(at sufficiently high temperatures). The sodium soaps are much more soluble in the glycol than the corresponding metal soaps. In the co-solvent mixtures, the optimum for the sodium soaps is towards the middle of the diagram, whereas for all the heavy metal soaps it lies well towards the chloroform side. The position of the optimum composition of co-solvent mixtures lies increasingly towards the side of chloroform as one passes from sodium to magnesium, calcium, barium, and lead, which is in accordance with increasing atomic weight. However, for zinc, with far lower atomic weight than the latter two, the optimum is still further towards chloroform. As far as actual solubility is concerned this decreases with increasing atomic weight, if the high solubility for lead and the extremely low solubility for zinc soaps are taken as exceptions. However, the solubility of lead laurate is less than that of all the other soaps except zinc if the glycol present exceeds 35%. The authors consider that such behavior can throw light upon the nature of the polarity of the valency bonds and the molecular structure of the soaps.

The heavy metal soaps show co-solvency in mixtures of benzene and alcohol, especially at higher temperatures, and more particularly magnesium and aluminum soaps. A stiff non-flowing gel or jelly of aluminum soaps in hydrocarbons may be converted into a thin clear fluid by addition of less than 1% of methyl alcohol.

Summary

The solubilities of the myristates, laurates, palmitates, and stearates of magnesium, lead, calcium, barium, and zinc have been measured at 25° C. in chloroform and in propylene glycol and in their mixtures. Even where they are sparingly soluble in the solvents separately, they dissolve freely in mixtures of the two.

For each metal the solubility is greatest for laurate and least for stearate and it is very low for zinc soaps, particularly zinc stearate.

Heavy metal soaps may be directly titrated with acid in mixtures of propylene glycol and chloroform using thymol blue as indicator (yellow to pink).

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An Investigation of the Crystalline Phases in the System: Sodium Myristate-Water*

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Introduction

ONLY recently has there been recognition of the fact that solid soaps are aggregates of crystalline phases and that the collection of phases in the aggregate differs with differing treatment. While the science of soap phases is in its infancy, it is now evident that soaps of different properties can be prepared from one and the same soap stock by varying their preparation.

In an earlier contribution (1) we have outlined the general occurrence of crystalline soap phases in simple soap-water systems. In this paper we discuss the conversion of one soap phase to another in such systems and give experimental results obtained in the system sodium myristate-water.

Soap phases are difficult to identify because they show more resemblances than differences. Their optical properties are nearly identical insofar as these have been investigated (2) and this is a consequence of the generally similar manner in which the molecules are packed in the structures of the soap crystals. It is only in detail that the packing schemes of the structures differ. One of the best ways of investigating differences in structure is by X-ray diffraction. "Powder" photographs of soap phases provide a means of "fingerprinting" them and thus of distinguishing between them as they occur in soaps.

Phase Transformations in Soap Systems

McBain has shown that simple soap-water systems conform with the phase rule insofar as the non-solid phase fields are concerned and has investigated the nature and distribution of the phase fields for a number of such systems (3). Our own investigations have been concerned chiefly with the regions of the phase diagrams in which solid phases predominate. These regions have not been discussed in detail by McBain. We now realize, in retrospect, that such regions cannot be investigated by the classical static methods for reasons which will appear very shortly.

To anticipate our general results somewhat, in order to make them the basis of discussion, we find that the predominantly solid regions of soap-water systems are partitioned into fields (1). In the cases of systems of pure soaps with water such fields are limited by phase rule considerations to solid solution fields and two-phase fields. In more complex soap-water systems additional phases may appear within a single field.

We have ascertained that it is not generally possible to shift the state of the system in these regions by merely changing its coordinates only, i.e., by merely adding or removing water or by changing its temperature (except as noted below). Indeed, *equilibrium can be attained, in general, following a change of coordinates, only when the change is accompanied by violent working.* (An exception to this is that equilib-

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rium is attained without working, provided that the new state involves a large proportion of a liquid phase.) This has been tested by the usual method of approaching equilibrium from different directions; the same phase collection is attained, in general, only with sufficient working.

