with the oil pump. Nine and eight-tenths grams of 2,4,6-triethylacetophenone came over at 112–114° (4–5 mm.). The distillation slowed up and was discontinued at this point. After standing overnight at room temperature, the flask contained yellow crystals. These were removed, filtered and washed with a little 85% alcohol. On recrystallization from petroleum ether, 7.75 g. of product was obtained. The yields of diketone and monoketone were 32.5 and 38.4%, respectively.

The monoketone was identified by means of a mixed melting point of its benzal derivative with an authentic specimen. The diketone crystallized in golden-yellow prisms melting at 75–75.5°.

Anal. Calcd. for $C_{26}H_{34}O_2$: C, 82.49; H, 9.06. Found: C, 82.53; H, 9.01.

2,4,6,2′,4′,6′-Hexamethylbenzil.—The Grignard reagent prepared from 23.7 g. of methyl iodide and 4.06 g. of magnesium diluted to 200 cc. with absolute ether was added with vigorous stirring over a period of seventy minutes to 10.95 g. of 2,4,6-trimethylbenzoyl chloride dissolved in 200 cc. of absolute ether. The reaction mixture was then decomposed and treated in a manner similar to that described for the triethyl compound. The yield of acetomesitylene was 3.44 g. and that of the benzil was 3.45 g., or 35 and 39%, respectively. The acetomesitylene was converted to the benzal derivative which was identified by means of a mixed melting point with an authentic specimen. The dimesityl diketone was likewise identified by comparison with an authentic specimen.

When the acid chloride was added to the solution of the Grignard reagent, it was not possible to isolate any benzil from the reaction products. Instead, acetomesitylene was formed in 88% yields.

Summary

2,4,6-Trimethylbenzoyl chloride and 2,4,6-triethylbenzoyl chloride are coupled by the action of methylmagnesium iodide to give, respectively, 2,4,6,2′,4′,6′-hexamethylbenzil and 2,4,6,2′,4′,6′-hexaethylbenzil.

URBANA, ILLINOIS RECEIVED MAY 23, 1938

[CONTRIBUTION FROM THE CHEMICAL DIVISION OF THE PROCTER & GAMBLE COMPANY]

A Phase Study of the System Sodium Palmitate–Sodium Chloride–Water at 90°

BY ROBERT D. VOLD[1] AND R. H. FERGUSON

It is the aim of this paper to present a complete equilibrium diagram of the system sodium palmitate–sodium chloride–water at 90° with greater precision than that which has characterized any previous published account of a similar system of soap, inorganic electrolyte and water. Especial emphasis is directed to the support of the interpretation of those parts of the diagram where the curd phase[2] is shown.

The practical soap maker has long been familiar with curd soap as an intermediate, distinctive form, differing markedly in its properties from neat soap, the usual finished product of the soap boiling process. However, the first clear concept of curd as a separate and discontinuous phase from neat soap, and of the relations of both these forms of soap to the other coexisting phases is of recent origin. This concept has been developed in a remarkable group of papers by McBain,[3] dealing with the properties and behavior of soap. In these papers both the experimental results and the imagination exhibited in the interpretation are of the first importance in the whole field of soap chemistry.

Inevitably, however, the evidence is not equally convincing with respect to all parts of the diagram constructed by McBain and his co-workers. For example, it is possible to derive conflicting views[4] relating to the presence of definite hydrates in the system at high temperatures, and the early dew-point results[5] do not support the existence of the three-phase invariant equilibrium, neat soap–curd phase–lye. In fact no definite constancy of phase composition has been clearly established hitherto for this equilibrium.

In general, the results of the present work, involving careful, systematic vapor pressure measurements of the system at 90°, are in agreement with McBain's conception of the equilibrium diagram. There are some quantitative divergencies, as may be noted by comparing the McBain diagrams with Fig. 6 below. In particular we have obtained definite proof that crystalline curd phase of sodium palmitate exists at 90° as a distinct phase different from neat soap, and that the neat–

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(2) The term *curd phase* will be used herein to refer to a homogeneous solid phase. In the literature, in addition to this meaning, the word curd has been used to describe variously a heterogeneous mixture of solid soap and other phases, any cooled and solidified soap system, and the upper curdy layer of soap in the soap kettle.

(3) Alexander, "Colloid Chemistry," Vol. I, Chapter by McBain; bibliography, McBain, Lazarus and Pitter, *Z. physik. Chem.*, **A147**, 87 (1930).

(4) Ostwald and Erbring, *Kolloid-Beihefte*, **31**, 345–346 (1930).

(5) McBain and Salmon, *J. Chem. Soc.*, **119**, 1374 (1921).

curd phase–lye equilibrium at this temperature is invariant. Contrary to the hypothesis of McBain, Lazarus and Pitter we find no evidence for the existence of stoichiometric hydrates of sodium palmitate at 90°.

Experimental

(a) **Methods Used.**—The solid nature of the systems encountered in highly concentrated soaps makes it virtually impossible to employ the method of phase separations developed by Ferguson and Richardson[6] for delimiting middle soap equilibria. Middle soap, while exceedingly gummy, is not as difficult to push to a condition of separation from other phases as is curd phase in the upper concentrated region of the diagram. Accordingly the phase separation method was used only to determine the boundaries of the middle soap and nigre fields.

For the various equilibria relating to curd phase and to check phase boundaries in the neat and middle soap fields an isopiestic vapor pressure method was devised. Essentially the method was adapted from that described by Collins and Menzies,[7] and has the advantage that it is independent of subjective visual observation of the appearance of the system, and is unaffected by whether or not the different phases present separate nicely or remain in intimate admixture.

A dew-point vapor pressure method was also employed in certain instances as discussed below.

(b) **Vapor Pressure Relations.**—The use of vapor pressure data to determine phase equilibrium diagrams is based directly on the requirements of the phase rule. A condition of invariance results whenever two condensed phases are simultaneously present in a binary system at constant temperature. Under such conditions the vapor pressure must remain constant despite changes in total composition, and thus give rise to flat portions in the vapor pressure–composition curve. The compositions at the ends of such "flats" give points on the phase boundaries of the two soap phases in equilibrium with each other.

In the ternary system soap–salt–water, at constant temperature, three condensed phases must be present before the pressure is independent of the total composition. In this case, however, the compositions at the ends of the flat in the vapor pressure curve give points on boundary lines connecting the compositions of the three phases present instead of giving the phase compositions themselves as in the binary system. This is equivalent to saying that "flats" in the vapor pressure curves in a ternary system are indicative of and specify the positions of triangles in the equilibrium diagram.

