

Vapor Pressure Data and Phase Diagrams for Some Concentrated Soap-Water Systems Above Room Temperatures

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Over twenty years of exacting studies have demonstrated that the phase rule applies to soap systems. The very different methods of investigation successively applied served to reveal, and to some extent clarify, a remarkably interesting array of phases. Many of these phases are of a type not previously known and their relations to each other are new and characteristic. As many as eleven phases may appear in a single anhydrous pure soap; and, in addition, there are several other liquid crystalline phases with well defined boundaries in the aqueous systems. The existence and some of the characteristics of all of these many phases have been definitively established by a number of investigators.

It proved comparatively easy to outline the phase diagrams at high temperatures, and then for less concentrated soaps at lower temperatures. However, each attempt to push the complete exploration into the region of concentrated systems at ordinary temperatures has met with increasing difficulty. Yet these are the regions of the greatest interest to the industry and to the manufacturers of soap products.

As a method of investigation, examination of vapor pressure has the advantage of yielding quantitative results of direct and unambiguous significance for phase rule and thermodynamic relations. Naturally, the results of all other methods, x-ray, dilatometric, calorimetric, and optical studies, must be taken into account in arriving at a definitive interpretation.

The unpublished vapor pressure data referred to here add substantially to our knowledge of the phase diagrams of concentrated systems of soap and water above the minimum temperatures for the existence of soap boiler's neat soap. The experiments required more than three years of continuous work and have become too voluminous for publication in full.* The two chief results are that, first, the so-called T_c curve or lower boundary of the "soap boiler's neat soap" field in the system soap-water is definitely confirmed; and, secondly, that this field is continuous within the range shown on the accompanying diagrams because the vapor pressure varies in a continuous manner right across this field. Use was made of these conclusions in establishing the diagrams published by R. D. Vold (1) for sodium oleate, and by McBain, Porter, and M. J. Vold (2) for a commercial toilet soap base, although through inadvertence due to acknowledgment was not made.

The object of this communication is to present the best binary phase diagrams of the six soap systems, utilizing all available information.

* Most of them are obtainable in detail from the U. S. Dept. of Agriculture, Wash., D. C., in the microfilm of the theses of Dr. W. W. Lee, where the experimental points are also numbered in chronological order. Details of some isotherms for low water content and low relative humidity are given in another communication.

Experimental

For all work up to about 96% relative humidity, the silica spring sorption balance of McBain and Bakr (3) was simple and effective. For near room temperature, however, it has proven necessary to use closely regulated liquid thermostats with the sorption balance. The springs were calibrated at a series of temperatures and their sensitivity was between 0.7 and 1.4 mm. per mg. The samples weighed about 30 mg. and were placed in buckets made of 0.0004 inch platinum foil welded by shaping over a carbon rod.

The springs were contained in a vertical sealed 30-inch Pyrex tube of 22 mm. diameter with some boiled out distilled water placed in the bottom of the tube before evacuation. The zero length of the spring was read with a dry sample while the water was kept frozen at -68° .

Two arrangements of air thermostats were employed. In one group, the upper half of the tube containing the spring was placed in a special air thermostat made by the Central Scientific Company. The lower part was immersed in an oil thermostat of adjustable temperature and the tube was surrounded by a small heating coil at a temperature intermediate between the oil and the air baths. In the other individual type of experiments, the upper and lower portions were independently heated by coils of chromel wire. The current was regulated by various transformers. Thermometers calibrated by the National Bureau of Standards were suspended in the tube.

One hour was sufficient to establish the same equilibrium content of water from either side when the soap was in the curd form, and less than a day for liquid crystalline forms or when a soap was in transition.

An unexpected and time consuming source of complication and error was found when silica springs are exposed to high humidities at high temperatures. Under these conditions they slowly stretch, even when carrying a constant weight such as platinum only. It was therefore necessary to check the length of every spring for the anhydrous sample from time to time by immersing the bottom of the tube in liquid air or dry ice, and correcting the readings accordingly where necessary.

The only other source of uncertainty has been the fact that several forms of curd can exist and it is not always certain that the curd was initially in the stable γ form of monoclinic fibrous crystal. The influence of the fibrous condition in inducing capillary effects will be discussed below.

The soaps used were the purest described in previous communications (4, 5, 6). For example, the sodium oleate was the specially pure water-white

sample made by Professors Brown and Foreman of Ohio State University, of molecular weight 282.3, iodine number 89.86 and thiocyanogen v. 89.74.

The error in the isotherms was usually less than 1% both in composition and in relative humidity.

The Binary Phase Diagrams for Soap-Water

A series of isotherms of vapor pressure data has been obtained for each of the five chief pure soaps, sodium laurate, myristate, palmitate, stearate, and oleate; and in addition some isotherms have been obtained for the typical commercial toilet soap base previously described (2). In every case the soap was watched to see whether it was in the opaque white curd condition or in the almost clear, liquid crystalline form (soap boiler's neat soap phase) or in a waxy crystalline form. A remarkable instance of the latter is photographed in Fig 1. Here the powdered curd of sodium stearate at 110°, originally lying on the bottom of the bucket, transforms to the subwaxy form above 50% relative humidity, having taken up between 3.0 and 4.5% of water. Thereupon, at still higher relative humidity, 89.5%, the subwaxy transforms into waxy soap containing 8.0 to 9.5% of water, after which neat soap is formed. In that waxy region, the extraordinary phenomenon is observed of the waxy crystals growing upwards for a centimeter or so from the top edge of the bucket, in stalagmitic, large, semi-transparent shapes, as shown in the photograph. In appearance they are definitely wax-like, like soft paraffin. At the ends of some of the crystals, clumps of finer crystals continue to grow. They are twisted slightly but with a smooth and glossy surface

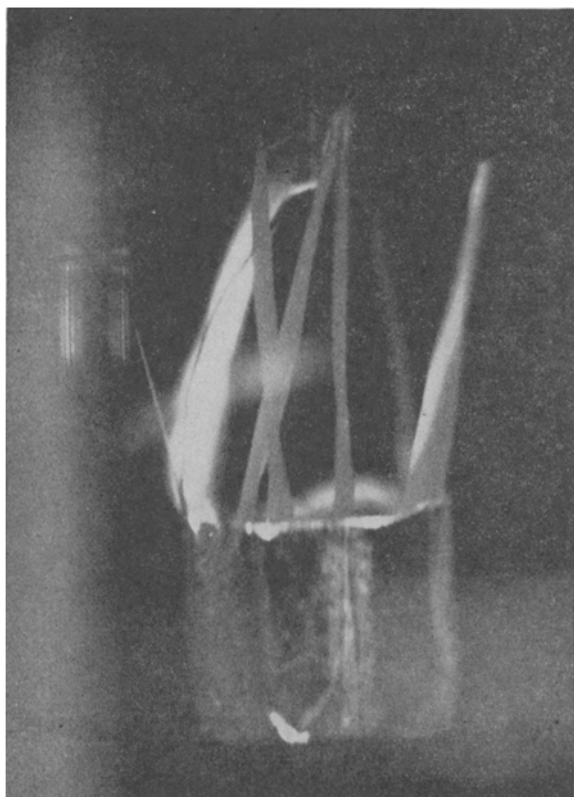


FIG. 1. Waxy sodium stearate at 110°C. and 90% relative humidity and containing between 8 and 9.5% of water, going upwards from a solid phase of sodium stearate placed in the platinum bucket.

