over the whole moisture range, as well as rehydration above 2.5% moisture. However, it should be noted that experiments starting with "Thiessen's beta" palmitate of 1.5% moisture, made by warming alcohol-crystallized alpha palmitate, showed that the structure could reincorporate a total of only about 2.2% moisture; at this composition the vapor pressure rises abruptly and the X-ray spacings cease changing, even when the soap mass attains a total moisture content of over 50%.

Discussion

A. Evidence for a Beta Solid Solution Phase.

—In accordance with the following interpretation of our results, a single crystalline phase of variable composition exists over the range from 0.2 to 2.5% water in the system NaP-H₂O at room temperature. Since this solid solution phase will be shown to include Thiessen's original beta phase, as well as beta-like phases of subsequent workers, we apply the term "beta" to the entire area.

It should be stated at the outset that beta is not necessarily the only, or even the most stable, crystalline phase obtainable in palmitate-water systems at room temperature; alpha, delta and omega persist for long periods under the proper conditions.

The X-ray evidence for solid solution is found in Fig. 1 and Table I, where the continuous spacing variations in the range 0.2 to 2.5% water appear analogous to those encountered with typical interstitial solid solution phases.¹¹ While we do

find some fixed spacings in this range, such a finding is consistent with the existence of a solid solution phase. Above 2.5% water all spacings are constant. Consequently, water in excess of 2.5% must either form a liquid phase or be associated with the crystalline phase in such a manner as not to affect the interplanar spacings.

The vapor pressure data substantiate the X-ray data in that the continuous variation in vapor pressure over the range 0.2 to 2.5% water (Fig. 2) signifies the existence of a single phase of variable composition, since a two-component system is involved. The vapor pressure data alone, of course, are not sufficient to reveal the reason for phase composition variability, but the X-ray evidence indicates that the water content varies not by adsorption, but by actual penetration of water into the unit cell resulting in alteration of interplanar spacings. The abrupt rise in vapor pressure at 2.5% water is in close agreement with the composition at which X-ray spacings cease varying, so that the latter effect can safely be attributed to attainment of the upper limit of solid solution.

In the absence of X-ray patterns of any new crystalline phases above 2.5% water, the abrupt rise in vapor pressure at this composition is tentatively attributed to the presence of a liquid phase. It is true that the simple form of the phase rule would call for a constant vapor pressure throughout the region of coexistence of a crystal phase and its saturated solution. Nevertheless, (a) the apparently continuous gradation in vapor pressure from 2.5% water to and beyond 30% water (where isotropic liquid can be filtered out with the aid of simple centrifugation), as well as (b) the X-ray spacing constancy and (c) the progressive increase in background scattering in X-ray patterns taken across the region, lead us to conclude that the depression of the vapor pressure below a theoretical flat is due to the presence of liquid throughout this range. That the simple phase rule is overlain with effects akin to adsorption is qualitatively in harmony with the conclusions of McBain, Vold and Johnston¹² who used vapor pressure experiments and sub-freezing dilatometry to show the existence of bound water in sodium palmitate and oleate systems. We find nothing above 3% water in any of our work, however, to indicate more than a smooth increase in the proportion of less firmly bound liquid as total water content increases.

The microscopic evidence likewise points to solid solution: a decrease in water content from about 3% to below 1% can be accomplished without breakdown of single crystals into polycrystalline aggregates (Fig. 3, A-D), a result supporting the continuity of the structure involved. Contrasting behavior is seen in the dehydration of alpha sodium palmitate (Fig. 3, E-H), in which conversion to the beta phase by room temperature desiccation over sulfuric acid leads to the formation of polycrystalline pseudomorphs after the alpha crystals. The latter behavior is that generally associated with the removal of water from a hydrate of definite composition, or in general from any crystal phase which converts discontinuously to a new phase as water is removed.

The single crystals of beta palmitate are grown by holding a hydrous system for days at such a temperature

(7) R. D. Vold and R. H. Ferguson, *THIS JOURNAL*, **60**, 2066-2076 (1938).