The composition at which transition from a one-phase to a two-phase region occurs in the ternary system at constant temperature may be determined from the vapor pressure–composition curve, since it is marked by a definite change in slope. This arises from the fact that in the one-phase region the rate of change of vapor pressure is directly dependent on the total composition, whereas in the two-phase region it is determined by the change of the compositions of the individual phases themselves.

Where lye (the technical name for any solution of electrolyte containing but little soap) is present, tie-line directions can be deduced from vapor pressure data. At equilibrium the partial pressure of water must be the same over all phases in the system. Consequently, the composition of a lye phase can be determined from the observed pressure in conjunction with standard recorded values for the vapor pressure of salt solutions, provided the solubility of sodium palmitate in the lye is not sufficient to change its vapor pressure appreciably. Lines drawn between the known composition of the total system and the composition of the equilibrium lye determined in this manner give the tie line upon which the composition of the equilibrium soap phase must lie.

That this procedure is valid in the present system was demonstrated by direct analyses of several lye layers which showed that sodium palmitate is practically insoluble in fairly concentrated salt solutions at 90°. Furthermore, it was found that the vapor pressure of systems consisting of curd phase, saturated lye and solid salt agreed exactly with that in the literature for the vapor pressure of a saturated salt solution at 90° and with our own values for the dew-point of saturated salt solution.

(c) **Procedure.**—In the more dilute systems phase boundaries were determined by methods of phase separation and analysis similar to those used with commercial soap systems.[8] In a few cases analyses were made of the partially separated phases, thus obtaining tie line directions. In all cases the visual appearance of the equilibrium systems was noted carefully in order to identify the phases present and facilitate interpretation of the vapor pressure curves.

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(6) Ferguson and Richardson, *Ind. Eng. Chem.*, **24**, 1329 (1932).

(7) Collins and Menzies, *J. Phys. Chem.*, **40**, 379 (1936).

(8) Ferguson, *Oil & Soap*, **14**, 115 (1937).

Studies by this (separation) technique were actually carried out at 100° instead of at 90°. The results were calculated to 90° for incorporation with the results of vapor pressure studies by use of temperature coefficients of phase boundary concentrations deduced from McBain's equilibrium diagrams at 90 and 100°. That no appreciable error is introduced by this procedure is evident since (a) the phase boundary concentrations for these phases—nigre, middle soap and neat soap—change but slowly with temperature, thus making the total correction small, and (b) for these phases the results obtained by McBain at 100° agree within 2% with those obtained in our study.

Phase equilibria in the more concentrated systems were deduced from vapor pressure curves as described above. After considerable preliminary work it was found that satisfactory results were obtained when 10-cc. portions of sulfuric acid solution were equilibrated with 1-g. soap samples in a closed system. During the experiment the acid concentration remains essentially constant while the soap system gains or loses water as required to make its vapor pressure the same as that of the acid.

In this work soap systems and sulfuric acid solutions were measured into the respective legs of an inverted Y-shaped Pyrex tube of about one inch (2.5 cm.) diameter. The tubes were then chilled in a salt-ice mixture and sealed off under vacuum from a water pump. After immersion in an oil-bath held at 90 ± 0.2° for a sufficient period to establish equilibrium (usually about five days) the two legs of the tube were simultaneously plunged into ice water thus preserving the compositions present at 90°. In this operation care was taken to make the level of the ice water the same as the level of the soap and acid in the respective legs in order to minimize distillation of water either into or out of the soap sample during the quenching process. The tube was then broken open and the contents of the two legs analyzed. The water content of the soap system was determined from the loss of weight on heating the *whole* sample to constant weight at 105°. The concentration of the sulfuric acid solution was determined by titration of a known weight of solution with standard alkali. Vapor pressures were obtained from the sulfuric acid concentrations of a plot of Collins'[9] vapor pressure results for such solutions at 90°.

A very large number of experiments was carried out with both binary and ternary systems over the whole composition range to test the validity of this method of vapor pressure determination as applied to soap systems and to establish the accuracy of the results. That the isopiestic method is satisfactory for use with soap systems is evident from the following experimental generalizations based on this work.

(1) Any two soap-water systems, one of higher and the other of lower water content, reach the same final concentration when sealed up in separate tubes with an acid of aqueous vapor pressure between the vapor pressures of the original soap systems.

(2) Duplicate soap samples sealed up in different tubes with the same acid reach the same equilibrium concentration at 90° even though one is brought to 90° by heating up from room temperature and the other by cooling down from 103°.

(3) Although the relative amounts of soap system and sulfuric acid were varied fivefold in some cases, the same vapor pressure and soap concentration were reached at equilibrium in all instances.

(4) Vapor pressures of salt solutions at 90° determined by the isopiestic method are in satisfactory agreement with the literature values, and with our dew-point determinations.

(5) Soap systems of widely differing initial concentration came to the same final concentration within a maximum deviation of ± 0.6% when equilibrated with the same acid. Some of the data on which this conclusion is based appear in Table I.

The reliability of the methods of analysis used was verified by analyzing samples of known composition and also by comparison of results with those obtained by analyses of samples for real soap content by standard methods.

To prove the absence of any systematic errors in the isopiestic vapor pressure method which conceivably could have led to erroneous vapor pressure–composition curves with resultant misconception of the nature of the phase equilibria involved, the vapor pressures of sodium palmitate–water systems at 90° were redetermined using an entirely independent method. For this purpose a dew-point method was used patterned after that described by McBain and collaborators.[10]

Use of the dew-point method for the determination of vapor pressures in the present work rests on the fact that the partial pressure of water vapor from a soap system at 90° is the same as that of pure water at some lower temperature. The temperature of pure water having the same vapor pressure as the soap system at 90° is given by the temperature at which dew just begins to form on a polished metal tube suspended in a closed space above the soap system. The vapor pressure of the soap system of known composition is then found simply from standard tables giving the vapor pressure of water at the dew-point temperature.

The technique of our determinations was essentially the same as that described by McBain, and modified by Ferguson and Vold.[11] The apparatus consisted of a glass tube closed at top and bottom with monel metal plates. These were equipped with circular grooves in which rubber washers were placed, and were held tightly against the glass by means of four "tie bolts." The top plate had a threaded hole through which the dew-point tube proper could be screwed down tightly against a rubber washer. The dew-point tube itself was a chromium-plated copper tube whose temperature could be varied by forced circulation of water from an auxiliary bath.

