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Detergent Fractionation of Tallow

D.A. GLASSNER and **E.A. GRULKE**, Department of Chemical Engineering, and **J.I. GRAY**, Department of Food Science and Human Nutrition, Michigan State University, East Lansing, MI 48824

ABSTRACT

The formation of an emulsified olein product can reduce the yield of the initial olein fraction in the detergent fractionation of tallow. Emulsion formation was linked to the crystal size obtained during partial crystallization and the surfactant concentration used for separation. Smaller crystal sizes in the partially crystallized oil caused the formation of more emulsified olein product, which would not coagulate during centrifugation. High surfactant concentrations inhibited the coagulation of olein drops during the centrifuging step. A rolling-up mechanism of detergency is proposed for the separation step, which explains the crystal size dependence of emulsified olein production.

INTRODUCTION

Three fat fractionation processes have been commercialized: dry, solvent and detergent (1). The dry fractionation process involves partial crystallization of the oil followed by vacuum filtration of the partially crystallized oil. The filtration yields clear oil but results in significant olein entrainment in the stearin fraction. Solvent fractionation of fats by hexane and other solvents yields fractions containing residual solvent. Process equipment must be explosion proof. Solvent recovery can be a significant portion of total process costs. In detergent fractionation, the liquid-solid separation is accomplished by adding an aqueous solution, containing a surfactant and an electrolyte, to a partially crystallized oil which preferentially wets the crystals into the aqueous solution. Detergent fractionation has the disadvantages of emulsified olein product formation and residual electrolyte and surfactant in the fractions obtained. The residual surfactant easily can be removed from the olein and stearin fractions by hot water washings, since the equilibrium is greatly towards water. Water washing also would remove any electrolyte present.

The detergent fractionation of a fat consists of a crystallization and a separation step. Previous researchers have given different recommendations for preferred conditions for the crystallization and separation steps. The crystallization step is a fractional crystallization at a specific temperature, resulting in a partially crystallized oil.

For palm oil fractionation, Haraldsson (2) reported the crystals should be β' or β type and that a 25 or 50 micron size was sufficiently large for the separation process to occur. Poot et al. (3) found that extremely small crystals, one micron and smaller, make efficient contact between the crystals and aqueous phase difficult, reduce the ability of the detergent to wet the crystals and lower the efficiency of the centrifugal separation. For tallow, Rek (4) and Bussey et al. (5) demonstrated that for lower temperature fractionations, 5 C to 25 C, the separation was more difficult to achieve than for higher temperature fractionations. This may have been due to differences in the crystals formed at the lower temperatures compared to those formed at 35 to 40 C. The importance of larger crystals was emphasized by this information, but was not explained.

The specific recommendations for the separation step vary widely. Kreulen (1) stated that the detergent solution generally contained 0.5% sodium dodecyl sulfate, but did not specify the basis. Rek (4) found that 0.6 wt % sodium dodecyl sulfate based on the weight of the partially crystallized oil was an optimum value. He also recommended a detergent solution to fat volume ratio of 0.2 to 0.8. The recommended concentration of electrolyte was 2.5 to 5.0 wt % based on the weight of the aqueous solution. Preferred electrolytes included sodium or magnesium sulfate or sodium citrate. Stein (6) showed that 1 to 2 wt % magnesium sulfate was a good electrolyte concentration and also recommended a 1:1 to 1:2 detergent solution to fat ratio, based on the volume fraction of the mixture. Bussey et al. (5) found that 4:1 electrolyte to surfactant ratio by weight was an optimum value. They used 0.6 wt % sodium dodecyl sulfate, based on the weight of the fat, as the surfactant.

