The Kettle Wax Phase in the System Sodium Laurate, Sodium Chloride and Water

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For over twenty years, McBain and collaborators have been publishing phase studies of pure and commercial soaps with and without the addition of electrolytes. The phenomena of soap boiling have been interpreted in terms of isotropic solutions (nigre and lye), anisotropic or liquid crystalline solutions (neat soap, middle soap), and crystalline curd. In 1938, K. Gardiner (1) noticed a wax-like phase, subsequently called "kettle wax", in the system sodium stearate-sodium chloride-water at 90°C., as well as in the system sodium oleate-sodium chloride-water.

Kettle wax has a soft waxy appearance and consistency. It is often dull white, but when homogeneous and clarified it is translucent to transparent, and is yellowish. In the stearate system, it was investigated visually, analytically and calorimetrically(1). In 1939, W. W. Lee (2) confirmed the presence of the new "island" phase in the stearate system by the study of vapor pressure. Kettle wax was found to occupy a dominant position in the middle of the phase diagram.

The present investigation substantiates the existence of the new kettle wax phase and partially delimits it for the lowest saturated soap, in the system sodium laurate-sodium chloride-water. The results are of general interest, since all soaps, pure, mixed and commercial, whether potassium or sodium, are of essentially the same type, differing in degree rather than in kind. Kettle wax has no connection with any of the anhydrous wax-like forms of soap, such as subwaxy, waxy, or superwaxy.

Material

The sodium laurate was prepared by neutralization of a hot alcoholic solution of lauric acid (Eastman Kodak) with sodium ethylate (3). It was dried at 105°C. to constant weight before being placed in the tubes used to determine the T_i points and dried at 105°C. for two hours before use in the tubes to be analyzed.

The sodium chloride was Merck's Reagent sodium chloride. It was fused before use and held over calcium chloride.

The tubes employed for the determinations of the nigre boundary were prepared during the winter of 1937-1938 by R. D. Vold. Kahlbaum's sodium laurate (excess lauric acid .38 equivalents %, water 08%) and sodium chloride were used.

Experimental Procedure

Weighed quantities of salt, water and soap, totalling about three grams, were sealed in thick-walled pyrex tubes, twelve centimeters long, fifteen millimeters o. d., and heated until all formed one homogeneous liquid. They were observed during slow cooling, between crossed Nicols, and the T_i point noted; that is, the temperature at which a separate

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liquid or liquid crystalline form just begins to appear on cooling. Experiments were carried out at least in duplicate.

The boundaries of the isotropic solution at 90°C. were interpolated from pairs of tubes whose T_i points were near the 90°C. isotherm.

The synthetic delimiting method is described later.

The oven was made of pyrex tubing (3 cm. o. d., 15 cm. long) wrapped with No. 24 A Nichrome wire and closed at each end with an asbestos wrapped cork. A standard thermometer was placed through one of the corks with the bulb very close to the glass tube for temperature observation. There was a temperature gradient of $\frac{1}{2}$°C. in the furnace but this was corrected by moving the thermometer close to the level at which the phase change was taking place. Temperature was controlled with an Adjust-A-Volt and stirring was accomplished by occasionally turning the small furnace upside down and back again. Two definite advantages of the oven were its good visibility and its simplicity.

The boundaries for the remaining part of the diagram were found from tie lines obtained by analysis of the phases that existed in the tubes at 90°C. and by visual observation of the tubes. Before the tubes were analyzed, they were heated until they were homogeneous, then cooled to 90°C., and when thermal equilibrium had been reached they were centrifuged at that temperature for fifteen minutes. The angle centrifuge was enclosed in a large thermostat, which stayed at 90°C.±2° during the entire centrifuging. After centrifuging, the tubes were quickly dropped into an acetone dry ice bath which froze the phases. The tubes were then cracked open and central slices of each phase cut out for analysis. This method was checked by removing phases at 90°C. in unfrozen tubes with similar results. Caution must be used, however, in not leaving the tubes in the dry ice bath too long as this gives results that are too high in percentage of salt and soap. This is probably due to the fact that water is squeezed out of the phase by expansion as it freezes. Likewise, water may be squeezed out or evaporated during the cutting and manipulation. The results for samples 7 and 8 of Table III are believed to be slightly too high in soap for this reason. The central slices were then analyzed for soap and chloride and the results plotted on a phase diagram. In analysis, soap was acidified with a known amount of sulfuric acid and the resulting fatty acid was filtered off, dissolved in boiled out, hot alcohol and titrated with standard sodium hydroxide in an 80% boiled out alcohol solution with phenolphthalein. The neutralized filtrate was analyzed for chloride, volumetrically, with standard silver nitrate solution, using sodium chromate as indicator.