This feature prevents the investigation of the phase diagram of a soap system by the mere process of preparing a soap-water mixture in a small container, such as a capillary, homogenizing it by melting it, and then taking X-ray photographs of the phases present at a sequence of lower temperatures. Such a preparation represents the equilibrium state only in the original melted state. At lower temperatures the equilibrium collection of phases can be attained only after a considerable period of violent working; a capillary merely cooled does not provide the required conditions.

On the other hand, the failure to attain equilibrium on cooling can be turned to advantage by a different procedure. A mixture of any desired amount of soap and water can be violently worked at the required temperature under such conditions that the water in the system cannot escape, and then the sample may be cooled without fear that the phases present will interact so as to shift the proportions of the phases present, or the chemical nature of each. The only possible changes which could occur would be (a) a polymorphic transformation of a phase or (b) a breakdown of a phase into two phases. We have never observed the breakdown of one soap phase into two others. This general type of investigation is discussed subsequently under the heading *Phase Maps.*

Phase Maps

Since lowering the temperature of a soap sample is not attended by a shift in the relative quantities of the phases in the collection at equilibrium at the elevated temperatures, it becomes possible to quench a sample worked at elevated temperatures and then to examine at lower temperatures the quenched equivalents of the phases which were at equilibrium at the elevated temperature. The quenched sample is not necessarily composed of the same phases which were present at the elevated temperature, but it is composed of phases which are at least descendants of these phases. If no transformations take place in the quenching process, the descendant phases are actually the same phases as the equilibrium collection at elevated temperature.

To avoid confusion between equilibrium phases and descendant phases we introduce the term *Phase Map.* A phase map is derived from a phase diagram by replacing the original equilibrium phases at all points by their descendant phases. The phase map is the representation of the system which is immediately obtained by recording the results of quenching experiments. It is not necessarily the phase diagram but is a map of the phases produced by working samples under the possible variations of the variables, composition and temperature. The phase map thus provides the room temperature phase compositions of soaps produced under these variations.

The Converter

The device for violently working soaps is here called a *converter* since its mechanical action facilitates conversion of phases. The essential features of the laboratory converter which we have employed in investigating phase maps is described in the following paragraphs and illustrated in the diagrammatic sketch and detailed drawing of Fig. 1.

The soap sample is contained in a cylinder *A* through which a perforated piston *B* is reciprocated. The piston is carried by a rod *C* drilled for thermocouple leads *D* and is driven by means of a motor *E,* gear reducer *F* and sliding crosshead *G*. The piston rod passes through a stuffing box *H* which prevents loss of soap and moisture.

The sample container is charged with soap of the desired composition and screwed into the block *J* against a recessed lead washer. The sample container and the block are surrounded by a constant temperature bath and brought to the desired temperature. The soap is then worked, usually for a period of 30 minutes, by forcing the perforated piston back and forth through it at a rate of about 12 strokes per minute. The length of the stroke is carefully adjusted so the piston traverses practically the entire volume of the sample holder, thus insuring thorough working of the entire charge. During working the temperature of the soap is checked by means of the aforementioned thermocouple. This couple, carried by the piston, is soldered into a small metal button *K* which is in direct contact with the soap and insulated thermally from the piston and piston rod by a hard rubber bushing *L.*

Since only a very small sample is required for the X-ray examination, it is convenient to run a series of tests at different temperatures with a single charge of given moisture content. After working at a desired temperature the piston is stopped and the bath lowered to expose the sampling vent *M* at the side of the sample container. This vent is normally closed by a rubber washer N, pushed tightly in place against the opening by a toggle arrangement *O* and a spring *P.* To open the vent a small key is inserted in the square hole shown in one arm of the toggle and given a quarter turn. A small, thin-walled tube is inserted through the opening thus exposed and withdrawn with a core of soap which can be expelled into a sample vial and quickly chilled to room temperature. Since the sampling vent need be opened but a few seconds, little moisture is lost from the remaining charge. When working at high temperatures, it is sometimes desirable to cool the apparatus somewhat before sampling. Upon completion of a temperature series it is customary to cool the sample cylinder before removing it from the apparatus and to run a moisture check on the unused soap.

