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216. *Phase-rule Equilibria of Acid Soaps. Part II. Anhydrous Acid Sodium Palmitates.*

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Acid soaps, *i.e.*, molecular compounds of neutral soap and fatty acid corresponding to the well-known acid acetates, were discovered by Chevreul and described or postulated by many subsequent writers. Crystalline specimens of constant composition (see, *e.g.*, McBain and Stewart, J., 1927, 1392), crystallising from solutions of varying composition, have been prepared, and studied by means of *X*-rays (Piper, J., 1929, 234); nevertheless, their existence is often disputed (for references, see Part I; McBain and Field, *J. Physical Chem.*, 1933, **37**, 675). This is largely due to the influence of an incomplete phase-rule study of the system palmitic acid–sodium palmitate by Donnan and White (J., 1911, **99**, 1668), who attained only a very imperfect separation of solid from liquid and did not carry their study beyond a mixture containing 38% of sodium palmitate, thus not attaining the composition even of the acid soap containing the smallest proportion of sodium salt.

We have shown (*loc. cit.*) by means of an elaborate phase-rule study, using visual, dilatometric, microscopic, and screw-press methods, that in the anhydrous system potassium laurate–lauric acid the only acid soap is the crystalline NaL,HL, which separates out pure, does not form solid solutions or isomorphous mixtures with either component, and exhibits a well-defined transition point at 91·3°. This and the following series of studies of the two- and three-component systems (anhydrous and aqueous) were completed at the University of Bristol in 1925—1927. Our findings differ greatly from those of Donnan and White, and appear completely to establish the existence of definite acid soaps of constant composition.

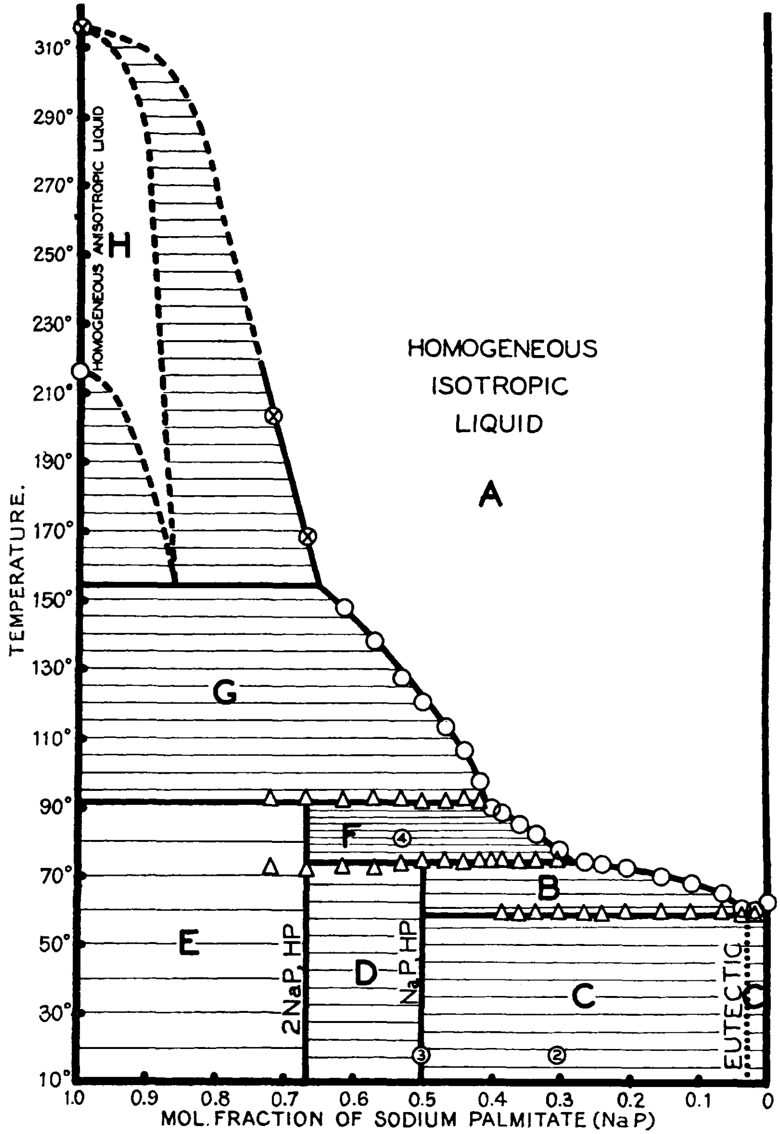
Experimental.

