4. A possible detailed mechanism for the bimolecular reaction has been discussed.

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Phase Rule Equilibria of Acid Soaps. IV. The Three-Component System Potassium Laurate–Lauric Acid–Water[1]

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In the past no attempt has been made to study the equilibria in aqueous solutions or suspensions of acid soaps by application of the phase rule. It is not surprising that this field has been neglected, because the phases which exist are in all cases very difficult to examine by the usual means. Generally, the separation even of two isotropic liquid phases is hindered by high viscosity. The authors have kept such systems for months in a thermostat at 90°, and in most cases at the end of this period very little separation had taken place.[2] We had to develop, therefore, a completely new technique.

Previous observations on the much disputed subject of acid soaps[3] mostly consist of analyses of sediments obtained from more or less dilute soap solutions. As found by Chevreul in 1823, and confirmed by Krafft and many others, these sediments exhibit a composition intermediate between that of neutral soap and fatty acid. However, in most cases this by no means indicates the composition or even establishes the existence of acid soaps because the sodium soaps and the higher potassium soaps are themselves fairly insoluble at room temperature and the sediments may consist of chance heterogeneous mixtures of variable composition usually containing both acid soap and soap itself.[4] On the other hand, the crystalline sediments from dilute solutions of a soluble soap such as potassium laurate are unquestionably acid soaps. However, in no case had sufficient care been taken to identify and characterize these different constituents.

In the corresponding anhydrous systems the acid soaps have now been definitely characterized as well-crystallized chemical substances of definite composition, not entering into isomorphous mixtures or solid solutions. Complete phase rule diagrams have been obtained for several of these anhydrous two-component systems.[1] Likewise, the other two-component system, potassium laurate–water, was mapped out in a previous study.[5]

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[1] This is the fourth of a series of studies of acid soaps carried out at Bristol University, England, in 1925–1927. For previous references see J. W. McBain and M. C. Field, *J. Phys. Chem.*, **37**, 675 (1933); J. W. McBain and M. C. Field, and J. W. McBain and A. Stewart, *J. Chem. Soc.*, 920, 924, 928 (1933); see also J. W. McBain and A. Stewart, *ibid.*, 1392 (1927).

[2] Compare R. H. Ferguson and A. S. Richardson, *Ind. Eng. Chem.*, **24**, 1329 (1932).

[3] See references given in the first communication of this series.

[4] Examples of such experiments leading to erroneous conclusions are R. Zsigmondy and W. Bachmann, *Kolloid-Z.*, **11**, 156 (1912); W. Prosch, *Z. deut. Öl- Fett-Ind.*, **42**, 450 (1922).

[5] J. W. McBain and M. C. Field, *J. Phys. Chem.*, **30**, 1545 (1926).

The present communication comprises systematic exploration of the three-component aqueous system for all proportions, over a range of temperature of several hundred degrees. At 370° lauric acid, water and potassium laurate are almost, but not quite, miscible in all proportions, this miscibility extending over nearly all of the three-component system, but breaking down in each of the two-component systems. As the temperature falls, miscibility rapidly decreases until most of the three-component system falls into heterogeneous mixtures of phases derived from the two-component systems, potassium laurate–water and potassium laurate–lauric acid, each of which is extended slightly into the three-component system; and the only important solubilities are those of potassium laurate in water and in melted lauric acid, respectively. Several of the phases are of great interest, such as the two immiscible conic anisotropic liquid phases, neat soap and middle soap, each of which can dissolve either fatty acid or any electrolyte. Finally, the types of equilibria and the forms of the phase boundaries are in many cases quite different from those met in phase rule studies of systems not involving soap.[6]

At room temperature solid is always present, because potassium laurate, potassium hydrogen dilaurate, and lauric acid are all separate solid phases, the two latter being almost insoluble in water. When a system is cooled from higher temperatures at which it may have existed in the form of two liquid layers, the upper one always containing much more lauric acid than the lower one, crystallization takes place from each layer, more or less separately, and often lauric acid crystals separate from the upper layer and acid soap crystals KL, HL from the lower layer. The equilibria from room temperature to 90° require further study for their representation. Those at higher temperatures are much more completely known and are the subject of the present communication.

Method of Investigation

The methods employed have been for the most part described in a series of previous communications.[7] One of them depends upon the fact that supersaturation with reference to the formation of a liquid phase or of a liquid crystalline phase cannot or does not occur.[8] This is made use of to determine the position of the boundary of the isotropic liquid (sometimes of the anisotropic liquid) by noting the temperature at which the whole of a known system just becomes isotropic or, more usually, where the whole

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(6) The validity of the application of the phase rule to a colloidal system such as this is a corollary of the fact, now carefully established, that true, reversible equilibria occur in soap solutions and that these equilibria determine all the colloidal as well as the crystalloidal constituents present. Hence a soap solution from the point of view of thermodynamics and the phase rule may be regarded as a single phase when discussing its equilibria with other solutions or solids, in spite of the presence of colloidal particles, even of several different kinds.

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

(8) See, for example, F. W. Küster and A. Thiel, "Lehrbuch der allgemeinen, physikalischen und theoretischen Chemie," 1, 327 (1913).

of the known system has been isotropic and, on cooling to a temperature T_i, just begins to separate out droplets of another phase, anisotropic liquid. This measurement may be made with the naked eye, with or without the aid of crossed nicols. Examination of a thin layer spread out under the polarizing microscope upon a heating stage with due precautions to prevent evaporation is necessary to determine when the whole of a given system of known composition just becomes or just ceases to be wholly anisotropic. Such microscopic examination is invaluable for determining whether a given system is homogeneous or heterogeneous.

Another method of determining points on the boundaries of the isotropic (or anisotropic) phase is to determine the temperature T_c at which on slow heating with good stirring the last traces of crystal dissolve completely to form one homogeneous isotropic liquid. The reverse process, cooling, is valueless on account of supersaturation.

In a few cases direct analyses of homogeneous samples of given phases were possible by decomposing with a known volume of standard aqueous sulfuric acid, and, after adding chloroform to dissolve the free fatty acid and separating the two layers, titrating the aqueous layer with sodium hydroxide, and the chloroform layer with alcoholic sodium hydroxide in the presence of excess of boiled out alcohol, using phenolphthalein as indicator.

The potassium laurate and lauric acid were those used in the study of the two-component systems.[9]

Series of systems were made up by weight in sealed glass tubes, each with the same concentration of potassium laurate (measured in weight normality, molality), and various concentrations of lauric acid. They were heated until the contents formed a homogeneous, isotropic liquid. Frequently temperatures of several hundred degrees were necessary in order to effect this. On cooling, the temperature T_i was detected by turbidity, followed in some cases at a slightly lower temperature by formation of visible globules of the second phase suspended in the first. These globules gradually separate into two or more liquid layers when the system is sufficiently fluid.

