TABLE VII

Elementary Composition of Sitosterol and Its Derivative From Filbert Oils

	(Chloroform Solution)	Melting Point °C.	C		H	
			Theory	Found	Theory	Found
			%	%	%	%
Barcelona sitosterol[1]	—25.6°	136-8	83.87	83.86	11.99	12.25
Du Chilly sitosterol[1]	—35.2°	135-7	83.87	83.95	11.99	12.09
Barcelona acetyl sitosterol[2]	....	118	81.25	81.27	11.29	11.32
Du Chilly acetyl sitosterol[2]	....	116-118	81.25	81.45	11.29	11.35

[1] Calculated as $C_{27}H_{46}O$.
[2] Calculated as $C_{29}H_{18}O_2$.

Discussion

In comparing the results obtained in this laboratory with those from the studies of Bertram (3) and Schuette and Chang (11), Barcelona and Du Chilly filberts are shown to contain slightly more oil than the European varieties. Other values except the iodine absorption value agree quite well with those European varieties reported in the literature. There are some variations in percentage of fatty acids in European oils as compared to those of Barcelona and Du Chilly filberts. Arachidic acid and C_{20-22} monoethenoid acids were found for the first time in Barcelona and Du Chilly filbert oils.

Bertram, in the separation of solid acids by the Twitchell method (3), reported that the solid acids had high iodine value and gave no explanation for this abnormal behavior. Similar results were observed in this study on both Barcelona and Du Chilly filbert oils. Fractional distillation of methyl esters of both fatty acids fractions revealed that this abnormal behavior probably was due to a high content of C_{20} monoethenoid acid. No attempt has been made to isolate and identify this acid.

The oils obtained by extraction gave a darker color and more free fatty acids than those obtained by cold expression. The amount of crude carotene in the samples obtained by these two different methods has shown no significant differences. It is then presumable that the darker color in extracted oil is due to other coloring matters.

The sitosterol of both oils possessed properties similar to those obtained from other vegetable oils.

Summary

Barcelona and Du Chilly filbert nuts have been analyzed for their principal constituents. The characteristics of the oils obtained by solvent extraction and by cold expression have been determined and their fatty acid composition has been ascertained. Most of the chemical and physical characteristics of the oils as determined in this laboratory agree well with values previously reported by other investigators on European varieties. However, our study of the oil components shows a considerable difference in fatty acid composition.

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The Stability of Sodium Stearate Gels[1]

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ONE of the methods used to estimate the stability of lubricating greases is a determination of the rate of expression and total quantity of syneretic fluid. Most properly formulated greases undergo syneresis quite slowly, hence various accelerated tests have been devised in an attempt to determine the syneresis within a few minutes to a day (4, 5). The present paper reports the results of pressure stability experiments on systems containing less than 40% sodium stearate and less than 10% water, undertaken with the hope that some correlation could be found between phase behavior (1, 2) and the ability of the gel to retain liquid.

Materials and Apparatus

The sodium stearate and cetane used in this study have been previously described (1, 7). The syneresis press is shown in Figure 1. A synopsis of the technique of operation follows.[2] The sample for the syneresis press consisted of a sandwich of the "molded" soap gel between two mats of filter paper. Each mat contained seven to ten sheets of filter paper and was weighed to a tenth of a milligram. Between weighing the first and second mat, the sample of the soap gel was put on top of the first and weighed. This sandwich was transferred to the base of the press, and the top was bolted on. The press was then placed in a constant temperature bath (± 0.2° C.). Fifteen minutes, which had been shown to be sufficient, were allowed to elapse in order to obtain temperature equilibrium, and then the valve was turned so as to lower the plunger onto the sample. Ordinarily a five-pound plunger was used although a few experiments were carried out at higher pressures. After the elapse of a measured time interval, the plunger was raised, the press removed from the bath, cooled, and dismantled. The cake was readily and cleanly removed from the

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[1] This paper was presented in part before the Division of Colloid Chemistry at the 110th meeting of the American Chemical Society in Chicago, Ill., in 1946.

[2] Complete details of the procedure are given by T. M. Doscher, Doctoral Dissertation, University of Southern California, 1946.