Experimental Results

The Boundary of the Isotropic Solutions of Soap and Salt. The T_i values as given in Table I serve to

TABLE I

T₁ Determinations

(T₁ value is the temperature at which a liquid or liquid crystalline form begins to appear on cooling the homogeneous isotropic solution.)

Composition of System			Composition of System		
Wt. % NaL	Wt. % NaCl	T₁ °C.	Wt. % NaL	Wt. % NaCl	T₁ °C.
20.00	9.42	109	7.47	11.52	108
19.95	14.50	217	9.95	11.10	99
9.95	11.45	112	7.48	12.60	144
2.92	10.60	81.5	28.00	7.51	98
7.50	12.20	136	2.96	13.14	148.5
4.87	12.30	131	19.95	12.50	204
7.53	11.92	132	2.96	12.00	150
10.10	11.30	104	20.00	9.42	91
35.00	5.60	97	9.95	11.70	121
28.00	8.00	114	3.01	13.60	164
13.95	10.80	107	2.99	13.20	148
2.98	10.80	98	35.00	6.00	99
3.02	12.45	140	14.00	10.20	89
7.48	12.60	145	9.97	12.00	137

plot the boundary of the isotropic solution or nigre, as in Table II.

The results at 90°C. are included in Figure 1 on a rectangular triangle whose ordinates are percent soap and abscissae percent sodium chloride, the balance being water, so that the total at any point is 100%. A single homogeneous phase is shown by a continuous area on such a diagram. For example, the isotropic solutions occupy the lower left hand part of the diagram. The larger area at higher temperatures as shown in Figure 3 correspond to the increasing solubility at higher temperatures.

TABLE II

Boundary of the Isotropic Solution at 90°C.

Composition of System		Composition of System	
Wt. % NaL	Wt. % NaCl	Wt. % NaL	Wt. % NaCl
37.40	1.00	9.40	11.00
45.00	1.50	7.00	11.20
35.00	5.20	5.20	9.80
30.00	6.80	3.00	10.10
15.80	9.80	......	

Equilibrium between two phases must be represented by straight tie lines between the compositions of the two phases, each passing through a point representing the total composition of the system in the heterogeneous region. Equilibrium between three phases is represented by a triangle of which they are the three apices. The left hand side of the diagram is the binary system sodium laurate-water, and where determinations overlap, the results agree to within ±2° with those previously published (4).

The Analytical Data for the Heterogeneous Equilibria. When it is seen that two phases are present, one being a clear fluid lye and the other a gel such as curd, kettle wax or neat soap, it is simple to secure a true sample and correct analysis of the separated lye, but difficult or impossible to ensure that the more solid phase does not include some of the lye. However, from the conservation of matter it results that the analysis of such a contaminated phase must lie upon the straight line through the point on the lye and the total composition of the system; one can be sure then that the tie line may be too short but cannot be too long, except through loss of water as already mentioned, and that the boundary of the more solid phase may either coincide with the analysis or lie further away from the lye. In Figure 1 the tie lines are shown accordingly.

When three phases occur, unless the separations are complete, only the analysis of the lye need be correct, but the other two analytical results must lie within the heterogeneous three phase region. Such compositions are likewise connected by dashed "tie lines" in Figure 1.

The analytical results are collected in Table III and IV.

The Synthetic Delimiting Method. To obtain visual evidence as to the limits of the region of existence of the island kettle wax phase, a series of tubes of concentrations near its boundary were prepared and observed at 80°, 90°, and 105°C. A special note was taken as to whether lye was or was not present. If

TABLE III

Analytical Data Obtained at 90°C.