The Experimental Data

Tables I–VI contain the data obtained by the visual method. These are then plotted in the corresponding working drawings, Figs. 1–6, each of which represents a cross section through the three-dimensional phase rule model whose height represents temperature and whose triangular edges represent the three components. N_w represents weight normality, molality, the number of gram equivalents per 1000 grams of water. At 18° the systems, with the exceptions marked by footnotes, constituted a white crystalline mass, but when there were two layers the upper one solidified to a straw colored crystalline mass.

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[9] J. W. McBain and M. C. Field, *J. Phys. Chem.*, **37**, 675 (1933).

The Equilibria in Tables I–VI and Figs. 1–6.—Three distinct types of equilibria between liquid and liquid crystalline phases have been identified.

(a) Equilibria between homogeneous anisotropic middle soap and homogeneous isotropic soap solutions. These are only observed in the

TABLE I

DESCRIPTION OF THE AQUEOUS SYSTEMS 0.25 N_w WITH RESPECT TO POTASSIUM LAURATE

N_w HL	At 90°	Turbidity temp., T_i
0.2564	Cloudy liquid, no separation into 2 layers	161.7
.5016	Ditto, very viscous	181.0
.7408	Ditto, very viscous	166.0
.9963	Two isotropic liquid layers	222.0
1.499		236.0

TABLE II

DESCRIPTION OF THE AQUEOUS SYSTEMS 0.50 N_w WITH RESPECT TO POTASSIUM LAURATE

N_w HL	At 90°	Turbidity temp., T_i
0.3035	Cloudy, fairly mobile liquid; no layer separation	125.0
.4989	Ditto, but incomplete layer separation	156.0
1.012	Cloudy viscous liquid, droplets of one phase suspended in the other giving an appearance of anisotropic liquid crystals	183.0
1.498	Cloudy viscous liquid, incomplete layer separation	186.3
1.758		179.0
1.987	Two isotropic liquid layers	180.7
2.245		195.0
2.496	Appeared to yield three liquid layers, the upper and lower isotropic and the middle cloudy	203.0
2.746		210.5
2.986		217.0
4.995	Cloudy viscous liquid droplets of one phase suspended in the second. No separation	239.0

TABLE III

DESCRIPTION OF THE AQUEOUS SYSTEMS 1.00 N_w WITH RESPECT TO POTASSIUM LAURATE

N_w HL	At 90°	Turbidity temp., T_i
0.2605	Homogeneous, isotropic liquid	None[a]
.5079	Cloudy viscous liquid, no separation of phases	121.5
.9924	Ditto, simulating anisotropic liquid crystals	162.5
2.005	Ditto, field lights up between crossed nicols[b]	182.5
2.620	Cloudy viscous liquid, no separation of the phases. Simulates anisotropic liquid crystals	172.5
3.007	Incomplete two liquid layer formation	114.0
3.510		138.5
3.990	Two isotropic liquid layers	157.0
4.971		180.0
6.977		206.8

[a] Isotropic until the crystalline phase separated.

[b] A well-known property of light reflected at interfaces in certain emulsions of two (ordinary) liquids.

TABLE IV

DESCRIPTION OF THE AQUEOUS SYSTEMS 2.00 N_w WITH RESPECT TO POTASSIUM LAURATE

N_w HL	At 90°	Turbidity temp., T_i
0.4965	Homogeneous, isotropic liquid	None[a]
1.011	Cloudy viscous liquid, two-phases but no separation	148.0
2.012	Ditto, simulates anisotropic liquid	180.3
2.975	Ditto, has consistency of vaseline	182.0
4.000		164.7
4.483	Turbidity appears due to an extremely finely divided solid in isotropic liquid	92.0
5.002	Homogeneous, isotropic liquid, but on cooling below 90° like above	86.5
5.254		80.3
5.511		81.0
5.996		85.0
6.466	Cloudy, fairly mobile, two-phase system. No separation	96.5
7.001		110.0

[a] Isotropic until the crystalline phase separated.

TABLE V

DESCRIPTION OF THE AQUEOUS SYSTEMS 3.00 N_w WITH RESPECT TO POTASSIUM LAURATE

N_w HL	At 90°	Turbidity temp., T_i
0.000[a]	Homogeneous, rigid, liquid crystalline middle soap	151.0
.4004[b]	Ditto, no isotropic liquid visible	146.5
.5157[b]	Ditto, no isotropic liquid visible	137.0
.5989	Ditto, no isotropic liquid visible	128.5
.7338	Cloudy, viscous two or three-phase system, no separation	115.0
1.007	Cloudy, viscous two-phase system, no separation. Looks anisotropic	154.5
1.486		179.5
2.000		185.5
2.914[c]		187.5
4.002		179.5
4.957	Ditto, but slight separation of the phases	164.0
5.431		149.0
5.973	Cloudy, almost rigid, two-phase system, no separation of the phases. Appears anisotropic	108.0
6.460		109.0[d]
7.008	Cloudy, almost rigid two-phase system. No separation	108.0
7.850		95.0
8.664	Isotropic liquid	82.0[d]
9.731	Isotropic liquid	84.0[d]

[a] At 18°, same as at 90°. [b] At 18°, fine hair-like needle crystals in bunches radiating from a central nucleus. [c] At 18°, two distinct layers of white crystals separated. Upper layer two-thirds and lower one-third by volume. [d] The turbidity temperature seems to be due in this case to an extremely finely divided solid phase of crystalline nature.

more concentrated soap systems, such as 3 and 4 N_w potassium laurate. Rigidity is characteristic of the middle soap phase; and on cooling a heterogeneous system containing middle soap and isotropic solution, the viscosity increases rapidly as the amount of isotropic solution decreases,

TABLE VI

DESCRIPTION OF THE AQUEOUS SYSTEMS 4.00 N_w WITH RESPECT TO POTASSIUM LAURATE

N_w HL	At 90°	Turbidity temp., T_i
0.000[a]	Homogeneous, rigid, anisotropic liquid crystalline middle soap	179.0
0.3307[b]	Homogeneous, rigid, anisotropic liquid crystalline middle soap	164.5
0.4949[c]		150.5
.7439	Highly viscous two or three-phase system. One phase has the appearance of anisotropic liquid crystals. No separation	150.0
.9879		176.0
1.522		196.5
1.975	Highly viscous two-phase system, simulating anisotropic liquid crystals	199.7
3.472		198.7
4.987		182.0
6.445		152.0

