Heat Treatment of Cream: A Model of the Butter Texture Response in Relation with Triglyceride Composition

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ABSTRACT: The effects of thermal treatments on butter texture are known and have been used since 1935 on an industrial scale, but without fundamental knowledge. Butter composition influences firmness, as observed through seasonal and regional variations. Experiments were carried out at 15°C by using a cone penetrometer and an industrial testing machine. A significant correlation between heat treatment efficiency and some prevalent triglycerides and fatty acids on butter firmness was outlined. Three fatty acids (myristic, oleic, palmitic) and four major groups of triglycerides mainly affected the firmness, sometimes leading to an inversion of the thermal effect, according to individual sample composition. A crystallographic and thermodynamic model based on triglycerides properties was developed.
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KEY WORDS: Butter, cream, crystallization, fatty acid, mixed crystal, texture, thermal treatment, triglyceride.

Usually, cream is rarely transformed into butter just after the pasteurization. A lag time, called "physical maturation," is generally observed to reach optimal equilibrium between liquid and solid components of fat in order to obtain a butter with a good consistency. Moreover, such a target is different, if the final product is a consumer who needs spreadability, or the food industry which needs some specific properties, such as higher firmness at room temperature, i.e., the pastry industry.

A physical treatment of cream is the best economic way to obtain the desired consistency of butter (1,2). Many workers have looked for the best thermal cycle to reach this goal. To satisfy butter makers in the last decade, most of the studies dealt with the obtention of a better spreadability of the final product (3–8). Very few works were done in the opposite way, that is higher firmness.

Through thermal treatments, some polymorphic forms are induced, as well as a composition and a specific concentration of crystals which, finally, influence the texture of the resulting butter (9).

Crystallization temperature affects polymorphic forms, the size and structure of the crystals formed and their physical properties (10–12). It is well known that the cooling speed influences the prevailing polymorphic forms. Thus, slow cooling induces the formation of β' and β crystals, whereas fast cooling results mainly in the α form (1). Deffense (13) shows that speed cooling mainly influences the size of crystals and thus the texture of butter fat (13–15). One of the first workers on this topic was Mulder (16), who established that the increase of solid fat during fast cooling is promoted by mixed crystals formation.

Therefore, the thermal treatment of cream simultaneously influences several parameters: crystal size, polymorphic forms, occurrence of mixed crystals, the composition and the specific concentration of the crystals, etc., which lead to a very complex situation and interpretation. It is the reason why, in most cases, the choice of a thermal treatment of cream is merely a know-how, rather than a fundamental understanding.

The first thermal treatment was set up in the 1930s (17). This treatment, known as the ALNARP method (heating–cooling–heating, or else 8–19–16), has been successfully improved, especially by taking into account the iodine value of cream. Having observed that different melting and solidification ranges may be obtained for creams with the same iodine value, Precht *et al.* (18) suggest another approach which consists in selecting the temperatures of the three steps of the ALNARP treatment, based on the diagram of the melting and solidification of milk fat.

In this paper, we shall deal with the increase of firmness, instead of the spreadability of butter. Referring to few available studies, originally done to correct the summer firmness of butter, seven thermal cycles and a reference one (raw cream) have been set up and applied on the same summer cream. The treatment with the best results, in terms of increasing firmness, has been selected for the maturation of the five different summer and winter creams, from five different areas and identified through their fatty acid (FA) and triglyceride (TG) composition. The quantified effect of this particular thermal treatment on butter firmness is related to the latter parameters. It allows, according to its composition, a specific textural response of the final product to the treatment.

MATERIALS AND METHODS

Materials. Creams from five different, specific areas in France, were collected in January (winter) and in July (sum-

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mer). They were assumed to be representative of the major dairy regions in France [details previously published (19)].

Buttermaking method. To avoid the effect of manufacturing on the consistency of butter, a laboratory-scale buttermaking method was set up and systematically applied (19). Each assay was done in duplicate. Dry matter was determined according to the standard method of the Association of Official Analytical Chemists (20). The results were in line with the recommended water content of 16%. The fresh butter was stored in 6 cuvettes (diameter, 5 cm; height, 3 cm) at 4°C for 20 h; then it was compressed and finally stored at 15°C for 2.5 h prior to analysis.