There appears to be no consistent choice for the chemical concentrations reported in the literature. The surfactant and electrolyte concentrations used during the separation and the crystals formed during the crystallization both are said to be important to conducting the fractionation. Some of the difficulty in choosing the amount of surfactant and electrolyte to use could be avoided, if the mechanism of the separation process was better understood. Such information also might help to control the formation of emulsified olein product. The electrolyte concentration was varied, but was not found to have an effect on emulsion formation (7). The purpose of this investigation of the fractionation process was to determine relationships between emulsified olein production, the surfactant concentration and the crystal size.

EXPERIMENTAL

Crystallization

Both a partial crystallization and a partial melting process were used. The crystallizations involved a number of common conditions. The tallow was crystallized and separated at 40 C. All samples comprising a trial, or trials directly compared, were prepared by melting a large quantity of tallow and keeping it well mixed while the individual samples were made. This procedure insured the production of uniform samples. The olein and stearin fractions produced were weighed to determine the yield of each product. Any emulsion produced was not included in the product yield calculation, so the total product yield could be less than 100%. The tallow, olein and stearin were characterized by fatty acid analysis and iodine value calculation.

The partial crystallization vessel was agitated by a turbine impeller, with the characteristic vessel dimensions shown in Figure 1. The vessel had constant speed controls for agitation so a constant RPM stirring rate could be maintained. The outside of the tank was insulated to reduce heat loss through the vessel walls. Tallow was charged to the vessel at 55 C so it was completely liquid. The tallow was brought to 40 C and maintained there while crystallization occurred. A constant stirring rate of 240 rpm was maintained throughout the 18-hr crystallization time in order to prevent build-up of tallow crystals on the vessel walls.

The partial melting vessels were 600 ml beakers in which tallow was crystallized and stored at 4 C. The tallow was partially melted by immersion of the beakers in a constant temperature water bath. The tallow temperature reached the bath temperature within 2 hr and remained within 1 C of the water bath temperature. An 18-hr period for the melting and equilibration of the liquid and crystal tallow phases finished the crystallization step. No stirring was used during the 18-hr melting period.

Separation

The separation step was carried out by adding the detergent solution to the partially crystallized tallow or (partially melted tallow) in the crystallization vessel. The aqueous solution was mixed in the partial melting vessels using hand stirring until a uniform dispersion was created. The mixture was remixed several times before the entire mixture was