(8) E. M. Collins, *J. Phys. Chem.*, **37**, 1191 (1933).

(9) Regnault, cited by Mellor, "Comprehensive Treatise on Inorganic Chemistry," Vol. X, p. 397.

(10) Sorel, *ibid.*, p. 399.

(11) C. H. D. Clark, "The Fine Structure of Matter," Part I, John Wiley and Sons, New York, N. Y., 1937, p. 166 ff.; C. S. Barrett, "Structure of Metals," McGraw-Hill, New York, N. Y., 1943, p. 203, 478.

(12) J. W. McBain, M. J. Vold and S. A. Johnston, *THIS JOURNAL*, **63**, 1000-1007 (1941).

that crystalline and neat soap co-exist, under which conditions soap fibers develop.⁷ At room temperature, these fibers can be separated easily into tiny ribbon- or lath-like units by suspending in an inert liquid and subjecting to a sliding motion of a cover-glass. These units are single crystals, since they exhibit a positive "sign of elongation" when lying flatwise on the slide and negative when edge-wise, as well as sharp (parallel) extinction for both these views. From this same information it follows that light vibrating parallel to the length corresponds to refractive index N_m ; an interference figure verifies this. The ribbon-like proportions of the crystals insure that their lengthwise axis will lie parallel to the slide. N_m can thus be determined accurately and is found to increase from 1.514 in fully hydrous crystals to 1.522 in fibers equilibrated against concentrated sulfuric acid. The other principal index for the flatwise view, while less certain of attainment because of the possibility of some tipping around the lengthwise axis, is found to be reproducible with care and to increase from 1.492 to 1.500 as water is removed. By brief examination on the universal stage, made possible by the courtesy of Profs. A. N. Winchell and R. C. Emmons, it was found that this lower index corresponds closely, if not exactly, to N_p . The increase in indices, in lieu of chemical analyses, serves to show the reduction in water content. Indices were determined by the Becke test using white light and Shillaber immersion fluids in index steps of 0.002.

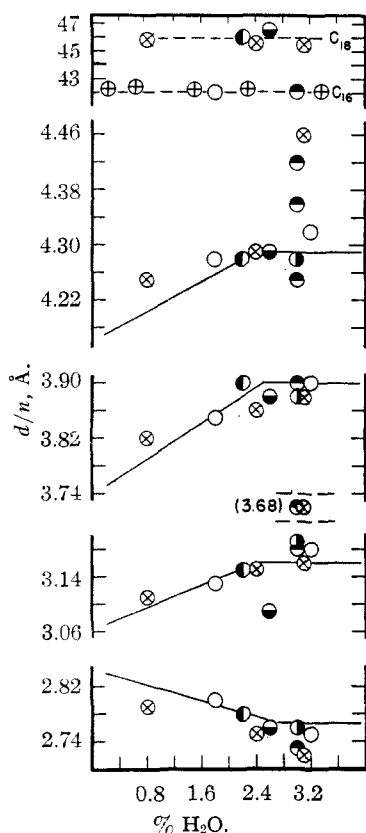


Fig. 4.—Summary of published interplanar spacings relating to beta sodium palmitate: — from data of Fig. 1; ⊕, from Table I; ⊗, Buerger, Smith, Ryer and Spike⁴ (stearate); ○, Ferguson, Rosevear and Stillman¹ (palmitate); ●, McBain, Bolduan and Ross¹⁷ (palmitate); ⊖, McBain, deBretteville and Ross¹⁴ (stearate); ⊙, Thiessen and Ehrlich¹⁶ (palmitate); ⊛, Thiessen and Stauff¹³ (stearate).

B. Compilation of Published Data Related to the Beta Phase.—Figure 4 summarizes the relation of previously published spacings of certain beta and beta-like structures to the beta solid solution, the full lines corresponding to those of Fig. 1. Short spacing data for palmitate and stearate have been used interchangeably.

