

Chloroplatinic Acid and Dithiane.—The mixing of dioxane solutions containing, respectively, four mols. of dithiane and one of chloroplatinic acid gave the yellow compound $\text{PtCl}_4 \cdot \text{C}_4\text{H}_8\text{S}_2$, reported by Husemann.⁵ This was removed by filtration after thirty minutes. In the filtrate, a finely divided lemon-yellow crystalline precipitate continuously formed for eighteen days. Analysis showed this precipitate to be $\text{PtCl}_4 \cdot \text{C}_4\text{H}_8\text{S}_2 \cdot \text{C}_4\text{H}_8\text{O}_2$. It is insoluble in water and common organic solvents and soluble in liquid phenol.

Anal. Calcd. for $\text{PtCl}_4 \cdot \text{C}_4\text{H}_8\text{S}_2 \cdot \text{C}_4\text{H}_8\text{O}_2$: Pt, 35.82. Found: Pt, 36.24, 36.31, 36.38.

Lead Perchlorate and Lead Ethyl Mercaptide.—Lead mercaptide⁸ was added to a very concentrated solution of lead perchlorate and the mixture heated on the water bath. After two days, the light yellow product was filtered, washed with cold water, and dried in air.

Anal. Calcd. for $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{Pb}(\text{SC}_2\text{H}_5)_2$: 1:3. Found: 1:3.02, 1:2.96, 1:2.98.

Chloroauric Acid and Aurous Ethyl Mercaptide.—To 1.09 g. of dry aurous ethyl mercaptide were added 1.72 g. of freshly prepared chloroauric acid and 50 ml. of chloro-

(8) Lead mercaptide was difficult to obtain in stable form, but was finally prepared with success by dissolving litharge in 6 *N* sodium hydroxide solution and adding an equivalent quantity of ethyl mercaptan, also dissolved in 6 *N* sodium hydroxide, the mixture being cooled by cracked ice. The bright yellow precipitate was washed with water and then dried over calcium chloride in a desiccator.

form, containing 0.75% alcohol. The suspension was stirred and, after three minutes, filtered. On standing the filtrate turned from red to yellow and bright yellow needles slowly deposited. The solid was washed with chloroform.

Anal. Calcd. for $\text{AuCl}_2(\text{SC}_2\text{H}_5)$: Au, 59.91; Cl, 20.93. Found: Au, 60.08, 60.05; Cl, 20.63, 20.26.

This compound is also obtained by heating aurous mercaptide with aqua regia, made from the 6 *N* acids.

Summary

1. The probable presence of soluble $[\text{Hg}(\text{HgS})](\text{ClO}_4)_2$ as an intermediate product in the precipitation of mercuric sulfide by the action of hydrogen sulfide upon mercuric perchlorate has been confirmed by the electrolysis of its solution.

2. The analogous oxygen compound has been prepared.

3. Addition compounds of dithiane and metallic salts corresponding to dioxane addition compounds have been prepared.

4. The metal salt addition complexes of ethyl mercaptides have been studied.

5. Lead mercaptide has been prepared in pure stable condition.

SEATTLE, WASH.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

A Phase Rule Study¹ of the Mixed Soap System Sodium Palmitate–Sodium Laurate–Sodium Chloride–Water at 90°

BY JAMES W. MCBAIN, ROBERT D. VOLD AND WALTER T. JAMESON

Proceeding from the known phase behavior of systems made from pure single soaps, the present work undertakes to ascertain the results of using the simplest mixture, that containing two single soaps. The correlation of these results with the properties of the two pure soaps is of interest.

Studies of commercial soap systems² have shown that where only liquid or liquid crystalline phases are involved, the behavior of a mixture of soaps with salt and water is qualitatively the same as that of a single soap. Quantitatively, the salt concentrations at the various phase boundaries are closer to the values for the soap of lower molecular weight than to the average of the values for the two separate soaps. In the system potassium oleate–potassium laurate–water, the same

phases are found as with either soap alone and here again, where the soap is an equimolar mixture of potassium oleate and potassium laurate, the phase boundaries occur at soap concentrations twice as close to those for $\text{KL}-\text{H}_2\text{O}$ as for $\text{KOL}-\text{H}_2\text{O}$.³

Sodium palmitate and sodium laurate were selected for the present study since their phase rule diagrams with salt and water are well known,⁴ and since the two soaps differ only in the length of the hydrocarbon chain. The isotropic solution boundary and the position of the neat–nigre–lye triangle are here determined in the $\text{NaP}-\text{NaL}-\text{NaCl}-\text{H}_2\text{O}$ system at 90° for the cases (a) that the soap is 50 wt. % sodium palmitate, 50 wt. % sodium laurate and (b) that the soap is 75 wt. % so-

(1) See THIS JOURNAL, 60, 1866 (1938), for preceding papers in this series.