Preparation of Sodium Myristate

Pressed fatty acids from *ucuhuba* butter were esterified with methyl alcohol. The washed and dried esters were passed through a Stedman-packed fractionating column and the methyl myristate fraction, amounting to approximately 73% of the total, was refractionated. On analysis the product showed a saponification value of 231.3 and an iodine value of 0.9. The molecular weight calculated from the saponification value equaled 242.5 (theoretical value for methyl myristate 242.2).

Six hundred grams of the ester were saponified directly with the calculated amount of approximately 25% sodium hydroxide, yielding a salt and glycerin free soap containing 0.11% free Na_2O and 0.10% un-

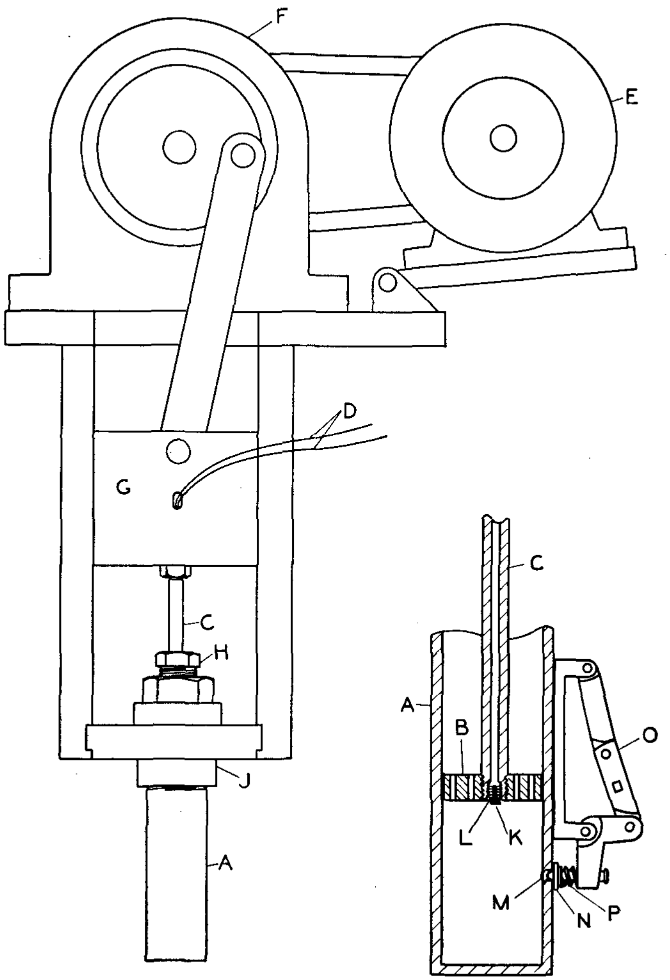

FIG. 1.

saponified ester. Drum drying, followed by heating at 105° C. overnight removed the last trace of methyl alcohol. After cooling, approximately 10% water was mixed in the soap and the mass homogenized by screening.

Processing of Soap and Water Systems

After obtaining an accurate moisture analysis on the soap stock, prepared as described above, charges of approximately 20 grams were weighed into the cylindrical working chamber and calculated amounts of water added from a burette to reach the processing concentrations.

This mass was worked at the desired temperatures for one-half hour by driving the perforated piston up and down through the soap, after which the small sample necessary for X-ray examination was extracted and quickly chilled.

The Phase Map of Sodium Myristate

In Fig. 2 we show the phase map of the system sodium myristate-water. Approximately 150 runs were made in accordance with the procedure above described and subsequently examined for phase content by making an X-ray powder photograph of a chilled sample of the run.

Fields containing the crystalline phases κ, μ, and ζ (1) occur on the map. With few exceptions, all experimental runs were found to contain phase collections the same as the label of the field in which they fall. The chief exceptions occur at high moisture where it is difficult to be certain of the identification of the phases *in the X-ray photograph*. The phase δ was encountered in one sample only which was prepared at 50% water and 68° F. Further experiments failed to duplicate this result.