Constant weight penetration. The instrument used was the P 41 1 penetrometer (Veb Feinmess, Dresden, Germany). The penetration time was 5 s (21,22). The cone was a commercial model according to the American Society for Testing and Materials (23) standard.

Three cuvettes were submitted to six penetrations each. Tests were performed at 15°C in a temperature-controlled laboratory room. The cone penetration gave the firmness index, which is the ratio of the mass of the cone assembly (w = 150 g) over the penetration depth (P is expressed as tenths mm). Yield value was calculated according to the formula of Haighton (24):

$$Y = K/P^{1.6} \qquad [1]$$

where Y is the yield value and K is a constant depending on the cone angle. Thus, average firmness was obtained from 36 (18×2) assays, with a satisfactory standard deviation of less than 7%.

Constant speed penetration. A computerized Instron® universal testing machine (model 1122; Instron, Buc, France) was used at a constant temperature (15°C). Three penetration tests were done in each of the remaining three cuvettes. The force required to drive a 28 mm^2 surface stainless-steel cylinder to a depth of 3 mm into the sample at a speed of 5 mm/min was measured by a load cell. The standard deviation was less than 7%.

Cream maturation. Maturation was done in a thermostated water bath. The seven thermal cycles experimented with are illustrated on Figure 1. The reference treatment set up to zero the thermal history of the cream and consisted in a heating up to 65°C, a rapid cooling to 5°C and immediate churning.

FA and TG composition. The FA and TG compositions of the different creams were determined according to a previous study (25).

Statistical tests. Statistical analyses were performed with STATITCF software (ITCF, Boigneville, France).

RESULTS AND DISCUSSION

Effect of the seven different maturation cycles on butter firmness. By comparison with reference treatment, treatments 2, 3 and 4 obviously lead to the best results in terms of stiffening: an increase of *ca.* 22% is obtained. The distinctive characteristic of these three treatments is that they present only

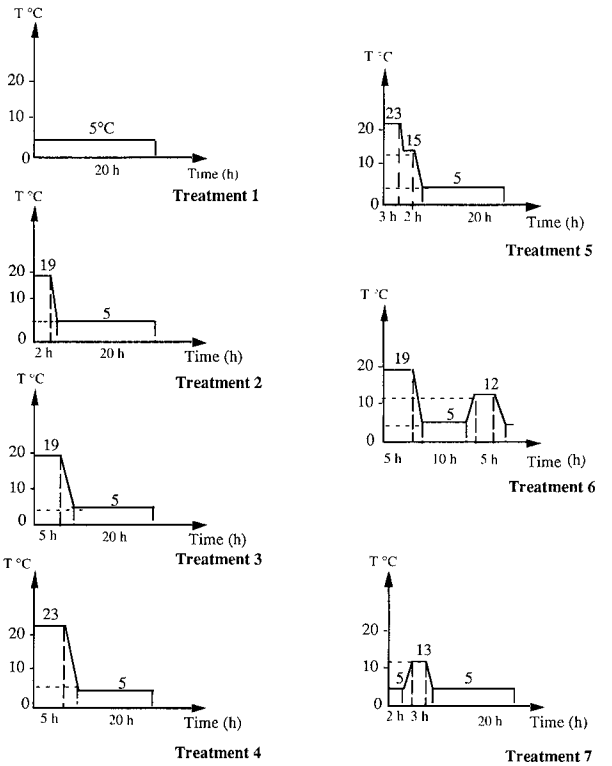

FIG. 1. The seven cream maturation treatments.

two steps: heating and cooling. The first step, 2 to 5 h long, is done within 19 and 23°C, whereas the second one is the same in all cases (20 h, 5°C). The aim of this first part of the study was the determination of the most efficient treatment for stiffening, in order to apply it afterwards to various creams. Treatment 2 was retained.

