Differential Thermal Analysis of Fats. I. Principle, Apparatus, and Procedure

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IN STUDYING the melting behavior of a fat, frequently the whole melting range is of interest. A review of dilatometric, calorimetric, and thermal methods for this purpose is given by Bailey (2).

In this article another method, *viz.*, the differential thermal analysis method (DTA), is suggested for the determination of melting curves. Although this method has been known for a long time in other fields (1), it was not applied to the investigation of fats until some of our laboratories started to use it a few years ago. The dynamic character of the DTA method has disadvantages in a quantitative sense, but, on the other hand, the conditions more closely resemble those obtained in practice. A great advantage is that analysis can be carried out directly with margarine, butter, soap, chocolate, etc., without destroying the original material.

Principle

A fat sample is placed in a copper block, which is heated at a constant rate, starting from a temperature at which the fat is solid. On melting, the temperature of the fat will be below that of the surroundings. Before and after melting, the difference in temperature between fat and surroundings has a constant value. Exothermic heat effects caused by polymorphic transitions during melting are also shown in the registered melting curves; the latter are more or less characteristic for a given fat. Some of these curves will be discussed in detail in II and III of this series.

The copper measuring block, placed in a Dewar vessel (Figures 2-3) is heated at a constant rate, which was found to be most favorable at 1–3°C./min. To adapt the reading of the recorder chart to the heating rate, the latter was chosen at 1.80 ± 0.03°C./min. since in that case one scale unit of the time coordinate corresponded with 2°C. In order to achieve a constant heating rate a resistance was used which decreased at 0.05 Ω/min. The resistance was wound on a drum driven by a slow-speed motor (¼ to 1 r.p.h.). The thermocouples used (Figure 4) are rigid and solid and consist of iron constantan wires (Honeywell Brown Type 9B 3N4). They are inserted into a narrow iron tube and are of identical construction and size, both for reference- and test-couples. The constantan wires are connected outside the calorimeter. The recorder calibration is performed by deriving a known voltage *via* shunts from a Weston cell (inset A in Figure 1). By means of the permanent resistances R_3–R_6, voltages can be obtained to correspond with differences in temperature of 5, 2, and 1°C. between the two couples. For oils and fats with wide melting ranges the calibration of 1°C. for full-scale deflection of the recorder is generally used, for samples with narrower melting ranges either 2 or 5°C.

Apparatus (Figure 1)

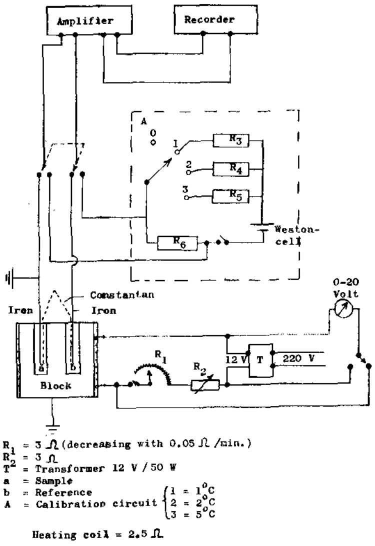

FIG. 1. Wiring diagram for D.T.A. apparatus.