Composition of System		Phases at 90°C.	Analytical Results	
Wt. % NaL	Wt. % NaCl		Wt. % NaL	Wt. % NaCl
40.1	5.0	neat	48.8	3.3
		nigre	31.6	6.6
6.0	12.0	neat		
		nigre		
		lye	0.6	12.8
32.0	7.1	neat	49.6	3.4
		lye	0.3	13.3
24.9	8.9	neat	52.7	3.4
		lye	0.8	14.2
25.0	10.0	neat	56.8	3.2
		lye	0.1	17.2†
20.0	12.5	neat		
		kettle wax		
		lye	0.1	17.0†
25.0	11.0	kettle wax (neat?)	67.5*	3.2
		lye	0.7	16.8†
25.0	13.0	kettle wax	67.8*	3.1
		lye	0.4	19.3
25.0	14.0	kettle wax	61.9	3.7
		lye	0.4	20.1
25.0	15.0	kettle wax	60.3	5.6
		lye	0.7	21.5
24.7	16.2	kettle wax	60.2	4.9
		lye	0.0	23.3
25.1	17.1	kettle wax	59.5	5.6
		lye	0.3	24.6
25.0	19.0	kettle wax	52.5	8.4
		lye		(28.1)
		salt		(100)
24.9	21.0	kettle wax	50.2	10.7
		lye		(28.1)
		salt		(100)
24.6	22.6	kettle wax	47.3	13.9
		lye		(28.1)
		salt		(100)
25.0	25.0	kettle wax	51.2	10.6
		lye		(28.1)
		salt		(100)
59.1	11.2	kettle wax	60.8	6.6
		salt		(100)
62.0	9.0	kettle wax	63.1	7.1
		salt		(100)
64.0	8.0	kettle wax–curd	68.0	6.5
		salt		(100)

* These two values occur on the left hand boundary of the kettle wax region but are believed to be slightly high through loss of water.

† These three, practically identical lyes from systems of divergent salt content, fix the lower point of the three phase triangle in Figure 1.

Note: Figures in parentheses are not actual analyses but represent saturated salt solution at 90° and pure salt.

TABLE IV
Analytical Data Obtained at 80°C. and 105°C.

Composition of System		Temp. °C.	Phases Present	Analytical Results	
Wt. % NaL	Wt. % NaCl			Wt. % NaL	Wt. % NaCl
25	12	75	curd lye	88.2 0.2	1.3 15.9
25	15	80	kettle wax lye	48.5 0.2	8.0 20.1
25	16	80	kettle wax lye	49.4 0.2	8.5 24.7
25	12	105	kettle wax lye	54.5 0.2	6.9 15.5
25	13	105	kettle wax lye	42.1 0.4	10.8 17.5
25	18	105	kettle wax lye	55.8 0.3	8.2 26.3
25	20	105	kettle wax lye salt	56.2	8.9 (28.4)* (100)*
25	25	105	kettle wax lye salt	55.3	11.1 (28.4)* (100)*

* Not analyzed.

TABLE V
Delimiting Data on the System, Showing the Phases Present:
(kw=kettle wax, l=lye, n=neat, c=curd, s=salt).

Composition of the System		80°C.	90°C.	105°C.
Wt. % NaL	Wt. % NaCl			
51.5	7.1	kw	kw-l	
54.0	7.0		kw-l	
55.0	6.0		kw-l	kw-n-l
59.9	4.1		kw-l	kw-n-l
70.3	4.6	c-kw	kw-c	kw
44	16	kw-l-c	kw-l-s	kw-l-s
50	15		kw-l-s	kw-l-s
51.5	6.8	l-kw-c		kw-l
56.6	6.8	c-kw		kw-l
46	16	c-kw		kw-l-s

any lye could be seen, obviously the boundary lay at a higher soap concentration. The results are collected in Table V.

At 75°C., both analysis and visual observation show that no kettle wax is present at any composition of the system. Systems which at 90°C. would have consisted of kettle wax are at 75° merely mixtures of curd and lye.

At 80°C., however, and at all higher temperatures probably up to 215°C., kettle wax does occur. It forms an island phase as is shown in Figures 1 and
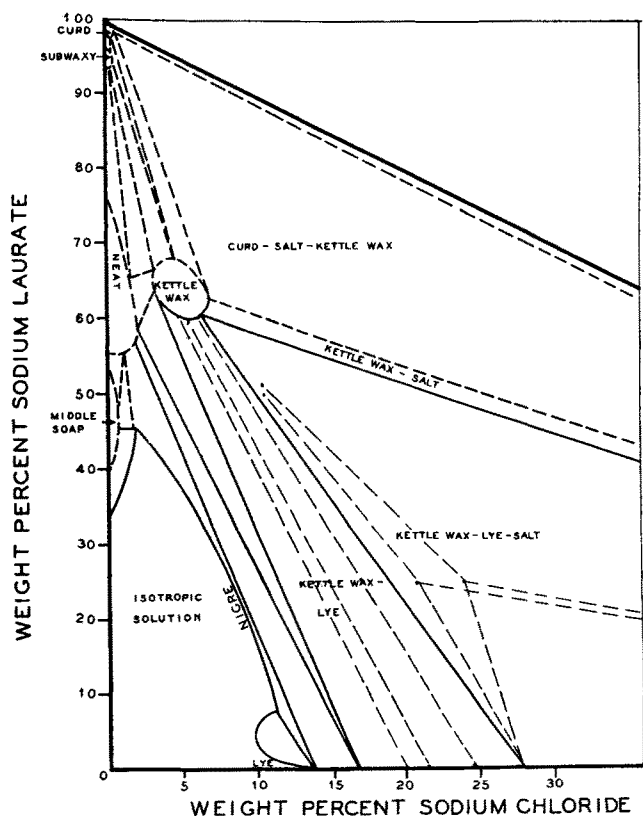