[a] At 18°, same as at 90°. [b] At 18°, as at 90° plus traces of hair-like needle acid soap crystals. [c] At 18°, two phases, white crystals and anisotropic middle soap.

until the whole system becomes quite rigid when the homogeneous middle soap region is reached.[10]

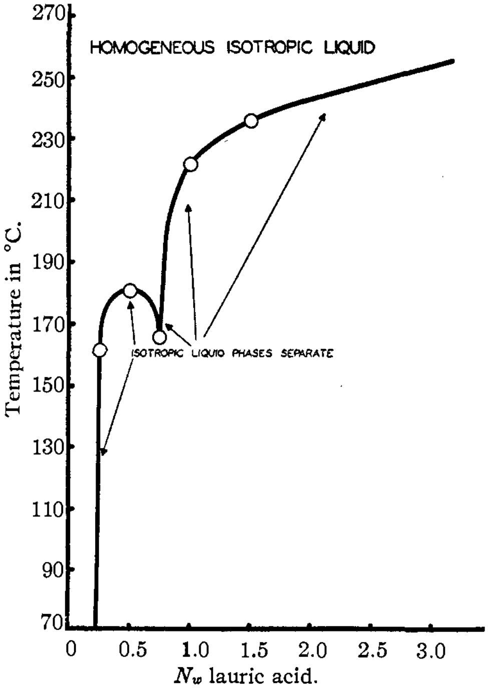

Fig. 1.—Lower boundaries of the isotropic aqueous phase containing 0.25 N_w potassium laurate.

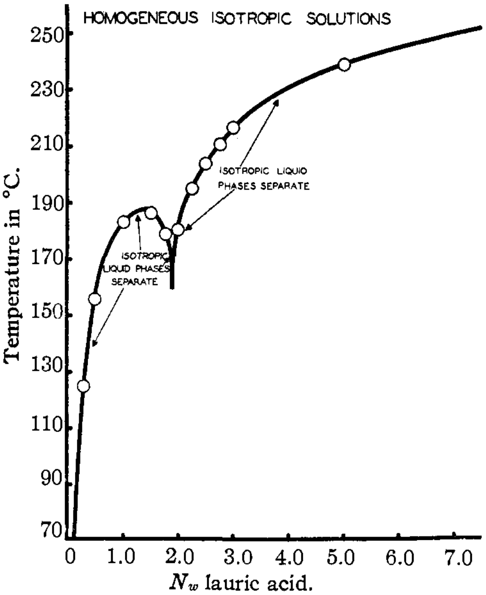

Fig. 2.—Lower boundaries of the isotropic aqueous phase containing 0.5 N_w potassium laurate.

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(10) For systematic measurements of the rigidity or structural viscosity of middle and neat soap, see J. W. McBain and O. O. Watts, *J. Rheol.*, **3**, 437 (1932).

The middle soap region is very much smaller in the system potassium laurate–lauric acid–water than in the system potassium laurate–potassium chloride–water.[5] McBain[11] gives a description of the conic anisotropic structure of middle soap for potassium laurate.

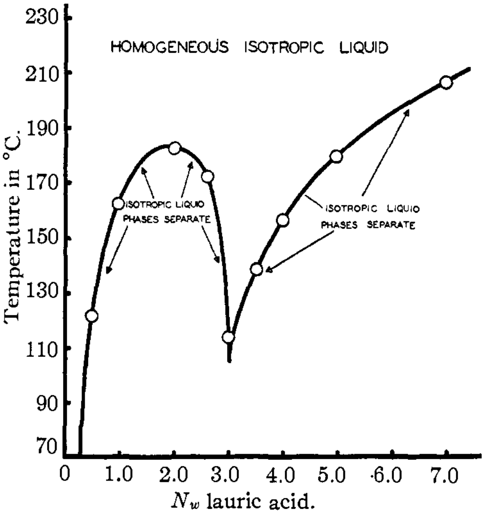

Fig. 3.—Lower boundaries of the isotropic aqueous phase containing 1.0 N_w potassium laurate.

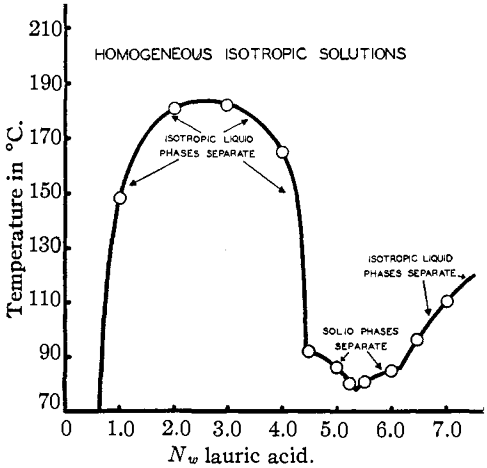

Fig. 4.—Lower boundaries of the isotropic aqueous phase containing 2.0 N_w potassium laurate.

(b) Equilibria between two isotropic liquid layers in which the layers separate readily. This type of equilibrium (analogous to the two layer formation, nigre–lye, met with in the salting out of soaps) occurs in the presence of excess lauric acid, which is the chief constituent of the upper layer; the lower layer is essentially a dilute aqueous solution of soap in which small quantities of fatty acid are dissolved. Certainly there is no reason to suppose that acid soaps exist in the liquid condition, especially above 91°, which is the decomposition or transition temperature of the acid soap in the solid state.

(c) Equilibria between two (apparently) isotropic liquids which scarcely ever separate owing to their being highly viscous. These are the most typical systems met with in the study of acid soaps. They are very similar to the anisotropic neat soap systems[12] in their properties although they are less rigid. A noteworthy feature is that in polarized light they exhibit double refraction, and yet, in the cases where separation of the two phases has been obtained, the two layers produced are isotropic. The anisotropic appearance is due to the polarization of light reflected at the surfaces of globules of one phase suspended in the other.

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(11) J. W. McBain, *Nature*, **114**, 49 (1924).

(12) Compare J. W. McBain and W. J. Elford, *J. Chem. Soc.*, 421 (1926).

The Triangular Diagrams.—The boundaries of the two isotropic liquid phases which can exist in the three-component system may be deduced, for representative temperatures, from the working graphs of Figs. 1–6. It is therefore possible from these numbers to draw isotropic boundaries for all temperatures up to 250° and this is done in Fig. 7.

