REFERENCES

1. Baer, E., and Fischer, H. O. L., J. Biol. Chem., *128*, 475–489 (1939).
2. Bates, F. J., "Polarimetry, Saccharimetry, and the Sugars," Circ. C440, Natl. Bur. Standards, p. 174, Washington, D. C., U. S. Government Printing Office, 1942.
3. Doerschuk, A. P., J. Am. Chem. Soc., *74*, 4202–4203 (1952).
4. Kent-Jones, D. W., and Amos, A. J., "Modern Cereal Chemistry,"

5th ed., p. 301, Liverpool, England, The Northern Publishing Company, 1957.
5. Mehltretter, C. L., Alexander, B. H., Mellies, R. L., and Rist, C. E., J. Am. Chem. Soc., *73*, 2424–2427 (1951).
6. Ofelt, C. W. Mehltretter, C. L., MacMasters, M. M., Otey, F. H., and Senti, F. R., Cereal Chem., *35(2)*, 142–145 (1958).
7. Ralston, A. W., and Selby, W. M., J. Am. Chem. Soc., *61*, 1019–1020 (1939).

Differential Thermal Analysis. III. Melting Curves of Oils and Fats

J. HANNEWIJK and A. J. HAIGHTON, Unilever Research Laboratory, Vlaardingen, The Netherlands

IN THE FIRST PART of this series (1) the principle, apparatus, and procedure of the differential thermal method for the analysis of fats are described. In addition, examples of melting curves of water and of some fats are included. In the second part (2) a description of melting curves of a number of pure glycerides is given. In the present paper the various factors influencing the shape of the melting curves are discussed in detail. These factors may be based on the apparatus (height and diameter of fat layer, rate of heating), but they can be kept constant, and therefore the manner in which crystallization takes place is of much greater importance. The pretreatment of the fats is also considered. Reproducibility of the measurements is checked, using different sample holders and thermocouples. Finally some DTA curves of natural oils and fats are given.

Influence of Cooling and Tempering on DTA Curves

In order to be able to draw the base line of a melting curve the determination should start from about 10° to 20°C. below the temperature at which melting sets in. Cooling to this temperature may be performed in the following ways.

a) The fat or fatty mixture is introduced into the sample holder and is rapidly cooled. The melting curve obtained gives information about the fatty portion as such. Figure 1a shows the curve of a chocolate with cocoa butter and a curve of chocolate with a substitute.
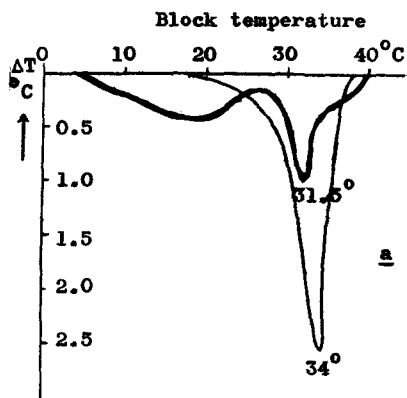

Block temperature

Fig. 1a. ———— pure chocolate, fat phase = 100% cocoa butter
▬▬▬ chocolate, fat phase = 50% cocoa butter, 50% substitute (hardened fat).

b) The sample holder, filled with premelted fat, is placed in the copper block, which is rapidly cooled subsequently until the fat is completely solid. In this way often metastable crystals will be formed, resulting in exothermic transformation peaks (maxima) in the curve. This method is particularly suitable for studying the polymorphic

behavior of fats. The positions of these peaks can be useful for the identification of pure triglycerides and of fats and oils. The curves for such unestablished fats are drawn as dotted lines.

