sis agree with the values calculated from random distribution (Table V).

Palmitic acid-rich Sal fat and stearic and palmitic acid-rich Mowrah fat may be useful for making high stability bakery fat, a new kind of vanaspati, tropical margarines, confectionery fats and other food fats.

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Iso-Solid Diagrams of Fat Blends from Thermal Analysis Data

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ABSTRACT

The use of spline interpolation between solid fat index (SFI) values obtained from calorimetric experiments to determine iso-solid data is described. Computer programs control both the sampling of the data from the calorimeter and the calculation of iso-solid values. This approach allows us to plot iso-solid diagrams fully automatically. Examples for cocoa butter/milk fat mixtures are given.

INTRODUCTION

For a range of mixtures of two components such as fat blends, iso-solid diagrams define curves indicating the temperatures at which constant solid to liquid ratios can be found as a function of the mixture composition.

Iso-solid diagrams are practical for illustrating the behavior of two constituent systems. In the case of fats, they are useful for determining factors relating to melting or crystallization behavior as well as to determine the fat compatability (1). Thus, iso-solid diagrams help fat technologists to choose the appropriate fat blend needed for a particular formulation.

The solid to liquid ratio in a fat or in a fat blend (solid fat index or SFI) can be determined by several methods: dilatometry (2), wide-line (3) or pulsed (4) nuclear magnetic resonance (NMR) spectroscopy, differential scanning calorimetry (DSC) (5) or densitometry (6).

Constructing iso-solid diagrams manually from data obtained with one of the abovementioned techniques is tedious and time-consuming, due to the fact that each point of the diagram must be calculated by interpolation between the experimental SFI values. Recently, Timms (7) described a partially automatic method based on a quadratic interpolation between the experimental SFI values determined by NMR, which facilitates this task.

We report below a fully automatic method for calculating iso-solid diagrams from DSC data, based on the rather sophisticated spline interpolation. An iso-solid diagram of cocoa butter/milk fat mixtures is shown.

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MATERIALS AND METHODS

Materials

Cocoa butter (CB) was supplied by De Zaan (Zaandan, Netherlands). Milk fat fraction (MFF) was prepared by Corman (Goe, Belgium) by milk fat dry fractionation at melting point 41 C.

Principle of the Method

The SFI depends on the fat temperature. SFI values can therefore be expressed as a function of the temperature. This function is calculated by sequentially integrating the DSC melting curve and normalizing the values obtained by the total surface englobed by the DSC curve (8) (see Fig. 1).

$$SFI\,(T) = \frac{\int_{T_0}^{T} H\,(T)\,dT}{\int_{T_0}^{T_1} H\,(T)\,dT} \qquad [1]$$

In order to calculate iso-solid diagram of a system of two fats A and B, SFI curves are determined for a series of mixtures representing, say, 10% composition intervals. A convenient SFI value, e.g., 20%, is then chosen and the temperature at which each mixture has this SFI value is calculated by interpolation and reported against sample composition (see Fig. 2).

This procedure is repeated for a series of SFI values, and in this way a set of iso-solid lines is obtained.

Data Acquisition

Data acquisition from the differential scanning calorimeter (Mettler TA 2000B) was carried out using a Hewlett-

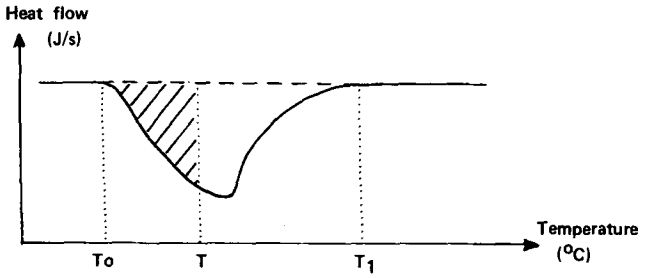

FIG. 1. Determination of SFI from DSC melting curve.

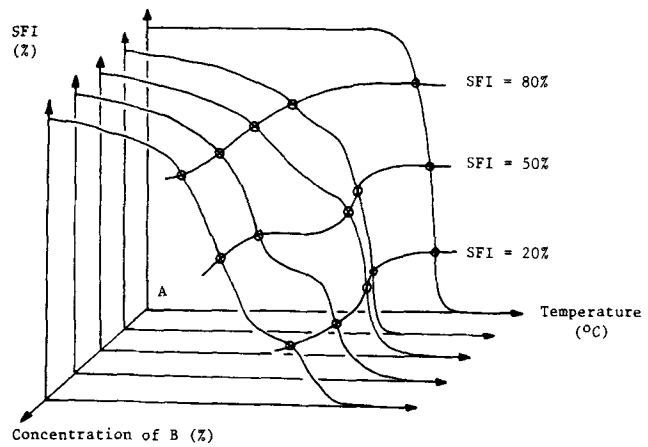

FIG. 2. Determination of iso-solid data for a system of two fats, A and B, from a set of SFI curves.

Packard 3356 Laboratory Automation System (LAS) according to the scheme described in Figure 3. During the calorimeter scan, the raw melting curve of the sample was recorded using an A/D converter (Hewlett-Packard 18652A) which discontinuously sampled the heat flow from the calorimeter at a rate of 0.5 Hz and transferred these data into the HP 3356 system. As the A/D converter accepts only positive voltage, a constant tension is added to the DSC signal by using a positive tension source connected between the calorimeter and the A/D converter (see Fig. 3).

Numeric Calculations

We have written a Basic program for the HP 3356 computer (LAS), based on those (9) supplied by the HP3350 series users group for the integration of the raw melting curves obtained from the calorimeter. This program corrects the data according to the thermal lag effect and the variation of calorimeter sensitivity with temperature. The base line for the integration of the DSC melting curve is determined by the straight line between the experimental points corresponding to the start and the end of the peak, the temperatures of which are chosen by the operator.

