LV.—*The Equilibria underlying the Soap-boiling Processes. The System Potassium Oleate–Potassium Chloride–Water.*

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THE study of soap solutions has shown that they exist in a number of forms, each with very striking characteristics. In pursuing the systematic study of the constitution of these liquids, jellies, liquid crystals, and curds, it is essential that the conditions under which each exists should be exactly delimited. Further, the processes of soap-boiling depend on the existence of this series of well-defined equilibria, which have, however, received very little systematic study.

We are now in a position to state that all soaps, pure, mixed commercial, whether potassium or sodium, are essentially of the same type. The differences are in degree and not in kind and the equilibria are so similar in the various cases that by means of numerical factors the effect of any electrolyte or mixture of electrolytes can be fairly closely predicted. Finally, to a large extent, the behaviour of a mixture of soaps can be inferred from that of its pure constituents taken separately. It is found also that the results from such small-scale laboratory experiments as are described in the present paper are in numerical agreement with similar results obtained on a full commercial scale.

Two previous contributions (McBain and Burnett, J., 1922, **121**, 1320; McBain and Langdon, J., 1925, **127**, 852) have dealt with the preliminary studies of sodium laurate and sodium palmitate in which the chief results were to show the various kinds of soap systems which exist, and to indicate some of the limits for the existence of ordinary isotropic soap solutions. The present instalment is an account of a more thorough study of systems derived from potassium oleate,* which possesses the advantage of being so soluble that all the possible systems can be observed at room temperature. Further, application of the new methods of optical investigation that were developed in a previous study of potassium laurate have enabled progress to be made with the delimitation of the two important anisotropic liquids, neat soap and middle soap.

All these phases exist equally well in the absence of salt and the simplest procedure is to begin with the two-component system oleate and water, in which most of the typical equilibria appear. Accordingly, this will be discussed first, together with observations made upon individual phases, followed by the data obtained with systems in which potassium oleate is the third component.

Materials.—Kahlbaum's ordinary potassium oleate was found to be unsuitable, as it was not homogeneous and contained excess of acid and not only did the concentrated solutions on warming become dark reddish-brown but they sometimes differed in physical state from those of purer potassium oleate. Our preparations were therefore made by neutralising oleic acid " Kahlbaum " with potassium ethoxide and when carefully dried remained as white powders. The oleic acid in each case had a nearly correct iodine value and a molecular weight (by titration) about 1% too high (compare Laing and McBain, J., 1920, **117**, 1506). Potassium chloride " Kahlbaum " was used. Solutions were prepared in sealed thick-walled tubes of Duro glass by weighing in the requisite quantities and heating to whatever temperature was necessary to transform the contents into a single homogeneous liquid. Heating up to 170° was best carried out in a bath of glycerol, but for heating aqueous solutions to temperatures up to 400° an electric oven with mica windows was used and care was taken to heat and cool very slowly in order that adequate time should be allowed for the soap system to acquire the successive temperatures. Stirring was effected by slowly shaking the furnace as a whole, formation of air bubbles being avoided. In some cases a bath of the eutectic mixture of the nitrates of sodium and potassium was employed.

Methods of Observation.—In every soap system it is possible to observe a temperature, T_i, on heating to which it becomes a single homogeneous, isotropic liquid. For example, pure dry potassium oleate melts at 235—240° to form liquid crystal which, as will be shown, represents a point in the neat soap field, but on further

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* A preliminary study was carried out by F. T. Maggs, who determined a number of points on the boundaries of the region of isotropic soap solutions.

heating to 300° this melts sharply to form an ordinary clear isotropic liquid. This liquid is miscible with water in all proportions; the more water present, in general the lower the temperature T_i, and at room temperature potassium oleate solutions up to $0{\cdot}7N_w$ are clear and isotropic.

All subsequent experience has confirmed the observations of McBain and Burnett (*loc. cit.*) that no supersaturation occurs, with respect to formation of anisotropic liquid, upon cooling the isotropic solution, but supersaturation readily occurs with respect to formation of either true lamellar crystals or crystalline curd fibres or needles. The sudden change in viscosity which occurs when anisotropic liquid appears, and the even more sudden change accompanying the completion of its formation upon cooling sufficiently, serve as useful although very rough checks upon the optical observations.

We have found it essential to use polarised light both for macroscopic and for microscopic observation. It is possible to examine a number of systems at room temperature and up to 80°, using an ordinary object slide and cover glass and a Guttmann heater (see Maclennan, *J. Soc. Chem. Ind.*, 1923, **42**, 393T), but it is essential that a truly representative sample should be taken and that the whole of the sample be examined. It is necessary also to ensure that the conditions observed in the calibration of the temperature scale be maintained throughout. When a mixture of isotropic and anisotropic soap solutions is thinly spread out and thus examined between crossed Nicols, the dark isotropic patches are seen to be sharply differentiated from the illuminated anisotropic portions of the field.

For work at higher temperatures no suitable substance could be found for sealing the cover glass to the object slide, as in some cases the properties of the soap were much affected by it as well as by evaporation. Professor Kenrick of Toronto University kindly supplied a cell, made by fusing together two optically ground plates of pyrex glass, with narrow side tubes sealed in, and such a cell has been used up to 120°. Latterly we have used small flattened glass cells made from tubing, 2·5 mm. in diameter, blown into a small bulb which during the process of blowing is squeezed flat between two hot carbon blocks, leaving room for only a thin film therein. The cell could be filled with a representative sample by suction and then sealed off. Such cells were very readily annealed, any optical evidence of strain being thus removed. They could be employed in a small electric furnace on the stand of the microscope, and the temperatures there observed agree closely with those obtained by a macroscopic study of large tubes.

