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I.—THE PHYSICAL PROPERTIES OF PURE TRIGLYCERIDES.

*By R. B. Joglekar and H. E. Watson.**

Since the publication of Scheij's exhaustive paper on the physical properties of the fatty acids and the triglycerides (*Rec. trav. chim.*, 1899, **18**, 169), various more or less detached observations have been made in which the values recorded do not always agree with this author's figures. As a part of the general scheme of work on oils and fats and their derivatives which is being conducted in these laboratories, it seemed desirable to revise this branch of the subject and simultaneously to determine additional physical properties. The principal results together with some data on binary mixtures are given in the present paper.

EXPERIMENTAL.

The acids used for preparing the glycerides were the purest commercially obtainable. Stearic and palmitic acids were crystallized from 95 per cent. alcohol and myristic and lauric acids from 75 per cent. alcohol until three consecutive crystallizations gave a product with the same solidifying point. The acids formed large crystals and appeared to be very pure. The molecular weights agreed with the calculated values. The solidifying points and refractive indices are given in Table I and compared with those of de Visser (*Rec. trav. chim.*, 1898, **17**, 182), Scheij (*loc. cit.*) and Pascal (*Bull. Soc. chim.*, 1914, [iv], **15**, 360).

TABLE I.

Solidifying Points and Refractive Indices of Acids.

Acid		Lauric	Myristic	Palmitic	Stearic
Solidifying point ...	de Visser ...	...	...	62·6°	69·32°
	Scheij ...	43·4°	53·8°	62·6°	69·3°
	Joglekar and Watson.	43·4°	53·8°	62·2°	69·35°
		60°	60°	80°	80°
Refractive index ...	Scheij ...	1·4266	1·4307	1·4269	1·4300
	Pascal ...	...	...	1·4269	1·4296
	Joglekar and Watson.	1·4264	1·4305	1·4266	1·4296

* *Reprinted with additions from Journal of the Society of Chemical Industry*, 1928, **47**, 365 T.

The low solidifying point of palmitic acid is noticeable. The same value was obtained from three different original samples after 12 crystallizations from 95 per cent. alcohol.

Two methods were adopted for preparing the triglycerides, the first a modification of Bellucci's process (*Atti. R. Accad. Lincei*, 1911, **20**, i, 125). Three molecules of glycerin and one of the acid were heated to 180° and the temperature slowly raised to 215° during two hours at 30–40 mm. pressure; the temperature was then raised to 250° in one hour and maintained at that point for one hour, the pressure being reduced to 6 mm. The second method was that of Partheil and Velson (*Arch. Pharm.*, 1900, **238**, 261), using tribromhydrin and the silver salt of the acid. The first method gave a larger yield of a purer product but after final purification, the glycerides obtained by the two processes had identical physical properties.

The crude product was crystallized six or seven times from concentrated alcohol in which the triglycerides are sparingly soluble and recrystallized from ligroin and ether. In the cases of palmitin and stearin, acetone and chloroform were subsequently used as solvents, but no further change in physical properties was brought about. The last traces of solvent were removed by heating for 2 to 3 hours at 100° under reduced pressure.

Physical Properties.

An examination of the physical properties of several of the substances during the course of their purification showed that the melting points and refractive indices afforded little criterion as to purity, but the densities, viscosities and solidification points varied appreciably even when a fair degree of purity had been attained. For example, two samples of tristearin with m.p. 71·7° and refractive index 1·4395 did not change these values after repeated purification. The densities which were 0·8622 and 0·8619 changed to 0·8631, the viscometer flow-times of 582·5 and 577·8 seconds changed to 591·4 and the solidifying points 69·4° and 69·6° to 71·3°. The viscosity is thus, perhaps, the most sensitive indication of impurity, but its determination requires a very careful temperature adjustment and for practical testing the solidifying point is nearly as accurate and much easier to measure. The solidification of the triglycerides is, however, as is well known, of a complex nature, and the determination of the solidifying point requires certain precautions. On heating a crystallized sample of, say, tristearin, melting occurs at 71·7°, but if the sample has been previously melted and suddenly cooled, it first melts at about 55°, then solidifies and again melts at 71·7°. This double melting point has formed the subject of several investigations (Vandevyer, *Ann. Chim. analyt.*, 1900, **5**, 321; Guth, *Z. Biol.*, 1902, **44**, 78; Kremann, *Monatsh.*, 1912, **33**,

063; Bokhörst, *Diss. Amsterdam*, 1916; Nicolet, *Ind. Eng. Chem.*, 920, **12**, 761; Grün, *Ber.*, 1921, **54**, 290; Klimont, *Oesterr. Chem.-Ztg.*, 1922, **25**, 22), but no very definite conclusions regarding the composition of the two modifications appear to have been reached. Additional data have been collected during the present series of experiments, and this aspect of the subject is still under investigation. For practical purposes it is sufficient to regard the glycerides as existing in two forms, the α-form obtained by crystallization from solvents and the β-form by heating the α-form to its melting point which appears to be a transition temperature. On cooling, crystallization does not occur at all readily and in some cases, the transformation is so slow that the liquid appears to be the stable form. In order to examine this point more closely, a sample of tristearin melting at 71·8° was divided into 3 portions of about 1 g. each and placed in covered glass dishes. Two of these were heated until the glyceride was completely melted, and all three were then placed in an oven at 65°. The solid did not melt even on prolonged heating but the liquid began to crystallize in about half-an-hour, crystallization starting usually from one point. If the liquid was seeded with a crystal of the α-form, crystallization started at once; but the rate of growth was very slow, some 10–15 minutes being required for complete solidification. To ensure that the initial crystallization was not due to accidental contamination, some of the substance was filtered into glass tubes which were sealed and then placed in boiling water for some time. The onset of crystallization was delayed but not inhibited, solidification occurring in 2 to 3 hours at 65°.

It is conceivable that the change of form may take place in one of two ways; either crystals of the α-form may grow directly from the liquified β-form or, less probably, the β-form may change to the α-form in a super-cooled liquid state, slow crystallization ensuing subsequently. That the latter hypothesis is untenable was shown by melting the glyceride in sealed tubes and maintaining the liquid at 65° during two hours. The tubes were then chilled in cold water. The solid melted at 55° the melting point of the β-form, but resolidified in a few moments showing that numerous nuclei of the α-form had been produced by chilling. This formation of nuclei is, no doubt, responsible for the change of the β into the α-form in the solid state at room temperature frequently observed during the experiments. When it takes place there is a remarkable swelling into sponge-like formations, and the containing vessel is often broken.

It appears probable that what we have termed the α and β-forms are not single substances but mixtures of two or more varieties in internal equilibrium. This is almost certainly so in the case of the β-form after solidification. More detailed knowledge is not, however,

necessary for the determination of the solidifying point as a physical constant. What is essential is a recognition of the fact that the transformation from β to α requires a considerable time and the heat evolved is not very great. Consequently, if the quantity of substance is too small or the jacket round the tube is at too low a temperature, low values are obtained for the solidifying point. It was found that consistent values can be obtained if 3 g. or more of the glyceride are used in a 2 cm. tube surrounded by an air jacket which, in turn, is immersed in a bath the temperature of which is raised during the experiment so as to be not more than 4° below that of the substance. Stirring has no effect in the case of tristearin, but it should be adopted with the lower members as it decreases the time required for the temperature rise. Owing to transformation taking place, the lower solidification points could not be definitely measured but only showed as slight breaks in the time-temperature curve. As the substance frequently did not melt completely, the melting points for the β-form were taken as the temperature of initial softening in a capillary tube on raising the temperature about 1° per minute. The melting points for the α-form are the temperatures of complete liquefaction under similar conditions.

Refractive indices were determined with an Abbé refractometer checked against a standard piece of fluorite. As has been remarked previously (*J. Indian Inst. Sci.*, 1922, **5**, 50), the use of this instrument at high temperatures is attended by some uncertainty as regards the temperature of the prisms. Most of the present measurements were made with heating water flowing at a definite rate and the temperature taken as the mean of the inlet and outlet temperatures. A small correction was subsequently applied by circulating the water very rapidly with a pump so that the temperature drop in passing through the prism heaters was less than 0·1° at 80°. The exposed prism face was covered with a plug of cotton wool except just at the moment of reading and the prism temperature assumed to be the same as that of the water, a correction being applied for the emergent stem. Scheij when measuring the refractive index of water at 80° obtained values 4 units in the fourth place of decimals lower than the accepted values, owing to the change in refractive index of his prism. A similar experiment with the Abbé refractometer used in the present experiments, gave correct values and so no correction has been applied.