with faint striations parallel to their length. Upon dehydration, they retain their shape but progressively lose transparency, the striations becoming more pronounced so as to give a fibrous appearance. Upon hydration, they melt to the clear gel of neat soap, but reappear when the relative humidity is again lowered.

All other available evidence has been utilized in drawing the isotherms as, for example, in placing the "flats" and intersections and in making up the final phase diagrams. Many more points and isotherms were determined than those shown, but those given are chronologically consecutive points from samples of known zero point. Many further points served to study hysteresis and to confirm the curves as shown. Likewise, the course of each isotherm was compared with all similar cases, both at the same and at other temperatures. There is no hysteresis in going back and forth along the isotherm in the neat soap field, except that when the pressure has been reduced to a point where curd should appear, transformation does not always take place and the neat soap curve may be continued as if extrapolated. The slope of the curve in the neat soap region is approximately that calculable from Raoult's law. The hysteresis effects in connection with the hydration of curd are discussed in a separate communication (7).

Some of the isotherms are collected in abbreviated form in Figs. 2, 4, 6, 8, 10, and 12. For convenience each portion of the vapor pressure curve has been labeled according to the soap phase present, according to the following scheme: C = curd fiber phase; SC = supercurd phase; H = hemihydrate; SW = subwaxy soap; W = waxy soap; N = soap boiler's neat soap; M = middle soap.

The Phase Diagrams

I. Sodium Laurate ($C_{11}H_{23}COONa$) and Water—Figs. 2 and 3.

A few isotherms may be discussed in detail as illustrations. Take, for example, the isotherms at 65° in the lower right hand corner of Fig. 2. The sample began at zero relative humidity and zero content of water in the lower left hand corner. The steeply rising sorption curve for the curd bends over towards the right at high humidities owing to capillary liquid forming in the interstices of the ultramicroscopic fibrous crystals. At 92.5% relative humidity the curd is transformed to neat soap (labeled N) containing 63% of soap. The horizontal flat on the isotherm, corresponding to a constant relative humidity of 92%, indicates the existence of two phases. As soon as either phase has disappeared, there is one more degree of freedom and the flat is replaced by a sloping curve traversing the range of existence of the new phase beginning at 63% and ending at 58% sodium laurate.

The boundary at 63% soap is very important. It agrees with the T_c boundary for 65°C. previously determined visually by McBain, Brock, and Vold (8). The right hand boundary at 58% again confirms the data of McBain, Brock, and Vold. A further flat at 97% relative humidity brings us to the middle soap region beginning at 53% soap, above which the present technique is not accurate. The boundary at 53% soap, likewise, agrees with the previous value (8) from the very different kinds of experiments.

SODIUM LAURATE

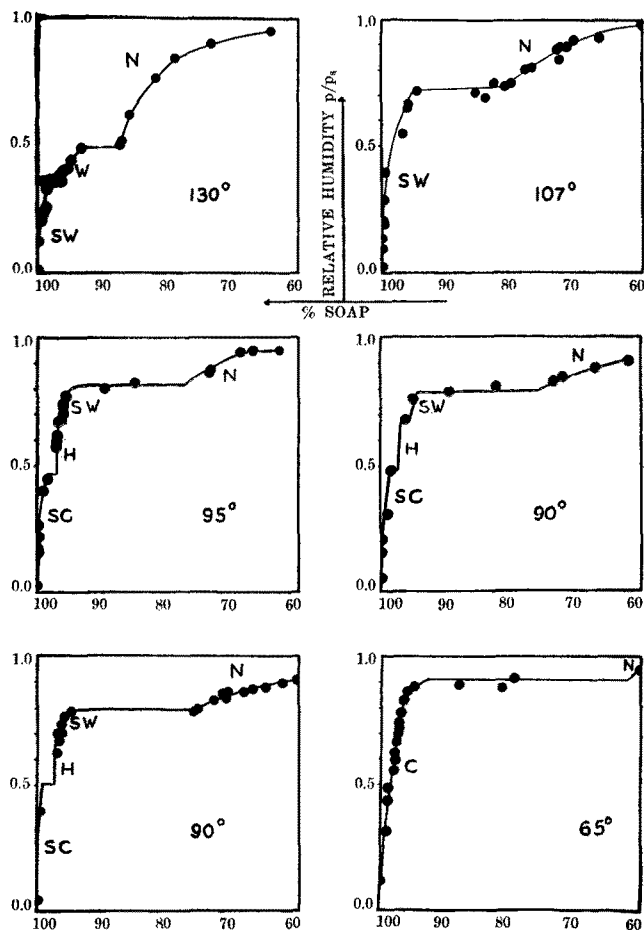


FIG. 2. Some of the isotherms whose results are utilized in the phase diagrams. N = neat soap, C = curd, SC = supercurd, SW = subwaxy, W = waxy, H = hemihydrate of 1 mol. of curd or supercurd with $\frac{1}{2}$ H₂O.

In transferring this information to the phase diagrams, Fig. 3, the flats on the isotherms correspond to the heterogeneous regions of two coexistent condensed phases and the intersections of the flats with the rising curves show the boundaries of the homogeneous regions of such phases as subwaxy or neat soap.

From the 90° isotherms (see Fig. 2) we obtain the values 55.5% and 52.0% for the right hand boundary of neat soap and the left hand boundary of middle soap, respectively, agreeing fairly well with the boundaries of Vold and Vold (6), who obtained 54% and 52%, respectively, by their isopiestic method. We have convinced ourselves that their data above 75% soap are in error, probably because their samples were thirty times larger and must require much more time to reach equilibrium.

Some of the numerical data derived from the isotherms are recorded in Table I.

The two most important results of the present study are that the region of soap boiler's neat soap in the soap-water diagrams is shown in all cases to be a single homogeneous phase; and that its left hand boundary agrees with the T_c curve determined by any visual or other methods.

