159. *Higher Aliphatic Compounds. Part IV. Systems with Ethyl Margarate and Heptadecyl Alcohol.*

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THE study of binary systems of long-chain compounds has now been extended to mixtures of substances with even and with odd numbers of carbon atoms in the molecules.

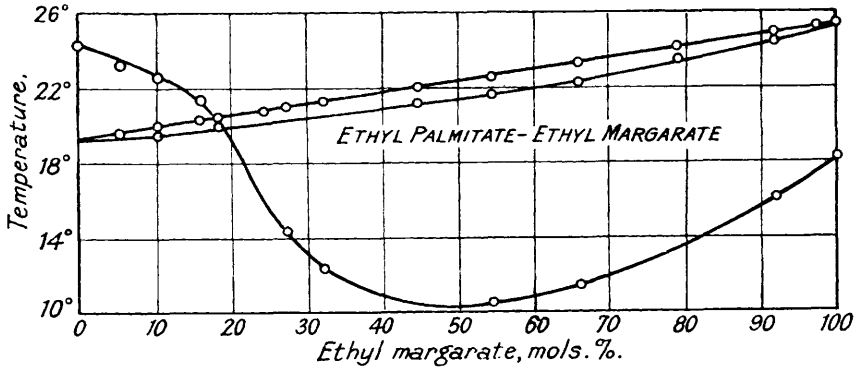
In the systems ethyl palmitate–ethyl margarate (see Fig. 1) and ethyl margarate–ethyl stearate, the transparent forms of these polymorphous esters give continuous series of solid solutions, the liquidus curves being straight lines. The transparent forms of ethyl palmitate and ethyl stearate, first described in Part I of this series (J., 1931, 803), were supplied for *X*-ray analysis to Dr. T. Malkin, who reported (*Nature*, 1931, **127**, 126; J., 1931, 2796) that they contained " vertical chains." It is significant that those forms in which the general direction of the carbon chains is at right angles to the crystal face should be those which form the simplest systems of solid solutions.

The opaque forms of the esters have " inclined chains," and their mixtures give systems of Type III (with a minimum). In the even–odd mixtures, the curve for opaque crystals

lies mainly below the solidus of the transparent system, because the opaque is the lower-melting form of ethyl margarate (Malkin, *loc. cit.*; Phillips and Mumford, J., 1931, 1736).

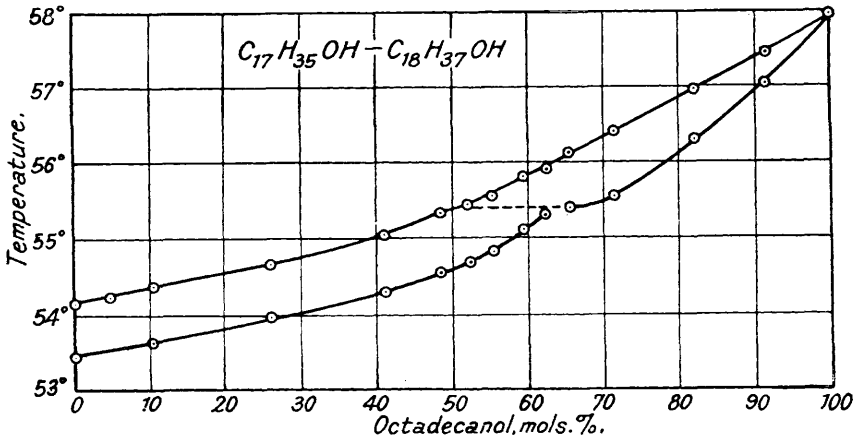
The system heptadecyl alcohol–octadecyl alcohol (see Fig. 2) is not a continuous series of solid solutions, as there is a transition at 50 mols. %. Polymorphism of the heptadecyl

FIG. 1.



alcohol complicates the solidus curve. Repetition of part of the even–even system, hexadecyl–octadecyl alcohols (Part I, *loc. cit.*) confirmed the smooth curves previously found, but the system hexadecyl alcohol–heptadecyl alcohol (not yet completed) gives indication of two series of solid solutions. These systems will shortly be discussed in Part V.

FIG. 2.



EXPERIMENTAL.

Ethyl Margarate.—Margaric acid was synthesised from pure cetyl iodide (Part II; J., 1932, 738) and crystallised from EtOH and then C_6H_6 to const. f. p. 61·10°, m. p. 61·12° (m. p. in capillary tube, 62°). Garner and King (J., 1929, 1860) give f. p. 60·81°. The ethyl ester crystallised from EtOH to const. f. p. 25·37°, m. p. 25·40° (m. p. in capillary tube, 26°). This transparent (α-) form passed into an opaque (β-) form at approx. 16° on cooling, the reverse change occurring at approx. 19°, in agreement with Phillips and Mumford (*loc. cit.*). Hydrolysis of the ester of f. p. 25·37° gave margaric acid, which, once crystallised from EtOH, had f. p. 61·1°. The value 25·2° given by Phillips and Mumford is thus too low.

Ethyl Palmitate.—This was crystallised to const. f. p. 19·34° (α-), m. p. 24·16° (β-) (Part I; *loc. cit.*).

