# Dilatometric Investigations of Fats

# II. Dilatometric Behavior of Some Plastic Fats Between O° C. and Their Melting Points[1]

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IN a previous communication (1) methods were described for the dilatometric examination of fats, which yield data from which curves may be constructed representing the volume of the fats as a function of temperature. These methods have been applied to obtain dilatometric curves for a number of fats, between 0°C. and their melting points. The curves are reproduced in Figures 1 to 6, inclusive. Some of the fats, including the all-hydrogenated shortening (Spry), the margarine oil (Nucoa), and the three samples of hydrogenated soybean oil, had previously been examined (2) by the micropenetration method.

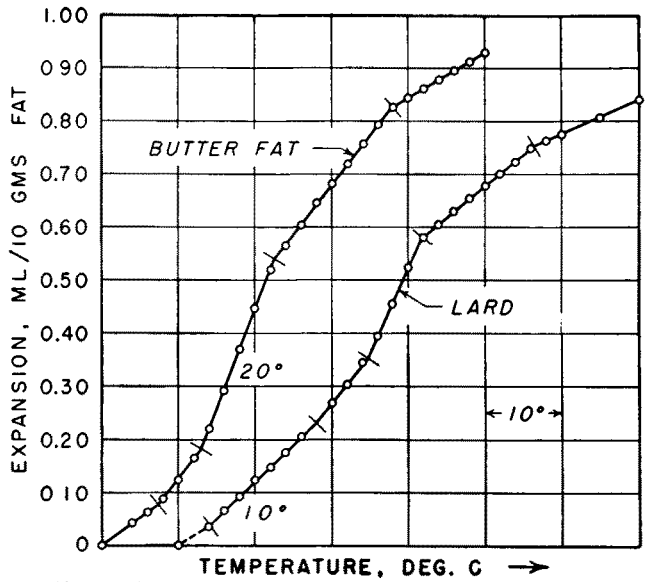


FIG. 1. Dilatometric curves, butter fat and lard, rapidly solidified.

All of the fats were plastic within the above-mentioned range of temperature, i.e. they consisted of a mixture of solid and liquid glycerides. The dilatometers employed were in all cases of the volumetric type, with water being used as the confining liquid.

### Relation Between the Dilatometric Curves and the Consistency of Fats

Since the consistency of a fat is determined by its relative proportions of solid and liquid glycerides, the dilatometric curve of a fat will obviously furnish an indication of the body characteristics of the fat. A steep curve is characteristic of fats with a narrow plastic range, whereas fats with an extended plastic range yield dilatometric curves with relatively low slopes. On the basis of characteristics of their dilatometric curves, certain of the fats examined may be ranked in the following order with respect to length of plastic range: (a) hard "butter" from peanut oil, (b) butter fat, (c) margarine oil, (d) lard, (e) vegetable oil shortening, and (f) mixture of tristearin and soybean oil.

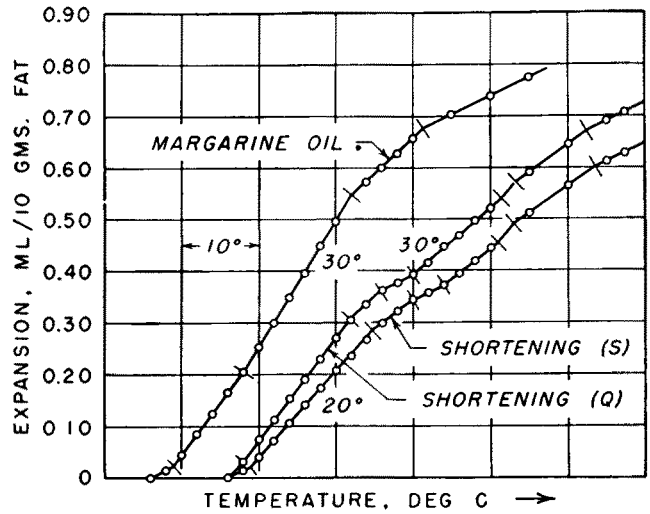


FIG. 2. Dilatometric curves, margarine oil, slowly solidified; and all-hydrogenated shortening, (S) slowly solidified and (Q) rapidly solidified.

### Relation Between the Dilatometer Curves and the Glyceride Composition of the Fats

IT was observed by Hofgaard (3) that dilatometric curves of fats, particularly in the upper temperature ranges, are often composed of a series of linear sections, with abrupt inflections or transition points occurring between the sections. The present results amply confirm Hofgaard's observations, and indeed suggest that dilatometer curves of plastic fats may be made up of linear sections throughout. An appearance of non-linearity in some dilatometric curves is the result of the presence of so many linear sections that the latter are not clearly indicated by a limited number of experimentally determined points. It may be mentioned, for example, that Hofgaard observed but one linear section, immediately below the melting point, in his curves for butterfat, whereas experiments (Figure 1) reported here clearly reveal the presence of four linear sections between 0°C. and the melting point of 37.7°C., with transition points at 7.5°, 13.0°, and 22.5°C.

