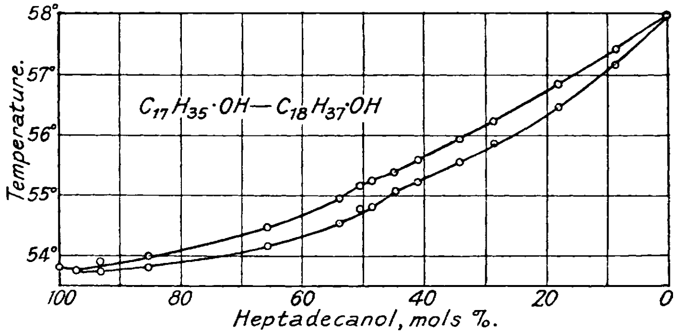
# 315. *Higher Aliphatic Compounds. Part V. Systems with Heptadecyl Alcohol and Heptadecane. Polymorphism of Octadecane.*

By Peggy C. Carey and J. C. Smith.

Mixtures of heptadecyl alcohol with its nearest homologues differ from other systems described in these memoirs in that there are sudden changes at the equimolecular composition. The " even–even " mixtures hexadecyl and octadecyl alcohols (Part I; J., 1931, 802) gave a clear Type III system. Malkin (*J. Amer. Chem. Soc.*, 1930, **52**, 3739) has concluded from *X*-ray measurements of alcohol crystals that there are two molecules in the unit cell. From a mixture of alcohols A and B there is thus the possibility of A–A, B–B, and A–B crystal units. In the system hexadecyl alcohol–octadecyl alcohol the smooth curves indicate that A–A can form a continuous series of solid solutions with B, and B–B likewise with A, these passing smoothly from one to the other at 50 molecules %. Here the big gap between liquidus and solidus may indicate the absence of A–B forms.

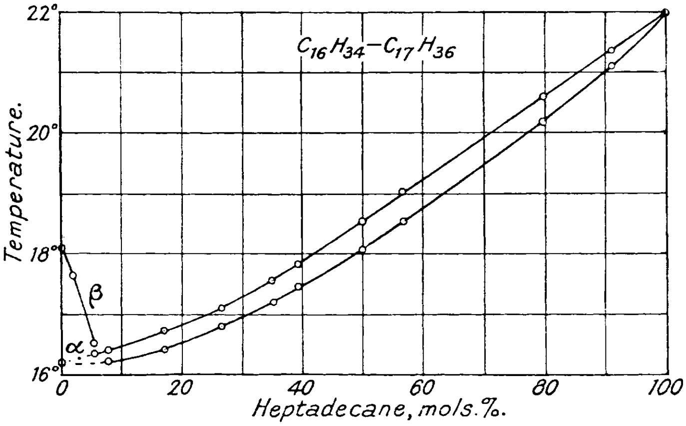
Fig. 1.



In the even–odd system, heptadecyl alcohol–octadecyl alcohol (Fig. 1 : the system hexadecyl alcohol–heptadecyl alcohol is very similar) the break in the curve is capable of at least two explanations. (i) The mixed crystals A–A with B do not approach the same crystalline form as those of B–B with A, so that at the equimolecular composition there is a *sudden* change from one type to the other. This implies a difference in crystalline form between even and odd alcohols which is not obvious in the thermal behaviour of those studied, but the *X*-ray data (Malkin, *loc. cit.*, p. 3740) show definitely that at the melting point the crystal form with a " vertical chain " is stable for the odd, and the form with a " tilted chain " stable for the even alcohols. (ii) Another explanation of the discontinuity in the even–odd systems is that A–B crystal units may be relatively stable and crystallise in the middle portion. This would give a system in which a " compound " A–B formed a continuous series of solid solutions with both A and B. No example of this type in a solid–liquid phase system has hitherto been recorded.

The transition temperatures for mixtures of hexadecyl alcohol and heptadecyl alcohol (in the solid phase) fit on a smooth curve showing no complication at the equimolecular composition. This is probably due to the fact that these temperatures are well below the solidus and that changes have already occurred in the solid + liquid field. In the same way the *X*-ray photographs of palmitic and stearic acid mixtures (Piper, Malkin, and Austin, J., 1926, 2316), taken apparently at room temperature, gave no indication of the well-authenticated $C_{16}H_{32}O_2,C_{18}H_{36}O_2$ compound. Investigation of the problems by the thermal method is rendered difficult by the small temperature differences involved compared with those met with in systems of inorganic substances. It is hoped to gain more information by a crystallographic study of the alcohols.

