890. *Melting-point Diagrams for Binary Triglyceride Systems.*

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Phase diagrams, constructed by the thaw–melt method, show that each of the mixtures, tristearin–tripalmitin, tripalmitin–trilaurin, tristearin–trilaurin, and tripalmitin–2-oleo-1 : 3-dipalmitin is of the eutectic type with partially miscible solid solutions.

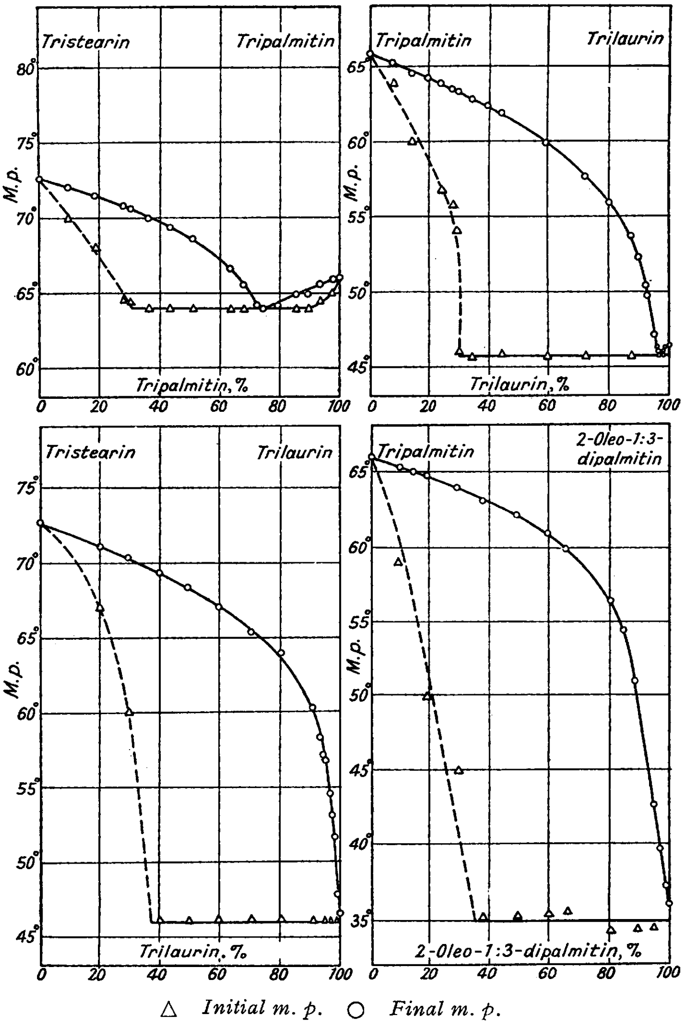
ACCORDING to Bailey ("The Melting and Solidification of Fats," Intersci. Publ., Inc., New York, 1950) the only reliable melting-point data for binary triglyceride mixtures are those by Joglekar and Watson (*J. Soc. Chem. Ind.*, 1928, **47**, 365T) who determined melting and solidification curves for tristearin–tripalmitin. Efremov *et al.* (*Akad. Nauk S.S.S.R.*, 1948, **16**, No. 3, 142; *Chem. Abs.*, 1950, **44**, 10352) have studied the same system by thermal analysis.

In the present investigation, the initial and final melting points have been determined for tristearin–tripalmitin, tripalmitin–trilaurin, tristearin–trilaurin, and tripalmitin–2-oleo-1 : 3-dipalmitin. The results (Figure) show each system to be of the eutectic type with partially miscible solid solutions. The eutectic point is progressively displaced to the lower-melting side of the diagram as the difference in melting point of the two pure components increases. Indeed the last two systems closely approach the monotectic type since the eutectic composition is virtually 100% of the low-melting component. The four eutectic points are :

	Eutectic point	
System	Composition	Temp.
Tristearin–tripalmitin	Tripalmitin 74·5%	63·9°
Tripalmitin–trilaurin	Trilaurin 97%	45·6
Tristearin–trilaurin	Trilaurin 99%	46·0
Tripalmitin–2-oleo-1 : 3-dipalmitin	Oleodipalmitin 100%	35·0

In each diagram the solidus curves (broken lines) are rather indefinite, but indicate that the high-melting triglyceride dissolves 30—40% of the low-melting triglyceride in the solid state at the eutectic temperature. By comparison the solubility of tristearin in tripalmitin in the solid state is about 10% and of tripalmitin in trilaurin is 1% or less. The solubilities of tristearin in trilaurin and of tripalmitin in oleodipalmitin are negligible.

For the system tristearin–tripalmitin, Joglekar and Watson (*loc. cit.*) obtained a curve of final melting points similar to that of our Figure, but lying about 0·6° below it on the tristearin side of the eutectic point and about 0·3° below it on the tripalmitin side. A minimum point at 72% of tripalmitin and 63·6° is in fair agreement with the eutectic point shown above at 74·5% of tripalmitin and 63·9°. Joglekar and Watson's solidification-point curve is roughly parallel to their melting-point curve but lies several degrees below it because of supercooling. As pointed out by Bailey (*op. cit.*, pp. 81—82) this does not represent a true phase boundary. On the other hand, the initial melting curves in the present work mark the first appearance of a liquid phase.