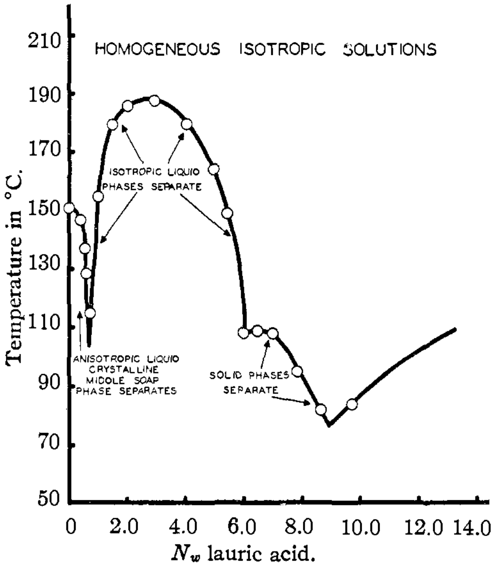

Fig. 5.—Lower boundaries of the isotropic aqueous phase containing 3.0 N_w potassium laurate.

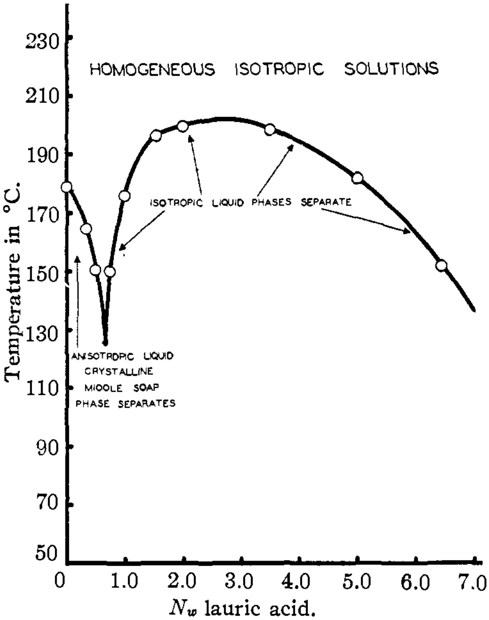

Fig. 6.—Lower boundaries of the isotropic aqueous phase containing 4.0 N_w potassium laurate.

For convenience of reference the two isotropic liquid phases are referred to as A and B, respectively. The existence of phase A is a proof that fatty acid dissolves in soap solutions,[13] although the internal constitution of these solutions has still to be accorded detailed investigation. Presumably they contain neutral colloid, ionic micelle and simple ions and molecules. The ready solubility of fatty acid in aqueous soap solutions, which at sufficiently high temperatures becomes complete miscibility, when compared with the immiscibility of fatty acid with water, can only be due to interaction between the dissolved soap and the fatty acid. This lends further support to our long maintained view that acid soap and not free fatty acid is the chief product of hydrolysis in soap solutions.

Phase B is the anhydrous solution of soap in fatty acid, which can dissolve water in curiously restricted fashion to form, at first, a narrow curved tongue whose base widens rapidly with increase of temperature and whose tip becomes remarkably elongated until just below 180° it has reached

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[13] See also C. Bergell and N. Baskin, *Seifensieder-Ztg.*, **56**, 157 (1929).

phase A. At all higher temperatures phases A and B are thus bridged, the bridge widening until at 370° it almost fills the diagram.

Liquid B is generally slightly yellowish because any colored impurity goes into it rather than into the more aqueous layer A.

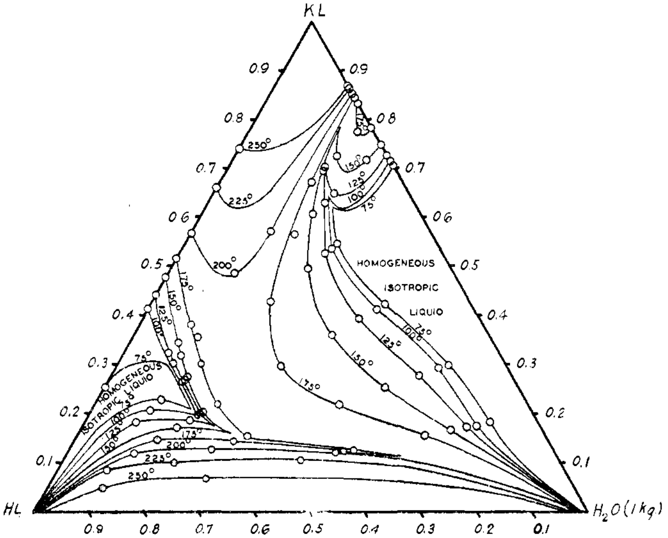

Fig. 7.—The boundaries of homogeneous isotropic liquid phases in the system potassium laurate–lauric acid–water. Isotherms for temperatures at intervals of 25°, from 75 to 250°.

Our triangular diagrams here and in previous studies of soap resemble those of Willard Gibbs with the exception that the unit of weight is not the gram but that two corners represent one gram molecular weight of lauric acid and potassium laurate, respectively, and the third corner is one kilogram of water. Intermediate points represent weights of each directly proportional to their nearness to these three corners. The total composition of the system lies upon a straight line connecting the points representing the composition at the two phases. Hence all tie lines are straight. Following previous usage, all compositions are represented in terms of "fractional proportions" of the three respective units, the whole adding up to unity for each point in the three-component system.

It will be noted that since the same units are here used as in studies of the three-component systems, soap–water–electrolyte, the triangular space model for that three-component system has one face in common with the present three-component system, namely, the two-component system soap–water. This is of very great assistance in identifying the three-component phases which extend out into the respective triangular prism models or, for a given temperature, triangular isotherms. We have found it useful to construct tetrahedral models (one tetrahedron for each temperature) in deducing the four-component systems potassium laurate–lauric acid–potassium chloride–water of which the four three-component systems are restricted cases and form the faces of the tetrahedra.

For lack of more precise knowledge the neat soap and the hydrated soap crystal boundaries are assumed to extend into the acid soap system in a manner similar to that in the aqueous electrolyte system.

Separation at 90°.—Thirty-three sealed up systems were placed in a thermostat at 90° for three or four months, at which time they were examined visually and carefully described with a view to identifying the nature of the phases present. In twenty-one cases there was either no separation in bulk, although the presence or absence of anisotropic liquid in the heterogeneous mixture was detectable, or in two cases the whole system formed one mobile isotropic liquid (Phase B). In the other cases there was more or less separation, sometimes into two isotropic liquids but sometimes one of the layers being definitely anisotropic. Always in the latter case, and frequently in the former, one or both of the layers was contaminated by droplets of the other. Five of these systems were analyzed in order to determine the gross composition of each layer.