c) The liquid fat is introduced into the sample holder and stabilized at a given temperature. On stabilizing, the following takes place. If a fat with a number of triglycerides of different melting points is rapidly cooled, a great variety of mixed crystals will be formed, resulting in a regular melting range (Figure 1b, dotted line). If such an unstabilized fat is tempered at, e.g., 29°C., part of the mixed crystals will melt, and the more saturated glycerides will be reassociated to form new series of mixed crystals, having higher melting points. This is illustrated by two minima in Figure 1b (at 27° and 37°C.). Hence, by the selective stearin formation during tempering, the final melting point is increased from 39° to 42°C., and the initial melting point is decreased
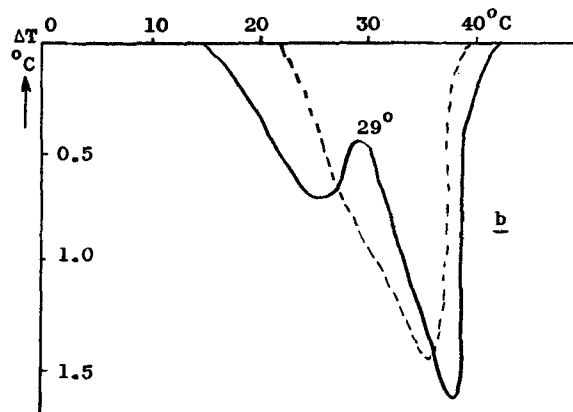

Fig. 1b. Cocoa butter substitute (based on coconut oil):
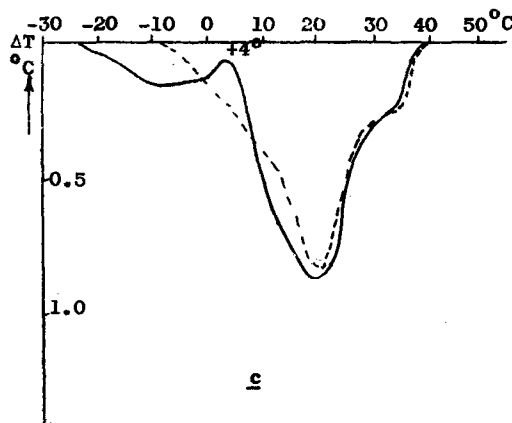------- rapidly cooled.
———— tempered at 29°C.

Fig. 1c. Margarine fat blend:
------- rapidly cooled (directly after Votator)
———— after 1 hr. of tempering at 5°C.
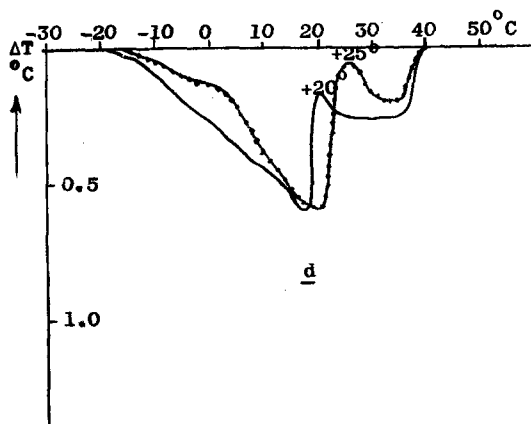
Fig. 1d. Margarine fat blend (as 1c):
         -------- after 1 hr. of tempering at 25°C.
         ———— after 1 hr. of tempering at 20°C.

from 22° to 15°C. The stabilization temperature is found as a maximum in the curves. Similar explanations are given by Bailey (3) and McMichael (4). Such reassociations, which are, in our opinion, of equal or even greater importance than polymorphic phenomena are frequently overlooked. As a result of tempering the temperature range at which fats are plastic is enlarged. Generally the fat becomes softer by crystal growth and formation of liquid oil and harder by stearin formation. The latter case occurs at high, the first at low temperatures.

The tempering period is mainly determined by the time necessary to obtain a constant temperature in the fat mass. The influence of the temperature during tempering is illustrated in Figures 1c and 1d. The maxima are clearly shown. X-ray analyses have revealed that all samples were in the β'-form after cooling and that in about 14 days no transitions have taken place.

d) A sliding stabilization of the fat results in more reproducible results. The liquid fat is in this case gradually cooled to −70°C. (2 days). The cooling must be carried out under standardized conditions. The curves obtained with fats stabilized in this way are particularly suitable for identification purposes.

