metric endpoint of the titrations and consequently represent the true iodine numbers of the unsaturated substance because of a) the absence of the subjective factor in fixing the disappearance of the starch-iodine blue color, b) the impossibility of using an excess of thiosulfate solution (the endpoint is not actually reached with the thiosulfate reagent but is calculated from an extrapolation to a point of zero potential), and c) the absence of errors arising from adsorption phenomena, such as occur in the iodine-starch system.

A useful application of dead-stop titrimetry could be found in micro iodine value titrations. It has been demonstrated (Foulk and Bawden) that in titrating iodine with a thiosulfate solution, the endpoint, as shown by the instrument, occurs 4 drops of 0.001N thiosulfate solution after the blue starch-iodine color disappears. This is probably due to the removal of iodine from the titration by adsorption on the starch. The value of the instrument in micro iodine number determinations is obvious.

Summary

The amperometric (dead-stop) method has been applied to iodine value determinations of fatty acids and oils. The values obtained agree with those arrived at by the starch end-point method. The use of this simple instrument appears to give however more accurate results since the endpoint is determined by the extrapolation of the linear response of the galvanometer with small increments of added thiosulfate to a zero galvanometer reading which corresponds to a zero iodine concentration. The fluctuations of the galvanometer needle give visible evidence of the approach of the endpoint, thereby facilitating the titration.

Acknowledgments

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Dilatometric Studies of Pure Triglycerides and Mixtures[1,2,3]

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THE volume-temperature relationships of various natural fats and some synthetic triglycerides have been studied with volumetric and gravimetric dilatometers by several investigators. Coffey and Spannuth (4) employed a simple volume dilatometer to determine these relationships in various fats and fat mixtures having widely different fatty acid compositions and found that the measurements in a general way reflected the fatty acid composition of such systems. Bailey and his co-workers (2,3,6,8) employed a gravimetric dilatometer to measure the volume changes associated with phase transformations, the coefficients of expansion in the solid and liquid states, and the melting dilations for several simple triglycerides. They calculated the percentage of solids at various temperatures for several fats and fat mixtures from dilatometric data on the assumption that all triglycerides present in such mixtures possessed equal melting dilations. The results appeared to be in agreement with calorimetric data which they had previously obtained.

Inasmuch as the melting dilations of individual triglycerides have been shown to vary quite considerably, depending on their fatty acid composition, Bailey (1) has recently indicated that the exact calculation of the proportion of the solid and liquid phases in the complex mixtures that constitute natural fats is impossible. This is also true of a simple binary mixture of triglycerides unless *a priori* knowledge of the identity, proportions, and properties of the individual components is available.

The work reported here was undertaken to extend the available information on the coefficients of expansion and melting dilations of individual triglycerides and to determine the effects of triglyceride composition on the melting range and on the proportion of solids within the melting range in synthetic mixtures of pure triglycerides.

Materials

Eight simple and mixed triglycerides were employed. The pure symmetrical mixed triglycerides, oleodistearin, oleodipalmitin, stearodiolein, palmitodistearin, and stearodipalmitin were prepared as described in another paper (5). The simple triglycerides, tristearin, tripalmitin, and triolein were prepared by reacting purified methyl esters of the fatty acids with triacetin using sodium methoxide as a catalyst (7). The properties of these simple triglycerides agreed with those reported in the literature for the pure compounds.

Various mixtures of the simple and mixed triglycerides containing two, three, four, and eight components were prepared. The mixtures of triglycerides examined contained $33\frac{1}{3}$ mol per cent of saturated fatty acids and $66\frac{2}{3}$ mol per cent of oleic acid.

Apparatus and Methods

A gravimetric type of dilatometer was used, similar to that described by Bailey and Kraemer (2), and is

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[1] Paper No. 2703 of the Scientific Journal Series. Minnesota Agricultural Experiment Station, and Hormel Institute publication No. 73.

[2] Submitted as part of Ph.D. Thesis by B. M. Craig, University of Minnesota, 1950.

[3] Presented at meeting of the American Oil Chemists Society, San Francisco, Calif., September, 1950.

