Dilatometric Investigations of Fats

II. Dilatometric Behavior of Some Plastic Fats Between 0°C. and Their Melting Points

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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.

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

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...
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°C, 23.7°C, and 36.0°C, in the case of the quickly chilled sample, and at 12.7°C, 25.7°C, 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°C, or below, and at approximately 15°C, 24.5°C, 31.5°C, and 46.5°C.

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°C and 10°C, at 18°C, at 32°C, and at 41.5°C. 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.

In the series of oils shown in Table 1 the transition point at 21.0°C, 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,