FIG. 1. Phase diagram of the system sodium laurate-salt-water at 90°C. The heavier dashed lines indicate boundaries whose position is uncertain. To avoid unnecessary complication the boundaries in the neat-nigre-lye area have been omitted.
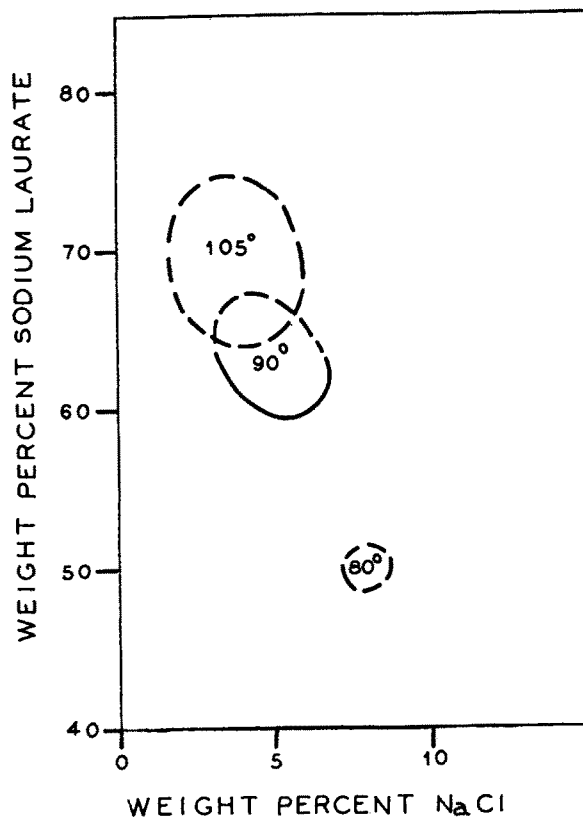

FIG. 2. Approximate positions of kettle wax in the system sodium laurate-salt-water at 80°C., 90°C. and 105°C.

2. Figure 2 represents the change in position of this phase between 80°C. and 105°C.

Upper Temperatures of Initial Formation of Curd. (Curd Solubility, T_c.) Figure 3 gives the compositions and temperatures T_c from 35°C. to 65°C. at which, upon slow heating with good mixing, the last trace of curd disappears into solution. The points on the graph are mainly based upon the previous determinations of Brock and the Volds[4]. Their observations of "T_c" at temperatures above 65°C. need reexamination as to their significance now that the existence of kettle wax has been discovered.

The indications are that kettle wax extends to a definitely lower soap concentration at 80°C. as compared with 90°C. or 105°C. The graph of the T_i values, that is, the boundaries of the isotropic solutions at temperatures from 80° to 250°C. are also contained in reference 4. Tubes that showed presence of lye at 90°C. showed none at 80°C.; similarly, tubes that showed distinct lye at 105°C. had none at 80°C. However, the position of the kettle wax does not appear to change much further, at least up to 150°C.
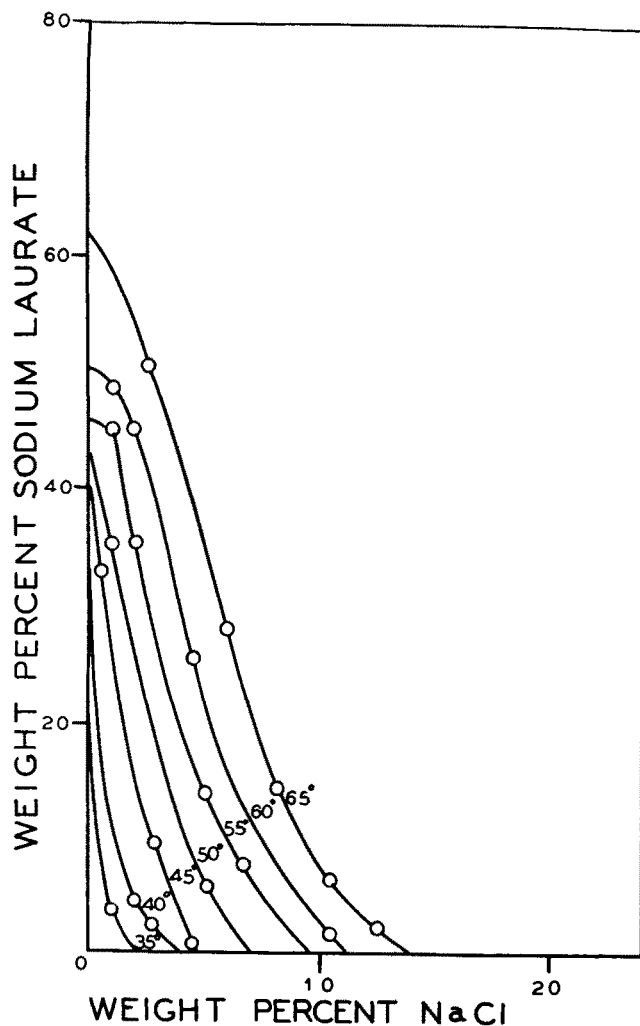
FIG. 3. T$_c$ curves for the system sodium laurate-salt-water.