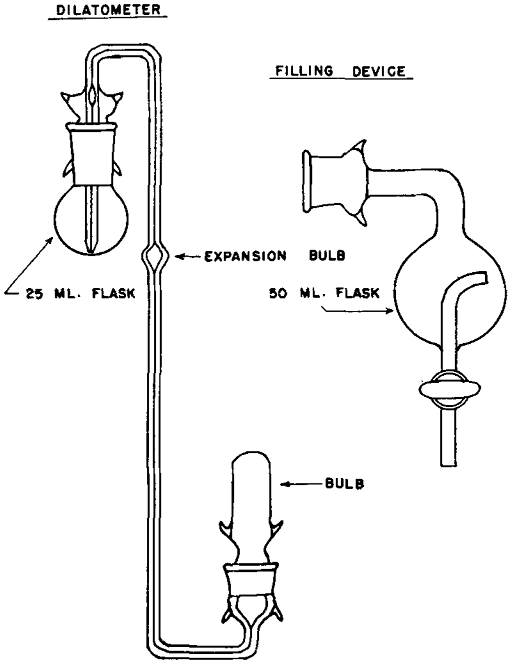

FIG. 1. Gravimetric dilatometer and filling device.

illustrated in Figure 1. The dilatometer was immersed in a thermostatically controlled bath to within 8 centimeters of the expansion bulb. The capillary tubing connecting the dilatometer bulb and the mercury receiving flask had an inside diameter of one-half millimeter. It was found that the use of tubing of this small size made it unnecessary to apply a correction for the so-called "stem emergence." However the usual volume corrections for expansion of the mercury and glass were made in all the measurements.

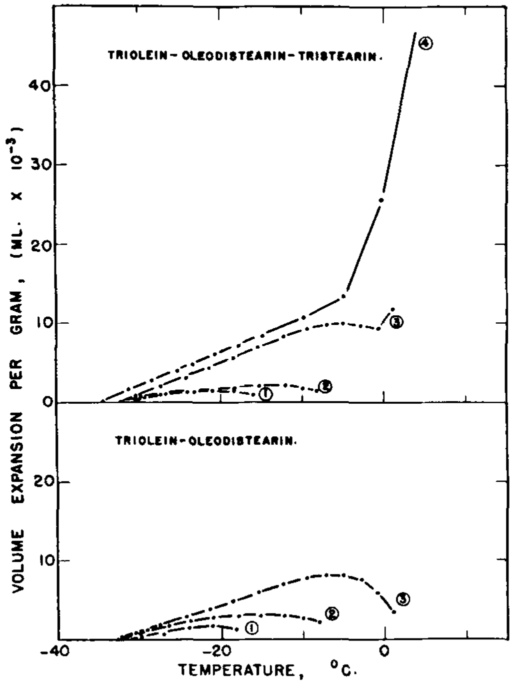

FIG. 2. Volume expansion of two glyceride mixtures, showing vacuole formation and the effect of tempering the samples for 6-hour periods at 5° and —5°C.

In initial studies with individual simple triglycerides, difficulties were encountered with a phenomenon that has been called "vacuole" formation when the sample was solidified in a single mass. This phenomenon was encountered in triglyceride mixtures in the temperature region below the melting point of the lowest melting triglyceride. In the latter case the difficulty could be overcome by alternate partial melting and solidification of the mixture. This is illustrated for two mixtures in Figure 2, which show an apparent contraction when the triolein began to melt. Curves 1, 2, 3, and 4 for the ternary mixture illustrate results that were obtained after successive treatments of partial melting and resolidification. In curve 4 all of the "vacuoles" had apparently been eliminated. However the difficulties were more satisfactorily overcome in a manner suggested by Bailey and Singleton (3) for the treatment of saturated triglycerides.