Extraordinary precautions were required to obtain accurate rather than merely reproducible results by this method. Soap samples (about 15-g. systems) were homogenized by heating to 295° in sealed tubes in a rotating autoclave prior to studying them in the dew-point apparatus. It was shown experimentally that the composition of the sample in the dew-point apparatus did not change during the time of the experiment. This is important since a small change in total composition may give rise to a

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[9] Collins, *J. Phys. Chem.*, **37**, 1191 (1933).

[10] McBain, Bull and Staddon, *ibid.*, **38**, 1075 (1934).

[11] Ferguson and Vold, *Oil & Soap*, in press.

surface layer of sufficiently different composition from the bulk of the sample to cause a serious error in the dew-point. At least fifteen hours was allowed for attainment of equilibrium since preliminary experiments showed that in many cases shorter periods of time were inadequate.

The validity of the technique finally evolved was confirmed by several tests. The vapor pressure of salt solutions at 90° determined by this dew-point method agreed within 1 mm. with the values listed in the "International Critical Tables."[12] In several experiments the equilibrium temperature was approached from higher and lower temperatures without causing any change in the observed dew-point of the soap sample at 90°. Finally, it was shown with several samples that the dew-point remained unchanged for periods of time running up to a week in the apparatus at 90°.

As appears from the results shown in Fig. 1, vapor pressures determined by the dew-point technique agree within the experimental error of that method with those obtained by the isopiestic method. Both series of experiments for systems containing NaP and H_2O alone, *i. e.*, along the left axis of the ternary phase diagram, show a step in the vapor pressure–composition curve, thus furnishing proof of the simultaneous presence of curd phase and neat soap as distinct phases.

It is of interest that the same result is obtained despite the fact that homogenized samples were used in the dew-point experiments whereas soap systems used in the isopiestic experiments had never been heated much above 105° and were used directly without preliminary equilibration. This fact would seem to show that we are dealing with the same equilibrium solid phase in both cases despite the difference in initial treatment.

(d) **Materials.**—The sodium palmitate used in these experiments was prepared by neutralizing (to phenolphthalein) a hot alcoholic solution of palmitic acid with a nearly saturated carbon dioxide-free aqueous solution of sodium hydroxide. The resulting soap was dried at 130–140°.[13] The palmitic acid was Eastman best product. The two lots used to prepare the sodium palmitate at different times during the course of the experimental work had the following characteristics.

Iodine value	0.09	0.05
Incipient fusion	61.5	61.9
Complete fusion	62.6	63.0
Molecular weight (by titration)	260	261

Sodium palmitate–water samples of the same composition made up from the two different preparations of sodium palmitate had the same vapor pressure.

Coleman and Bell C. P. sodium chloride was used throughout.

(e) **Results.**—The vapor pressure data obtained for the sodium palmitate–water system at

TABLE I

VAPOR PRESSURE OF SODIUM PALMITATE–WATER SYSTEMS AT 90°

Tube	Original % soap	% soap at equil.	Vapor press., mm.	Av. % soap at equil.	Av. vapor press., mm.	Phases present
E_6B	15.0	17.7	523			Nigre
E_4A	24.0	29.1	521			Middle soap and nigre
E_4B	28.0	31.1	521			
E_3A	33.8	37.7	519	37.7	519	Middle soap
E_3B	37.9	37.6	519			
1X	51.8	52.2	510			Middle soap and neat soap
21X	54.8	55.9	510			
21Y	51.8	54.7	510			
2X	64.0	56.3	510			Middle soap and neat soap
2Y	59.8	54.0	510			
22X	64.0	52.5	510			
22Y	59.8	52.3	510			
23X	67.8	60.8	505			Neat soap
23Y	. .	60.3	505	60.6	505	
9A	62.7	60.9	505			
9B	57.3	60.8	505	60.9	505	
5RY	74.0	67.6	497			Neat soap
4X	73.4	68.4	495			Neat soap
4Y	68.2	67.8	495	68.1	495	
24X	73.4	68.1	495			
24Y	68.2	68.0	495	68.1	495	
5X	79.6	68.4	495			
5Y	74.0	69.4	495	68.9	495	
25X	79.6	68.0	495			
25Y	74.0	68.2	495	68.1	495	
1B	73.3	69.9	491			Neat soap
6X	80.9	73.3	481			Neat soap
6Y	77.2	73.4	481	73.4	481	
26X	80.9	71.6	481			
26Y	77.2	72.4	481	72.0	481	
5A	77.5	74.0	481			
5B	80.6	73.4	481	73.7	481	
4B	90.0	73.2	479			Neat soap
8A	88.8	73.9	477			
8B	83.2	73.2	478	73.4	478	
14A	76.1	74.2	474			Neat soap
14B	84.0	74.3	474	74.3	474	
7A	93.2	86.9	471			Neat soap and curd phase
7B	85.7	85.5	471			
16A	76.2	79.3	472			
16B	81.2	80.4	471			
17A	83.0	80.8	471			
17B	95.0	83.2	471			
13A	86.8	92.1	467			Curd phase
13B	93.3	93.0	466	92.5	467	
12A	89.1	92.7	463			Curd phase
12B	94.5	92.3	462	92.5	463	
27X	85.3	93.0	458			Curd phase
7Y	81.1	93.0	458	93.0	458	
9X	90.3	93.6	436			Curd phase
9Y	93.9	93.2	436	93.4	436	
29X	90.3	93.4	436			
29Y	93.9	93.5	436	93.5	436	
28Y	86.5	94.5	410			Curd phase
38Y	86.5	95.2	410	94.9	410	
6A	95.3	96.3	381			Curd phase
6B	100.0	96.2	380	96.3	380	
11A	91.3	95.4	381			
11B	96.0	95.9	380	95.7	380	
10B	94.8	98.2	328			Curd phase

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[12] "International Critical Tables," Vol. III, 1928, p. 370.

[13] A dilatometric investigation of sodium palmitate has indicated the existence of more than one form of anhydrous solid soap, and additional liquid crystalline phases. Transitions from one phase to another may be slow (or incomplete) with the result that the modification obtained may depend on the experimental conditions of the preparation. The curd phase under discussion in this paper always contained some water: it formed spontaneously in the system and so must be the stable equilibrium solid phase at this temperature. Furthermore, equilibria involving curd phase at 90° were shown experimentally to be perfectly reversible. Hence, it is difficult to imagine that the results obtained with aqueous systems at this temperature are subject to any uncertainty arising from possible differences in the initial crystalline modification of the anhydrous sodium palmitate.