Over the solid solution range below 2.5% moisture, patterns can be fitted to the curve at their proper moisture content, even when the latter has not been published, by taking advantage of the decrease in one short spacing while the other three increase. The data corresponding to the X-ray flats above 2.5% water have necessarily been plotted at arbitrary compositions. If some moisture contents appear unexpectedly high, reference to Fig. 2 will reveal that exposure to a relative humidity as low as 15% should allow beta palmitate to absorb over 2% moisture; in addition, we have found that conversion of alpha (3.1% water) to beta by warming in a closed tube yields a fully hydrated beta, while the water content of beta obtained by such heat-conversion in open systems depends on the surrounding humidity.

Data for the original beta phase as discovered by Thiessen and Stauff¹³ had to be derived from their Fig. 12, as it has been demonstrated by two laboratories^{1,14} that Thiessen's detailed numerical data do not apply to beta prepared according to his directions. Buerger¹⁵ later showed beta to be somewhat hydrous and we find that Thiessen's data fit ours well at about 2.2% water. Other data for beta derived from alpha according to Thiessen's directions are taken from references 1 (their Table II), 14, and 4. The spacings from the latter paper have been placed in Fig. 4 at 0.8% water corresponding to Buerger's assigned composition of $\text{NaSt} \cdot \frac{1}{8} \text{H}_2\text{O}$, although a better correspondence for this particular pattern would be obtained at about 1.4% water.

Data from beta-like soaps prepared other than from alpha are taken from references 1 (their Table V), 16 (their Fig. 5), and 17. Since the latter data are taken from a sharp fiber pattern, it is not surprising to find the largest of the four spacings resolved into three. Of particular interest because of their supposed hydrate nature are Buerger's proposed zeta and epsilon phases.^{4,5} When plotted at 2.4% water, corresponding to $\text{NaP} \cdot \frac{3}{8} \text{H}_2\text{O}$, the zeta spacings are found to fall close to the upper end of the solid solution region. Epsilon, however, exhibits a distinct departure from our 4.29 Å. spacing and a prominent addi-

(13) P. A. Thiessen and J. Stauff, *Z. physik. Chem.*, **A176**, 397-429 (1936).

(14) J. W. McBain, A. deBretteville and S. Ross, *J. Chem. Phys.*, **11**, 179-183 (1943).

(15) M. J. Buerger, L. B. Smith, A. deBretteville and F. V. Ryer *Proc. Nat. Acad. Sci., U. S. A.*, **28**, 526-529 (1942).

(16) P. A. Thiessen and E. Ehrlich, *Z. physik. Chem.*, **A165**, 464-471 (1933).

(17) J. W. McBain, O. E. A. Bolduan and S. Ross, *THIS JOURNAL*, **65**, 1873-1876 (1943).

tional ring at 3.68 Å., though there is fairly good agreement with our 3.90, 3.16 and 2.77 Å. spacings.

The agreement between published data and the reference curves of Fig. 4 seems sufficient to justify the conclusion that all these samples, with the possible exception of epsilon, correspond to various members of the continuous beta solid solution.

In support of this conclusion based on short spacings, it is evident in Fig. 4 that, when long spacings are available, they are constant at 42.1 Å. for the palmitates and 46.0 Å. for the stearates (± 0.5 Å.).

C. Examination of Related Definite Hydrate Proposals.—For characterizing crystalline soaps, the phase type most frequently proposed in the soap literature is the hydrate of definite soap: water ratio.^{4,5,12,15,18-21} For sodium palmitate some sixteen hydrates from $\text{NaP}\cdot\frac{1}{8}\text{H}_2\text{O}$ to $\text{NaP}\cdot 30\text{H}_2\text{O}$ have been tabulated (Table IV in ref. 3) as representative of the literature; other hydrates corresponding to $\frac{1}{6}$, $\frac{1}{4}$, and $\frac{3}{8}$ molecules of water have appeared later.⁵ While some of these are stated not to be hydrates in the strict phase rule sense, the over-all picture is in great need of clarification.

