SYMPOSIUM: MILK LIPIDS

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Crystallization and Fractionation of Milk Fat[1]

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ABSTRACT

Recent progress in understanding milk fat crystallization and fractionation is reviewed. Extent of fat solidification in butter can be altered by variations in thermal treatment of cream prior to churning. Because of its compositional complexity, milk fat rarely exhibits polymorphism. As with mixtures of closely related triglycerides, milk fat forms solid solutions. A typical milk fat begins melting below -40 C, maximum melting occurs at 15-18 C, and the highest melting fraction appears 20-37 C as a shoulder on the main peak. Dispersion of fat in emulsions increases its tolerance to supercooling, thereby altering the properties and composition of the solid phase. Most studies of milk fat fractionation have used progressive fractional crystallization, either of the melt or of solutions. Both procedures result in fractions showing larger changes in mp than in composition. The high melting glyceride fraction, ca. 5% total fat, influences crystallization out of proportion to concentration. The Alfa-Laval system, using an aqueous suspension of partially crystalline fat, produces two fractions. Typical high melting fractions have softening points ca. 3 C higher than the original fat. The softening point of typical low melting fractions is lowered 10 C. Refractionation is easier with the high melting fraction. Melting thermograms of these fractions show them as resembling fractions prepared from melted fat.

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INDEX

INTRODUCTION

The study of milk fat crystallization has been prompted by interest in controlling and improving butter spreadability. The emphasis has been upon processing effects because of restrictions upon alteration of the chemical composition of the fat. The knowledge gained from such research is useful. Maximum benefits of cream treatment do not appear to achieve all of the softening that might be desired for competitive purposes. Techniques now have become available for fractionation of milk fat on a commercial scale. So far, the fractions obtained are still defined as milk fats with respect to U.S. import regulations. This widens the range of butter spreadability that is achievable. There is also the possibility of producing special milk fats having physical properties designed for specific uses.

Processing factors for controlling butter consistency include thermal treatment of the cream, thermal treatment of the butter, and mechanical treatment of the butter (1). Thermal treatment of the cream has received the greatest emphasis. Butter firmness can be increased by cold tempering prior to churning (2). Butter firmness can be decreased by cooling cream to below 8 C to initiate fat crystallization then tempering at 19 C for 4-6 hr (3). The effectiveness of such treatments is consistent with Mulder's theory of mixed crystal formation (4). Quickly cooled milk fat has a larger solid fat content than when slowly cooled (5), with the major part of the solidification completed during the first 30 min after cooling (6). Mechanical reworking has been shown to decrease butter hardness through a reduction in crystal size and in the solid/liquid fat ratio (7).

MILK FAT CRYSTALLIZATION

Since the purpose of milk fat fractionation is to alter the physical properties, largely the extent of crystallization, it is important to review the nature of triglyceride crystallization. The most remarkable property of such crystals is monotropic polymorphism. The nomenclature used is confusing since there has been a long standing disagreement upon correlations of mp, names, and X-ray diffraction data. Chapman (8) suggests, on the basis of IR spectroscopy, that the Lutton scheme is more correct and

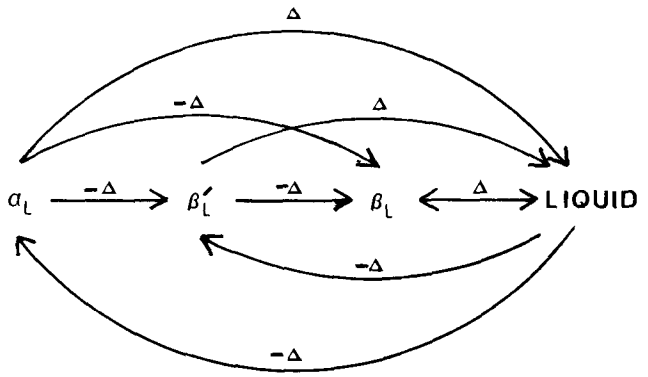

FIG. 1. Transitions between α_L, β'_L, and β_L crystals of triglycerides.

