Using the formula given by Gerhard and Dennison[6] and our calculated values of I_A and I_C, we have evaluated for parallel bands the separation in cm.$^{-1}$ of the maximum of a P branch from that of a R branch at 27° as 20 cm.$^{-1}$. The observed value of this separation for the parallel band with its center at 951 cm.$^{-1}$ is 21 cm.$^{-1}$. This agreement between observed and calculated separations indicates that the moments of inertia of nortricyclene do not differ greatly from those calculated and that its actual shape does not differ much from that of structure II.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

An X-Ray Diffraction Study of Calcium Stearate Monohydrate–Cetane Systems[1,2]

BY ROBERT D. VOLD AND THOMAS D. SMITH[3]

This paper describes a study by X-ray diffraction methods of the system calcium stearate monohydrate–cetane as conditioned by variations in composition and thermal history. These systems are particularly interesting, as it is known that the addition of water to anhydrous calcium stearate–cetane systems results in a considerable increase in stability,[4,5] and it is important to attempt to discriminate between phase state and colloidal structure as the primary cause of this effect. A similar study of the anhydrous system has already appeared.[6]

The X-ray experiments were carried out at room temperature on quenched systems subjected to different temperatures of initial heating, and on systems subjected to controlled slow cooling. It is possible to derive information on the possible phase state of the system both at room temperature and at elevated temperatures from the resultant patterns, although this process is complicated by the question of degree of reversibility at transitions on cooling through a succession of phases.

A comparison of the behavior of anhydrous and hydrous systems was made, and the role of water and cetane in the system is discussed. The conditions of decomposition and formation of the hydrate were examined and are discussed in relation to the degree of dehydration at elevated temperatures. The occurrence of a hitherto unreported modification[7] of calcium stearate in systems containing both cetane and water is also reported. This modification appears to differ from the usual form of calcium stearate VI-H only in the degree of randomness of its crystal structure. Consequently the possibility must be considered that *different types of disorder* of the crystal structure of a single phase as well as *different sorts of orderly arrangement* (different phases) can contribute to the number of realizable, discrete, solid modifications.

Experimental Methods

Materials.—Calcium stearate monohydrate (laboratory no. 5R3AH) was made from stearic acid by metathesis with calcium chloride in aqueous methanol.[8] The acid had been purified from Armour Neofat 1–65 by two recrystallizations from acetonitrile and had the following characteristics: iodine value (Wijs), 0.34; equiv. wt., 286.5. The hydrate contained 2.97% water, determined by drying to constant weight at 110° (calcd. 2.88%), and was in a crystal form which, on dehydration, gave the anhydrous soap in the VIA crystal form.[8,9]

The cetane was obtained from the du Pont Co., freed from dissolved air by sweeping with nitrogen, and dried over calcium chloride.

Procedure.—Calcium stearate monohydrate, taken directly from the stock bottle, and cetane, were weighed into dry, Pyrex glass tubes, mixed thoroughly and sealed. For systems which were to be cooled from temperatures greater than 130°, the tubes were maintained at the desired temperature for 2 hours before being quenched in a Dry Ice–acetone freezing mixture, or before being cooled slowly at 0.5° per minute. If the systems were to be heated at lower

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(1) Presented in part before the Division of Colloid Chemistry at the 115th Meeting of the American Chemical Society, San Francisco, Calif., March, 1949.

(2) This work is part of a project "Phase Studies of Greases" supported by the Office of Naval Research, Contract No. N6-onr-238-TO-2; NR057057.

(3) Department of Colloid Science, Cambridge University, England.

(4) D. H. Birdsall and B. B. Farrington, *J. Phys. Colloid Chem.*, **52**, 1415 (1948).

(5) R. J. Coswell, "A Study of the Pressure Stability of Calcium Stearate–Cetane Systems Containing Additives," M.S. Thesis, University of Southern California, 1949.

(6) R. D. Vold and M. J. Vold, *J. Phys. Colloid Chem.*, **52**, 1424 (1948).

(7) The term "modification" is here used in a sense similar to that of K. J. Mysels and J. W. McBain [*ibid.*, **52**, 1471 (1948)] to denote a material having clearly different properties but without commitment as to its phase nature.

(8) M. J. Vold, G. S. Hattiangdi and R. D. Vold, *J. Colloid Sci.*, **4**, 93 (1949).

(9) X-Ray diffraction patterns of the polymorphic forms of anhydrous calcium stearate designated as VI-A, VI-H and VI-N are presented in reference 8. The long spacing given by the present preparation of calcium stearate is slightly shorter than the previously reported value,[10] possibly because of traces of impurities,[11] and there are indications of some slight tendency toward a VI-H rather than a VI-A pattern, such as the abnormal weakness of the usual peak at 3.70 Å.[6,8,10,12] although in general the remainder of the pattern is similar.