No hydrates in the region above 3% water, the composition corresponding to hemihydrate, have been encountered in the present study as we find only one X-ray pattern type above 2.5% moisture. Furthermore, there is no published X-ray evidence by which such higher hydrates may be identified.

McBain and Lee^{18,19} present vapor pressure evidence at 84° and higher temperatures for the existence of a sodium palmitate hemihydrate, while Lee's Master's thesis²² vapor pressure isotherms at 75, 65, 60, 40, and 30° are given. The last two temperatures fall fairly close to our 27° and both of his isotherms do exhibit a rounding at high humidities and an abrupt vertical rise at about 4% water, features which afford fair qualitative agreement with our isotherm. Lee's data do not point to a solid solution below 2.5% water, but this is probably because his isotherms go no lower than 15% humidity. The resemblance between Lee's data and ours might conceivably be extended through 75°, where his isotherm is still similar to that at 30° but, in the absence of X-ray data by which phases can be identified, comparison of our results with the more complex isotherms at higher temperatures has not been attempted.

Buerger's beta and zeta phases, which in respect to the four principal short spacings have

(18) J. W. McBain and W. W. Lee, *Oil & Soap*, **20**, 17-25 (1943).

(19) J. W. McBain and W. W. Lee, *Ind. Eng. Chem.*, **35**, 784-787 (1943).

(20) J. W. McBain, H. T. Bull and L. S. Staddon, *J. Phys. Chem.*, **38**, 1075-1083 (1934).

(21) J. W. McBain, L. H. Lazarus and A. V. Pitter, *Z. Physik. Chem.*, **A147**, 87-117 (1930).

(22) W. W. Lee, Master of Arts thesis, Stanford University, Aug., 1940.

been shown in the preceding section to correspond to certain members of our beta solid solution, require brief further consideration from the standpoint of hydrate formation.

Coexistence at room temperature of a pair of hydrates at definite ratios of water to soap would call for distinctive X-ray patterns at each hydrate composition, and between such compositions coexistence of the patterns of the two hydrates. No such complication of spacings has been encountered in our work, even though our 10-cm. technique is adequate to resolve the spacings which we have obtained at Buerger's specified hydrate compositions of 0.8 and 2.4% water for beta and zeta, respectively. In this connection it should be stated that our 10-cm. technique would not resolve mixtures of phases corresponding to Buerger's published beta and zeta patterns¹ but, as has already been pointed out, the sample from which his particular beta pattern was obtained appears to have been at about 1.4% rather than 0.8% moisture. In the absence of published numerical values, we measured the patterns and computed the spacings concerned to be 4.25, 3.82, 3.11, and 2.79 Å. for the beta pattern and 4.29, 3.86, 3.15, and 2.75 Å. for zeta.

Moreover, on the vapor pressure-composition curve, coexistence of definite hydrates would call for a constant vapor pressure over the composition range between each pair of adjacent hydrates. In the beta-zeta case, then, Fig. 2 should show a constant vapor pressure value between 0.8 and 2.4% water; instead, the data show a continuous variation.

Thus, while our vapor pressure evidence is not directly comparable with that of Buerger⁵ at higher temperatures, it is evident that, as far as the beta-zeta relationship is concerned, the respective conclusions drawn: solid solution *vs.* definite hydrates, are incompatible. We feel that the case for a solid solution, resting as it does on proof of continuity by both X-ray and vapor pressure techniques, receives stronger support than the case for definite hydrates, for which their discontinuities were apparently not tested at close enough intervals by the X-ray method.

The foregoing evidence emphasizes the need for scrutinizing, particularly by more than one method at a time, the claims for other definite soap hydrates, but does not eliminate the possibility of their existence.

D. Implications of the Existence of a Beta Solid Solution Phase.—Around the nature of beta sodium palmitate revolves the whole question of whether solid soaps are to be understood in terms of a few basic crystalline structures with the flexibility necessary to accommodate the effect of such variables as fat stock, water content and temperature, or whether every slight variation encountered in X-ray pattern or other property is to be attributed to the occurrence of another phase.