Slow cooling (23–15–6°C, treatment 5) leads to a firmness increase of about 15%, whereas heating up to 12°C after a two step treatment (19–5°C, treatment 6) leads to a minimal effect, that is to say 8%. More complex cycles (5–13–5°C, treatment 7) result in a firmness increase of no more than 10% (Fig. 2).

A comparison with literature results is not made easily, since buttermaking, sample conditioning and measuring methods are not standardized and have a high influence on the measured textural parameters. All things considered, buttermaking protocols have been the same throughout the present study. In such an instance, the conclusions should be restricted to this work.

Danmark and Bagger (7,8) show that the stiffest butter is obtained after a cream treatment without temperature variation (only one step: 8.6°C, 19 h). Another "summer treatment" (two steps: 19°C, 2 h; 8.6°C, 19 h) leads to a butter with a "good consistency." Most authors confirm this trend (2,3,26), but they generally diverge in terms of steps parameters and in the amplitude of the effect.

The interpretation of firmness variation due to thermal treatment has been extensively studied. However, the pro-

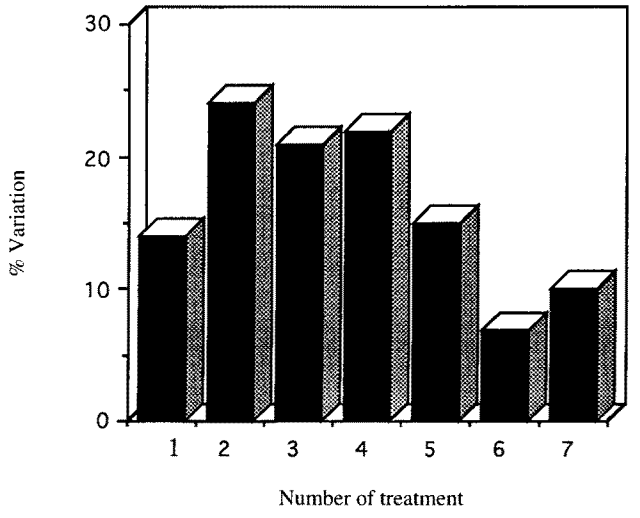

FIG. 2. Variation of butter firmness after a cream treatment by comparison with reference firmness.

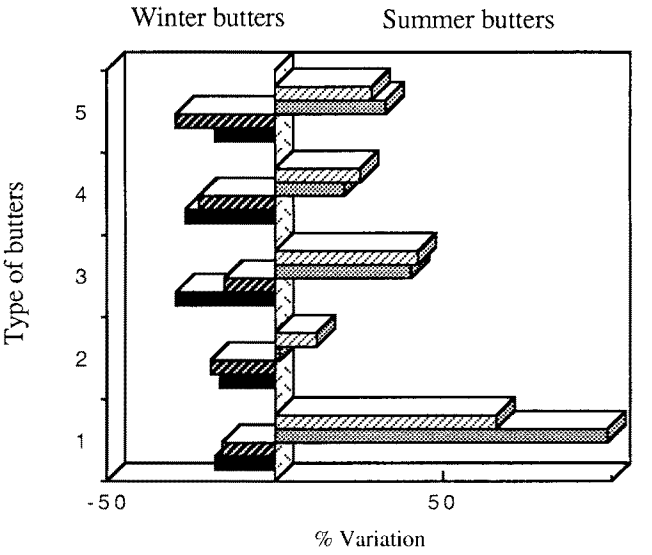

FIG. 3. Effect of a two-step cream maturation on the firmness of five butters by comparison with the reference treatment: (shaded) variation of summer butter firmness measured with the Instron® universal testing machine (model 1122; Buc, France); (light diagonal lines) variation of summer butter firmness measured with a cone penetrometer (P 411; Veb Feinmess, Dresden, Germany); (solid) variation of winter butter firmness measured with the Instron universal testing machine; (dark diagonal lines) variation of winter butter firmness measured with a cone penetrometer.