The methods employed have already been described (McBain and Field, *J. Physical Chem.*, *loc. cit.*, and 1926, **30**, 1545; for other references, see McBain, Lazarus, and Pitter, *Z. physikal. Chem.*, 1930, *A*, **147**, 87).

Materials.—The palmitic acid used was carefully recrystallised and had m. p. (capillary) 62·8°

(Millikan and Beilstein give 62·6°). The sodium palmitate (Kahlbaum; special preparation September, 1925) gave on analysis 1·0NaP + 0·0086NaOH + 3·47%H_2O. It was thought that the water would be negligible because, under the conditions of the experiments, it might have been in the vapour. However, subsequent results showed that this is not the case, for systems containing more than 75% sodium palmitate gave appreciably distorted results, which are therefore not included in the data now submitted.

Fig. 1.



Phase-rule diagram for stable equilibria in the anhydrous two-component system sodium palmitate–palmitic acid.

○, T_c; ⊗, T_i; △, *temperature at which a change was observed microscopically on heating*; ②, ③, ④ *systems photographed in the Figs. of corresponding number.*

Visual Method.—First, a delimitation of the boundaries of the homogeneous isotropic liquid was made. The systems were prepared by weighing the constituents directly into thick-walled glass tubes, sealed at the bottom like a test-tube, of diameter $\frac{1}{2}$—$\frac{3}{4}$ in. and 9 in. long; these were then evacuated and sealed. The tubes were next heated to approximately 250°, until all solid had melted or dissolved to form a homogeneous isotropic liquid, and then cooled.

Observations were made to determine the temperature, T_c, when the last trace of crystal dissolves to form a homogeneous isotropic liquid. These were carried out by careful heating in either a glycerol-bath or an electric furnace. No observations were made on cooling, owing to the undercooling when solid phases are due to separate. Results obtained in this manner are given in Table I and represented diagrammatically in Fig. 1. In most cases these values were checked by the microscopic method given below. Description of the individual systems has been omitted to save space.

TABLE I.

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

Mol. fractions.			Mol. fractions.			Mol. fractions.			Mol. fractions.			
NaP.	HP.	T_c.	NaP.	HP.	T_c.	NaP.	HP.	T_c.	NaP.	HP.	T_c.	T_i.
0·0000	1·0000	62·8°	0·2074	0·7926	72·3°	0·3850	0·6150	88·4°	0·5310	0·4690	127·8°	—
0·0175	0·9825	60·7	0·2404	0·7596	73·6	0·3995	0·6005	90·0	0·5709	0·4291	138·0	—
0·0364	0·9636	61·1	0·2747	0·7253	74·2	0·4161	0·5839	97·8	0·6155	0·3845	147·8	—
0·0665	0·9335	65·2	*0·3034	0·6966	77·5	0·4395	0·5605	106·2	0·6682	0·3318	†	168·5°
0·1119	0·8881	67·9	0·3335	0·6665	82·5	0·4673	0·5327	113·2	0·7188	0·2812	†	203·5
0·1555	0·8445	70·0	0·3599	0·6401	85·1	0·5010	0·4990	120·5	1·0000	0·0000	216 ‡	316 ‡

* Compare Fig. 2.

† These temperatures could not be determined accurately owing to the cloudiness of the conic anisotropic liquid crystals formed.

‡ Taken from Vorländer, *Ber.*, 1910, **43**, 3120.