Speculation upon the precise significance of the linear sections and transition points appears premature; however, as pointed out by Hofgaard, the conclusion can hardly be escaped that each transition point represents the disappearance of a different class of solid glycerides or glyceride complexes. It is to be particularly noted that the complexity of the dilatometric curves increases in accordance with the

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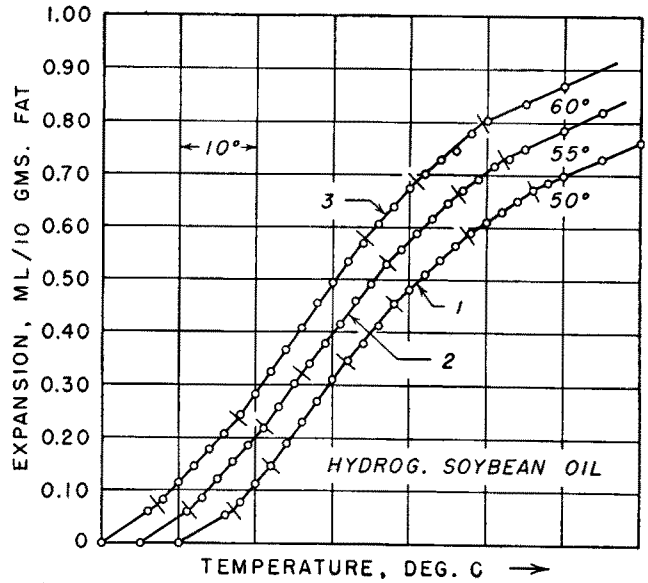


FIG. 3. Dilatometric curves, soybean oil hydrogenated to different degrees: (1) I. V. = 80.1; (2) I. V. = 74.4; (3) I. V. = 69.6. (All samples rapidly solidified.)

known degree of heterogeneity of the glyceride mixture in the fat. The simplest mixture of those examined is undoubtedly that occurring in the synthetic fat prepared from oleic and stearic acids, the dilatometric curve of which is shown in Figure 5. This fat was prepared by the co-esterification of equal molar proportions of the two acids, employing an excess of fatty acids over glycerol, to avoid the formation of mono- and diglycerides, hence its composition, in terms of mol percentages, was theoretically as follows: tristearin, 12.5 percent; distearo-olein, 37.5 percent; dioleostearin, 37.5 percent; and triolein, 12.5 percent.

A plot of dilatometric data for this fat yielded a curve above 0°C. composed of but two sections, with a transition point at about 46°C., and the melting point at about 56°C.

Also undoubtedly of simple composition was the artificial hard butter represented in Figure 4, which was prepared by fractionally crystallizing highly hydrogenated peanut oil (4). A plot of similar dilatometric data for this fat produced a curve having three linear sections above 0°C. (Figure 4). Transitions in the curve appear at 12.7°, 23.7°, and 36.0°C. in the case of the quickly chilled sample, and at 12.7°, 25.7°, and 35.7°C. in the case of the slowly chilled sample. With this fat, as with most of the others, the melting point is indicated quite precisely by the dilatometer curves. Lard, which might logically be expected to be simpler in composition than hydrogenated vegetable oils, yields a curve (Figure 1) with four linear sections above 0°C., the transitions being at 4°, or below, and at approximately 18°, 24.5°, 31.5°, and 46.5°C.

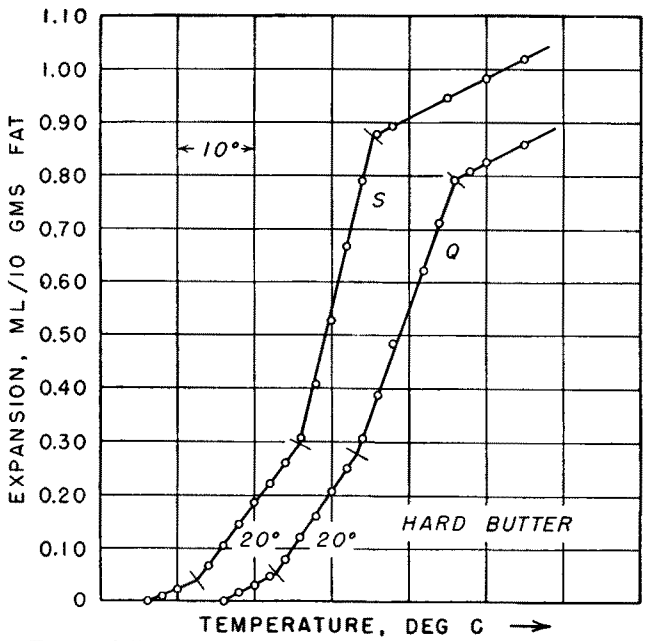


FIG. 4. Dilatometric curves, artificial hard butter from peanut oil; (S) slowly solidified and (Q) rapidly solidified.

