The Four Known Crystalline Forms of Soap

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I. Introduction

The constitution of solid soap products has remained notably obscure during a decade or more of continued progress in the development of comprehensive interpretations of the more liquid forms of soap. The original and penetrating observations of Zsigmondy and Bachmann in 1912 (1) were followed by numerous researches on the physical nature of solid soaps, but as a general statement it may be said that no very significant advance resulted until Thiessen and Stauff (2), in 1936, announced the discovery of two distinctive crystalline forms, called the alpha and beta, for pure sodium palmitate and stearate. This and subsequent papers from Thiessen's laboratory (3), while containing what now appear to be certain fundamental errors, at once pointed to more profitable avenues of approach to the problems concerning solid soaps, and suggested why so much previous effort had been relatively fruitless through failure to recognize the role of polymorphism in soap-water systems.

It is of course true that between 1912 and 1936 a considerable body of information had accumulated in the literature with respect to solid forms of soap. Several stimulating descriptions of soaps in fiber and lamellar crystalline condition had appeared (4).

One of these latter papers (by Maclennan), which as much as any in the soap literature deserves the name "classic," brought together so many acute and useful descriptions, that today, after twenty years of further advances, it still remains an outstanding suggestive source for the student of soap technology.

It is natural and logical that early workers should have placed emphasis on microscopic and ultramicroscopic techniques, and in the absence of methods which were capable of dealing with highly concentrated, non-equilibrium soap systems, it was a matter of necessity that the results obtained on relatively dilute systems be used as a basis for inferential conclusions as to the structure of bars, flakes and powders which were far from dilute. To a great extent, microscopic and hydration studies led to the description of a cake of commercial soap (5) as "hydrated curd fibers, with enmeshed liquor, which is a sol or more frequently gel of the various more soluble soaps and salts present." Such a definition of bar soaps was indeed an improvement on the vaguer ideas of earlier times, and has survived into the very recent literature.

Once the x-ray method had been applied to soaps (6), (7), and developed into the pioneer work of Thiessen on polymorphism, it became possible to gain a more precise view of the structure and behavior of solid soaps. In considering the later information on the known crystalline forms of soap, it is useful to note that when sodium soap is allowed to crystallize freely, a fiber form of crystal is usually obtained. Microscopic as well as macroscopic fibers may be observed (8), and McBain (5) has shown that the ultramicroscopic units are likewise of fiber character.

As to the often mentioned lamellar soap crystals, there is no clear evidence that this form plays any part in commercial sodium soaps. While reported in numerous connections (4) (9), lamellar crystals of neutral sodium soaps seem to be found only when soap is crystallized from alcoholic solution to form the alpha phase. Many earlier observations of lamellar crystals were concerned with the potash soaps, and probably with acid soaps.

Well formed crystals are of course not generally seen in soaps and especially in the concentrated systems of commercial soap products, although fibers have often been observed under special conditions (4) (8).

II. The Solid Modifications of Sodium Soaps

That the fibers or crystals of soap may exist in distinctive modifications, with differing properties has now been established for commercial soaps of widely differing types (11).

The first positive demonstration of polymorphism was concerned with pure single soaps (sodium palmitate and stearate), and brought to light two modifications only, the alpha and beta (2). Before the literature contained any clear disclosure of more than these two distinctive crystalline forms of soap, a third type had been established by two independent groups of investigators. Research in the Procter & Gamble laboratories had shown that this third form, called the omega phase, accounted for a large proportion of commercial soap. Peculiarly enough, the first published description of the omega phase happened to appear in a patent to Mills (12) covering a process which had been found to produce an unusually small proportion of this phase.

The Mills patent was issued on September 15, 1942. Shortly thereafter McBain and deBretteville (13), as a result of experiments with single pure soaps in anhydrous condition, announced the existence of a so-called gamma form, and some months later published a more complete description of the same soap (19). The description of the gamma form is based on a still earlier thesis of deBretteville. The question of the possible identity of the omega and the gamma forms is not considered in the papers by McBain and deBretteville, but careful consideration of the x-ray diffraction patterns and of the methods of preparation of the samples examined leaves little room for doubt that the two are essentially the same.

Although credit for developing adequate means of identifying omega or gamma soap should be given to the two groups working independently on the subject, it should be recognized that soap in the omega form has long been commercially available, and it would be surprising if the published literature older than the Mills patent failed to contain any description of soap which, in the light of later knowledge, can be taken as applying to omega soap. We originally discarded the use of the term gamma so as to avoid suggesting any relation to the very unstable gamma form of fats, with which it has so little in common.

The fourth known form, the delta, still more recently has been described by Ferguson, Rosevear, and Stillman (11).