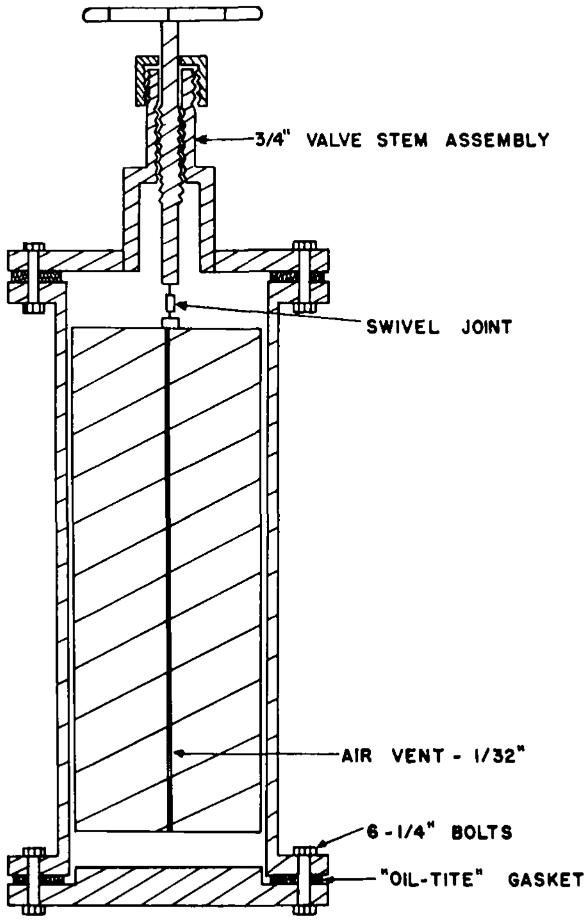

FIG. 1. Syneresis press. Diameter of chamber, 1⅞"; height of chamber, 6¾"; weight of plunger, 5 lb.; all parts of brass; plunger makes sliding fit in chamber.

mats of filter paper with the aid of a spatula. The top and bottom mats were weighed separately, the gain in weight representing liquid loss of the soap gel. This quantity divided by the initial weight of the gel sample is reported as the percentage loss. Occasionally the cake was also weighed to obtain an overall weight balance.

The soap samples were prepared in the following manner: The powdered soap was dried at 105°C., weighed into a constricted 19-mm. i.d. pyrex tube, and cetane, previously dried over calcium chloride, was added with a long capillary to give a total system of about 10 grams. After evacuation the lower part of the tube was immersed in a dry ice-acetone mixture and the tube sealed under vacuum. Since two grams of soap in a typical unsealed sample tube without cetane increased in weight 0.07% in five minutes, and only 0.14% after an hour, it seems reasonable to assume that the presumed anhydrous systems contained about 0.1% water.

The samples were then heated to a temperature above their melting point (1), allowed to cool slowly in the oven to about 100°C. with constant agitation, and then quenched in ice water. Only in this manner could reproducible results be obtained. Most of the molded soap gel samples for use in the press were formed in a washer (4) although samples containing more than 30% soap were sufficiently rigid to be sawed or cut from the cylinder of the gel formed in the glass tube upon cooling.

Usually systems were studied immediately on reaching room temperature after quenching. Where this was not possible, they were stored at 0° to 5°C. to prevent undue liquid loss due to spontaneous syneresis. That this procedure was effective was indicated by the unchanged melting point after storage.

In most cases Whatman No. 3 filter paper was used for the mats. Substitution of the fine No. 42 paper caused a decrease in liquid loss of about 10%. It was found necessary to control the weight of the samples for the press to within a tenth of a gram in order to obtain reproducible values for the percentage of syneresis, the usual weight being 1.2 ± 0.1 gram. The overall precision of the method amounted to ± 0.5 absolute per cent when working with systems containing 30% or more of soap. The precision fell off gradually as the soap concentration was lowered; at 3% soap it was only ± 4.0%.

Results

Sodium Stearate-Cetane Gels: Due to rapid spontaneous syneresis anhydrous systems containing less than 20% sodium stearate could not be run in the press with any precision. The results on systems containing 30% and 44% sodium stearate are summarized in Figures 2, 3, and 4.