The bath used for measurements of density, viscosity and surface tension, consisted of a 2 litre beaker of water heated electrically and fitted with a stirrer, standing in another beaker as an air jacket and carefully covered. With a steady source of heating current and hand regulation, the temperature remained constant to 0·01° and could be readily varied through a wide range.

Densities were determined in a 5 cc. pyknometer with two fine capillary limbs calibrated with water at each temperature employed. The values obtained are given in Table II.

TABLE II.

Densities of triglycerides at different temperatures.

Temp.	Caprin.	Laurin.	Myristin.	Palmitin.	Stearin.
40°	0·9204	...	...	...	...
60°	0·9059	0·8943	0·8860	...	...
70°	0·8986	0·8872	0·8790	0·8730	...
80°	0·8913	0·8801	0·8722	0·8663	0·8632
Mean change per 10°	0·0073	0·0071	0·0069	0·0067	0·0067

Viscosities were measured in a modified Ostwald viscometer with a trap in the upper bulb to enable a constant volume of liquid at the required temperature to be taken. This was calibrated at 30° with solutions of glycerin in water varying in concentration from 59 to 62 per cent., Muller's (*Wien. Ber.*, 1924, **133**, 133) figure 0·0857 for the viscosity of a 61·44 per cent. solution having $d^{30°}$ 1.1517 being taken as standard. A small correction was applied for the expansion of the glass at the higher temperatures. Table III shows the values obtained.

TABLE III.

Viscosities of triglycerides at different temperatures.

Temp.	Caprin.	Laurin.	Myristin	Palmitin.	Stearin.
40°	0·1879	...	...	...	...
45°	0·1006	0·2198	...	...	...
60°	0·0777	0·1359	0·1771	...	...
70°	0·0688	0·1030	0·1342	0·1679	...
75°	0·0625	0·0911	0·1170	0·1467	0·1850
80°	...	0·0809	0·1035	0·1292	0·1621
85°	0·0551	0·0722	0·0920	0·1144	0·1431

Surface tension was determined by the maximum bubble pressure method (*cf.* Sugden, *J.C.S.* 1924, **125**, 27, etc.), the apparatus being standardized with carefully purified benzene. The surface tension of this was assumed to be 27.58 at 30°. The results are given in Table IV.

TABLE IV.

Surface tension of triglycerides (dynes/sq. cm.) at different temperatures.

Temp.	Caprin	Laurin	Myristin	Palmitin	Stearin
40°	28·7	...	...	...	...
60°	27·3	27·9	28·7	...	...
70°	26·6	27·3	27·7	28·3	...
80°	25·9	26·6	27·2	27·6	28·1
P	1404	1648	1892	2134	2376
P (calc.)	1399	1633	1867	2101	2335
diff.	5	15	25	33	41

The parachors $P = M\gamma^{\frac{1}{4}}/d$. (*cf.* Sugden, *J.C.S.*, 1924, **125**, 1184) have been calculated from the surface tensions at 80° and form a very uniform series, the mean difference for C_2H_4 being 81. There is however a marked difference from the values calculated with Sugden's data according to which the difference for C_2H_4 is 78. Taking Walden's values for density and surface tension at 80° (*Z. physikal Chem.*, 1910, **75**, 560) the parachors for tripalmitin and tristearin are 2120 and 2360. Sugden gives the values from the same data as 2252 and 2380, the former value being due to an error in the formula assumed for tripalmitin.

A summary of the above results, with figures for the melting and solidifying points and values given by other observers is shown in Table V.

Scheij's values are thus mainly confirmed, the chief differences being in the densities of palmitin and stearin. These were determined in an air-bath by Scheij, and it is possible that the temperature of the glyceride was not exactly that of the bath. With regard to the lower melting points of laurin and myristin, the same author mentions that laurin softened at 44° and myristin between 35° and 45°, but does not state that these are the lowest temperatures at which softening was observed. The densities calculated from Jæger and Kahn's figures

TABLE V.

Physical properties of triglycerides.

—	Author	Caprin	Laurin	Myristin	Palmitin	Stearin
Melting point (1)	B[1].	...	...	...	61	71·0
	S[2].	31·1	46·2	56·5	65·1	71·6
	G[3].	...	...	...	65·5	71·5
	J. & W.	31·6	46·2	56·5	65·6	71·8
Melting point (2)	B.	...	...	...	..	55·0
	S.	...	44	35	45	55
	J. & W.	...	18·0	33·0	46·2	55·0
Solidifying point	K[4].	...	...	...	62·6	56·0
	N[5].	...	...	...	...	69·0
	J. & W.	30·3	45·3	56·1	65·2	71·3
Refractive index	S.	1·43697 (60°)	1·44039 (60°)	1·44285 (60°)	1·43807 (80°)	1·43987 (80°)
	P. & N[6].	...	...	...	1·4371 ,,	1·4396 ,,
	P[7].	...	...	...	1·4377 ,,	1·4385 ,,
	J. & W.	1·4370 ,,	1·4402 ,,	1·4428 ,,	1·4376 ,,	1·4395 ,,
Density	J. & K[8].	0·9056 ,,	0·8945 ,,	...	0·8671 ,,	0·8672 ,,
	S.	0·9057 ,,	0·8944 ,,	0·8848 ,,	0·8657 ,,	0·8621 ,,
	W[9].	...	...	...	0·8666 ,,	0·8624 ,,
	J. & W.	0·9059 ,,	0·8943 ,,	0·8860 ,,	0·8663 ,,	0·8632 ,,
Surface tension	W.	...	...	...	26·87 ,,	27·21 ,,
	J. & W.	27·3 ,,	27·9 ,,	28·7 ,,	27·6 ,,	28·1 ,,
Viscosity	W.	...	...	...	0·1456 (70°)	0·1741 (70°)
	J. & W.	0·0688 (70°)	0·1030 (70°)	0·1342 (70°)	0·1679 ,,	0·1850 (75°)

[1] Berthelot. *Ann. Chim. Phys.* 1854, (3) **41**, 240.
[2] Scheij. *loc. cit.*
[3] Guth. *Z. Biol.*, 1902, **44**, 78.
[4] Kremann, *Monatsh.* 1912, **33**, 1063.
[5] Nicolet, *Ind. Eng. Chem.*, 1920, **12**, 761.
[6] Partheil and Nelson, *Arch. Pharm.*, 1900, **238**, 261.
[7] Pascal, *Bull. Soc. chim.*, 1914, **15**, 360.
[8] Jæger and Kahn, *Proc. K. Akad. Wentensch. Amsterdam*, 1915, **18**, 285.
[9] Walden, *loc. cit.*

agree for the two lower glycerides but appear distinctly high for the upper members of the series. Details as to the purity of their compounds are not available. Walden's values for density agree fairly closely, but his figures for viscosity and surface tension are much lower than those we have obtained. The melting points of his glycerides were 65·0° and 71·2° (unc.) so that they do not appear to have been as pure as our samples and this would account for his low results.

Binary Mixtures.

The solidification points of mixtures of tripalmitin and tristearin were determined hy Kremann (*loc. cit.*) with the object of ascertaining if there was a flat portion on the curve as there is in the case of palmitic and stearic acids. His results appear to refer to mixtures of tripalmitin with the two modifications of tristearin in indefinite proportions, the low melting variety predominating.