Calibration

For calibration purposes a standard fat was used with a short melting range, obtained by repeated crystallization of hardened cottonseed oil from acetone. The temperature at the minimum is block tem-
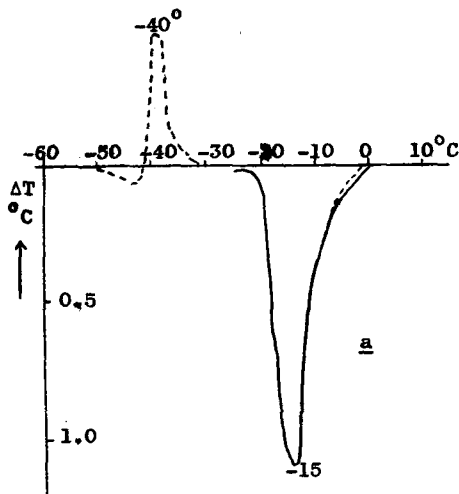

Fig. 2a.

Fig. 2. DTA curves of various oils (———— stabilized; -------- nonstabilized): a) safflower oil; b) sunflower oil; c) corn oil.

perature $-\triangle T = 46.1 - 1.6 = 44.5°C$. To carry out successive analyses a number of sample holders and thermocouples of sufficient uniformity must be available. A number of determinations was carried out
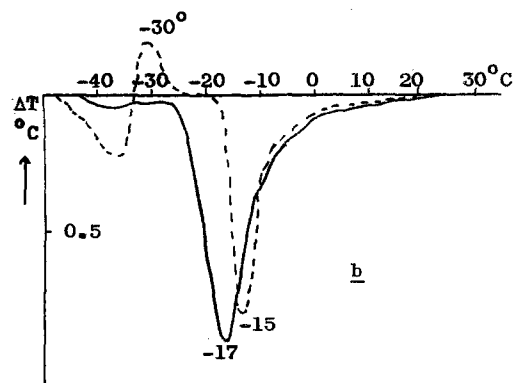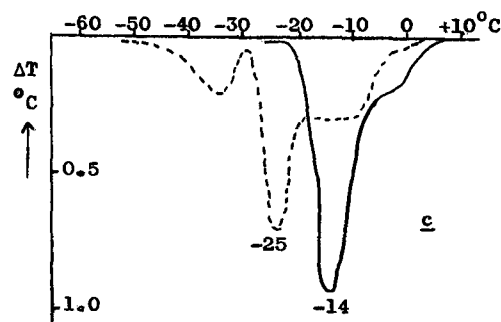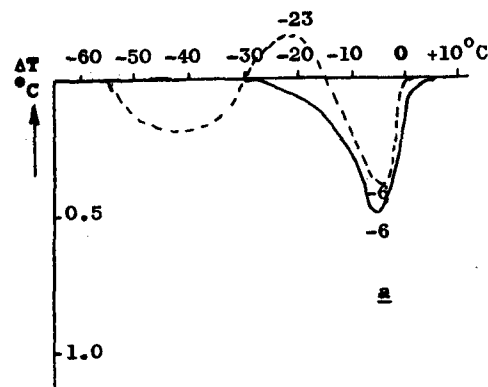

Fig. 2b.

Fig. 2c.

Fig. 3a.

Fig. 3. DTA curves of various oils (———— stabilized; -------- nonstabilized): a) tung oil; b) teaseed oil; c) linseed oil; d) soybean oil.
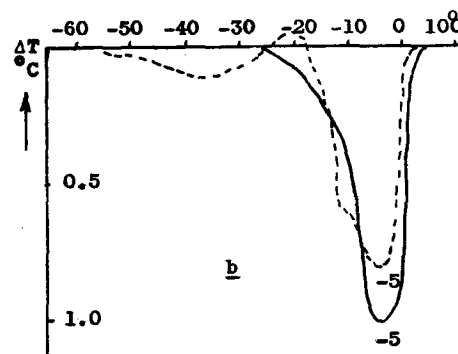

Fig. 3b.

with the standard fat, using a selection of 10 sample holders and eight thermocouples, to check the scattering in the results. The following mean values were found (standard deviation between brackets): Peak area 23.8 cm.^{2} ($\sigma = 1.6$), temperature difference at melting minimum 1.61°C. ($\sigma = 0.09$), melting minimum at 44.5°C. ($\sigma = 0.1$).