Sodium Stearate-Cetane-Water Gels: The results for these systems are summarized in Figure 5. Table I contains data on the appearance, tendency toward spontaneous syneresis, rate of loss of liquid, and soap content of the residual cake for 20% soap-cetane-

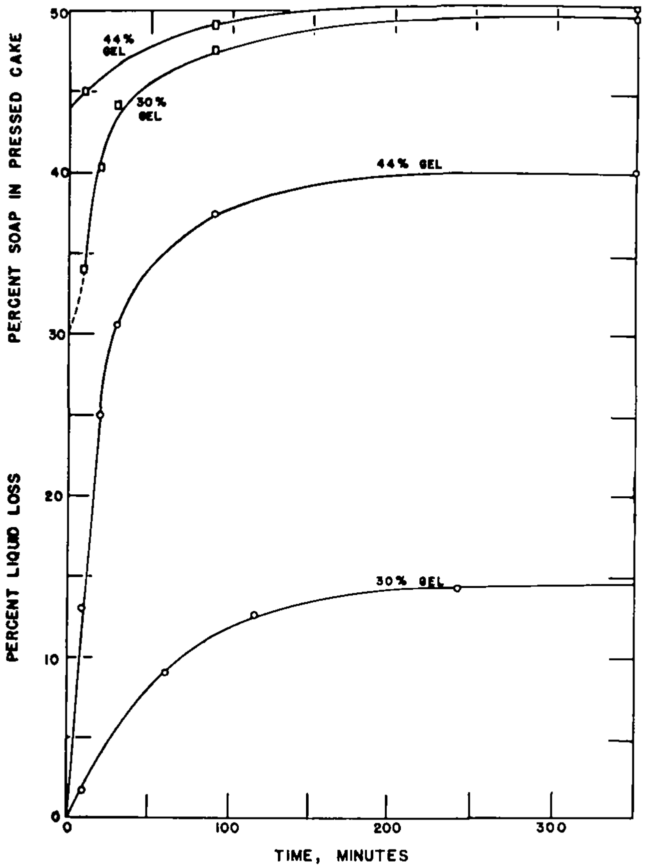

FIG. 3. Liquid loss and residual soap content of 30% and 44% sodium stearate-cetane gels at 25°C.