The diffraction pattern of the anhydrous VI-H form is indistinguishable from that of calcium stearate monohydrate. However, in the present work calcium stearate crystallized dominantly in the VI-A form which has a pattern easily distinguishable from that of the hydrate, thus permitting recognition of changes in the extent of hydration of the system.

(10) R. D. Vold, J. D. Grandine, 2nd., and M. J. Vold, *J. Colloid Sci.*, **3**, 339 (1948).

(11) R. D. Vold and G. S. Hattiangdi, *Ind. Eng. Chem.*, **41**, 2311 (1949).

(12) M. J. Vold and R. D. Vold, *J. Am. Oil Chem. Soc.*, **26**, 520 (1949).

TABLE I

TYPICAL X-RAY DIFFRACTION DATA FOR SYSTEMS OF CALCIUM STEARATE HYDRATE–CETANE QUENCHED FROM VARIOUS TEMPERATURES

Composition, wt. % soap hydrate	Quenching temp., °C.	Long[a] spacing Å.	I/I_0[b]	Cetane[c] halo, I/I_0	A peak d/n	A peak I/I_0[d]	B peak d/n[j]	C peak d/n	C peak I/I_0	D peak d/n	D peak I/I_0	Other weak spacings
14.5[e]	90	50.0	4.25	8.00	4.46	(1.50)	4.19	3.96	(0.75)	3.41	(0.75)	2.29
27.9	90	49.9	10.55	2.55	4.44	(1.22)	4.15	3.89	(.33)	3.43	(.55)	
44.2	90	50.0	8.00	1.46	4.41	(1.15)	4.16	3.89	(.53)	3.42	(.47)	3.15
14.6	110	50.1	3.00	5.60	4.41	(1.40)	4.16	3.86	(.40)	3.40	(.60)	
28.6	110	49.9	4.66	2.33	4.42	(1.11)	4.15	3.88	(.44)	3.41	(.22)	
44.4	110	50.0	7.07	1.15	4.41	(1.23)	4.16	3.86	(.61)	3.41	(.38)	
14.7	130	50.0	0.25	1.80	4.39	(0.55)	4.19	3.87	(.10)	..	....	
28.9	130	49.9	.41	1.17	4.39	(.50)	4.18	3.91	(.21)	3.42	(.12)	
44.0	130	49.9	.47	1.00	4.39	(.86)	4.20	3.91	(.67)	3.40	(.24)	
58.0	130	49.7	.91	0.31	4.37	(.20)	4.17	3.85	(.20)	3.41	(.14)	3.97
100	130	49.3	2.47	..	4.36	(1.04)	4.13	3.83	(.42)	3.40	(.23)	2.49; 2.37; 2.28; 2.18
58.4	140	50.0	0.25	.32	..	....	4.17	3.86	(?[f])	3.44	(.07)	3.95
78.1	140	49.9	0.24	.23	4.38	(0.30)	4.18	3.86	(0.14)	3.42	(.14)	
Calcium stearate hydrate (cetane-free)		49.9	3.11	..	4.40	(1.38)	4.12	3.86	(.55)	3.41	(.38)	3.15; 2.51; 2.43; 2.38; 2.28
Anhydrous calcium stearate[g] (cetane-free)		49.0	2.09	..	..	....	4.18	3.92	(.28)	..	....	3.51; 2.75; 2.45; 2.33; 2.24; 2.18; 2.08
Anhydrous calcium stearate[h] (cetane-free)		50.2	2.70	..	..	....	4.11	3.97	(.08)	..	....	3.68[i]; 3.49; 2.48; 2.36; 2.20; 2.12; 2.06

[a] Values reported are mean of those obtained from 2–6 orders. [b] Relative amplitude given for third order of long spacing. [c] Cetane halo is centered at 4.66 Å. in all cases. [d] I/I_0 in all cases is the ratio of the height of the given peak to the height of the B peak. [e] Polystyrene cover used on this specimen. [f] Query signifies an intensity too weak to estimate. [g] Obtained from the present preparation of calcium stearate monohydrate. [h] From reference 6 for a non-interacting paste of 38.5% calcium stearate in cetane at room temperature. [i] Unlike the other weak spacings, this line has an amplitude 0.19 times that of the B peak. [j] I/I_0 = 1 for all values of d/n given.

temperatures, the following procedure was used to ensure complete mixing. The tubes were maintained at the desired temperature for one hour, cooled, broken open and thoroughly mixed with a spatula, then resealed, heated for a further 2 hours, and either quenched or slow cooled. Longer periods of heating of such samples caused no further change in the diffraction pattern obtained.

