Dilatometric Investigations of Fats. V. Volume Changes Associated With the Polymorphism and Melting of Monostearin

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THAT 1-monostearin is capable of existing in three different crystalline forms has been established by several investigators (1, 2, 3, 4), using x-ray diffraction and thermal techniques. Lutton and Jackson (5) in a recent publication present the x-ray spacing measurements and thermal data for four distinct polymorphic modifications of 1-monostearin.

In the investigation reported here the expansibilities of the four established polymorphic forms of 1-monostearin were determined over the complete melting range from solid to liquid, thus relating the specific volume of each form to temperature. The volume change associated with the transition of one crystalline form to another and the melting dilation of each crystalline form was calculated from the observed expansibilities of the solid and liquid states.

Experimental

Materials. 1-Monostearin was prepared by reacting purified stearic acid with 36.2% U.S.P. glycerol in the presence of 0.1% sodium hydroxide, at 200°C. for 3 hours. Soaps and catalyst were removed by acidifying with acetic acid, and the crude product was washed several times with hot water. Di- and triester reaction products were removed by fractional crystallization from a 70% isopropanol-water solution. The monostearin fraction was further purified by slow separation from commercial hexane at 25°C. at a product-solvent ratio of 1:6 by weight. The purity of the monostearin was at least 99% as indicated by its heating curve (6), and 99.2% by periodic acid oxidation analysis (7). During the course of the investigation the purity of the material decreased to 94%, probably due to thermal decomposition.

The polymorphic forms of the purified monostearin were obtained by the method of Lutton and Jackson (5), by which the α_s-(sub-alpha)-form results from rapid cooling of the melt, the β'-(beta prime)-form by fairly rapid crystallization from 1:300 commercial hexane solution, and the β-(beta)-form by slow crystallization from 1:6 commercial hexane solution. The α-(alpha)-form is not obtained directly at room temperature but exists only when the α_s-form is warmed to approximately 49°C. Capillary melting points as determined in a fixed-temperature bath were 74.2°, 77.8°, and 81.8°C., for the α-, β'-, and β-forms, respectively, closely agreeing with 74°, 78°, and 81.5° C. as reported by Lutton and Jackson (5).

The α_s-, β'-, and β-forms of monostearin are illustrated by the x-ray diffraction patterns which are reproduced in Figure 1.

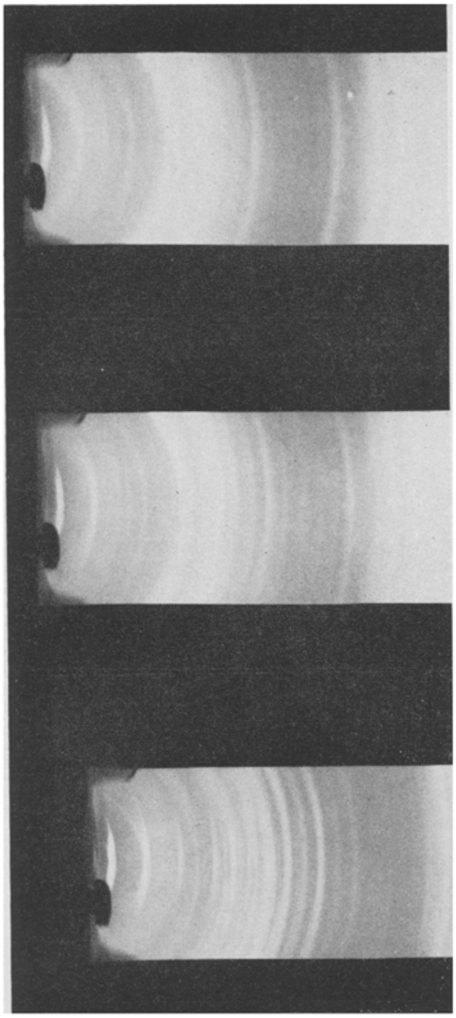

FIG. 1. X-ray diffraction patterns of monostearin: (1) beta form, (2) beta prime form, (3) sub-alpha form.

Expansibility. The expansibility of monostearin was measured with gravimetric-type dilatometers, and melting dilations of the various crystalline forms were calculated by the method described in previous publications (8, 9). The α_s-, β'-, and β-forms of monostearin were placed in dilatometers, which were then evacuated and filled with mercury. Expansibilities were determined for each sample, beginning at —38.86°C. and proceeding by small temperature increments to approximately 8° beyond the melting point of the highest melting sample (β-form). Measurements of the expansibility of both the α- and β'-forms of monostearin in the temperature range from about 50°C. to their respective melting points had to be made rapidly because these two forms are known to transform (5) to the β-form at some temperature below their melting points. However the transitions are somewhat sluggish as the α- to β-transition in a capillary tube required from 4 to 6 hours at 70°C. Measurement of the expansibility of the α-form of monostearin from the solid to the liquid state was made rapidly enough to avoid substantial transition,

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but the β′-form began to transform to the β-form before the determination of the expansibility of this form could be completed.