For the benefit of those wishing to identify these phases in the future their X-ray photographs are recorded in Fig. 3 which has been prepared directly from the original films to exactly natural size. The photographs were made with copper radiation in a cylindrical camera of the standard diameter 114.6 mm., (where 1 mm. on the film is equivalent to ½° for the Bragg angle θ, or to 1° for the deviation angle 2θ).

Isotropic solution occurs as a phase of the phase map in increasing quantities toward the right of the diagram. This phase has not been entered in the labels since it is not certain how far toward lower moistures the isotropic solution persists. That it occurs at the higher moisture values is indicated by the facts that (a) it can be squeezed out of the obviously wet samples and (b) that for water contents of more than about 40% the intensities of the diffraction lines of the crystalline phase become obviously weakened (and also show preferred orientation of the crystals). No appreciable *diffraction due to liquid water* is evident to the eye within the region sampled.

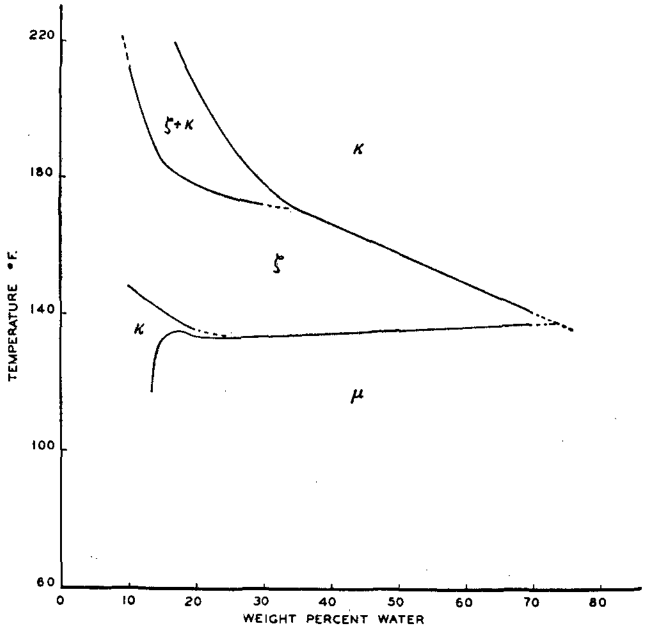

FIG. 2.

In the lower temperature regions of the diagram there occur three single phase fields without obvious solid solution areas between them. The substantially horizontal boundary between μ and ζ corresponds with the temperature of ready solubility of sodium myristate (4). A similar horizontal boundary occurs in other saturated sodium soap-water systems. In this system the κ field is inserted as a wedge at low moistures, with its apex at this horizontal boundary. It is roughly suggestive of one of the "tongues" which appear near the zero moisture axis of the McBain phase diagrams (3).

The phase κ not only appears in the aforementioned wedge-shaped field but also in a high temperature field, limited beneath by a boundary sloping