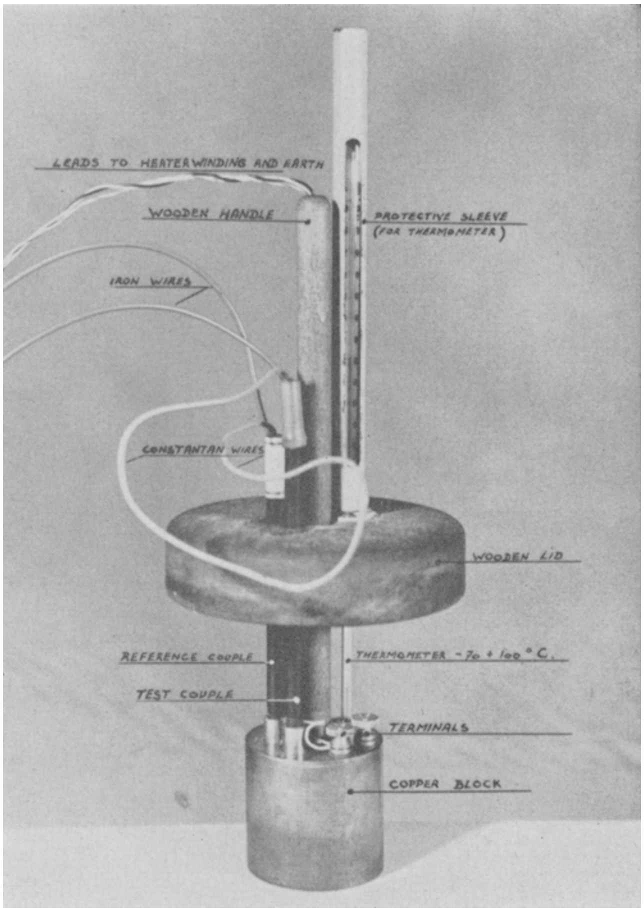

FIG. 2. Copper block with thermocouples and thermometer.

The sample holder is made of the same material as the block. Care should be taken that both the internal and external bottom of the sample holder and the cavity into which it is placed are flat.

The reference tube, having the same dimensions as the sample holder, is filled with an inert liquid which should neither solidify nor boil between —70 and +100°C. Dioctylphthalate (DOP) satisfies these con-

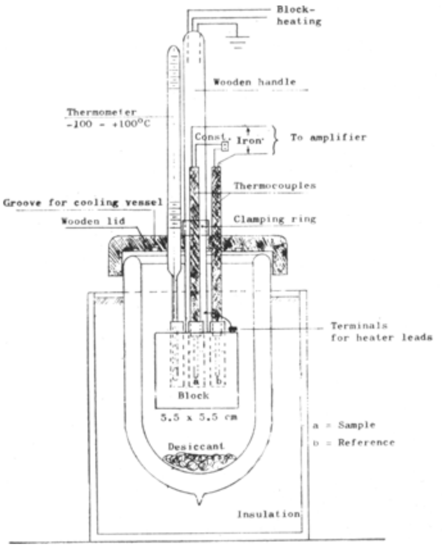

FIG. 3. Copper block with Dewar vessel.

ditions. The amount of DOP in the tube influences the course of the base line, thus enabling slight corrections to be made.

The recording unit consists of a recorder (Honeywell Brown, variable span 1–50 mV) and an amplifier (W. G. Pye-Cambridge D. C., 1–1000 μV). The latter serves to cause a sufficient deflection of the recorder. When working at the highest sensitivity, a full-scale deflection of the needle corresponds with 0.1°C. Normally sensitivities from 1–10°C. are used.

There is no fully linear relationship between the temperature and the EMF of the thermocouples. Calibration curves have been plotted, but in practice this irregularity was generally neglected. The position of the temperature axis of a minimum in the curve is far more important than its precise depth. Correction factors for the conversion of △T of a certain pair of thermocouples to a standard temperature can be derived from tables issued by the manufacturers of couple-wires.

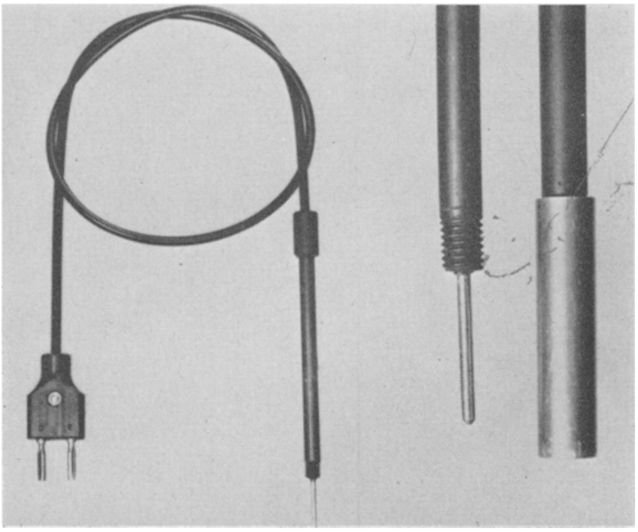

FIG. 4. Thermocouple: left—couple with Bowden cable and plug; middle—couple; and right—couple screwed in the sample holder.