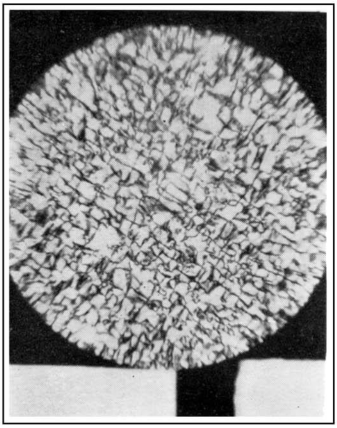
Equilibria in the System Water–Potassium Oleate.

Dilute aqueous potassium oleate is a homogeneous isotropic liquid which freezes with separation of ice, and at temperatures above 300° may without losing homogeneity be concentrated to 100% potassium oleate in the isotropic liquid condition. At all lower temperatures, potassium oleate is not miscible with water, but other intermediate phases are successively formed. Thus at 20° the highest concentration at which a homogeneous isotropic solution of potassium oleate can be prepared is $0{\cdot}70N_w$ (g.-mol. per 1000 g. of water). Above this concentration, an upper layer of higher concentration separates. This phase is a conic, anisotropic liquid and has been called in this laboratory " middle soap " (*Nature*, 1924, **113**, 534; **114**, 49 ; *Science*, 1925, **61**, 613; McBain and Langdon, *loc. cit.*). Middle soap exists over a limited range of concentrations as a homogeneous phase which constitutes, like the isotropic solutions, a colloidal electrolyte. There is no great difference in molar conductivity between soap in the middle soap phase and soap in the isotropic phase. Middle soap up to $1{\cdot}25N_w$ shows no structure in the cardiod ultramicroscope, but above this concentration diffuse granular patches begin to show against the dark background.

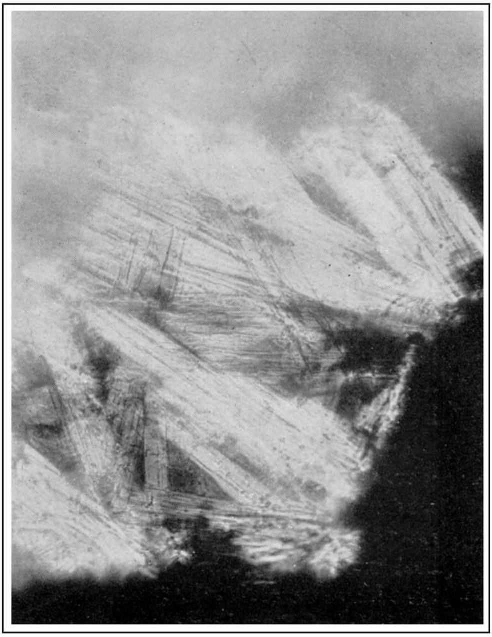
Middle soap exists over only a limited range of concentrations, above which another distinct phase of still more concentrated solution appears. To this phase we have extended the term " neat soap." Neat soap resembles middle soap in being a conic anisotropic liquid and in being plastic; that is, devoid of noticeable elasticity. Each is rigid, the neat soap much less so with about the consistency of vaselin. Middle soap is darker than neat soap (due to presence of impurity). A moderately thin specimen of middle soap is clear and transparent, whereas neat soap is better described as semi-transparent and somewhat turbid. The heterogeneous mixture of these two is rigid and turbid, the turbidity being at a maximum between the normalities $5N_w$ and $6N_w$. The exact range of concentrations for the existence of these phases has still to be determined, but for middle soap it lies between about $0{\cdot}9N_w$ and $3{\cdot}4N_w$ and for neat soap between $7{\cdot}5N_w$ and $12N_w$, within which limits a uniform field is obtained (see photograph I).

In many of the otherwise clear systems described above, small, white, star-like growths develop with time. Examination in the ultramicroscope shows them to consist of small rods plaited together to form branching structures. They probably consist of acid soaps produced by hydrolysis.

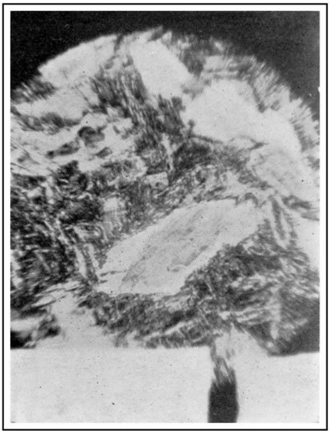
Photograph I, of $9N_w$-potassium oleate in polarised light, shows that neat soap, like middle soap, is a homogeneous, conic, anisotropic liquid soap with uniaxial interference figures. Further, on



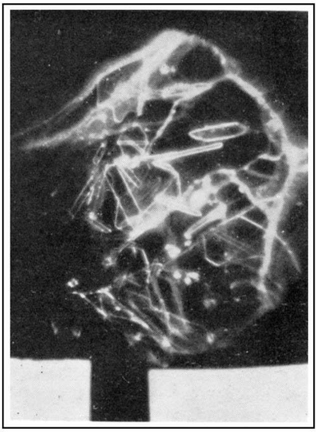
I.—$9N_w$ Potassium oleate at room temperature. Crossed nicols. × 250.



II.—Concentrated aqueous potassium oleate. Crystal phase. Crossed nicols. × 250.



III.—$25N_w$-Potassium oleate at room temperature. Showing crystalline flakes and anisotropic fluid. Crossed nicols. × 60.



IV.—$13{\cdot}3N_w$-Potassium oleate at room temperature. Crystals as seen under cardiod ultramicroscope.

