# **140.** *Higher Aliphatic Compounds. Part VII. The Binary Systems, Palmitamide–Stearamide, Palmitanilide–Stearanilide, and Methyl Palmitate–Methyl Stearate. Purification of Palmitic and Stearic Acids.*

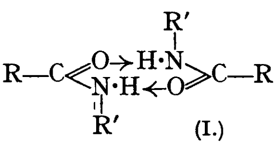
By J. B. Guy and J. C. Smith.

Amides and anilides of palmitic and stearic acids give mixed melting-point curves similar to the palmitic acid–stearic acid curve but with less depression of melting point. An equimolecular compound is formed in each case.

Methyl palmitate and stearate are polymorphous, yielding transparent (metastable) and opaque crystals; in mixtures the transparent form is stabilised. The binary system yields inconclusive evidence on the problem of compound formation between methyl esters raised by the *X*-ray measurements.

The purification of palmitic and stearic acids is described, and the elimination of homologues has been carried further than previously recorded.

The survey of the binary systems of derivatives of hexa-, hepta-, and octa-decane is now extended to the amides, anilides, and methyl esters of the acids. Amides and anilides yield systems similar to those of the acids (see Part VI, J., 1936, 625), eutectic systems of solid solutions, 1 : 1 compounds being indicated by non-congruent melting points. Anilides are known to be associated in solution (Auwers, *Z. physikal. Chem.*, 1897, **23**, 454) and can be represented by a formula (I) similar to that proposed by Sidgwick (*Ann. Reports*, 1933, **30**, 115) for the carboxylic acids. (Rodebush and Buswell, *J. Physical Chem.*, 1939, **43**, 219, regard amides as chain-like polymerides.) When two substances exist as double molecules, A—A and B—B respectively, 50/50 mixtures of them should yield some of the compond A—B.



(I.)

The depressions of melting point in the amide and the anilide systems are smaller than in the acid system, and the melting points of homologous amides lie closely together. Consequently neither the amide nor the anilide is a very suitable derivative for identification of a long-chain acid. Anilides, probably because of their less compact structure, are lower-melting than the corresponding amides.

Special interest attaches to the methyl esters since it has been inferred from the *X*-ray measurements (Malkin, J., 1931, 2796) that methyl palmitate and stearate crystallise in double molecules; the difference from the ethyl esters, which certainly crystallise in single molecules, is thought to be due to the greater affinity of the carbomethoxy-group. Actually, the *X*-ray measurements quoted (the $d_1$ spacings) merely give the length of the repeating units, and afford no information about the arrangement of the carbomethoxy-groups in space. It may be that the symmetry of the molecule requires an arrangement with the carbomethoxy-groups adjacent, but on the other hand, the recorded cases of double molecules are of substances with fairly reactive end groups: $CO_2H$, $CO_2Me$ (but not $CO_2Et$), COMe (but not COEt), I, $CH_2{\cdot}OH$, $CH_2Ph$; this seems to indicate that chemical affinity is involved, and makes the methyl esters an interesting test case.

Examination of the binary system methyl palmitate–methyl stearate, which might be expected to show the presence of double molecules as with acids and amides, has not given a really satisfactory answer. These esters, like nearly all other long-chain compounds, are polymorphous, but they differ from the acids, amides, and anilides in that the opaque form becomes metastable near the middle of the system. If a compound existed it would more likely be manifested in the opaque crystals than in the transparent ones, which probably have rotational freedom. (It is assumed from the similarity of appearance of the transparent forms to those of the ethyl esters and the paraffins, and also from their high rate of crystallisation, that they have "vertical" rotating chains; see *Ann. Reports*, 1938, **35**, 254.) The only evidence of compound formation between the methyl esters came from a series of points obtained in a preliminary examination of the system with slightly impure esters; these points seemed to indicate a 1 : 1 compound, but the observations could not be repeated. When pure esters were used only the transparent crystals could be obtained (near the middle of the system); the melting-point curve then showed a discontinuity between 50 and 60% of methyl stearate, owing probably to a slight change in the crystal lattice. The greater stability of the transparent form seems itself to be evidence of the weakness of any tendency to form double molecules, and this view is supported by the fact that molecular weights of methyl esters in solution are normal.

More light might be thrown on the problem by a redetermination of the *X*-ray data of films of the pure esters (opaque forms) and also of mixtures (both transparent and opaque forms), but for the solution of this problem and many similar ones detailed analysis of single crystals would seem to be necessary.