Diffraction patterns were obtained immediately after the systems regained room temperature using the North American Philips Co. X-ray spectrometer as previously described.[10] In the present work positions of the peaks were determined from the midpoint not at half intensity but as near the maximum as feasible, thus minimizing errors due to peak asymmetry arising from either unresolved components or instrumental lags. All values reported are based on at least two different runs with good internal consistency. The average long spacing values were reproducible within ±0.05 Å. on patterns given by highly crystalline samples but the error increased to ±0.15 Å. with peaks of very low intensity. As in previous work[6,11] short spacings were reproducible within ±0.01 Å. in the case of the more pronounced peaks regardless of their width. With respect to the limit of resolution, Miss Dorothy Wallace of this Laboratory has shown that sodium sulfate and disodium hydrogen phosphate lines differing in position by only 0.018 Å. are nicely resolved in the pattern of a 50–50 mixture examined under standard operating conditions without use of especially fine slits.

Experimental Results

Visual Observations.—Depending on the soap concentration, room temperature mixes of the hydrate and cetane vary from very fluid suspensions to powders in which the cetane has been absorbed into the interstices of adjacent particles. No obvious macroscopic changes occur until a temperature of 130–150° has been reached, when the mixtures clear, yielding a viscous, translucent, anisotropic material. The appearance of the systems was noted at Dry Ice temperature and after warming to room temperature. In contrast to the behavior of the systems of anhydrous soap in cetane,[6] the appearance of these systems, after quenching, seemed to indicate a fairly smooth transition from soft, coherent greases to hard, brittle gels. Certain of the quenched systems containing between 60 and 80% soap by weight of system, crumble into highly charged particles (tribo-electric effect). A few of the more concentrated slow-cooled gels also showed this phenomenon.

X-Ray Diffraction Results

Systems Quenched in Dry Ice–Acetone and Studied at Room Temperature.—X-Ray data for systems quenched from 90, 110, 130 and 140° are presented in Table I. Included in this table are the data for cetane-free crystalline hydrous and anhydrous calcium stearate. The series of patterns in Fig. 1 illustrates the typical variation in pattern with increase in quenching temperature (*i.e.*, temperature from which the sample is quenched).

Patterns of the systems quenched from 90 and 110° may be interpreted as that of crystalline soap hydrate superposed on that of liquid cetane. Cetane itself gives a very broad halo with a maximum at an angle corresponding to a 4.66 Å. spacing.

The patterns of systems quenched from 130° cannot be interpreted simply as hydrate and cetane patterns superimposed. The long spacing

TABLE II

X-RAY DIFFRACTION DATA ON CALCIUM STEARATE MONOHYDRATE–SYSTEMS QUENCHED FROM 155°

Composition, wt. % soap hydrate	Long spacing Å.	I/I_0 3rd order	I/I_0 cetane halo, 4.66 Å.	A peak		B peak			C peak		D peak		Other weak spacings
				d/n	I/I_0	d/n ($I/I_0 = 1$)	d/n[a]	I/I_0	d/n	I/I_0	d/n	I/I_0	
15.5	49.9	0.22	2.00	..	....	4.22	4.03	(0.16)	3.85	(0.22)	..	....	
19.1	50.8	.29	1.87	..	....	4.21	3.94	(?)	..	....	..	....	2.2–2.5(H)[b]
20.2	50.7	.35	1.78	4.42	(0.58)	4.23	4.02	(0.21)	..	....	3.41	(0.21)	
20.6	50.4	.31	1.68	..	....	4.20	..	....	..	....	..	....	
22.3	49.9	.70	2.00	4.37	(1.00)	4.21	3.97	(?)	..	....	3.42	(.18)	3.77
22.7	49.9	.38	1.48	..	....	4.20	..	....	..	....	..	....	
24.2	50.7	.41	1.50	4.40	(0.66)	4.18	3.96	(?)	..	....	3.42	(.20)	
29.4	50.3	.23	0.77	4.29	(0.13)	4.15	3.92	....	..	....	..	....	2.1–2.5(H)
38.3	49.8	.35	.76	..	....	4.17	..	....	3.87	(?)	..	....	
50.5	49.9	.20	.52	..	....	4.18	..	....	..	....	..	....	
60.8	50.2	.39	.33	4.35	(0.69)	4.15	..	....	3.85	(0.14)	3.41	(.14)	3.16
78.8	49.8	.14	.14	4.38	(0.11)	4.15	..	....	3.85	(0.11)	3.44	(.09)	
84.3	49.4	.27	..	..	....	4.15	..	....	3.80	(?)	3.42	(.05)	2.27
89.2[c]	48.7	.29	..	4.34	(?)	4.15	3.91	(?)	3.81	(?)	3.40	(.13)	
89.2[c]	49.4	.35	..	4.40	(0.06)	4.15	3.96	(?)	3.84	(?)	3.41	(.06)	2.28
89.2[c]	49.6	..	..	Not measured beyond 15°									
95.7	49.9	.30	..	..	....	4.16	3.9	(?)	..	....	3.42	(.06)	2.71, 2.34
100	49.7	.49	..	4.42	(0.08)	4.15	..	....	3.86	(0.20)	3.42	(.11)	

[a] The position of this peak is rather uncertain due to its occurrence as a "shoulder" on the side of the rather broad B peak. [b] Halo. [c] Variations in long spacing at this composition were due to the presence of unresolved peaks.