Mixtures of Ethyl Palmitate and Ethyl Margarate.—These crystallised readily in transparent plates. In mixtures containing more than 80% of the palmitate, a change to opaque occurred

on keeping, while the other mixtures were transformed on cooling sufficiently. The β- m. p.'s recorded are very approx. and are the averages from arrests on heating and cooling curves.

Mixtures of Ethyl Margarate and Ethyl Stearate.—Only sufficient points were determined on the liquidus curve to show that this was a straight line, and the system must be very similar to the preceding one. The ethyl stearate was a pure specimen used in Part I (*loc. cit.*).

Ethyl margarate–ethyl palmitate.

Margarate, mols. %.	F. p. (α).	M. p. (α).	M. p. (β).	Solidus.	Margarate, mols. %.	F. p. (α).	M. p. (α).	M. p. (β).	Solidus.
100	25·37°	25·40°	18·3°	—	27·3	20·95°	21·0°	14·3°	—
97·5	25·19	25·20	—	—	24·4	20·7	—	15·5	—
91·7	24·81	24·86	16·1	24·5°	18·5	20·36	20·39	—	20·0°
79·0	24·10	24·16	—	23·5	15·9	20·16	—	21·4	—
65·9	23·24	23·31	11·5	22·25	10·2	19·91	20·04	22·6	19·5
54·0	22·51	22·54	10·5	21·6	5·3	19·60	19·64	23·21	—
44·7	22·02	22·06	—	21·2	0·0	19·34	—	24·16	—
32·3	21·24	21·28	12·3	—					

Ethyl margarate–ethyl stearate.

Margarate, mols. %	0·0	21·5	51·8	62·1	100
F. p.	30·95°	29·75°	28·10°	27·49°	25·37°

Heptadecyl Alcohol.—Reduction of ethyl margarate (f. p. 25·4°) with Na and EtOH and distillation of the product with superheated steam gave heptadecyl alcohol of f. p. 53·4° (yield 80%). The alcohol crystallised from EtOH to f. p. 54·2°, m. p. 54·3° (m. p. in capillary tube 55°). Levene, West, and van der Scheer (*J. Biol. Chem.*, 1915, **20**, 531) give m. p. 54° (capillary tube). As the cooling curves showed a change of direction at 53·8° and a distinct arrest at 43·5°, the alcohol is polymorphous. In the system with octadecyl alcohol, the shape of the solidus curve also indicates a modification of f. p. 53·5—53·8°. Some specimens, moreover, which were unlikely to contain much impurity had f. p.'s 53·8° and a slow rate of crystn. Several recrystns. from C_6H_6 and ligroin were needed to raise the f. p. to 54·2°. This matter is being reinvestigated.

Heptadecyl Acetate.—The alcohol of f. p. 53·8° gave an *acetate* which, twice cryst. from acetone, had f. p. 24·60°, m. p. 24·62° (transparent form, α-). The substance is very easily sol. in C_6H_6. After distillation (150°/*ca.* 1 mm.) and recrystn. from much acetone, it had f. p. 24·62°, m. p. 24·64° (capillary tube 25·5°) (Found: C, 76·6; H, 12·7. $C_{19}H_{38}O_2$ requires C, 76·5; H, 12·7%). On standing, the substance changes into an opaque form (β-), m. p. 30·2° (capillary tube, 30·5—31°). The β-form is also deposited from *dilute* acetone solutions in dense prisms, but cooling to below 5° produces a fine opaque form (γ-), the existence of which is also indicated by an arrest at 10·0° in the cooling curve (compare the polymorphism of cetyl and octadecyl acetates, Phillips and Mumford, *loc. cit.*). Hydrolysis gave alcohol of f. p. 53·8°.

Mixtures of Heptadecyl and Octadecyl Alcohols.—These crystallised fairly rapidly, and the f. p.'s were concordant if the temp. of the air-jacket surrounding the f. p. tube was kept less than 0·6° below that of the alcohols.

$C_{18}H_{37}$·OH, mols. %.	F. p.	Solidus.	$C_{18}H_{37}$·OH, mols. %.	F. p.	Solidus.	$C_{18}H_{37}$·OH, mols. %.	F. p.	Solidus.
0·0	54·18°	53·5°	48·4	55·36°	54·55°	65·6	56·15°	55·4°
5·0	54·27	—	52·2	55·46	54·7	71·2	56·40	55·6
10·6	54·40	53·7	55·3	55·55	54·8	82·0	56·96	56·3
25·9	54·67	53·95	59·3	55·81	55·1	91·5	57·45	57·05
41·2	55·05	54·3	62·5	55·90	55·3	100	57·93	57·7

Mixtures of Hexadecyl and Octadecyl Alcohols.—New values of f. p. and solidus temps. supplement those of Part I in the 50% region and lie on smooth curves.

$C_{18}H_{37}$·OH, mols. %	63·5	52·0	48·1	45·0
F. p.	52·86°	51·40°	51·01°	50·65°
Solidus	51·2°	50·0°	49·7°	49·5°

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