Several explanations could be offered for the synergism exhibited by NaOH and surfactant in solutions maintained below the cloud point. These include lowering of the surface tension, so permitting the solution to make closer contact with the soil, and the probability that hydroxide ion and surfactant remove various soil fractions at different rates. Harris and Satanek (10) found that surfactants were more effective in removing fatty soils than protein deposits. It is probable that the surfactant and hydroxide ion alternate at being the more effective detergent at any one site of the deposit, depending on the nature of the soil exposed to the solution.

The apparently anomalous behavior of the surfactant with relation to cloud point might be explained if the active form consisted of micelles distributed through the continuous phase. Ionic surfactants form micelles when the energy released by aggregation of the hydrophobic hydrocarbon chains balances the electrical repulsion of the ionic groups and the decrease in entropy resulting from the more highly organized state of the detergent. Nonionic surfactants generally have a lower cmc, probably because the energy from aggregation must balance only the entropy decrease. The resulting uncharged micelles could form loose clumps, separated by a network of water bound to the exposed hydrophilic groups. Reich (7) indicated that nonionic micelles were spherical, and the individual hydrocarbon chains were tightly coiled within the micelle. At cloud point temps, the increased thermal agitation of the molecules may be sufficient to break the individual micelles within a clump, and form free globules of surfactant that account for the turbidity. Surfactant confined to the interior of these globules would contribute little or nothing to detergency. This would explain the following observations: a) the detergent efficiency of the nonionic decreases as the solution transcends the cloud point temp, b) the magnitude of this decrease is lower for more concentrated solutions, c) very dilute solutions do not exhibit the cloud point phenomenon (8), d) the temp of the cloud point varies inversely with surfactant concentrations (8), e) cloud points are exhibited only by nonionics—ionic surfactants produce micelles that would resist clumping. Cloud formation, then might be represented as

$$\begin{array}{c}\text{molecularly}\\ \text{dispersed}\\ \text{surfactant}\end{array} \underset{\longleftarrow}{\xrightarrow{\text{CMC}}} \begin{array}{c}\text{micellar}\\ \text{aggregates}\end{array} \underset{\longleftarrow}{\xrightarrow{\begin{array}{c}\text{Cloud}\\ \text{Point}\end{array}}} \begin{array}{c}\text{globules of}\\ \text{surfactant}\end{array}$$

This would explain not only the results obtained in this study, but the observations of Ginn et al. (9) that solubilization of a fatty soil by a nonionic surfactant was maximal at cloud point temps, and decreased at higher temps.

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Study of Kettle Wax in the Sodium Palmitate-Water-Electrolyte System at 90C

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Abstract

An X-ray diffraction study has been carried out on kettle wax occurring at 90C for the ternary system sodium palmitate-water-sodium chloride.

It was found that kettle wax is not a simple phase, according to Gibb's phase rule, but a mixture of curd, neat and lye.

Introduction

A GREAT DEAL of the work carried out by McBain and coworkers (1,2,3) concerns the study of the phases present in the ternary systems soap-water-electrolyte at high temp. Several experimental techniques were employed including visual observation, thermal analysis and vapor pressure measurements. The existence of kettle wax amongst the phases identified was noted only when electrolyte was present, the other phases (curd, neat soap, middle soap) being also present in the binary soap-water systems.

The structure of all the liquid-crystalline phases existing in the soap-water systems has been thoroughly investigated in Strasbourg recently (4,5). We describe here very briefly the structure of middle and neat soap, which are the most important phases occurring in soap-water systems. Middle soap is formed by a set of indefinitely long cylinders, arranged in a regular two-dimensional hexagonal array, and separated from one another by water. The polar groups of the soap molecules lie at the surface of these cylinders and the hydrocarbon chains are in a liquid state filling the interior of the cylinders. The neat soap consists of a set of plane parallel equidistant sheets, each formed of a double layer of soap molecules, and separated from each other by a layer of water. The hydrocarbon chains are in the "liquid" state and the polar groups lie at the surface of the sheets.

As an extension to this work it was decided to complete these results by determining the structure of kettle wax.

To this end, a study was undertaken of both the sodium palmitate-water-sodium chloride and sodium laurate-water-sodium chloride systems at 90C. Only the results of the first system will be presented in this note, the two systems being very similar to each other.

Attention was not paid as to an accurate definition of the phase diagram boundaries nor as to the structure of phases other than kettle wax.

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TABLE I

Wt Composition of Samples Corresponding to Black Dots in Figure 1

Sample	% NaP	% H_2O	% NaCl
1	90.0	10.0	0.0
2	71.0	29.0	0.0
3	61.8	38.2	0.0
4	50.6	49.4	0.0
5	40.3	59.7	0.0
6	31.2	68.8	0.0
7	69.6	29.5	0.9
8	50.3	48.8	0.9
9	39.7	59.6	0.7
10	29.5	69.7	0.8
11	68.4	29.7	1.9
12	49.8	48.1	2.1
13	45.1	52.6	2.3
14	39.5	58.5	2.0
15	68.0	29.0	3.0
16	65.1	31.5	3.4
17	61.8	35.1	3.1
18	48.3	48.9	2.8
19	39.7	57.4	2.9
20	29.8	66.9	3.3
21	67.4	28.8	3.8
22	39.5	56.6	3.9
23	31.1	64.6	4.3
24	66.3	28.8	4.9
25	47.5	47.6	4.9
26	38.0	57.2	4.8
27	66.3	27.3	6.4
28	42.3	51.3	6.4
29	64.2	27.5	8.3
30	41.7	50.2	8.1
31	36.6	55.8	7.6
32	68.7	21.5	9.8
33	67.6	22.4	10.0
34	35.5	54.6	9.9
35	30.4	59.9	9.7