posed hypotheses are often contradictory. Four fat globules types, based on electron microscopic observations, have been defined in the cream by Precht *et al.* (18). Each type has a typical membrane and contains specific fat crystals. Their occurrence merely depends on temperature and on the thermal treatment of cream. During a "summer treatment," which is similar to a slow cooling, "type 2" fat globules are favored. This type is defined by a thin crystallized membrane and irregular crystals entrapping liquid fat. The membrane of these globules is easily broken by churning, so that very few of them remain intact in the resulting butter. The presence of many membrane fragments would increase the viscosity and, finally, the firmness of the product (18,27). Moreover, the crystals formed inside the fat globules are associated with a large quantity of liquid fat, which leads to a decrease of the exudation phenomenon and a weak fractionation of high and low melting TGs (2,28).

Conversely, by using electron paramagnetic response, Szekaly and Schaeffer (26) say that the maturation giving the hardest butter is the one which leads to the highest liquid fat in the continuous phase.

By using X-rays diffraction, De Man (1) shows that a slow cooling promotes β and β′ polymorphic forms crystallization, whereas fast cooling induces the transitory α form which is progressively replaced by the β′ form (27). Slow cooling would permit a temperature melting increase of high melting TGs (29).

Effect of thermal treatment 2 on creams of various composition. Each set of cream has been divided into four samples: the first two were processed as references. They were cooled to 5°C and directly churned after pasteurization; the average firmness obtained was called "reference firmness" (Fr or Yr). The two other ones were submitted to thermal treatment 2 (2 h, 19°C; 20 h, 5°C), and the medium firmness obtained was called "after-treatment firmness" (Ft or Yt).

Summer butters, resulting from treatment 2, are in keeping with the a foresaid results: they are stiffened by comparison with reference firmness (Fig. 3).

The effect of stiffening is as more pronounced as the butter is naturally soft at the beginning. By comparison with the reference treatment, a soft butter (summer butter) is stiffened—positive variation—whereas a hard one (winter butter) is softened—negative variation (Fig. 3). This aspect may be

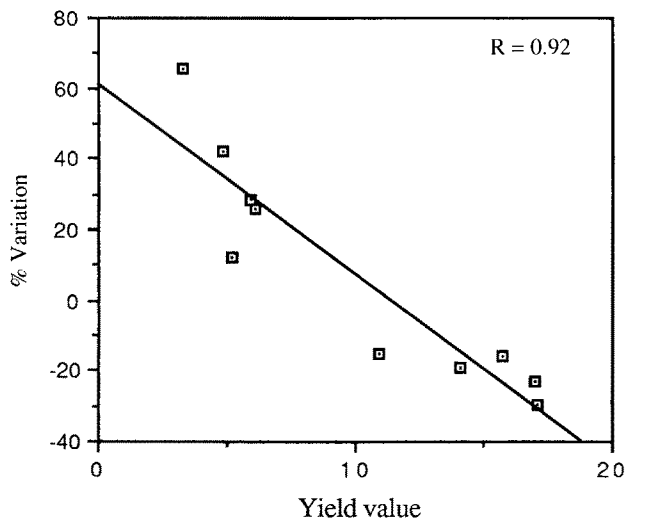

FIG. 4. Percentage of firmness variation vs. yield value of the different type of butters. R, correlation coefficient.

highlighted by studying the variation of firmness of each kind of butter through the firmness expressed as its yield value (Fig. 4).

Relation between the effect of treatment 2 and fat composition. In a previous study (25) it has been shown that the three major fatty acids (C_{14}, C_{16}, $C_{18:1}$) mainly contribute to regional and seasonal variations. Figure 5 shows the effect of treatment 2 by comparison with reference treatment, according to the respective levels of the three FAs. These results confirm obviously that the increase of C_{14}, the lowering of $C_{18:1}$ and the increase of the $C_{16}/C_{18:1}$ ratio increase butter firmness. More precisely, the results of the present work allow the determination of a critical composition in each of these FAs, from which an inversion of treatment 2 effect vs. reference can be observed.