(2) J. W. McBain in Alexander's "Colloid Chemistry," Vol. 1, 1926, p. 160; R. H. Ferguson and A. S. Richardson, *Ind. Eng. Chem.*, 24, 1329 (1932).

(3) J. W. McBain, L. H. Lazarus and A. V. Pitter, *Z. physik. Chem.*, A147, 87 (1930).

(4) Cf. reference 3; R. D. Vold and R. H. Ferguson, THIS JOURNAL, 60, 2066 (1938); J. W. McBain, G. C. Brock, R. D. Vold and M. J. Vold, *ibid.*, 60, 1870 (1938).

dium palmitate and 25 wt. % sodium laurate. In the latter case we have also examined the boundary of the field neat-lye corresponding to the neat-lye edge of the triangle neat soap-curd fibers-lye of the simple ternary system.

Materials and Procedure.—The sodium laurate was from the same stock used for previous phase rule studies.^{4c} It was dried to constant weight at 105° shortly before use. That this procedure results in very nearly anhydrous soap was proved directly by analysis of the product for fatty acid content and for combined sodium, and by the fact that the loss of weight on subsequent heating under vacuum to 260° was only 0.5%, and by the agreement between the melting point to isotropic liquid of this material (313° corr.) and the value for anhydrous sodium laurate (310°).^{5, 5a} This result is at variance with the behavior described by Lawrence,⁶ who believes that drying of sodium soaps at temperatures slightly above 100° results in a monohydrate rather than in anhydrous material.

The sodium palmitate was a special preparation made by Kahlbaum and found by analysis to be exactly neutral. It was dried to constant weight at 105° shortly before use.

Kahlbaum sodium chloride "for analysis" was dried and used throughout. It was found unnecessary to take special precautions to exclude carbon dioxide from the distilled water that was used.

The experimental methods employed closely resemble those previously described.^{4c} In all cases the calculated quantities of salt, water and soap, total 5 g., were weighed into Pyrex tubes (12 cm. long, 16 mm. o. d., walls 3 mm. thick) which were sealed off immediately to prevent changes in composition. The mixed soap was prepared by weighing out the requisite amounts, mixing, grinding and redrying.

In determining the isotropic solution boundary both the delimiting and the synthetic methods were used. All the T_1 values (temperatures at which a liquid or liquid crystalline phase forms in the isotropic solution on cooling) recorded in the tables are the average of two or more determinations. Duplicate determinations usually agreed within 2° except when middle soap was the saturation phase. In this case the transition temperature was marked only by the appearance of small globules of clear middle soap around the walls of the tube rather than by the usual development of cloudiness throughout the system. Consequently, these temperatures may be in error by as much as 5°. However, since the position of the isotropic solution boundary with middle soap as the saturation phase changes very slowly with temperature, this experimental uncertainty introduces no significant error in the phase rule diagram calculated from the data.

With some of the more dilute systems, determinations of T_1 were difficult because even the isotropic solution was slightly hazy due to the presence of finely divided suspended acid soap. This haziness was removed by using 0.005 *N* sodium hydroxide solution instead of water. Tests made on four otherwise identical systems showed

(5) Vorländer, *Ber.*, **43**, 3120 (1910).

(5a) Recent work has thrown considerable doubt on all previous determinations of the melting point of anhydrous sodium laurate, including that published from this Laboratory. An account of this work will be published shortly.

(6) A. S. C. Lawrence, *Trans. Faraday Soc.*, **34**, 660 (1938).

that the same value of T_1 was obtained within one degree regardless of whether water or the dilute alkali was used in the preparation of the tubes.

That the delimiting and the synthetic methods yield strictly comparable results is evident from the following table which gives concentrations on the isotropic solution boundary for the system (50 wt. % NaP-50 wt. % NaL)-NaCl-H₂O at 90°.

Delimiting % soap	method % salt	Synthetic method		
		% soap	% salt	Tubes used
35.0	5.37	35.0	5.35	M25 and M28
		35.0	5.41	M25 and M26
		35.0	5.31	M26 and M28
25.0	7.3	25.0	7.35	M7 and M8
		25.0	7.10	M8 and M18
		25.0	6.94	M7 and M18

The concentration range in which neat soap, nigre and lye coexist was determined by the delimiting method. The increase in accuracy because of the fact that the sides of this triangular region in the phase rule diagram must be straight lines made it possible to locate this area within 0.1% as regards salt concentration. In the case of the 75 wt. % NaP-25 wt. % NaL soap the accuracy of this determination was checked by preparation of three three-phase systems which were equilibrated at 90° and then the lye analyzed. The salt concentrations in the lye were 9.59, 9.61 and 9.57 wt. %, respectively; values in good agreement with the figure previously deduced from the delimiting experiments, 9.6%.