For example, since the beta structure in sodium palmitate incorporates up to 2.5% water in solid solution with accompanying continuous changes in interplanar spacings and other properties, a similar behavior would be expected in sodium stearate and other beta-forming single or commercial soaps. In addition, Ferguson and Nord-sieck have demonstrated⁶ the actuality of solid solution among crystalline soaps of different chain lengths, including even complex mixtures. It is then reasonable to expect in the sodium soaps, a comprehensive beta phase continuous with respect to both chain length and water content. The possibility of a similar phase continuity should be considered for the omega and delta structures.

Contrasted to this point of view is that of Buerger and his co-workers who have assigned distinct phase designations to each of ten X-ray patterns,⁴ some distinguished by relatively slight differences, leading to a phase situation of considerable complexity. That some of this complexity has been introduced needlessly is evident from our more detailed exploration of the beta-zeta relationships, which has revealed a single solid solution phase. Consequently, epsilon, and also the several phases showing pattern resemblances to omega, should be studied further in the hope that simplifying relationships will be discovered there also.

In any case we propose, as a guiding principle, that the number of crystalline soap structures be kept at the minimum consistent with available

evidence, in order that the subject of solid soaps may develop with greater simplicity and clarity. The final section of reference 4 with its tentative phase map is an indication of the predicament into which the multiphase concept can lead.

It is not, of course, necessary that each of such basic crystalline structures be capable of forming solid solutions with water. As a matter of fact, the alpha structure seems well established as a hydrate.^{15,23,24}

Acknowledgment.—The writers wish to acknowledge the advice of Dr. A. S. Richardson in developing the subject matter of this paper.

Summary

On the basis of X-ray, vapor pressure and microscopic evidence, certain minor variations previously encountered among X-ray patterns of beta sodium palmitate are accounted for by the existence of a beta solid solution phase extending at room temperature from about 0.2 to 2.5% water.

This beta structure is shown to embrace previous beta palmitates and stearates as well as the zeta, and possibly the epsilon, phase. Beta and zeta are therefore not hydrates of fixed composition.

Some justification is offered for keeping the number of distinct crystalline soap structures as few as consistent with available evidence.

(23) M. J. Buerger, *Proc. Nat. Acad. Sci., U. S.* **28**, 529-535 (1942).

(24) M. J. Buerger, *Am. Mineral.*, **30**, 551-571 (1945).

IVORYDALE, OHIO

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[CONTRIBUTION FROM SOCONY-VACUUM LABORATORIES, A DIVISION OF SOCONY-VACUUM OIL CO., INC., RESEARCH AND DEVELOPMENT DEPARTMENT]

Decenes Formed from *t*-Amyl Alcohol and from 2-Methyl-2-butene. Composition of the Hydrogenated Products

BY GEORGE C. JOHNSON

The formation of decenes from *t*-amyl, *i*-amyl and optically active amyl alcohol and the dimerization of isopentenes in the presence of catalysts was investigated for a century.¹⁻⁵ However, after this time the structures of the resulting decenes remained in doubt.⁶ The close y similar reaction of the formation of decenes from methyl *i*-propyl carbinol in the presence of sulfuric acid was studied in greater detail.⁶⁻⁸ In an effort to

establish the decene structures more definitely the present studies have been undertaken. In these studies decenes have been formed from *t*-amyl alcohol in the presence of sulfuric acid and from 2-methyl-2-butene in the presence of an alumina-silica catalyst.

The procedure for investigating the structures consisted of the hydrogenation of the decenes to decanes and subsequent analysis of the decanes by efficient fractional distillation accompanied by the determination of the physical properties of the fractions. This same procedure has been used in the studies of similar nonenes prepared by the reaction of *t*-butyl alcohol with *t*-amyl alcohol and of *i*-butene with 2-methyl-2-butene.⁹

Experimental

Reaction of *t*-Amyl Alcohol in the Presence of Sulfuric Acid.—The material used for this study was the decene fraction formed when *t*-amyl alcohol and *t*-butyl alcohol reacted together with the object of making the nonenes.⁹

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