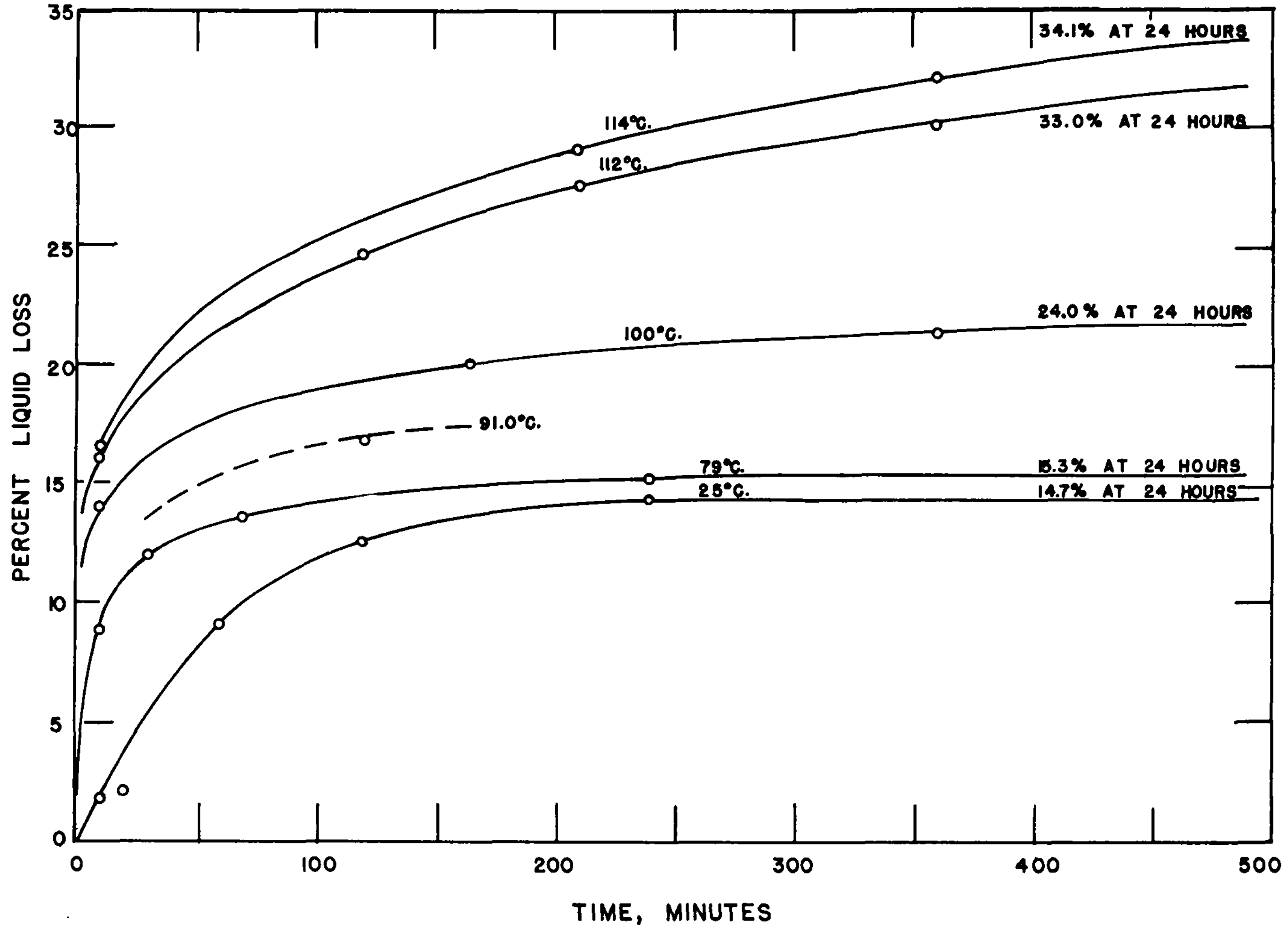

Fig. 2. Rate of liquid loss by 44% sodium stearate-cetane gels at various temperatures.

water gels. The behavior of the other compositions studied is qualitatively similar. Experiments were conducted on systems containing as little as 2.5% soap but, as pointed out previously, the precision at this low concentration of soap is only of the order of magnitude of ± 5%.

Discussion

Before discussing the experimental results, it is valuable to consider the significance of these measurements. The data permit estimation of the total quantity of liquid expressed at a given pressure and of the rate of expression. Farrington and Humphries have shown (4) that in some cases the initial rate of liquid loss of commercial greases can be related to storage instability, i.e., spontaneous loss of liquid from greases that have been stored six months. It is possible that the total amount expressed may be related to the amount of liquid lost under pressure in an operating bearing.

The nature of the expression of fluid from soap gels can be expected to depend upon the following factors:

Free Liquid: Fluid that is mechanically interspersed or held in the pores and channels of the gel structure may be considered to come under this designation. The total amount of liquid expressed is controlled by the difference between the pore capacity of the initial gel structure and the gel structure produced by compression. The free fluid will be exuded