The synthetic method was used for determination of the limiting concentrations of the neat-lye field in the (75 wt. % NaP-25 wt. % NaL)-NaCl-H₂O system. Tubes were first heated to homogeneity and then cooled to room temperature where the system was a white solid. They were then heated gradually and the temperature T_0 noted at which the last trace of white "solid" disappeared. To avoid error due to slow "melting" of the "solid," the tubes were usually left for a half hour or so at each temperature, the temperature being raised in steps of one or two degrees. These observations, unlike the determinations of T_1 in which transmitted light was used, were best made by reflected light.

Determinations of T_0 on systems of a single soap with salt and water at concentrations similar to those involved in the present work are made easily since the white crystals or curd fibers are readily distinguishable from the mixture of translucent plastic neat soap and clear lye present after melting. The neat soap to which the "solid" melted in the 75 wt. % NaP-25 wt. % NaL system is itself rather white and "grained" in appearance. Rapid heating to a temperature almost high enough to cause further melting to nigre and lye caused no change in appearance, but long standing at 90° (two weeks) resulted in a decrease in opacity and a close approach to the usual appearance of settled neat soap. In the 50 wt. % NaP-50 wt. % NaL system the change in appearance from the white solid at room temperature to the less opaque plastic substance of higher temperatures occurred so gradually that the transition temperature could not be determined visually.

A New Soap Phase—Waxy Soap.—Interpretation of these determinations of T_0 , previously defined^{4a} as temperatures at which the last trace of curd fibers disappears on heating, is complicated by the presence of a previously unknown phase in the sodium laurate system at 90° .^{7a} Its existence in this system has been established by dilatometric and vapor pressure measurements.^{7b} This new phase, which we shall call waxy soap on account of its general appearance, occurs in the case of anhydrous soaps at temperatures intermediate between the melting point of the curd fibers (curd phase) and the solidification point of the liquid crystal. Its appearance is often so similar to that of curd phase that the transition temperature between the two cannot be determined at all accurately by visual observation. In the NaL-H₂O system at 90° waxy soap occurs at concentrations between the fields, curd fibers and neat soap. It is not present in the NaP-H₂O system at this temperature.

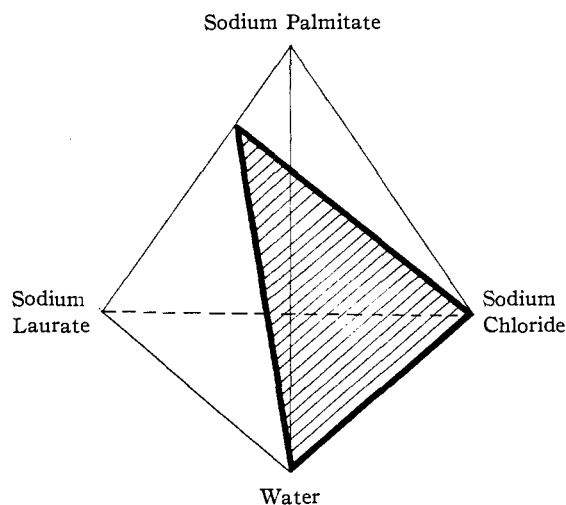


Fig. 1.—The relation of a section showing the phase behavior at a constant concentration ratio of sodium palmitate and sodium laurate to the tetrahedron showing the complete isothermal phase behavior of the quaternary system.

In the ternary system NaP-NaCl-H₂O at temperatures around 90° it is known that the temperature of disappearance of the last curd fiber gives a point on the neat-lye edge of the triangle neat-curd phase-lye. In the system NaL-NaCl-H₂O the corresponding T_0 determinations probably serve to locate the neat-lye edge of a triangle neat soap-waxy soap-lye, rather than of neat soap-curd fibers-lye, as reported in our preceding paper.^{4a} In the mixed soap systems the T_0 values determine the limiting concentrations of soap and salt at which the system exists as neat soap and lye, but leave unspecified the nature of the last trace of white "solid" which disappears. Although the following possibilities are not equally probable, it might be a curd phase of sodium palmitate, or of sodium laurate,

(7) (a) The discovery of this phase in the sodium palmitate system, and also of several other new phases, is described in a paper by R. D. Vold, R. Roseveare and R. H. Ferguson, presented at the Chicago meeting of the American Oil Chemists' Society, October, 1938. (b) R. D. Vold and M. J. Vold, *THIS JOURNAL*, **60**, 37 (1938).

or a waxy form of either soap, or a "solid solution" of the two, or a mixture of two waxy or curd phases.

Results

Since the system NaP-NaL-NaCl-H₂O is one of four components a tetrahedron (Fig. 1) is required for complete representation of the phase behavior at constant temperature. Since plane projections of such a figure are difficult to read we have chosen instead a series of triangular sections through the isothermal tetrahedron at different constant ratios of sodium palmitate to sodium laurate. Consideration of these diagrams together with the previously published data for NaP-NaCl-H₂O and NaL-NaCl-H₂O, permits a fair estimate to be made of the course of the boundaries within the solid figure.

