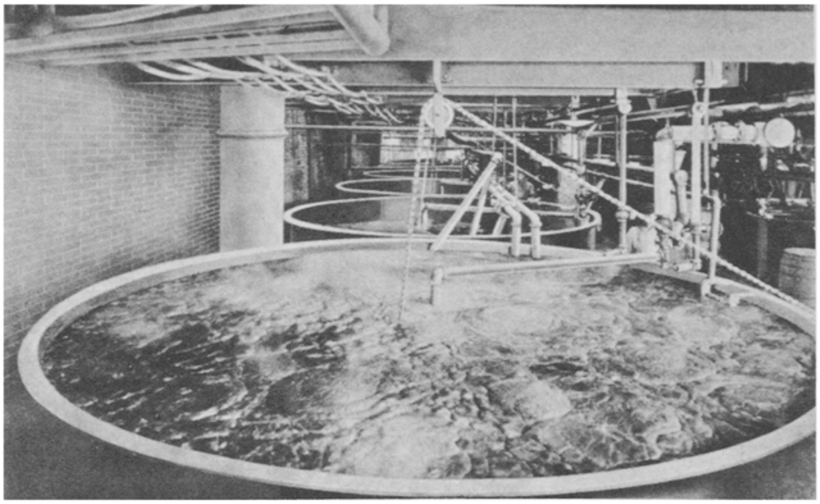

Typical Settled Soap Boiling Kettle Installation

Phase Phenomena in Commercial Soap Systems

By R. H. FERGUSON*

The Procter and Gamble Company, Ivorydale, Ohio

Complex Soaps Found Susceptible to Much the Same Rules of Phase and Equilibrium as Are Single Salts of Fatty Acids

THAT the phase phenomena exhibited by soaps are related directly to well known physical chemical principles of solubility and equilibrium has been firmly established, in this and in other laboratories, by studies on many different types of soap systems. Complex commercial soaps are found to be susceptible to much the same interpretation accorded the more simple single salts of fatty acids, with the result that the fields of soap chemistry and soap technology achieve a unity hitherto sadly lacking.

In order to arrive at a basic understanding of the nature and make-up of commercial soaps, it is helpful to consider them as systems of matter, composed essentially of salts of various fatty acids (i. e., soaps), water and electrolyte. Glycerine, unsaponifiable matters, etc., which are usually present, exert specific influences on phase relations, but are not important in the present connection. The equilibria which occur in such systems of soap, water and electrolyte, give rise to a multiplicity of soap forms and phases, and likewise are definitely responsible for the somewhat involved nature of the soap boiling process.

In the present very general paper, the several phases characteristic of a typical commercial soap (tallow) will be considered in the light of the solubility relations of the dry soap in water and in salt water solutions. Thus figure 1 represents equilibrium conditions at the single temperature 100° C. in a system whose components are pure, dry tallow soap, water and sodium chloride. The vertical or Y axis denotes per cent soap, the horizontal or X axis per cent salt; hence the origin refers to 100 per cent water, and any point within the interior of the diagram corresponds to a definite proportion of soap, salt and water.

The justification for the use of such a three component diagram in a mixed soap system lies in the fact that the various constituent soaps of tallow (sodium stearate, palmitate, oleate, etc.) behave for all practical purposes as a single soap, both in the presence of water alone and in the presence of salt solutions. When tallow soap solutions are salted out into two liquid layers, the most insoluble soap does not salt out first, but all the soaps come out together as a

---

*Presented at the Fall Meeting of the A. O. C. S., Chicago, Oct. 29-30, 1931.

single soap. This point, while usually unrecognized, has always been more or less tacitly assumed by the soap manufacturer in "pitching" soaps and in blending different stocks.

In the present soap system the assumption appears to be justified, for the molecular weights and iodine values of the fatty acids in the liquid layers produced by salting out are quite similar in each layer. In general, even with those soaps in which marked fractionation is known to occur, its extent is not serious enough to vitiate the application of the phase point of view.[1]