Microscopic Examination between Crossed Nicols.—In order to understand and plot the equilibria present in the solid phases, the microscope method, previously described, was used. Very thin samples of the systems placed between a microscope slide and cover glass were observed between crossed Nicols on the microscope stage (magnification × 55). The temperature was gradually raised by a small electric heater. The results obtained are plotted in Fig. 1.

DISCUSSION.

In Fig. 1 the boundary of the liquid field A shows four definite breaks at 59·2°, 74·2°, 91·1°, and 154°. Each of these must, therefore, represent a change of the phases in contact with the liquid. The first of these is the eutectic point. The second is a transition point, also noted by Donnan and White but called by them " the second eutectic point." It is a typical transition point, and marks the highest temperature at which the acid soap NaP,HP can exist and above which it immediately breaks down into a mixture of the acid soap 2NaP,HP and liquid.

Similarly, the break at 91° must be recognised as the transition temperature above which the acid soap 2NaP,HP immediately decomposes into a mixture of solid NaP and liquid. There is no name for the break at 154° that represents the lowest temperature at which liquid crystalline soap can exist. Such points have been observed hitherto only in our phase-rule studies involving soaps, and they arise from the fact that, as shown in field H, fatty acid can dissolve in liquid crystalline soap, extending the range of existence of homogeneous conic anisotropic liquid outwards and downwards as indicated in the broken-line boundaries of field H. Above 316° sodium palmitate is an isotropic liquid miscible in all proportions with palmitic acid.

Below the eutectic point at 59·2° exists the field C, consisting of a heterogeneous mixture of the pure crystalline acid soap NaP,HP and pure crystals of palmitic acid. Likewise, the fields D and E represent binary heterogeneous mixtures of the two acid soaps, and of NaP with 2NaP,HP, respectively.

The field B is separated from the field C by the experimental points which demonstrate along most of the boundary a sharp break, thus disproving the hypothesis of Donnan and

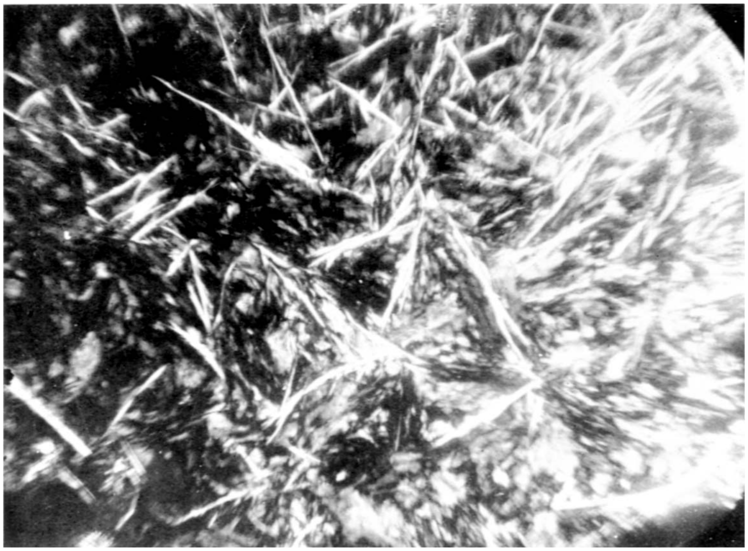


FIG. 2.—*The heterogeneous system* $0{\cdot}303NaP + 0{\cdot}697HP$ *at room temperature, showing needle crystals of the acid soap* NaP,HP *against darker background.*