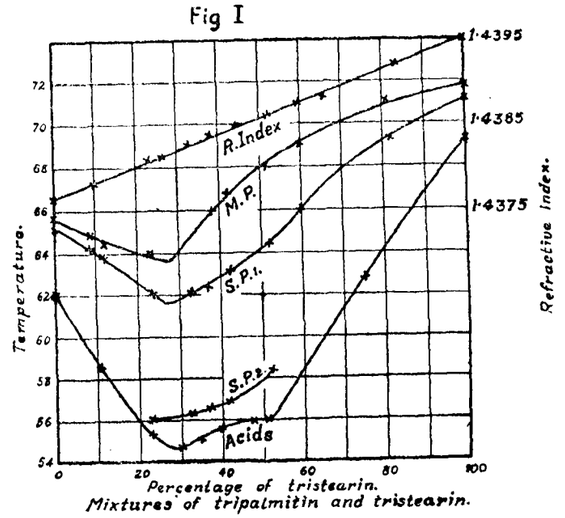
We have succeeded in obtaining figures which appear to be characteristic of the mixture of the high melting modifications and also a few points for which at least one constituent is in the β-form. Some care seems to be necessary in preparing the mixtures as the glycerides do not mix readily, and it was found advisable to shake the molten mixtures in a stoppered bottle.

With mixtures containing from 25 to 50 per cent. of tristearin, if the molten mass is cooled until solidification takes place and is then vigorously stirred, definite solidification points in the neighbourhood of 58° are obtained. If, on the other hand, the liquid is kept at 56° for some minutes before stirring and not allowed to cool below this temperature, much higher solidification points are found. Double solidification points could not be obtained for the other mixtures. Fig. 1 shows the results graphically and it may be seen that the curve is characteristic of a simple mixture and does not resemble the one for the corresponding acids which is given in the same diagram. The latter was determined in the same apparatus and with the acids from which the glycerides were prepared. The figures are slightly lower than those given by de Visser (*loc. cit.*) owing to the lower solidification point of the palmitic acid used.

The refractive indices of mixtures of tripalmitin and tristearin were measured by Pascal (*loc. cit.*) who found a minimum in the curve at 80° and a maximum at 60°, while at 70°, the relation was approximately linear. The refractive index of the tristearin used by this author was only 1·4385 at 80°, considerably lower than the value obtained by other observers, and although the preparation is described as synthetic, no details are given, and its purity must be regarded as doubtful. We

have been unable to confirm Pascal's values, but find a relation between refractive index and composition which is linear within the limit of experimental error both at 70° and 80°. The results at 80° are shown in Fig. I. The figures for 70° are 0·0036 higher. Measurements could not be made at 60° owing to solidification.

Fig I



Mixtures of tripalmitin and tristearin.

Determinations of the density, viscosity and surface tension of palmitin-stearin mixtures have also been made, but these present no unusual features. The solidifying points of caprin-stearin mixtures have been investigated and exhibit certain peculiarities which will be dealt with in detail on another occasion.

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II.—THE PREPARATION AND PHYSICAL PROPERTIES OF α-MONOGLYCERIDES.

By R. S. Rewadikar and H. E. Watson.

Simultaneously with the investigation of the triglycerides outlined in the previous paper, experiments of a similar nature were conducted with the α-monoglycerides, the literature of which is even more scanty than that of the triglycerides. The glycerides of acids with an even number of carbon atoms from lauric to stearic have been previously prepared, but in most cases, the melting point is the only physical constant which has been measured and the figures given by different authors vary considerably as shown in Table I.

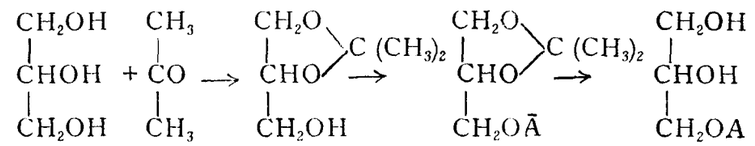
TABLE I.

Melting Points of α-Monoglycerides.

...	Berthelot.	Hundeshagen.	Smith.	Thieme.	Guth.	Krafft.	Grün.	Fischer.	Brash.	Adam, Berry and Turner.
Laurin ...	...	...	...	58·9	...	59	61	62–63	...	...
Myristin ...	...	...	...	...	...	68	69	...	...	70-71
Palmitin ...	58	...	63	...	65	72	74	78–79	68	76–77
Stearin ...	61	60–62	...	...	73	78	80	81–82	...	...

Berthelot (*Compt. rend.*, 1853, **37**, 398) was the first to attempt the synthesis of the monoglycerides from the acids and glycerin. His work was repeated more systematically by Chittenden and Smith (*Am. Chem. J.*, 1885, **6**, 225) and Belucci (*Gazzetta*, 1912, **42**, 283), but the products obtained were found to be mixtures. Guth (*Z. Biol.*, 1902, **44**, 78), Krafft, (*Ber.*, 1903, **36**, 4342) and Grün (*Ber.*, 1910, **43**, 1288; 1912, **45**, 3421) used the chlorhydrins as starting materials by allowing them to react with the sodium or potassium salts of the acids or by esterifying a di-halogen hydrin and then converting the halogens into hydroxyl groups. Thieme (*Ber.*, 1913, **46**, 1653) pointed out that reactions of this type were not simple, but yielded other products as well as those desired, and Fischer (*Ber.*, 1920, **53**, 1589, 1621) showed that the acid radicle might change its position during the course of the reaction so that the constitution of the glyceride produced in this way could not be definitely established.

Abderhalden (*Ber.*, 1914, **47**, 2888) appears to have been the first to prepare α-monoglycerides of definite constitution. He isolated the optically active epihydrin alcohol and esterified the lower members of the fatty acids, with it. The products were purified by distillation in vacuo. Fischer and his collaborators (*Ber.*, 1920, **53**, 1589) achieved the same result by using as starting material isopropylidene glycerin, the constitution of which had been definitely established by Irvine, Macdonald and Soutar (*J.C.S.*, 1915, **107**, 342). This was condensed with fatty acid chloride and the isopropylidene linking removed, giving the α-glyceride.



The glycerides could be readily condensed with acetone giving the intermediate isopropylidene glyceride thus showing that the acid radicle had not changed place on hydrolysis, since acetone will only condense with two adjacent hydroxyl groups. (*Ber.*, 1920, **53**, 1606.)

Fischer (*Ber.*, 1920, **53**, 1640) also prepared the α-monoglycerides by the alcoholysis of alkyl esters of fatty acids with glycerin and by the degradation of triglycerides using excess of glycerine. Bergmann and Sabety (*Z. physiol. Chem.* 1924, **137**, 47) prepared optically active α-monolaurin from 2-phenyl 5-chlormethyl oxazolidine. While the present experiments were in progress, Brash (*J. Soc. Chem. Ind.*, 1927, **46**, 481 T) prepared α-monopalmitin by a method which he considered superior to that of Fischer, *viz.*, by heating the lead salt of the fatty acid with α-monochlorhydrin. His palmitic acid was admittedly impure and this was no doubt a contributory cause to the low melting point (68°) of his product. Still more recently Adam, Berry and Turner (*Proc. Roy. Soc. A.* 1928, **117**, 540) have prepared monomyristin and palmitin by Fischer's method. The only property recorded was the melting point as given in Table I.

We have now prepared in a pure state the α-monoglycerides of acids with an even number of carbon atoms from C_8 to C_{18} and determined their melting points, refractive indices, densities, viscosities and surface tensions. As far as possible, alternative methods of preparation have been adopted in order to compare the products obtained in different ways.

It has been shown by Fischer (*loc. cit*) that on replacement of the iodine in α-iodo-βγ-acylated glycerin by hydroxyl, the αγ-acylated

glycerin results. It appeared of interest to see if a similar change would take place with a di-halogen compound and consequently allyl laurate and stearate, and their dibromides were prepared. Attempts to prepare the monoglycerides by substituting hydroxyl groups for the bromine were not successful as the bromine could not be completely removed.

EXPERIMENTAL.

Isopropylidene glycerin was prepared by Fischer's method (*Ber.* 1920, **53**, 1607) and obtained in 70 per cent. yield; b. p. 79°/9 mm.

α-monostearin.—The stearic acid used for this preparation was crystallized 3 times from 90 per cent. alcohol and melted at 69·3°. Its equivalent weight agreed with theory.

(*a*) Stearyl chloride was condensed with isoproplylidene glycerin dissolved in dry quinoline by standing at room temperature (25°) for 48 hours according to Fischer's method. The yield of acetone compound was 80 per cent. of the theoretical value and the crude product was used as such, since recrystallization seemed liable to produce hydrolysis. α-monostearin was obtained in 80 per cent. yield on hydrolysis with concentrated hydrochloric acid (1·19) at 20–25°. After washing with ether and crystallizing from the same solvent, the melting point was 82°, agreeing with Fischer's value.