TABLE VII

ANALYSES OF MORE OR LESS COMPLETELY SEPARATED TWO LAYER SYSTEMS

		A	B	C	D	E
Total composition	N_w KL	0.2525	0.04940	0.5046	0.5037	2.997
	N_w HL	1.499	1.498	1.758	2.496	1.486
Upper layer	N_w KL	4.093	11.60	1.574	3.265	3.181
	N_w HL	26.46	59.17	6.759	17.04	1.534
Lower layer	N_w KL	0.0222	0.3867	0.3242	0.1496	2.204
	N_w HL	.0410	.9738	.8800	.5715	0.7158

In systems A, B, C and D the upper layer was moderately mobile, fairly clear and straw colored, the lower layer being much more viscous, being cloudy in A but exhibiting visibly suspended droplets in the other cases. In system E the lower layer was a clear isotropic liquid, the upper four-fifths of the system being a cloudy, highly viscous, anisotropic mixture.

Separation in system A is almost perfect, exactly placing the tie line, each end of which falls on the boundary of homogeneous, isotropic liquid phase as already determined.

Separation in B and D is good as regards the upper layer, whose composition lies on the liquid boundary previously determined. The lower layer, however, is sufficiently viscous to have retained droplets of the upper layer. The analysis, therefore, gives the direction of the tie line but does not reach its extremity.

Separation in C is imperfect as regards both layers, therefore merely giving the direction of the tie line.

Separation in E has yielded only the lower phase pure, for this is a three-phase system of which the third phase is presumably neat soap.

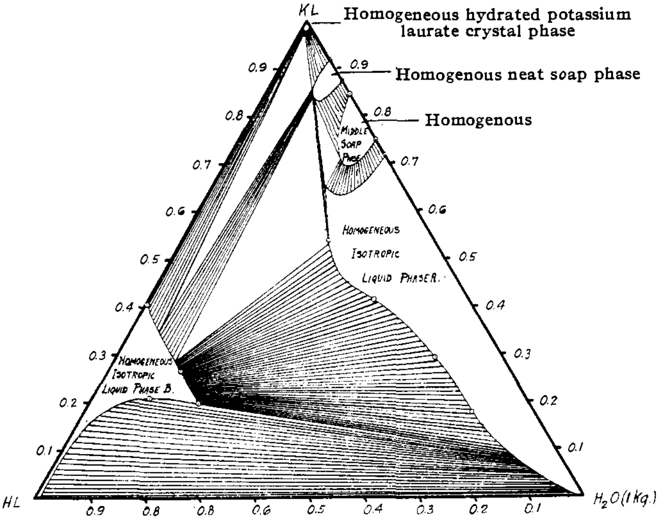

Fig. 8.—Equilibria at 100°.

Discussion

Before presenting the phase rule diagrams for representative temperatures from 100 to 370°, it may be recalled that middle soap is a plastic, conic anisotropic liquid, turbid if stirred but often quite transparent. Its apparent or structural viscosity is of the order of a hundred million times that of water and greater than that of vaseline.

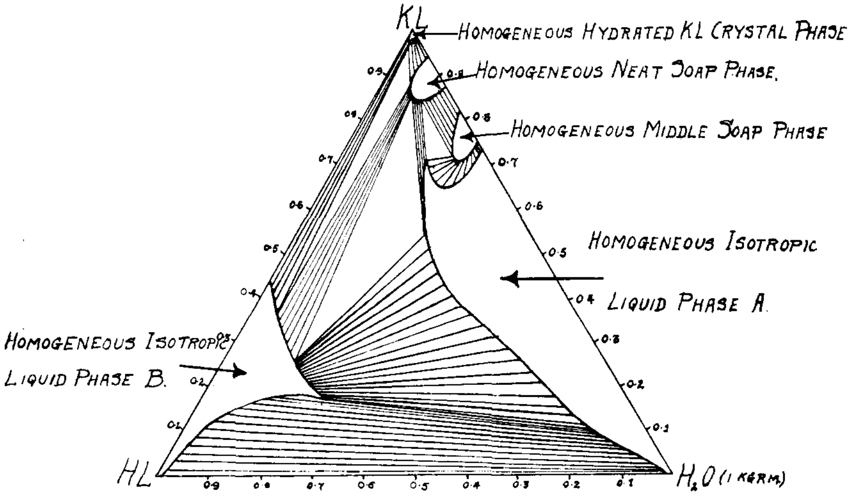

Fig. 9.—Equilibria at 125°.

Neat soap is also a conic anisotropic liquid, more turbid than middle soap with which it is immiscible. We (like Ferguson and Richardson[2]) were under the impression that it was less rigid than middle soap, but the quantitative examination of McBain and Watts demonstrated that it was even more rigid.

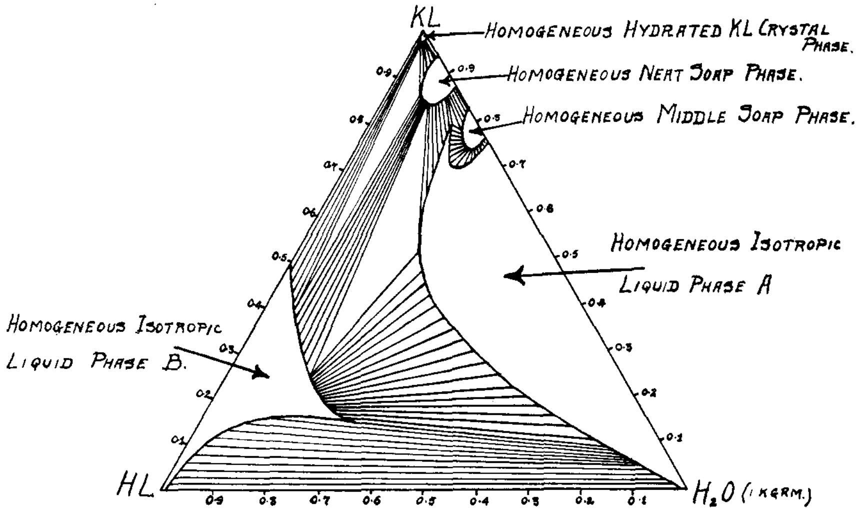

Fig. 10.—Equilibria at 150°.