The establishment of the four known modifications of solid soap has stemmed directly from x-ray diffraction work, although there is now considerable corroborative evidence. The primary principle of applying the x-ray diffraction pattern to phase identification problems in soaps is the essential constancy of most of the short or side spacings for a given solid phase, independent of fat composition or moisture content.* The long spacings are useful in a correlative or differential way, but require more discrimination in their use since they vary with the composition of the soap. In composition studies they are of course of great importance.

In Piper's early application of x-ray methods to soaps (7) attention was focused on long spacings, and although the data now appear to support the conception of constancy of short spacings for a given phase, this was not sensed by Piper, and later phase investigations have been circumscribed by failure to recognize that long spacing data are of limited value for phase identification especially in the complicated fat mixtures of commercial soaps.

III. Properties of Crystalline Phases of Soap

The crystalline phases present in a soap product depend on the fat, moisture and electrolyte composition of the system. But this is not all; the processing methods used to make the product may exert considerable influence, not only on the phases finally present, but also on the condition or state of these phases. Such factors as the crystal size, orientation, and coherence between crystals, may vary widely, and bar soap properties for example may be influenced by these factors. Thus it is usually difficult to give strict comparisons of soap properties for the various phases, because in general the same conditions will not have prevailed during their production, and consequently other factors than phase nature exert effects on the properties of the product.

For example when neat soap is cooled a mixture of phases may result. As a general rule very rapid chilling induces the formation of omega crystal phase, while slow cooling increases the amount of beta. The melting properties and the final melting point of the product will depend on, and vary with, the phases so produced. The firmness of the bar or cake will be affected by the coherence of the crystals, crystal size, etc., so that the effect of phase on firmness, and other properties, may be obscured by many other factors.

The working or agitation of plastic soap compositions induces profound changes in properties. Soap milling and extrusion are examples of such processing methods. Extrusion of soap through an orifice, or intense mixing, enables a nearer approach to phase equilibrium to be attained. As an example of the changes produced by extrusion the results in Table I should be noted.

TABLE I

19% H_2O, 80% Tallow, 20% Coconut Soap

Number of Extrusions Through Small Orifice at Room Temp.	Phases Present in Soap	Lather (Relative Amt. Soap Rubbed Off Bar) at 70°F.	Firmness (Arbitrary Units)
0	omega	.20	6.7
10	75% beta 25% omega	.87	8.2
30	95% beta 5% omega	.91	8.3

Illustrating extrusion as an equilibrium device, the following results show that mixing under appropriate conditions may induce the reverse change, from beta to omega. Thus if an 80 Tallow-20 Coconut oil soap of 6% H_2O, containing a considerable proportion of beta, is extruded at room temperature, conversion to omega is obtained, and the lather power of the soap reduced.

TABLE II

	Lather (Relative Amt. of Soap Rubbed Off Bar in Test)
Bar containing 70% beta-30% omega....	2.1
Same soap after sufficient extrusion to convert to 75% omega....................	.5

From similar experiments it appears that working of omega per se without production of beta does not markedly increase lather. However, in cases where beta is obtained, its further processing under certain conditions may lead to further changes in properties.

The production of delta phase results from rapid cooling of fairly dilute NaP solutions, or it is formed in some systems by extrusion, especially at relatively high moistures. High molecular weight soaps favor its formation.

As an example of the effect of phase on properties, an actual difference in complete melting point between samples of identical soap-water content, but of different phase, can be demonstrated in the system NaP-H_2O. At 10% soap, a sample sealed in a glass capillary will melt at 65°C. if it has been first crystallized (from nigre) by slow cooling. But the same sample will melt at 61°C. if it has been first crystallized by quenching in ice water. X-ray examination shows that the crystals in the slowly cooled sample are beta, while in the rapidly cooled sample they are delta phase. Delta is apparently the stable phase at room temperature in dilute NaP-H_2O systems as shown by (1) extrusion, and (2) by mixing beta, omega or alpha phase with various amounts of H_2O and allowing the mixes to stand for considerable lengths of time.

The x-ray diffraction patterns of the crystal phases of soaps have been described in other publications (11), but for purposes of comparison the identifying spacings are shown in Table III.

TABLE III

Phase	Lattice Spacing Å
	d/n
Alpha..	2.45 and 3.65
Beta..	2.75
Delta...	2.85 and 3.55
Omega...	2.95

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* In the omega structure one of the important short spacings (about 4.7Å) shows small but real variations which, in certain commercial soaps, can be correlated with cooling rate and other treatment.

