92. *Higher Aliphatic Compounds. Part II. The Systems Hexadecyl Iodide–Octadecyl Iodide and Hexadecane–Octadecane.*

By John Charles Smith.

The frequent use of cetyl (hexadecyl) iodide both in synthetic work and in measurements of reactivity renders desirable an exhaustive purification of the substance, and also a knowledge of the effect of octadecyl iodide on the melting point.

It soon became evident that the discordant values of the freezing point recorded in the literature (Delcourt, *Bull. Soc. chim. Belg.*, 1931, **40**, 284, gave 21·15°; Phillips and Mumford, J., 1931, 1735, gave 22·5°) were due, not to a real depression of the freezing point, but to a diminution of the rate of crystallisation by small amounts of impurity. This large effect on the rate of crystallisation appears to be connected with a tendency to crystallise in a second form, for although Phillips and Mumford (*loc. cit.*) did not obtain evidence of polymorphism from the cooling curves of the purified iodide, the binary system shows that some change takes place in the crystals soon after formation.

A second feature of the binary system is the formation of an equimolecular compound of the two iodides (non-congruent melting point). Molecular combination between alkyl halides, although not hitherto recorded, might have been predicted, since other long-chain compounds with reactive end groups tend to combine. Morgan and Bowen (*J. Soc. Chem. Ind.*, 1924, **43**, 346T) and Bhatt and Watson (*J. Indian Inst. Sci.*, 1930, **13**, *A*, 141) have shown that higher fatty acids form molecular compounds, and the *X*-ray analysis of films (Müller, J., 1923, **123**, 2042; Müller and Shearer, *ibid.*, p. 3162) shows that these acids crystallise in double molecules with the carboxyl groups adjacent. The methyl (but not ethyl) ketones (Saville and Shearer, J., 1925, **127**, 593), the methyl esters, and the alkyl iodides (Malkin, J., 1931, 2796; compare *Nature*, 1931, **127**, 928) also show this tendency to unite end to end.

The system hexadecane–octadecane is one of solid solutions (Type III; Roozeboom, *Z. physikal. Chem.*, 1899, **30**, 385) complicated by polymorphism of both substances. Müller and Saville (J., 1925, **127**, 602) noticed that different spacings were given by octadecane at different temperatures, but observed only one spacing for hexadecane. Phillips and Mumford (*loc. cit.*) found no evidence of polymorphism in pure hexadecane, but it is now shown that about 5% of octadecane is required to stabilise the metastable (transparent) form. In Part I (J., 1931, 803) it was shown that the metastable form of ethyl palmitate was stabilised by the presence of ethyl stearate.

EXPERIMENTAL.

Cetyl Iodide.—Cetyl alcohol (f. p. 49·27°) (12·7 g.), red phosphorus (0·7 g.), and pure iodine (10 g.) were heated for 2 hours at 150°. The reaction mixture was extracted three times with ether (filtering), and the ethereal solution washed with water, sodium hydroxide solution, and water, and dried over anhydrous sodium sulphate. After removal of the ether the iodide distilled at approximately 150°/1 mm. (yield, 16·6 g.; 90%. F. p. 22·95°, m. p. 23·05°). Twice recrystallised from ether–methyl alcohol, it froze at 23·28°; m. p. 23·33° (m. p. in capillary tube 23·5—24°) (yield, 7 g.), unchanged by further crystallisation (yield, 2·5 g.) (Found : I, 36·0. Calc. : I, 36·0%). Krafft (*Ber.*, 1886, **19**, 2219) gives m. p. 23°; Phillips and Mumford (*loc. cit.*) give f. p. 22·5°; Delcourt (*loc. cit.*) found f. p. 21·15°. Another specimen (yield, 95%) was recrystallised from acetone to constant f. p. 23·28°; m. p. 23·33°. Cetyl iodide is very soluble in most solvents, sparingly soluble in even hot methyl alcohol, and easily soluble in *n*-propyl alcohol. Either in the solid state or in solution this iodide is quite stable to light.

Octadecyl Iodide.—Octadecyl alcohol (f. p. 57·95°, m. p. 58·00°) (9 g.), red phosphorus (0·5 g.), and pure iodine (6 g.), heated for 1 hour at 170°, gave 11·4 g. (94% yield) of distilled iodide, f. p. 32·5°. Twice recrystallised from ether–methyl alcohol, it had f. p. 32·90°, m. p. 32·94° (yield, 9·4 g.), and then twice from acetone, it had f. p. 32·91°, m. p. 32·94° (yield, 7 g.) (Found : I, 33·4. Calc. : I, 33·4%). A second preparation made from slightly impure octadecyl alcohol (f. p. 57·87°, m. p. 57·95°) gave an 85% yield of distilled iodide, f. p. 31·9°. After recrystallisation from the mother-liquors of the first preparation the new specimen had f. p. 32·92°, m. p. 32·94° (m. p. in a capillary tube 33·5°). Levene, West, and van der Scheer (*J. Biol. Chem.*, 1914, **20**, 521) give m. p. 34° (rapid heating). Octadecyl iodide is much less soluble at the ordinary temperature than is cetyl iodide.

