Phase Boundaries in Ternary Systems of Sodium Oleate, Compared With Other Soaps

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A long series of investigations since 1919 has established the conditions of existence of various soap phases, with and without water, and with both salt and water. Many different experimental methods have been described in previous communications, mostly developed especially for this purpose . The results have amply demonstrated that the ordinary phase rule applies strictly to the phase diagrams of soap.

The number of soap systems is so great, and the field to be covered so extensive that only portions of a few typical systems have as yet received quantitative study. We therefore now supply some data for the important but completely neglected systems of sodium oleate in the presence of salt and water.

1. *Isotropic Solutions of Sodium Oleate Containing Salt.* One of us [3] in an extension of a study of sodium oleate in water found the boundaries surrounding homogeneous isotropic soap solutions of sodium oleate containing sodium chloride at 90°C. and 100°C. respectively, using both delimiting and synthetic methods. However, when an attempt was made to confirm and extend these results, it was found that they changed with time of heating in the sealed glass tubes. The apparent solubility becomes less with time, although it is nearly constant after a month and a half. The temperatures, T_i, above which the system consists of a single clear liquid soap solution, but below which other phases begin to separate, rises at first rather rapidly by about twenty or thirty degrees in ten days at 105°C. However, it should be noted that this drift in T_i values only occurs while the solution is hot, and does not continue at ordinary temperatures. Anhydrous sodium oleate does not change its properties upon heating in a sealed tube at 105°C., because solutions made before and afterwards from such a sample showed the same initial T_i value.

Reaction with glass was suspected, and indeed some silicate does slowly dissolve. However, when experiments were carried out with systems to which known amounts of silicate are added, the value of T_i is actually lowered, and the drift with time is still observed. The silicate used was "N" brand, containing 28.3% SiO_2 and 8.9% Na_2O, and it was added in quantities sufficient to supply between 0.1 and 1% of SiO_2 in the soap system.

Several systems were made up containing 10% sodium oleate and using "N" brand sodium silicate as electrolyte instead of sodium chloride, in concentrations of 3.6% and 5.6% respectively. However, instead of the sodium silicates salting out the sodium oleate, the silicate salted the soap "in," and on cooling to 90°C., an elastic, transparent jelly resulted, with no visible separation of any other phase. At room temperature they formed a solid white curd.

It was concluded that it is the sodium oleate solution itself that is unstable on prolonged heating. Hence the determinations of values of T_i, shown in Figure 1, were taken from the initial values observed with freshly made systems. Figure 1 shows the boundaries of the homogeneous, liquid solutions of sodium oleate at a series of temperatures derived in the usual way by interpolation between the observed T_i values for individual systems. The solubility of course increases with increasing temperature, and the boundaries move correspondingly outwards towards higher concentrations of salt and soap. The upper right hand boundary corresponds to soap boilers' nigre. Below it is the bay region, in which two liquid layers are formed, one containing much more soap than the other, but not differing greatly in salt content. On the lower right this isotropic region extends with less and less of soap through the range called lye out to saturated sodium chloride solution. This extension is not included in Figure 1.

