# 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**, 1063; Bokhörst, *Diss. Amsterdam*, 1916; Nicolet, *Ind. Eng. Chem.*, 1920, **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 $P = M\gamma^{1/4}/d$. (*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.

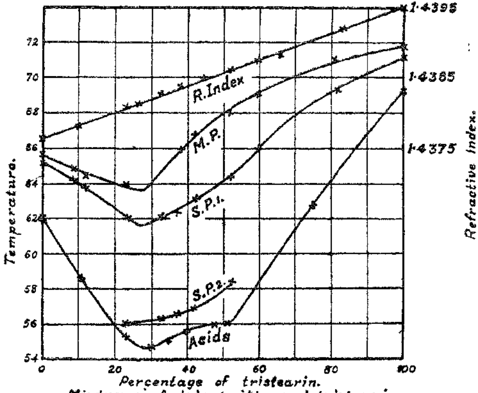
The solidification points of mixtures of tripalmitin and tristearin were determined hy Kremann (*loc. cit.*) with the object of ascertaining if there was a flat portion on the curve as there is in the case of palmitic and stearic acids. His results appear to refer to mixtures of tripalmitin with the 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 $\beta$-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.

*Department of General Chemistry,*
*Indian Institute of Science,*
*Bangalore.*

[Accepted, 19-6-30.]