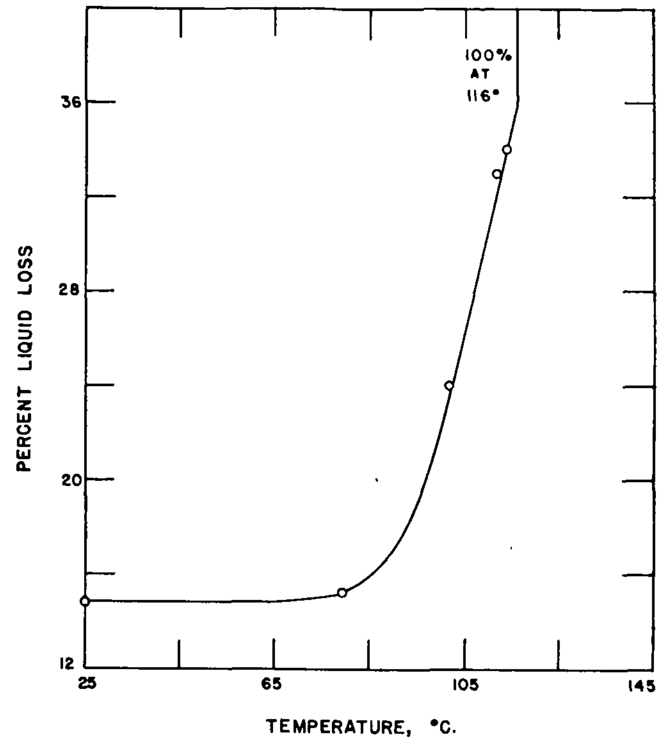

Fig. 4. Liquid loss of 44% sodium stearate-cetane gels after 24 hours at various temperatures.

in proportion to the collapse of the gel structure with consequent decrease in pore capacity. The quantity of liquid expressed would be expected to vary with temperature to the extent that such variation causes phase changes or differences in the structure of the compressed gel at the surface of the filter paper mats.

The rate of expression of free liquid is controlled chiefly by viscosity of the liquid itself and therefore increases with increasing temperature. In addition, as the cake is compressed, it offers greater resistance to fluid flow with a resultant decrease in the rate of expression.

Adsorbed Liquid: Liquid that is held by the soap molecules as a result of van der Waal's forces is designated as adsorbed liquid. Only in so far as an increase in temperature or pressure results in desolvation will the adsorbed liquid contribute to the total loss of liquid.

Water-free Systems: Below 80°C. the curves of per cent liquid loss vs. time are similar to those which have been obtained with commercial greases (4). Increasing temperature appears to affect only the viscosity, the rate of loss of liquid increasing with no significant change in the total amount expressed. It is interesting to observe that both the 30% and 44% soap systems yielded residues (compressed gels) of approximately the same soap content (50 ± 1%) after ten hours. This final composition is not to be construed as a phase boundary but is probably that of the equilibrium gel structure produced under the conditions of the experiment. An increase in pressure (two and one-half times the pressure used for the reported results) resulted in an increase in the amount of expressed fluid of both the 30% and 44% systems so that the final composition of the pressed gels was raised to 61 ± 1%. It is possible that, by continuing to raise the pressure, phase boundaries might be reached, but this was not attempted.

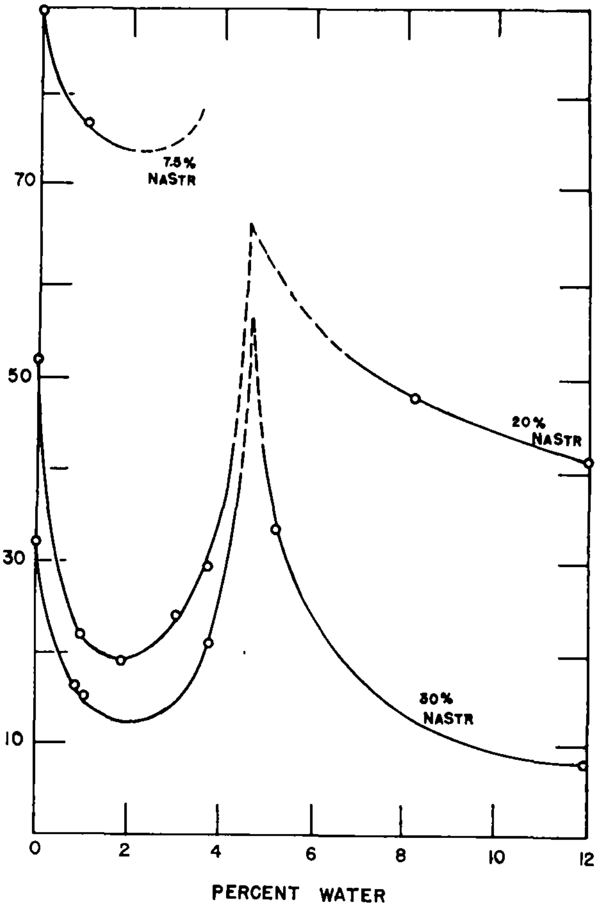

Fig. 5. Effect of water on the liquid loss of sodium stearate-cetane gels after 30 minutes at 25°C.