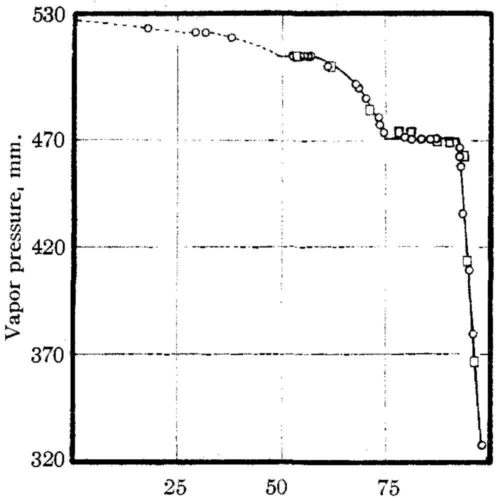

Fig. 1.—The vapor pressure of sodium palmitate–water systems at 90°: ○, points by the isopiestic method; □, points by the dew-point method.

90° are assembled in Table I. To conserve space the data for ternary systems are shown graphically in Figs. 2, 3, 4 and 5. The compositions at which phase changes occur, deduced from the vapor pressure curves and from the phase analysis and delimiting experiments, are given in Table II.

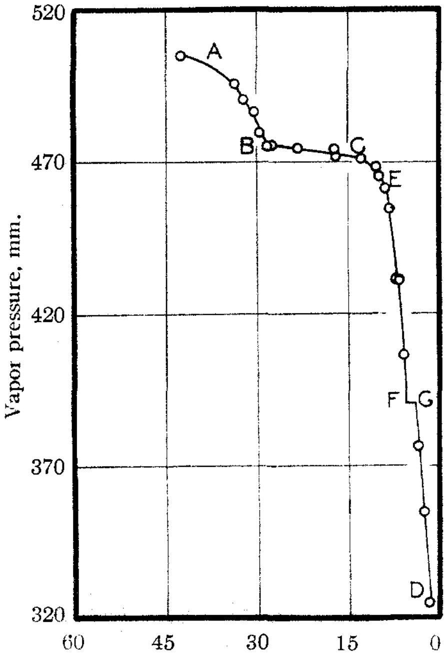

Fig. 2.—The vapor pressure of sodium palmitate–sodium chloride–water systems at 90°: sodium chloride concentration equals 0.80% sodium palmitate concentration.

In Fig. 1 the partial pressure of water vapor is plotted as a function of composition for the sodium palmitate–water system at 90°. The three flats in the curve correspond respectively to the coexistence of middle soap–nigre, middle soap–neat soap and neat soap–curd phase. The compositions of the phases in equilibrium, determined from the ends of the flats in the vapor pressure curve in the case of middle soap–nigre and middle soap–neat equilibria, are in good agreement with the values found directly by the delimiting method. The flat for the neat soap–curd phase equilibrium constitutes conclusive experimental proof of the existence of these two forms of soap as independent phases.

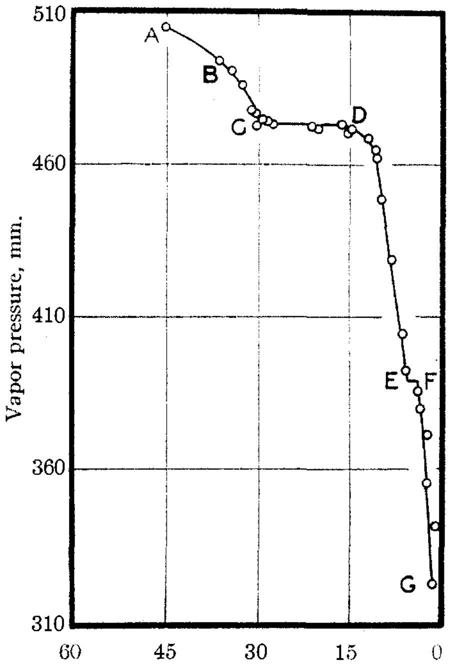

Fig. 3.—The vapor pressure of sodium palmitate–sodium chloride–water systems at 90°: sodium chloride concentration equals 1.22% sodium palmitate concentration.

Figure 2 shows the change in partial pressure with change in water content for systems in which the ratio of salt concentration to soap concentration is held constant at 0.0080. The application of phase rule principles to this curve, coupled with visual observation of the phases present, leads to the following interpretation. Above 28.5% water (point B) neat soap is present. Between 28.5% and 12.5% water (B to C) neat soap and curd phase are present. Since three condensed phases are required for a condition of invariance in a ternary system at set temperature, the pressure is not constant but changes slowly with the total composition. After all the neat soap has disappeared (point C) curd phase alone remains and the pressure falls more rapidly with further decrease in water content. At 9.0% water (point E) a two-phase region, curd phase–lye, is again entered with a resultant slight change in slope of the vapor pressure curve. Between 5.1 and 3.9% water (points F and G) the vapor pressure remains constant, thus showing three condensed phases are present in the system. These are curd phase, saturated lye and solid salt. Below 3.9% water only the two solids, curd phase and crystalline salt, remain and the vapor pressure decreases rapidly and continuously with further decrease in water content.

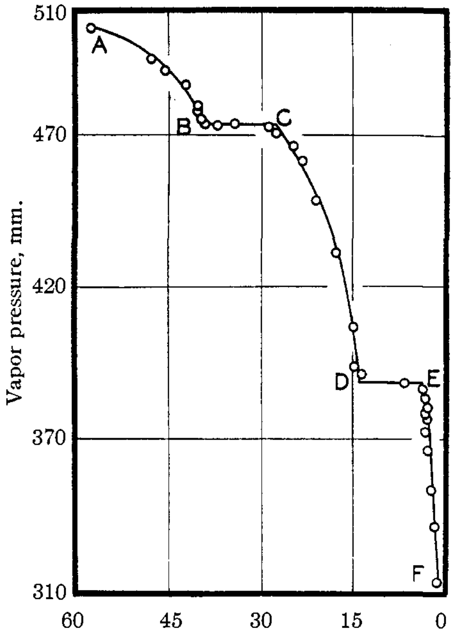

Fig. 4.—The vapor pressure of sodium palmitate–sodium chloride–water systems at 90°: sodium chloride concentration equals 5.27% sodium palmitate concentration.

The change from curd phase to curd phase–lye, evidenced by the inflection in the curve at E, is so slight that it was identified as such only after subsequent work determining the equilibrium diagram had shown the necessity for its existence. The compositions at the ends of flats, indicative of the presence of three condensed phases, are much more accurately determined than are the compositions of inflections representing transitions from one-phase to two-phase regions.