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cooling $4N_w$-potassium oleate below its critical temperature, T_i 240°, the drops of neat soap which begin to appear separate in the form of the double cones which Lehmann (*Weid. Ann.*, 1895, **56**, 771, etc.) gave as a classical illustration of liquid crystals in systems containing ammonium oleate. Ethyl azoxybenzoate likewise separates in the form of these double cones when cooled from the isotropic, amorphous liquid condition. Friedel (*Ann. Physique*, 1922, **18**, 273) terms this structure " batomet " and regards it as proof that such systems are to be included in his so-called " smectic " group. Evidently both neat soap and middle soap are anisotropic liquids which would be included in the smectic group, and no soap systems are yet known which could be classified as " nematic." The fact that curd fibres have been shown by Mr. S. H. Piper to give radiograms with lines corresponding to spacings in three dimensions is a positive disproof of Friedel's contention that they were to be included in his " smectic " group, although he renamed the " liquides à conique " (conic anisotropic liquids) specially to include them.

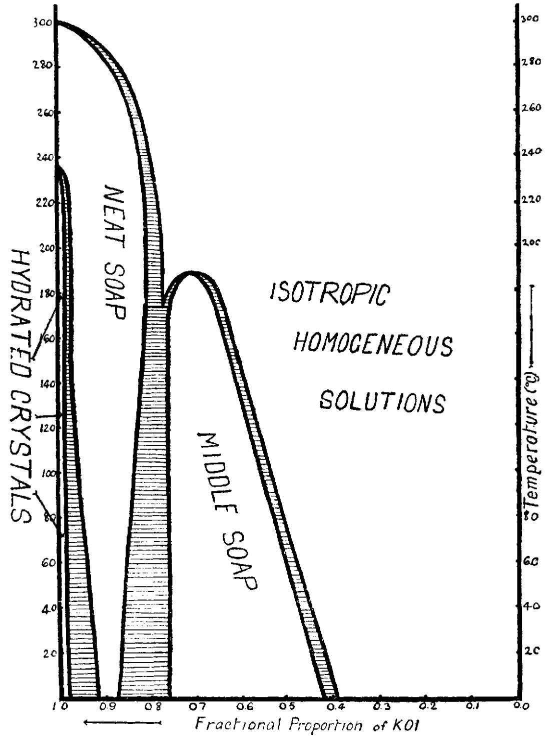
At temperatures between 240° and 300° neat soap may be concentrated up to 100% anhydrous potassium oleate, but at lower temperatures there is an upper limit fixed by the separation of crystalline potassium oleate, usually in the form of extremely thin, hexagonal flakes. In the $50N_w$-solution there is still some neat soap left, showing that the hydration of the crystals cannot exceed 1 mol. of water per mol. of soap. It is not known whether these crystals of slightly hydrated potassium oleate can be dehydrated to anhydrous potassium oleate without any new phase separating. The excessively thin crystal plates are readily bent and are illustrated in photograph II.

The sharply outlined hexagonal lamellæ are sometimes thin enough to give interference colours in ordinary light, and under a polarising microscope exhibit polarisation colours and give sharp uniform extinction in four positions. A mass of the crystals has a wax-like consistency and presents a silvery appearance. Photographs III and IV show these crystals mixed with neat soap in the heterogeneous systems.

Thus in passing from one pure component, water, to the other pure component, potassium oleate, at 20°, at least four different phases are met with and the solutions are alternately homogeneous and heterogeneous. At temperatures above 180°, the very remarkable behaviour is met with that there is a region of homogeneous isotropic phase above the middle soap as well as below it, so that, for example, at 177°, on steadily concentrating an isotropic solution the anisotropic middle soap separates, and after its formation is completed and the solution is slightly more concentrated, isotropic solution of still higher concentration begins to appear but exists over a narrow range, whereupon neat soap appears.

All these relations are shown in Fig. 1 and some of the numerical data from which the figure has been plotted are in Tables IA, B, C and D. The temperatures there recorded are T_i, the minimum temperature at which the system is a homogeneous isotropic liquid, determined visually or with the aid of optical apparatus; T_h, the temperature on heating to which anisotropic plastic liquid shows, by a marked fall in rigidity, that isotropic liquid is beginning to separate; and T_c, the temperature on heating to which crystals just disappear to form homogeneous neat soap. Concentrations are expressed in weight normality (N_w), and also in "fractional proportions" of potassium oleate, $N_w/(N_w + 1)$, for use later in the triangular diagram of the three-component system.

FIG. 1.



Equilibrium diagram for the two-component system water–potassium oleate, showing the stable, homogeneous phases that occur at various temperatures. The boundary of the isotropic solution only is accurately known.

TABLE IA.

Appearance of aqueous potassium oleate at room temperature and phases present, together with temperatures, T_i, *on heating to which the system becomes a clear homogeneous liquid.*

Series a. *Tubes partly evacuated before sealing.**

System (N_w).	Fractional proportion of K oleate.	Description of material at room temp.	T_i (visual).
0·70	0·412	Viscous, colourless, isotropic liquid.	12°
0·72	0·419	Hetero. M. soap and isotropic liquid.	22
0·75	0·429	Hetero., etc., very viscous.	33
0·78	0·438	Clear, firm M. soap.	42
1·00	0·500	Clear, rigid M. soap, yellowish-brown.	72
1·50	0·600	,, ,, ,, ,,	138
2·00	0·667	Clear, rigid, M. soap, deep colour.	185
2·50	0·714	,, ,, ,, ,,	173
3·00	0·750	Hetero.†	175
3·50	0·778	Hetero.‡	184

Homo. = homogeneous. Hetero. = heterogeneous. M. soap = "middle soap." N. soap = "neat soap."