Experimental

X-ray diagrams were obtained by means of a Guinier-type focusing camera used with a bent-quartz monochromator. A detailed description of this apparatus appears elsewhere (6). Samples were prepared by mixing known amounts of soap, salt and water. After homogenization at high temp (150C for 48 hr) the samples were enclosed in a cell consisting of two thin mica windows clamped tightly in metal holders and then subjected to X-ray examination. Equilibrium was assumed to be reached when the diffraction diagrams taken at the same temp did not vary with time.

The composition of the samples was checked before and after X-ray examination.

Results and Discussion

The portion of the phase diagram ranging from 30–100% of soap and from 0–10% of salt was examined (Table I). A certain number of phases can be identified by their diffraction diagram, namely curd, neat soap, middle soap, as well as two intermediate phases (complex hexagonal phase and deformed middle soap) that appear in the binary soap-water systems (4) (Figure 1). Although the experimental techniques used allowed the easy detection of the neat, middle, curd and intermediate phases, it was more difficult to determine the presence of lye, of isotropic solution or of excess salt; this being due to the fact that the latter phases produce diffraction diagrams which do not show sharp lines in their central portion. In diagram I, in the areas where the different phases are localized the system may equally consist of the mixture of these phases with lye, salt (or with both).

It will be noted that the phases appearing in the presence of electrolyte all derive from the phases already appearing in the binary soap-water systems and that no new stable phase appears in the presence of electrolyte, as claimed by McBain and coworkers.

In the region of the phase diagram where these authors had localized kettle wax, the system is not a simple one but shows the neat phase and the curd phase and probably a third one, the lye, which is invisible under X-ray.

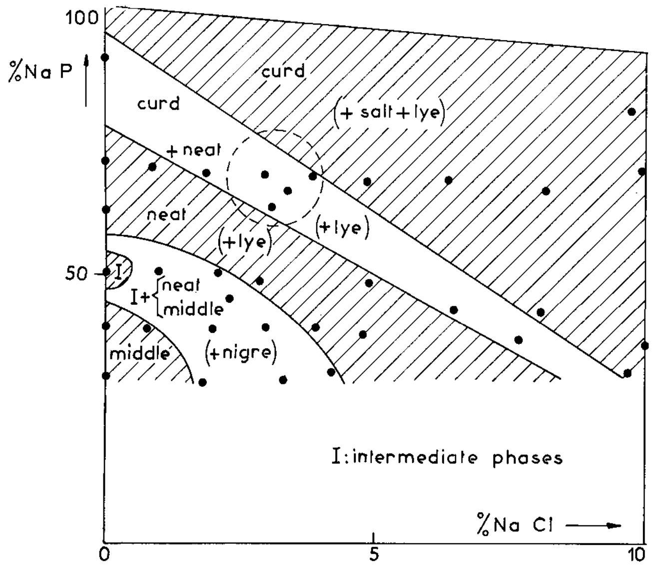

FIG. 1. Phase diagram of the system Na palmitate, NaCl and water at 90C. The dotted circle contains the kettle wax region as determined by McBain. For wt composition of samples corresponding to black dots see Table I.

Moreover, the examination of a kettle wax sample identical to that met in the soap manufacturing industry, confirms this fact.[2]

Kettle wax therefore cannot be considered as a simple phase according to Gibb's phase rule, as are the neat and middle phases.

Even though X-rays cannot show us whether kettle wax is a mixture of two or three phases, a simple reasoning shows that kettle wax consists of a mixture of neat, curd, and lye. Indeed, according to the observations made by McBain and his colleagues (3), the neat phase cannot incorporate more than about 2 or 3 % of salt (this percentage varies according to the type of soap), because it demixes with lye in the same way as curd demixes with salt and lye. The area where curd and neat soap coexist must therefore be limited to 2 or 3% of salt also, and the area of the phase diagram where the simultaneous presence of curd and neat was observed by X-ray diffraction must, in fact, for a salt content greater than approx 3%, be a triple curd-neat-lye demixing area. This is the very area where McBain and coworkers place kettle wax.

This definition of kettle wax is in compliance with all observations made by the various authors quoted in this note; these have noted, for instance, that kettle wax does not appear below 70C, that it contains a relatively large amount of salt, and has a granulous and mottled appearance. In fact, kettle wax consists of an intimate mixture of neat, which does not appear below 70C; of lye, which is rich in salt; and of curd, which is finely divided and suspended in the rather viscous neat phase, lends to the whole this granulous and mottled aspect, this being obviously due to optical effect.

Though they apply only to one system, our results could quite likely be extended to other soap-water-electrolyte systems and only the scope of the area where these phases appear would then change.

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[2] This sample was kindly obtained for us by Mr. Bergeron (Cie. Cadum-Palmolive, Courbevoie) to whom we extend our thanks.

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