## EXPERIMENTAL.

*Purification of Materials.*—*Palmitic acid.* The final stage of the purification of palmitic acid involves the elimination of small amounts of stearic acid with which it forms solid solutions. A gradual approach to a maximum f. p. would be expected rather than the attainment of constant f. p. after 13 crystallisations previously observed (Part I; J., 1931, 802). In the present investigation, palmitic acid was crystallised 22 times and three solvents were used; the product was distilled after each 4—6 crystallisations; cooling of the solution was slow (at least 6 hours) with frequent agitation.

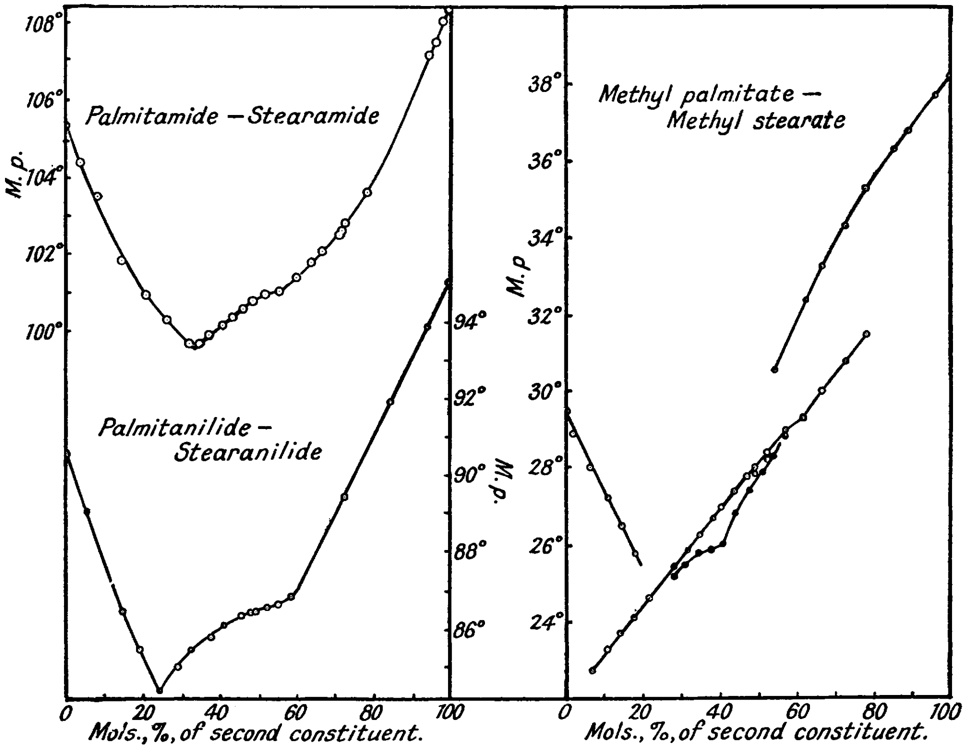
Palmitic acid (50 g., f. p. 61·0°, m. p. 61·8°, thermometer in the liquid), after 4 crystallisations from ethyl alcohol (250—200 c.c. each time), followed by distillation at 0·2 mm., melted at 62·4° (28 g.); after 4 crystallisations from benzene (200—150 c.c. each time) this gave 17 g., m. p. 62·58°. After 6 more crystallisations from benzene there remained 6·7 g., m. p. 62·70°, and a further 3 crystallisations from benzene gave 4·0 g., m. p. 62·74°. Three crystallisations from acetone gave 2·1 g., m. p. 62·76°, and finally, two crystallisations from acetone left 0·8 g., m. p. 62·76°, f. p. 62·74°. In Part I (*loc. cit.*) the specimen had f. p. 62·66°; de Visser (*Rec. Trav. chim.*, 1898, **17**, 182) gave 62·62°; Francis, Collins, and Piper (*Proc. Roy. Soc.*, 1937, *A*, **158**, 707) gave f. p. 62·53°; 1% of stearic acid would lower the m. p. by 0·36° (de Visser, *loc. cit.*).

*Stearic acid.* The "purest" commercial acid (50 g., f. p. 67·7°, m. p. 68·4°, thermometer in the liquid) after 6 crystallisations from alcohol, followed by 4 from benzene, gave 13 g., m. p. 69·40°; after 4 more crystallisations from benzene there remained 9 g., m. p. 69·47°, and another 4 crystallisations gave 5·2 g., m. p. 69·56°. Two further crystallisations from benzene failed to raise the m. p., but 2 crystallisations from acetone gave 2·9 g., m. p. 69·61°, and finally, 2 more crystallisations from acetone gave 1·9 g., m. p. 69·62°, f. p. 69·60°. The specimen described in Part I (*loc. cit.*) had m. p. 69·41°; de Visser (*loc. cit.*) gave 69·32°; Francis, Collins, and Piper (*loc. cit.*), who purified the acid through the ethyl ester, gave 69·32°. The presence of 1% of palmitic acid would lower the m. p. by 0·24° (de Visser, *loc. cit.*). Thus, after 24 crystallisations and 3 distillations the stearic acid seems to have reached a fairly high degree of purity, as is indicated by the changes of m. p., but it is quite probable that an improved technique or work on a larger scale would yield still higher-melting specimens of stearic and palmitic acids.