tween them on the lower boundary, the relatively high percentage of salt in kettle wax, its sudden disappearance below 80°C., and the unexpected direction of shift of its boundaries with rise of temperature as shown in Figure 2, all point to kettle wax and neat soap being separate phases.

In a paper by J. W. McBain, W. J. Elford and R. D. Vold (5), the analytical results from samples taken during the actual soap boiling processes were given for several soaps.

The results of samples from the soap layer of palm oil soap, soya bean oil soap and tallow soap were all too high in salt per cent to fit the soap boiler's neat-soap boundary and too low in soap per cent to be curd. At that time kettle wax was not known, and this high salt content was assumed to be caused by the fact that the glycerin of saponification was present in the system when the samples were taken. It was probably due however to the existence of kettle wax. During "graining out" the salt and water content is higher than in any other step and is in the range of kettle wax existence. The following steps in soap boiling process, boiling, fitting and settling, are all in the region of neat soap—nigre equilibrium. The results from analyses of these steps fit the phase diagram.

Tubes were set up in the region between the kettle wax island and the upper corner of the diagram, 100% soap, and observed visually at a series of temperatures up to 120°C. These tubes therefore passed the transition temperature of the anhydrous soap between curd and supercurd and between supercurd and subwaxy, the latter at 100°C., but they remained visibly heterogeneous. By these observations it was demonstrated that kettle wax is a separate phase from those observed in the anhydrous pure soap. Kettle wax phase is therefore an island, as shown in the diagram.

Discussion

It is evident from Figure 1 that kettle wax occupies a dominant position in the middle of the phase diagram. In fact the "equilibria" commonly assumed to be the result of "graining out" into soap, curd and lye are now shown to be more commonly equilibria between kettle wax and lye. Even in the highest salt concentration these equilibria are predominant; curd is not produced at 90°C. by salting out sodium laurate. This result should also obtain for coconut or palm kernel oils. This is a different type of equilibrium than is involved in the sodium stearate system, whose phase diagram has tie lines in the higher salt concentrations connecting lye with soap curd (1). The fact that kettle wax is usually formed instead of curd during "graining out" is of technical importance. For one thing, it sets a low upper limit to the percent of soap which can possibly be obtained by graining out.

The kettle wax phase region might have been explained as an extension of the neat soap phase, although perhaps entitled to a separate designation, much in the same way that one part of the isotropic phase is called lye and another called nigre, although these two are merely different boundaries of the same phase. However, the difference in appearance of kettle wax and neat soap, the definite indentation be-

Summary

A study of the new phase, kettle wax, in the system sodium laurate, sodium chloride and water has been carried out using analytical and visual methods. The lower boundaries of kettle wax and its equilibria were established and when plotted occupy a highly dominant island region on the phase diagram. It occupies a portion between 60 and 70 wt. % soap and about 3 and 7 wt. % of salt.

The effects of temperature on kettle wax in this system have also been studied. It was found that kettle wax existed above 75°C. and below 215°C. and has the same type of equilibria with lye throughout this temperature range.

In the system sodium laurate, sodium chloride and water, curd is not formed, even by saturating the lye with salt at 90°C. Hence graining out results only in the formation of kettle wax and lye.

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