Since milk fat is a complex mixture of TGs, the relation between treatment 2 and the TG composition is particularly interesting to investigate. Two previous studies (19,25) have shown that, among butter TGs, four groups contribute to seasonal and regional variation and mainly influence butter firmness. These groups are the following: TG1 mainly represented by POO; TG2 mainly represented by MyOO; TG3 mainly represented by CLaO + CyMO + CoPO +BuSO; and TG4 mainly represented by BuPO + CMO + CoPL where P is palmitic acid, O is oleic acid, M is myristic acid, La is lauric acid, Cy is caprylic acid, Co is caproic acid, Bu is butyric acid, S is stearic acid, C is capric acid, and L is linoleic acid.

As observed in Figure 6, it can be seen that there exists a good linear correlation between butter firmness and the respective level of the four TG groups; as for the fatty acids, the effect of the process is sharply linked to the percentage of the TG groups. Two ranges can be separately observed: (i) a first range where TG1 is <5%, TG2 is<3.5%, TG3 is >5.5% and TG4 is >4.5%: the butter obtained is winter type and can be softened by the process; (ii) a second range where TG1 is >5%, TG2 is <3.5%, TG3 is >6% and TG4 is <4.5%: the butter is summer type and can be stiffened by treatment 2. Therefore, the knowledge of the composition can be used as a predictive variable for the effect of the thermal treatment on butter firmness.

As for the FA composition (Table 1), a similar study of the relation between the firmness variation and the TG composition was done, and high correlation was found (Table 2). Thus, the effect of thermal treatment 2 (summer treatment) is sharply related to the raw fat composition: the more the cream naturally leads to a soft butter, the more the effect of the thermal treatment is important in terms of stiffening.

Interpretation: *(i) A crystallization kinetics model.* A first possible interpretation takes into account the well known discrepancy between winter and summer butter viscosities and resorts to crystallization kinetics. On a low-viscosity summer cream, a rapid cooling favors crystal germination by overcooling, instead of crystal growth (15). Such a situation leads to a large quantity of small α entangling crystals (1) so that a very large sorption surface is offered to the liquid fat still existing. However, despite this physical adsorption for most of