In sodium palmitate and sodium stearate there are small but important differences between the beta structure obtained by warming of alpha in the manner of Thiessen and Stauff (identifying spacing 2.80Å), and that obtained by crystallization of a hydrous melt (identifying spacing 2.75Å), including the growth of single fibers. In sodium palmitate, x-ray and vapor pressure studies of progressive dehydration of hydrous fibers and bulk soap show that below about 2.9% H_2O the more hydrous structure converts to Thiessen's beta which exists as a phase of variable water content from about 2.2% H_2O almost to the anhydrous axis. Similarities in fiber patterns indicate that, though not continuous, the two structures may be quite similar. It is apparently Thiessen's beta which is dealt with by McBain, deBretteville, and Ross (14), by Buerger (15), and in Tables II and IV of Ferguson, Rosevear, and Stillman (11); it appears to be the more hydrous beta which is dealt with by Bolduan, McBain, and Ross in a recent paper, and which is encountered in commercial soaps, e.g. Tables V and VI of Ferguson, Rosevear, and Stillman (11).

The crystalline system and unit cell dimensions for the various phases have been worked out only in part. It should be recalled, however, that in matters of phase identification only one or two characterizing rings in the diffraction pattern are needed and that nothing whatever need be known of the structure itself.

Thiessen and Stauff (2) assigned the alpha phase to the orthorhombic system and the beta to the monoclinic, but Buerger (15) has shown, by more careful work, that the alpha form is monoclinic. For purposes of classification the angle of tilt system evolved by Ferguson, Rosevear and Stillman (11) is useful independently of the actual crystal systems involved.

IV. The Effect of Moisture

Each crystal modification has its own field of stability. Its composition and temperature range and the possible equilibria with other soap phases constitute the phase diagram for the particular soap-water system involved in a given soap product. Without knowledge of the fields of stability in the system it is futile to speak of one phase as a stable phase and another as a metastable phase. For example beta phase in the NaP-H_2O system is able to exist, either alone or in equilibrium with other phases, from below 2.4% H_2O to at least 95% H_2O at certain temperatures, while omega has a much more restricted range. The opposite condition exists in coconut oil soap; here omega predominates.

While no phase diagram has yet appeared in the literature, showing the fields of existence of the four recognized solid modifications in soap-water systems, there are several publications which purport to show the presence of definite stoichiometric hydrates in such systems (16) (17).

By way of example, in Table IV are brought together a partial list of the hydrate compositions which have been variously reported or inferred for the system NaP-H_2O.

Taken alone, the great prolixity of these compositions, to say nothing of the apparent lack of reproducibility over the years, would cast some doubt on the reality of their existence, and indeed Ferguson and Rosevear (18) have been unable to find any such multiplicity of definite hydrates by x-ray analysis. The thousands of patterns examined here can be interpreted in terms of alpha, beta, omega, and delta structures only.

In Table V are reproduced data from the above paper. It will be observed that no new crystal phase appears where the moisture content of a NaP-H_2O system in beta form is varied over wide limits. The beta phase is able to vary continuously in moisture content over its field of stability, and when the moisture content is changed from this range the new phases that appear are equilibrium phases, neat, nigre, middle, etc. The x-ray evidence would seem to show that the beta, delta and omega forms are independent of any published hydrate compositions. In commercial soaps, the various crystalline phases are found to vary continuously in moisture over their fields of stability, and no evidence indicating any definite hydrate has been found.

TABLE IV

Definite Hydrates Reported in Literature for Sodium Palmitate

NaP·⅛ H_2O
NaP·½ H_2O
NaP·H_2O
NaP·2.1 H_2O
NaP·2.2 H_2O
NaP·2.6 H_2O
NaP·3.2 H_2O
NaP·4.0 H_2O
NaP·4.36 H_2O
NaP·4.6 H_2O
NaP·5.2 H_2O
NaP·6.7 H_2O
NaP·8.0 H_2O
NaP·9.0 H_2O
NaP·9.9 H_2O
NaP·30 H_2O

Again, when compositions representing exactly those of the definite hydrates listed in the most complete paper extant (16) on NaP are examined by x-ray, only the beta pattern is found. Patterns of compositions on either side of the supposed hydrates do not give evidence of the presence of two definite compounds as demanded by the phase rule. If such compositions are heated the x-ray pattern provides no confirmation of the hydrate transitions called for by the phase diagram.

It is only when moisture addition or subtraction brings about a change in crystal modification beta, delta or omega, that the x-ray pattern changes significantly. When the modification begins to transform, the moisture content where this occurs is merely the limiting boundary of the phase field of stability.

While alpha is not under consideration here, it should be pointed out that Buerger (15) has indicated that this form of NaP is a hemi-hydrate, and that the beta form is the ⅛ hydrate. While this may well be true of the alpha structure, our experience in the system NaP-H_2O indicates that beta is a phase of continuously variable composition.