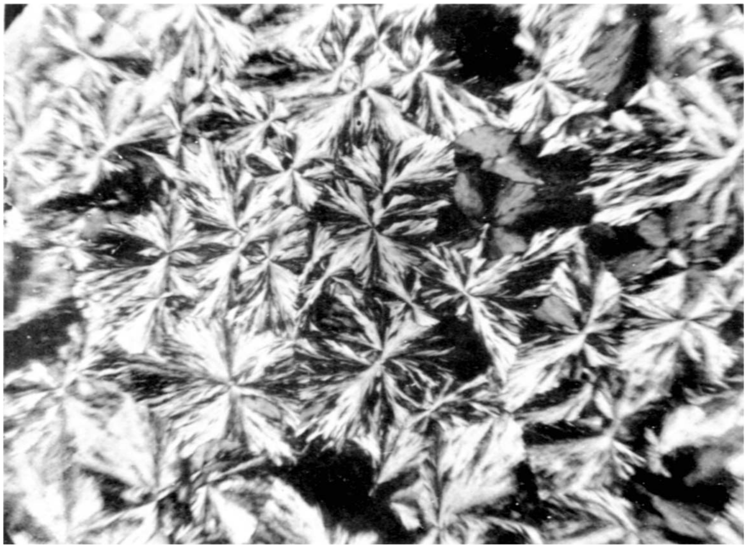


FIG. 3.—*The homogeneous system* NaP,HP *at room temperature, consisting entirely of bunches of radiating crystals and showing no change until heated to* 74·2°.

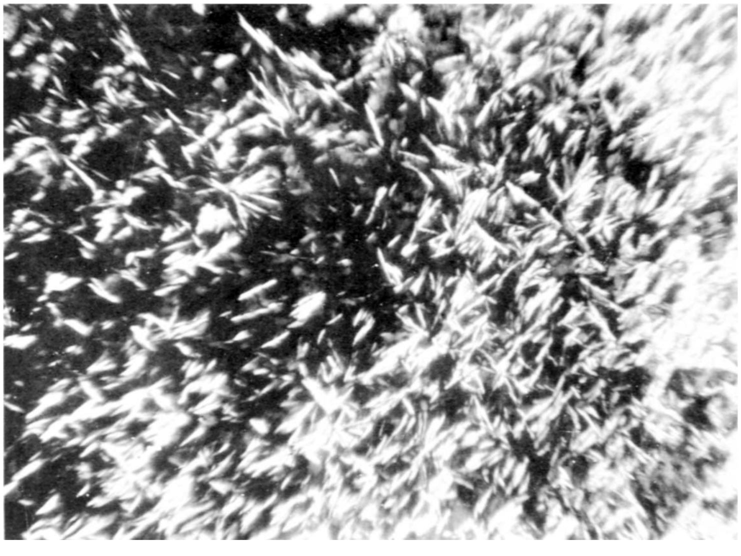


FIG. 4.—*The heterogeneous system* $0{\cdot}531NaP + 0{\cdot}469HP$ *at* 81°, *consisting of rods of crystalline* 2NaP,HP *in isotropic liquid.*

White * that these systems are homogeneous solid solutions instead of heterogeneous mixtures as shown by our results.

The same result follows from inspection of the photographs (Figs. 2 and 3). The latter consists entirely of crystals of the pure acid soap NaP,HP, whereas the former obviously is heterogeneous, consisting of comparable amounts of needles of NaP,HP and of a background of palmitic acid. Field C, like fields B and F, is therefore heterogeneous, field B representing mixtures of NaP,HP with the isotropic liquid on its right-hand boundary, which is its solubility curve, and field F mixtures of 2NaP,HP with the isotropic liquids bounding this field on the right. The heterogeneity of field F is evident in the last photograph (Fig. 4).

Throughout the diagram, heterogeneous fields are marked by horizontal (isothermal) tie lines, whose two ends represent the phases present in the heterogeneous mixture. Thus field G consists, in so far as we have investigated it, of a heterogeneous mixture of pure soap with its saturated solution in palmitic acid represented by the solubility curve separating G from A.

It was our intention to insert Donnan and White's incomplete data for the liquid boundaries in our Fig. 1, but the results are so close to ours that an enlarged diagram would be necessary to distinguish them. Their temperatures ranged only from 60° to 82°. The portion of the boundary between fields A and F is identical with ours; that between A and B runs smoothly parallel with ours but is for the most part 1° lower.