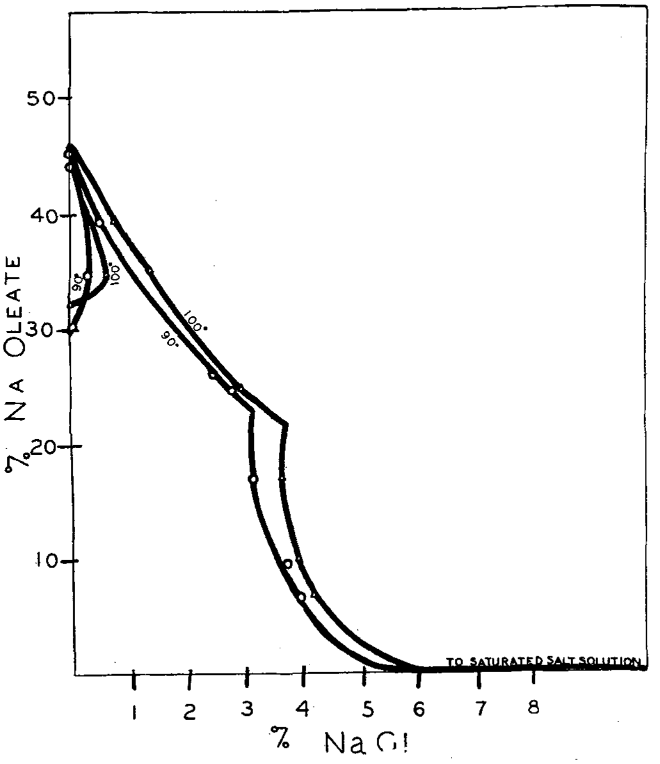

FIG. 1. The boundaries of homogeneous isotropic solutions of sodium oleate containing salt at 90° and 100° C.

2. *Comparisons of the Solubilities of Typical Soaps in Water and Chloride Solutions.* All the existing published data for the boundaries of isotropic solutions of pure soaps of single fatty acids are collected for comparison with each other in Figure 2, where they are all drawn to the same scale and recalculated

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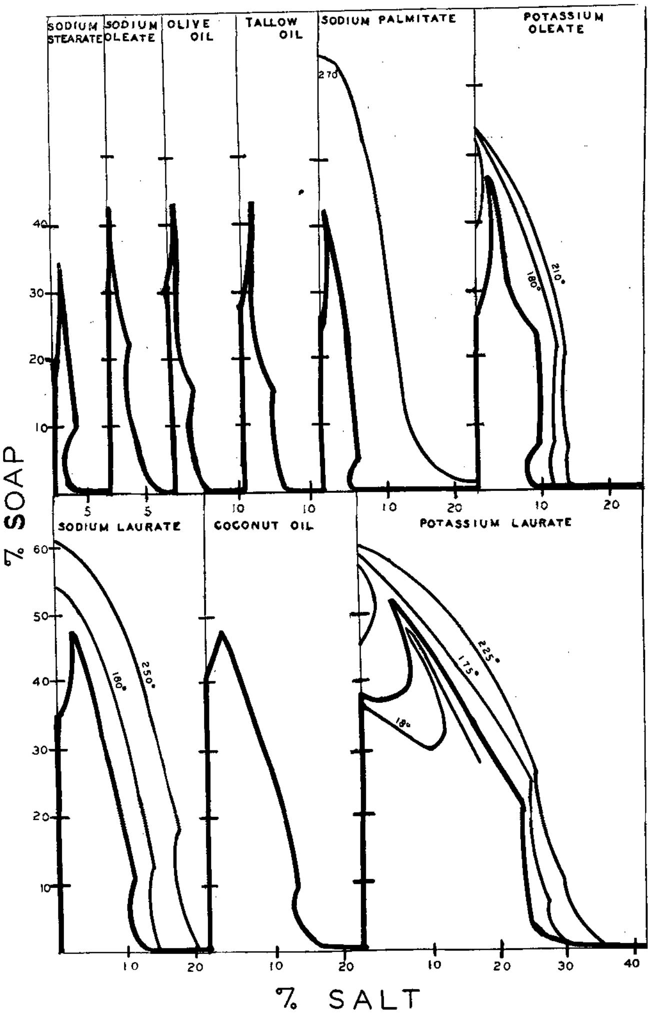

FIG. 2. The boundary of isotropic solution of soaps containing added sodium (or potassium) chloride at 90° C. for the six pure soaps so far studied, together with examples of sodium soap of single commercial oils or fats. The 90° boundaries are drawn in heavy line. Lighter lines indicate their position at some other temperatures.

in the same units. Even now, such data are available for only six pure soaps. We have added the boundary at soap boiling temperature for sodium soaps made from tallow, olive oil, and coconut oil respectively. No data have yet been published for any commercial soap or for soap made from a mixture of oils and fats.

First we may consider the solubility of all these soaps in water at 90°C. This is shown in Figure 2 from the percentage of soap at which the isotropic boundary begins for 0 percent salt (point A in reference 4). It ranges from 21% for sodium stearate to 45% for potassium laurate.

In a previous paper [5] the symbol T_s was introduced to characterize the temperature of ready solubility of soaps. Above T_s, soaps are fairly soluble in water in amounts of at least 15%. Below T_s the solubility falls rapidly to very small values at lower temperatures. Usually the soap is still soluble to the extent of several percent at a temperature of about ten degrees below T_s. T_s may be read from binary phase diagrams as the lower left hand corner of the isotropic field where the soap solution is in equilibrium with curd fibers and middle soap (point I_{CM} in reference 6). These values are collected in Table 1.