Procedure

Prior to the actual determination of the melting curve, the copper block with sample and also the Dewar vessel have to be cooled to at least 20°C. below the starting temperature of the curve. Pre-cooling of the copper block is performed by putting it in a hollow cylinder (placed on a prop) in an insulated cooling vessel. After having been cooled, the block is rapidly transferred to the cold Dewar vessel.

The Melting Curve of a Pure Substance

In Figure 5 the melting of ice is schematically represented. The copper block is heated at a constant rate of 2°C./min, from —20° to +20°C. The thermocouple (B) is placed at a distance of 2 mm. from the wall of the sample holder (A). From experiments it appeared that, on heating the block from —8° to 0°C., there is a constant temperature gradient between A and B (△T = —2°C.). At further heating from 0° to 7.6°C. the ice melts gradually. In this range △T is not constant but increases with the increasing wall temperature. At a wall temperature of 7.6°C. (A) the temperature at B is 0°C. (melting is completed), and the temperature gradient has reached its maximum value. From a wall temperature of 7.6° to 10°C. onward the temperature gradient decreases until a constant value is obtained.[1] The constant gradient will be steeper in water (xy) than in ice (pq) because of the higher specific heat and the lower heat conductivity of water as compared with ice. When T_A is plotted against △T, the melting curve is obtained. The characteristic points of Figure 5 can be readily recognized in Figure 6a ($\triangle T_L > \triangle T_S$).

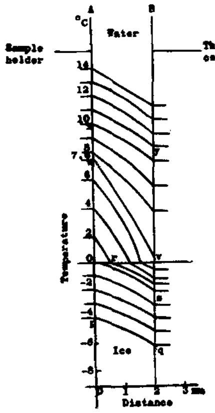

FIG. 5. Temperature gradients in ice.

Figure 6b shows a melting curve of water, which was determined in practice. The absolute values of $\triangle T_S$ and $\triangle T_L$ of Figure 5 are unknown. The dotted line through *s* and *y*, called the "base line," is usually drawn by free hand. In practice however the base line is projected on the abscissa, which is demonstrated in Figure 6c, where the distance between the curve and the base line at a given block temperature T_A (*m* or *n* in Figure 6b) is transferred at corresponding temperatures (m′ or n′), after which the new curve can be drawn (m = m′ or n = n′).

It appears from Figure 6a that, at the melting point of pure substance (*i.e.,* at 0°C.), the curve will

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[1] The importance of a low heat capacity of the thermocouple is clear because then the line *vy* (Figure 6c) would be steeper.

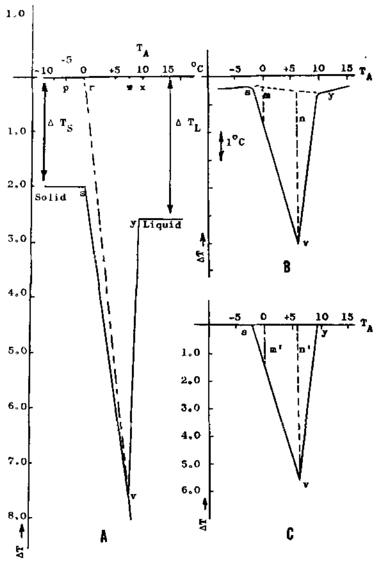

FIG. 6a. Course of the temperature on plotting the melting curve of ice.

FIG. 6b. Same from direct experiment.

FIG. 6c. Same base line transposed on horizontal.

leave the base line. In Figures 6b, 6c however this takes place at −2°C., which is caused by melting-point depression, etc.

It is therefore better to start from point *v*, at which the thermocouple has the temperature of the melting point. This temperature is then found by subtraction of the absolute value of △T at that point from the temperature on the abscissa (block temperature).

In Figure 6c point *v* lies on the abscissa at 5.6°C., △T is here also 5.6°C. Actual melting point = 5.6–5.6 = 0°C.

Melting Curves of Fats

Figure 7 is an example of the DTA curve of a margarine fat mixture with a melting range between −20° and +32°C. The mixture was well tempered and stable so that the maximum at 16°C. was not caused by exothermic transitions but by a "melting-gap" between two groups of glycerides.