FIG. 2.



Heptadecane crystallises in transparent plates (α) which change reversibly into the opaque (β) form of *lower* melting point. This enantiotropic polymorphism is parallel to that of ethyl margarate, which also has an odd number of carbon atoms, just as the monotropic polymorphism of hexadecane resembles that of ethyl palmitate (Parts I and II). Octadecane crystals (α- and β-forms) resemble those of ethyl stearate, but the α-form of the hydrocarbon is less stable, changing quickly to the β unless impurity is present.

Both the hydrocarbon systems, hexadecane–heptadecane and heptadecane–octadecane, are of Type I (Fig. 2). As the dominant form is the transparent α-crystal common to both even and odd hydrocarbons, the systems differ little from that of hexadecane–octadecane (Part II; J., 1932, 740). Near the extreme compositions hexadecane and (more slowly) octadecane undergo monotropic change to the β-forms. It is evident that most mixtures of paraffins of about these chain lengths will set to a transparent mass. Piper, Chibnall, and collaborators (*Biochem. J.*, 1931, **25**, 2088) showed that mixtures of hydrocarbons of about thirty carbon atoms give the simplest possible systems. Near the melting point, both the even and the odd hydrocarbons with *more* than eighteen carbon atoms exist in the α-forms and the melting points of mixtures plotted against composition fall on a straight line.

## EXPERIMENTAL.

*Heptadecyl Alcohol.*—Several preparations of the alcohol have been made (*a*) from pure margaric acid, f. p. 61·1°, and ethyl margarate, f. p. 25·40° (α-form), and (*b*) from margaric acid of f. p. 60·7—60·8°, ester f. p. 25·5—25·55° (raised probably by the presence of ethyl nonadecoate). Reduction with sodium and ethyl alcohol gave in the (*b*) series products of f. p. 52·9°, which were fractionated with a 60 cm. column at 0·1 mm. pressure: first fraction, f. p. 52·1°; main, f. p. 53·5°; third fraction, f. p. 53·4°. Crystallisation of any of these fractions or of the products of the (*a*) series from benzene or acetone gave heptadecyl alcohol of constant f. p. 53·80°, m. p. 53·83° (m. p. in capillary tube 54·5°) (Found: C, 79·7; H, 14·2. Calc.: C, 79·7; H, 14·1%).

If instead of fresh solvents the mother-liquors employed in Part IV (this vol., p. 637) were used for these crystallisations, the products melted at 54·0—54·2°. Specimens of m. p. above 53·8° are now believed to be impure because (i) the behaviour on cooling is anomalous, solid of f. p. 54·2° changing, still in contact with liquid, to stable solid of f. p. 53·8°; (ii) 2·45 g. of alcohol, f. p. 54·2°, recrystallised from ethyl alcohol, gave 2·19 g. of f. p. 53·8° and evaporation of the solvent left 0·26 g., melting at 50—56° to a cloudy liquid (Found: C, 79·1; H, 13·6. Calc. for $C_{17}H_{36}O$: C, 79·7; H, 14·1%); (iii) alcohol of f. p. 54·2° gave an acetate, f. p. 24·9°, falling during several crystallisations and a fractional distillation to 24·70° (the stable solid of f. p. 53·8° gives an acetate of constant f. p. 24·61°). Hydrolysis of the acetate, f. p. 24·7°, gave alcohol of f. p. 53·9°, and f. p. 53·8° after recrystallisation; (iv) the iodide from "54·2°" had m. p. 33·5°, and f. p. 33·9°, m. p. 34·1° after two crystallisations from acetone (Found: I, 34·6. Calc.: I, 34·7%). "53·8°" gives iodide (m. p. 34·0°) which, recrystallised once from acetone, melts at 34·1°.