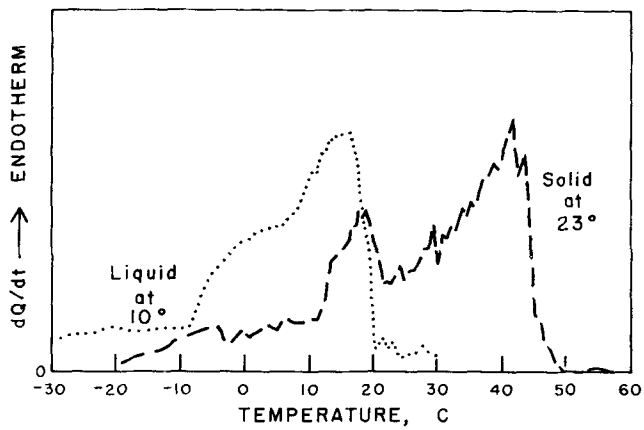

FIG. 2. Fats solid at 23 C and liquid at 10 C obtained during fractional crystallization of melted milk fat (27).

that all references include the subscript L to signify that his system is being used. As a first approximation, the α_L form has hexagonally packed hydrocarbon chains, the β'_L has orthorhombic packing, and the β_L form has triclinic chain packing (8). The chains of the β_L are tilted with respect to the base plane, defined by the end groups, while the α_L and β'_L are not. The permitted transitions between forms are shown in Figure 1. Thermal detection of polymorphism is based upon the exothermic nature of the unstable to stable form transition. The heating or cooling rate is the major factor controlling the pathway used, the faster the heat transfer, the longer the jump. A particular triglyceride may not show all possible forms. Thermal techniques usually detect only two forms during the course of melting of an α_L crystal, since fat is not able to disperse rapidly the energy released by polymorphic transitions. The more complex the composition of the fatty mixture, the less likely it is to exhibit monotropic polymorphism (9). Woodrow and DeMan (10) have shown that milk fat can be crystallized in an unstable form. The occurrence of such forms, however, is rare. There is apparently no relationship between polymorphism and butter hardness (11).

Although milk fat is composed largely of triglycerides, the large number of fatty acid residues present result in a wide variety of crystallization patterns. Both optical and positional isomerism affect mp. Rossell (12) stated, "Mixtures of triglycerides similar in melting points form solid solutions over extensive, but not usually complete, ranges of composition. This leads to several types of phase behaviour, eutectic formation being the most common, although peritectics and monotectics are also formed." He then presents a comprehensive review of triglyceride phase diagrams. Such solid solutions have been detected in mixtures of high and low melting fractions of milk fat (13). Establishment of equilibrium between different solid phases of fats (13) and between solid and liquid phases is sluggish (6); thus, solid fats usually contain inclusions of liquid. With the complexity of solid phases possible (14), due both to solid solution formation and to polymorphism of the simpler triglyceride mixtures, it is not surprising to find many contradictions in the literature on milk fat crystallization.

Melting patterns of milk fat have been studied since the 1930's (15,16). Crystallization conditions and fat composition will modify the details, as will experimental technique. Basically, milk fat shows three important melting ranges. The first range begins at less than -40 C, and the amount of fat melting increases gradually to ca. 0 C. The most significant region is 0-20 C, with the maximum occurring at 15-18 C and a minor peak at ca. 8 C. The position of the maximum depends both upon cooling conditions and fat composition. The highest melting region is 20-37 C and appears as a shoulder on the main melting peak (17-19). The temperature at which melting is completed is relatively constant and does not reflect seasonal changes in fat composition. The softening point of milk fat has been found to correspond to a solid/liquid ratio of 5:95 (20). Thermal patterns such as this are useful for following changes in type and extent of fat crystallization but indicate nothing about crystal size.

Dispersion of the fat in emulsions strongly influences its crystallization. Both in model systems (21-23) and in cream (16), more finely dispersed fat will tolerate a higher degree of supercooling. When crystallization eventually does occur, the lower temperature influences the nature of the crystalline phase. Polymorphism seems more likely; in the case of milk fat, the composition of the solid phase also may be altered. The three aspects of an emulsion, water, oil, and interface, also lead to the formation of liquid crystals, thereby modifying the properties of the emulsion (24). Since dispersion effects have been noted both for pure triglycerides and for milk fat, it is not surprising to find emulsions of milk fat fractions also are affected similarly (25).

FRACTIONATION OF MILK FAT

Many different fractions of milk fat have been prepared in laboratories over the years. Almost without exception, these have been prepared by progressive fractional crystallization, both from the melt and from solutions using solvents, such as ethanol or acetone. At the risk of stating the obvious, the nature of the fractions obtained depend upon the experimental conditions. The most important of these are crystallization temperatures, the temperature difference used between consecutive crystallization steps, cooling rates, and, in the case of solvent fractionations, the concentration of fat.