peaks are unchanged in position but greatly weakened in intensity and broadened. In the original hydrate the order of intensities of the short spacing peaks is A > B > C > D, these letters referring to the four most conspicuous lines at 4.40, 4.12, 3.86, and 3.41 Å. in the hydrate pattern.[8] Systems quenched from temperatures above 130° give patterns which show a regular increase in intensity of the B peak and decrease in intensity of the A, C and D peaks, suggestive of partial dehydration to the VIA anhydrous form (or the VIN form when heated above 150°), (*cf.* Figs. 1 and 2).[13] This same change of pattern is also found when systems are dehydrated in open tubes at 110° and, as is shown in Fig. 2, when oil-free systems are heated in sealed tubes.

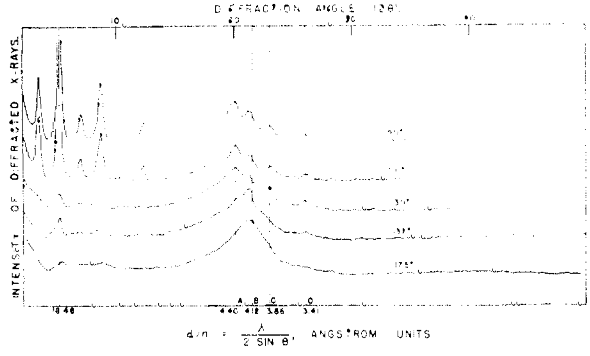

Fig. 1.—Effect of increasing the quenching temperature on patterns of 45% systems of calcium stearate hydrate in cetane.

A more complete composition range was covered for systems quenched from 155° in order to investigate whether the phases present at room temperature depended on the soap concentration of the system. The X-ray data for these systems are given in Table II.

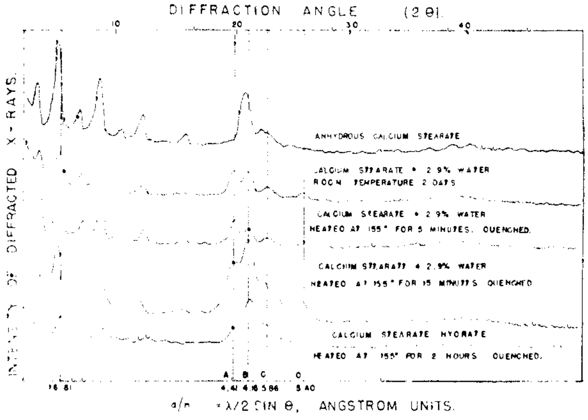

Fig. 2.—X-Ray diffraction patterns illustrating the hydration and dehydration of calcium stearate. These systems contained no cetane and were heated in closed tubes for the times indicated in the Fig.

Systems Cooled at a Half Degree per Minute.—Samples of the hydrate in cetane which had been cooled slowly from 155° showed, in addition to the hydrate spacings, a very prominent peak at 4.55 Å. and a weaker line at 2.90 Å. (listed in the tables but not apparent in the one to five pantograph reductions shown in the figures). Compared with the hydrate pattern the A peak had become considerably diminished in intensity, and the C and D peaks had become more pronounced. This pattern (hereinafter referred to as the VIS pattern) could not be interpreted as being due to the presence of a hydrolysis product. Although the patterns

[13] The extent to which rehydration occurs on cooling is apparently very sensitive to slight differences between different preparations of calcium stearate. Although the present calcium stearate monohydrate invariably was found to be partially or wholly dehydrated after heating in closed tubes, in later work in this Laboratory by Mr. Henry Coffer with another preparation of calcium stearate of similar analytical purity, the soap was frequently found to be hydrated after cooling to room temperature.

Table III

Typical X-Ray Diffraction Data on Calcium Stearate–Water–Cetane Systems, Cooled at 0.5°/Minute from 155°