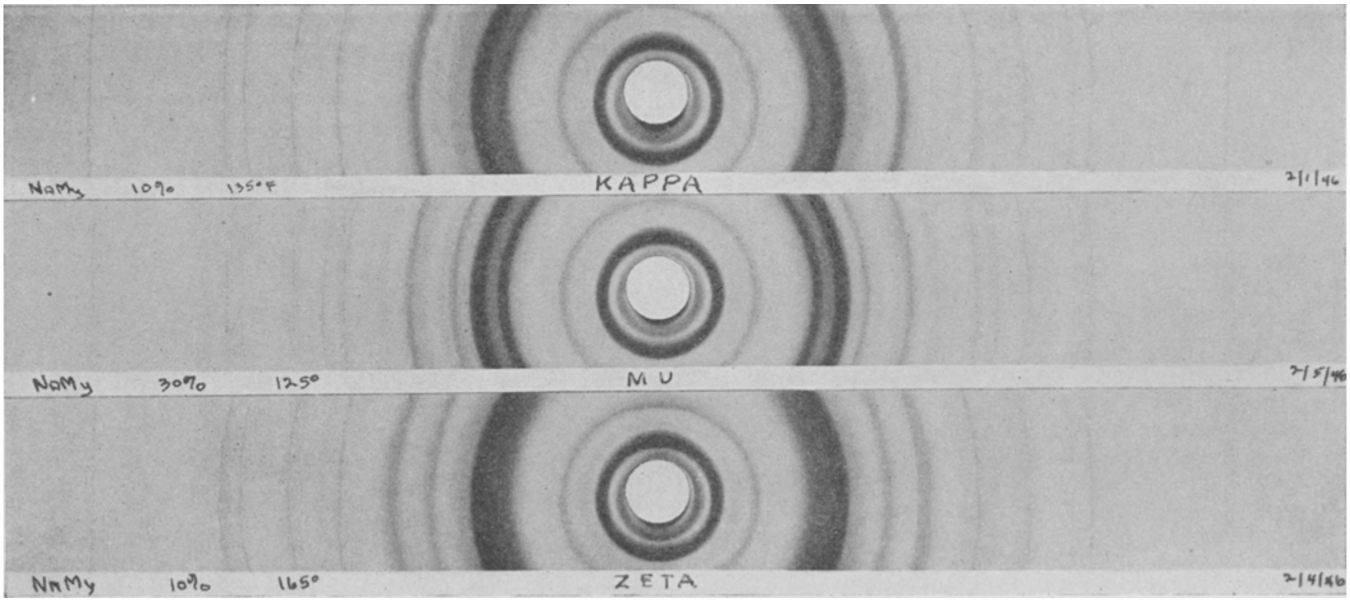

FIG. 3.

down to higher moisture values. This boundary corresponds with McBain's T_c, the temperature of final melting of the curd soap. It is apparent that the phase κ is not an equilibrium phase in this second field. Evidently the equilibrium phase is liquid crystal and κ is a descendant phase.

This T_c boundary is composed of two segments. At moistures higher than about 35%, the boundary is substantially a straight line. At lower moistures the boundary curves sharply upward. The straight part of the boundary has below it a phase field containing the phase ζ plus solution while below the curved boundary lies a two-phase field containing ζ plus κ. If the latter field represents an equilibrium collection of phases, it can contain no solution phase in addition since three-phase fields cannot occur in a two-component system. The question, therefore, arises whether the lower boundary of the ζ plus κ field represents the composition of the ζ crystals.

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The Non-Uniformity of B-Linoleic Acid[1]

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THE linoleic acid isolated from natural oils (1, 2) and the α-linoleic acid[3] obtained on the debromination of crystalline tetrabromostearic acid (3) are believed to be identical (4, 5, 6). However, the identity of the β-linoleic acid obtained on the debromination of liquid tetrabromostearic acid is still subject to speculation. This acid is believed to be either an isomer of α-linoleic acid (6, 7, 8, 9) or α-linoleic acid contaminated with conjugated acids (10) or products of the brominating reaction (5).

In the characterization of new vegetable oils the linoleic acid content has usually been reported as α-linoleic acid. In the case of sorghum grain oil, however, the presence of β-linoleic acid has also been reported (11). Biological assays have indicated that α-linoleic acid was more effective than β-linoleic acid in the prevention of dermatitis in rats (12). Interest in the composition and nutritive value of sorghum grain oil (13, 14) prompted a reinvestigation of the identity of β-linoleic acid.

Experimental

Preparation of the methyl esters: The α- and β-methyl linoleate were prepared according to the method of Rollett (3) from corn, cottonseed, and sorghum grain oil. In each case the α-methyl linoleate, iodine value 170.3 (theory 172.4), was prepared from recrystallized tetrabromostearic acid (m.p. 114° C.). The β-methyl linoleate, iodine value 147.0, was prepared from liquid tetrabromostearic acid according to the modification of McCutcheon (4).

The esters were saponified and converted to the free acids when needed. The methyl esters and free

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[2] Contribution No. 323 from the Department of Chemistry.

[3] The term "α" and "β" as such have no proven structural significance. The term "α" refers to the acid obtained from crystalline tetrabromostearic acid and the term "β" refers to the acid obtained from the Skellysolve B soluble residue or liquid tetrabromostearic acid.