DTA Curves of Natural Oils and Fats

The DTA curves, both for stabilized and unstabilized fats, give information about their melting and polymorphic behavior. The curves can therefore be used for identification. In Figures 2 to 6 a number of such curves is given. The dotted lines refer to unstabilized (rapidly cooled) fats, the drawn lines to slowly-sliding stabilized fats. Samples of 400-mg. fat were used in all cases while the heating rate amounted to 1.8°C./min.

DTA curves of oils and fats which have a more complicated character, such as whale oil, herring oil,
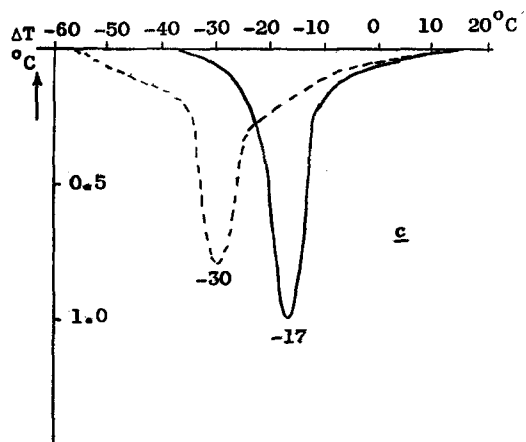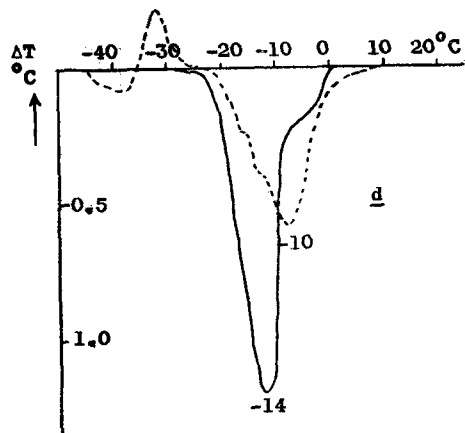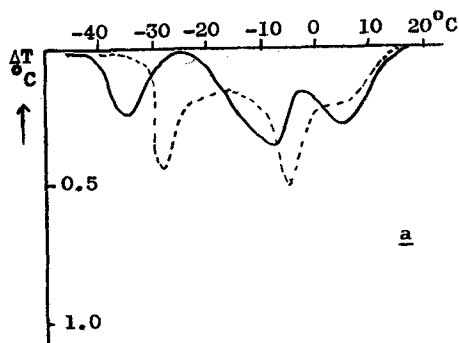

FIG. 3c.

FIG. 3d.

FIG. 4a.

Fig. 4. DTA curves of various oils (———— stabilized; -------- nonstabilized): a) cottonseed oil; b) peanut oil; c) sesame oil; d) olive oil.
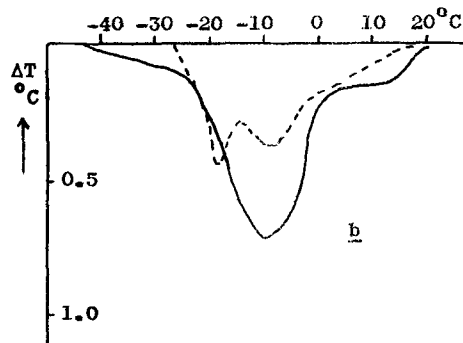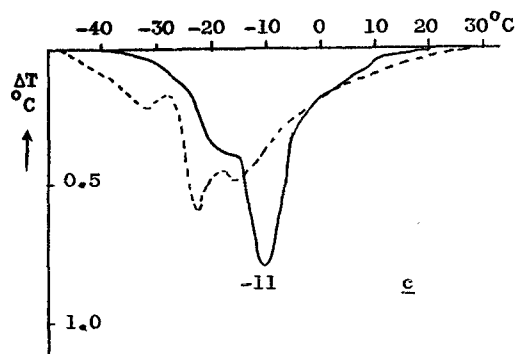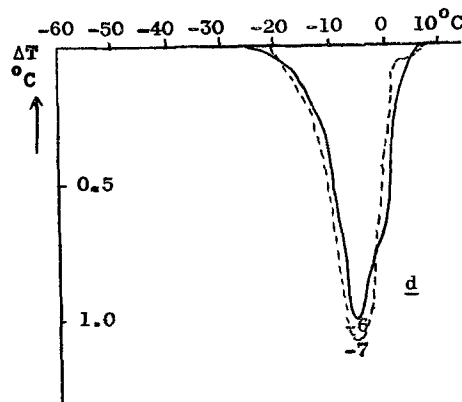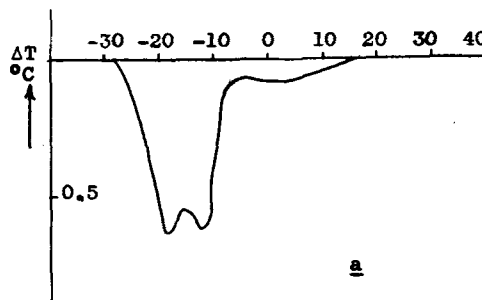