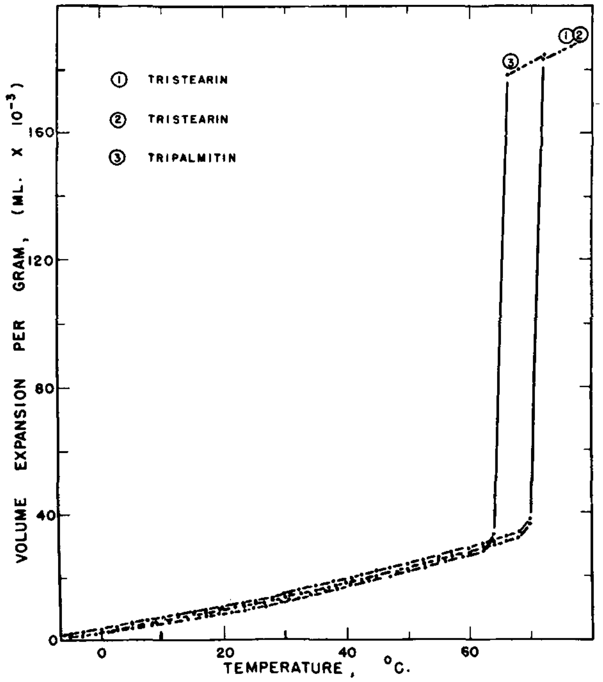

FIG. 3. Volume expansions of tripalmitin and tristearin.

Pretreatment of Samples

In measurements with individual triglycerides the samples were solidified in small globules on a glass plate and then placed in the dilatometer bulbs. After the dilatometer had been filled with mercury, the samples were equilibrated for 12 hours at a temperature slightly above the melting point of the beta prime (next to the most stable) polymorphic modification. The dilatometers were then kept in a cold room at —15°C. for 12 hours prior to being placed in the bath for the measurements.

The triglyceride mixtures were similarly solidified in globular form with some additional precautions to prevent any gross separation of the components and, after being placed in the dilatometers, were cooled to —60°C. before the dilatometers were filled with mercury. The dilatometers were placed in a room at 5°C. for two hours and then kept at —6°C. for 12 hours before the measurements were started. By employing this procedure no deviations in the dilatometric curves were apparent that could be attributed to vacuole for-

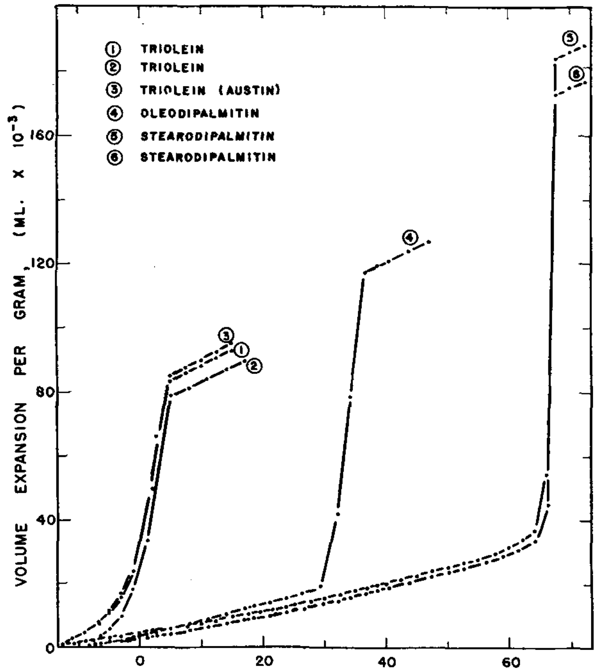

FIG. 4. Volume expansions of triolein, oleodipalmitin, and stearodipalmitin.

mation or to first order polymorphic transitions. After preliminary work had shown that the volume expansion of all the triglycerides, including triolein, was linear from —35° to —6°C., all measurements were started either at —10° or —15°C. Measurements were made at 2° intervals. The sample was allowed to equilibrate at each temperature for 40 minutes.

Volume Expansion of Individual Triglycerides

The volume expansions of the individual triglycerides are shown graphically in Figures 3, 4, and 5.