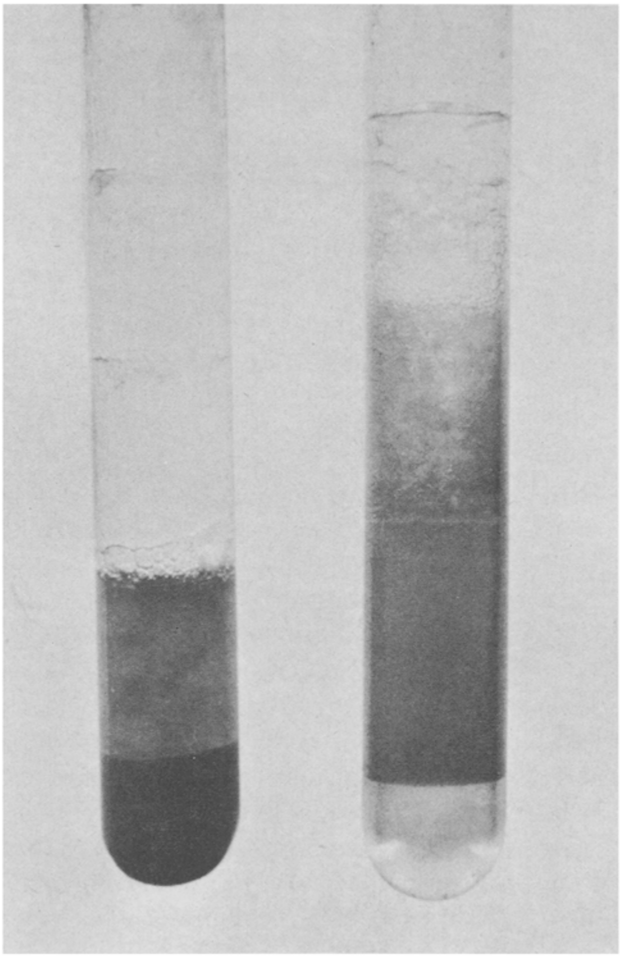

Fig. II—Neat Nigre and Neat Nigre Lye

The phase theory accordingly constitutes a most valuable tool in studying commercial soaps.

Referring to diagram 1, it is evident that a saturated salt solution at 100° C. would be repsented by a point at 28.3 per cent NaCl on the horizontal axis extended and, in the same way, a saturated soap solution corresponds to a point at 26.5 per cent soap (point R) on the vertical axis.

Accordingly, if dry tallow soap (represented by 100 per cent soap on the vertical axis), is added to water so as to make a soap solution of less than 26.5 per cent soap, the phase present is an ordinary soap solution or "nigre." When the concentration reaches 26.5 per cent soap, the solution becomes saturated. That is to say, it no longer consists of one homogeneous phase, but is a heterogeneous emulsion, and any composition between 26.5 per cent soap and 33.5 per cent soap (on the Y axis) is composed of two phases, middle soap and nigre.

The saturation phase, middle soap, is not the original dry soap added to the system, but is a viscous (or plastic), almost transparent form of soap. It was discovered by McBain[2] as a distinct soap phase, and later work has shown it to be identical with the so-called "gum" or "gummy" soap of the soap boiler.

Middle soap flows only with difficulty, yet through its ability to form droplets, and other properties, it must be called a liquid phase. However, due to its anisotropic nature under the polarizing microscope, which sharply distinguishes it from nigre, it is best defined as a liquid crystalline solution, differing from the conventional "liquid crystal" in that its composition varies over wide limits of soap and salt. (Area D.) Middle soap as a phase forms the basis for several commercial products, but its main importance in the system under discussion derives from undesirable "gummy" properties if it separates in the soap kettle through accident or through incorrect procedure during the boiling process. In the usual sodium soaps, of which tallow soap is a representative, middle soap exists at high temperatures only, and disappears completely at ordinary temperatures.

Nigre or soap solution, one particular com-

---

[1] In a tallow soap system, fractionation is a considerable factor when the soap becomes curded, and under certain conditions may cause trouble in the more dilute portions of the system. Although usually slight, it is probably always sufficient in any mixed soap system to cause the boundaries of the various fields to exist as narrow zones instead of lines as demanded by theory.

[2] The reader will find the best discussion extant on equilibria in soap systems in the various papers of McBain and his students. Particular reference may be made to McBain's fundamental contributions contained in *J. Chem. Soc.* 127, 852-70 (1925).

The original application of the phase theory to soap is described in "Die Kernseifen," Merklen, Germ. Trans. by Goldschmidt, Halle, 1907.

Middle Soap Phase

The saturation phase, middle soap, is not the original dry soap added to the system, but is a viscous, almost transparent form of soap, identical with the so-called "gum" or "gummy soap" of the soap boiler.

position of which constitutes the saturated solution in equilibrium with middle soap in a soap-water system (point R), is isotropic in polarized light. It is the name given to all the various soap solutions usually studied by the physical chemist, as well as to the less known soap phase which separates as a dark, impure liquid layer in the soap kettle during the pitching operation. Every composition falling within area F is "nigre" at 100° C. This area illustrates the extent also of the solubility of tallow soap in salt water solutions. Although all compositions in area F correspond to a single homogeneous phase, yet this phase varies enormously in physical properties, such as viscosity, as the composition varies.