For the most part the hydrogenated vegetable oil products are evidently more complex. The margarine oil (Figure 2), which appears to consist of a single "all-hydrogenated" vegetable oil, yields a curve of four sections, with breaks between 8° and 10°, at 18°, at 32°, and at 41.5°. At least six sections can be distinguished in the case of the curves obtained with the hydrogenated soybean oils (Figure 3), with transition and melting points occurring approximately as shown in Table 1.

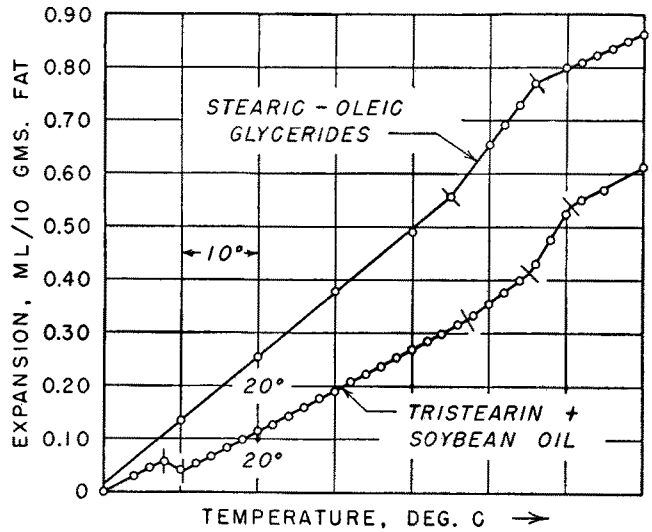


FIG. 5. Dilatometric curves, 10 percent tristearin plus 90 percent soybean oil (rapidly solidified); and synthetic fat prepared by co-esterification of equal molar proportions of oleic and stearic acids (slowly solidified).

TABLE 1

Transition and Melting Points From Dilatometric Curves for Hydrogenated Soybean Oil.

| Sample No. | Iodine value | Transition points, °C. | | | | | Melting point, °C. |
|---|---|---|---|---|---|---|---|
| 1 | 80.1 | 6.7 | 11.6 | 21.0 | 28.0 | 37.5 | 46.5 |
| 2 | 74.4 | 6.3 | 14.0 | 21.0 | 32.0 | 41.0 | 47.0 |
| 3 | 69.6 | 5.5 | 17.5 | ..... | 34.0 | 41.5 | 49.0 |

In the series of oils shown in Table 1 the transition point at 21.0°, which is poorly defined in the first sample, became even more indistinct in the second sample, and disappeared altogether in the third sample.

The all-hydrogenated vegetable oil shortening, which was probably made by blending two stocks hydrogenated to different degrees, yielded a dilatometric curve (Figure 2) composed of at least seven sections. In the case of the slowly solidified sample,

there were transition points at approximately 9°, 25°, 30°, 34°, 42°, and 44°C. and complete melting at 53°C.

The mixture of 10 percent tristearin and 90 percent soybean oil (Figure 5) contained but a single high melting glyceride, yet in this fat transition points were observed at 47.3° and 55.3°, as well as at 60.5°C. Obviously at least a portion of the tristearin had formed high melting mixed crystals with glycerides in the soybean oil. The irregularity in the curve at 8° to 10°C., appears to be due to a polymorphic transformation.

It is interesting to note that calorimetric investigations carried out in this laboratory (5) also reveal the apparent tendency of fats to undergo melting in a series of successive phases in each of which the amount of melting is linear with temperature. The heat content of a sample of cottonseed oil is plotted as a function of temperature in Figure 7. The curve

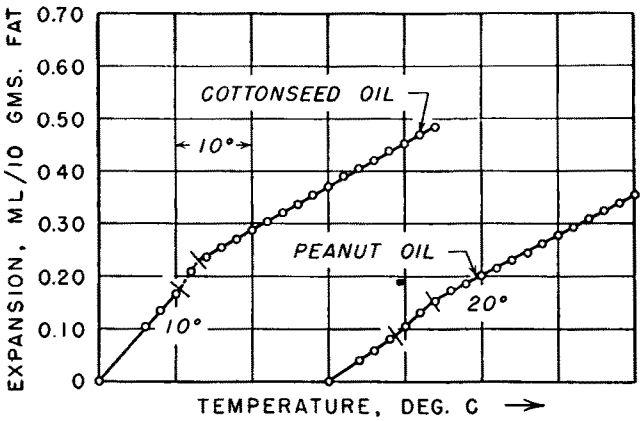


FIG. 6. Dilatometric curves, cottonseed and peanut oils, rapidly solidified.