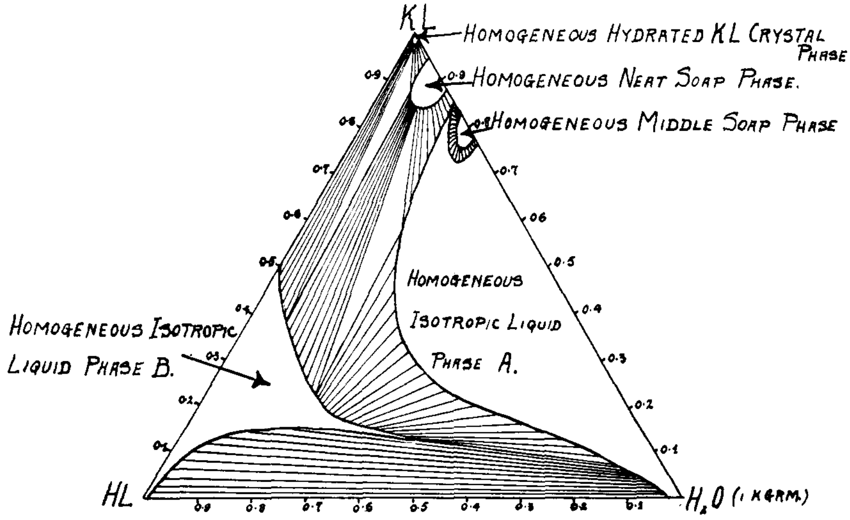

Fig. 11.—Equilibria at 164°.

Crystals of potassium laurate are transparent, hexagonal lamelae, giving a silvery white paste. They are only slightly hydrated.

Figures 8–21 present the results of this investigation, outlining the equilibria met with at 100, 125, 150, 164, 175, 178, 180, 183, 200, 225, 239, 250, 275 and 370°. Of these the diagrams at 100, 175 and 250° are worked out with the most care. The notes and comments already made in this paper, together with the annotations upon the diagrams, will enable those conversant with the phase rule to read the qualitative and quantitative significance of the various equilibria, in spite of the unique and highly interesting phenomena presented.

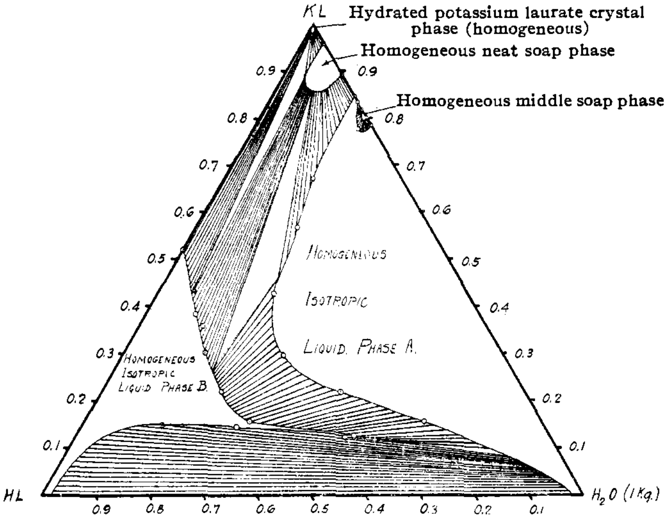

Fig. 12.—Equilibria at 175°.

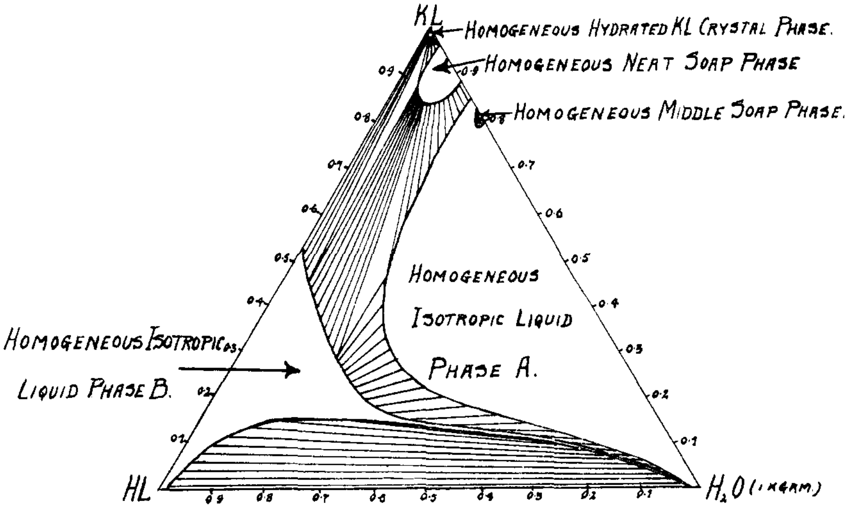

Fig. 13.—Equilibria at 178°.

At 164° the middle soap phase becomes completely surrounded by isotropic liquid phase A. At 178° the isotropic liquid phase A unites with (reaches) the liquid phase B. At 180° the middle soap phase vanishes. At 376° neat soap vanishes and only isotropic liquids survive.

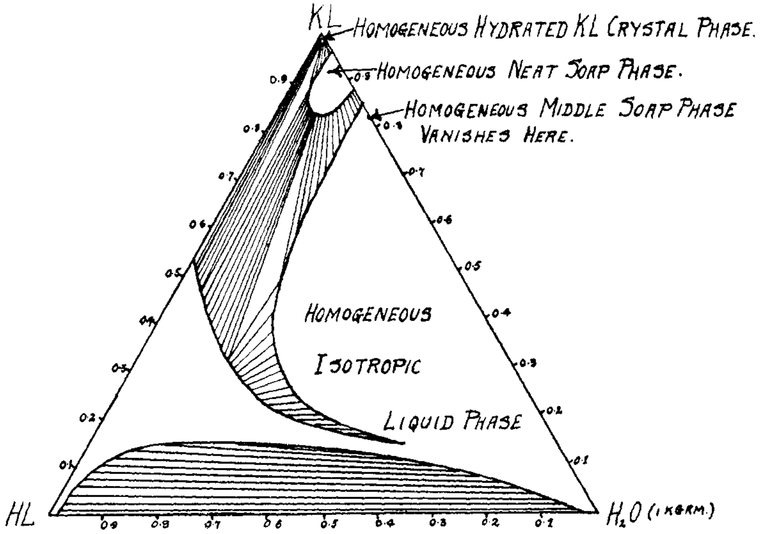

Fig. 14.—Equilibria at 180°.