* The above systems were prepared from oleic acid of mol. wt. 285 and were all more deeply coloured than those prepared with 1924 (B) and 1925 soaps, possibly owing to a very slight amount of free oleic acid, which becomes oxidised at high temperatures. This would provide a possible explanation of the marked difference between $3{\cdot}5N_w$-solution prepared with this sample of soap and that prepared with succeeding samples.

† Minute droplets of a lemon-white phase in a brownish-red phase; system still rigid and plastic.

‡ Two immiscible plastic fluids, one lemon-coloured and tending to accumulate at the surface, the other deep reddish-brown and accumulating at the bottom of the tube.

TABLE IB.

*Tubes not evacuated.**

System (N_w).	Fractional proportion of K oleate.	Description of material at room temp (18—20°).	T_i (visual).
0·80	0·444	Hetero. M. soap and isotropic liquid.	34·5°
0·85	0·458	Homo. clear firm M. soap.	57
0·91	0·476	,, ,, ,,	67
1·25	0·556	,, ,, ,,	118
2·00	0·667	,, ,, ,,	183·5
2·50	0·714	,, ,, ,,	188
2·75	0·733	,, ,, ,,	188·15
2·98	0·748	,, ,, ,,	186
3·20	0·762	,, ,, ,,	185
3·50	0·778†	,, ,, ,,	200
4·00	0·800	Rigid, anisotropic, definitely turbid.	237·5

* Prepared from oleic acid of mol. wt. 286.

† Not quite as transparent as the $3{\cdot}2N_w$-solution.

TABLE IC.

*Tubes not evacuated.**

System (N_w).	Fractional proportion of K oleate.	Description of material at room temp. (18—20°).	T_i (visual).	T_s (opt.).	T_c (visual).	T_h (opt.).
0·80	0·444	Viscous, hetero. M soap and isotropic liquid.	31·5°	32·5°.	—	—
1·00	0·500	Clear, rigid M. soap.	72	76	—	55°
1·50	0·600	,, ,, ,,	139	142·5	—	127
1·75	0·636	,, ,, ,,	161	173	—	163
2·00	0·667	,, ,, ,,	180	184	—	174
2·50	0·714	,, ,, ,,	188	—	—	—
2·75	0·733	,, ,, ,,	190	187·5	—	187
3·00	0·750	,, ,, ,,	185·5	—	—	—
3·10	0·756	,, ,, ,,	184·5	185·5	—	181
3·20	0·762	,, ,, ,,	183	—	—	—
3·28	0·766	,, ,, ,,	179·5	—	—	—
3·40	0·773	,, ,, ,,	178·5	—	—	—
3·50	0·778†	,, ,, ,,	194·5	200·5	—	173
4·00	0·800	Rigid, turbid N. soap and M. soap.	235·5	242	—	—
5·00	0·833	Hetero. rigid N. soap and M. soap.	261	—	—	—
6·00	0·857	Firm, hetero. N. soap and M. soap.	274·5	—	—	—
7·00	0·875	Semi-transparent N. soap.‡	283	—	—	—
8·00	0·889	Semi-transparent N. soap.§	280	—	—	—
9·00	0·900	Soft, semi-transparent N. soap.	287	—	—	—
10·00	—	,, ,, ,,	288·5	—	—	—
12·00	0·923	,, ,, ,,	291	—	26°	—
15·00	0·937	Hetero. N soap and cryst. flakes.	291·5	—	55	—
25·00	0·962	,, ,, ,,	293	—	98	—
30·00	0·968	,, ,, ,,	291	—	118	—
40·00	0·975	,, ,, ,,	303	—	132	—
50·00	0·980	,, ,, ,,	305	—	150	—

* Prepared from oleic acid of mol. wt. 286.

† Reproduction of 1924 (B).

‡ Turbidity subdued, and consistency less firm; can just be displaced by shaking.

§ Fluid, soft and non-homogeneous in appearance.

TABLE ID.

Systems prepared from pure aqueous potassium hydroxide and Kahlbaum's oleic acid, mol. wt. 285.

System (N_w).	Fractional proportion of K oleate.	Description of material at room temp. (18—20°).	T_i (visual).
1·15	0·535	Rigid M soap.	93·0°
1·24	0·552	,, ,,	115

Effect of the Presence of Potassium Chloride in Isotropic Solutions of Potassium Oleate.

Qualitative observations have been described by M. H. Fischer ("Soaps and Proteins," New York, 1921) on the effect of adding salts to ordinary soap solutions. Some of his experiments were repeated by Miss King (*J. Soc. Chem. Ind.*, 1922, **41**, 147T). Fischer's observations were confined to fairly dilute soap solutions and were evidently influenced by the difficulties of ensuring adequate mixing and avoiding oxidation of soap, which greatly affect the results. The following observations were made by Miss King and F. T. Maggs as well as by ourselves.

The most important effect is that, whilst moderate additions of such salts as potassium chloride and potassium thiocyanate progressively increase the viscosity of the liquid, there is an ill-defined range of concentrations of salt for which the potassium oleate solutions set to a clear, transparent, elastic jelly like table jelly. For potassium chloride and potassium thiocyanate these concentrations are between about 0·4 and $0{\cdot}8N_w$. This range is somewhat wider if sufficient time is given for gelatinisation; the whole system remaining homogeneous and clear if hydrolysis and oxidation are avoided.