(*b*) Methyl stearate m. p. 38·5–39° made from the stearic acid and methyl alcohol was heated with 4 mols. of glycerin containing 4 per cent. hydrochloric acid on the water-bath for various periods, moisture being excluded, but no alcoholysis took place.

(*c*) A mixture of methyl stearate (7g.) and glycerin (9·2g.) was dissolved in 8·7 g. of acetone containing 2 per cent. of hydrochloric acid and refluxed for 5 hours. The product was poured into water, and the solid which formed was recrystallized repeatedly from ether. 1 g. of a substance melting at 82° was obtained and the melting point did not change on mixing with the specimen obtained by method (*a*).

A similar experiment with 15 g. of methyl stearate in which the refluxing was continued for 48 hours, acetone removed by distillation and the residue dissolved in ether, yielded 2 g. of α-monostearin and 8 g. of a neutral product m. p. 40°–50° (probably crude isopropylidene monostearin which gave 3 g. of α-monostearin after hydrolysis and recrystallization from benzene.

(*d*) An attempt to obtain the glyceride by heating methyl stearate with isopropylidene glycerin in benzene solution containing hydrochloric acid was unsuccessful.

(*e*) Methyl stearate (10 g.) and anhydrous glycerin (9 g.) were dissolved in dry pyridine (50 cc.) and 1 cc. of a 7 per cent. solution of sodium methylate added. The mixture was heated for 24 hours on the water-bath, the pyridine distilled and the residue treated with a mixture of N/2 sulphuric acid and ether. 4·5 g. of α-monostearin with the same melting point as before were obtained.

(*f*) An alternative method of producing the glyceride was by oxidation of allyl stearate.

Allyl stearate was obtained in 80 per cent. yield by the action of allyl iodide on silver stearate suspended in benzene. It forms shining plates from methyl alcohol m. p. 35°. (Found: C, 77·6; H, 12·3. $C_{21}H_{40}O_2$ requires C, 77·7; H, 12·3).

Allyl stearate dibromide was prepared by adding a solution of bromine (1 mol.) in dry chloroform to a solution of allyl stearate (1 mol.) in the same solvent cooled to −3° with stirring. The reaction is very slow but the yield is quantitative. The substance forms a white solid from methyl alcohol; m. p. 45°. (Found: Br. 33·3. $C_{21}H_{40}O_2Br_2$ requires Br, 33·1.)

Oxidation of allyl stearate.—An attempt at oxidation with benzoylhydroperoxide was not successful, but a small yield of glyceride was obtained by permanganate oxidation in acetone solution at room temperature (30°). After a number of trials, the best yield (30 per cent.) was obtained as follows:—Allyl stearate (4 g.) was dissolved in acetone (700 cc.) containing 1·2 g. of magnesium sulphate at 2° (this amount of acetone is necessary to keep the ester in solution) and potassium permanganate (1·6 g.) equivalent to 1 atom of oxygen per 1 mol. of ester added slowly with stirring, the temperature being kept at 2°. The manganese dioxide was separated by filtration, suspended in water, dissolved by passing sulphur dioxide and the solution extracted with ether. This solution was washed with 10 per cent potassium bicarbonate solution and the ether distilled. The acetone solution was distilled and the residue taken up in ether. After recrystallization, the product melted at 82° and mixture with α-monostearin produced no change. (Found: C, 70·2: H, 11·7. $C_{21}H_{42}O_4$ requires C. 70·4; H, 11·7.) Experiments with larger quantities of permanganate did not result in increased yield but caused the formation of stearyl glycollic acid previously obtained by Grün (*loc. cit.*) by the oxidation of α-monostearin.

α-monopalmitin.—The palmitic acid used for this preparation was a specially pure sample recrystallized 3 times from 90 per cent. alcohol. It had the correct equivalent weight and melted at 62·5°.

(*a*) A quantitative yield was obtained by condensing the acid chloride with isopropylidene glycerine. After recrystallizing from ether, the melting point was 76°.

(*b*) 5·4 g. of methyl palmitate gave by glycerolysis in pyridene solution (*cf.* α-monostearin (*e*)) 2·5 g. of glyceride with the same melting point. Glycerolysis in acetone solution gave a small yield.

(*c*) Equimolecular proportions of potassium palmitate and α-monochlorhydrin (b. p. 115°/7 mm.) were heated in a sealed tube at 180° for 6 hours and the product treated according to the method of Krafft. (*Ber.* 1903. **36**, 4342.) A very low yield of an impure product melting at 72–73° was obtained.

α-monomyristin.—Myristic acid was recrystallized from alcohol and melted at 53·6°.

(*a*) Myristyl chloride prepared from the above was redistilled and boiled at 169°/15 mm. A 75 per cent. yield of myristyl isopropylidene glycerin was obtained on condensation and a 90 per cent. yield of the glyceride on hydrolysis with hydrochloric acid (1·19) at −5°. The product was recrystallized from a mixture of ether and petroleum ether in which it is not very soluble and melted at 70°.

(*b*) 1 g. of the monoglyceride with the same melting point as the above was obtained from 7 g. of trimyristin and 2·8 g. of glycerin in a pyridine solution containing sodium methylate after standing for 3 days at room temperature (25°).

α-monolaurin melting at 63° was obtained in 90 per cent. yield by Fischer's method. The lauric acid was made from a pure specimen of methyl laurate prepared in the laboratory and melted at 43°. The acid chloride boiled at 123–124°/7 mm.

Allyl laurate.—Laurylchloride (13·2 g.) and quinoline (8 g.) were dissolved in dry chloroform (30 cc.). Allyl alcohol (3·5 g.) was gradually added at 0° while stirring and the mixture allowed to stand for 24 hours at room temperature. It was then extracted with chloroform and the solution shaken in succession with half-normal sulphuric acid, 10 per cent. potassium bicarbonate solution and distilled water. After drying with anhydrous magnesium sulphate and distilling the solvent, a neutral pale brown liquid (13·1 g.) was obtained which

became semi-solid at −6°. The distillate was a colourless, mobile liquid boiling at 162–164°/20 mm.

Allyl laurate dibromide—Allyl laurate (9 g.) was dissolved in dry chloroform (50 cc.) and cooled in ice; bromine (6 g.) dissolved in the same solvent (10 cc.) was added while stirring and the reaction flask allowed to stand for 4 hours in ice. After removing the chloroform, the residue distilled at 220–222°/10 mm. as a pale yellow mobile liquid. (Found: Br. 39·3; $C_{15}H_{28}O_2Br_2$ requires 40·0.)

Attempts to prepare halogen hydrins from the above two compounds were not successful, inseparable mixtures only being obtained.

α-monocaprin.—Kahlbaum's synthetic capric acid boiling at 140–141°/6 mm. was used for this preparation. The acid chloride boiled at 97°/8 mm. The condensation of the acid chloride with isopropyliden glycerine was effected at −10° giving a 75 per cent. yield. Some difficulty was experienced in hydrolysing the acetone compound, but an 80 per cent. yield was finally obtained by treating an ethereal solution with 30 per cent. hydrochloric acid at −10° to −15° for 1 hour. The product after recrystallization from petroleum ether melted at 54°, and had saponification value 227·3 (calc. 228·1).

Diphenylurethane—α-monocaprin (1 mol.) was mixed with phenyl isocyanate (2 mols.) and the mixture allowed to stand during 48 hours at 25°. It was then made into a paste with carbon tetrachloride and filtered. The residue was dissolved in hot benzene and filtered and an 80 per cent. yield of a colourless substance melting at 101° obtained from the filtrate. (Found: C, 67·1; H, 7·4; $C_{27}H_{36}O_6N_2$ requires C, 66·9; H, 7·5.) The substance is therefore the diphenyl urethane of α-monocaprin.