Richardson (26) has presented results obtained when milk fat was fractionated from the melt at 30, 25, 20, and 15 C. The fraction crystallizing at 30 C had the largest yield. The slipping points varied from 38.5-17 C. The long chain saturated residues decreased, and the unsaturated and short chain residues increased as the mp of the fraction decreased. Both free and esterified cholesterol tended to concentrate slightly in the lowest melting fractions. Thermograms of the highest and lowest melting fractions from a similar fractionation scheme producing five fractions (although done at 23, again at 23, 17, and 10 C) are presented in Figure 2 (27). The shoulder caused by the high melting fat has become the dominant feature in the first fraction, but a considerable amount of low melting fat is still evident. The fraction remaining liquid at 10 C reflects the increased concentration of low melting fat but shows an abrupt cessation of melting well above the fractionation temperature. This is typical of residual fats throughout fractionation schemes. Commercial scale fractionations from melted milk fat have been done (28). As could be

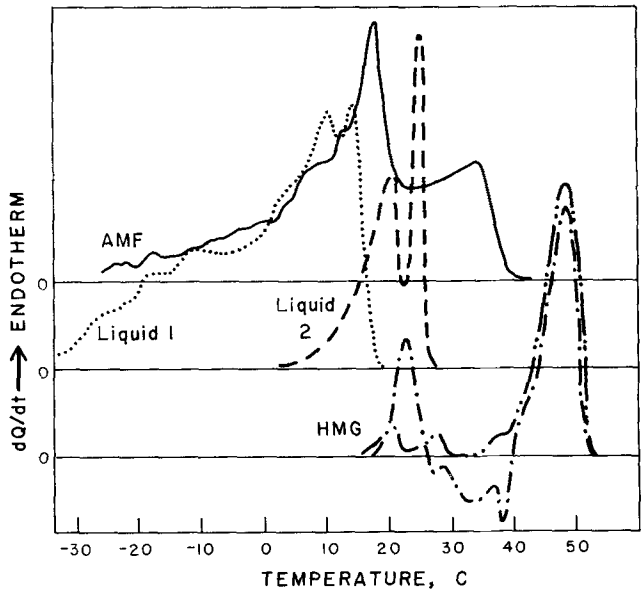

FIG. 3. Thermograms of fractions of anhydrous milk fat obtained during the preparation of high melting glyceride (30).

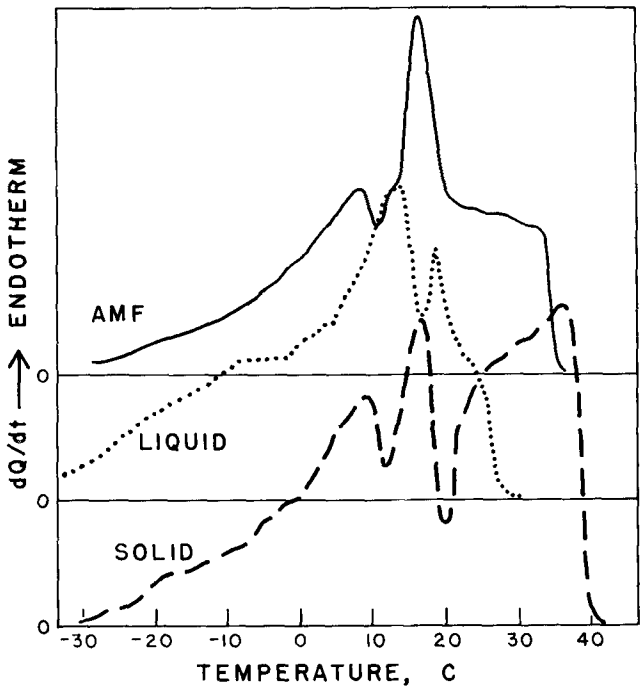

FIG. 4. Thermograms of anhydrous milk fat and two fractions made by the Fjaervoll process (20).

expected, control of crystallization conditions is critical.

DeMan (29) has reported on the composition and properties of eight milk fat fractions progressively crystallized from acetone. Crystals were collected at succeeding 10 C drops between 15 and -45 C. There were no sharp changes in fatty acid composition, but the same trends for increasing unsaturated and short chain acids and decreasing long chain saturates with decreasing mp of the fraction were noted. The trisaturated glyceride contents decreased smoothly throughout the fractionation. The free cholesterol and mono- and diglycerides concentrated in the low melting fractions, while the esterified cholesterol tended to crystallize with the intermediate fractions. The highest melting fraction was the only one containing substantially more *trans*-unsaturation than the original milk fat. Ca. 80% unsaturation in this fraction was *trans*. Although melting behavior of these fractions was not reported, it has been my experience that fractions prepared in this manner melt at temperatures considerably higher than the fractionation temperature. Although the compositions of the fractions are as complex as native milk fat, the melting patterns are simplified. Antilla (17) obtained similar results on 4 fractions prepared from milk fat by crystallization at -9 C, then successively fractionating the solid phases at 0 and 10 C.