FIG. 4b.

FIG. 4c.

FIG. 4d.

FIG. 5a.

FIG. 5. DTA curves of various oils (———— stabilized; -------- nonstabilized): a) castor oil; b) rapeseed oil; c) antarctic whale oil; d) Norwegian herring oil.
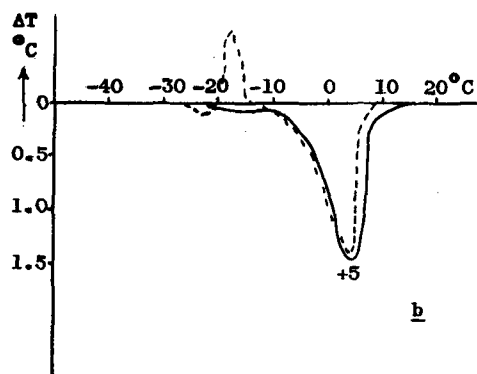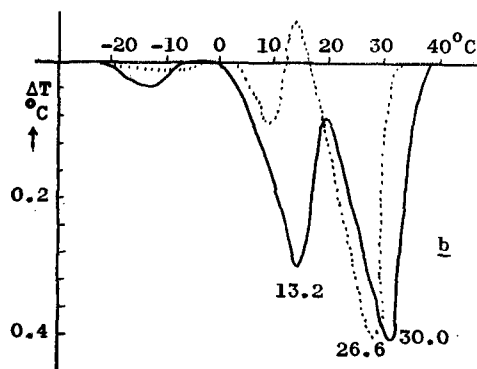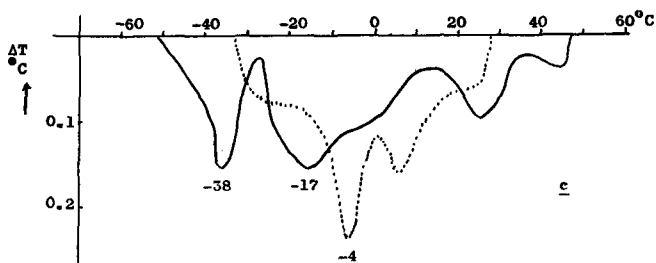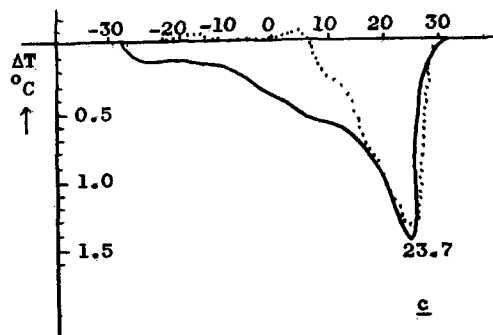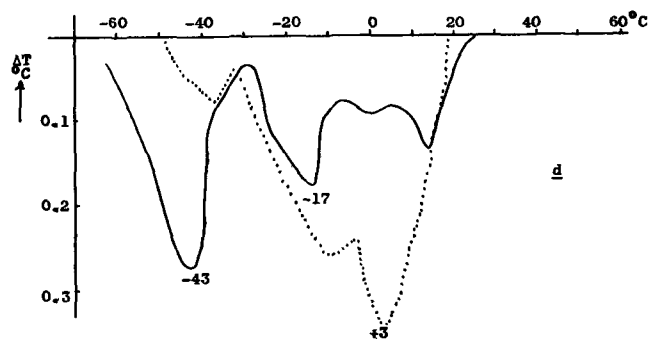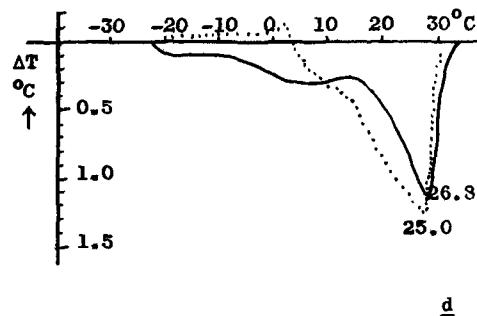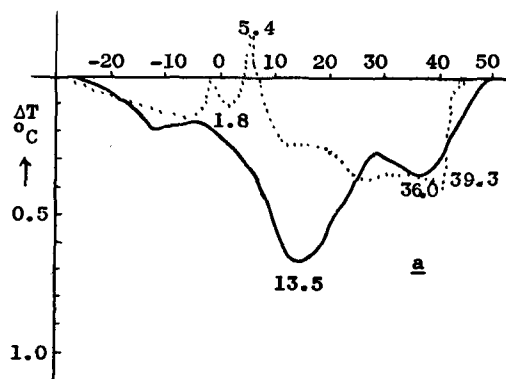
FIG. 5b.