TABLE I

Characteristics of Soap-Cetane-Water Gels at 25°C.

% Water	Appearance at 25°C. (After homogenization)	Liquid Loss 10′	30′	After 120′	% Soap in the pressed cake 30′	120′
0.0*	Liquid separates, solid has a paste-like consistency.	13.0	31.8	35.5	44.1	46.5
0.9	Trace of syneresis, solid has duller appearance, unctious.	....	16.1	....	40.0	....
1.1	No syneresis, dull appearance, has grease-like consistency.	9.6	15.3	22.7	34.1	37.4
3.8	As above, even more grease-like, but softer	13.0	21.0	22.6	38.0	39.9
4.7	Large amount of free liquid. Solid separates as globular, lustrous particles.	....†	....	....	....	....
5.2	Free liquid, but can be quenched to homogeneous solid. Is not lustrous, and less tendency to form globular particles.	....	34.0	38.0	45.4	48.4
17.5	No syneresis, hard, cake-like appearance.	....	7.5	11.1	32.4	33.7

* The soap content in all cases was 30 weight per cent on the basis of total system.

† This system was not sufficiently homogeneous, even on quenching, to obtain a homogeneous sample.

Above 80°C., the effect of temperature is to increase the total quantity of liquid expressed without affecting the initial rate. This behavior is indicative of the fact that the final gel structure is being continuously altered by the increase in temperature or that more liquid is "freed" by desolvation. The phase behavior of this system is such that there is a transition at about 80°C. from crystalline soap to a wax-type soap (1). Taking into consideration the structure proposed for this wax-type soap (2), the transition would lead to the possibility of closer packing of the soap aggregates under pressure; in other words, a greater collapse of the gel structure. It is noteworthy that the amount of liquid exuded in five or ten minutes above 80°C. is almost equal to the total final amount below 80°C. This again indicates a more readily collapsible gel structure.

At 114° to 116°C. a further phase change occurs with the formation of non-aqueous middle soap (1). Under these conditions the entire gel, both soap and oil, is completely absorbed within the filter paper in less than 10 minutes. This is in accord with the micellar structure previously proposed (2) for this phase.

Hydrous Systems: In all cases studied the effect of adding water is first to cause a decrease in the rate at which liquid is expressed and then an increase upon further addition of the water. With still more water the nature of the system changes again (cf. Table I), and in some cases the amount of liquid lost actually decreases again. It is difficult to make comparisons in the rates of liquid loss of most of these systems because of the relatively rapid rate of spontaneous