Thermograms for each fraction obtained during the preparation of the high melting glyceride (HMG) fraction (30) are shown in Figure 3. This fraction first was isolated from fat globule membrane by Jenness and Palmer (31), but it is now apparent that its occurrence in membrane preparations is coincidental. The HMG fraction is defined by the scheme (32) used for its preparation, and it probably does not exist as a discrete entity in milk fat, either in bulk or in globules (33). As defined, it amounts to ca. 5% fat, and its chemical composition is strikingly similar to the highest melting fraction described by Chen and DeMan (34). Its influence upon butter hardness, however, is far out of proportion to its concentration (35). As can be seen in Figure 3, its removal causes the disappearance of the high melting shoulder in the thermogram of milk fat. This shoulder accounts for ca. 30% area under the curve. Part of the discrepancy is resolved when it is realized that the heat of fusion of low melting fats is much lower than that of high melting fats (36). Additional high melting fat, besides the HMG, crystallizes in the first step of HMG preparation, as shown in the curve for liquid 2 in Figure 3.

Solvent crystallization results in cleaner cuts, thermally more so than chemically, than does crystallization from melted fat. Thus, there is greater opportunity to tailor the products for the intended uses. On a commercial scale, however, the cost of solvent recovery is said to be prohibitive.

The most successful procedure for fractionation of fat on a large scale appears to be that described by Fjaervoll (37) and marketed by Alfa-Laval. It is in commercial operation in Sweden and under pilot plant evaluation in New Zealand. In this process, anhydrous milk fat is tempered at 25-28 C to crystallize the fat partly. An aqueous solution of a surfactant and an electrolyte is mixed in thoroughly. The resultant mixture appears to have two phases. The lighter phase is melted fat, the low melting fraction. The heavy phase is suspended crystals of the high melting fraction in the detergent solution. A special separator is used to remove the light phase. The other phase is heated to melt the fat, and a second separator is used to remove the molten high melting fat. The detergent solution is recirculated. The two oils are dried in vacuum chambers prior to packaging. The physical and chemical properties of the two fractions have been reported by Norris, et al. (38). As could be expected, the chemical differences are smaller than the physical differences. The hard fraction typically has a softening point ca. 3 C higher than the original fat, while the soft fraction typically has a softening point ca. 10 C lower. Exact values depend upon the composition of the starting fat, the setting temperature, and the cooling treatments given the final products. Setting temperatures should be chosen so that yields of the two fractions are somewhat equal.

The melting thermograms of an anhydrous milk fat and the two fractions made from it by this process are shown in Figure 4 (20). Both fractions show that the low melting region essentially is unaltered. The soft fraction has the abrupt cessation of melting typical for residual fats obtained by both crystallization from the melt and from solution. The hard fraction is enriched considerably in the fats responsible for the shoulder present in normal milk fat. The melting gap at 20 C is not altered by tempering at 20 C, so it does not represent an exotherm superimposed on an endotherm, as could be produced by polymorphic transitions (20,38).

Refractionation of the hard phase removes a liquid fat having thermal properties strikingly similar to intact milk fat but does not alter the resulting solid phase materially, unless the setting temperature is increased (20). Refractionation of the soft phase is more difficult to accomplish. It tends to form crystals that are too small for efficient processing. Furthermore, the major part of the liquid phase melts just below the softening point, so that efficient fractionation demands small changes in setting temperature. Notice the small temperature difference between maximum melting and completion of melting.

It is not difficult to imagine a few uses for fractions of milk fat. Butters of highly modified spreadability may now be possible. Hard fractions are suitable as ingredients in coatings and bakery products. HMG makes a fine candle. We still need much research into the characteristics desired for many applications, and we still need much imagination for entirely new uses.

In reading the literature on crystallization and fractionation of milk fat, one is left with several strong impressions. First, a surprising amount of information is available on crystallization of pure triglycerides. Second, progress is beginning to be made on the details of crystallization of complex triglyceride mixtures, such as milk fat. Third, much work on fractionation of milk fat suddenly has found processing importance since the development of commercial fractionation procedures. Much is yet to be done, but the progress is heartening.

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