FIG. 5c.

FIG. 5d.

FIG. 6a.

FIG. 6. DTA curves of various oils and fats (————— stabilized; - - - - - - - nonstabilized: a) palm oil; b) Shea butter; c) coconut oil; d) palm kernel oil; e) tallow; f) cocoa butter.

FIG. 6b.

FIG. 6c.

FIG. 6d.

tallow, lard etc., may differ, according to the origin.

For unstabilized castor oil (Figure 5a) no curve could be drawn. This is because of the transformation into a glassy mass after shock-cooling, which does not show thermal effects upon heating. In most liquid oils two distinctly different crystal forms are detected; the first is unstable. This form is rapidly transformed into the second, more stable one. Sometimes this transition takes place so rapidly that a sharp maximum above the zero line is achieved (safflower, sunflower, rapeseed, and soybean oils: Figures 2a, 2b, 3d, 5b).

In other cases transition and melting take place simultaneously, and the transformation maximum is less distinct or much flatter (corn oil, tung oil, and teaseed oil: Figures 2c, 3a, 3b). Sometimes the curves do not indicate whether metastable forms are formed or not (cottonseed, peanut, and sesame oil: Figures 4a, 4b, 4c).

Only for linseed oil (Figure 3c) was it possible to record the metastable form. For olive oil only one form could be detected (Figure 4d).

Most of the liquid oils start melting between −50° and −30°C. Exact temperatures however cannot be given because small deviations from the zero line can be caused by drift of this line as well as by small amounts of melting fat. This is in agreement with an investigation into the thermal properties of fats and oils carried out in the Southern Regional Research Laboratory, New Orleans (5-8). The workers stated that cottonseed oil starts melting at about −75°C. However it is still an open question whether these
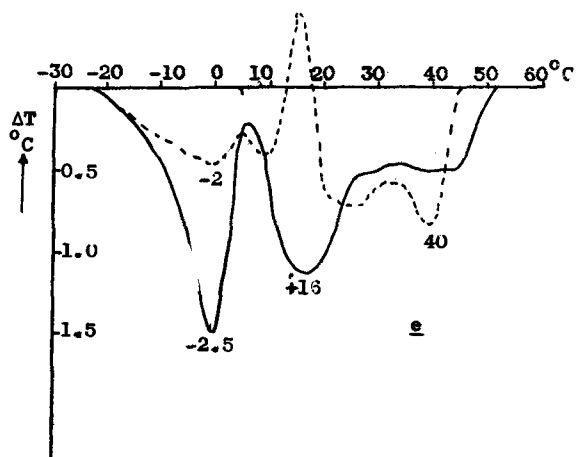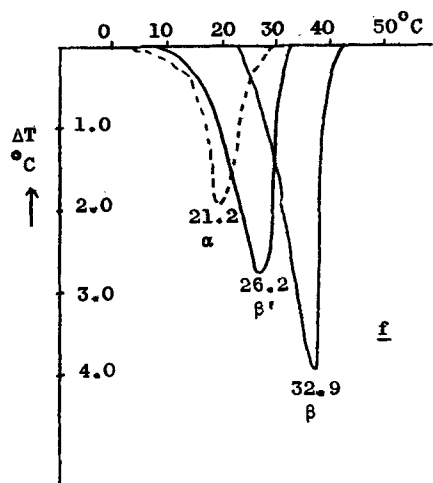
FIG. 6e.