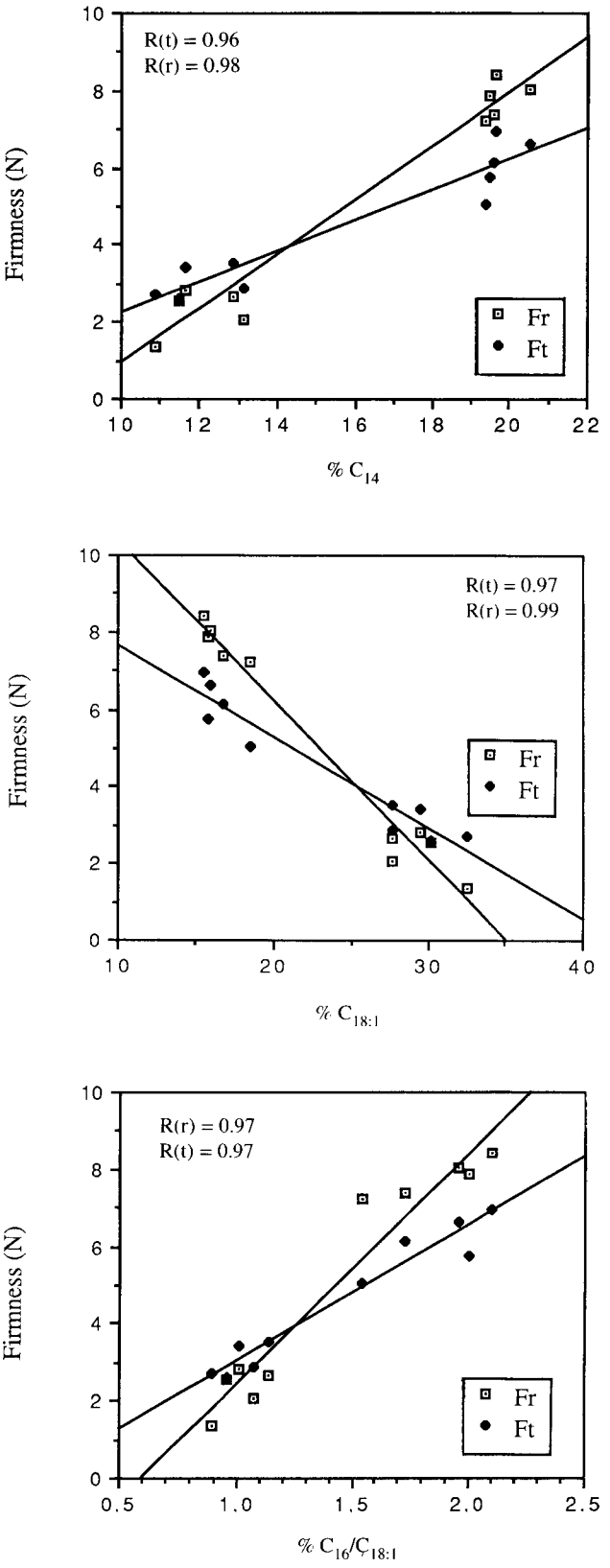

FIG. 5. The relationship between firmness and the percentage of the prevalent fatty acids: (⊡) butter firmness after reference treatment; (◆) butter firmness after a two-step cream maturation. The relationship between firmness and the percentage of fatty acid fraction (a) C_{14}; (b) $C_{18:1}$; (c) $C_{16}/C_{18.1}$. Fr, reference firmness; Ft, aftertreatment firmness; N, Newtons.