However, in determining the constitution of the solid phases, they trusted to mere draining and filtration through a Gooch crucible to separate these from the viscous liquid. This process must have been extremely incomplete, as demonstrated by our present results as well as by the direct observations, using a screw press, in the other studies of this series. They greatly under-estimated the extent to which a finely divided solid can soak up a liquid. Examination between crossed Nicols readily reveals the presence of liquid because of its isotropic nature in contrast to the doubly refracting crystals.

The demonstration of the extent to which acid soaps separate out pure has not been made as complete in this as in the other studies of this series, but the latter have yielded much further support for the present findings.

Two points on Fig. 1 represent observations that are not completely in accord with the identification of the second acid palmitate as 2NaP,HP. They are the two left-hand points at 72°, representing microscopic observations of a detectable change at this temperature, impossible if no NaP,HP is present. However, this is undoubtedly due to insufficient time having been allowed for complete formation of the 2NaP,HP when cooling the systems from the liquid condition.

Formation of the acid soap when cooling these particular systems from the homogeneous liquid state well above 200° is a very complicated process. The first thing that separates is highly viscous liquid crystal during perhaps 50° of cooling. Next comes anhydrous soap itself, the system still being extremely viscous. Except with very slow cooling it would, therefore, be unlikely that the reactions would be completed between the solid phases so as quantitatively to produce the theoretical yield of 2NaP,HP without extraneous admixture.

McBain, Taylor, and Laing (J., 1922, **121**, 621), in the three-component system sodium palmitate–water–palmitic acid, found that the conductivity and osmotic effects disappeared linearly upon addition of palmitic acid down to the proportion 2NaP,HP, which would substantiate the present result, although presumably this acid soap would be hydrated in presence of water. They worked at 90°, only just within the range of possible existence of 2NaP,HP with its transition point at 91°. They could not, therefore, have discovered NaP,HP which does not exist above 72·1°. Piper states that he carried out his *X*-ray examinations at 80°. If so, the specimens of NaP,HP prepared for him by Dr. Malkin must have been decomposed before examination, and the spacings given on

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* Potts (Donnan and White, *loc. cit.*, p. 1669) observed " the appearance of a second halt at this temperature in some of the cooling curves," which extended from 0 to 40% of sodium palmitate, but did not state in which of the cooling curves this eutectic break was observed.

p. 238 of his paper must refer to the second acid soap in the decomposition mixture. Similarly, acid potassium oleate KOl,HOl cannot exist above 47°, KL,HL not above 91·3°, and the acid stearates not above 81° and 96°, respectively.

Ekwall and Mylius (*Ber.*, 1929, *B*, **62**, 1080; cf. Malkin, *Ber*, 1930, *B*, **63**, 1807) obtained only 2NaP,HP and NaP,HP by crystallisation from mixtures in absolute alcohol, but from 96% alcohol containing 32·5 times as much palmitic acid as sodium palmitate they derived at 10·5° a solid of the composition NaP,2HP. Their microscopic examination was always carried out while the original crystals were still suspended in the alcoholic mother-liquor. We do not account for their NaP,2HP (compare our Fig. 2, which is certainly heterogeneous), but it is just possible that it may be formed at low temperature. If so, it must decompose below the eutectic temperature, according to the liquid curves both of Donnan and White and of ourselves. In favour of its existence is the molecular-weight determination in camphor, but all other physicochemical checks are lacking. The melting points they give are seen to be incorrect, and a compromise with partial liquefaction. Donnan and White found that an appreciable excess of the viscous liquid had to be present before the mixture would even flow down into a Gooch crucible. None of the acid soaps has a true melting point.

SUMMARY.

It is shown that the two definite crystalline compounds NaP,HP and 2NaP,HP exist without forming solid solutions or isomorphous mixtures with either component, sodium palmitate, palmitic acid, or with each other. They decompose at well-marked transition temperatures of 74·2° and 91·1°, respectively. The liquid crystalline or conic anisotropic phase is extended down to 154° in this anhydrous two-component system.

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