*Palmitamide.* Palmitic acid (m. p. 62·6°) *via* the acid chloride gave palmitamide, which, after 2 crystallisations from alcohol and 1 from benzene, followed by distillation at 0·2 mm., melted at 105·3° (m. p. in a capillary tube, 105—106°, uncorr.). A second preparation had the same m. p. Krafft and Stauffer (*Ber.*, 1882, **15**, 1728) gave m. p. 106—107°.

*Stearamide.* Stearic acid (m. p. 69·4°) gave the amide, m. p. 107·3°; after 2 crystallisations from benzene and 1 from alcohol, followed by distillation, the substance melted at 108·4° (capillary tube, m. p. 108—109°, uncorr.). Krafft and Stauffer (*loc. cit.*) gave m. p. 108·5—109°.

*Palmitanilide.* Palmitic acid (m. p. 62·53°) was converted into the acid chloride, which was added to ice-cold aniline (f. p. — 6·3°). The product, crystallised from benzene and then twice from alcohol and distilled, melted at 90·6° (capillary tube, 91°). Hell and Jordanoff (*Ber.*, 1891, **24**, 943) give 90·5°.



*Stearanilide.* Prepared from stearic acid, m. p. 69·4°, this was crystallised from benzene and then twice from alcohol. After distillation it melted at 95·05° (capillary tube, 95·5°). Robertson (J., 1919, **115**, 1210) gives m. p. 94°.

| Stear-amide, mols. %. | M. p. | Stear-amide, mols. %. | M. p. | Stear-amide, mols. %. | M. p. | Stear-amide, mols. %. | M. p. | Stear-amide, mols. %. | M. p. |
|---|---|---|---|---|---|---|---|---|---|
| 100 | 108·4° | 71·6 | 102·6° | 56·2 | 101·05° | 40·3 | 100·15° | 20·95 | 100·95° |
| 98·1 | 108·0 | 70·1 | 102·5 | 52·0 | 101·0 | 37·45 | 99·9 | 14·35 | 101·85 |
| 96·35 | 107·45 | 66·9 | 102·1 | 48·35 | 100·8 | 34·6 | 99·7 | 7·3 | 103·5 |
| 94·35 | 107·15 | 63·9 | 101·8 | 46·1 | 100·6 | 31·75 | 99·7 | 3·85 | 104·35 |
| 78·6 | 103·6 | 60·0 | 101·4 | 43·1 | 100·4 | 26·4 | 100·3 | 0·0 | 105·3 |
| 72·6 | 102·8 | | | | | | | | |

| Stear-anilide, mols. %. | M. p. | Stear-anilide, mols. %. | M. p. | Stear-anilide, mols. %. | M. p. | Stear-anilide, mols. %. | M. p. | Stear-anilide, mols. %. | M. p. |
|---|---|---|---|---|---|---|---|---|---|
| 100 | 95·05° | 58·15 | 86·9° | 48·0 | 86·45° | 37·9 | 85·8° | 19·2 | 85·5° |
| 94·2 | 93·9 | 55·0 | 86·7 | 46·3 | 86·4 | 32·25 | 85·5 | 14·8 | 86·5 |
| 84·65 | 91·95 | 52·1 | 86·6 | 44·8 | 86·4 | 29·3 | 85·05 | 5·35 | 89·1 |
| 72·25 | 89·5 | 49·3 | 86·5 | 41·0 | 86·15 | 24·3 | 84·4 | 0·0 | 90·6 |

Mixtures of the two amides or of the two anilides crystallised readily and gave sharp m. p.'s throughout the systems.