The relation between the plane diagrams by which the present data are expressed and the total system is shown in Fig. 1. The actual diagrams which were constructed differ from this schematic section only in that the triangle has been distorted to give a right triangle for greater ease in plotting and reading the data, and in that the whole triangle is not shown. Where only liquid and liquid crystalline phases are involved, fractionation of the two soaps does not occur, so the composition of all such phases lies in the plane of the section which is then similar in all respects to an isothermal section through the triangular right prism used for depicting the phase behavior of ternary systems over the whole range of temperature. Where solid or waxy phases are involved fractionation may occur with the result that tie lines may not lie in the plane of the section, but may run to phase compositions located elsewhere in the tetrahedron.

The delimiting data on the system (50 wt. % NaP-50 wt. % NaL)-NaCl-H₂O, together with a few observations of the temperatures T_i at which neat soap or middle soap just separate from the isotropic solution, are assembled in Table II. Some idea of the relative amounts of the different phases may be obtained from their apparent volumes as indicated by their linear heights in the tube, recorded in the fifth column. The phase diagram shown in Fig. 2 was obtained by plotting these points and drawing in boundaries concordant with all the data, except for the boundary of the isotropic solution in equilibrium with middle soap, which was obtained by the synthetic method.

TABLE II
DELIMITING DATA ON THE SYSTEM (50 Wt. % NaP-50 Wt. % NaL)-NaCl-H₂O

Tube	Composition		T_i	State of the system at 90°
	Soap wt., %	NaCl wt., %		
M1	4.72	7.77	..	Homogeneous nigre
M2	4.99	8.90	..	Homogeneous nigre
M3	11.6	8.55	..	Homogeneous nigre
M4	11.5	9.22	..	Homogeneous nigre
M5	11.5	9.83	..	On neat-nigre boundary
M6	25.1	5.70	..	Homogeneous nigre
M7	25.1	6.40	65.5	Homogeneous nigre
M8	25.0	7.00	81	Homogeneous nigre
M9	25.0	7.70	..	31 mm. nigre; 14 mm. neat
M11	24.9	8.46	..	18 mm. neat; 28 mm. lye
M12	11.5	10.3	..	8 mm. neat; 34 mm. lye
M13	5.00	9.70	..	Homogeneous nigre
M14	5.00	10.6	..	15 mm. nigre; 25 mm. lye
M15	5.00	10.4	..	14 mm. nigre; 33 mm. lye
M16	5.00	11.0	..	13 mm. nigre; 35 mm. lye
M17	25.0	8.00	..	20 mm. neat; 15 mm. nigre; 13 mm. lye
M18	25.0	7.32	109	2 mm. neat; 50 mm. nigre
M19	5.00	10.0	..	Homogeneous nigre
M20	10.0	9.60	..	Homogeneous nigre
M21	9.00	9.80	..	Homogeneous nigre
M22	8.50	10.0	..	Homogeneous nigre (opalescent)
M23	35.1	6.5	..	30 mm. neat; 23 mm. lye
M24	8.00	10.2	..	34 mm. nigre; 10 mm. lye
M25	35.0	5.20	79.5	Homogeneous nigre
M26	35.0	4.81	61	Homogeneous nigre
M27	35.0	6.20	..	27 mm. neat; 20 mm. nigre; 5 mm. lye
M28	35.1	5.50	100	44 mm. nigre; 1 mm. lye
M31	4.95	9.96	..	Homogeneous nigre
M47	32.5	0.00	83	Homogeneous nigre
M47a ^a	32.5	.00	83	Homogeneous nigre
M48	34.5	.00	100	Nigre and middle
M48a ^a	34.5	.00	100	Nigre and middle
M49	36.0	1.00	110	Nigre and middle
M49a ^a	36.0	1.00	110	Nigre and middle
M50	35.0	1.20	95	Nigre and middle
M50a ^a	35.0	1.20	95	Nigre and middle

^a Tubes prepared using 0.005 *N* sodium hydroxide solution instead of distilled water.

Table III contains the data for the system (75 wt. % NaP-25 wt. % NaL)-NaCl-H₂O at 90°. All systems listed in this table were prepared using 0.005 *N* sodium hydroxide solution instead of water.

Additional data on this system are presented in Table IV. This table gives the temperatures T_c at which the last trace of white "solid" disappears. The upper concentration limit of the neat-lye field at 90° was constructed from these data. The table also contains values of T_i , T_Δ and T'_Δ from which it is possible to calculate the boundary of the isotropic solution field and the position of the neat-nigre-lye triangle at elevated temperatures. T_i in this instance is the temperature at which nigre and lye were formed on cooling the isotropic solution. T_Δ is the temperature

at which on further cooling the nigre-lye system began to separate neat soap. T'_Δ is the temperature at which the neat-lye systems just began to form nigre on very slow heating.