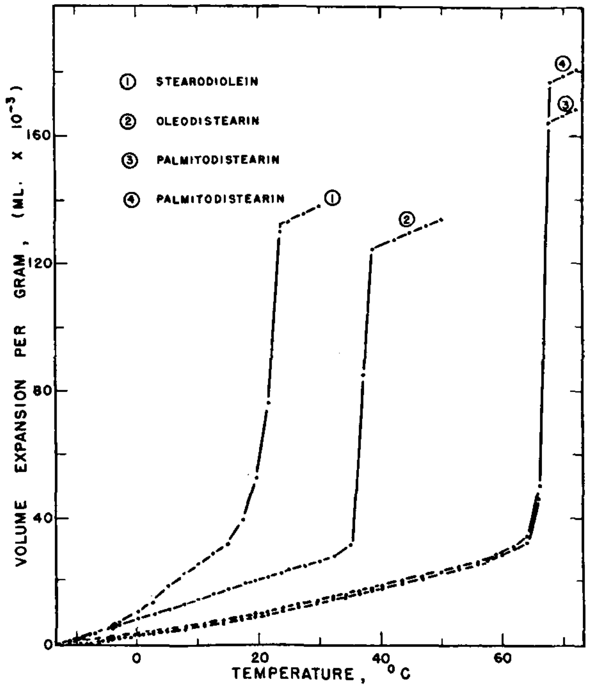

FIG. 5. Volume expansions of stearodiolein, oleodistearin, and palmitodistearin.

Figure 3 shows curves for the two saturated simple triglycerides. It should be pointed out that a slight and abrupt change of the slope occurs with all the saturated triglycerides during expansion of the solids. The reason for this change in slope is not known since presumably the triglycerides existed in their most stable polymorphic modification. Similar changes of slope are apparent in curves that have been published for saturated triglycerides by other investigators (3) and have been attributed to second order phase transformations.

Duplicate determinations for the tristearin gave melting dilations of 0.1512 and 0.1517 ml. per gram. Duplicate determinations on one sample of triolein, illustrated in Figure 4, gave melting dilations of 0.0585 and 0.0610. A third determination with another sample of triolein prepared in another laboratory gave a melting dilation of 0.0665.

Duplicate determinations of the melting dilations of the mixed triglycerides showed somewhat poorer agreement; values of 0.1526 and 0.1395 were obtained for stearodipalmitin. The results of two experiments with palmitodistearin, shown in Figure 5, gave values of 0.1360 and 0.1452.

In all cases duplicate values for the coefficients of expansion of the liquid and solid states, respectively, agreed very closely.

Table I summarizes the average values for the coefficients of expansion of the liquid and solid states and the melting dilations of the individual triglycerides. Two values are given for the coefficients of expansion of the solid saturated triglycerides because of the change in slope referred to earlier.

TABLE I

Melting Dilations and Coefficients of Expansion of Single Triglycerides

Triglyceride	Melting Dilation		Coefficient of Expansion			
			Solid State		Liquid State	
	Found	Reported	Found	Reported	Found	Reported[a]
	ml./gm.		*ml./gm./°C.*		*ml./gm./°C.*	
Triolein (a)	0.0597	0.0830	0.00071	0.00038	0.00093	
Triolein (b)	0.0665	0.0830	0.00100	0.00038	0.00099	
Stearodiolein	0.0905		0.00118		0.00105	
Oleodistearin	0.0925		0.00060		0.00092	
Oleodipalmitin	0.0965		0.00053		0.00091	
Palmitodistearin	0.1406		0.00032 0.00043		0.00093	
Stearodipalmitin	0.1460		0.00033 0.00047		0.00097	
Tristearin	0.1516	0.1671	0.00034 0.00044	0.00023	0.00095	0.00092
Tripalmitin	0.1621	0.1619	0.00031 0.00044	0.00022	0.00097	0.00092

[a] Values reported by Kraemer and Bailey (6).

The coefficients of expansion of the liquid state are very nearly the same for all of the triglycerides, but in the solid state the coefficients for the saturated triglycerides are appreciably lower than those for the triglycerides that contain oleic acid. The values for liquid tripalmitin and tristearin agree well with those reported by others (6), but the values for the solid state are considerably higher than previously reported.

The values for the melting dilations increase with increasing saturation of the triglycerides. Triolein has the lowest value and tristearin and tripalmitin the highest. The agreement with values found by others is reasonably good for the latter two compounds, but the values do not agree well in the case of triolein. The causes of these discrepancies are not known.