We may now present Fig. 3 which summarizes the more definitive data obtained by all methods up to

TABLE I

The Range of Composition for the Stable Existence of Phases of Aqueous Sodium Laurate at a Series of Temperatures

Temperature	Phase	Range (wt. % soap)
65°	Middle	(36) to 53
	Neat	58 to 63
	Curd	93 to 100
90°	Middle	(38) to (52)
	Neat	(54) to 76
	Subwaxy	94 to 96.5
	Curd	97 to 100
95°	Neat	(55) to 77
	Subwaxy	94 to 96
	Curd	97 to 100
100°	Subwaxy	94 to 100
	Neat	(65) to 80
107°	Neat	(60) to 82
	Subwaxy	94 to 100
130°	Neat	(62) to 89.5
	Waxy	93.5 to 96.5
	Subwaxy	98.5 to 100

the present time. Previous publications contain also less definite indications which are not reproduced here.

The boundaries in the phase diagrams that are to be regarded as definitive are drawn in full lines, whereas others that are less well established are indicated by dashed lines or left blank. For example, no boundary is inserted between aqueous superneat and soap boiler's neat soap.

As has been shown by several authors, following Vold, Rosevear, and Ferguson (9), the effect of the addition of water to anhydrous soap at various temperatures is to bring the phases which exist in anhydrous soap slightly within the hydrous region in the form of hanging "tongues."

II. Representation of Curd Fibers, Curd Phases and Curd Hydrates on the Phase Diagrams—Figs. 3, 5, 7, 9, 11, and 13.

The exact representation of the curd mass, and of the fibers therein, on the phase diagrams depends upon whether one prefers to record the observed gross composition of the curd, including sorbed and capillary water as well as hydrate water, or merely to represent the composition of the fibers themselves and their hydrate water, if any. Both are done on the binary diagrams, Figs. 3, 5, 7, 9, 11, and 13. The tie lines, however, are drawn to the boundaries representing the total gross composition of the phases just as observed.

In the left hand lower triangle for sodium stearate, Fig 9, at 91° there is a vertical line at 93% soap representing the hemi-hydrate, $\text{NaStr} \cdot \frac{1}{2}\text{H}_2\text{O}$, discussed in another communication (7); but the dashed line to its right includes the bound, sorbed and capillary water at which the tie lines end. Other measurements at lower temperatures in presence of middle soap and isotropic solutions will be required to complete this picture by including any hydrates which lie to the right of the dashed gross curd field.

For sodium laurate there is as yet no evidence for the formation of a hemi-hydrate from curd; and the lower left hand portion of the diagram for this soap is likewise still very incomplete.

The myristate forms a hemi-hydrate, $\text{NaMyr} \cdot \frac{1}{2}\text{H}_2\text{O}$, whose fibers likewise enmesh capillary liquid

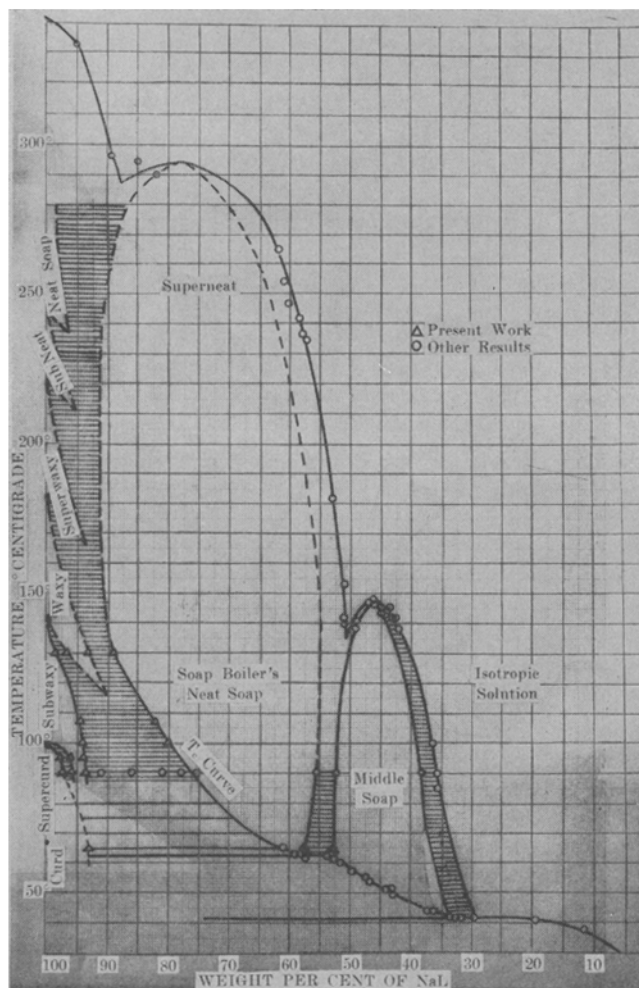


FIG. 3. Phase diagram for sodium laurate showing homogeneous fields of each of the different phases and the isothermal tie lines connecting the phases in heterogeneous equilibria.

water at a relative humidity below 82%, whereas the saturation pressure would have been p/p_s equal to 100%.

The palmitate likewise forms a hemi-hydrate, $\text{NaP} \cdot \frac{1}{2}\text{H}_2\text{O}$, which encloses capillary liquid below 90% relative humidity, and there is good evidence for the formation of a hydrate such as $\text{NaP} \cdot 9\text{H}_2\text{O}$ or $\text{NaP} \cdot 10\text{H}_2\text{O}$ in contact with isotropic solutions at temperatures between 0° and 70° . There are indications of other hydrates containing 6.6 and 4.4 H_2O at progressively lower vapor pressures, but there is no evidence for the existence of the monohydrate $\text{NaP} \cdot 1\text{H}_2\text{O}$ alluded to by McBain, Vold, and Johnston (10).

The highest hydrates can exist only when the vapor is practically saturated, as in the presence of liquid solution. All of them dehydrate very readily when the vapor pressure is lowered by only a few per cent, leaving then the hemi-hydrate $\text{NaP} \cdot \frac{1}{2}\text{H}_2\text{O}$.

Hemi-hydrate apparently does not exist for sodium oleate, but the evidence in Reference 10 indicates that two other hydrates containing 3 H_2O and 25 H_2O , respectively, can exist, the latter only in contact with aqueous solution of nearly saturated vapor pressure.