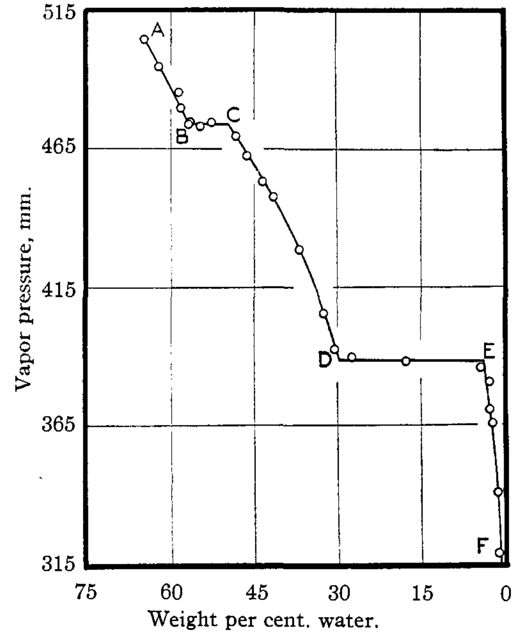

Fig. 5.—The vapor pressure of sodium palmitate–sodium chloride–water systems at 90°: sodium chloride concentration equals 17.70% sodium palmitate concentration.

Figures 3, 4 and 5 show the results at higher relative salt concentrations where progressive decrease in water content results in the formation of two different three-phase equilibria. The compositions at the ends of the higher flat in each curve represent the range within which neat soap, curd phase and lye exist in equilibrium with each other. The lower flat determines the composition range of coexistence of curd phase, saturated lye and solid salt.

The phase equilibrium diagram at 90° is shown in Fig. 6. This diagram is simply a modification of the customary Gibbs triangle for representation of the equilibria in ternary systems and is especially convenient in representing soap systems. Ordinates show the weight per cent. of sodium palmitate and abscissas the weight per cent. of sodium chloride, the per cent. water being obtained by difference. A straight line, passing through the origin and any given composition, represents the compositions of all systems which can be obtained by altering the water content of the original system.

The experimental data on which the equilibrium diagram is based are assembled in Table II. The compositions of the curd phase and neat soap corners of the curd phase–neat soap–lye triangle were determined within about 2% by comparison of the vapor pressure curves for systems with salt to soap concentration ratios of 0.008 and 0.012. On the first curve (Fig. 2) the compositions of curd phase and neat soap at the inflection points (C and B) lie just outside the triangular area; on the second curve (Fig. 3) corresponding points (D and C) lie just inside this area. The composition limits of the neat soap–middle soap–nigre and neat soap–nigre–lye triangles at 90° were obtained indirectly from values for these points at 100°. These compositions at 100° were corrected for the 10° decrease in temperature by the same relative amounts deduced for corresponding points in phase rule diagrams of the system: tallow soap–sodium chloride–water at 100 and 80°.[14] Use also was made of McBain's data showing the change in the isotropic solution boundary in the sodium palmitate–sodium chloride–water system from 100 to 90°.

The following considerations establish the validity of the present experimental results. Theoretically two of the lines forming the boundaries of the neat soap–curd phase–lye triangle should converge to a point on the lye axis corresponding to a lye composition above which curd phase is in equilibrium with lye and below which neat soap is in equilibrium with lye. It is clear from Fig. 6 that the experimental points do fall nicely on straight lines which intersect exactly at a point on the water–salt axis. In all cases the same vapor pressure (473–474 mm.) was found experimentally for all systems having compositions within the triangle.

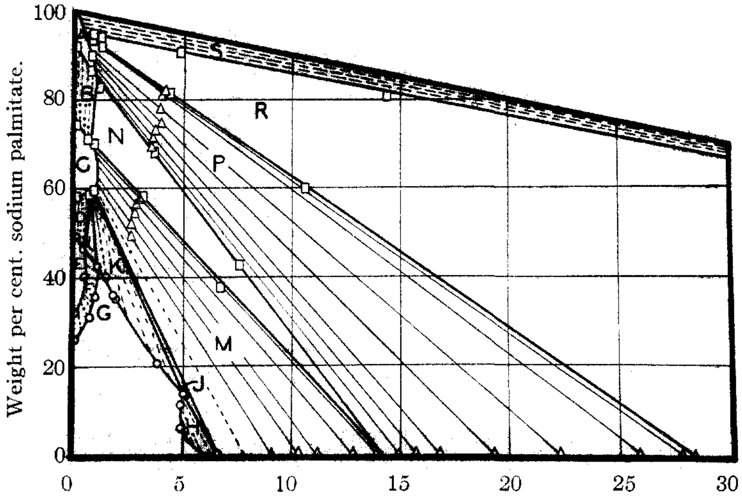

Fig. 6.—The system sodium palmitate–sodium chloride–water at 90°: ○, points from delimiting experiments; □, points from vapor pressure data; △, points from tie line determinations. A, curd phase; B, curd phase–neat; C, neat; D, neat–middle; E, middle; F, middle–nigre; G, nigre; H, nigre–lye; J, neat–nigre–lye; K, neat–nigre; L, middle–neat–nigre; M, neat–lye; N, neat–curd phase–lye; P, curd phase–lye; R, curd phase–lye–salt; S, curd phase–salt.

In the curd phase–saturated lye–solid salt equilibrium theoretically one of the lines forming the sides of the triangle should run to the point representing pure salt and another to the composition of a saturated lye solution (28.4%). As appears in Fig. 6 the experimental points do define two straight lines which satisfy these requirements. Here again the same vapor pressure was found experimentally for all systems within the triangle regardless of wide variations in total composition. Furthermore, the value found for this vapor pressure, 389 mm., is in good agreement with the literature value for the vapor pressure of a saturated salt solution at 90°.[12]

The accuracy of the results by the analytical and phase-delimiting method for equilibria involving fluid soap phases is attested by their self-consistency. Furthermore, the boundaries obtained by this method are in relatively good quantitative agreement with those obtained by McBain[3] by an entirely different method.

Discussion

(a) Description of Phases.—Descriptions of the physical nature of equilibria involving liquid and liquid crystalline soap phases have already been given in considerable detail for several systems, notably tallow soap–sodium chloride–water,[6,15] potassium oleate–potassium chloride–water[16] and potassium laurate–lauric acid–water.[17] Since the corresponding phases in the sodium palmitate–sodium chloride–water system at 90° closely resemble those referred to above, it will be unnecessary to describe them here in detail.