Di-p-nitrobenzoyl derivative.—*p*-nitrobenzoyl chloride b. p. 156–157°/6 mm. was prepared from the acid and phosphorus pentachloride and a chloroform solution added to a solution of α-monocaprin in dry pyridine cooled to −10°. After standing for 3 days the pyridine was removed with acid and an almost theoretical yield of the mixed triglyceride obtained. Crystallised from hot alcohol it forms small pale yellow needles m. p. 94°. (Found: C, 59·4; H, 6·1, $C_{27}H_{32}O_{10}N_2$ requires C, 59·6; H, 5·9.)

α-monocaprylin was prepared from a sample of synthetic caprylic acid b. p. 115°/7 mm. the acid chloride of which boiled at 77°/8 mm. in the same way as α-monocaprin. The theoretical yield of an oil was obtained and this solidified on keeping in a vacuum desiccator for

three days. On filtering at 0°, white shining plates m. p. 40° were separated and a further yield obtained by stirring the slightly acid filtrate with a little sodium carbonate and extracting with ether. The melting point was not raised on recrystallizing from petroleum ether. The saponification value was 257 agreeing with theory.

The *diphenyl urethane* was obtained in 80 per cent. yield in the same way as the caprin derivative. It forms a fine colourless powder from benzene m. p. 114°. (Found: C, 65·9; H, 7·2; $C_{25}H_{32}O_6N_2$ requires C, 65·8; H, 7·0.)

The *di*-p-*nitrobenzoyl derivative* was prepared in 80 per cent. yield in the same way as the caprin derivative. It forms pale yellow needles from alcohol m. p. 91·5°. (Found: C, 58·9; H, 5·6; $C_{25}H_{28}O_{10}N_2$ requires C, 60·0; H, 5·6.)

Physical Properties.

Melting points were determined in a capillary tube with a standard thermometer and corrected for exposed stem.

Refractive indices were measured on an Abbé refractometer at 93·1°, 85·7°, 78·7° and 65·0° except those of palmitin and stearin which could not be determined at the lowest temperature.

Densities were determined at the boiling point of water (97·3°) in a pyknometer consisting of a glass bulb of approximate volume 4 cc. with two capillary tubes of measured bore attached to it. This was calibrated by filling it with mercury at the temperature employed. After cleaning it was placed in a steam oven with one limb dipping into a vessel containing the molten glyceride and filled by suction. Caps were then placed over the ends of the side tubes and the instrument immersed almost completely in boiling water. When equilibrium was attained the distances of the liquid in the limbs from two marks was measured thus giving the volume.

Viscosities were measured in an Ostwald's viscometer with a second bulb containing an overflow device so that a constant volume of the hot liquid could be run through. The constant was determined at 30° with a 61·44 per cent. solution of glycerin as described in the previous paper.

Surface tensions were determined by Sugden's maximum bubble pressure method (*J.C.S.*, 1924, **125**, 28), the radii of the tubes used being approximately 0·018 and 0·335 c.m. The apparatus was

calibrated at 30° with benzene and the value obtained used for the measurements at the higher temperature.

Table I summarises the values obtained for the physical properties.

TABLE I.

Physical properties of α-monoglycerides.

Glyceride	M. P.	$n_D^{85·7}$	$d^{97·3}$	$\eta^{97·3}$	$\gamma^{97·3}$	P.	P. calc.	Diff.
Caprylin ...	40°	1·4309	0·9646	0·0603	26·69	514	529	−15
Caprin ...	54°	1·4331	0·9399	0·0772	25·43	588	607	−19
Laurin ...	63°	1·4350	0·9248	0·0985	25·28	664	685	−21
Myristin ...	70°	1·4366	0·9121	0·1210	24·88	740	763	−23
Palmitin ...	76°	1·4484	0·9014	0·1472	25·54	823	841	−18
Stearin ...	82°	1·4400	0·8959	0·1691	25·07	894	919	−25

Temperature coefficient of refractive index 0·00038.

The variation with the number of carbon atoms is regular as may be seen from Fig. I except in the case of the surface tension which appears to fall to a minimum for myristin. The parachor P ($M\gamma^{\frac{1}{4}}/d$) has been calculated and the value compared with those computed from Sugden's data as in the case of the triglycerides, the value 20·0 being assumed for both the non-ester oxygen atoms. The differences show a regular increase except for palmitin, and it is possible that the specimen was not sufficiently pure in spite of the special attention bestowed upon it in view of the variation of the melting point from Fischer's value.

It is noteworthy that the values found for the parachor are all lower than those calculated, whereas with the triglycerides the reverse is the case. The difference for C_2H_4 is 76, compared with 81·0 for the triglycerides and Sugden's value of 78. If the values for the monoglycerides are all raised by 2·8 per cent., the agreement between the theoretical and measured values is almost exact, but such a change would require a constant error of 11·2 per cent. in the surface tension determinations which can hardly be regarded as probable. It is possible that when dealing with these large molecules certain factors enter which are not apparent with substances of smaller molecular weight.

Double Melting Points and Solidifying Points.

It is well known that triglycerides exhibit double melting points, but little attention has been drawn to the corresponding phenomenon in the case of monoglycerides. Fischer (*Ber.* 1920, **53**, 1591) remarked that α-monostearin which melted at 81–82°, melted after solidification at 75–76° and similarly α-monopalmitin exhibited two melting points 78–79° and 72–73°. Brash, however (*loc. cit.*), stated that he was unable to obtain double melting points with his preparation of monopalmitin, the reason probably being that it was impure.

We have succeeded in obtaining two well-defined melting points for each of the four higher monoglycerides examined and they thus resemble the triglycerides. Measurements were made by means of the capillary tube method, a small quantity of the substance being melted in each of several thin-walled, narrow capillaries, retained above the melting point for five minutes and chilled in a freezing mixture. The tubes were then plunged into baths differing slightly in temperature in the neighbourhood of the expected melting point and the temperature of the bath which caused melting to take place within three seconds taken as the melting point of the β-form. The results appeared to be correct to within a degree.

The stability of the β-form varied greatly for different glycerides and showed a regular gradation. Thus, in the case of monostearin, the melting point was 74° and on warming to 75°, no solid appeared in 45 minutes. With monopalmitin the lower melting point was 65° and at 68° a trace of solid formed which increased very slowly. After half-an-hour at the same temperature, the contents of the tube were mainly solid. Monomyristin melts at 57° and resolidifies at a temperature just above this in about 2 minutes. On keeping the chilled melt at room temperature, a slow transformation takes place, as the melting point is found to rise with time, and on rubbing or grinding the change into the α-form is rapid. In the case of monolaurin β, melting and resolidification are almost simultaneous while with monocaprin no double melting point could be detected, doubtless owing to the extreme rapidity of the change from one form to the other.

Table II gives the melting points of the glycerides, their solidifying points (see next section) and the melting points of the fatty acids with 4 more carbon atoms than the acids from which the glycerides are derived. The corresponding values are nearly the same, a fact which is worthy of note although possibly due merely to coincidence.

TABLE II.

Melting points of α-monoglycerides and fatty acids.

Glyceride	M. P. α	M. P. β.	S. P.	Acid	M.P.
Caprylin ...	40	...	...	Lauric ...	43·5
Caprin ...	54	...	...	Myristic ...	53·6
Laurin ...	63	45	60·0	Palmitic ...	62·5
Myristin ...	70	57	67·0	Stearic ...	69·5
Palmitin ...	76	65	70·2	Arachidic (*n*) ...	75·5
Stearin ...	82	74	...	Behenic (*n*) ...	82·0

The value found for palmitin β is 8° lower than Fischer's figure while with stearin the difference is only 2°. The discrepancy in the former case may be due to the different methods employed, but considering the comparative stability of palmitin β, it appears unduly large. It has already been pointed out that the parachor for our sample is high, but at the same time the melting point agrees with that of the material used by Adam Berry and Turner and in spite of several attempts, we have been unable to obtain a specimen with a higher melting point. It seems unlikely that the true melting point could be two degrees higher as given by Fischer. To settle the question, it is intended to make another preparation using an entirely different sample of palmitic acid as the starting material.

Solidifying Points.

Attention has been drawn to the fact that in the case of triglycerides (*cf.* preceding paper), preparations of one substance with the same melting point may vary several degrees in their solidifying points and only after repeated recrystallization is it possible to produce a specimen with a solidifying point approximating to the melting point. Even then the two do not coincide. The same phenomenon is met with in a more marked degree with the α-monoglycerides and the present experiments point to the conclusion that the solidifying points observed are those of an equilibrium mixture of the two forms, the exact proportion depending upon very small traces of unidentifiable impurity.