*Mixtures of Heptadecyl Alcohol (f. p. 53·8°) with Hexadecyl and with Octadecyl Alcohol.*—The mixtures all crystallised readily, although not as quickly as those with the impure alcohol, f. p. 54·2°. As the solidus curves lie so close to the liquidus, special care has to be taken to determine the solidus points under standard conditions. The 50–50 composition has been passed through six times in these alcohol mixtures and every time a medial change of direction in the liquidus curve has been observed; the changes in the solidus curves are not outside the limits of experimental error. In each system there is a minimum which is slightly below the f. p. of the lower alcohol.

Hexadecanol–Heptadecanol.

| $C_{17}H_{35}$·OH, mols. %. | F. p. | M. p. | Solidus. | $C_{17}H_{35}$·OH, mols. %. | F. p. | M. p. | Solidus. |
|---|---|---|---|---|---|---|---|
| 0·0 | 49·22° | 49·27° | (49·1°) | 49·5 | 50·73° | 50·76° | 50·3° |
| 3·3 | 49·19 | 49·24 | 49·1 | 53·4 | 50·92 | 50·95 | 50·5 |
| 8·7 | 49·29 | 49·32 | 49·1 | 57·4 | 51·13 | 51·15 | 50·7 |
| 24·0 | 49·62 | 49·66 | 49·4 | 64·3 | 51·55 | — | 51·2 |
| 35·0 | 49·94 | 49·97 | 49·65 | 80·15 | 52·42 | — | 52·1 |
| 45·2 | 50·45 | — | 50·05 | 93·4 | 53·27 | 53·30 | 53·1 |
| 46·8 | 50·56 | — | 50·1 | 100 | 53·80 | 53·83 | (53·7) |

*Transitions in the solid.*

| $C_{17}H_{35}$·OH, mols. % | 0·0 | 42·5 | 58 | 82 | 86·5 | 100 |
|---|---|---|---|---|---|---|
| Temp. | 40° | 34° | 35·8° | 40° | 41·3° | 43·5° |

Octadecanol–Heptadecanol.

| $C_{17}H_{35}$·OH, mols. %. | F. p. | Solidus. | $C_{17}H_{35}$·OH, mols. %. | F. p. | Solidus. | $C_{17}H_{35}$·OH, mols. %. | F. p. | Solidus. |
|---|---|---|---|---|---|---|---|---|
| 0·0 | 57·95° | — | 40·95 | 55·58° | 55·2° | 65·75 | 54·46° | 54·15° |
| 8·6 | 57·40 | 57·15° | 44·7 | 55·38 | 55·1 | 85·2 | 53·98 | 53·8 |
| 17·9 | 56·82 | 56·45 | 48·5 | 55·24 | 54·8 | 93·1 | 53·88 | 53·7 |
| 28·5 | 56·22 | 55·85 | 50·4 | 55·15 | 54·75 | 97·2 | 53·73 | 53·7 |
| 34·0 | 55·90 | 55·55 | 53·8 | 54·94 | 54·5 | 100 | 53·80 | — |

*Heptadecyl Iodide.*—Heptadecyl alcohol (f. p. 53·8°), heated with phosphorus and iodine, gave the iodide, which, crystallised from *n*-propyl alcohol–methyl alcohol and then acetone, had constant f. p. 34·05°, m. p. 34·13° (m. p. in capillary tube 35°) (Found: I, 34·6. Calc.: I, 34·7%). Gascard (*Compt. rend.*, **1911**, **153**, 1486) gives m. p. 33·6°. The substance is very stable to light; it is sparingly soluble in acetic acid and in methyl or ethyl alcohol.

*Heptadecane.*—Reduction of the iodide with zinc dust and acetic acid (Part III; this vol., p. 346) gave heptadecane (95% yield), which after crystallisation from propyl alcohol–methyl alcohol and then acetone had constant f. p. 21·92°, m. p. 21·97° (m. p. in capillary tube 23°). Krafft and Weinlandt (*Ber.*, 1896, **29**, 1323) gave m. p. 22·5°. This paraffin crystallises in transparent plates which become opaque at *ca.* 10°. It is sparingly soluble in methyl and ethyl alcohols and in acetic acid; moderately easily soluble in *n*-propyl alcohol, acetone, and ether, and easily soluble in benzene and ligroin.