FIG. 6f.

small thermal effects are caused by real melting or by increasing rotation in the crystal lattice.

According to the observations of Oliver et al. (6), it was also found that DTA curves often have a long "tail," which points to melting processes within a temperature range in which the oil is visually clear. For example, the curve of cottonseed oil (Figure 4a) ends at 17°C. although the oil was visually clear at 0°C.

Contrary to Ward et al. (8), a metastable form was found for a-tung oil (Figure 3a). Apparently this form melts between −60° and −30°C. but could not be obtained in a pure state because of its low stability. Since Ward et al. found a melting of a-tung oil over two principal temperature ranges (viz., for the first component from −43° to −10°C. and for the

second from −10° to +3°C.), it should be assumed that the oil was not completely stable on measuring. For coconut oil (Figure 6c) two forms exist; when cooling rapidly, the a-form is obtained, which has a final melting point of 13°C. The transition to the β'-form however obviously starts below 0°C. so that transition and melting take place simultaneously and none or very little of the a-form can be observed in the DTA curve.

Remarks

One of the most interesting possibilities of the DTA method is the calculation of the heat of melting of a sample from the actual area between the curve and the base line. In the case of fats with narrow melting ranges (pure glycerides, cocoa butter) a correlation exists between the surface area of the curve and the heat of melting. Problems encountered with the establishment of such correlations are discussed by Erikson (9) and other workers.

Analogous to the determination of melting curves, it is also possible to plot cooling curves. In this case the copper block with a sample is first heated and subsequently cooled at a constant rate.

Summary

The application of the differential thermal-analysis method for studying the melting behavior of oils and fats has proved very useful. The shapes of the curves depend largely on the pretreatment of the fats. From these curves, indications regarding the tempering of the fats can be obtained. DTA curves show the frequent occurrence of mixed crystals in fats. The curves are satisfactorily reproducible, provided that a carefully identical pretreatment is given.

Acknowledgment

REFERENCES

1. Haighton, A. J., and Hannewijk, J., J. Am. Oil Chemists' Soc., in press.
2. Lavery, H., J. Am. Oil Chemists' Soc., in press.
3. Bailey, A. E., "Industrial Oil and Fat Products," 2nd ed., Interscience Publishers, New York, p. 218 (1951).
4. McMichael, C. E., J. Am. Oil Chemists' Soc., 33, 512–516 (1956).
5. Bailey, A. E., and Oliver, G. D., Oil and Soap, 21, 300–302 (1944).
6. Oliver, G. D., Singleton, W. S., Todd, S. S., and Bailey, A. E., ibid., 297–300.
7. Ward, T. L., and Singleton, W. S., J. Am. Oil Chemists' Soc., 27, 423–426 (1950).
8. Ward, T. L., Singleton, W. S., and Planck, R. W., J. Am. Oil Chemists' Soc., 29, 155 (1952).
9. Erikson, E., Annals of the Royal Agriculture College of Sweden, vol. 19, 129 (1952); vol. 20, 117 (1953); vol. 21, 189 (1954).

[Received August 12, 1957]

Detergent Bars from Salts of a-Sulfonated Tallow Acids[1,2]

J. K. WEIL, A. J. STIRTON, E. W. MAURER, W. C. AULT, and W. E. PALM, Eastern Regional Research Laboratory,[3] Philadelphia, Pennsylvania

A SYNTHETIC DETERGENT BAR is expected to equal or approximate the excellent characteristics of soap in soft or moderately hard water, to be more efficient than soap in very hard water, and perhaps to be useful in sea water as well. Detergent bars are judged with reference to soap as a standard. From

consideration of the many problems encountered in