Mixtures of Cetyl Iodide and Octadecyl Iodide.—Except near the extreme compositions the mixtures crystallise slowly and concordant values of the freezing points are difficult to obtain. The melting points (temperatures at which the last fine crystals dissolve on slow heating) are quite definite, except in the region 10—22% of octadecyl iodide. In this indefinite portion supercooling of 2—3° is necessary to cause crystallisation; moreover, if the mixture is heated immediately after solid has separated, low m. p.'s are obtained. If, on the other hand, the heating is slow or if complete solidification is allowed before heating, higher m. p.'s are shown.

The crystals, which at first are almost transparent, rapidly become opaque. In the table individual values of the temperatures are given for the indefinite portion. Heating- and cooling-curves fail to give a definite eutectic temperature, a slow change from 18·8° to 19·4° and vice versa being observed; this and the absence of a eutectic halt at 20·1° are regarded as due to polymorphism of cetyl iodide.

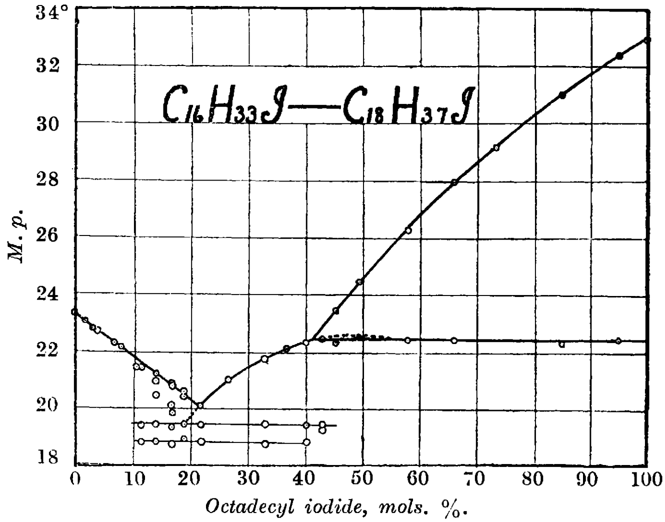
Octadecyl iodide, mols. %.	M. p.	Lower arrest.
0·0	23·33°	—
1·85	23·05	—
3·0	22·80	—
3·9	22·72	—
6·7	22·30	—
7·95	22·15	—
10·6	21·45	—
11·5	21·42	18·8—19·4°
14·25	20·45; 20·95; 21·2	18·8—19·4
16·9	19·8; 20·1; 20·8; 20·9	18·7—19·3
19·0	19·45; 20·4; 20·6	18·9—19·4
21·8	20·10	18·8—19·4
26·75	21·00	—
33·24	21·73	18·7—19·3
37·33	22·15	—
40·4	22·30	18·8—19·4
43·2	22·45	19·2—19·4
45·55	23·45	22·3
49·6	24·43	22·5
58·05	26·25	22·4
66·24	27·95	22·4
73·4	29·20	—
85·0	31·00	22·3
95·0	32·4	22·4
100	32·94	—

Temperature differences, Δ, between m. p. and f. p.

Cetyl iodide, mols. %	100	98·1	96·1
Δ	0·05°	0·4°	0·7°
Octadecyl iodide, mols. %	100	95·0	85·0
Δ	0·03°	0·3°	0·65°

Hexadecane and Octadecane.—These paraffins were prepared by the hydrogenation of hexadecene (cetene) and octadecene obtained by the distillation of spermaceti (Krafft, *Ber.*, 1883, **16**, 3022; Gault and Hessel, *Ann. Chim.*, 1924, **2**, 319; Waterman, van 't Spijker, and van Westen, *Rec. trav. chim.*, 1929, **48**, 1109). The semi-solid mixture of olefins and acids (from spermaceti distilled at 200 mm.) was dissolved (100 g. lots) in 3 volumes of *n*-propyl alcohol, and palladised barium sulphate added. Hydrogen (3·9 litres) was rapidly absorbed, corresponding to 39 g. of cetene. After filtration of the mixture and removal of the solvent, the residue was fractionated at 0·1 mm. through a 60 cm. column of glass rings. The fractions of b. p. 105—110° (m. p. 10—13°) contained most of the hexadecane, and those boiling between 120—130° (m. p. 9—14°) most of the octadecane. These, redistilled, melted at 13·5° and 12° respectively. To remove acids it is not necessary to use alkali. The hexadecane fraction, twice extracted with hot methyl alcohol, melted at 15°, and was then crystallised four times from *n*-propyl alcohol containing a little methyl alcohol (m. p. raised to 18·03°; f. p. 18·00°). Twice recrystallised from the same solvent, it had m. p. 18·08°, f. p. 18·05°, and twice from acetone–benzene, 18·12° and 18·10° respectively (m. p. in a capillary tube 18—19°). Two further crystallisations from acetone–benzene did not change these values (Phillips and Mumford, *loc. cit.*, give f. p. 17·6°). By extrapolation (see Fig. 2) the m. p. of the metastable form is 16·2°.