Still further small additions of salt reduce the jelly to a more or less viscous, homogeneous liquid. In solutions of such soaps as do not gelatinise under the given conditions, for example, sodium palmitate at 81°, the viscosity rises to a maximum and then falls off very greatly before any salting-out takes place (compare Miss King's graph, *loc. cit.*). Similar behaviour is observed within the whole range of isotropic solutions.

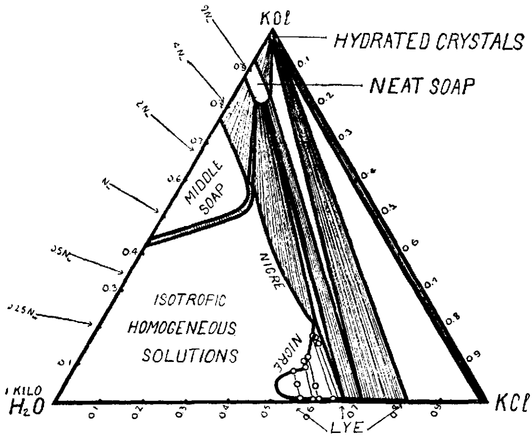
Still higher concentrations of salt cause separation of the soap solution into two layers. The concentration of salt necessary to effect this depends, in a rather complicated way, on the concentration of the soap, as is seen in Figs. 2, etc., in which the boundaries of the isotropic field are accurately mapped. If the solutions are sufficiently dilute, say below $0{\cdot}6N_w$-potassium oleate, the two liquid layers formed are both isotropic and are represented on the diagram within an indentation in the isotropic liquid boundary. The upper layer is "nigre" and contains most of the soap; the lower layer is "lye" containing a minute concentration of soap and a concentration of salt slightly higher than that in the nigre.

If the soap solution is more concentrated, say between $0{\cdot}75N_w$ and $3N_w$, the two phases separating out are neat soap and nigre. It will be noted that the presence of the salt greatly increases the possible concentration of soap in the isotropic solution; thus at 20° in the absence of salt the highest concentration at which potassium oleate forms a homogeneous isotropic liquid is $0{\cdot}70N_w$, whereas in the presence of $0{\cdot}176N_w$-potassium chloride the concentration of the soap may be increased to $3N_w$. As in the two-component system, so in the three-component system, increasing temperature extends the boundaries of the isotropic field.

Equilibria in the System Water–Potassium Oleate–Potassium Chloride.

Middle soap and neat soap, like isotropic solution, extend from the two-component system, aqueous potassium oleate, into the three-component system; thus not only is the two-component system the limiting boundary of the three-component system, but the same phases occur in each and no new ones appear through addition of salt. Discussion of the three-component system is thus reduced to delimiting the boundaries for the existence of the phases, the appearance and properties of which have previously been dealt with. In other words, a reference to the foregoing discussion of the two-component systems shows that solutions of pure soap spontaneously " salt out " in the absence of salt.

FIG. 2.



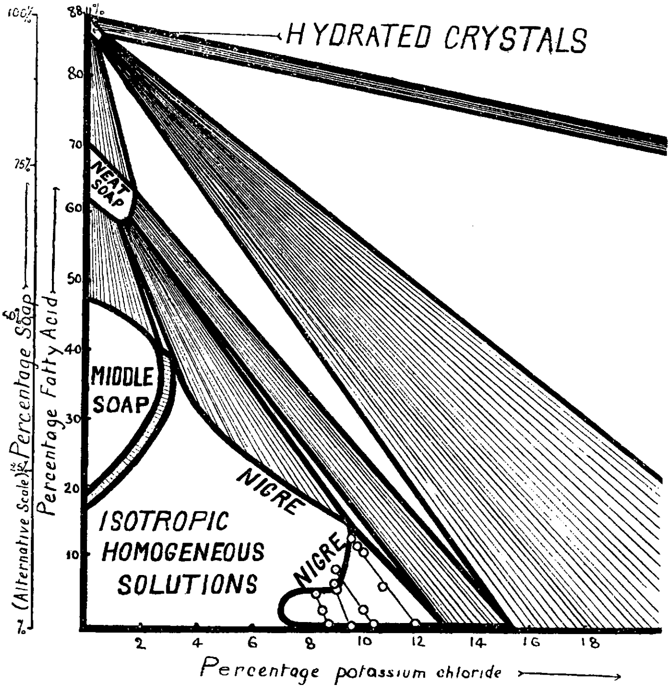
Phase rule diagram at 20°. Potassium oleate–potassium chloride–water; concentrations being expressed in fractions of mols. of potassium oleate and potassium chloride, but in fractions of one kilogram of water. The shaded areas represent the approximate direction of the tie lines in the two-layer systems.

Most of the observations consisted in noting carefully the temperatures, T_i, at which heterogeneous systems just became isotropic, and it was found that these homogeneous isotropic solutions separated again at the same temperatures on cooling. It is only when the true crystalline lamallæ are due to appear that supersaturation has ever been observed.

Addition of salt to middle soap lowers the temperature, T_i, at which it becomes isotropic. Likewise, at higher temperatures, its field of existence progressively diminishes until at 189° it is reduced to a single point in the two-component system.

In most cases separation of the phases was so imperfect that they remained permanently in intimate mixture as a rigid, or extremely viscous mass, so that samples could not be separated for analysis. Indeed, the complete separation of neat soap from nigre, even in full-scale commercial work, is an art which calls for the highest skill on the part of the soap boiler, and middle soap has never been studied on the commercial scale. Apart from the extremely ready separation of lye from nigre, it has been considered impossible to effect separations in small-scale experiments. However, recent experience indicates that at high temperatures certain of these separations may be possible which will then permit of direct analyses of the separated layers.