A Fortran program is used for the subsequent calculations which are performed on a HP 3000 computer. SFI curves are obtained according to the formula [1], and the iso-solid diagrams are calculated using a spline interpolation function (10) between the calculated SFI values for each fat blend of the two-fat system.

RESULTS

The method described here has been tested with several cocoa butter/milk fat sample systems.

In Figure 4, we report the iso-solid diagram of milk fat fraction/cocoa butter mixtures stored at 15 C for 4 weeks. On the left part of this graph (e.g., up to 30% milk fat fraction) the iso-solid lines are very close together, indicative of a sharp melting fat (nonplastic fat). In this area the blends have similar physical properties to cocoa butter. At the other end of the graph, say below 30% milk fat fraction, the iso-solid lines are far apart. In this area, the physical properties of the blends are similar to those of the milk fat fraction, and correspond to a broad melting fat (plastic fat).

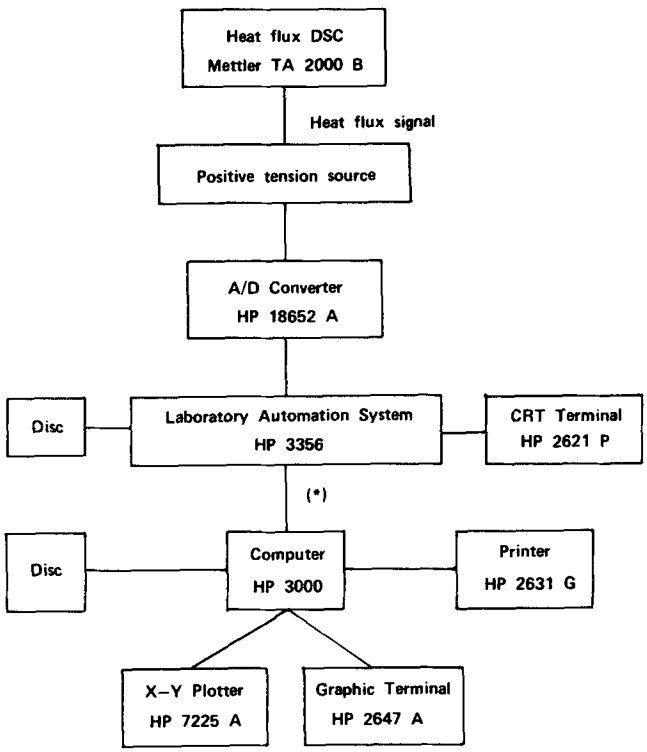

FIG. 3. Scheme of connections between calorimeter and computer. *There is no direct connection as yet between the Laboratory Automation System HP 3356 and the computer HP 3000. Data are presently transferred via magnetic cartridge tapes.

The iso-solid lines illustrated on this figure also show a minimum which reveals a eutectic between the milk fat fraction and the cocoa butter. This means that these fats are not completely compatible.

These results are in good agreement with those obtained when studying similar binary systems by NMR spectroscopy (7), (11) and (12).

DISCUSSION

Many different approaches have been taken towards the determination of SFI of fats, but none of the techniques gives absolute SFI values. The oldest method, dilatometry, is an official AOCS method (2). This is tedious and time-consuming, and is now being more and more frequently replaced by quicker methods.

For fats in a stable polymorphic form, dilatometry and calorimetry give similar results, whilst results obtained with NMR spectroscopy are somewhat different (13) and (14). Calorimetry, on the other hand, has the advantage over the other techniques of giving a melting pattern of the fat investigated in addition to SFI data.

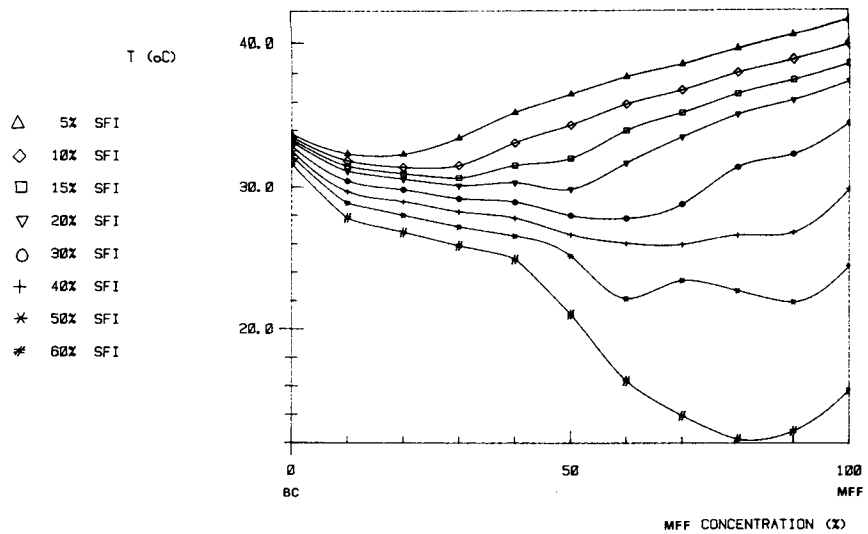

FIG. 4. Iso-solid diagram: CB-MFF system.

Calorimetry has been little used in the past to determine iso-solid diagrams of fat blends, because the procedures are tedious and the manual calculations impracticably long. Using available computer facilities for both data sampling and for calculating the iso-solid temperatures facilitates the task a great deal and makes such a method accessible.

Copies of the computer programs described in this study may be obtained from the authors.

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M.C. Malherbe performed the DSC measurements and J. Löliger and I. Horman helped with constructive discussions.

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