The pseudo-binary diagram for the commercial soap is still incomplete and the interpretation of some of

the isotherms is still uncertain. It must, however, be remembered that when a definite boundary is obtained, this represents the actual gross composition of the system. Such a total composition is an average, summing up the total weight of the various soaps and the respective amounts of water associated with each. Their individual compositions, therefore, in such cases may lie well to the right and left of the actually observed average recorded.

III. Sodium Myristate ($\text{C}_{13}\text{H}_{27}\text{COONa}$) and water— Figs. 4 and 5.

The isotherm for 82° shows two transitions. The anhydrous supercurd sorbs water until at about 78% relative humidity it transforms to hydrated supercurd, appearing as yellowish translucent needles. At 90% relative humidity, the hydrated curd containing 95% water transforms to neat soap, whose nearest boundary is at 70% soap.

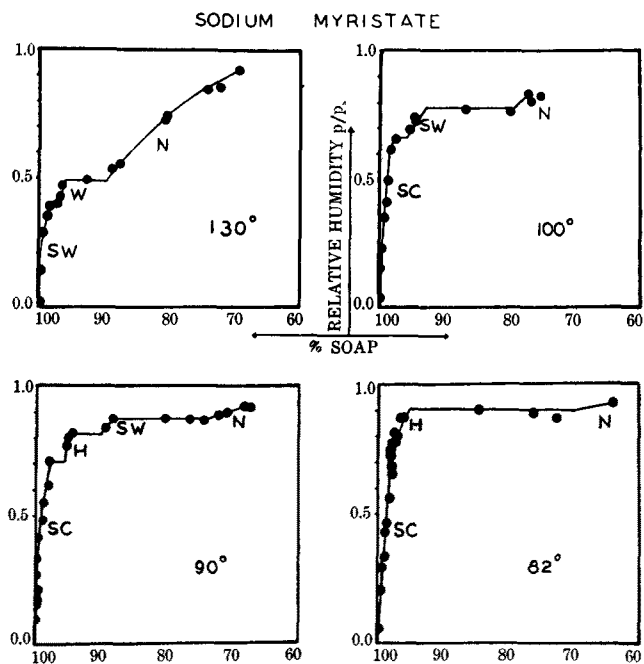


FIG. 4. Some of the isotherms whose results are utilized in the phase diagrams.

The isotherm for 90° shows three flats. The anhydrous supercurd sorbs up to 2% water at 70% relative humidity and then hydrates. At 81.5% relative humidity, transformation occurs from hydrated supercurd containing 9.5% soap to subwaxy soap existing between 10% and 12% water. The neat soap field begins at 74% soap.

At 100° the supercurd transforms directly to subwaxy soap whose field, from 93% to 97% soap, overlaps the expected composition for hydrated supercurd. The subwaxy soap transforms to neat soap containing 80% soap at 77.5% relative humidity. The data for the range of existence of the above soap phases are collected in Table II.

The phase diagram, as far as it has been completed, is given in Fig. 5. Once more the narrow tongues of

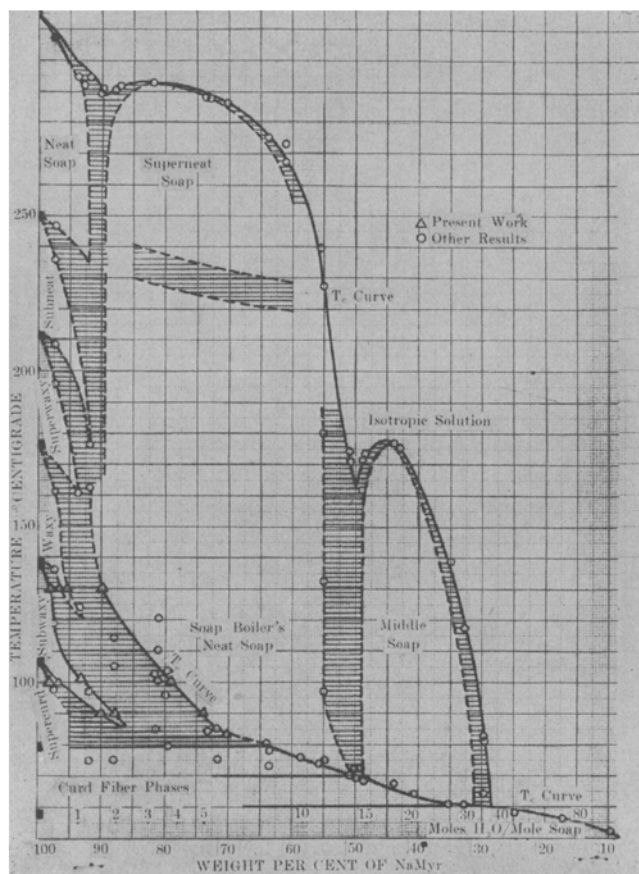


Fig. 5. Phase diagram for sodium myristate showing homogeneous fields of each of the different phases and the isothermal tie lines connecting the phases in heterogeneous equilibria.

TABLE II

The Range of Composition for the Stable Existence of Phases of Aqueous Sodium Myristate at a Series of Temperatures

Temperature	Phase	Range (wt. % soap)
82°	Supercurd	95 to 100
	Neat	(53) to 70
90°	Supercurd	95 to 100
	Subwaxy	88 to 90
	Neat	(54) to 74
100°	Supercurd	98 to 100
	Subwaxy	93 to 97
	Neat	(55) to 80
130°	Subwaxy	98 to 100
	Waxy	96 to 97
	Neat	(< 70) to 90

the waxy forms of soap are characteristic. The left hand boundary of the neat soap field agrees well with that indicated by previous methods of investigation.

IV. Sodium Palmitate ($C_{15}H_{31}COONa$) and Water—Figs. 6 and 7.

Sodium palmitate was the first pure soap to be investigated from the standpoint of the phase rule in binary systems with water (11). The phase diagram has not been revised since the publication of McBain, Lazarus, and Pitter (12) in 1930. We have obtained isotherms at several temperatures below 75°, and then at 84, 90, 100, 102, 105, 107, 112, 130, and 145°.