*Methyl palmitate.* Palmitic acid (m. p. 62·6°) and pure methyl alcohol gave the methyl ester, which, once crystallised from methyl alcohol, melted at 29·35° (clearing point, thermometer in the liquid); after distillation and 3 crystallisations from methyl alcohol, it melted at 29·55° (f. p. 29·35°; m. p. in a capillary tube, 29·5—30·5°). The pure ester easily supercools by 1° and the temperature rises rather slowly after crystallisation has begun. When the tube is placed in the Beckmann apparatus with the bath temperature 1—2° above that of the melt, there is a gradual rise of temperature as the opaque solid disappears, but the final clearing point is fairly sharp (29·55°). This behaviour is similar to that of ethyl stearate (Part I, *loc. cit.*) and indicates a polymorphic change near the m. p. The binary system with methyl stearate reveals the existence of a transparent form of f. p. 22° (by extrapolation), but it is doubtful whether the existence of this form can explain the behaviour of the ester near 29°. Phillips and Mumford (J., 1934, 1662) quote Watts's "Dictionary of Chemistry," vol. IV, p. 385, as stating that methyl palmitate solidifies at 22° and melts at 28° (capillary tube); these would be the values for a specimen of about 90% purity. King and Garner (J., 1936, 1372) give f. p. 29·05°; Adam (*Proc. Roy. Soc.*, 1922, *A*, **101**, 516) gives m. p. 30°.

*Methyl stearate.* Stearic acid (m. p. 69·45°) and pure methyl alcohol yielded the ester, which, after crystallisation from methyl alcohol, melted at 37·7°. After distillation and 3 more crystallisations from methyl alcohol, the ester had clearing point 38·25°, f. p. 37·83°, and m. p. in a capillary tube 38·5—40°. King and Garner (*loc. cit.*) give f. p. 37·78°; Whitby (J., 1926, 1458) gives m. p. 38·8° (capillary tube). As with methyl palmitate, the liquid supercools readily and the almost transparent crystals formed at about 36·8° change at 37·5° into a fine, opaque form; on heating, there is a gradual rise of temperature, but a sharp clearing point at 38·25°. Extrapolation of the curve in the binary system indicates a transparent form of m. p. approx. 34—35°.

*Mixtures of Methyl Palmitate and Methyl Stearate.*—Near the extreme compositions, the mixtures crystallise first in transparent plates which soon become opaque; as the rise to the freezing point is slow, it is more convenient to determine clearing points than f. p.'s of the opaque form. Mixtures containing 25—90% of methyl palmitate crystallise in transparent needles or thin plates; there is little supercooling, and the f. p. is usually within 0·03° of the m. p. When the transparent crystals are rubbed with the thermometer, they form bunches or lumps and may change into the opaque form, so giving two m. p.'s. Several attempts were made to map the section where the opaque form melts below the transparent, and with slightly impure esters (clearing points 29·3° and 37·9° respectively) the following points were obtained by rather rapid heating of the crystals:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Methyl stearate, mols. % | 27·2 | 30·8 | 34·7 | 38·0 | 40·95 | 44·2 | 47·8 | 51·2 |
| M. p. | 25·2° | 25·5° | 25·8° | 25·9° | 26·05° | 26·85° | 27·45° | 27·9° |
| Methyl stearate, mols. % | 54·65 | 59·65 | | | | | | |
| M. p. | 28·3° | 29·2° | | | | | | |

In the figure these points are marked as full black circles; and in the following table the m. p.'s of the transparent and of the opaque form are denoted by (i) and (ii) respectively. The thaw-point method of Rheinboldt and Kirscheisen (*J. pr. Chem.*, 1926, **113**, 348) was not suitable for investigating the mixtures.

| Methyl stearate, mols. %. | M. p. (i). | M. p. (ii). | Methyl stearate, mols. %. | M. p. (i). | M. p. (ii). | Methyl stearate, mols. %. | M. p. (i). | M. p. (ii). |
|---|---|---|---|---|---|---|---|---|
| 0·0 | — | 29·6° | 34·8 | 26·25° | — | 57·4 | 28·8—29·05° | — |
| 2·1 | — | 28·9 | 38·5 | 26·7 | — | 62·25 | 29·3 | 32·4° |
| 6·8 | 22·7°(?) | 28·0 | 40·2 | 27·0 | — | 67·0 | 30·0 | 33·25 |
| 11·0 | 23·3 | 27·25 | 43·9 | 27·4 | — | 73·0 | 30·8 | 34·3 |
| 14·65 | 23·75 | 26·5 | 47·3 | 27·8 | — | 78·35 | 31·5(?) | 35·3 |
| 18·2 | 24·2 | 25·8 | 49·4 | 28·0 | — | 85·4 | — | 36·3 |
| 21·8 | 24·7 | — | 51·0 | 28·1—28·25 | — | 89·4 | — | 36·85 |
| 28·35 | 25·5 | — | 52·8 | 28·3—28·55 | — | 96·3 | — | 37·7 |
| 32·0 | 25·9 | — | 54·9 | 28·2—28·7 | 30·55° | 100 | — | 38·25 |

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