In addition to the work on the mixed soap systems a few tubes were prepared using pure sodium laurate. In general the values obtained from these tubes agreed exactly with the results already published.^{4c} However, a small but, for purposes of the present paper, significant shift was made in the salt concentration of the isotropic solution boundary at 35% soap (from 5.4 to 6.09%) in the NaL-NaCl-H₂O system at 90°.

The equilibrium phase diagrams for the two mixed soap systems are shown in Figs. 2 and 3. The concentration limits of the existence of isotropic solutions and the concentration range

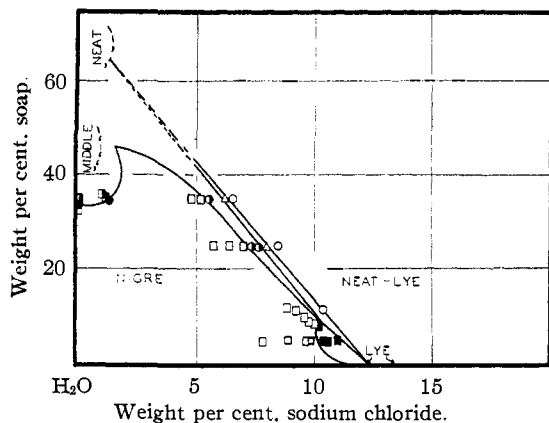


Fig. 2.—Phase equilibria in the (50 wt. % NaP-50 wt. % NaL)-NaCl-H₂O system at 90°: ●, points on the boundary, calculated by the synthetic method; □, nigre; ■, middle soap and nigre; ○, neat soap and nigre; ■, nigre and lye; △, neat soap, nigre and lye; ○, neat soap and lye.

within which the three phases neat-nigre-lye co-exist at 90° are shown for both systems of mixed soap. In addition, in Fig. 3, the concentration

limits are shown above which solid or waxy soap appears in the system.

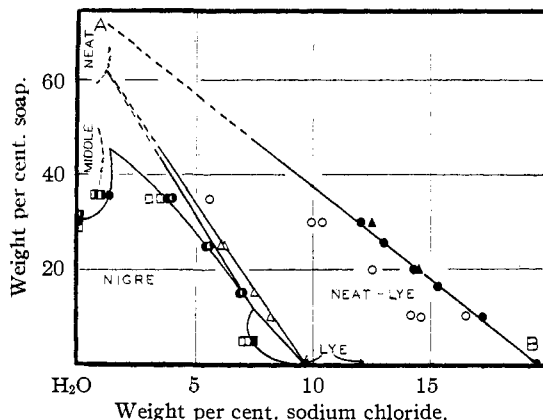


Fig. 3.—Phase equilibria in the (75 wt. % NaP-25 wt. % NaL)-NaCl-H₂O system at 90°: ●, points on the boundaries, calculated by the synthetic method; □, nigre; ■, middle soap and nigre; ○, neat soap and nigre; ■, nigre and lye; △, neat soap, nigre and lye; ●, point obtained by analysis; ○, neat soap and lye; ▲, neat soap, lye and a solid or waxy phase.

TABLE III
THE SYSTEM (75 WT. % NaP-25 WT. % NaL)-NaCl-H₂O.
TEMPERATURES AT WHICH ISOTROPIC SOLUTION SEPARATES
A LIQUID CRYSTALLINE OR A SECOND LIQUID PHASE

Soap wt., %	NaCl wt., %	T _i	State of the system at 90°
34.9	2.97	...	Homogeneous nigre
34.9	3.50	72	Homogeneous nigre
35.0	4.01	102	Neat and nigre
25.0	5.59	103	Neat and nigre
25.0	6.10	133	Neat, nigre and lye
15.0	7.00	94	Neat and nigre
15.0	7.50	120	Neat, nigre and lye
35.0	5.59	...	Neat and lye
5.00	6.99	68	Homogeneous nigre
5.01	7.51	112	Nigre and lye
29.0	0.00	80	Homogeneous nigre
31.0	.00	102	Nigre and middle
35.4	.70	131	Nigre and middle
35.5	1.00	108	Nigre and middle
5.00	7.30	75	Homogeneous nigre
25.0	6.28	...	Neat, nigre and lye

TABLE IV
ADDITIONAL TEMPERATURES OF PHASE CHANGES IN THE
SYSTEM (75 WT. % NaP-25 WT. % NaL)-NaCl-H₂O

Soap wt., %	NaCl wt., %	T _i	T _Δ	T' _Δ	T _c
10.75	14.3	280	225	218	80
9.90	14.6	276	224	211	83
29.8	9.95	253	231	224	82
30.0	10.4	258	230	217	84
9.96	16.5	300	237	234	88
30.0	12.5	300	245	234	92
20.0	12.5	277	228	218	85
20.0	14.5	305	242	237	91

Figure 4 shows the boundary of the isotropic solution field for the two systems of mixed soap and for the two systems of pure soap. This dia-