TABLE 1

Temperature of Ready Solubility, T_s, of Various Soaps in Water, and Solubility of Soaps in Water in True Percent by Weight at 90°C., Including Sodium Soaps of Various Single Oils and Fats

Soap	T_s	% Soap at 90°C.	Maximum % Salt in Nigre
Sodium Laurate	42°C.	36	11.2
Potassium Laurate	17	36	23.6
Sodium Myristate	60	30	......
Sodium Palmitate	70	26	5.4
Sodium Stearate	77	19	2.8
Potassium Oleate	Below 0°C.	26	9.5
Sodium Oleate	32	30	3.2
Palm Oil	52	31	4.6
Whale Oil, semi-hardened		35	5.2
Green Sulfur Olive Oil	27	33	3.5
Tallow	53	29	4.2
Soya Bean Oil	....	34	2.9
Pressed Coconut Oil	....	42	13.3
Tallow-Coconut	48	28	......
¾ Palm, ¼ Coconut	49	....	......

The most soluble soap at 90° is that from coconut oil, and the least soluble is that of sodium stearate. The lowest temperature of ready solubility, T_s, is that of olive oil soap, 27° C.; the highest is again sodium stearate, 77°C.

Although sodium oleate appears so soluble because its value of T_s is so near room temperature, 32°C., whereas that of the stearate is 77° and the laurate 42°, nevertheless sodium laurate is more soluble than oleate at 90°C. Again, although the solubility of oleate in pure water is so much higher than that of stearate, the oleate is almost as easily salted out by salt. The maximum concentration of salt in the nigre (usually corresponding to point C in Reference 4) is 3% for stearate and oleate; this is only a fraction of that which sodium laurate and potassium laurate will bear, 11 and 23% respectively. This much greater sensitivity of oleate to salt as compared with the lower saturated soaps is graphically reflected in the narrowness of the fields of isotropic solution at 90°C., as shown by the heavily drawn boundaries in Figure 2.

For a few soaps in Figure 2 the boundaries of the field of existence of isotropic soap solutions is shown also for much higher temperatures, by drawing them lightly. The solubility of the soap in water is greatly increased and they will dissolve more salt at higher temperature.

3. *Effect of Salt Upon the Sodium Oleate-Water Phase Diagrams.* In soap boiling the final product at the boiling temperature is neat soap phase, but it always contains a little salt. Otherwise the subsequent procedures relate to the simpler binary system soap-water. The question arises as to how this strictly binary phase diagram is modified by the salt present. Such information also relates to the initial trend of the boundaries of soap phases with the addition of salt in the ternary system.

Here we show in Figure 3 the comparison between the binary diagram found for Merck's sodium oleate [3] and that obtained when similar systems are investigated, in which a constant addition of sodium chloride is made to the sodium oleate in the proportion of 1.5 parts by weight of chloride to 100 parts of sodium oleate throughout. This proportion was chosen because at 70% soap the salt is then 1.05% of the system, ap-

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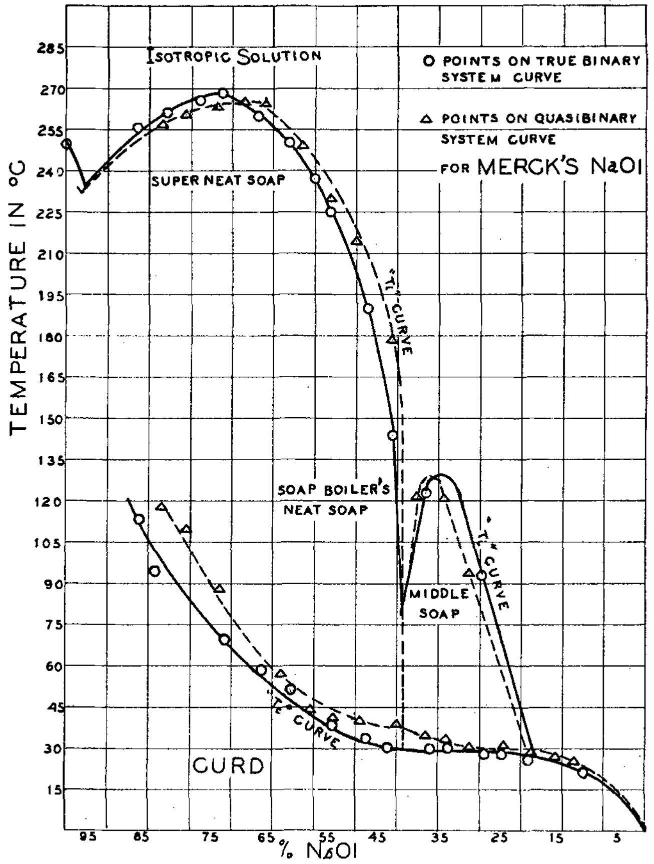