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(14) Unpublished data obtained in this Laboratory.

(15) Ferguson, *Oil & Soap*, **9**, 4–8 (1932).

(16) McBain and Elford, *J. Chem. Soc.*, 424 (1926).

(17) McBain and Field, THIS JOURNAL, **55**, 4786 (1933).

More attention will be devoted to equilibria involving curd phase since these have not been so adequately described.

As appears in Fig. 6 sixteen different equilibrium conditions are possible at 90°, the particular state of any given system being determined by the relative amounts of soap, salt and water present. Inspection of the phase diagram shows the concentration limits for the existence of these various equilibria.

1. Nigre, or isotropic solution of soap and salt (Field G), is a single homogeneous phase, despite its colloidal nature and capacity for existing as mobile liquid, thick viscous liquid or even elastic transparent jelly.

2. Middle soap (Field E) is also a single phase of variable composition, a liquid crystalline solution. It combines the mechanical properties of a stiff fluid having a pronounced yield value[18] with certain of the optical properties of a crystal. Generally it occurs as clear gummy lumps of very great viscosity.

3. Neat soap (Field C), a single phase of variable composition, is another liquid crystalline solution. It is more turbid and at 90° in this system is less viscous than middle soap.

4. Curd phase (Field A) is another single phase of continuously variable composition. It is a crystalline form of solid soap. When formed in the presence of neat soap it is characterized by

TABLE II

EQUILIBRIUM DATA FOR THE SYSTEM NaP-NaCl-H_2O AT 90°. A. PHASE BOUNDARY DATA FROM VAPOR PRESSURE RESULTS

Phases	Composition, % NaP	NaCl
Points on the neat soap boundary	58.0	0.00
	71.4	.57
	74.5	.00
Points on the curd phase boundary	92.5	.00
	90.3	.72
	86.8	.69
	100.0	.00
Points on the neat–lye edge of the neat–curd phase–lye triangle	37.3	6.60
	58.0	3.06
	70.1	0.86
Points on the curd phase–lye edge of the neat–curd phase–lye triangle	42.9	7.60
	68.4	3.60
	83.0	1.03
Points on the curd phase–lye edge of the curd phase–lye–salt triangle	59.9	10.6
	81.7	4.30
	92.4	1.14
	94.2	0.76
Points on the curd phase–salt edge of the curd phase–lye–salt triangle	81.0	14.4
	91.2	4.81
	94.8	1.17
	95.2	0.77

B. PHASE BOUNDARY DATA FROM PHASE RULE REQUIREMENTS AND EXTENSION OF RESULTS FROM VAPOR PRESSURES

Description of point	Composition, % NaP	NaCl	Source of data
Lye apex of neat–curd phase–lye triangle	0	14.3	Vapor pressure of flat confirmed by intersection of sides of triangle
Saturated lye	0	28.4	"I. C. T." data
Solid salt	0	100	Visual observation; assumes no solid solution formation by NaCl
Neat soap in equilibrium with curd phase and lye	70.8	0.65	Intermediate between composition on neat soap boundary just outside the neat–curd–lye triangle and composition just inside the triangle (see Figs. 2 and 3)
Curd phase in equilibrium with neat soap and lye	85.0	.90	Intermediate between composition on curd phase boundary just outside the neat curd–lye triangle and composition just inside the triangle (see Figs. 2 and 3)
Curd phase in equilibrium with lye and solid salt	95.5	.30	Intersection of sides of curd–lye–salt triangle

C. DATA FOR EQUILIBRIA INVOLVING FLUID SOAP PHASES

Phases	Composition % NaP	% NaCl
Points on middle soap boundary	32.0	0
	40.0	0.4
	49.0	0
Points on isotropic solution boundary	6.0	4.9
	11.2	4.9
	13.7	5.0
	20.5	3.8
	35.1	1.9
	35.5	1.8
	40.0	1.4
	40.0	0.8
	35.5	.9
	31.0	.7
	26.0	.0
Apices of neat–middle–nigre triangle	59.0	.7
	46.5	.4
	42.5	1.0
Apices of neat–nigre–lye triangle	59.5	0.8
	13.5	5.1
	0	6.6

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[18] McBain and Watts, *J. Rheology*, **3**, 437 (1932).

TABLE II (*Concluded*)

D. TIE LINE DIRECTIONS DETERMINED FROM TOTAL SYSTEM COMPOSITIONS AND VAPOR PRESSURES

1. Systems in which NaCl concentration = 5.27% soap Concentration. (NaP)

Total system		Vapor pressure, mm.	Lye phase, % NaCl
% NaCl	% NaP		
Phases in equilibrium: neat soap–lye			
2.58	49.2	495	9.1
2.59	51.7	491.5	10.3
2.74	54.5	487	11.2
2.83	56.4	480	12.8
2.98	56.7	478	13.2
3.02	57.5	475.5	13.9
Curd phase–lye			
3.38	67.5	473	14.4
3.49	69.5	471	14.9
3.58	71.7	567	15.7
3.66	73.5	462	16.8
3.97	74.9	449	19.3
3.92	78.3	432	22.3
4.05	81.2	407.5	25.9
4.16	82.5	392	27.8
2. Systems in which NaCl concentration = 17.70% NaP concentration.			
Neat soap–lye			
4.88[a]	32.7	495	9.1
5.44[a]	36.3	486	11.4
6.80	35.2	480	12.8
6.60	37.1	474.5	14.1
Curd phase–lye			
7.80	44.3	470	15.1
8.12	46.0	463	16.55
8.55	48.6	454	18.3
8.80	49.6	448.5	19.4
9.50	53.7	430	22.6
10.2	57.9	406	26.1
10.5	59.3	393	27.8

[a] In these systems salt concentration was only 15% of soap concentration.

the presence of long, lustrous fibers and tufts of shorter, finer fibers. We have obtained these fibers in lengths up to two or three centimeters.

Analysis of fibers in the binary system shows that they consist of neutral soap and water, thus proving that their development is not due to the formation of acid soap. Expulsion of water by drying to constant weight at 105° results in no change in the appearance of the fibers nor are they affected by cooling from 90° to room temperature. Fibers developed in binary systems of sodium palmitate–water were no different in appearance from those formed in the ternary system.