At 84° the curd forms the hemi-hydrate $NaP \cdot \frac{1}{2}H_2O$, or 96.8% soap, at 67% relative humidity and

this, at 91% relative humidity, goes to neat soap containing 64% soap on the T_c boundary. At 90°, the supercurd hydrates at 72% relative humidity, and at 80% relative humidity the hydrate containing 93% soap goes to neat soap at 76% soap on the T_c boundary. Vold and Vold (6) obtained almost the same

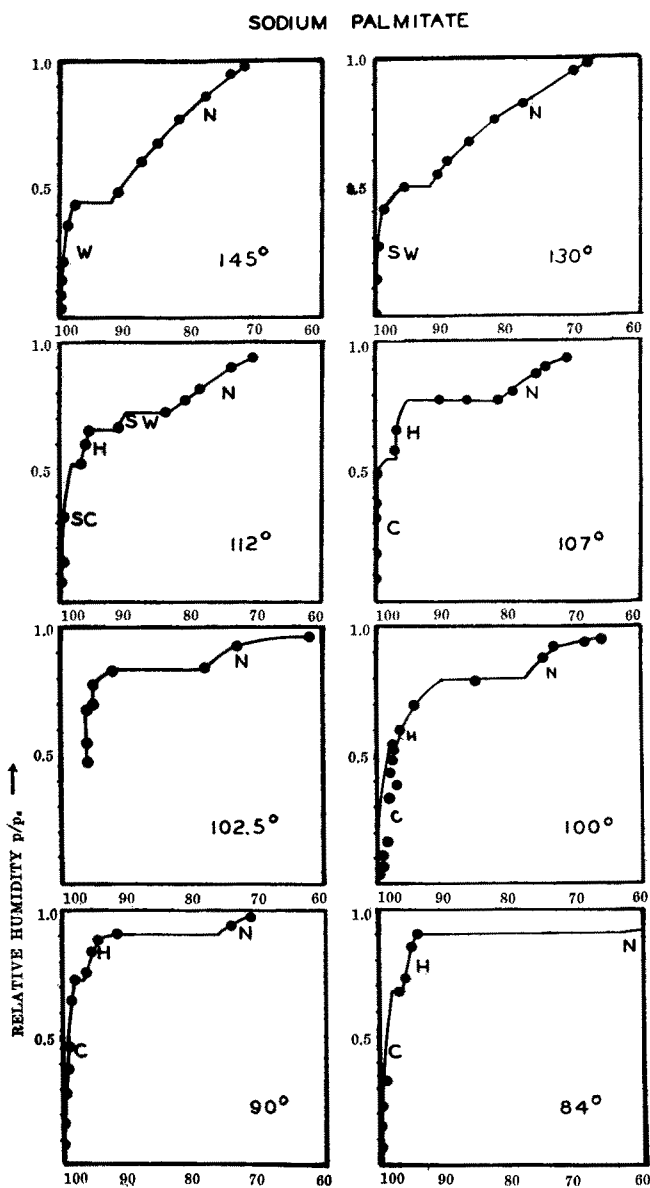


Fig. 6. Some of the isotherms whose results are utilized in the phase diagrams. The 100° isotherm is taken from earlier work where the zero point had shifted at least 1%, but was not rechecked.

value by the isopiestic method. The neat soap field extends continuously to 38% water. Again at 100° the supercurd sorbs only about 2% water before transforming to a hemi-hydrate and the nearest boundary of the neat soap field is at 77% soap, whereas at 102.5° it is 78% soap and the neat soap field is continuous to at least 38% water. At 107° the behavior is still similar and the left hand boundary of the neat soap is 81.5% on the T_c curve. At 112° subwaxy soap intervenes between hemi-hydrate and neat soap. The slope of the isotherm in this subwaxy tongue is drawn to conform to Raoult's law, neat soap beginning at

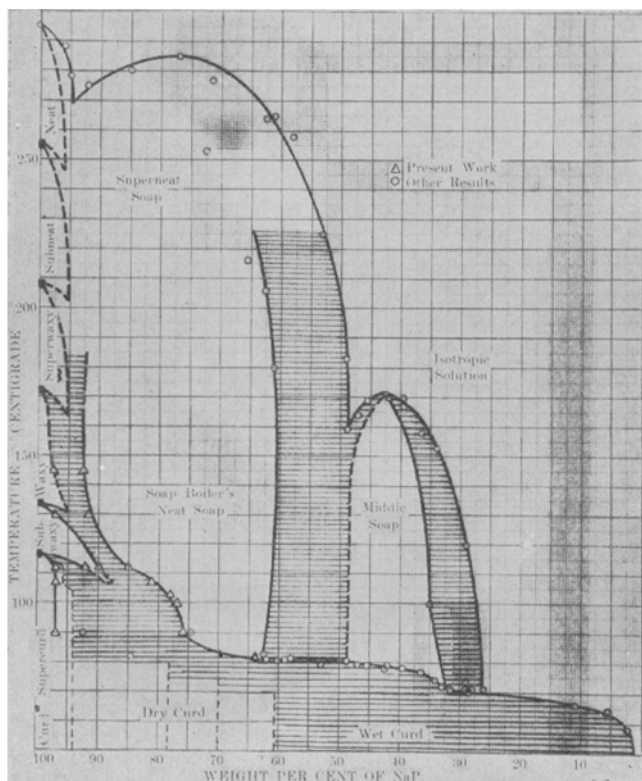


FIG. 7. Phase diagram for sodium palmitate showing homogeneous fields of each of the different phases and the isothermal tie lines connecting the phases in heterogeneous equilibria.

84% soap and extending to at least 39% water. At 130° anhydrous soap is subwaxy and when this has taken up 4% of water, it transforms to neat soap containing 92% soap on the T_c curve, the transition occurring at 50% relative humidity. At 145° the sodium palmitate is waxy, taking up 2.5% water and then transforming to neat soap containing 88% water at 45% relative humidity.

The isotherms between 30° and 75° show that the curds undergo no transition until the relative humidity is within a very few per cent of saturation. Furthermore, the curd takes up only a very few per cent of water over almost the whole range of relative humidity. This will be discussed in another communication. Hydrates occur at very high relative humidity as, for example, where the curd is in contact with the solution (10).

The range of existence of some sodium palmitate phases is summarized in Table III. The phase diagram for the binary system, sodium palmitate and water, is given in Fig. 7, which revises and extends the earlier work of McBain, Lazarus, and Pitter (12).