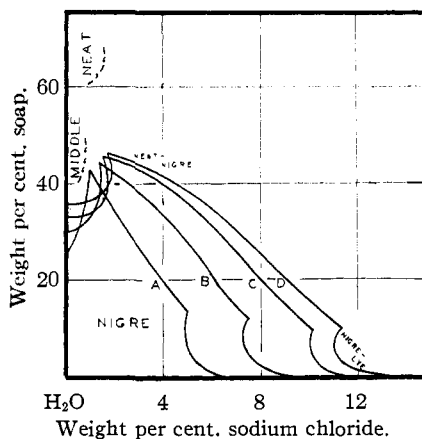


Fig. 4.—Isotropic solution boundaries at 90°: A, NaP-NaCl-H₂O; B, (75 wt. % NaP-25 wt. % NaL)-NaCl-H₂O; C, (50 wt. % NaP-50 wt. % NaL)-NaCl-H₂O; D, NaL-NaCl-H₂O.

gram is the basis for the comparison of the different systems and was used in the construction of Fig. 5.

Comparison of the position of any given phase boundary in the four systems is made most conveniently in terms of the weight per cent. of salt at constant total soap concentration required to

effect a given phase change. In Fig. 5 this limiting salt concentration, expressed as the percentage of the total difference between the salt concentrations for pure palmitate and pure laurate, is plotted against the percentage of laurate in the soap. The curves shown in Fig. 5 all refer to salting out of isotropic solution into neat soap and nigre, but at different total concentrations of soap. It is clear that these three curves might be replaced by a single curve which would give the position of this portion of the isotropic solution boundary within 5% at any total soap concentration.

Furthermore, this same single curve holds equally well for the neat-nigre-lye triangle and for the isotropic solution boundary of the nigre-lye "bay" region. Consequently, Fig. 5 makes it possible to predict the phase behavior—so far as liquid and liquid crystalline phases are concerned—of any mixtures of sodium palmitate and sodium laurate from a knowledge of the phase diagrams of the two soaps separately. Generally speaking, determination of the phase behavior of two or three mixtures of any two soap stocks with salt and water will permit construction of a diagram similar to Fig. 5 from which the phase behavior of any mixture of the two soaps can be ascertained.

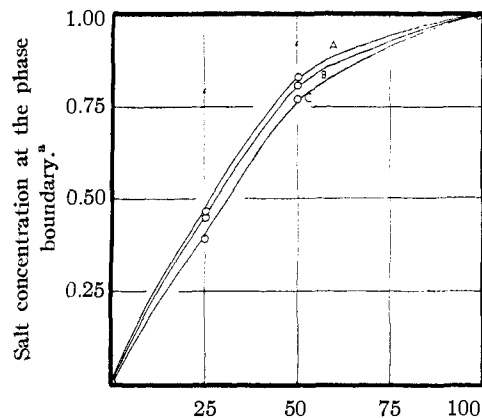
The utility of Fig. 5 is brought out clearly by the following additional experiment with a 25 wt. % NaP-75 wt. % NaL soap. According to Fig. 5 the isotropic solution boundary at 90° for such a system at 25 wt. % total soap should occur at a salt concentration equal to that of the palmitate system alone plus 93% of the difference between laurate and palmitate, *i. e.*, at $3.2 + 0.93(8.0 - 3.2) = 7.7\%$ sodium chloride. To test this prediction two tubes were prepared each with 25% total soap but one with 7.00% salt and the other with 9.03% salt. The isotropic solution in the first tube separated into neat soap and nigre at 57°, while T_i for the second tube was 129°. The salt concentration, x , at the boundary at 90° is given by the expression

$$\frac{9.03 - 7.00}{9.03 - x} = \frac{129 - 57}{129 - 90}$$

Solving, $x = 7.78\%$ salt, a result which is in very satisfactory agreement with the value 7.7% predicted from the curve of Fig. 5.

Discussion

As is evident from Fig. 4 the isotropic solution boundary in the mixed soap systems occurs at salt



Weight per cent. sodium laurate in the soap.

Fig. 5.—Relation of the position of the phase boundaries in the mixed soap system to their position in the pure soap systems: A, total soap concentration, 35 wt. %; B, total soap concentration, 25 wt. %; C, total soap concentration, 15 wt. %.

^a Expressed in terms of additional salt concentration above the value for sodium palmitate, divided by the total difference between sodium palmitate and sodium laurate values.

concentrations intermediate between those found in the single soap systems. If the factor limiting the solubility of the soap in the salt solution is principally the necessity of having a certain minimum concentration of water per methylene group, then the solubilities of two saturated soaps would be expected to vary inversely as the length of the hydrocarbon chain. Also on this basis, the solubility of an equimolar mixture of two saturated soaps should be the arithmetic mean of the solubilities of the two pure soaps; *i. e.*, the curves of Fig. 5 would be replaced by a straight line between the values for the single soaps. The observed behavior is not additive in this sense, however, since the boundaries are considerably closer to the laurate than the palmitate. Thus, on the basis of additive behavior, the salt concentration at the phase boundary in the 50 wt. % mixture should occur 55.6% of the way from the palmitate to laurate whereas experimentally it is found to be about 76% of the way toward the laurate.