FIG. 3.



Phase rule diagram at 20°, potassium oleate–potassium chloride–water; concentrations being expressed in grams of fatty anhydride and grams of potassium chloride per 100 *grams of total system. The areas correspond to those in Fig.* 2.

The data are in Table II and the isotherms deduced therefrom are shown in Figs. 2 to 5, which should be compared with the corresponding diagrams for sodium palmitate (McBain and

Langdon, *loc. cit.*), where also a fuller introduction to the subject is given.

The five tie-lines between nigre and lye shown in Figs. 2 and 3, which illustrate the general equilibria at 20°, were obtained by direct analyses of the two phases in equilibrium with each other. The cross in the middle of each line represents the total composition of each system which should, of course, lie upon the straight line connecting the compositions of the two phases in each case.

TABLE II.

Effect of addition of potassium chloride to 0·1N_W*-potassium oleate; appearance and phases present at room temperature, and* T_i *the temperature on heating to which the system becomes a clear homogeneous liquid.*

Conc. of KCl (N_w).	Description of material at room temp. (18°).	T_i (visual).
0·00	Homo. transparent, isotropic liquid.	—
0·5	Isotropic, colourless, jelly-like system.	—
1·0	Moderately viscous, isotropic, opalescent liquid.	—
1·05	Two liquid layers; nigre and lye.*	25°
1·20	,, ,, ,, ,, Both isotropic.	119
1·30	,, ,, ,, ,, ,, ,,	127
1·50	,, ,, ,, ,, ,, ,,	156
1·80	Two layers, upper hetero.	185
2·0	Two layers, N. soap and lye.	205

* Upper layer the more viscous, lower limpid lye, both isotropic.

Effect of addition to 0·25N_W*-solutions of potassium oleate.*

0·25	Colourless, limpid liquid, isotropic.	—
0·50	Clear, viscous liquid, isotropic.	—
1·00	Clear, very viscous, isotropic liquid.	—
1·25	Clear, isotropic, viscous liquid.	—
1·50	Two liquid layers, both isotropic.	100
1·65	,, ,, ,, ,,	159
2·0	Two layers, upper hetero., lower lye	184
2·2	Two layers, upper viscous, lower lye.	204

Effect of addition to 0·50N_W*-solutions of potassium oleate.*

0·00	Clear, transparent, isotropic, mobile liquid.	—
0·25	Clear, isotropic, very viscous liquid.	—
0·50	Transparent, isotropic, elastic jelly.	—
1·00	Clear, viscous, isotropic liquid.	—
1·65	Two liquid layers, both isotropic.	75
1·67	,, ,, ,, ,,	124
1·70	,, ,, ,, ,,	120
1·80	Two layers, upper creamy, lower lye.	167
2·0	,, ,, ,, ,, ,, Lye increasing.	178
2·3	Two layers, N. soap and lye.	207

*Effect of addition to 0·75*N_w*-solutions of potassium oleate.*

Conc. of KCl (N_w).	Description of material at room temp. (18°)	*T* (visual).
0·00	Hetero. M. soap and isotropic liquid.	33
0·1	Clear, elastic jelly, isotropic.*	—
0·25	Clear, transparent, elastic jelly, isotropic.*	—
0·50	Clear, transparent, rigid jelly, isotropic.	—
1·0	Clear, transparent jelly, isotropic.*	—
1·5	Clear, viscous, isotropic liquid.	—
1·7	Viscous hetero. system.†	25
1·75	Hetero.; bad separation.‡	109
1·85	Hetero., three liquid phases.§	150
2·0	Viscous, turbid upper layer. ||	158
2·3	Turbid, aniso. upper layer and lye.	195
2·5	,, ,, ,, ,,	206
2·75	,, ,, ,, ,,	229·5

* Not perfectly rigid.

† Small amount of anisotropic phase at surface.

‡ Mainly clear, isotropic liquid of moderate viscosity; anisotropic phase near surface.

§ Middle nigre layer forms main bulk.

|| Lye growing at expense of nigre.

*Effect of addition to 1·0*N_w*-solutions of potassium oleate.*

0·00	Aniso. plastic fluid, rigid.	72
0·085	,, ,, ,,	65
0·10	Aniso. fluid, possessing elasticity.	60
0·17	Hetero. aniso. phase and isotropic jelly.	30
0·25	Clear, isotropic, transparent jelly.	—
0·50	,, ,, ,, ,,	—
1·00	Clear, viscous, isotropic liquid.	—
1·50	Viscous hetero. system.*	65
1·6	Viscous hetero. system.*	104·5
1·75	Viscous hetero. system, aniso. phase and nigre.	130
2·0	Two layers, upper turbid, lower lye.	156
2·5	Two layers, upper turbid and viscous, lower lye.	193
2·8	,, ,, ,, ,, ,, ,,	212·5

* Anisotropic phase tending to accumulate at the surface and viscous, isotropic liquid as lower layer; bad separation.

*Effect of addition to 1·5*N_w*-solutions of potassium oleate.*

0·00	Aniso. plastic fluid, rigid.	138
0·2	,, ,, ,,	129·5
0·40	,, ,, ,,	90
0·46	Clear, very viscous, isotropic liquid.	—
1·0	Hetero. system.*	60
1·35	Hetero., viscous, aniso. phase and nigre.	129
1·50	,, ,, ,, ,, ,,	136
1·78	Two layers, upper hetero., lower lye.†	160
2·0	Two layers, upper turbid and viscous.	163
2·3	Two layers, upper turbid, lower lye.	191
2·5	Two layers, upper viscous and turbid, lower lye.	205

* Small amount of anisotropic phase near surface, mainly viscous, isotropic liquid.