Composition wt. % Calcium stearate	Cetane	Water	Long spacing Å.	I/I_0 3rd order	I/I_0 cetane halo	S peak d/n	S peak I/I_0	A peak d/n	A peak I/I_0	B peak (I/I_0 = 1) d/n	C peak d/n	C peak I/I_0	D peak d/n	D peak I/I_0	Other weak spacings
33.3	61.6	5.1	50.0	1.88	2.22	4.55	(3.77)	..	....	4.20	3.85	(4.33)	3.39	(1.55)	2.89; 2.54; 2.48; 2.43; 2.34; 2.24; 2.16; 2.10
44.4	45.4	10.2	50.2	1.77	2.82	..	....	4.37	(3.63)	4.18	3.90	(2.33)	3.40	(1.33)	2.92
54.3	32.1	13.6	50.5	3.33	0.45	4.56	(4.00)	..	....	4.19	3.87	(3.12)	3.39	(1.50)	2.87; 2.69; 2.54; 2.49; 2.44; 2.35; 2.24; 2.10
78.5	21.8	0.7	49.5	0.90	0.21	4.53	(1.26)	..	....	4.15	3.85	(1.10)	3.38	(0.36)	2.87; 2.47; 2.24
77.6	22.4	..	49.4	0.31	..	..	....	..	....	4.16	..	....	..	....	2.23; 3.48; 3.94
79.6	..	20.4	49.6	1.87	..	..	....	4.43	(2.00)	4.13	3.94	(1.20)	3.40	(0.73)	2.90; 2.27; 3.99
Typical data on calcium stearate monohydrate–cetane systems, cooled at 0.5°/minute from 155°															
Soap hydrate	Cetane														
48.0	52.0		49.6	0.59	0.48	4.53	(0.69)	4.38	(0.90)	4.20	3.88	(0.90)	3.39	(0.45)	3.12; 2.90; 2.25
71.9	28.1		50.1	1.62	0.62	4.55	(2.15)	..	....	4.18	3.86	(2.31)	3.38	(0.85)	2.89; 2.48; 2.45; 2.24
97.9	2.1		49.8	0.76	..	4.52	(0.87)	4.39	(0.43)	4.14	3.88	(0.45)	3.39	(0.38)	2.90; 2.49; 2.24
100	..		49.6	0.38	..	..	....	4.40	(0.10)	4.16	3.88	(0.16)	3.40	(0.08)	2.72; 2.45; 2.32; 2.24

of some forms of stearic acid[14] do contain lines at 4.56 and 2.90 Å., more pronounced lines in the same patterns do not appear in the VIS pattern. No lines due to either calcium oxide or calcium hydroxide were detected. In addition, an attempt to increase any possible hydrolysis was made by maintaining a system containing 44.4% calcium stearate, 10.2% water and 45.4% cetane at 155° for 10 days. This resulted in a material giving a normal hydrate pattern, a significant result which will be discussed further. Moreover, a system containing 18.0% calcium stearate, 5.0% stearic acid and 77.0% cetane,[5] when cooled slowly clearly showed stearic acid lines in its diffraction pattern, thus proving that if stearic acid had been present in appreciable quantity in the preceding systems, it should have been recognized as such in the diffraction pattern.

Figure 3 illustrates the differences between the new pattern, and patterns of the oil-free soap and a quenched oil-containing system. In no case did the oil-free soap develop the new pattern on cooling slowly, nor did the most dilute oil-containing sample exhibit this pattern.

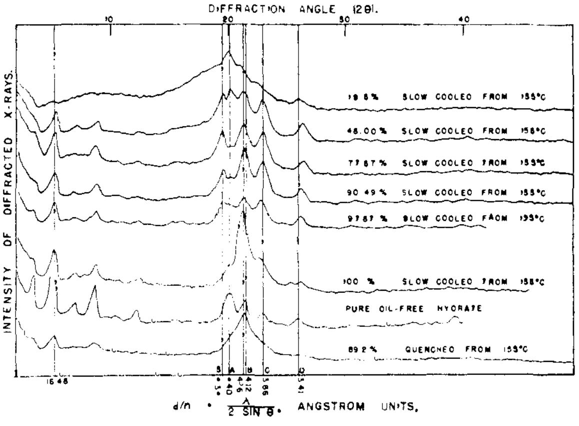

Fig. 3.—X-Ray diffraction patterns of calcium stearate monohydrate in cetane. Numbers give weight per cent. of soap hydrate.

Further samples of the development of the new pattern by systems of calcium stearate, water and cetane are shown in Fig. 4 and a small selection of typical data is given in Table III. Obviously the presence of both cetane and water is necessary for the formation of this modification, and it is formed over wide regions of the ternary system but with widely varying distribution of intensities between the A, B, C, D and S peaks depending on composition.

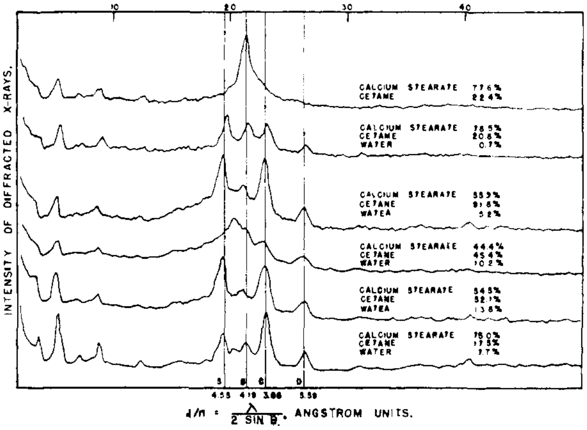

Fig. 4.—X-Ray diffraction patterns of systems cooled at 0.5° per minute from 155°.