As noted above, area D refers to those compositions of tallow soap, salt and water which yield the homogeneous phase middle soap. The addition of dry soap to water (along the Y axis) at first produces soap solutions (from the origin to R), then heterogeneous middle soap and nigre (area E), then homogeneous middle soap (area D).

When the concentration of soap is increased so as to fall within area B, a second liquid crystalline phase separates, and now two liquid crystalline solutions exist in equilibrium. They are middle soap and neat soap. When the soap concentration is further increased to area A, homogeneous neat soap exists alone. Neat soap, which is the phase separating as the upper layer in the soap kettle during the pitching operation, forms the basis for bar soaps and, to a large extent, for flakes and chips. It has widely varying properties as the total composition varies over area A. Ordinarily, at 100° C. neat soap flows readily. Middle soap, on the other hand, will hardly flow at all, and it is to the phase change, from middle to neat soap, that the lessened viscosity of concentrated soap systems must be attributed.

The Soapmakers' Base-Material

Neat soap, which is the phase separating as the upper layer in the soap kettle during the "pitching" or finishing operation, forms the basis for bar soaps and, to a large extent, for flakes and chips.

When the concentration of soap is raised to about 72 per cent, a more crystalline form of soap separates. Its relation to neat soap seems somewhat doubtful and, as yet, there is no exact correlation between crystals or curd fibres as defined by the physical chemist and the "curd" or "grain" soap of the soap chemist. Hence the upper and extreme right portions of the diagram are not drawn in.

So far, the concentrations lying on and close to the vertical axis have been discussed. If sodium chloride is introduced into the system in sufficient quantity, the soap is "salted out." It is clear from the diagram, and should be emphasized, that "salting out" is not a precise term. A salted out soap system can exist as any one of several different sets of phases, and, in addition, the presence of salt may produce homogeneity as well as heterogeneity.

Phase Relations in the Soap Kettle

The equilibria which occur in systems of soap, water and electrolyte, give rise to a multiplicity of soap forms and phases, and are definitely responsible for the somewhat involved nature of the soap boiling process.

As an example, suppose sodium chloride to be added in gradually increasing quantities to a 40 per cent tallow soap solution. (During the addition, all changes in total composition of the system will take place along a straight line from 40 per cent soap on the Y axis to 100 per cent salt on the X axis extended.) A 40 per cent tallow soap system at 100° C. exists in the form of homogeneous middle soap (since it lies in area D), and remains so until about 0.5 per cent NaCl is present. Additional NaCl causes the formation of middle soap and nigre (area E), but further increase in salt content again brings about complete homogeneity, as the total composition changes to area F.

A large number of physical separations of middle soap and nigre of a high degree of completeness have been obtained, and the resulting analyses of the separated phases, together with the known total compositions at which one of the phases forms or disappears, yield the necessary data for the boundary lines of areas D and E. Similar separations of phases in equilibrium in the other fields involving middle soap (B and C), make it evident that this form of soap is a separate and distinct soap phase, thus confirming and amplifying the results of McBain.[2] When enough salt is added to a 40 per cent tallow soap solution to change the total composition to area G, again the system "salts out" into two phases. The phases now present are neat soap and nigre (see 1st tube in fig. 2). The ends of the tie lines give the composition of the phases in this and other heterogeneous two-phase areas.

It should be noted that the nigres (along lower boundary of G) in equilibrium with neat soap are quite different in composition and properties from the nigres (lower boundary of E) in equilibrium with middle soap.

So far, the addition of salt has brought about several diverse phenomena, changing the system from a homogeneous phase (area D) to a heterogeneous system (area E), then to a homogeneous form again (area F), and finally to a different heterogeneous two-phase condition (area G). If still more salt is added, so as to cause the total composition to fall in H, then a three-phase separation occurs (tube 2 of fig. 2). The phases in equilibrium are neat soap, nigre and lye,[3] their compositions being given by the apices of the triangle.

Area H, from a theoretical standpoint, is most important. Any total composition of soap, salt and water lying within this area should yield three phases, each of constant composition, no matter what the original total system.[4]

Many experimental results have shown that, if equilibrium conditions are controlled carefully, any total composition within area H yields a lye which approximates 7.0 per cent NaCl within very narrow limits. Although analyses of the other two phases do not indicate such a degree of constancy of composition for them, this is probably due to phase contamination and not strictly to deviation from theory. In addition, by varying the total composition of the system in a systematic manner, the outline of area H can be determined without resort to analysis of the segregated phases. This indirect method places the area as triangular in form and of the position shown. Such evidence again points to the conclusion that tallow soap, in the main, constitutes a single component in the system and that the various soaps of tallow do not act independently.