of this figure is analogous to the dilatometric curves, with melting of the sample being indicated by the absorption of heat rather than dilation. In this case, the complete melting of the sample is indicated, inasmuch as the latter was completely solid at the lowest temperature. Transition points are to be seen at approximately 225°K.(—48°C.), 252°K.(—21°C.), 269°K.(—4°C.), 281°K.(8°C.), and 286°K.(13°C.). The dilatometric curve of cottonseed oil (Figure 6) shows only the three highest sections of the curve, but is consistent with the calorimetric curve insofar as these sections are concerned.

It is to be hoped that the dilatometric method may be developed to eventually produce both qualitative and quantitative information concerning the glyceride composition of fats and oils. The first step in further elaboration of the method would logically involve the examination of simple mixtures of synthetic glycerides of known constitution, at temperatures down to their points of complete solidification.

### Polymorphism in the Fats Examined

In most cases the fats of the present series were not polymorphous, even though they were in most instances solidified quite rapidly by plunging the dilatometer containing the molten sample into ice water. Two fats (Figures 2 and 4) were tested after both rapid and very slow solidification. The two methods of solidification yielded curves of essentially similar form.

The rapidly chilled mixture of tristearin and soybean oil apparently underwent a polymorphic change

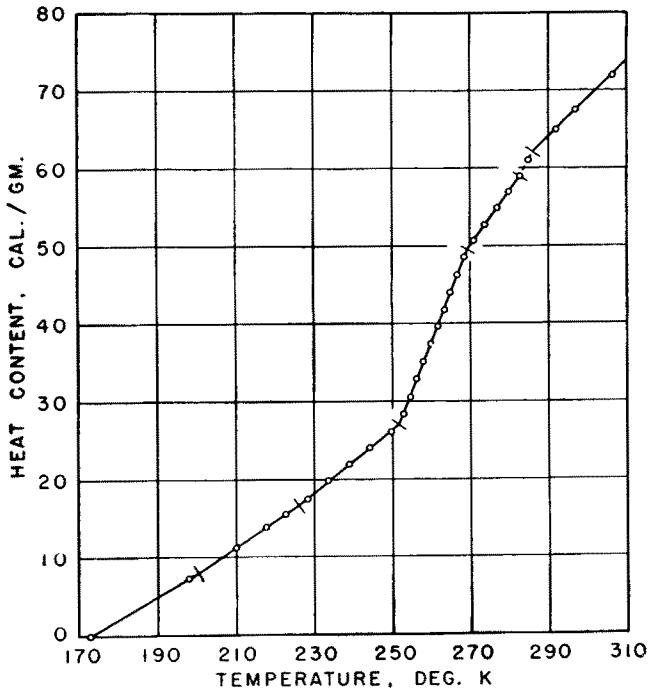


FIG. 7. Heat content vs. temperature of cottonseed oil.

at 10°C. In a test of the synthetic stearic-oleic glyceride mixture after rapid solidification (not shown in the figures) pronounced polymorphic transformations occurred at 48° to 52°C.

### Summary

1. Dilatometric curves between 0°C. and their melting points have been obtained for the following fats: lard, butterfat, cottonseed oil, peanut oil, a commercial margarine oil, a commercial all-hydrogenated vegetable shortening, three samples of soybean oil hydrogenated to different degrees, a hard butter fractionally crystallized from hydrogenated peanut oil, a mixture of tristearin and soybean oil, and a synthetic fat containing equal molar proportions of stearic and oleic acids.

2. The dilatometric curves, of volume change in the fat against temperature, were in every case composed of a series of straight lines, separated by sharp breaks or transition points.

3. The number of linear sections in the dilatometric curves corresponded in a general way with the known degree of complexity in the glycerides of the fats, and varied from two in the case of the relatively simple stearic-oleic glyceride mixture, to at least seven in the case of the all-hydrogenated shortening. Since each break in the curve must correspond to the disappearance of a distinct class of solid glycerides or glyceride complexes, the application of dilatometry to the qualitative and quantitative determination of glyceride composition in fats is suggested.

4. Only two of the fats examined, the mixture of tristearin and soybean oil, and the synthetic stearic-oleic glyceride mixture, exhibited polymorphism, even after rapid solidification in ice water.

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