Volume Expansion of Triglyceride Mixtures

Figure 6 shows the dilatometric curves for two binary and one ternary mixture. Several points of interest are apparent from these curves. 1. In these three cases there are distinct phases that melt discretely, each containing a preponderance of one or another of the triglycerides in the mixture. 2. The triolein phase in these three mixtures has the same melting point as the pure triglyceride, i.e., about 4.8° C. 3. The melting points of the phases that contain mainly a saturated triglyceride are lowered 5° or more by the presence of triolein in the mixture. The melting ranges, of course, are lowered correspondingly on the temperature scale and are also broadened to some extent.

It is of interest to determine in these cases whether a constant solid-to-liquid ratio exists in those portions of the curves immediately following the complete melting of the triolein phase. Assuming a constant solid-to-liquid ratio, the theoretical expansion curves in this region were calculated for the two binary mixtures from the previously determined coefficients of expansion of the individual triglycerides and are represented by the dotted lines in Figure 6. If any decrease in the solid-to-liquid ratio had occurred in this region, that is, if any of the saturated triglycerides had liquefied, the observed expansion curves should have fallen above the theoretical curves. Since the reverse was true, it is likely that no appreciable liquefaction of the saturated triglycerides occurred in this region.

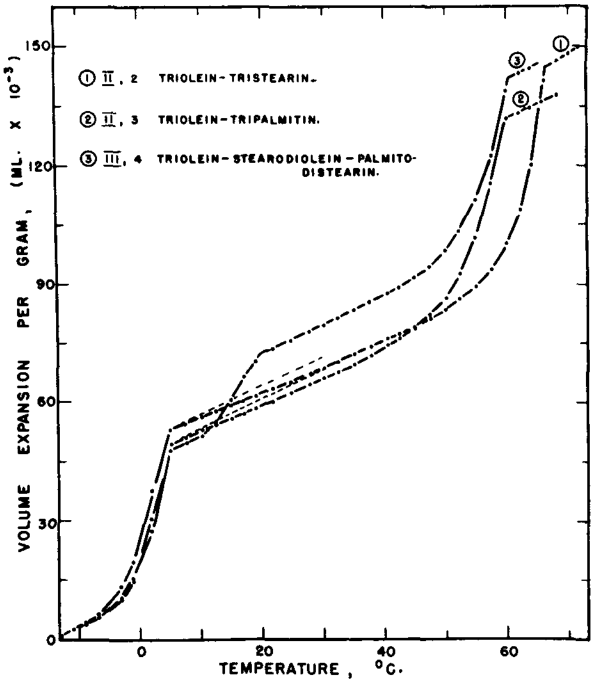

Fig. 6. Volume expansions of glyceride mixtures:
II, 2 triolein 66.5%; tristearin 33.5%.
II, 3 triolein 68.7%; tripalmitin 31.3%.
III, 4 triolein 57.4%; stearodiolein 25.2%; palmitodistearin 24.4%.

The observations that the actual curves fall below the theoretical curves and that the melting points of the saturated triglycerides are lowered in the presence of triolein indicate that there is probably some solution of triolein in the solid saturated triglycerides. On the other hand, the fact that the melting point of the triolein is not altered in these mixtures suggests that the saturated triglycerides do not form a solid solution in the triolein phase.

The proportion of the preponderant triglyceride in each discretely melting phase was further examined by means of simple calculations. First, it was assumed that the discretely melting phases consisted of single triglycerides. Then from the observed melting dilations in the discrete melting segments of these curves and from the known melting dilations of the pure individual triglycerides, a calculation of the triglyceride composition of the mixtures was made. In Table II the calculated compositions are compared with the known compositions of the three mixtures. In the two binary systems there is close agreement between the calculated and known values. Hence in these systems the assumption that the discretely melt-

TABLE II

Calculated and Actual Percentages of Glycerides in the Mixtures Shown in Figure 6

Glyceride Mixture	Glyceride	Percent Glyceride	
		Actual	Calculated
II, 2	Triolein Tristearin	66.5 33.5	64.5 34.1
II, 3	Triolein Tripalmitin	68.7 31.3	65.4 27.5
III, 2	Triolein Stearodiolein Palmitodistearin	50.4 25.2 24.4	57.4 18.2 27.9