The melting of palm oil (Figure 8a) is more complicated. Here the base line deviates more from a horizontal line which may be caused by differences in the thermocouple-pair or by irregularities in the fat mass because of quick cooling from +60° to −70°C. (*e.g.*, the air space, which occurs between the wall of the sample holder and fat on cooling, disappears on melting). Transposing the base line onto a horizontal line so that p = p', q = q', etc., as shown in Figure 8b, is more illustrative. Melting of the palm oil starts at −32°C. At b' (and possibly at a') there is an exothermic transition from a metastable to a more stable configuration.

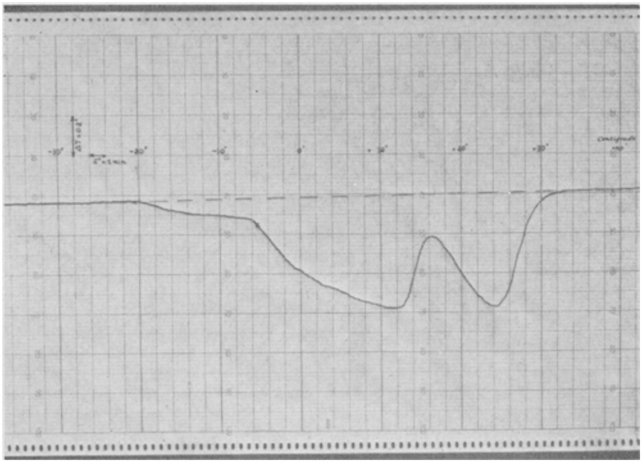

FIG. 7. Melting curve of a margarine fat, starting at −20°C. up to +32°C. (heating rate 2°C./min.)

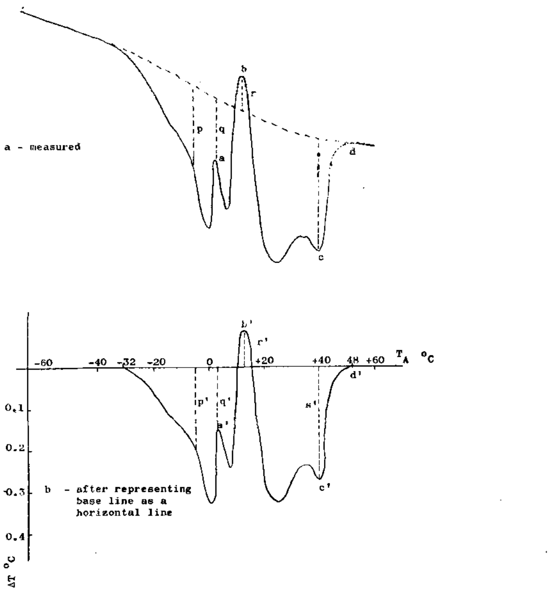

FIG. 8. Melting curve of palm oil (nonstabilized).

Figure 9 shows the DTA curves of fully hardened peanut oil. The polymorphic forms, as identified by X-ray analysis, are given in the figure. On rapidly cooling the α-form is obtained; after melting of the α-form, an instantaneous transition to the β'-form at 58°C. takes place. The β-form occurs on prolonged tempering at 65°C. By judicious tempering, the three forms can be shown simultaneously in one curve (Figure 9c).

Summary

The differential thermal method is particularly suitable for investigating the melting and polymorphic properties of fats. An apparatus for regis-

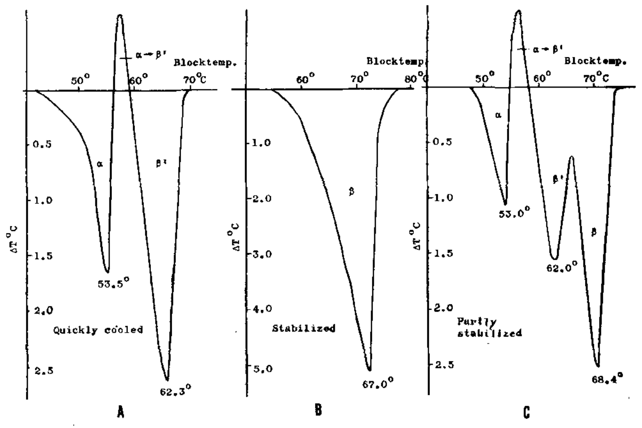

FIG. 9. Melting curves of fully hardened peanut oil.

tering differential thermal analysis curves is described. In addition, examples of melting curves of water and of some fats are given.