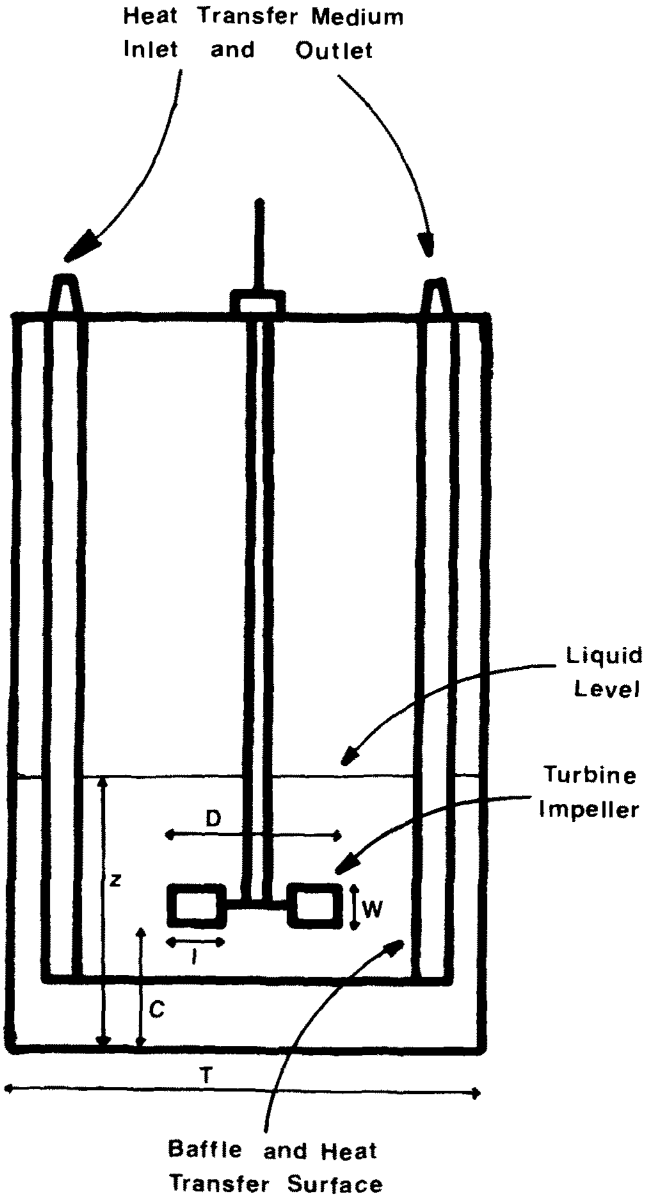

FIG. 1. Partial Crystallization Vessel. The heat transfer medium is circulated through the baffles. D, the impeller diameter, is 12 cm; T, the tank diameter, is 20 cm; z, the liquid depth, is 15 cm; C, the clearance of the impeller from the vessel bottom, is 7.6 cm; W, the blade width, is 2.0 cm; N, the number of blades, is 4, and l, the blade length, is 3.0 cm.

centrifuged. In the partial crystallization vessel, a gentle mixing using a 40 RPM impeller speed for 30 min is used. The mixture was then centrifuged, using 4000 × g relative centrifugal force.

Materials

The materials used in the experiments were obtained from the following sources: antioxidant-free tallow from a commercial supplier, sodium citrate from Mallinckrodt and sodium dodecyl sulfate from Fisher Scientific. Distilled water was used for the aqueous solutions.

Characterization of Tallow

The original tallow and the fractions obtained were characterized by fatty acid analysis and iodine value determinations. The methyl esters of the fatty acids were prepared by the method of Morrison and Smith (8). The methyl esters were then analyzed on a HP 5840A gas chromatograph using a column packing of 15% diethylglycol succinate (DEGS) on 80 to 100 mesh chromosorb WA (acid washed).

Flowrate of the carrier gas was 25 ml/min of nitrogen, and the column operating temperature was isothermal at 190 C. Iodine values were calculated from the fatty acid data. An average molecular weight and an average number of double bonds per triblyceride were calculated from fatty acid analysis data. The number of milliequivalents of iodine reacted per gram of triglyceride was then calculated.

RESULTS AND DISCUSSION

Crystal Size Effects

Two different crystal sizes were formed by the 2 different crystallization procedures. The partial crystallization procedure produced small, single fiber crystals. The partial melting procedure produced large polycrystalline agglomerates. The agglomerates form because an existing crystal is a good nucleation site for another crystal. Agglomeration did not occur in the partial crystallization procedure because the high rate of stirring broke apart any crystals that were agglomerated. A partial crystallization procedure was not used for the nonagitated system because the crystal nucleation and growth rates were too slow. The partial melting procedure is not recommended for large quantities of fat because of heat transfer problems in the viscous, partially melted fats.

In the partial crystallization process, the average crystals were cylindrical, with a diameter of 2 microns or less and a length of 10 microns. The crystal lengths ranged from 5 to 20 microns. Crystals recovered during the partial melting process had cylindrical diameters of 2 microns or less and averaged 50 microns in length. The crystal length ranged from 20 to 80 microns. The agglomerates of these crystals were considerably larger than the individual crystal size and were irregular spheres. The major differences between the 2 crystalline products were the much longer crystal sizes and the presence of agglomerates from the partial melting process. The agitation in the partial crystallization process apparently prevented crystal agglomeration.

The crystallization temperature of 40 C was chosen because the tallow fractionated at this temperature yields 20-40% solids. More solids would make the partially crystallized tallow too viscous. The mixing methods used for the 2 separation procedures are believed to be equivalent. This is because the wetting of the crystals into the aqueous phase is a very fast process. A short period of mixing is all that is necessary for the wetting to be accomplished.