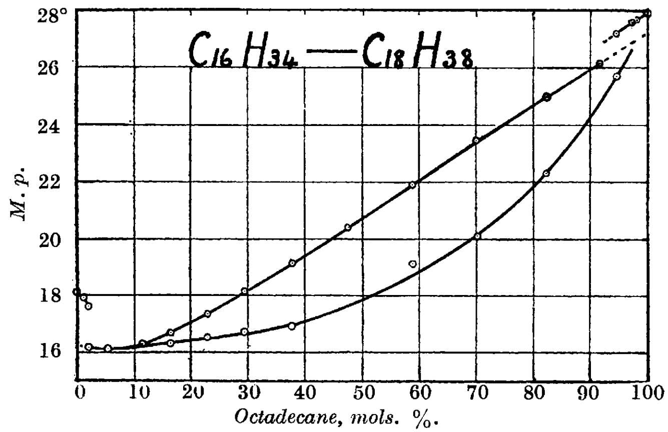
FIG. 1.



The much smaller octadecane fraction, m. p. 12°, after two extractions with hot methyl alcohol melted at 24·6°. Recrystallised six times from propyl alcohol–methyl alcohol, it melted at 27·75° (f. p. 27·68°); then, after four crystallisations from benzene–acetone, it had constant m. p. 27·90° and f. p. 27·82° (m. p. in a capillary tube 28—28·5°; Müller and Saville, J., 1925, **127**, 600, give 28°). The metastable form melts at 27·3° (by extrapolation; see Fig. 2). Both octadecane and hexadecane are readily soluble in hot *n*-propyl alcohol and less soluble in hot absolute ethyl alcohol.

Mixtures of Hexadecane and Octadecane.—Although pure hexadecane does not supercool readily, a mixture containing 1% of octadecane can easily be supercooled 1°. Large transparent crystals then appear and rapidly become opaque, the temperature rising immediately. A mixture containing 2 mols. % of octadecane cools to 16·14°, and the temperature remains constant while the transparent form separates. These crystals can be kept for several minutes, but when pressed with the thermometer they immediately become opaque, the temperature rising 1·2°. In a mixture containing 5·3 mols. % of octadecane the transparent form can be kept for several hours and the m. p. (16·11°) is the minimum for the system. From mixtures of increasing content of octadecane the transparent form continues to separate, giving sharp m. p.'s and f. p.'s (compare the system ethyl palmitate–ethyl stearate; Part I, *loc. cit.*). Above 92% of octadecane, crystals separate in transparent curving clusters, becoming opaque on stirring. A larger difference is shown between the f. p. and m. p., 0·4° and 0·2° at 95% and 97% respectively. Apparently the metastable form of octadecane (m. p. 27·3° by extrapolation) cannot exist near 27° unless more than 8% of hexadecane is present.

FIG. 2.



The solidus points. (approximate only) are the means of the temperatures of complete solidification after slow cooling (40 mins.) with constant stirring, and the temperatures at which liquid appears on slow heating.

Octadecane, mols. %.	M. p.	F. p.	Solidus.	Octadecane, mols. %.	M. p.	F. p.	Solidus.
0·0	18·12°	18·10°	—	47·74	20·40°	20·40°	—
1·0	17·90	17·80	—	58·8	21·92	21·90	19·1°
2·0	17·6	17·45	—	70·1	23·44	23·41	20·1
	(16·15)	(16·13)		82·45	24·97	24·95	22·3
5·3	16·11	16·10	16·1°	91·5	26·17	26·15	—
11·25	16·30	16·30	16·2	94·7	27·20	26·80	25·7
16·45	16·68	16·68	16·3	97·3	27·58	27·40	—
22·8	17·35	17·32	16·5	98·05	27·65	27·50	—
29·4	18·12	18·10	16·7	100	27·90	27·82	—
37·75	19·13	19·12	16·9				

THE DYSON PERRINS LABORATORY,
OXFORD UNIVERSITY.

[*Received, February* 17*th*, 1932.