The determination of the solidifying point offers considerable difficulty owing to the presence of two forms of the substance and the

small amount of heat evolved on solidification. In order to obtain consistent values, it was necessary to follow the procedure adopted in the case of the triglycerides, of conducting the determination in a water-bath the temperature of which could be closely controlled so as to be always cooler than the melt but never more than 1° less. This was effected by using a comparatively small beaker of water (500 cc.) mechanically stirred and electrically heated, with hand regulation. A supplementary gas burner was used for increasing the temperature rapidly during solidification. Not less than 3 g. of the substance was filtered hot into a 3 × ½ inch hard glass test-tube fitted with a very small thermometer and placed in an air jacket in the bath. Scarcity of material precluded the use of larger quantities which would have been desirable, but the results, as well as unpublished results with triglycerides, indicate that the amount taken was sufficient to yield accurate values.

A sample of carefully purified α-monomyristin melting at 70° was first examined because the transition from one form to the other takes place fairly rapidly. A definite maximum at 62·4° was obtained in a number of experiments even when the bath was at room temperature (30°). On raising the bath temperature as previously described, the maximum rose to 63·4°, as shown in Fig. II, curve VIII. The cross on the curve marks the point at which the liquid was seeded with a crystal of the α-form. If this was not done, excessive supercooling was apt to result or a delay to occur in the transition.

On recrystallizing the specimen from ether, the melting point remained unaltered, but the maximum temperature reached rose to 65·2°. After allowing the substance to stand during 24 hours and repeating the experiment, an identical value was obtained as shown in curve X. After another recrystallization the value rose to 67·0° (curves XI & XII, the slight difference in position being due to different seeding temperatures). Further crystallization produced no appreciable change (curve XIV).

An inspection of the curves in Fig. II suggests that the maximum temperature depends to some extent upon the temperature at which a seeding crystal was added. This was shown not to be the case both in preliminary experiments and in a test made by adding some of the original material to the specimen used for experiment XII. Seeding was performed at 58°, but no temperature rise occurred until the melt had cooled at 52·4°, and the maximum attained was only 65·2°. It appears fairly certain therefore that the maximum depends upon traces of impurity too small to affect the melting point. The same impurity also seems to retard the transition to the α-form because, in general, the less pure samples had to be cooled to a lower temperature before

Fig. I

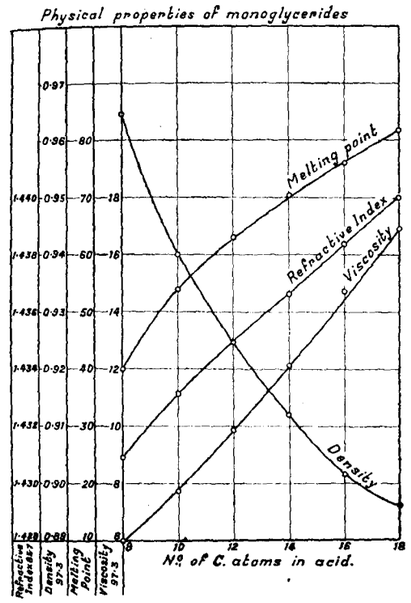


Fig. II

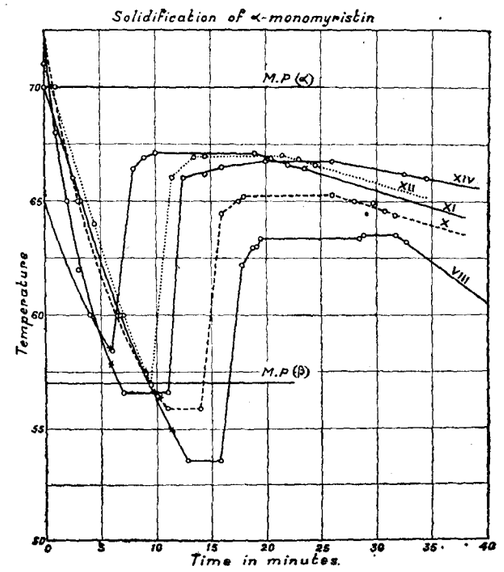


Fig. III

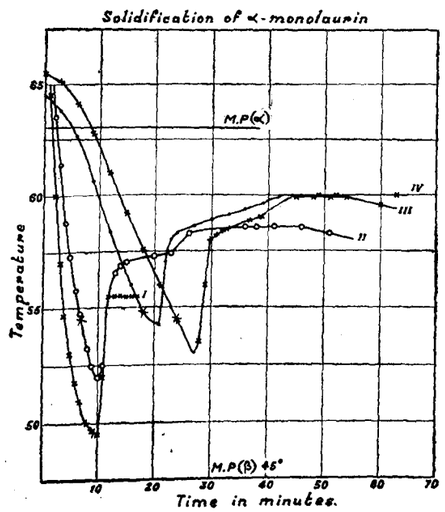
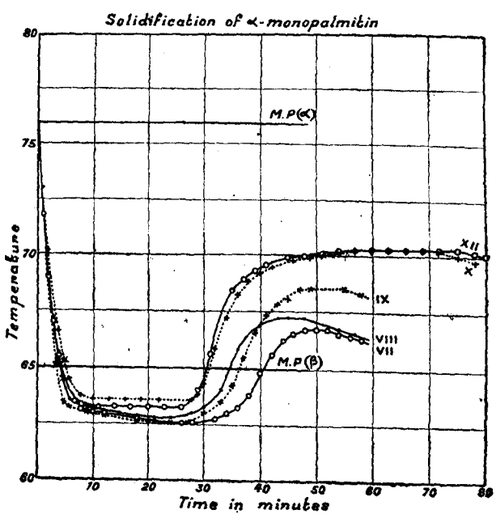


Fig. IV



liberation of heat occurred. A specimen of the solid after the conclusion of experiment XIV was heated in a capillary tube and found to melt at 67·0°, the maximum temperature reached during solidification. It is thus evident that it must be an equilibrium mixture of the two forms, since the α-form melts at 70°.

Similar phenomena were observed with α-monopalmitin but owing to the slow rate of transition very careful regulation of the jacket temperature was required. For example, the first sample tested, melting at 76°, rose in temperature from 60·9 to 64·8° when the temperature of the bath was kept within 1° of that of the melt, but with the bath maintained at 55° no rise at all could be recorded. Crystallization from benzene raised the maximum temperature to 66·7 (Fig. IV curve VII) but it is doubtful if this is a true solidifying point as the maximum temperature was not maintained for any length of time. The same applies in a less degree to curve VIII obtained after a crystallization from ether. In experiment IX with the same substance the bath was maintained still nearer to the temperature of the melt and a higher maximum was reached. Three more recrystallizations from ether resulted in a steady maximum 70·3° (X), this value then remained unchanged on further crystallization (XII). The solid from this experiment melted at 70·2°.

With α-monolaurin the rise in temperature was much more sudden as might be expected from the rapidity with which the β-form changes to the α-form. After the initial rise, however, a period of slow increase in temperature was observed as may be seen in Fig. III. This suggests that there may be a third form of α-monolaurin just as there appears from the work of Loskit (*Z. physical Chem.*, 1928, **134**, 135), to be a third form of some of the triglycerides. No definite opinion can be expressed, however, without further experimental data.

The first sample rose to a maximum temperature of 55·5°; successive crystallizations from ether raised this to 58·6°, 59.9°, 60·0° and 60·0° as shown by curves I, II, III and IV in Fig. III. The curve for the last experiment was practically identical with IV and has not been drawn.

On comparing the solidifying points and melting points shown in Table II, it will be noted that the depression from the melting point of the α-form is 3° for laurin and myristin and 6° for palmitin. It has been found that the initial depression in the melting point of laurin mixed with a small quantity of palmitin or *vice versa* is 0·9° for 1 per cent. impurity in both cases, so that if the assumptions are made that the solidifying point is that of an equilibrium mixture of the α and β-forms and that the depression produced by the presence of β-form is of the

same order as by the addition of a second monoglyceride (an admitted approximation), the quantity of β-form in the mixture would be about 3 per cent for laurin and myristin and 6 per cent. for palmitin.