*Polymorphism of Octadecane.*—All the specimens of this hydrocarbon after repeated crystallisation show a melting point of 27·9—28·0°, but may be cooled (unstirred) to as low as 27·4°. Transparent (α) crystals then suddenly appear, the temperature rising usually only 0·1° to f. p.'s 27·4—27·8°; heating gives m. p. 27·9—28·0° in each case and the crystals become opaque. The f. p. of the α-form can better be estimated by extrapolation of the curve for the α-forms in the system heptadecane–octadecane, and the value 27·0° is then obtained; similarly the system with hexadecane gives f. p. 27·2° (Part II, *loc. cit.*), so that octadecane appears to have f. p. *ca.* 27·1°.

One specimen of octadecane (Part III, *loc. cit.*) showed after the m. p. (28·0°) a clearing point at 29·8°, and addition of heptadecane (2%) lowered this point to 28·6°. A very small portion of the specimen after distillation melted at 28·0° (β-form) to a clear liquid. Possibly a small amount of impurity is the cause of the original clearing point at 29·8°.

*Mixtures of Hexadecane and Heptadecane.*—These crystallise in the transparent α-form except when more than about 95% of hexadecane is present.

Hexadecane–Heptadecane.

| $C_{17}H_{36}$, mols. %. | F. p. | Solidus. | $C_{17}H_{36}$, mols. %. | F. p. | Solidus. | $C_{17}H_{36}$, mols. %. | F. p. | Solidus. |
|---|---|---|---|---|---|---|---|---|
| 0·0 | 18·1° (β) | — | 17·1 | 16·7° (α) | 16·4° | 49·95 | 18·5° (α) | 18·1° |
| 2·3 | 17·6 ,, | — | 26·7 | 17·05 ,, | 16·8 | 56·6 | 19·0 ,, | 18·5 |
| 5·7 | 16·5 ,, | — | 35·0 | 17·55 ,, | 17·2 | 79·9 | 20·55 ,, | 20·2 |
| | 16·35 (α) | | 39·2 | 17·8 ,, | 17·5 | 90·8 | 21·35 ,, | 21·1 |
| 8·0 | 16·4 ,, | 16·2° | | | | 100 | 21·92 ,, | — |

*Mixtures of Heptadecane and Octadecane.*—When more than 90% of octadecane is present, long branching needles (α) grow in the melt and appear to change slowly to thin plates (β). The f. p.'s and m. p.'s in this region vary with the procedure. Where the α-form is stable there is less than 0·1° between f. p. and m. p. The transition points are the temperatures at which there is an inflexion in the cooling curve for the solid, and correspond to the change from transparent to opaque form. These points fall on a smooth curve (not shown) similar to that in the system ethyl palmitate–ethyl margarate (Part IV, *loc. cit.* Compare also Piper, Chibnall, and collaborators, *loc. cit.*; Mumford and Phillips, *Rec. trav. chim.*, 1933, **52**, 185).

Heptadecane–Octadecane.

| $C_{17}H_{36}$, mols. %. | F. p. (α). | M. p. (β). | Transition. | Solidus. | $C_{17}H_{36}$, mols. %. | F. p. (α). | M. p. (β). | Transition. | Solidus. |
|---|---|---|---|---|---|---|---|---|---|
| 100 | 21·92° | — | 10° | — | 7·9 | 26·54° | 26·76° | — | 27·35° |
| 96·6 | 21·96 | — | 5 | 21·9° | 5·85 | 26·63 | 26·95 | — | — |
| 90·5 | 22·16 | — | 3 | — | | | 27·15 | | |
| 77·2 | 22·76 | — | — | 22·5 | 4·2 | — | 27·13 | — | — |
| 61·25 | 23·49 | — | — | 23·0 | | | 27·45 | | |
| 50·8 | 24·04 | — | — | 23·4 | 2·0 | — | 27·50 | — | — |
| 40·85 | 24·60 | — | 5 | 24·0 | | | 27·80 | | |
| 30·76 | 25·15 | — | 11·5 | 24·8 | 1·9 | — | 27·43 | — | 27·4 |
| 18·0 | 25·91 | — | — | 25·65 | | | 27·77 | | |
| 9·2 | 26·47 | 26·55° | — | — | 0·0 | — | 28·02 | — | — |

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