217. *Phase-rule Equilibria of Acid Soaps. Part III. Anhydrous Acid Potassium Oleate.*

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IN a previous communication (J., 1927, 1392) we described the pure crystalline compound potassium hydrogen dioleate, showing that its composition is unaltered on recrystallisation from oleic acid or from various concentrations of alcoholic solution. We now present a more extended phase-rule study of the anhydrous two-component system. The results are very similar to those obtained by McBain and Field (*J. Physical Chem.*, 1933, **37**, 675) with potassium laurate and lauric acid, in that the only solid phases are the pure components and this one acid soap (containing equimolar proportions of soap and fatty acid), there being no evidence for the occurrence of solid solutions or isomorphous mixtures.

EXPERIMENTAL.

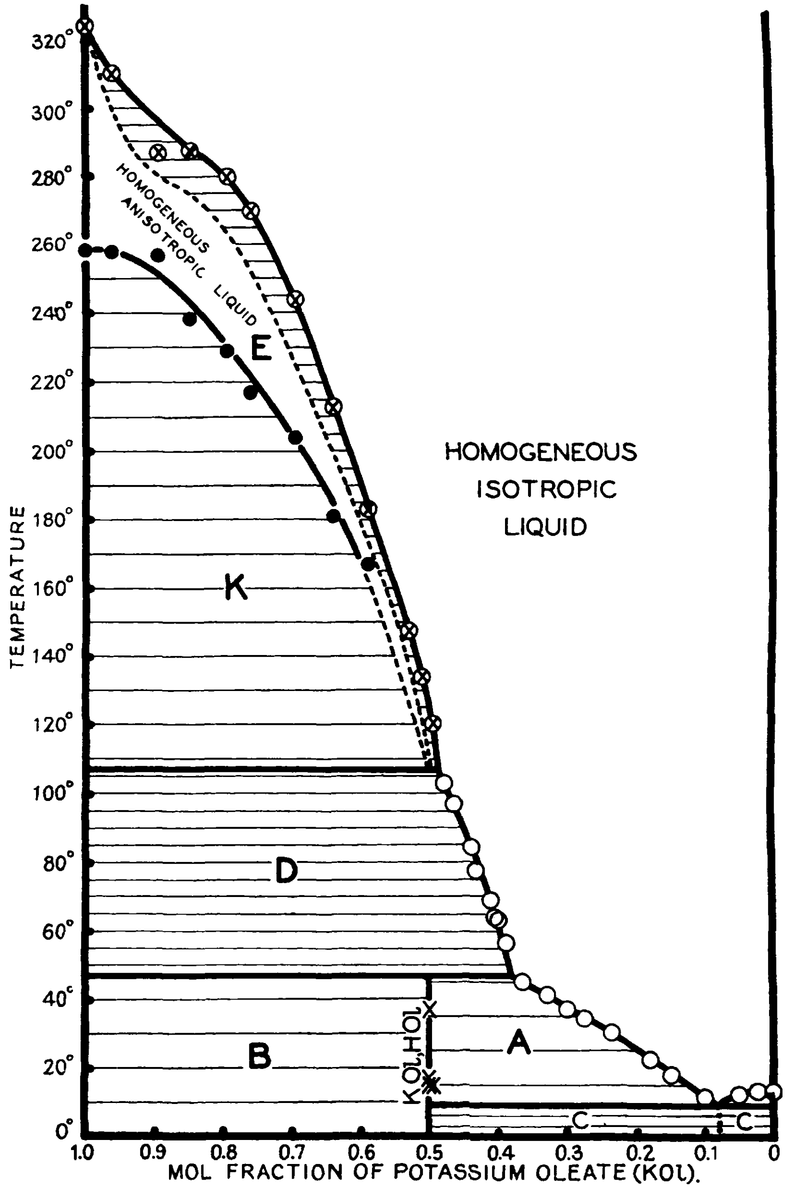
Preparation and Purity of Materials.—Lapworth, Pearson, and Mottram (*Biochem. J.*, 1925, **19**, 12) and Scheffers (*Rec. trav. chim.*, 1927, **46**, 293) have shown that commercial oleic acid contains considerable amounts of impurity, and we have followed essentially the former workers in preparing our pure acid. Oleic acid, obtained by the action of hydrochloric acid upon the sodium salt (Kahlbaum), on standing deposited a solid, which on recrystallisation from alcohol had a fairly sharp m. p., giving at 51° a slightly cloudy liquid which cleared sharply at 53·5°. This agrees with the m. p. of elaidic acid (Saytzeff, *J. pr. Chem.*, 1894, **50**, 73). The impure oleic acid was therefore converted into its ethyl ester by means of alcohol and sulphuric acid, and distilled at 4 mm., the middle fraction, b. p. 185—192°, being collected.

	First fraction.	Main fraction.	Residue.
Weight, g.	30	310	170
Refractive index (μ^{19°)	1·4451	1·4525	1·4649

Dr. Malkin has obtained for ethyl oleate, by repeated fractional distillation, $\mu^{15^\circ} = 1{\cdot}4536$.