V. Sodium Stearate ($C_{17}H_{35}COONa$) and Water—Figs. 8 and 9.

At lower temperatures the sodium stearate isotherms resemble those of sodium palmitate. At 91° the anhydrous supercurd sorbs water continuously up to 1.5%, then transforms to $NaStr \cdot \frac{1}{2}H_2O$. At relative humidity of 35.5% white, short, fine, fuzz-like fibers developed from the dry white powder until at 87% relative humidity the entire exposed surface resembled white velvet, retaining that appearance

TABLE III
The Range of Composition for the Stable Existence of Phases of Aqueous Sodium Palmitate at a Series of Temperatures

Temperature	Phase	Range (wt. % soap)
84°	Curd Neat	94 to 100 (64) to 75
90°	Supercurd Neat	94 to 100 (62) to 76
100°	Supercurd Neat	90 to 100 (< 65) to 77
102.5°	Neat	(< 62) to 78
107°	Supercurd Neat	95 to 100 (< 70) to 81
112°	Supercurd Subwaxy Neat	94 to 100 90 to 92 (< 61) to 84
130°	Subwaxy Neat	96 to 100 (< 68) to 92
145°	Waxy Neat	97.5 to 100 (< 70) to 92

even to 95% relative humidity. At 97% relative humidity it was a clear gel of neat soap whose boundary lies at about 70% soap. At 100° the subwaxy tongue intervenes between the hemi-hydrate and neat soap. At 105° the supercurd first forms hemi-hydrate, then subwaxy, and then waxy soap, before transformation to neat soap at 80% soap. At 110° the supercurd is transformed to subwaxy soap before it can change to the hemi-hydrate. Then it is converted to waxy soap before forming neat soap. Its left hand boundary is 84% soap.

The data for the range of existence of the chief phases are collected in Table IV.

The phase diagrams for sodium stearate and water, Fig. 9, differ from that for sodium palmitate chiefly in the long slender extensions of the waxy and subwaxy forms into the aqueous region. Thus the aqueous subwaxy form for stearate occurs well below 100° in contradistinction to that for sodium palmitate.

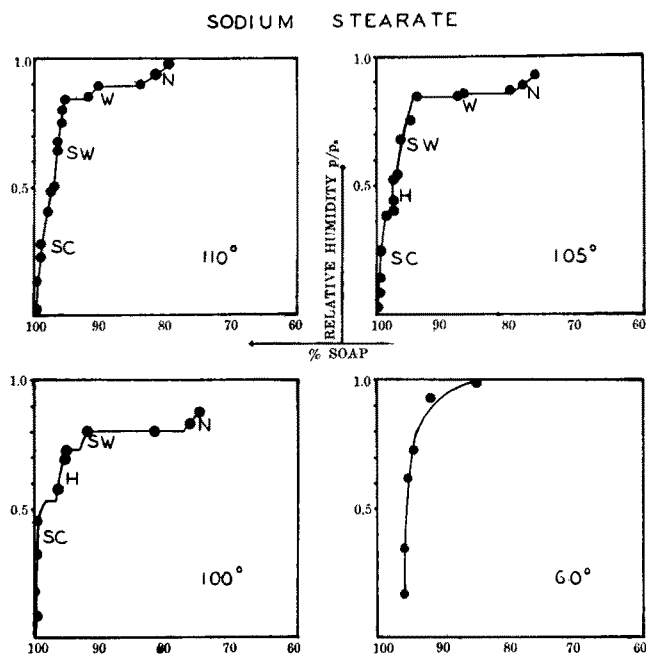


FIG. 8. Some of the isotherms whose results are utilized in the phase diagrams.

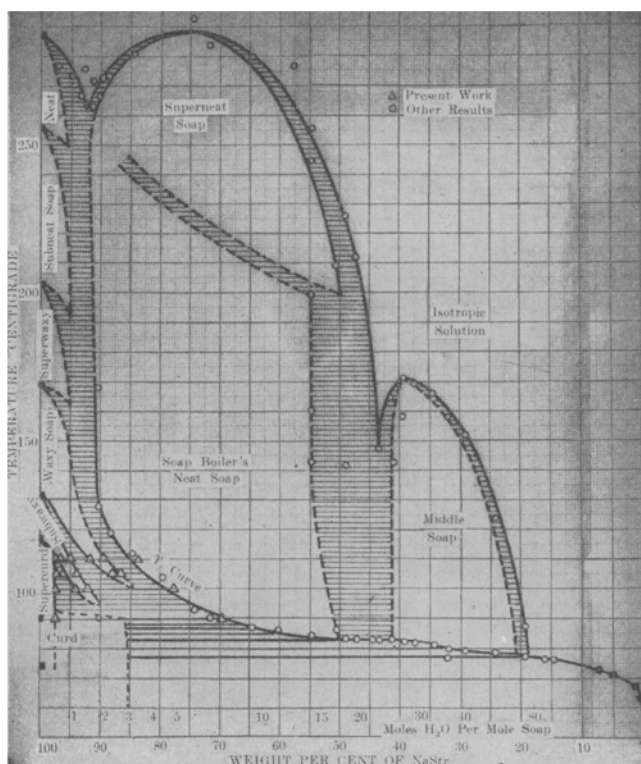


Fig. 9. Phase diagram for sodium stearate showing homogeneous fields of each of the different phases and the isothermal tie lines connecting the phases in heterogeneous equilibria.

TABLE IV

The Range of Composition for the Stable Existence of Phases of Aqueous Sodium Stearate at a Series of Temperatures

Temperature	Phase	Range (wt. % soap)
91°	Supercurd	87 to 100
	Neat	(<67) to 70
100°	Supercurd	97.5 to 100
	Subwaxy	92.5 to 93.5
	Neat	(<75) to 77.5
105°	Supercurd	97.6 to 100
	Subwaxy	94 to 97
	Waxy	87 to 88
	Neat	(<76.5) to 80
110°	Curd	97.5 to 100
	Subwaxy	95.5 to 97
	Waxy	90.5 to 92
	Neat	(<80) to 84

This subwaxy form has been shown by another vapor pressure study (by W. W. L.) and by other experiments (by K. Gardiner) to exist as an island in the ternary diagram, and hence to occur in soap boiling.

VI. Sodium Oleate ($C_{17}H_{33}COONa$) and Water—Figs. 10 and 11.

Sodium oleate is so much more soluble than the saturated soaps that the soap boiler's neat soap region extends down to as low as 34°. Hence the method here employed is applicable to fairly low temperatures. Otherwise the isotherms and phase diagrams follow the same general pattern. The subwaxy tongue projects further than usual into the aqueous system and the aqueous neat soap region is unusually narrow with a wide gap between it and middle soap.

The 60° isotherm indicates no formation of hydrate, but after taking up 2% of water continuously

a direct transition to subwaxy soap occurs at 82% relative humidity, this subwaxy soap containing between 12.5 and 13.5% water. Then at 85% relative humidity, the left hand boundary of the neat soap is at the composition 77% soap. All the curves for neat soap show that it extends continuously over the field indicated, and this was one of the bases of the original diagram published by Vold.