EXPERIMENTAL

Preparation of Pure Triglycerides.—Trilaurin, tripalmitin, and tristearin. The pure acids were prepared from the pure distilled methyl esters, recrystallised, and converted into the triglycerides by glycerol at 180° in the presence of 1% of toluene-*p*-sulphonic acid (Clarkson and Malkin, *J.*, 1934, 666). These were repeatedly recrystallised from absolute alcohol. Tristearin required further recrystallisation from 1 : 1 toluene–alcohol and then from toluene.

2-*Oleo*-1 : 3-*dipalmitin.* Oleic acid was prepared by low-temperature fractional recrystallisation of the tallow fatty acids (linoleic, *ca.* 5%; oleic, *ca.* 40%) from acetone, followed by low-pressure fractional distillation (Brown and Shinowara, *J. Amer. Chem. Soc.*, 1937, **59**, 6), and then converted into oleyl chloride by thionyl chloride (Human and Mills, *Nature*, 1946, **158**, 877). 1-Monopalmitin was prepared by the action of palmityl chloride on 1 : 2-*iso*propylidene glycerol (Averill, Roche, and King, *J. Amer. Chem. Soc.*, 1929, **51**, **866**), and converted into 1 : 3-dipalmitin by palmityl chloride (Malkin, Shurbagy, and Meara, *J.*, **1937**, 1409). Finally 1 : 3-dipalmitin and oleyl chloride gave 2-oleo-1 : 3-dipalmitin (Jackson, Daubert, King, and Longenecker, *J. Amer. Chem. Soc.*, 1944, **66**, 289) which was purified by repeated recrystallisation from 1 : 1 alcohol–ether.

The analytical constants of the various acids and glycerides are tabulated.

	M. p.	A.V. found	S.V. found	S.V. calc.	I.V. found	I.V. or SCN.V. calc.	OH.V. found	OH.V. calc.
Lauric acid	43·8° *	279·6	280·2	280·3	—	—	—	—
Palmitic acid	62·5 *	218·7	219·1	219·0	0·0	0·0	—	—
Stearic acid	69·5 *	196·8	197·2	197·3	—	—	—	—
Oleic acid	12·7	199·0	199·4	198·8	89·9	89·9 †	—	—
Trilaurin	46·4	0·0	263·6	263·6	0·0	0·0	0·0	0·0
Tripalmitin	65·9	0·0	208·6	208·6	0·0	0·0	0·0	0·0
Tristearin	72·6	0·0	188·9	189·0	0·0	0·0	0·0	0·0
1-Monopalmitin	77·0	—	—	—	—	—	343·0	340·0
1 : 3-Dipalmitin	72·5	—	—	—	—	—	99·0	98·8
2-Oleo-1 : 3-dipalmitin ...	36·1	0·0	201·8	202·1	30·4	30·5	0·0	0·0

* Setting point. † SCN.V., found: 89·4. A.V. = acid value (mg. of KOH/g.). S.V. = saponification value (mg. of KOH/g.). SCN.V. = thiocyanogen value (g. of iodine/100 g.). I.V. = iodine value (g. of iodine/100 g.). OH.V. = hydroxyl value (mg. of KOH/g.).

Construction of Phase Diagrams.—The thaw-melt method (Bowden, "The Phase Rule and Phase Reactions," Macmillan and Co. Ltd., London, 1938, p. 208) was modified. Mixtures (total wt. *ca.* 0·15 g.), in small stoppered tubes, were melted, mixed, and allowed to solidify by storage in a large Dewar flask filled with hot water which cooled very slowly overnight. This procedure was intended to avoid the unstable, low-melting, polymorphic forms which are produced by rapid cooling and can persist for a long time, particularly in the presence of an impurity such as another triglyceride. It was successful, except for tristearin–tripalmitin which exhibited double melting if the content of tripalmitin was 50—90%. The last-mentioned mixtures melted to a clear liquid at 58—62° and then partly resolidified before becoming clear at a higher temperature. This corresponds to the double solidification points observed by Joglekar and Watson (*loc. cit.*) and indicates the presence of unstable forms. Tristearin–tripalmitin mixtures were therefore remelted and left to solidify overnight in a thermostat at 60°, yielding then only the stable form. For each system the solidified mixtures were thoroughly powdered and their m. p.s determined as follows.

A 1-mm. capillary tube containing a small quantity of the mixture was slowly heated in a stirred oil-bath. The final m. p. was taken as the temperature at which the turbid liquid finally became clear whilst being thoroughly mixed with a nickel-wire stirrer and illuminated by a spotlight. The determination was repeated at reduced heating rates with freshly filled capillaries until a constant minimum value was obtained. All the final m. p.s, except those shown on the very steep portions of the curves, were reproducible within ±0·1°.

Accurate observation of initial melting in a capillary tube was difficult and was replaced by a microscopic method. A thin layer of the powdered mixture, pressed on to a glass disc 4 mm. in diameter, was carefully observed for first signs of melting whilst being slowly heated in a specially designed hot stage between crossed Nicols which gave dark-background illumination. All the initial m. p.s were sharp and reproducible within ±0·1°, except that those forming the broken curves were indefinite and gave duplicate determinations differing by 1—2°.

The thermometer used throughout had been calibrated against an N.P.L. standard.

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