FIG. 3. Phase diagram of the system sodium oleate-water, before and after adding sodium chloride to the extent of 1.5% by weight of the soap to simulate the difference between the pure soap and a commercial settled soap.

proximately the upper limit in the final stages of a commercial soap boiling process. The technique was that previously described. All systems were first homogenized in sealed tubes by heating until they formed a clear single liquid phase. Two determinations were made on each tube. The temperature T_c is that at which on slowly heating and stirring the last of the solid (curd, supercurd or subwaxy phase, respectively, according to the range of temperature) just disappears to complete the formation of the single liquid or anisotropic liquid phase. The curve of T_c values is therefore a solubility curve. The other temperature, T_i, is the lowest temperature to which the initial hot homogeneous isotropic liquid system can be cooled before another phase begins to separate, showing saturation or equilibrium with neat, superneat or middle soap phase, respectively. These values of T_i and T_c are tabulated in Table 2.

The results are very readily read from Figure 2; all the observed points except one are in the expected direction and correspond to the slopes which we have been accustomed to assume for the initial portions for the boundaries in the ternary phase diagrams. These effects are: (a) to lower the solubility of the solid soap in all phases; (b) to enable neat soap to take up more water as salt begins to be added, thus lowering correspondingly the percent of soap in the lower part of the neat soap phase of the ternary system, while (c) the diminished solubility of the solid soap is likewise reflected in the rapid decline in percentage of soap in the upper part of the neat soap phase as salt is added in the ternary system. Hence the neat soap phase has the form of a pendant drop in the ternary system. The middle soap boundary rises fairly rapidly to higher percentage of soap as its field is quickly narrowed and then completely eliminated by the addition of salt. The single unexpected observation is the T_i value for 39% oleate. This lies in Figure 3 to the left of the middle soap region, as if in the ternary system middle soap extends slightly upwards. Practically no quantitative measurements have been made in any ternary system between the middle and the neat ternary soap phases.

TABLE 2

% NaOl	% NaCl (0.015 × %NaOl	T_i °C.	T_c °C.
5.03	0.07	......	......
11.70	.15	......	23.6
15.30	.23	......	25.6
18.70	.29	......	27.1
24.70	.38	......	28.5
30.00	.44	98	29.7
34.70	.54	123	31.5
39.00	.61	123	36.4
43.30	.68	178.5	41.4
49.10	.78	215	42.4
53.20	.82	232.4	43.3
59.30	.94	251.5	48.3
63.80	1.02	263.5	56.3
69.60	1.15	266.5	64.3
73.70	1.14	266.5	88.0
78.70	1.21	262.5	109.0
82.40	1.36	257.5	118.0

Summary

1. The boundaries of isotropic solutions of sodium oleate containing salt have been determined over a series of temperatures. Prolonged heating in glass tubes alters sodium oleate solutions, rendering the soap less soluble.

2. It is found that when sodium silicate replaces sodium chloride in the same percentage by weight the sodium oleate is not salted out, but tends on cooling to set to a clear jelly.

3. The phase boundaries for soap solutions containing chloride have been assembled and recalculated to the same units for comparison with each other and with the results for soaps made from a few single commercial oils and fats. In spite of its solubility in water, sodium oleate is readily salted out by electrolytes.

4. The effect of small amounts of salt such as are retained in commercial soap systems upon the boundaries of the strict binary phase diagram have been determined.