To sum up the question of soap hydration: there can be no doubt that soap crystallizing from water solution or from melt may form a crystal phase containing water. That the hydrated crystal phase is a definite hydrate compound seems very doubtful. The positive evidence for hydrate formation comes largely from vapor pressure and similar curves, which in some cases exhibit very ill defined and dubious breaks (17). [There is some indication (19) that this evi-

TABLE V

Constancy of Beta Pattern with Moisture Variation Na-Palmitate-H_2O

3.0% H_2O		8.5% H_2O		15.1% H_2O		45% H_2O		58% H_2O		85% H_2O		95% H_2O	
I	*d/n*	*I*	*d/n*	*I*	*d/n*	*I*	*d/n*	*I*	*d/n*	*I*	*d/n*	*I*	*d/n*
W	8.45	W	8.55	W	8.55	W	8.50	W	8.35	W	8.50	....	......
W	4.78	W	4.77	W	4.80	W	4.80	W	4.92	W	4.78	VW	4.80
S	4.33	S	4.28	S	4.25	S	4.32	S	4.28	S	4.33	M	4.35
S	3.87	S	3.80	S	3.80	S	3.92	S	3.88	S	3.93	M	3.90
W	3.52	W	3.45	....	......	W	3.50	W	3.55	....	......	....	......
W	3.13	W	3.08	W	3.08	W	3.13	W	3.13	....	......	....	......
M	2.76	M	2.75	M	2.75	M	2.80	M	2.78	M	2.78	VW	2.78
VW	2.35	....	......	....	......	....	......			....	......	....	......

dence has not been substantiated by the original workers.]

Also there is the fact that at the time of the main body of work on hydration no knowledge of the particular crystal modification was available, and some supposed breaks in property curves which were attributed to formation of definite hydrates could quite reasonably have resulted from transformation of one crystal phase to another. Hence the earlier work on hydration must be examined critically from the standpoint of what phase or phases were present in each sample taking into account the processing methods by which the given systems were produced.

Pointing to the non-existence of definite hydrates is the failure of such compounds to respond to x-ray analysis. An exceedingly large number of x-ray diffraction patterns fail to reveal the presence of any definite hydrate compounds, over the range from 2.5% to 95% H_2O. The total evidence to date seems consistent with the conception that the solid modifications of soaps are of the nature of solid solutions. They are crystalline phases of variable composition in soap-water systems. It appears that no sol, gel or mother liquor exists in many types of bar soap, hence earlier definitions require alteration. Many solid soap products appear to be made up solely of crystalline phases which are able to vary continuously in water content over their certain ranges of stability. Products containing sufficient water to bring about the formation of liquid phases may contain sols or gels in addition to crystalline phases.

V. The Effect of Fat Composition

Similarly, the conception of commercial soaps in bar form containing "fibers of the more insoluble soaps enmeshing a gel or sol of the more soluble soaps" can be regarded as valid in a limited sense only. In most commercial soap compositions fractionation of the fatty acid salts, as called for in the above definition, does not seem to occur (20). Such soaps for example exhibit but one set of long spacing rings corresponding closely to the value of c sin β which would be derived from the average molecular weight of the constituent soaps of the mixture. In other words the fat mixture in such commercial soaps crystallizes as a unit.

TABLE VI

Showing Spacings of Commercial Soaps

Soap	c sin β	Mol. Wt.	
		Calculated from c sin β	Chem. det'd.
Tallow (omega)	43.8 Å	299	300
60% T-40 C.N.O. (omega)	38.8	267	267
Soap A (omega)	41.1	283	281
Soap B (omega)	42.0	288	283

As an example of solid solution formation, a mechanical mixture of anhydrous NaSt-NaL will yield a diffraction pattern showing the characteristic long spacings of each constituent, but if the mixture is now heated to melting and then crystallized by cooling, the pattern no longer shows the two sets of long spacing rings of the two components. Now there appears only one set of rings intermediate between the two original values.

TABLE VII

	c sin β
NaL	31.9 Å
NaSt	44.9 Å
Solid Solution 42.2 mol % NaSt	38.5 Å

These and similar data (20) indicate the formation of a solid solution phase which may exist in the appropriate modification corresponding to the composition and temperature. The undoubted experimental fact that a bar of commercial soap when placed in water yields a solution richer in the more soluble soaps is not inconsistent with the presence of solid solution phases, and is not proof of fractionation into the single soaps as some have thought. Solubility relations in 3 component systems containing solid solution phases readily account for such phenomena.

That a certain degree of fractionation may occur between two different solid solutions is indicated by studies on such systems as NaL-NaSt (20). Here three different types occur under some conditions, and at some composition ranges it appears that crystallization simultaneously into two solid solution phases may take place. On the basis of this and related work (20) many bar soaps may be considered as made up solely of crystalline phase without any apparent separation of liquid crystalline or liquid phases. The crystalline phase is in the form of a solid solution of the various constituent soaps, and this solid solution may exist in one or more of the crystalline modifications described above.

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