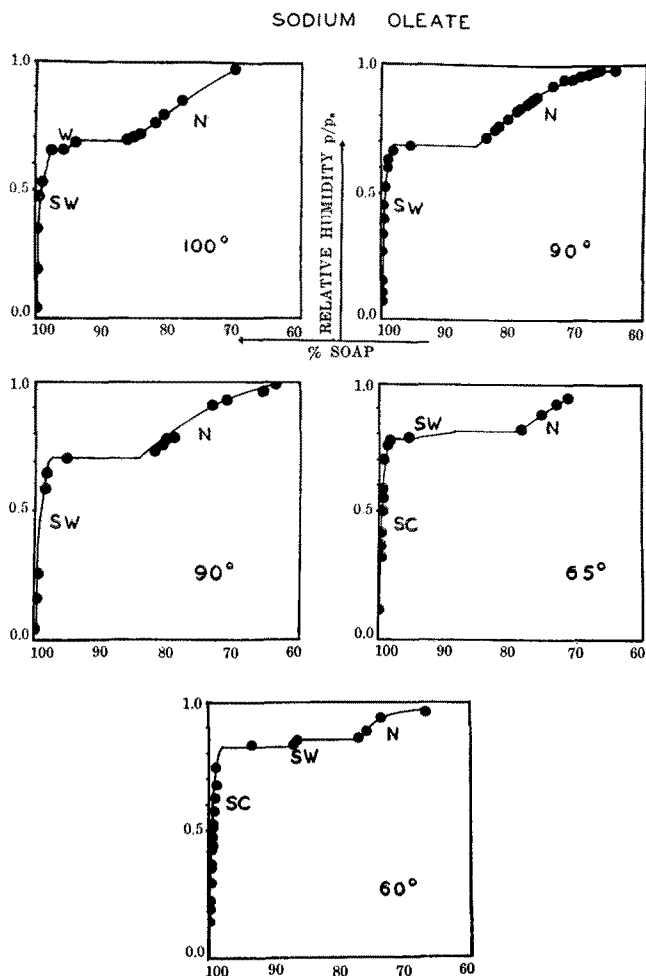


Fig. 10. Some of the isotherms whose results are utilized in the phase diagrams.

At 90° the isotherms from the very pure preparation made from Brown and Foreman oleic acid agree with our less pure preparation from Lapworth oleic acid, obtained through British Drug Houses, Ltd. Here the anhydrous soap is already in the subwaxy form, and this does not take up more than 2.5% water for transformation to neat soap at 70% relative humidity. These isotherms indicate that the neat soap field might extend even further to the right than the boundary taken from Vold's diagram, but the transformation to middle soap occurs too near to saturation for the present method to be certain. The data for the range of existence of the sodium oleate phases as shown by the isotherms are given in Table V, once more demonstrating that the observed T_c curve truly represents the left hand boundary of neat soap.

The phase diagram is given in Fig. 11, which constitutes a revision of the lower left hand corner of that previously published by Vold. In neither of

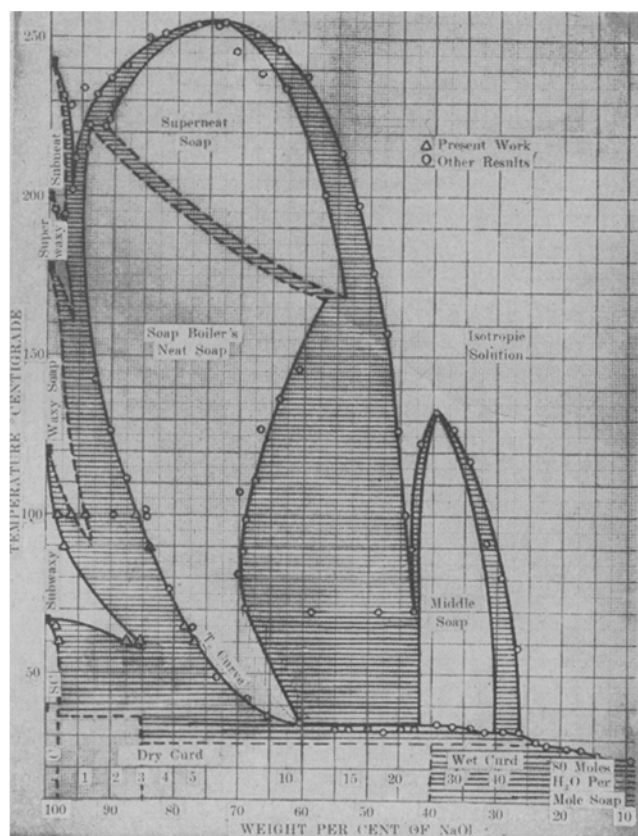


FIG. 11. Phase diagram for sodium oleate showing homogeneous fields of each of the different phases and the isothermal tie lines connecting the phases in heterogeneous equilibria. The point at 130° and 98% soap is a subsequent determination by George Shreve in this laboratory showing where the dashed right hand boundary of the waxy soap region should have been placed.

these is provision made for the heat change which Dr. Vold (unpublished) has found at 110° .

VII. Toilet Soap Base and Water—Figs. 12 and 13.

Commercial soaps are usually composed of the sodium salts of a complex mixture of fatty acids. It has been found that in certain regions of composition and temperature, such a complex mixture can be considered as a single component, an assumption which has been substantiated by the successful application of the phase rule to soap boiling processes. Recent studies have indicated that, under some other conditions, constituents of a commercial mixture may partially fractionate, thereby increasing the number of components of such portions of the phase diagram.

For anhydrous commercial sodium soap alone, the phases at different ranges of temperature resemble in general those of pure soaps; but below 200° , the changes occur over a range of temperature instead of sharply, indicating partial fractionation.

The 40° isotherm cannot be definitely interpreted without supplementary x-ray data. The soap takes up only a few per cent of water up to 85% relative humidity, where it may change to a hydrate well over towards the middle of the diagram (compare the results in reference 10). In any case, for ordinary temperatures, the concentrated systems are pseudo-binary except for the field of soap boiler's neat soap,

TABLE V
The Range of Composition for the Stable Existence of Phases of Aqueous Sodium Oleate at a Series of Temperatures

Temperature	Phase	Range (wt. % soap)
60°	Curd	98 to 100
	Subwaxy	86.5 to 87.5
	Neat	(< 69) to 77
65°	Curd	98.5 to 100
	Subwaxy	not determined
	Neat	69° to 78.5
90°	Subwaxy	97.5 to 100
	Neat	(< 64) to 84
100°	Subwaxy	98 to 100
	Waxy	94 to 96
	Neat	(< 70) to 86.5

* Value uncertain.

which is delimited on the left hand side by the T_c curve. At 60° and 65° , the soap is nearly anhydrous up to high values of relative humidity. Although at 60° a flat in the isotherm did not clearly develop, at 65° it ends definitely at 73.5% soap on the T_c boundary of soap boiler's neat soap at 85% relative humidity. Possibly the difference between the isotherm at 60° and 65° may be due to the known transition of sodium oleate to subwaxy form at the higher temperature, the other soaps present remaining unaltered.