Acknowledgment

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Reactions of Unsaturated Fatty Alcohols. V. Preparation and Properties of Some Copolymers of Unsaturated Fatty Vinyl Ethers with Lower Alkyl Vinyl Ethers[1]

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IN PREVIOUS PUBLICATIONS (6, 7) we have described the preparation, polymerization, and polymer film properties of soybean and linseed vinyl ethers. The fatty vinyl ethers were prepared from the corresponding alcohols, using acetylene and an alkaline catalyst at atmospheric pressure. Polymerization of the vinyl ethers was accomplished by using the Lewis-acid type of catalysts and a flash technique at temperatures down to —30°C. in solvents. Polymers of highest molecular weight were obtained at —30°C. in methylene chloride, using boron trifluoride-etherate catalyst.

Baked films of these polymers containing metallic driers showed promise as protective-coating materials although improvement of their properties was indicated in two areas: (a) retarding oxidative degradation of the films, and (b) preventing the wrinkling and what appears to be "gas-checking," as manifested by tung oil, or dried films more than 2 mils thick. Oxidative degradation of fatty vinyl ether polymer films, which was especially pronounced when cobalt drier was used, led to the formation of free acids and esters that resulted in poor alkali resistance. Stability to alkali was improved by suitable formulation, for example, by adding antioxidants or by using driers other than cobalt. Properly prepared films resisted 5% alkali for over 24 hrs.

It was believed that modification of fatty vinyl ethers by copolymerization with other vinyl ether monomers would improve alkali resistance and other properties of films from the polymers. This paper describes the preparation and properties of copolymers of unsaturated fatty vinyl ethers with several lower alkyl vinyl ethers and reports the results from a study of the effects of structure on the oxidative stability and wrinkling of copolymer films.

Preparation and Properties of Copolymers

Starting Materials. Soybean vinyl ether was prepared from a commercial sample of the fatty alcohol (Unadol 40, Archer-Daniels-Midland Company[2]), using acetylene at atmospheric pressure (7). The product analyzed as follows: vinyl ether, 94.5%; conjugated diene, 32.2%; conjugated triene, 1.3%; soybean alcohol, 3.8%.

Ethyl, butyl, isobutyl, 2-ethylhexyl, and 2-chloroethyl vinyl ethers were obtained from commercial sources and used as received. 2-Methoxyethyl vinyl ether was distilled before use to improve the color.

Nopol vinyl ether was prepared from nopol (obtained from Dow Chemical Company) by a modification of a transvinylation technique (8) as follows: 83 g. (0.5 mole) of nopol, 500 g. (5 moles) of n-butyl vinyl ether, and 5.1 g. (0.016 mole) of mercuric acetate were mixed in a round-bottom flask and refluxed for 10 hrs. Analysis for vinyl ether content by an iodometric method (7) showed that the mixture contained 80.4% Nopol vinyl ether. Potassium carbonate, 4.4 g. (0.032 mole), was added to neutralize the catalyst, and the butyl vinyl ether was distilled off to yield a dark residue. Distillation of the residue gave 64 g. of a water-white distillate (88.4% vinyl ether), which was purified further by stirring with sodium ribbon for 4 hrs. at room temperature. The final product was 97.5% vinyl ether.

Anal. Calcd.: C, 81.2; H, 10.48
Found: C, 80.6; H, 10.47

Polymerization Procedure. A typical copolymerization was carried out in the following manner. A mixture of lower alkyl vinyl ether and soybean vinyl ether (10 to 15 g. total charge) was dissolved in 50 ml.

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[1] Presented at the fall meeting, American Oil Chemists' Society, Cincinnati, O., September 30–October 2, 1957.

[2] Since the Department of Agriculture does not recommend the products of one company over those of another, the names are furnished for information only.