Discussion

The important results of the present investigation are the determination of the conditions under which calcium stearate monohydrate is decomposed or formed in oil-containing systems, and the demonstration that by slowly cooling ternary systems of calcium stearate, water and cetane a hitherto unreported modification of calcium stearate is formed. In addition it has been possible to extend the use of diffraction patterns of soap-oil systems beyond mere identification and characterization of the phases present[15,16] to arrive at a new significant concept of the nature of these solids.

The patterns of systems quenched from temperatures between 130 and 155° can be identified as

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[14] J. D. Grandine, II, Research Report, University of Southern California Library, June, 1948.

[15] R. H. Ferguson, F. B. Rosevear and R. C. Stillman, *Ind. Eng. Chem.*, **35**, 1005 (1943).

[16] M. J. Buerger, L. B. Smith, F. V. Ryer and J. E. Spike, Jr., *Proc. Nat. Acad. Sci.*, **31**, 226 (1945).

mixtures of the established patterns of the hydrous and anhydrous soap. The behavior of this mixture can be followed by examining the intensity of the B peak (Fig. 1). In patterns of the anhydrous soap this is very intense. The increase in intensity of this peak has just commenced at 130° indicating that decomposition of the hydrate has begun. It was also observed that water droplets were present in the tubes after quenching from above 130°. Quenched from above 155° the systems gave patterns closely resembling those of the anhydrous soap quenched from the same temperature (form VI-N). The soap is therefore present predominantly in the anhydrous form. Systems quenched from 180° show no detectable indications of the presence of the hydrate.

Quenched systems (originally in the VI-N form) were found to have partially rehydrated after standing in laboratory air for a month and to have become considerably more crystalline as judged by the "sharpness" of the diffraction pattern. The oil-free anhydrous soap (in the VI-A form) remained unchanged on standing in laboratory air, but hydrated completely on standing at room temperature in a closed tube with the theoretical amount of water required to form the monohydrate (Fig. 2). The more rapid rate of rehydration here found compared to previous results[10] may possibly be attributed to traces of the VI-H form in the present preparation of calcium stearate which may have provided nuclei at the phase interfaces facilitating hydration.

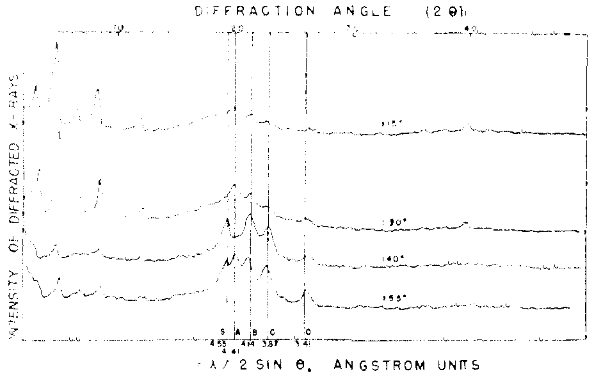

Fig. 5.—X-Ray diffraction patterns of 48% systems of calcium stearate monohydrate in cetane which have been cooled at 0.5° per minute from various temperatures.

Monohydrate–cetane systems quenched from 155° show the same dependence of long spacing on composition as do anhydrous systems,[6] further indicating that the present soap is dehydrated in the solid resulting after quenching from an elevated temperature. Below 25% calcium stearate the values of the long spacing are somewhat higher than in the oil-free system (except at 22%), between 25 and 80% they fluctuate considerably, around 85% abnormally short values are obtained, with longer values again in the more concentrated systems. Long spacing variations may be caused by changes in the angle of inclination of the hydrocarbon chains with respect to the planes containing the polar groups, the values being quite reproducible for a given composition although varying in so apparently erratic manner as composition is changed.

A distinctively different diffraction pattern (VI-S) is obtained when ternary systems of calcium stearate, water and cetane are cooled at a rate of 0.5° per minute from 155°. If water is not present the normal anhydrous pattern (VI-A) is produced; if cetane is not present the hydrate pattern is obtained. However, neither cetane nor water appear to be necessary for preservation of the soap lattice of the VI-S modification although required for its formation, since the pattern remained unaltered except for slight sharpening of the peaks after complete removal of cetane and water. Cetane was removed by *n*-heptane in a Soxhlet extractor and water by heating *in vacuo* at 40–50° for several hours, the completeness of removal being shown both by analysis of the residue for calcium and by comparison of the weight losses on extraction with the weights of liquid initially present.

As is evident from Fig. 4, the VI-S pattern was developed over a wide composition area of the ternary system, although occasionally (*cf.* 44% calcium stearate, 10% water, 46% cetane) a normal hydrate pattern was obtained. It is apparent from Fig. 5, which shows the patterns of a number of 48% calcium stearate monohydrate systems in cetane cooled slowly from various temperatures, that the new structure is not formed unless the temperature has been greater than 130° which, as has already been shown, just suffices to permit decomposition of the original hydrate in sealed tubes. Slow cooling then permits development of the VI-S structure when cetane is simultaneously present.