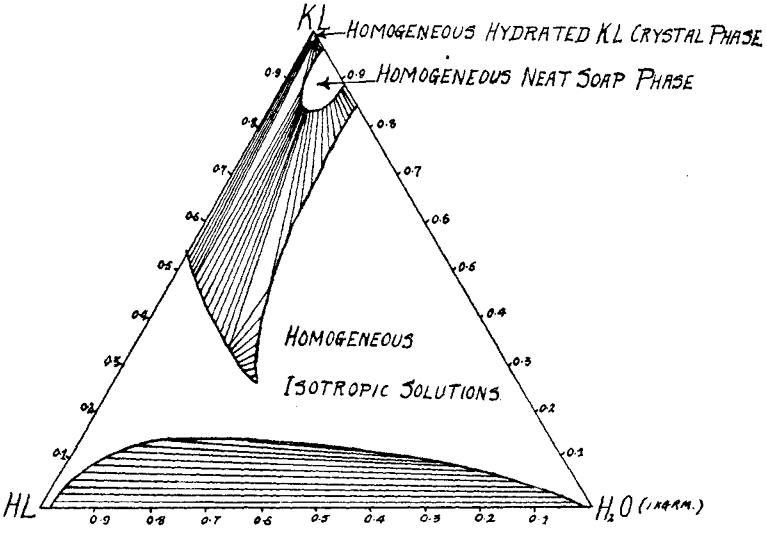

Fig. 15.—Equilibria at 183°.

It may be helpful to point out that eleven types of two- or three-phase equilibria occur at 100°, types 5 and 6 having disappeared by 175° and only types 1, 3 and 9 remaining at 250°. The types are listed as follows:

1. Two-phase equilibria between homogeneous, isotropic liquid phase A and the lower boundary of homogeneous, isotropic liquid phase B. The limiting case of these heterogeneous equilibria is between liquid lauric acid and water.

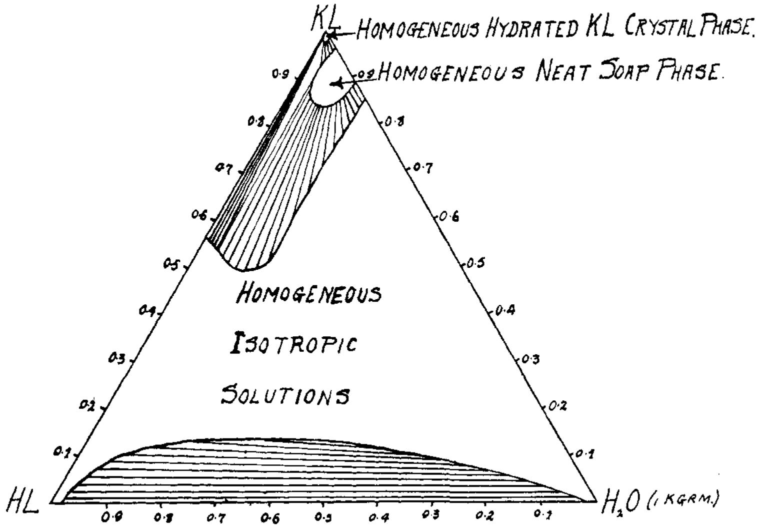

Fig. 16.—Equilibria at 200°.

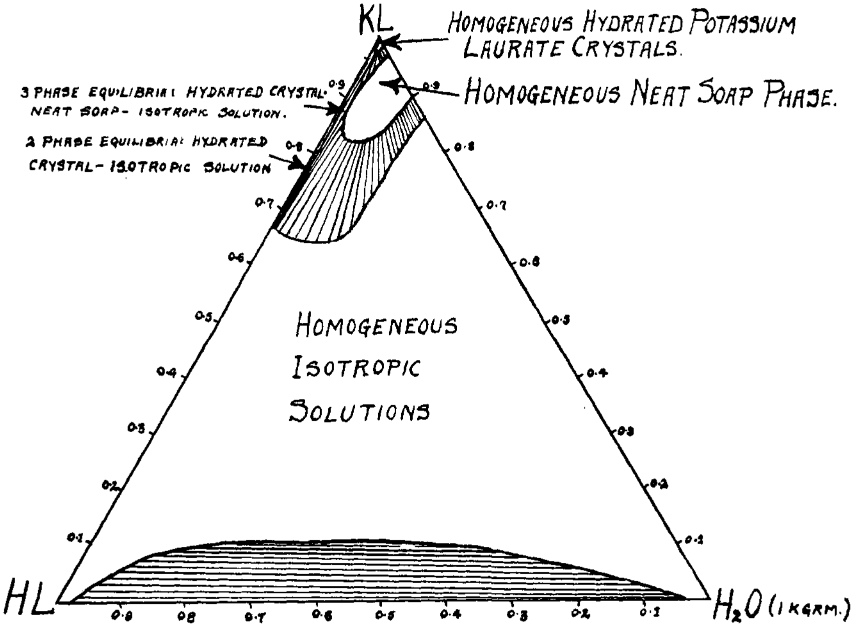

Fig. 17.—Equilibria at 225°.

2. Two-phase equilibria between homogeneous, isotropic liquid A and the upper boundary of homogeneous isotropic liquid B.

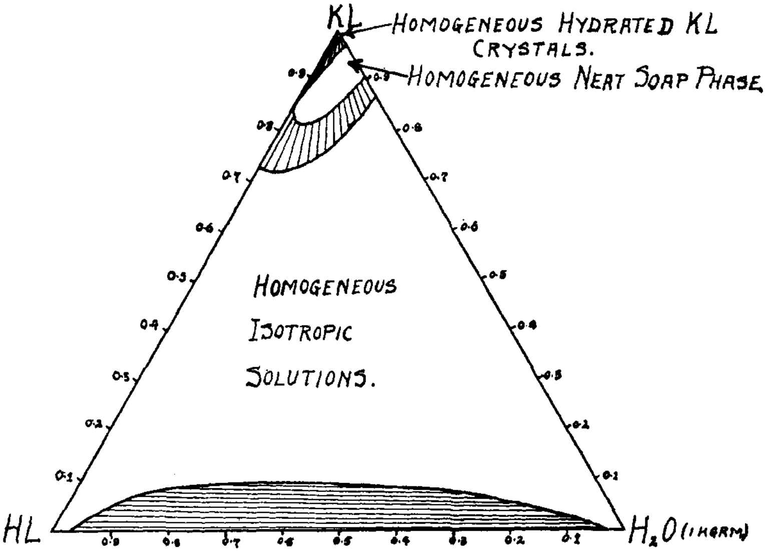

Fig. 18.—Equilibria at 239° at which neat soap just appears in the two-component system KL, HL.