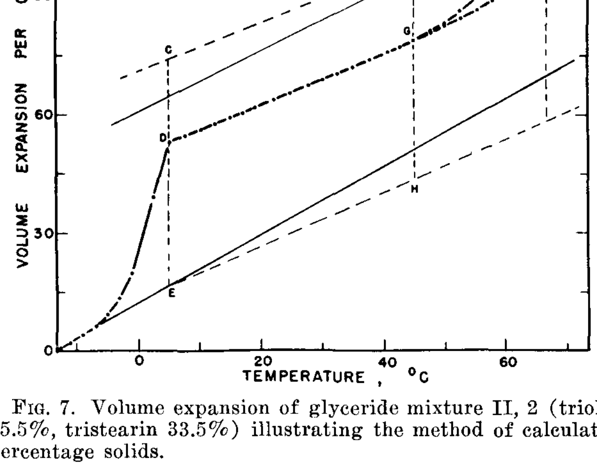

Fig. 7. Volume expansion of glyceride mixture II, 2 (triolein 65.5%, tristearin 33.5%) illustrating the method of calculating percentage solids.

ing phases consisted of single triglycerides was very nearly correct. In the ternary system there was less agreement between calculated and observed values, and therefore even though there are three discrete melting segments in the curve, the discretely melting phases must contain appreciable proportions of other triglycerides in addition to those that are preponderant.

For simple mixtures in which the melting of several phases occurs discretely and where the identity and melting dilations of the preponderant triglycerides in those phases are known, it is possible to determine with a fair degree of accuracy the solid-to-liquid ratio in some regions of the curves. The procedure is illustrated in Figure 7 for the binary system containing triolein and tristearin. The method is similar to one recently suggested by Bailey (1).

The method will be described only briefly. Section B in Figure 7 is an adjusted curve, obtained by multiplying the observed melting dilation in this temperature region by the ratio of the melting dilations of pure triolein, and pure tristearin. The effect of this adjustment is to make the melting dilations of triolein and tristearin equal and thus facilitate the calculation of the solid-to-liquid ratio. The line for the completely solid system is then extended, and from the point E corresponding to the melting point of triolein a line is drawn parallel to segment DG. Similarly from a point on the adjusted curve, representing the temperature at which the system becomes completely liquid, another line is drawn parallel to line DG. The ratio of the segments CD to DE, or FG to GH then represents the solid-to-liquid ratio in the temperature range of DG.

It is apparent that calculations of the solid-to-liquid ratio will be reasonably accurate only in mixtures that contain discretely melting phases and where the phases consist predominantly of single triglycerides.

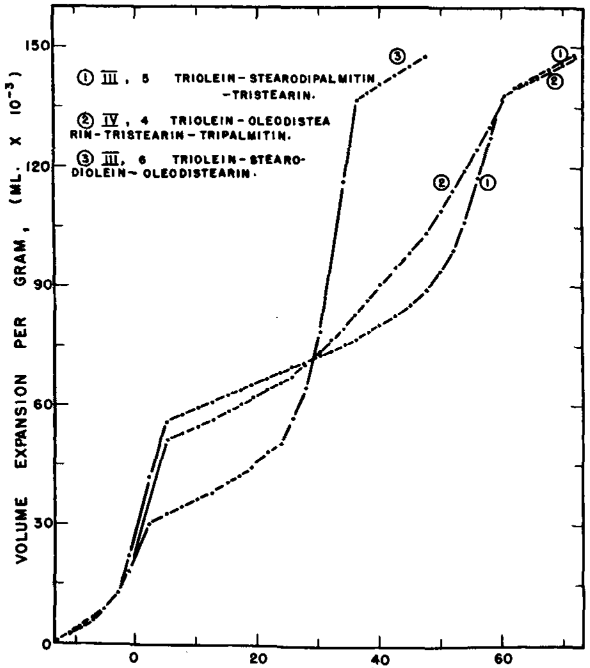

FIG. 8. Volume expansions of glyceride mixtures:
III, 5 triolein 65.0%; stearodipalmitin 17.1%; tristearin 17.9%.
IV, 4 triolein 60.4%; oleodistearin 20.2%; tristearin 10.2%; tripalmitin 9.2%.
III, 6 triolein 33.3%; stearodiolein 33.3%; oleodistearin 33.4%.