This involves the assumption that what have been termed the α and β-forms are single bodies. According to Smidts (*Allotropy*) it is more probable that both are equilibrium mixtures. The formation of a definite equilibrium mixture with a melting point lower than that of the α-form makes it appear unlikely that the α-form itself is another equilibrium mixture, but the composition of the β-form cannot be decided without further investigation.

Another noteworthy feature is the very considerable super-cooling which appears to be necessary before the change $\beta \longrightarrow \alpha$ takes place even in presence of the α-form. This is probably a spurious effect due to the slow rate of transformation and the tendency of the β-form to remain in the metastable state and has been already discussed in the case of tristearin (p. 121).

In conclusion we wish to express our best thanks to Dr. J. J. Sudborough and Dr. J. L. Simonsen for valuable assistance during the course of this work.

SUMMARY.

The α-monoglycerides of the fatty acids with an even number of carbon atoms from caprylic to stearic have been made in a state of high purity and their densities, refractive indices, viscosities and surface tensions measured.

The glycerides of the four higher acids exhibit two definite melting points corresponding with those of two forms α and β. The rate of the change $\beta \rightleftharpoons \alpha$ increases with decrease in molecular weight and is almost instantaneous in the case of α-monolaurin.

The solidification point of the fused glyceride always lies below the melting point of the α-form indicating that the transformation $\beta \longrightarrow \alpha$ is not complete.

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III.—THE SOLIDIFYING POINTS OF BINARY MIXTURES OF FATTY ACIDS AND ESTERS.

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A knowledge of the solidifying point of binary mixtures of fatty acids or of their esters is of value for determining the proportion of the constituents in mixtures such as those obtained while fractionating a mixture of esters during the investigation of an oil. (*Cf.* Patel, Sudborough & Watson, *J. Indian Inst. Sci.*, 1923, **6**, 120.) The solidifying point of a mixture being much more sharply defined than the melting point, gives more accurate results than those which can be obtained by determining the latter property, but apart from measurements made in this laboratory very few data appear to exist except the figures for palmitic and stearic acid of de Visser (*Rec. trav. chim.*, 1898, **17**, 182).

In addition to their value for analytical purposes, solidifying point curves should give information regarding the state of molecular aggregation of the constituent substances, a problem of some complexity where the fatty acids are concerned. We have consequently made determinations for several mixtures and have compared the results with those previously obtained in this laboratory and elsewhere.

EXPERIMENTAL.

Preparation of Materials.

Acetic acid.—The purest commercial sample obtainable was fractionally distilled four times, the middle fraction twice partially frozen and the crystals separated, great care being taken to exclude moisture during the whole of the operations. In spite of this there appears to have been slight contamination as the product solidified at 16·4°, 16·7° being the accepted value.

n-*Butyric acid.*—A pure specimen was fractionally distilled 3 times yielding a product boiling sharply at 163° and solidifying at −8·1°.

Capric acid.—A synthetic specimen was fractionated and the middle fraction boiling at 136° at 5 mm. recrystallized 12 times from absolute alcohol. The product melted at 31·4° the accepted value, but the solidifying point was only 30·9°.

Methyl laurate and methyl myristate were prepared from fairly pure samples which had been made by fractionation of the methylated fatty acids from hydrogenated *Salvadora oleoides* (*cf.* Patel, Iyer, Sudborough and Watson, *J. Indian Inst. Sci.*, 1926, **9**A, 117). The solidifying points of these preparations were 2·5° and 14·5°. Attempts at purification by freezing were not successful and consequently the esters were fractionated at 7 mm. pressure through a four-bulbed column filled with Lessing rings. After four distillations the methyl laurate boiled within 1° and its solidifying point remained unchanged at 4·4° on refractionation. The methyl myristate required only two distillations to reach a steady solidifying point 15·9°.

Lauric and myristic acids were prepared from the purified esters by saponification with alcoholic potash and recrystallized twice from alcohol. Their solidifying points were 43·5° and 53·0°, respectively. In spite of the apparent purity of its ester, the solidifying point of the myristic acid was low, 53·8° being a better value. (*cf.* Joglekar and Watson, *J. Indian. Inst. Sci.*, 1930, **13**A. 119.)

Stearic acid.—A pure sample was recrystallized five times from 95 per cent. alcohol and the last traces of solvent removed by heating to 50° in a vacuum for some hours. The solidifying point was 69·2°.

Lignoceric acid from *Adenanthera pavonina* was twice ground with acetone and the liquid separated by suction in order to remove lower acids. The solid portion was then crystallized twice from toluene and three times from carbon disulphide. The product melted sharply at 80·8° but the solidifying point was only 79·3°. It may be mentioned that this acid is not *n*-lignoceric acid which melts at 80·5°, but appears to have a side chain, the position of which is under investigation.

Determination of solidifying points

Solidifying points were determined by the usual method of observing maximum temperature reached by the molten substance on solidification. Temperatures were measured with thermometers divided to 0·2° or 0·1° and calibrated against standards.

For temperature control, a bath of calcium chloride solution was used above 10° and ice or a freezing mixture of ice and salt down to −15°. Between −15° and −25° calcium chloride hexahydrate and ice were found suitable and for still lower temperatures the vessel to be cooled was suspended in a tall vacuum vessel with a small quantity of liquid air at the bottom. In all cases the test tube containing the substance was surrounded by a wider one to form an air jacket. In the case of mixtures liquid at room temperature, stirring was effected with a

magnetic stirrer to avoid condensation of moisture. Numerous experiments were made with different quantities of material, different bath temperatures and different degrees of supercooling. It was found that results reproducible to 0·1° could be obtained with 3 grams of material provided that the bath temperature was maintained not more than 2 or 3 degrees below that of the melt and supercooling was not excessive (about 2 degrees). All mixtures were made by adding successive weighed quantities of one constituent to the other; those containing approximately 50 per cent. of each constituent were thus arrived at in two ways, by adding A to B, or B to A, and a considerable overlap was usually allowed between the two series.

The following tables give values for the solidifying points of different mixtures, and Figs. I and II show the shape of the curves obtained on plotting these points against the percentage compositions of the mixtures. The points marked show composition by weight and the second curves drawn in several cases refer to molecular proportions. In both tables and curves, a small correction has been applied where necessary to bring the solidifying points of the pure acids to their accepted values:—

TABLE I.

Solidifying points of binary mixtures of acids and esters.

Percentage weight of first-named compound	Behenic —stearic	Lauric —stearic	Capric —stearic	Lauric —lignoceric	Lauric —myristic	Butyric —acetic	Me-laurate —me-myristate
100	79·3	43·5	31·0	43·5	43·5	− 8·1	4·4
90	76·9	38·6	26·6	43·8	39·3	−16·2	0·4
80	74·4	38·3	35·6	51·5	36·0	−24·5	−2·8
70	71·7	41·5	43·8	58·2	33·8	−33·0	−4·8
60	68·5	47·9	49·5	63·0	35·7	−28·6	−2·2
50	64·8	53·1	53·9	66·6	36·4	−18·2	1·0
40	63·6	57·9	57·4	69·5	39·2	− 8·2	4·1
30	62·3	61·6	60·8	72·2	43·3	− 1·6	7·2
20	63·0	64·5	63·7	74·6	47·0	5·0	10·4
10	65·2	67·0	66·6	76·9	50·6	11·0	12·5
0	69·3	69·3	69·3	79·3	53·8	16·7	15·9

De Visser's figures for palmitic and stearic acids and those for the pairs methyl palmitate-methyl stearate and methyl stearate-methyl behenate which have been published previously (*J. Indian Inst. Sci.*, 1923, **6**, 120 and 1926, **9**, 69) are not given in the table, but the corresponding curves are shown for the sake of comparison.

It will be noticed that the curves for all the acids are of a similar type. Starting with the higher melting acid the curvature is concave towards the X-axis. A break then occurs which appears to be more pronounced the closer the acids are to each other in the homologous series. Lauric and myristic acids are the only two exhibiting a definite minimum; palmitic and stearic acids have a distinct flat portion in the curve; the curves for stearic-lauric and stearic-behenic acids tend to become flat, while in the case of the others a fairly well-defined break alone is observable. After reaching a eutectic point the curves rise and are convex to the X-axis.