Table I shows the separation results for the different crystal sizes. The results indicate a relationship between the formation of emulsified olein product and crystal size. Small crystals apparently cause an increase in the amount of emulsified olein if the surfactant and electrolyte concen-

TABLE I

Separation Results for Different Crystals

	Small crystals	Large crystals
TALLOW SAMPLE		
Approximate weight	4,000 g	200 g
Per cent unsaturated fatty acids	51.2	51.2
Per cent saturated fatty acids	48.8	48.8
Iodine value (meq I_2/g fat)	47.4	47.4
Crystal size and habit	Needles 10-20 microns in length, less than 2 microns in diameter	Spherulites 25-125 microns in diameter
SDS concentration (by weight of tallow)	0.6%	0.6%
Sodium citrate concentration (by weight of water)	3.6%	3.6%
Aqueous to fat volume ratio	0.6:1.0	0.6:1.0
OLEIN		
Yield	5 to 45%	65-70%
Per cent unsaturated fatty acids	54.2	54.9
Per cent saturated fatty acids	45.8	45.1
Iodine value (meq I_2/g fat)	49.9	50.5
STEARIN		
Yield	20%	30-35%
Per cent unsaturated fatty acids	39.2	42.6
Per cent saturated fatty acids	60.8	57.4
Iodine value (meq I_2/g fat)	37.4	40.2
Emulsified olein yield	35 to 75%	0 to 2%

trations are held constant. The saturated and unsaturated fatty acid contents of the fractions and the tallow indicate that the fractions have different properties than the original tallow.

At 40 C, the solid recovered from a partial crystallization process is less than the solid recovered from a partial melting process. In the partial crystallization experiments the temperature of the crystallizing fat was never below 40 C. The solids formed by crystal nucleation and growth. However, the partial melting samples are brought from storage at 4 to 40 C without completely melting the solid fat. The partial melting procedure results in a higher percentage of stearin product. The unsaturated fatty acid content of the olein in the 2 procedures was not much different. A larger difference in the unsaturated fatty acid content of the stearin fractions was noted. This larger difference in the fatty acid content is due to the smaller amount of stearin present.

The 3.6% electrolyte and 0.6% surfactant concentrations used in the partial crystallization experiments do not necessarily represent optimum values. They are in the range of values reported by other investigators (1,4,5).

The polymorphic type of the crystals (α, β or β') obtained in the crystallization process was not determined. It was observed by light microscopy that the individual crystals from either process were similar in cylindrical diameters. The crystals obtained from the partial melting process were much longer than those from the partial crystallization process. Even if the polymorphic type of the 2 crystal products was different, the effect of the polymorphic type on the crystal size should be minimal. Our hypothesis is that crystal size has the major effect on the separation efficiency.

Surfactant Concentration Effects

The effect of various surfactant concentrations on the olein and emulsified olein yields is shown in Figures 2 and 3. All trials indicated that the olein yield increased as the surfactant concentration rose. However, at higher levels of surfactant concentration, 1 to 2 wt %, an emulsion formed which was not disrupted by centrifugation. A marked drop in olein yield was observed at the higher surfactant concentrations, which was due to the presence of emulsified olein after centrifugation.

Two different partial melting temperatures, 38 C and 40 C, were used. Trials 1, 2 and 5 were replicates at 40 C. Trials 3, 4 and 6 were performed at 38 C. Trials 5 and 6 were conducted over an expanded surfactant concentration range compared to the earlier trials. The expanded surfactant range was used because emulsion formation for trial 4 had not occurred at 1.5 wt % surfactant.

The maximum olein yields for trials 1, 2 and 5 were 69.9, 69.2 and 68.7% respectively. The yields for trials 3, 4 and 6 were (62.8, 64.0 and 62.2%) reduced because of the lower fractionation temperature used. Each trial consisted of 6 separate fractionation experiments. All samples for a given trial were in the constant temperature bath at the same time, thus assuring that the temperature of each experiment in a trial was the same.