The very fact that the observed behavior is so far from additive may be taken as evidence for the interaction of the two soaps in solution. In these solutions it is well established⁸ that most of the soap is present as colloidal micelles. It seems likely, as has been suggested previously,⁸ that the presence of short laurate molecules among the longer palmitate molecules decreases the stability

(8) J. W. McBain and C. S. Salmon, *THIS JOURNAL*, **42**, 426 (1920).

of the micelle in solution. Consequently, a higher soap concentration or a lower activity of the water (higher salt concentration) is required before the structure of the mixed micelles becomes sufficiently organized to permit separation from the solution as a different phase.

Exactly the same relations hold for the position of the neat-nigre-lye triangle in the mixed soap system as for the isotropic solution boundary. Here again the solubility of the mixed soap, regarded as proportional to the salt concentration required for formation of neat-nigre-lye is considerably greater than would be the case if the palmitate and laurate were behaving independently in the liquid and liquid crystalline phases.

Where phases other than nigre, lye, middle soap or neat soap are involved, as in the limit of the neat-lye field shown in Fig. 3, the phase boundaries in the mixed soap system no longer bear the relation to their position in the pure soap systems shown in Fig. 5. In this case the solubility in the mixed soap system is proportionally greater; *i. e.*, a much greater salt concentration is required to cause the formation of solid or waxy soap than would be predicted from Fig. 5. With a 75 wt. % NaP-25 wt. % NaL soap, formation of white "solid" does not occur until the salt concentration is very nearly as high as that required for formation of waxy soap in the pure sodium laurate system. In other words, the solubility of sodium palmitate is effectively raised to that of sodium laurate. This is a matter of considerable practical importance since it shows that a less soluble soap can be prevented from separating as "curd" simply by addition to the system of a soap of shorter chain length. This is a part of the art of the practical soap boiler which assumed great importance after the introduction of oils and fats hardened by hydrogenation.

The boundary of the neat-lye field, line AB of Fig. 3, is a *straight line*. Furthermore, its intersection with the salt-water axis in this quaternary system, rich in sodium palmitate, occurs at identically the same salt concentration as the lye corner of the neat-waxy soap-lye triangle in the ternary NaL-NaCl-H₂O system. It is conceivable that either or both of these experimental facts is a chance occurrence of no phase rule significance. If, however, significance can be attached to both facts there is only one plausible interpretation.

The fact that the boundary is a straight line

means either that (1) it is the edge of a triangle representing an isothermally invariant equilibrium in a pseudo-ternary system between three condensed phases, or (2) it is one edge of a region of four condensed phases formed by the intersection of the plane section of Fig. 1 with a solid figure representing an invariant four-phase equilibrium within the isothermal tetrahedral model of the quaternary system. The first alternative is highly improbable because, first, it requires that the identity in composition of lye be regarded as a coincidence. Secondly, it requires the assumption that sodium palmitate and sodium laurate can form a continuous series of solid solutions despite their different chain length and despite any difference between curd fiber and waxy form, in order to maintain the condition of no fractionation. It should be noted that extensive fractionation has been found experimentally with sodium oleate-sodium palmitate solutions on formation of curd.⁹ Lastly, if there is no fractionation on formation of curd fiber or waxy phases this boundary in the mixed soap system, contrary to the observed behavior, should have occurred at the same position relative to the pure soap systems as do the other phase boundaries in the mixed soap system.

If the boundary line AB marks the intersection of the plane section shown in Fig. 3 with a four phase region,¹⁰ one apex of this region is located almost on the salt-water axis at 19.55% salt. It is not possible on the basis of the evidence at hand to say anything conclusive about the positions of the other three corners. One possibility, sketched schematically in Fig. 6, suggested by the fact that the lye concentration here is practically identical with that found in the neat-waxy soap-lye region of the system NaL-NaCl-H₂O, is that the other three corners are waxy sodium laurate, sodium laurate neat soap (both of the same composition as are in equilibrium with lye in the ternary system) and a solid solution of sodium laurate in sodium palmitate. This behavior would

(9) M. E. Laing and J. W. McBain, *J. Chem. Soc.*, **117**, 1525 (1920).