Figure 8 contains dilatometric curves for two other systems with three components and a system with four components. In these cases, partly because the melting ranges of individual triglycerides have been extended by the presence of small amounts of other triglycerides in the same phase, the melting ranges overlap and triolein is the only discretely melting phase that is evident. It is also noteworthy in these cases that the melting point of the triolein is not appreciably affected by the other triglycerides in the mixture.

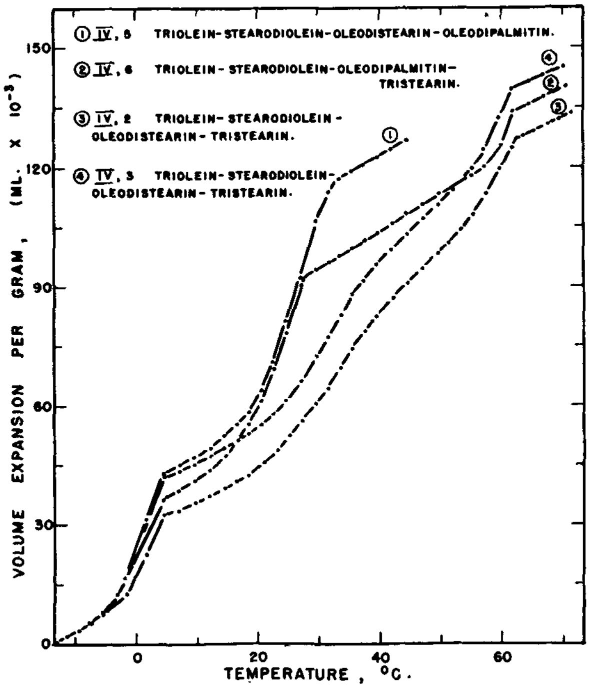

FIG. 9. Volume expansions of glyceride mixtures:
IV, 5 triolein 40.4%; stearodiolein 20.2%; oleodistearin 20.3%; oleodipalmitin 19.1%.
IV, 6 triolein 47.2%; stearodiolein 20.2%; oleodipalmitin 19.0%; tristearin 13.6%.
IV, 2 triolein 38.5%; stearodiolein 23.0%; oleodistearin 23.0%; tristearin 15.5%.
IV, 3 triolein 46.6%; stearodiolein 20.0%; oleodistearin 20.0%; tristearin 13.4%.

Figure 9 represents additional systems with four components. The observations made in connection with Figure 8 apply here also. Curves 3 and 4 in this figure represent systems containing the same four triglycerides but in different proportions. The two curves are similar in shape, but the melting point of the tristearin phase in curve 3, representing a system containing 8% less triolein, is slightly higher than in curve 4. In both cases, of course, the melting point is lower than that of pure tristearin, as was observed in the binary systems.

Figure 10 shows curves for systems with four and eight components and also a curve for a commercial hydrogenated vegetable shortening. In the first two cases the melting point of the triolein phase appears to have been affected by the presence of the other components. No identifiable discreet melting dilations appear in the curve for the commercial shortening although there are changes in slope in portions of the curve.

On the basis of solid-to-liquid ratio calculations in relatively simple systems where the different melting