A drop in the olein yield with an increase in the surfactant concentration, for a given trial, indicates that some of the olein was emulsified at the higher surfactant concentration. The various surfactant concentrations causing emulsion are believed to be due to different crystal sizes present in different trials. Although the general procedures used on each sample were the same, various cooling stage times were used, which probably resulted in different crystal sizes forming. This occurred during the sample preparation time, not during the partial melting time.

Since the partial crystallization process resulted in small crystals and emulsion formation, the effects of surfactant concentration on olein recovery were not investigated for

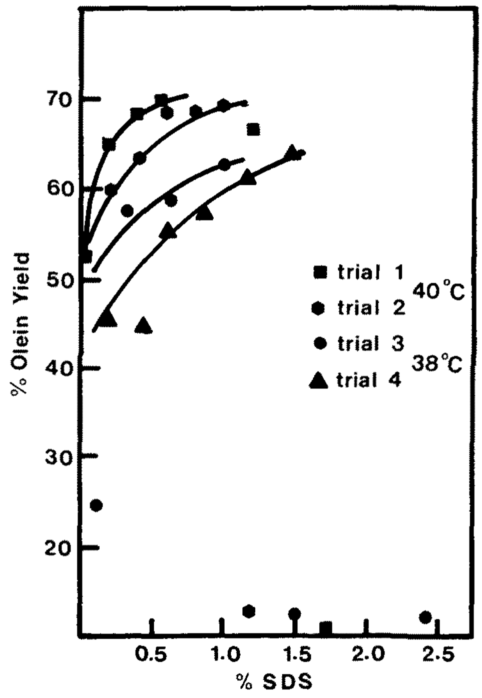

FIG. 2. Olein yield versus the percentage sodium dodecyl sulfate in the aqueous solution for the partial melting process. Trials 1 and 2 were replicate experiments with the fractionation temperature at 40 C. Trials 3 and 4 were replicate experiments with the fractionation temperature at 38 C.

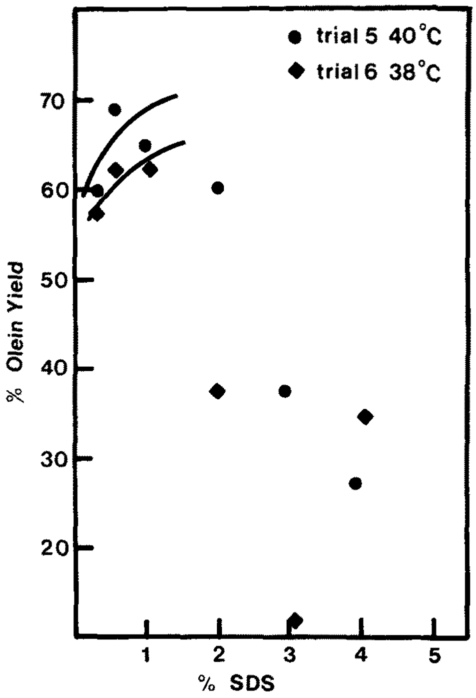

FIG. 3. Olein yield versus percentage sodium dodecyl sulfate in the aqueous solution for the partial melting process. Trials 5 and 6 were conducted with the fractionation temperature at 40 C and 38 C respectively.

this process. When a emulsion forms, olein yields vary greatly and seem to be dependent on mixing during the separation step (3).

Detergency Theory

The partially crystallized oil is considered to consist of fat crystals surrounded by oil. The crystals are recovered by the displacement of the oil by an aqueous solution containing surfactant and electrolyte. This suggests a detergency phenomenon. There is theory describing the displacement of an oil-fiber interface by a water-fiber interface if the water contains a sufficient amount of surfactant (9).