This ester was converted into the barium salt and thence into the free acid, which had m. p. 12·0—12·4° (Lapworth and co-workers give 12·0—12·8°).

Fig. 1.



Phase-rule diagram for stable equilibria in the anhydrous two-component system potassium oleate–oleic acid. The composition of the eutectic mixture of solid HOl *and* KOl,HOl *is denoted by the vertical dotted line in field* C.

○, T_c; ⊗, T_i; ●, *temperature at which the last trace of crystal disappeared on slow heating, leaving the system wholly anisotropic*; ×, *compositions confirmed by the screw-press method.*

Potassium oleate was prepared by the method of McBain and Taylor (*Z. physikal. Chem.*, 1911, **76**, 179), and the pure acid potassium soap by the method of McBain and Stewart (*loc. cit.*). Both salts and the acid were kept in evacuated desiccators over calcium chloride and potassium hydroxide.

Analysis.—Two methods of analysis were used. (*a*) Direct titration of acid and acid soap with standard sodium hydroxide solution (from sodium drippings) free from carbonate, in 70—80% boiled-out aqueous alcohol (phenolphthalein). The alkali was standardised against standard hydrochloric acid prepared by dilution of the constant-boiling mixture (Hulett and Bonner, *J. Amer. Chem. Soc.*, 1909, **31**, 390), and also against Bureau of Standards benzoic acid, with agreement to within 0·06%. (*b*) Neutral and acid soaps were analysed as described by Laing (*J. Physical Chem.*, 1924, **28**, 681). The potassium oleate had M, 316·6, 316·1, 316·1 by the potassium value, and 321·6, 320·4, and 320·3 by the oleic acid value; value used, 319·3. Similarly, the molecular weights of the oleic acid and the acid soap were 286·1 and 602·4, respectively, the ratio of oleate to potassium in the latter being 1·985, 1·992.

Procedure.—All thermometers, weights, etc., were standardised. Systems were prepared by weighing the two components into glass tubes, and evacuating and sealing them. They were then heated until the contents formed a single homogeneous liquid. After cooling, they were heated, and the temperature T_c observed at which on very slow heating with constant shaking the last trace of solid just disappeared to leave only isotropic liquid (reproducibility within 0·5° up to 100°, decreasing to about 2° at 300°).

In systems containing more than 50% of potassium oleate, anisotropic liquid appeared at high temperatures, completely to disappear again at still higher temperatures, T_i, forming isotropic liquid, since above 324·4° potassium oleate and oleic acid are ordinary liquids miscible in all proportions.

The formation of anisotropic liquid is clearly visible to the eye because of the turbidity of this plastic phase (liquid crystal, conic anisotropic liquid, one of the smectic states). One cannot see the wires of an electric lamp bulb placed behind the tube when either pure potassium oleate or the two-component system is in this state. Similarly, the disappearance of the last of the anisotropic liquid is clearly visible. Supersaturation does not take place with reference either to formation of anisotropic liquid or its conversion into isotropic liquid. The results of this examination are given in Table I and Fig. 1.

TABLE I.

Visual Observations of the Temperature T_c *at which the Last Trace of Solid Crystal disappears on Heating to leave only Isotropic Liquid, and of* T_i, *the First Temperature at which the Homogeneous Isotropic Liquid becomes Turbid or Non-homogeneous on Cooling.*

Potassium oleate, %.	Potassium oleate, mol. fraction.	T_c.	Potassium oleate, %.	Potassium oleate, mol. fraction.	T_c.	Potassium oleate, %.	Potassium oleate, mol. fraction.	Crystals dissolve to anisotropic liquid at	T_i.
0·0	0	13·1°	39·10	0·3653	45·3°	52·35	0·4961	*	120·5°
2·500	0·0225	13·2	41·61	0·3884	56·7	53·79	0·5107	*	134
5·491	0·0495	12·1	42·60	0·3994	63·4	55·56	0·5285	*	147·7
10·87	0·0985	11·5	43·17	0·4050	64·0	61·37	0·5873	167°	183
16·13	0·1470	18·0	43·82	0·4114	69·0	66·34	0·6384	181	213
19·64	0·1797	22·4	45·95	0·4325	77·6	71·63	0·6936	204	244
25·60	0·2357	30·4	46·55	0·4384	84·7	77·80	0·7584	217	270
29·63	0·2739	34·6	49·16	0·4643	97·0	81·06	0·7936	229	280
32·43	0·3007	37·2	50·62	0·4788	103·1	86·10	0·8474	238·5	287·4
35·33	0·3287	41·7				90·36	0·8939	257	287
						96·40	0·9601	258	310·5
						100·0	1·000	258·5	324·4

* Temperature uncertain.

DISCUSSION.

The isotropic liquid phase exhibits three breaks in its boundary, at 9° (mol. fraction 0·08 KOl), at 47° (mol. fraction 0·38 KOl), and at 107° (mol. fraction 0·49 KOl).