If the curves showing molecular percentage are examined it is seen that although the flat portion for the pairs stearic-behenic, stearic-palmitic and lauric-myristic acids corresponds very nearly to the equimolecular mixture, in no case do the two coincide. The nearest approach is shown by the last mentioned pair for which a maximum occurs at 53 mols. per cent. of lauric acid. Compound formation is thus in all probability best defined with these two acids. When the quantity of compound is relatively small, the flat portion appears when the molecular proportion of lower-melting acid is greater than 50 per cent. i.e., 60 per cent. of stearic when mixed with behenic acid and 57 per cent. of palmitic when mixed with stearic acid. For the lauric-stearic acid mixture the curve indicates a compound at about 80 per cent. of the former acid or 4 mols. to 1, while with capric and stearic acids, the ratio is still higher. It is not possible to decide whether compounds of this nature are really formed or whether the bend in the curve is displaced owing to the fact that compound formation is incomplete and that a ternary mixture of unknown composition is being dealt with.

The curves for the esters are of the simple eutectic type, methyl palmitate and stearate being the only pair with a definite break while the small inflection for methyl laurate and myristate may be due to experimental error.

The depressions in the solidifying points of pure acids on the addition of a second substance might be expected to yield data of some interest, but the results are so irregular that no deductions can be made without further experimental values. Table II gives Δ, the depression which would be produced by 100 g. of acid dissolved in 100 g.

Fig. 1

Solidifying points of binary mixtures with stearic acid

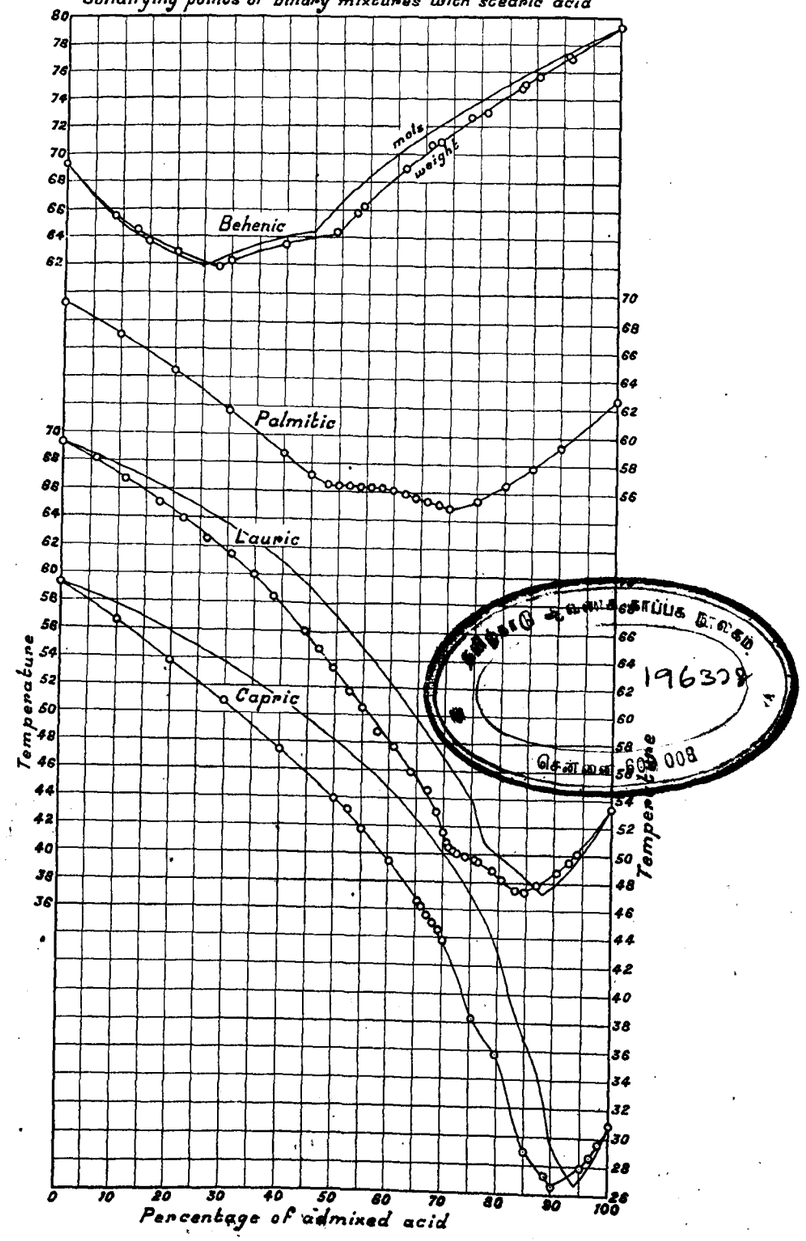
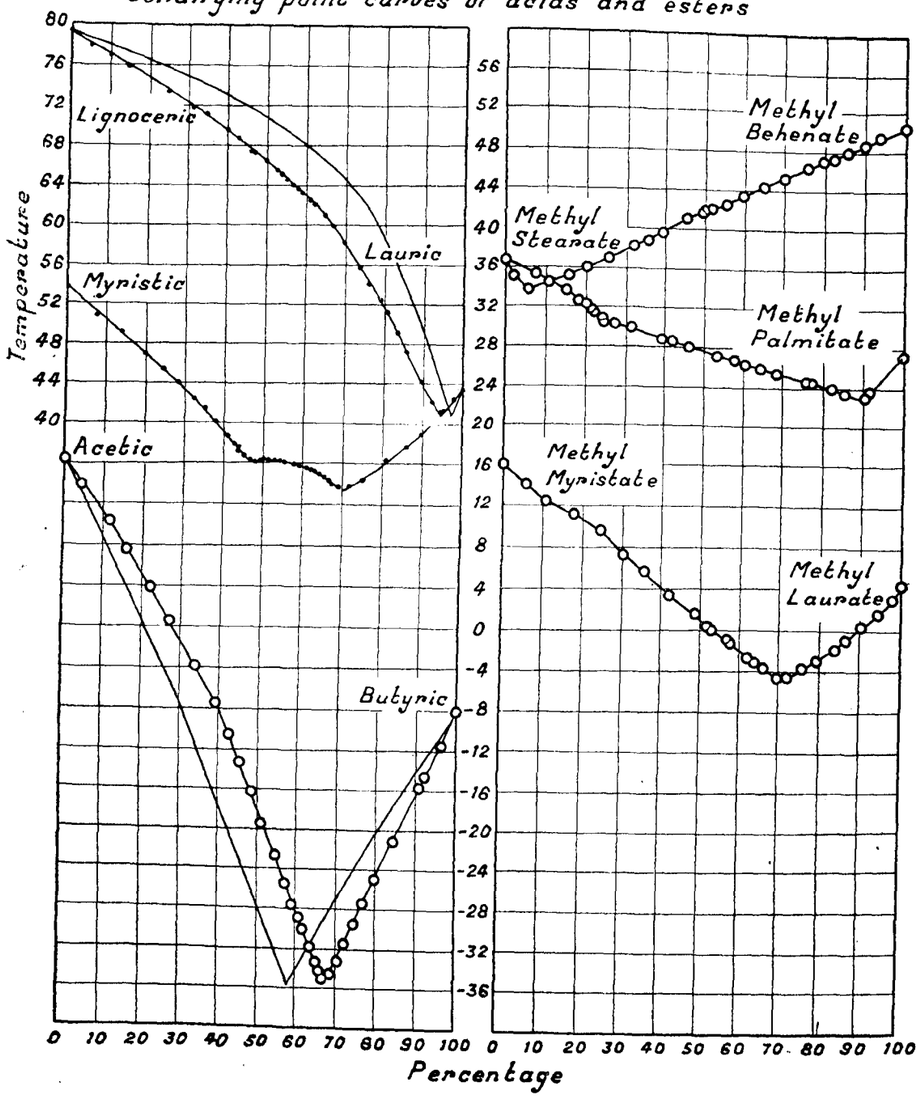


Fig. II

Solidifying point curves of acids and esters



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