† Upper layer forms main portion.

Note.—Only results obtained with systems prepared in non-evacuated tubes are recorded in this and the following sections, *i.e.*, results are those with 1924 (B) soap.

Effect of addition to 2·0N_W-solutions of potassium oleate.

0·00	Clear, aniso., plastic fluid, rigid.	183·5
0·1	Aniso., plastic fluid, rigid.	178·5
0·2	,, ,, ,,	167
0·3	,, ,, ,,	159
0·4	,, ,, ,,	153
0·5	,, ,, less rigid.	136
0·6	Aniso. plastic fluid.	91
0·7	Mainly clear, isotropic jelly.*	—
0·8	Clear, viscous, isotropic liquid.	—
1·0	Hetero.; bad separation.†	110·5
1·2	,, ,, ,,	143
1·3	,, ,, ,,	154
1·5	,, ,, ,,	160
1·65	Two layers, upper viscous and turbid, lower lye.	183
2·0	,, ,, ,, ,, ,, ,,	—
2·2	,, ,, ,, ,, ,, ,,	—

* Little anisotropic phase near surface.

† Anisotropic phase and viscous, isotropic solution.

Effect of addition to 2·5N_W-solutions of potassium oleate.

0·0	Aniso. plastic fluid.	188
0·1	,, ,, ,,	186
0·2	,, ,, ,,	179
0·3	,, ,, ,,	166
0·4	,, ,, ,,	154
0·5	,, ,, ,,	108
0·6	Heterogeneous.*	86
0·7	Heterogeneous.*	121
0·79 †	Hetero. aniso. phase and nigre; bad separation.	142
1·0	,, ,, ,, ,, ,, ,,	163
1·3	,, ,, ,, ,, ,, ,,	188
1·5	Three phases, lye just appearing.	197·5
1·65	Two layers, viscous turbid layer and lye.	215
3·5	,, ,, ,, ,, ,,	247

* Anisotropic phase near surface, mainly clear, viscous nigre.

† 0·79N_w-KCl with 2·47N_w-K oleate.

Effect of addition to 2·75N_W-solutions of potassium oleate.

0·0	Aniso. plastic fluid, rigid.	188·5
0·2	,, ,, ,,	170
0·25	,, ,, ,,	164
0·30	,, ,, ,,	158
0·40	,, ,, ,,	144·8
0·50	Turbid, aniso., plastic fluid.	125
0·60	Hetero. aniso. phase and clear, viscous nigre.	150·5
0·80	,, ,, ,, ,, ,,	175
1·0	,, ,, ,, ,, ,,	184
1·65	Two layers, upper turbid and viscous, lower lye.	217

Effect of addition to 3·0N_W*-solutions of potassium oleate.*

Conc. of KCl (N_w).	Description of material at room temp. (18°).	T_i (visual).
0·0	Aniso. plastic fluid.	186
0·1	,, ,, ,,	172
0·2	,, ,, ,,	168
0·3	,, ,, ,,	156
0·4	,, ,, ,, Slight turbidity.	158
0·5	Viscous, semi-transparent system.	176
1·0	,, ,, ,, ,,	208
2·19	Turbid fluid, upper layer and lye.	—
3·0	,, ,, ,, ,,	237·5

Effect of addition to 3·5N_W*-solutions of potassium oleate.*

Conc. of KCl (N_w).	Description of material at room temp. (18°).	T_i (visual).
0·0	Aniso. plastic fluid.*	200
0·15	,, ,, ,, Quite firm.	210·5
0·20	,, ,, ,, ,, ,,	216·5
0·40	,, ,, ,, ,, ,,	224·5
0·50	,, ,, ,, ,, ,,	228·0

* Rigid but tending to turbidity.

Effect of addition to 4·0N_W*-solutions of potassium oleate.*

Conc. of KCl (N_w).	Description of material at room temp. (18°).	T_i (visual).
0·0	Rigid, aniso., plastic fluid.*	237·5
0·5	,, ,, ,, ,, Turbid.	240
1·1	Two layers, neat soap and nigre.†	238

* Definitely turbid.

† Good separation of brown nigre, forming about ¼ of system.

Effect of addition to 5·0N_W*-solutions of potassium oleate.*

Conc. of KCl (N_w).	Description of material at room temp. (18°).	T_i (visual).
0·0	Very turbid, aniso., plastic fluid, rigid.	261
1·0	Two layers, N. soap and nigre.*	260

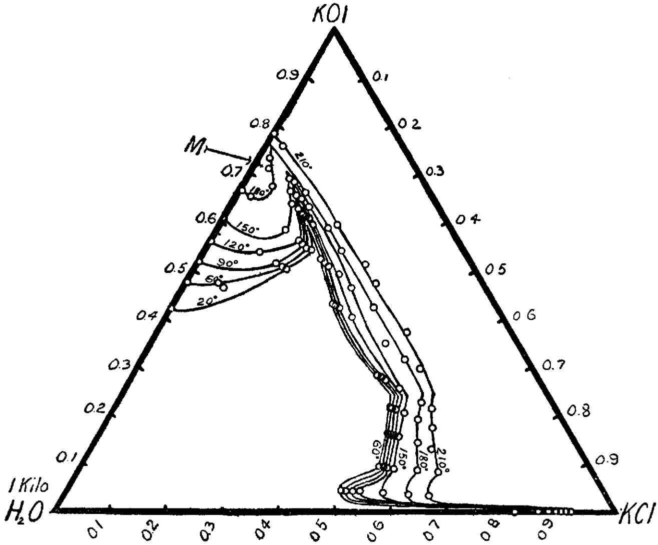
* Good separation of brown nigre, ⅕ of system.