The first is the eutectic point at temperatures below which only mixtures of solid oleic acid in solid acid soap KOl,HOl can exist, as shown in the fields marked C. The second, 47°, is a typical transition point and is the temperature above which the acid soap KOl,HOl cannot exist. Field A represents mixtures of this solid with the liquid represented by the boundary on the right for each temperature. Field B would represent heterogeneous mixtures of pure potassium oleate and pure acid soap, existing at all temperatures below the transition temperature. This field has not been especially studied in this system, but its interpretation is doubtless the same as in the other two-component systems investigated.

The field D between the transition temperature, 47°, and 107° will be shown to consist of mixtures of pure potassium oleate with the liquid which forms its right-hand boundary.

The break at 107° is due to the appearance of liquid crystal, field E. In all the systems so far investigated we have found that the pure soaps, which Vorländer has shown to exist as liquid crystals over a range of temperature between that for the solid crystal and the ordinary liquid, will dissolve the corresponding fatty acid whilst still retaining the liquid crystalline state. The field of anisotropic liquid not merely extends out into the two-component system but is prolonged downwards, in this case apparently from 258·5° down to 107°. The heterogeneous region to the left of this tongue consists between 107° and 258·5° of crystals of pure soap in equilibrium with the two-component anisotropic liquid at the right-hand boundary of this field. The heterogeneous region at the right hand of the tongue at 107° right up to 324·4° consists of mixtures of the two immiscible phases, liquid crystal and anisotropic liquid. The anisotropic liquid field E requires further examination, especially on account of its narrowness and the comparatively low temperatures to which it has been brought. Its right-hand boundary can be determined by a microscopic examination between crossed Nicols on a heating stage.

The field C is visibly heterogeneous at room temperature. For example, the system containing 0·4 mol. fraction of potassium oleate is seen to contain a crystalline solid enmeshing an oily liquid.

Direct proof that the acid soap KOl,HOl does not form solid solutions or isomorphous mixtures in the fields A or C is given by the screw-press method developed by Field (*loc. cit.*) for squeezing out any liquid enmeshed by the solid, thus enabling the press-cake residue to be analysed. Four such experiments were carried out at 15°, 15°, 17°, and 37°, the original composition being 0·24, 0·24, 0·25, and 0·37 mol. fraction of potassium oleate, respectively. In each case the press-cake residue had the composition KOl,HOl, the mol. fractions actually determined being 0·494, 0·499, 0·50, and 0·50, respectively.

Likewise, the same method yields conclusive proof that the transition temperature has been correctly interpreted. Here, three experiments were carried out at 49°, 60°, and 103°, the original compositions being 0·50, 0·50, and 0·54 mol. fraction of potassium oleate, respectively. In each case pure potassium oleate crystals were left as press-cake residue, the actual compositions as determined being 1·000, 0·999, and 1·00 mol. fraction of potassium oleate, respectively.

Preliminary Results with the Anhydrous Two-component System Sodium Stearate–Stearic Acid.

Using Kahlbaum's sodium stearate and stearic acid without purification, we outlined the form of the liquid boundary. The soap contained 1·273% of moisture, which appreciably affects the results, as well as the ease of working, at higher proportions of soap. The soap was imperfectly crystalline and tended to pass out from the screw press with the liquid. The results, which need confirmation, would indicate that the acid soap NaStr,2HStr (or, just possibly, NaStr,HStr) may exist with a transition point at about 80°, and the acid soap 2NaStr,HStr with a transition temperature of about 97°. We did not find NaStr,HStr, but the separation of liquid from the apparent 2NaStr,HStr may have been imperfect. The liquid boundaries are outlined by the following provisional determinations of T_c. Besides the transition points indicated by the breaks in the liquid boundary at 97° and 80°, there is a eutectic point at 67° close to the stearic acid boundary. The nature of the transition points was confirmed by screw-press experiments with analysis of the residue.

Mol. fraction NaStr	0·0	0·022	0·050	0·069	0·124	0·156	0·205
T_c	68·4°	68·6°	71·5°	72·6°	74·7°	75·8°	77·7°
Mol. fraction NaStr	0·239	0·270	0·301	0·350	0·375	0·422	0·427
T_c	78·1°	79·3°	82·0°	86·8°	91·7°	107·4°	109·6°
Mol. fraction NaStr	0·444	0·450	0·508	0·554	0·663	0·666	0·777
T_c	113·9°	118·0°	136·0°	152·2°	188°	240°	242·5°

The soap itself became anisotropic at 260° and isotropic at 400°.

SUMMARY.

It has been shown that potassium oleate, oleic acid, and the acid soap, which contains equal proportions of the two, each crystallise out pure without forming isomorphous mixtures or solid solutions with each other. The acid soap KOl,HOl exists only below its transition temperature, 47°.

The anisotropic liquid or liquid-crystalline form of potassium oleate, which exists between 258·5° and 324·4°, is extended by addition of oleic acid into the two-component system and there begins to appear at a temperature as low as 107°.

Some preliminary results have been obtained for acid sodium stearates.

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