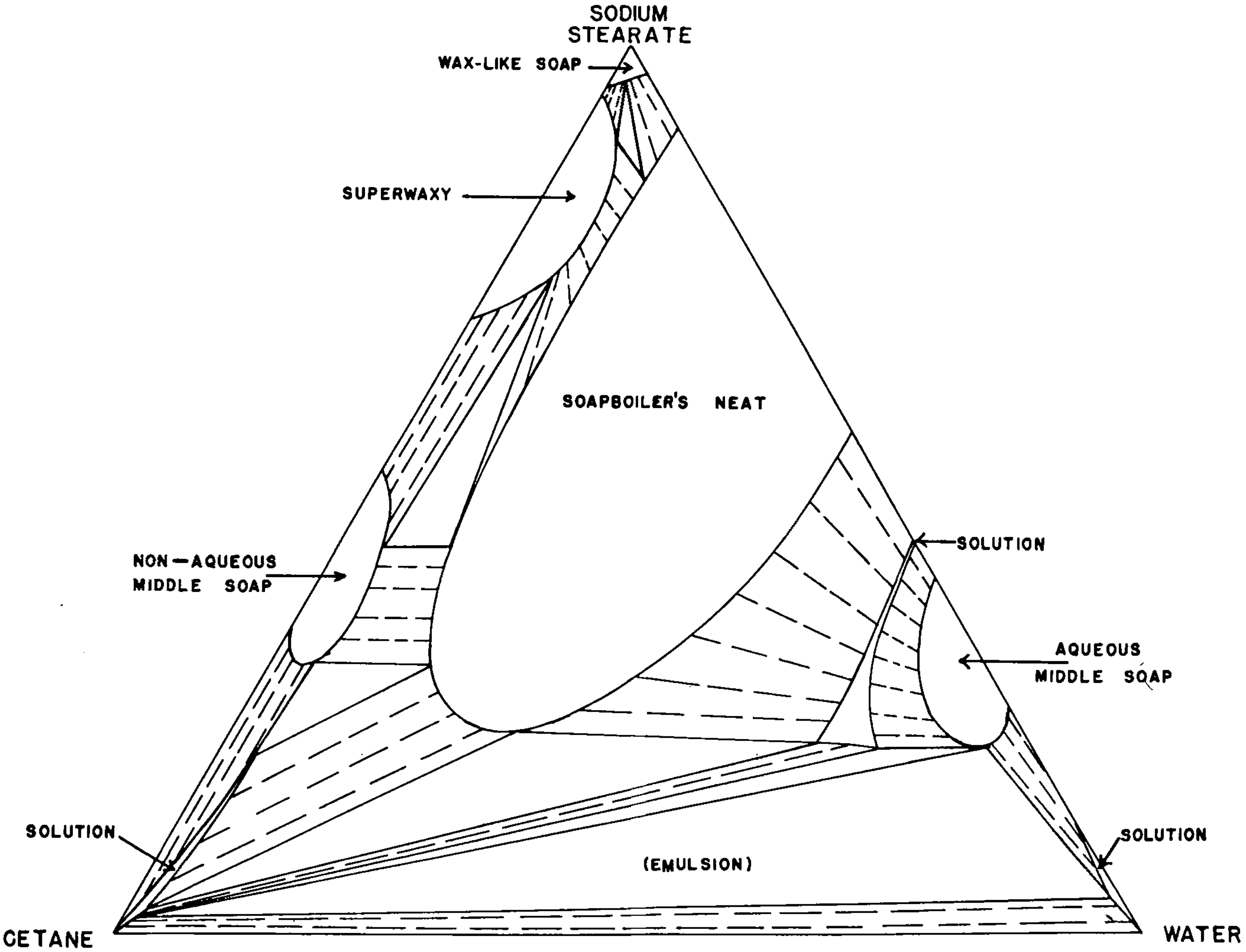

FIG. 6. Tentative phase diagram for the system: Sodium stearate-cetane water at 150°C.

syneresis at the lower soap concentrations which were of chief interest.

The sensitive dependence of syneretic behavior on water content may reflect either a difference in the particle size or degree of aggregation of the gel, or the presence of metastable phases "frozen in" on cooling from the higher temperatures where they are the stable form. At equilibrium at room temperature these systems consist of a mixture of crystalline soap phases and dilute solutions of oil or water (3, 6, 8). At higher temperatures, however, rather complex phase behavior is encountered as shown in Figure 6, which presents a tentative phase diagram for sodium stearate-cetane water at 150°C. Which structures are actually realized at room temperatures depends on both the conditions during cooling and on the composition of the system. Microscopic observations (3) show that anhydrous systems of sodium stearate and cetane cooled from 150°C. revert rapidly to crystalline soap which separates from the liquid whereas the addition of water results in persistence of the liquid crystalline appearance for long periods of time at room temperature. It is not yet known, however, whether the phase actually present at room temperature is really liquid crystalline or merely crystals showing pseudomorphism with the liquid crystal structure.

In any case addition of water apparently stabilizes a structure, either crystalline or liquid crystalline or a mixture of both, in which the cetane is more stably dispersed. The opacity of the water-containing systems as compared with the transulency of the water-free systems is further evidence that some type of aggregation has been induced by the water. It seems likely that the ability of water to form complexes or aggregates in this system may well be related to its ability to form hydrogen or hydroxyl bridges with other polar groups.

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