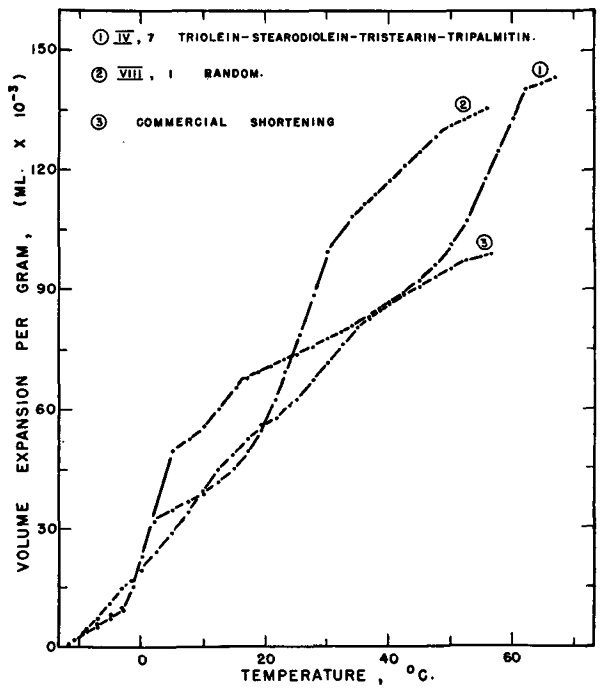

FIG. 10. Volume expansions of glyceride mixtures IV, 7; VIII, 1; and a commercial shortening:
IV, 7 triolein 54.0%; stearodiolein 20.2%; tristearin 13.6%; tripalmitin 12.2%.
VIII, 1 triolein 38.4%; stearodiolein 29.1%; oleodistearin 14.4%; oleodipalmitin 13.5%; palmitodistearin 1.7%; stearodipalmitin 1.7%; tristearin 0.6%; tripalmitin 0.6%.

dilations of the individual triglycerides are known, and on the basis of our observations that in more complex systems the melting ranges are extended, and except in the simplest systems, overlap, we concur in Bailey's conclusion (1) that the calculation of solid-to-liquid ratios from the dilatometric curves of natural fats is not possible with any degree of accuracy unless information from other types of measurements is available.

Summary

The melting dilations and the coefficients of expansion of the solid and liquid states have been reported for five symmetrical mixed triglycerides and three simple triglycerides. The melting dilations were found to decrease with increasing proportions of oleic acid in the triglyceride molecule. In some simple mixtures the melting dilations of the several phases were found to occur discretely, but in the more complex systems there was an extension and overlapping of the melting ranges. In the mixtures of triolein with more saturated triglycerides, the melting point of triolein was found to be generally unaffected, but the melting points of the more saturated glycerides were lowered by the presence of triolein. Calculations of the solid-to-liquid ratios from dilatometric data were found to be impossible in the more complex mixtures due to wide variations in the melting dilations of the several phases and to the overlapping of their melting ranges. Approximate calculations of solid-to-liquid ratios in simple systems in which melting dilations occur discretely can be accomplished if the melting dilations of the individual triglycerides are known.

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Sweetwater Deionization on a Plant Scale[1]

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THE ion exchange phenomena and the basic process have been described in innumerable publications and have been thoroughly discussed at various meetings similar to this over the last decade. The process itself has been applied to water and many other purifications, of which one of the most recent and novel is the treatment of glycerol sweetwaters and crude glycerols.

Kahler (1) described the purification of crude glycerol by ion exchange, and recently Caskey (2) delivered a general treatise covering ion exchange purification of various impure glycerols. Reents and Stromquist (3) lately published a more detailed study of treatment of crude glycerols and glycerol sweetwaters by ion exchange to produce a C.P. product. There are other articles in the literature regarding glycerol purification, but none of them concerned the production of C.P. or U.S.P. glycerol by ion exchange and evaporation. All previous work on the ion-exchanging of glycerols to produce a C.P. product necessitated distillation as a final measure. The production of a chemically pure glycerol by ion exchange and evaporation with the subsequent elimination of distillation has led several firms to purchase and install large scale equipment for the treatment of both glycerol sweetwaters and crude glycerols. The Archer-Daniels-Midland Company plant at Wyandotte, Michigan, treating glycerol sweetwaters obtained by hydrolysis, has been in successful operation for over a year, the operation of which will be discussed in a later portion of this paper. A similar installation on the west coast has been in operation for several months. A soap lye crude ion exchange purification unit has been operating successfully over a period of a few months. This is also located on the west coast, and a discussion of the characteristics of this unit will be presented at this meeting by a member of the company concerned.

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[1] Presented at the 25th Annual Fall Meeting, American Oil Chemists' Society, Chicago, Ill., Oct. 8-11, 1951.