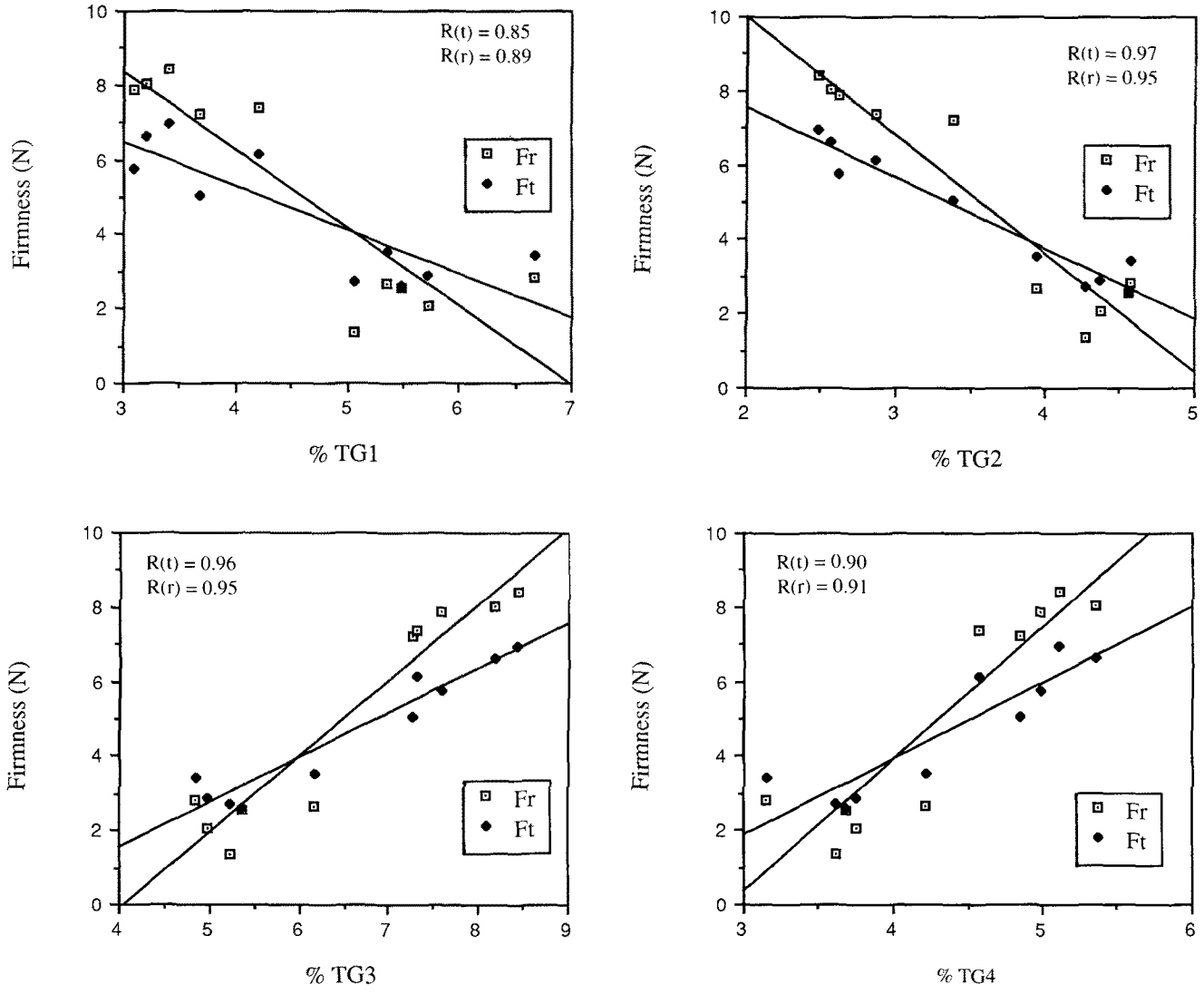

FIG. 6. The relationship between firmness and the percentage of the prevalent triglyceride fraction in butter: ⊡, butter firmness after reference treatment; ◆, butter firmness after a two-step cream maturation. (a) The relationship between firmness and the percentage of triglyceride fraction (TG1); (b) the relationship between firmness and the percentage of triglyceride fraction (TG2); (c) the relationship between firmness and the percentage of triglyceride fraction (TG3); (d) the relationship between firmness and the percentage of triglyceride fraction (TG4). See Figure 5 for abbreviations.

the liquid fat on the crystal skeleton, a small part of this fat remains free (30): a "solidification" of the structure occurs, represented by a higher solid-fat content (SFC) at a given temperature. On a more viscous winter cream, the heat transfer slows down, growth is induced rather than germination of the crystals, which are mainly β′ forms (1). Therefore, since the adsorption of liquid fat is less important on larger crystals, the global texture is softer. This assumption is in keeping with Foley (30) and DeMan and Beers (9) studies. It can be discussed, at least, on one point: if the fast cooling of a light viscous fat favors the polymorphic α form still existing, such a form is known to induce softening of the products (15). Moreover, it is unstable and leads, after a few hours, to the β′ and β forms (27) which have different properties.

TABLE 1
Correlation Coefficients Between Variation of Firmness (F) or Yield Value (Y) and the Percentage of the Prevalent Fatty Acids in Butter

	C_{14}	$C_{16}/C_{18:1}$	$C_{18:1}$
% Variation (Y)	0.91	0.88	0.92
% Variation (F)	0.80	0.76	0.83

TABLE 2
Correlation Coefficients Between Variation of Firmness (F) or Yield Value (Y) and the Percentage of the Prevalent Triglycerides (TGs) in Butter

	TG1	TG2	TG3	TG4
% Variation (Y)	0.78	0.84	0.87	0.83
% Variation (F)	0.63	0.68	0.73	0.70

(ii) A crystallographic and thermodynamic model. In the disordered liquid state, TGs are considered as totally miscible, thus leading to a perfect continuum. A singularity occurs through germination of high melting triglycerides (HMTG) in the process of cooling: If the cooling is slow in a viscous liquid, HMTGs crystallize and, while growing, reject foreign TGs because the energetic barrier corresponding to this discrimination matches the crystallization speed. The crystals obtained in such a medium (winter cream-like) are mainly nonmixed crystals, as observed from their melting points. If the cooling is rapid, the rejection of foreign crystals is no longer possible because the crystal growth kinetics is by far higher than the kinetics of rejection. Therefore, the growing crystals absorb some foreign molecules and lead, to a certain extent, to mixed crystals. According to Mulder (16), mixed crystals are responsible for butter stiffening.