Plates 1, 2 and 3 are typical of the appearance of these fibers. Plate 1 shows a mixture of macroscopic curd phase fibers and neat soap. Plates 2 and 3 are photomicrographs of curd phase fibers at successively higher magnifications. They illustrate the similarity in form between the large fibers visible to the unaided eye and the finer ones visible with the microscope. This same structural form also has been observed in the ultramicroscope.[19]

Curd phase formed without contact with neat soap, as by diffusion of water vapor into anhydrous sodium palmitate, does not develop visible fibers. Under these circumstances the appearance is that of a white solid of granular formation.

5. Two-phase equilibrium between nigre and middle soap (Field F). It is of interest here that addition of salt to the soap solution actually results in an increase in the solubility of the soap.

6. Two-phase equilibrium between nigre and neat soap (Field K). Here increased salt concentration in the soap solution results in a rapid decrease in the solubility of the soap, the saturation phase being liquid crystalline neat soap.

7. Two-phase equilibrium between nigre and lye (Field H). At low soap concentrations sufficient increase in salt concentration results in separation into two isotropic liquid phases.

8. Two-phase equilibrium between neat soap and lye (Field M). Reasonably good separations of molten liquid crystalline neat soap over isotropic lye occur throughout this range of concentrations.

9. Two-phase equilibrium between neat soap and middle soap (Field D). This is a very difficult field in which to obtain separation of phases.

10. Two-phase equilibrium between neat soap and curd phase (Field B). Complete separation of phases was never attained in this range, although a fairly good degree of segregation was obtained in a centrifuge. Even systems of total composition such that they were mostly neat soap appeared to the naked eye to consist primarily of fibrous solid material.

11. Two-phase equilibrium between curd phase and lye (Field P). As the total soap concentration is increased, the appearance of the curd phase changes from a feathery white solid, covered with a fuzz of fine whiskers, to a damp granular solid of no pronounced structure. Sometimes a clear lye layer separated below the soap

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(19) McBain, Darke and Salmon, *Proc. Roy. Soc.* (London), **A98**, 395 (1921).

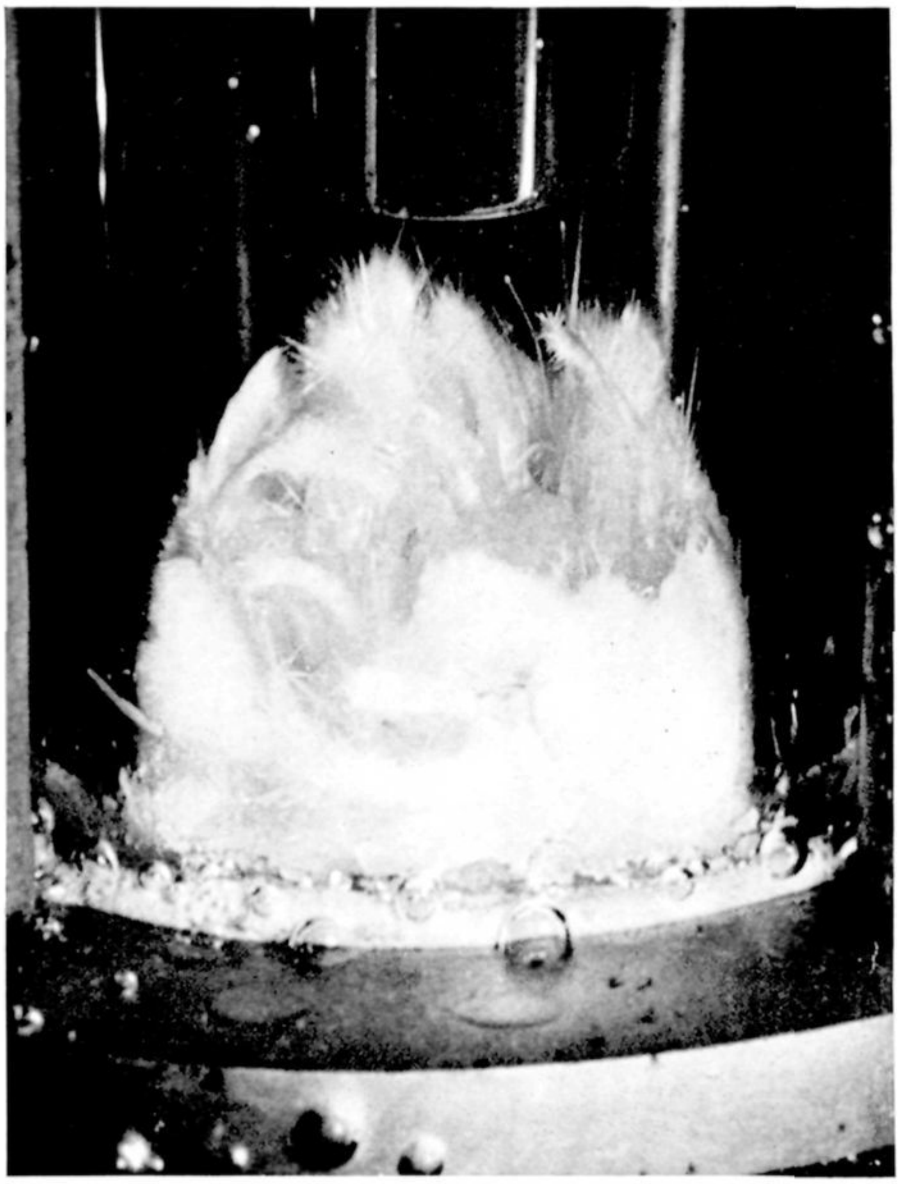

Plate 1.—Macroscopic fibers at 90°: NaP–H_2O system, 76.9% NaP after a few days at 90°.

Plate 2.—Photomicrograph of macroscopic curd fibers: NaP–H_2O system, about 76% NaP, polarized light ×13, crossed Nicols.

Plate 3.—Photomicrograph of macroscopic curd fibers: reflected light ×42.

layer; at other times all the lye was mechanically enmeshed in the curd phase forming a macroscopically homogeneous mass.

12. Two-phase equilibrium between curd phase and solid salt (Field S). The appearance of these systems is very similar to the soap layers found in the region of curd phase–lye equilibria. As the water content is decreased the soap gradually becomes drier and changes from a loosely caked solid to a granular dry free-flowing solid. In most cases crystals of salt can be seen mixed with the soap.

13. Three-phase equilibrium between neat soap, middle soap and nigre (Field L). (Separations have been obtained in certain commercial soap systems.[6])

14. Three-phase equilibrium between neat soap, nigre and lye (Field J). The relatively low soap content of the neat soap separating in the sodium palmitate system compared to that separating in this region in systems of ordinary commercial soaps is of technical interest.