When the addition of salt has proceeded to such an extent that the composition of the system changes to area K, only two phases remain, neat soap and lye, the nigre having disappeared. Further increase in the percentage of salt causes the soap to become curdy (area M). As noted above, this portion of the diagram is incomplete, but tie line directions in M, while not shown, are roughly parallel to and consistent with those in area K, and yield information as to the compositions of the separated phases, i. e., "curdy" or "grainy" soap and lye.

The upper portions of areas G, H, K and M are the important regions involved during the pitching or finishing operation of the soap boiling process. The progress of the "pitch," as indeed the changes in phases which must and do occur during any of the operations of soap boiling, can be followed schematically on the diagram by applying the usual graphic methods, some of which have been outlined above. The diagram also gives the solubility of tallow soap in various concentrations of salt water. An interesting point arises if one considers the solubility of dry tallow soap in 1.0 and 2.0 per cent NaCl solutions. From the diagram it will be observed that the soap is even more soluble in the salt solutions than it is in pure water alone.

Again, the diagram explains the peculiar results which are obtained with certain nigres when they are "salted out." Thus, if a nigre of total composition lying in the uppermost apex of area F is treated with salt, it separates into neat soap and nigre. If water is added to the original nigre, it again "salts out," but this time into middle soap and nigre (area E). Finally, if soap is added to the original solu-

(*Continued on page* 25)

---

[3] "Lye" refers to any electrolyte solution; in the present system to a sodium chloride solution. Called also "pitchwater" and "seat" in the soap industry.

[4] In the discussion the vapor phase is omitted. If the system is of three components, then

$$C - P + 2 = F$$
$$3 - 3 + 2 = 2$$

but the temperature is constant and the system is condensed; hence $F = 0$, and the composition of each phase must be constant.

clusion to be reached, either by design or accident. Several of the most recent articles in the technical journals almost directly contradict each other because the standards of comparison chosen were quite different. Perhaps the practical laundry operator is right in his assumption that laboratory studies are of little value to him.

Perhaps the best approach is by way of practical studies aided by scientific instruments. The maintenance of the highest grade of whiteness during actual operation has frequently been the basis of constructive work. Unless all operating conditions are carefully noted, however, erroneous conclusions can be drawn because of the difficulty in controlling all possible variables entering into the washing formula. The final judgment of this procedure is the whiteness of the washed fabric. Here, again, the variables enter. Bluing, sizing, finishing, and personal taste enter into the conclusions. Some of these can be eliminated by the employment of complicated photometers. Finally, as the differences in results become small, as we approach the perfect process, the par in laundering, the method of measurement breaks down and leaves us still groping for the ideal procedure. As we approach more perfect work we must be increasingly careful in the method of measurement.

In conclusion, I would like to stress the necessity of studying this problem with the practical limits in view. Elimination of irrelevant factors will do much toward avoiding the present state of confusion regarding basic principles of detergency. Unprejudiced cooperative work should arrive at more definite statements of fact for the ultimate consumers of soap products, who in this discussion are the laundry operators. Perhaps I am leaning too heavily toward their viewpoint. If so, it is because I have spent a number of years in intimate association with them trying to fully appreciate their problems in their way.

Agash Refining Company, Brooklyn, New York, have recently installed a new winterizing plant for cottonseed oil, giving them over double their former capacity for salad oil production.

PHASE PHENOMENA IN COMMERCIAL SOAP SYSTEMS

(*Continued from page* 8)

tion, a separation of neat soap and nigre is obtained. Hence it appears that this particular soap solution can be ''salted out,'' i. e., separated into layers, by addition of salt, water or soap.

Area N delimits those concentrations which give rise to two phases, nigre and lye. Equilibria in this part of the system are not nearly so definite and precise as in the more concentrated portions. The area, however, lies completely outside the range of soap boiling practice and is of theoretical interest only.

Summary

TO sum up, it has been found that the phase theory is applicable to commercial soap systems. Tallow soap in particular behaves as a single component in most of its equilibrium relations.

A general discussion of the system tallow soap—NaCl—H_2O has been given, with a description of the various phases which occur. The fields of stability of these phases at 100° C. have been outlined.

[THE END]

The Peruvian customs regulations provide for a special import duty of 10 per cent ad valorem on a list of commodities as follows, when imported in quantities of more than 500 gross kilos for use in industries of Peru: Coconut oil, fish oil, and coloring matter which is soluble in fats but insoluble in water, ordinarily dutiable as follows: Coconut oil 0.04 and 0.06 sol per gross kilo according to capacity of container; fish oil, 0.10 sol per gross kilo; harmless coloring matter for foods and beverages, 6 soles per gross kilo except when derived from coal tar of sulphur coloring, in which case the duty is 1 sol per gross kilo.

Sol equals $0.3999 U. S. currency.

The modern whale oil industry is based upon a dual foundation of geographic exploration and laboratory research.