The limitations of mixed crystals composition are known in most binary mineral systems, but data on solid solutions of TG or hydrocarbons are rare. One can assume that the stability domains of TGs solid solutions which are very close, on a thermodynamic point of view, lead to mixed crystal domains larger than those observed on usual solid solutions. It is known that mixed TG solutions, favored by rapid cooling when compared to homogeneous crystal mixtures, lead to hard products. An extreme case is given by the "shock cooling" of melted butter oil which leads to very hard and brittle products (31).

It should be noted that the study of a theoretical binary diagram indicates that the melting point of a mixed crystal is, whatever the melting point of the components may be, always over the melting point of a simple mixture (Fig. 7).

Taking two pure TGs, one with a low-melting point (LMP) and the other with a high-melting point (HMP), the diagram indicates two possible ways of obtaining mixed structures: The "BB′" way, which corresponds to a continuous solid solution between LMP and HMP, is called "way of mixed crystals." According to Mulder and Walstra (15), mixed crystals appear when the viscosity is low, that is to say when the heat transfer is rapid. In such a case, on a low-viscosity summer cream, with high LMP level (SB on the diagram), the thermal treatment favors mixed crystals formation, i.e. solid solution.

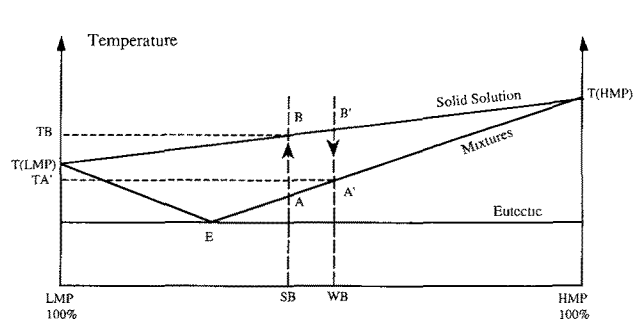

FIG. 7. Schematic phase diagram of two components, one with a low-melting point (LMP) and the other with a high-melting point (HMP); E, eutectic point; SB, summer butter; WB, winter butter.

The melting point of such a solution is $T_L > T_{LMP}$, the butter obtained will have a higher melting point and thus, the perception will be the one of a hard product. The "AA′" way: the mixture is homogeneous with a possible eutectic lowering melting point effect (point E). On a high-viscosity winter cream, with a higher level of HMP (WB on the diagram), the lower cooling speed favors the homogeneous mixture, rather than the solid solution. The representative point of this mixture is A′, and it can be seen that its melting point is below T_L: the butter obtained from this cream will be perceived softer.

Therefore, according to this thermodynamic interpretation of the thermal treatment effect, on a summer cream (SB), this effect displaces the point A up to B, resulting in a stiffening of the butter obtained, and on a winter cream (WB), the representative point slips backwards from B′ to A′ leading to a softening.

This assumption, based on Mulder (16), could explain the response discrepancy to the same thermal treatment of a two TGs model only by varying the respective proportions of the TGs. The complexity of milk fat does not allow further interpretation. Nevertheless, taking into account the large variation of only a few groups of TGs, such a thermodynamic model seems to be valid. However, it should be stressed that the model, although realistic, remains highly schematic. It should be taken more as a background for further studies than as a straight thermal process.

In accordance to this assumption, it would be of interest to study a binary HM and LM TG model, in order to point out the differences appearing during a slow or a rapid cooling and to determine the prevailing of the occurrence of mixed crystals over simple mixtures. An important part of the work, i.e., the relation between firmness and the thermodynamic equilibrium for the β and β′ forms should be done. The research should combine X-rays diffraction and differential scanning calorimetry. Such a study is under way at our laboratory.

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