The 83.0° isotherm more nearly resembles that of a single pure soap, the neat soap extending from 80% soap at least as far as 57% soap. The isotherm at 90°

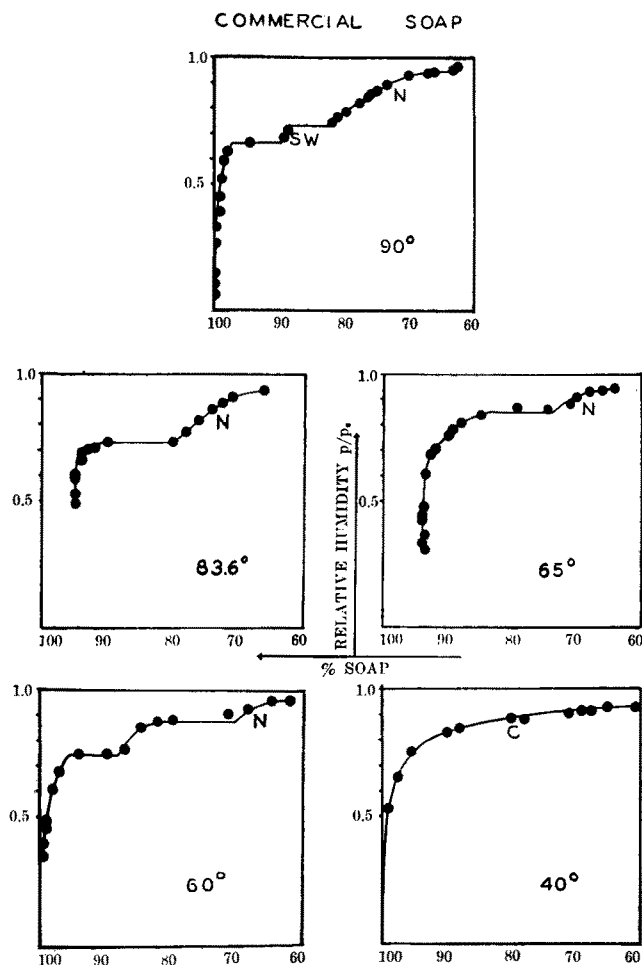


FIG. 12. Some of the isotherms whose results are utilized in the phase diagrams.

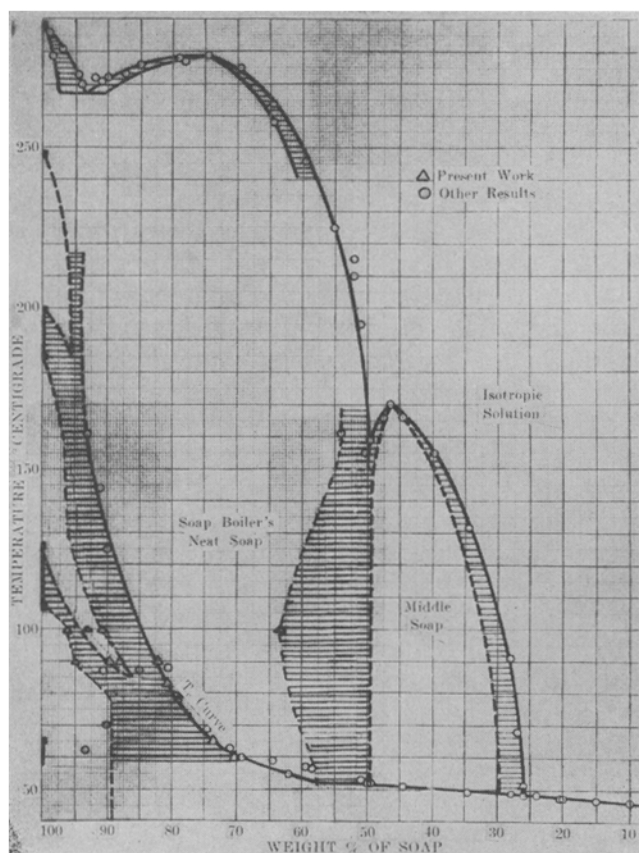


Fig. 13. Phase diagram for a commercial toilet soap showing homogeneous fields of each of the different phases and the isothermal tie lines connecting the phases in heterogeneous equilibria.

resembles that for sodium oleate except for the intervention of a homogeneous phase extending between 89.5% and 88.5% soap which may well be a waxy form. The anhydrous commercial soap presumably comprises a curd and subwaxy mixture which altogether takes up only 3% of water before transformation to the waxy form, followed by formation of neat soap at 73% relative humidity. The left hand boundary of the neat soap field lies at 82% soap in excellent agreement with the T_c curve and dilatometric data.

Fig. 13 presents the revised phase diagram for the typical commercial toilet soap base, which is a pseudo-binary system in the lower left region; and there its representation may well be oversimplified, since only gross compositions are recorded.

VIII. Some Comparisons for Different Soaps.

It is convenient to have for reference some of the chief values of the five most important pure sodium soaps and the typical commercial toilet soap base here studied. Some of these are assembled in Table VI, where many interesting relations are apparent.

TABLE VI
Comparison of Some Important Values for Five Pure Soaps and the Typical Commercial Soap

Soap	Ready soln. T_s	Lowest T or T_c for 70% neat	Lowest T for neat		Left or T_c boundary for neat at 100°	
			T	% soap	% soap	% humidity
NaL	42°	76°	62°	58%	80%	73%
NaMyr	60°	84°	70°	51%	79%	77%
NaP	71°	88°	80°	63%	78%	79%
NaStr	77°	91°	83°	50%	79%	82%
NaOl	32°	43°	34°	61%	86%	69%
Toilet	49°	60°	51°	58%	85%	65%
Commercial oils	45-55°

The "temperature of ready solubility," T_s , is the temperature at which a soap rather suddenly becomes highly soluble (usually 20-30%); whereas at a few degrees lower, its solubility is only slight (2). It is also the lowest temperature for the existence of middle soap, since a tie line of constant temperature connects the lowest right hand corner of the middle soap field with the lower left hand corner of isotropic solution. For sodium salts of most commercial oils and fats, T_s lies between 45° and 55°.

Summary

Vapor pressure data for a series of five pure soaps with water and for a typical commercial soap have been made the basis of a revision and extension of the less complete phase diagrams previously developed in investigations carried on by many different methods.

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