An examination of the pressure stability of quenched calcium stearate–cetane systems[5] in which the same preparation of calcium stearate was used as in the present investigation has shown that the presence of water causes a considerable increase in stability. The X-ray results reported above indicate that this increase in stability is not due to presence of the stoichiometric hydrate at room temperature in the quenched systems, since the present soap was found to be anhydrous after quenching when the system had been heated to 150° or higher. It is more probable that the presence of water conditions some modification of the structure of the aggregates in the system, without affecting the microcrystalline structure examined by X-ray diffraction. Thus it has been shown by the electron microscope[4] that in water-containing systems the soap is present in a fibrous habit as contrasted with a relatively amorphous appearance in anhydrous systems.

Interpretation of Diffraction Patterns in Terms of Stacking Disorder.—Considerable interest attaches to the question as to whether or not the new modification of calcium stearate (VI-S) should be regarded as a new phase. Diffraction patterns alone cannot settle this question. However, different phases have characteristically different X-ray diffraction patterns, and phase identification is often effected by an essentially empirical consideration of the positions of the more intense lines in the pattern.[15,17,18,19] In the present instance the VI-S pattern differs from the previously reported patterns by the appearance of a new intense line (4.53 Å.) as well as by a number of other less striking features, so at first it might seem plausible to regard this modification as a new phase. However, more detailed analysis of the patterns renders this conclusion unwarranted.

Consideration of the fact that diffraction patterns of both heavy metal and alkali metal soap phases characteristically show a series of sharp (001) long spacings at small angles, with only broad bands at higher angles together with some weak sharp lines, recently led Stosick[20] to postulate that these solids have a disordered structure in which micellar layers are superimposed with stacking disorder. Consequently, the (001) spectra remain sharp and intense as in a conventional crystal but lines due to the (*hk*) indices will be diffuse since they arise only from the two-dimensional lattice of the micellar layer, the index *l* which would normally contribute reinforcement and sharpness now being meaningless and continuously variable (here designated as ζ) because of the random orientation of the layers. A somewhat similar model has already been shown to be successful in interpreting the diffraction pattern of graphite.[21]

With Professor Stosick's collaboration we have analyzed the present patterns in terms of this concept with the results shown in Table IV. This hypothesis is successful in accounting for nearly all of the lines found in the diffraction patterns. Many of these appear to be due to higher orders of the long spacing, including many lines which have previously been regarded as side spacings. The remainder are indexed by taking the reciprocals of the observed values of d/n and by trial and error finding three vectors which permit construction of a two-dimensional reciprocal lattice net, in terms of which the other lines may be derived. This procedure involves the implicit assumption that the band maxima correspond to the region $\zeta = 0$ in each of the $(hk\zeta)$ bands, and failure of this condition may account for the presence of an occasional case of poor matching or an unmatched line.

TABLE IV

DIFFRACTION PATTERNS OF CALCIUM STEARATE MONOHYDRATE AND CALCIUM STEARATE VI-A AND VI-S INTERPRETED IN TERMS OF STACKING DISORDER IN THE CRYSTALS

Calcium stearate VI·A (present preparation)			Calcium stearate VI-A (from reference 6)		
Recognized long spacing			Recognized long spacing		
d/n, obsd.	n	d, calcd.	d/n, obsd.	n	d, calcd.
16.27	3	48.81	16.61	3	49.83
12.23	4	48.92	12.52	4	50.08
9.836	5	49.18	10.04	5	50.20
8.147	6	48.88	8.396	6	50.36
7.025	7	49.18	7.190	7	50.33
5.451	9	49.06	5.602	9	50.42
			4.59	11	50.4
	Av.	49.00		Av.	50.24

All other peaks					All other peaks				
d/n, obsd.	d/n, calcd.	Indices h	k	l	d/n, obsd.	d/n, calcd.	Indices h	k	l
4.18[a]	..	1	$\bar{1}$	ζ	4.11	..	1	$\bar{1}$	ζ
3.92	..	0	1	ζ		4.19	0	0	12
3.92	..	1	0	ζ	3.97	..	0	1	ζ
3.51	3.50	0	0	14	3.68	..	1	0	ζ
2.75	2.72	0	0	18	3.49[b]				
2.45	2.45	0	0	20	2.36	2.39	0	0	21
2.33	2.33	0	0	21	2.20	2.18	0	0	23
2.24	2.23	0	0	22		2.22	2	$\bar{1}$	ζ
2.18	2.22	1	1	ζ	2.12	2.15	1	1	ζ
2.08	2.09	2	$\bar{2}$	ζ	2.06	2.06	2	$\bar{2}$	ζ

Calcium stearate monohydrate (pattern indistinguishable from anhydrous calcium stearate VI-H)			Calcium stearate VI-S (71.9% system from Table III)		
Recognized long spacing			Recognized long spacing		
d/n, obsd.	n	d, calcd.	d/n, obsd.	n	d, calcd.
16.61	3	49.83	16.58	3	49.7
12.47	4	49.88	12.57	4	50.3
10.00	5	50.00	10.04	5	50.2
8.322	6	49.93	7.184	7	50.3
7.155	7	50.09			
	Av.	49.95		Av.	50.1