(10) It should be pointed out that immediately to the left of line AB the system behaves like one of three components. Only two condensed phases are present, and the compositions of these phases lie in the plane of the diagram. If, along line AB, four phases exist whose compositions are not necessarily in the plane of the diagram, and if the same discontinuity accompanies an infinitesimal temperature rise as accompanies an infinitesimal concentration change, then the phase change at 90° must involve an abrupt change in the relative amounts of the phases. Unfortunately, the difficulty of distinguishing sharply between the phases on the two sides of the line renders this deduction incapable of experimental test by the method of visual observation. However, there must also be a discontinuity in heat content and volume.

be comparable to that observed by Piper, Chibnall, *et al.*,¹¹ in the case of hydrocarbons, fatty acids, etc., where solubility of a substance of long chain molecules in one of short chain molecules is far less common than the converse.

Summary

Diagrams have been determined showing the phase behavior of the four component system sodium palmitate–sodium laurate–sodium chloride–water at 90° for two constant ratios of sodium palmitate to sodium laurate. From these data a curve has been constructed which permits fairly accurate prediction of the phase rule diagram for any mixture of the two soaps.

Corresponding phase boundaries in the mixed soap system occur at salt concentrations far nearer the values for pure laurate than for pure palmitate. This effect is probably due to interference of the shorter sodium laurate molecules with the degree of regularity in the sodium palmitate micelles.

The least soluble phase of sodium palmitate is

(11) S. H. Piper, A. C. Chibnall, S. H. Hopkins, H. Pollard, J. A. B. Smith and E. F. Williams, *Biochem. J.*, **25**, 2072 (1931).

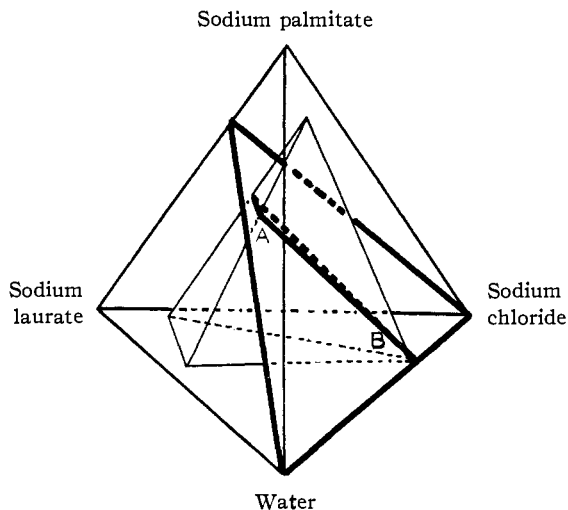


Fig. 6.—A possible relation of the phase boundary AB to the tetrahedron representing the quaternary system at constant temperature.

made actually as soluble as sodium laurate by the addition of sodium laurate to the system.

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Thermodynamic Behavior of Liquid Crystalline Solutions of Sodium Palmitate and Sodium Laurate in Water at 90°

BY ROBERT D. VOLD AND MARJORIE J. VOLD

The liquid crystalline states of aggregation¹ are characterized, as their name implies, by sets of mechanical and physical properties intermediate between those of true crystals and those of true liquids. From the theoretical standpoint, also, these states are intermediate between crystal and liquid. Corresponding to the definition of a crystal as an array of atoms or molecules in regular periodic order in all three coordinate directions and the definition of a liquid as an essentially chaotic or "zero dimensional ordered" array, liquid crystals can be defined as aggregates of atoms or molecules regularly arranged in only one or two directions, and randomly distributed with respect to the remaining coordinate or coordinates.

The most convenient identification of a particular state as truly liquid crystalline makes use of the property of spontaneous optical anisotropy, common to all liquid crystals. The fact that

optically homogeneous regions—"single liquid crystals"—seldom grow spontaneously to a size much greater in any dimension than the wave lengths of visible light, together with the fact that these homogeneous regions are readily deformable, gives rise to a very large variety of marvelously beautiful optical figures observable microscopically using polarized light. Study of the optical properties has given a great deal of information about the structure of various liquid crystals.² Still it is important to recognize that these optical properties are all consequences of the anisotropy and deformability of the liquid crystals and are *not* independent characteristics.³

(2) See, *e. g.*, A. van Wijk, *Ann. Physik*, [5] **3**, 879 (1929).

(1) For an excellent discussion and classification, see J. D. Bernal and D. Crowfoot, *Trans. Faraday Soc.*, **29**, 1032 (1933). For a detailed theoretical discussion see C. Hermann, *Z. Krist.*, **79**, 186 (1931).

(3) A. S. C. Lawrence, *Trans. Faraday Soc.*, **34**, 660 (1938), refuses to classify certain phases of the alkali soaps as liquid crystalline on the ground that the characteristic optical figures cannot be obtained. He attributes the spontaneous optical anisotropy that exists even in completely strain free masses prepared by undisturbed cooling of the isotropic liquid form to the presence of oriented sub-microscopic crystals, an hypothesis which established phase rule diagrams render completely untenable. Moreover, J. W. McBain and W. E. Elford actually have obtained excellent photographs of typical focal conic structures in the case of aqueous potassium oleate. One such photograph has been published [J. W. McBain, *Nature*, **114**, 49 (1924)].