15. Three-phase equilibrium between neat soap, curd phase and lye (Field N). As in the case of curd phase–neat soap equilibria, systems in this composition range usually developed pronounced macroscopic soap fibers. Occasionally a small amount of lye settled out beneath the soap layer but in general these systems appeared macroscopically homogeneous despite the actual presence of three phases.

16. Three-phase equilibrium between curd phase, saturated lye and solid salt (Field R). Here again most of the salt and lye are enmeshed in the curd phase forming a damp mass of white solid. Sometimes crystals of free salt were observed.

(b) **Comparison with Previous Work.**—The present results are in agreement with McBain's general concept of curd phase existing in true reversible equilibrium with neat soap and lye. In the fields of nigres, middle soap, neat soap, middle soap–nigre, middle soap–neat soap–nigre, neat soap–nigre, neat soap–nigre–lye and neat soap–lye our results by phase analysis and delimiting methods are in satisfactory quantitative agreement with McBain's results obtained by extrapolation from observations of temperatures at which phase changes occurred in systems of varying composition.

In the equilibria involving solid soap phases there are considerable discrepancies between the present results obtained by the vapor pressure method and the older work. For instance, our results show that the presence of small amounts of salt in curd phase actually increases the amount of water it can contain before "melting" to neat soap, whereas McBain tentatively drew the phase boundary as though the water content of curd phase decreased on addition of salt. However, this is not a difference in kind but only of degree. It is not surprising inasmuch as previous diagrams of the equilibria involving curd phase were derived from a few scattered incidental observations by a process of reasonable deduction rather than from systematic experimental data. The upper apex of our curd–lye–salt triangle is considerably different from McBain's. This may be due to a difference in the soap used, in the method of preparation of the soap before determining the vapor pressure, or to a systematic error in the older vapor pressure work.

(c) **Nature of Curd Phase.**—The present work, in agreement with the first work of McBain and collaborators, shows that curd phase in this system consists of sodium palmitate associated with varying amounts of salt and water. On the basis of the fact that at room temperature quite different amounts of water can be contained in the curd phase, McBain[3,10] tentatively assumed the existence of definite sodium palmitate hydrates. Contrary to this hypothesis all the present work favors the view that the curd phase of sodium palmitate at 90° is a single phase of continuously variable composition.

Let us consider the vapor pressure—composition curve for the binary system, sodium palmitate–water, at 90°. If there is a stoichiometric hydrate, application of the phase rule in its usual form necessitates a flat in the vapor pressure curve corresponding to the equilibrium between anhydrous sodium palmitate and the hydrate. Actually the vapor pressure of curd phase at 90° was found to decrease continuously with decrease in water content.

Points on the curd phase boundary could not be obtained directly by phase analysis or delimiting experiments because of incomplete separation of phases. However, in many cases tie-line directions could be ascertained by analysis even though the composition of the uncontaminated soap phase at the end of the tie-line remained unknown. All tie lines involving curd phase extrapolated to points of continuously variable composition on the curd phase boundary. If curd phase consisted of one or more definite hydrates these tie-lines would have had to converge to the points representing the compositions of the hydrates. In this connection it might also be mentioned that in an earlier paper McBain[5] himself has commented on the fact that the water content of soap curd appears to vary continuously with the concentration of the electrolyte used to salt it out.

Summary

An isopiestic vapor pressure method has been developed which is suitable for studying soap systems at high temperatures and high soap concentrations where the usual methods based on observation of phase changes or analysis of phases are inapplicable due to non-separation of phases. By means of vapor pressure measurements in a pure single soap system at 90°, it has been demonstrated (a) that curd phase can exist in true reversible equilibrium with neat soap, and that the two are separate phases; (b) that no stoichiometric hydrates occur in the system at 90°, the curd phase varying continuously in water content.

The complete equilibrium diagram has been drawn for the system sodium palmitate–sodium chloride–water at 90°.

The formation and appearance of curd fibers have been described.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

The Preparation of Some Higher Alkylglucosides

BY C. R. NOLLER AND W. C. ROCKWELL

The following records the preparation and some properties of *n*-hexyl-, *n*-octyl-, *n*-nonyl-, *n*-decyl- and *n*-dodecylglucoside. These compounds were synthesized in order to make available for physical-chemical investigations pure surface-active compounds of known constitution that have suitable solubility characteristics and do not ionize in aqueous solutions.

The method of synthesis was essentially that of Fischer and his co-workers,[1] namely, the condensation of acetobromoglucose with the appropriate alcohol and hydrolysis of the tetraacetyl derivative to the alkyl glucoside. One important change was made in the method of deacetylating the tetraacetates, namely, the replacement of hydrolysis using barium hydroxide or ammonium hydroxide by catalytic transesterification[2] with methyl alcohol and sodium methoxide. In this way the time of hydrolysis is greatly reduced and the isolation of the pure glucoside is simplified.

It will be noted from the tables that while the melting points of the tetraacetyl derivatives are fairly sharp, those of the alkyl glucosides especially from octyl up are over a very wide range. This was noted by Fischer and Helferich,[1] who stated that they were unable to explain the phenomenon. We have noted that during a melting point determination the solid changed to a semi-transparent state at the lower temperature noted. On further raising the temperature little change took place until the higher temperature was reached when sharp melting to a clear liquid occurred. It appears to us that the lower temperature marks the transition from the solid to the liquid–crystal state and the higher temperature the transition from the liquid–crystal to the liquid state.

n-Hexylglucoside is very soluble in water and its aqueous solutions show little tendency to foam on shaking. As the length of the alkyl group increases the foam-producing ability is greatly increased, the nonyl-, decyl- and dodecylglucosides giving very stable foams. The solubility in water decreases, the dodecylglucoside being only sparingly soluble in cold water but readily in hot water. Cetylglucoside was reported by Fischer and Helferich[1] as being insoluble in water.

It was not determined whether these glucosides are hydrolyzed by emulsion but the work of Fischer and Helferich and the observed negative rotations would indicate that they are β-glucosides.

Experimental

Pentaacetylglucose and Acetobromoglucose.—When pentaacetylglucose was prepared according to the proced-

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[1] Fischer and Raske, *Ber.*, **42**, 1465 (1909); Fischer and Helferich, *Ann.*, **383**, 68 (1911).

[2] Fischer and Bergmann, *Ber.*, **52**, 852 (1919); Zemplén and Pacsu, *ibid.*, **62**, 1613 (1929).