Fig. 2 represents the equilibria and the stable phases at 20°. It is the same equilateral triangle of unit height used in the previous papers, in which the respective corners represent 1 mol. of pure anhydrous potassium oleate, 1 mol. of potassium chloride, and 1 kilo. of water; and in which the co-ordinates are the fractions of these three quantities, the sum of which for each point on the diagram is unity. Although not so easily read as the rectangular diagram (Fig. 3), it is much more satisfactory for a complete survey of the field. In Fig. 3 technical units are employed for convenience of comparison with soap-boiling data.

Nearly half of each of Figs. 2 and 3 is occupied by the field of ordinary isotropic solutions. The general form of this extensive field resembles that for sodium palmitate (*loc. cit.*, Figs. 1 and 2), especially if the difference in temperature is taken into account. However, the greater solubility of potassium oleate is reflected in the distinctly larger amounts of salt which can be added without destroying the homogeneity of the solution. The field of middle soap, though in both cases only approximately delimited, is much more prominent with potassium oleate, whereas the neat soap fields, as far as known, are fairly similar. The field representing crystalline soap is confined to a small part of the uppermost corner of the diagram on account of the low degree of hydration of crystals of potassium oleate. This field likewise requires further study.

In the previous communication (*loc. cit.*, p. 858) the possibility of the existence of a three-phase system, *viz.*, neat soap, nigre and lye, is briefly discussed, and it is shown that it is confined to a negligibly narrow region. This is again the finding in the present case, but since a few instances have been met with where apparently these three phases stably co-exist over a very narrow range, corresponding provision has been made in Figs. 2 and 3 of the present paper by indicating the very narrow triangle connecting the compositions of these three phases immediately to the right of the projecting portion of the isotropic field. In Fig. 2 of the previous paper this triangle was represented by a single heavy tie-line, whereas, through inadvertence, in Fig. 1 it was omitted altogether.

FIG. 4.

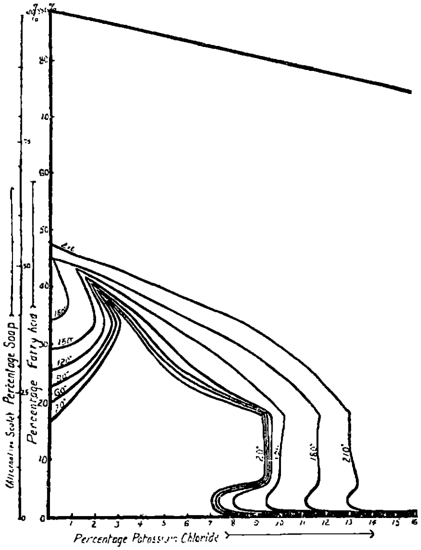


Solubility curves of potassium chloride and potassium oleate at 20°, 60°, 90°, 120°, 150°, 180°, *and* 210° *showing the extreme limits of the field of homogeneous isotropic solutions capable of existing at these temperatures. The point M is the only concentration at which middle soap can exist up to* 183°*; above this temperature it is isotropic.*

For practical purposes, whether this region is a single line or such a very narrow triangle is of no importance.

M. C. Field attempted to test this question for us by preparing five solutions each of which was $0{\cdot}5N_w$-potassium oleate and contained amounts of total potassium chloride ranging from $1{\cdot}70N_w$ to $1{\cdot}99N_w$. All five exhibited three layers, the proportion of the middle layer being greatest in the first and progressively less in the others and the amount of upper layer changing accordingly. This would at first sight appear to establish the existence of the suggested triangular field and give it a maximum width on the diagram extending from fractional proportion of potassium chloride = 0·53 to 0·57. However, the refractive index of the lye as well as of the middle layer changed progressively with the total composition of the system instead of each phase being identical in composition for all cases and varying only in amount. This is, then, direct proof that complete equilibrium was not attained and that the suggested triangle must be much narrower, having a width of only 1% or so of the total width of the diagram.

Fig. 5.



Limits of existence, in technical units, of homogeneous isotropic solutions containing potassium chloride and potassium oleate at 20°, 60°, 90°, 120°, 180°, *and* 210°, *showing the two regions in which solutions of pure soap form isotropic solutions at* 210°.

Figs. 4 and 5 present the isotherms which bound the field of isotropic solutions at various temperatures from room temperature up to 210°. These have been much more carefully worked out than in the case of palmitate, and in addition to the actual experimental points indicated in the diagram the position of the isotherms was checked by a series of graphs representing cross sections of the triangular space model for various normalities of soap.

Whereas the maximum temperatures at which middle soap can exist are lowered by the addition of salt, sections 11 and 13 of Table II indicate that in neat soap they are not much affected.

Summary.

1. The equilibria between the various forms of a potassium soap are very similar to those for a sodium soap.

2. All the soap phases that exist in the three-component system, including salt, are found in the simpler system, soap and water, where also their separation is spontaneous; that is, they "salt out" in the absence of salt and may even be observed at room temperature.

3. The limits of the field of existence of isotropic liquid solutions of potassium oleate with and without potassium chloride have been accurately determined for temperatures up to 210°. This single phase includes wholly crystalloidal solutions and ranges at sufficiently high temperatures from pure water up to pure anhydrous liquid potassium oleate, the two being miscible in all proportions above 300°.

4. Improvements in the methods of optical investigation have enabled progress to be made with the delimitation of the two important anisotropic liquids, neat soap and middle soap. Both neat soap and middle soap are typical conic anisotropic liquids.

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