3. Three-phase equilibria between homogeneous, anisotropic neat soap, and homogeneous, isotropic liquid phases A and B.

4. Two-phase equilibria between homogeneous, anisotropic rigid middle

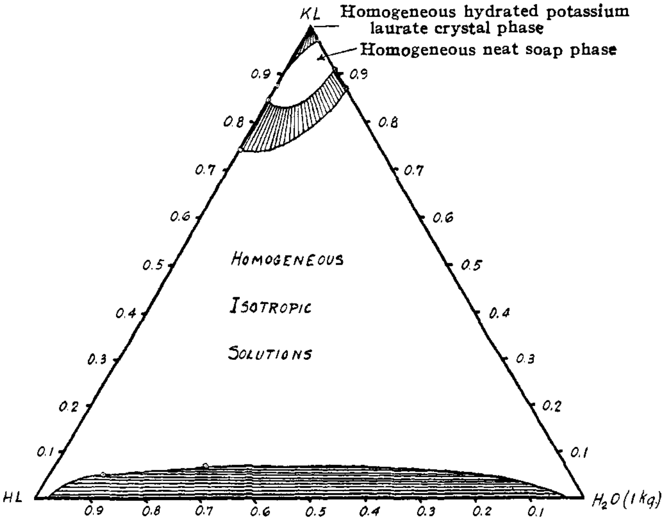

Fig. 19.—Equilibria at 250°.

soap, and homogeneous, isotropic liquid A, the limiting case of which occurs in the absence of lauric acid.

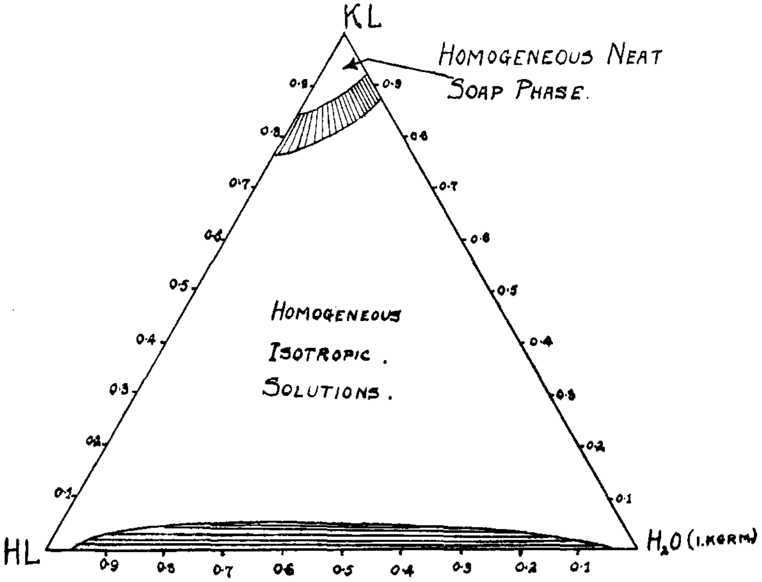

Fig. 20.—Equilibria at 275°.

5. Two-phase equilibria between homogeneous, anisotropic neat soap, and homogeneous, anisotropic rigid middle soap, the limiting case of which occurs in the absence of fatty acid.

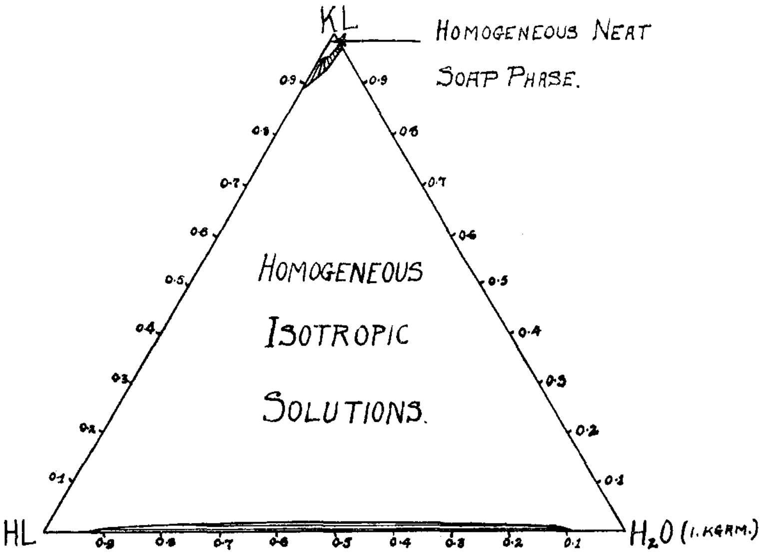

Fig. 21.—Equilibria at 370°.

6. Three-phase equilibria between homogeneous, anisotropic plastic neat soap, homogeneous, anisotropic middle soap, and homogeneous, isotropic liquid phase A.

7. Two-phase equilibria between homogeneous, anisotropic, plastic neat soap, and isotropic liquid phase A.

8. Two-phase equilibria between homogeneous, anisotropic, plastic neat soap, and isotropic liquid phase B.

9. Two-phase equilibria between homogeneous, anisotropic, plastic neat soap, and homogeneous, hydrated potassium laurate crystals, the limiting case of which occurs in the absence of lauric acid.

10. Three-phase equilibria between homogeneous, anisotropic, plastic neat soap, homogeneous, hydrated potassium laurate crystals, and homogeneous isotropic liquid phase B.

11. Two-phase equilibria between homogeneous, hydrated potassium laurate crystals, and homogeneous, isotropic liquid phase B, the limiting case of which occurs in the absence of water when the isotropic liquid phase B is in equilibrium with anhydrous potassium laurate.

Summary

It is attempted for the first time to map out with phase rule diagrams the equilibria existing in an aqueous three-component system of acid soaps. This is done from 100 to 370°, some remarkable and unique equilibria being exhibited.

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Solubility. XIII. The Solubility of Iodine in Certain Solvents

BY G. R. NEGISHI, L. H. DONNALLY AND J. H. HILDEBRAND

The solubility of iodine in a variety of solvents is unusually interesting because of the large number of "regular solutions"[1] it forms showing large deviations from Raoult's law. These solutions are particularly striking in the relationship they show between "regularity" and color. The investigations here described were undertaken for the purpose of including certain additional solvents: ethylene bromide, because of its high solvent power, isooctane, to compare with a normal paraffin, and two of the tetrahalides included under a comprehensive investigation now going on under the direction of the senior author,[2] *viz.*, the tetrachlorides of silicon and titanium.

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[1] J. H. Hildebrand, THIS JOURNAL, **51**, 66 (1929).

[2] J. H. Hildebrand and J. M. Carter, *ibid.*, **54**, 3592 (1932).