The absolute density of liquid monostearin was found by the pycnometer method to be 0.9039 g./ml. at 85°C.

The specific volume of the β′-form appears to be high, possibly on account of incomplete wetting of the powdered sample by the confining mercury. However the β′- and β-forms were confined under identical conditions, and no difficulty was experienced with the latter form.

Results and Conclusions

Data for the specific volumes of the polymorphic forms of monostearin at —38.86°C., the melting dilations of each form, and the expansibilities in the solid state are included in Table I. Discontinuity in the specific volume of all forms was detected at about 12.5°C. and tentatively assigned to premelting. The final melting points, determined dilatometrically, were 81.2° and 74.2°C. for the β- and α-forms of monostearin, respectively. The β′-form transformed before melting and the dilatometric melting point of this form was not determined. The melting dilation of the β′-form was calculated at the capillary tube melting point (77.8°C.). Expansibility of the liquid state, the same for all forms, averaged 0.000920 ml./g./°C. The specific volume at 85°C. was 1.1063 ml./g. The specific volume as a function of temperature of each of the polymorphic forms of monostearin is shown graphically in Figure 2. The β-form appears to be the most dense, unlike the results of Lutton and Jackson (5), who observed the β-form to be less dense than the α_s-form. However the spread in densities is very small.

TABLE I

Expansibility in the Solid State, Specific Volume, and Melting Dilation of the Beta-, Beta Prime-, and Sub-Alpha-Forms of 1-Monostearin

Form	Expansibility in solid state,[a]	Specific volume,[b]	Melting dilation,
	ml./g./°C.	*ml./g.*	*ml./g.*
Beta	0.000241	0.9419	0.1367
Beta prime	0.000291	1.0307	0.0610
Sub-alpha	0.000303	0.9515	0.1292

[a] —38° to +12°C.
[b] At —38.86°C.

Transition of the α_s- to the α-form of monostearin at 48-49°C. involved an increase in specific volume of 0.004 ml./g. and was found to be reversible, contracting about 0.008 ml./g. Lutton and Jackson (5) do not report a value for the α_s-α-transition but give the reversible contraction as 0.04 units.

A comparison of the melting dilations of the stable forms of stearic acid and tristearin, as reported in previous publications (9, 10), with the corresponding determination for monostearin, reveals an interesting relationship. The melting dilations of stearic acid, tristearin, and monostearin are 0.1857, 0.1671, and 0.1367 ml./g., respectively. On a weight basis, the content of stearyl groups in tristearin is 90.0% and in monostearin it is 74.6%. Multiplying the melting dilation of stearic acid by the stearyl group content of tristearin and monostearin yields values for the melting dilation of tristearin and monostearin of 0.1671 and 0.1385 ml./g., respectively. The observed and calculated melting dilations of tristearin are seen to be identical, whereas they differ only 1.4% for monostearin, which could be due to experimental error in determining the melting dilation. A plot of the melting dilations of stearic acid, tristearin, and monostearin as functions of the percentage of stearyl groups in each, yields a curve indicating that the melting dilations of stearic acid, tristearin, and monostearin are in proportion to the amount of stearyl groups present in these materials. If this method is used to calculate the melting dilation of distearin, the value of 0.159 ml./g. is obtained.

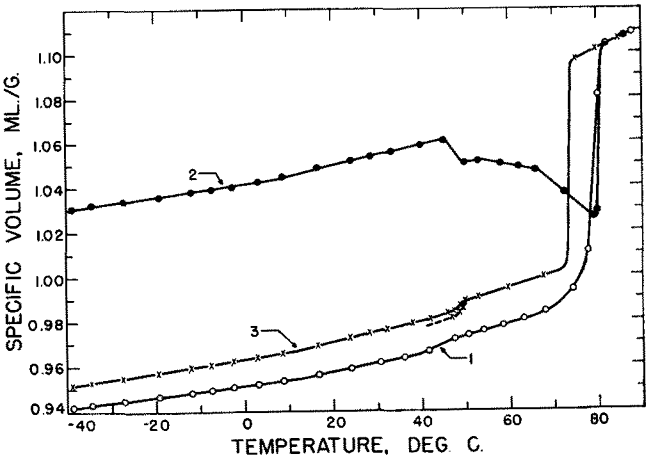

FIG. 2. Specific volume as a function of temperature of the polymorphic forms of monostearin: (1) beta form, (2) beta prime form, (3) sub-alpha form.

Summary

1-Monostearin of 99.2% purity was prepared and the polymorphic forms known as sub-alpha (α_s), alpha (α), beta prime (β′), and beta (β) obtained, and their expansibilities determined over the temperature range from the solid to the liquid state. The melting dilation of each form was calculated from the observed expansibilities.

From the values for the expansibility, density, and melting dilation, the specific volume of any of the polymorphic forms of monostearin at any temperature from the solid to the liquid state may be calculated.

The melting dilations of stearic acid, monostearin, and tristearin are in direct proportion to the mole percentage of stearyl groups present in each compound. By means of this relationship a melting dilation for distearin was calculated.

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