All other peaks					All other peaks				
d/n, obsd.	d/n, calcd.	Indices h	k	l	d/n, obsd.	d/n, calcd.	Indices h	k	l
5.58	5.55	0	0	9	4.55	4.55	0	0	11
4.40	..	0	1	ζ	..	4.40	0	1	ζ
4.12[a]	..	1	$\bar{1}$	ζ	4.18[a]	..	1	$\bar{1}$	ζ
	4.16	0	0	12		4.18	0	0	12
3.86	3.84	0	0	13	3.86	3.85	0	0	13
3.41	..	1	1	ζ	3.38	..	1	1	ζ
	3.47	2	0	ζ		3.47	2	0	ζ
3.15	3.12	0	0	16	2.89	2.89	0	0	17
2.51	2.50	0	0	20	2.48	2.51	0	0	20
2.43	2.48	2	1	ζ	2.45	2.46	2	1	ζ
2.38	2.38	0	0	21	2.24	2.28	0	0	22
2.28	2.27	0	0	22		2.25	1	$\bar{2}$	ζ
	2.23	1	$\bar{2}$	ζ					

[a] Packing considerations (10) suggest that this is a very plausible side spacing. [b] This weak line, which is not accounted for in the present assignment, may be an example of a case where the (*h k*) band maximum does not occur for $\zeta = 0$.

That the intensity of the successive orders of the long spacing does not decrease to zero at higher orders as would seem to be indicated from the trend at lower orders must be attributed to occurrence of some other regular distribution of scattering matter along the *c* axis of periodicity corresponding to the particular higher order of the long spacing. Thus it has been shown in the case of cetyl palmitate[22] that this sort of interaction due to carbon–carbon distance results in very high intensity of the thirty-fourth and thirty-sixth orders of the long spacing even though intervening orders are missing, and similar variations have also been

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noted with montmorillonites containing adsorbed water.[23] The fact that soaps of different chain length usually have lines at about the same position, even though such lines may be higher orders of the long spacing, is easily explicable in terms of the coupled geometry of the system. Thus calcium stearate of long spacing 49.0 Å. (Table IV) and calcium palmitate[12] of long spacing 45.5 Å. have diffraction peaks at 2.33 and 2.37 Å., respectively, corresponding, respectively, to the twenty-first and nineteenth orders of the long spacing.

Another anomaly which is explained by the present interpretation is the occurrence of rather large differences of several hundredths Å. between comparable short spacings of different soaps in the same crystal form, or of different samples of the same soap, these differences being far greater than the precision of the measurements. Where such spacings are in reality higher orders of the long spacing this would be expected since they must vary slightly if the long spacings do not remain constant, and these latter have been shown to be subject to erratic variation (within limits) with composition and sample preparation.

Examination of the data in Table IV shows that anhydrous calcium stearate VI-A differs greatly from calcium stearate VI-H in the reciprocal lattice vectors in terms of which its side spacings can be explained. However, calcium stearate VI-S appears to differ from calcium stearate VI-H only in which of the higher order peaks of the long spacing occur with marked intensity, and in the appearance of some different (*hk*) bands, the long spacing itself and the basic (*hk*) net being identical for the two. (Both calcium stearate VI-H and VI-S can contain one mole of water per mole of soap without any observed change in the diffraction pattern.) Hence despite the superficial marked differences between the two patterns, the two solids appear to differ only in some slight shift in packing or orderliness rather than involving any change in the basic unit cell. Consequently it seems unlikely that there would be here two discrete phases capable of existing in equilibrium with each other, even though it is still entirely possible that these two "modifications" may differ somewhat in certain physical properties, such as rate of inhibition of liquid.

Summary

Consideration of X-ray diffraction patterns of calcium stearate monohydrate–cetane systems quenched and cooled slowly from elevated temperatures shows that the monohydrate begins to decompose at 130° in sealed tubes, and that the resultant anhydrous soap in the present experiments did not rehydrate on quenching to room temperature. Cooling ternary systems of soap, cetane and water slowly from temperatures above 130° results in the formation of a new modification of calcium stearate (VI-S).

Postulation that solid soaps consist of regular micellar layers superimposed with stacking disorder shows that many of the so-called side spacings in their diffraction patterns are in reality higher orders of the long spacing. The pattern of the new VI-S modification of calcium stearate is shown to differ from that of the usual monohydrate chiefly in the intensities of varying orders of the long spacing despite a superficially great difference between the two patterns.

Evidence is discussed tending to show that the ability of water to enhance the stability of systems of calcium stearate and cetane is due primarily to its effect on the colloidal structure of the gel (size, shape, and manner and degree of association of the ultimate particles) rather than to its reaction to form calcium stearate monohydrate.

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