Surfactants are adsorbed at all kinds of interfaces (10). The adsorption of surfactants is important in the fractionation process because the interfacial properties of the crystal-olein, crystal-aqueous and aqueous-olein interfaces are altered by the adsorption. The degree of adsorption is dependent on the type of surfactant, the concentration of the surfactant, the other materials present in the solution and fat, and the material on which the surfactant is adsorbed (10). The adsorption of surfactants on carbon black increased with the addition of an electrolyte, sodium sulfate, and decreased with rising temperature.

The work of Adam (11) showed that oily soil was removed from fiber surfaces by wash water through a mechanism of preferential wetting. Kling (12) called the mechanism exchange wetting, because the oil-fiber interface exchanged to become a water-fiber interface.

Adam and Stevenson (13) and Moillet et al. (14) gave the following description of the preferential wetting or rolling-up mechanism. A fiber partly covered by a film of oil was immersed in a dilute aqueous surfactant solution, which did not completely displace the oil. A state of equilibrium resulted. The oil and the aqueous solution both remained in contact with the fiber. The surfactant molecules were adsorbed at the fiber-water and oil-water interfaces in a monolayer film. The film of surfactant molecules being adsorbed at the fiber surface displaced the oil because the surfactant adhered to the fiber surface more strongly than did the oil.

As the concentration of surfactant was increased, the oil was rolled up until it no longer was in contact with the fiber (11). The oil droplets were now surrounded by an aqueous phase. The surfactant was adsorbed at the oil-water interface helping to stabilize the oil-in-water emulsion (13).

If a smooth film of oil completely covers a fiber surface, an aqueous solution could not break through the oil to wet the fiber surface (15). A point at which the 3 surfaces meet was necessary to roll-up the oil. If a contact point for the 3 phases was established, the displacement of the oil-fiber interface by the aqueous-fiber interface could occur.

Proposed Mechanism for the Separation of Liquid and Solid Phases

Detergency theory can be used to explain the crystal size and surfactant concentration effects on the production of emulsified olein described earlier. Agitation provided after the addition of the detergent solution to the partially crystallized oil assists in contacting the oil, crystal and

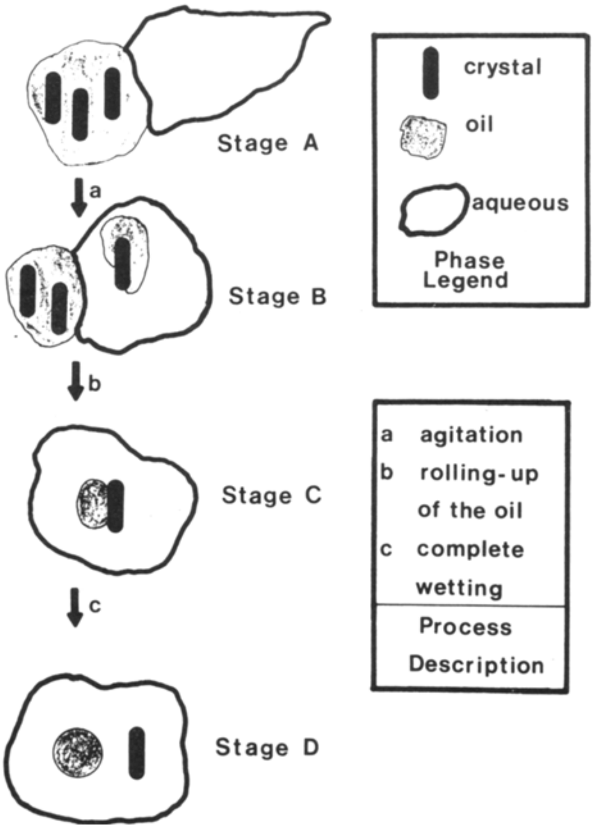

FIG. 4. Single Crystal Wetting Mechanism. The partially crystallized oil is mixed with the detergent solution. The mixing causes 3 phase contact points, allowing the oil to be rolled off the crystals and the crystals to be wetted into the detergent solution.

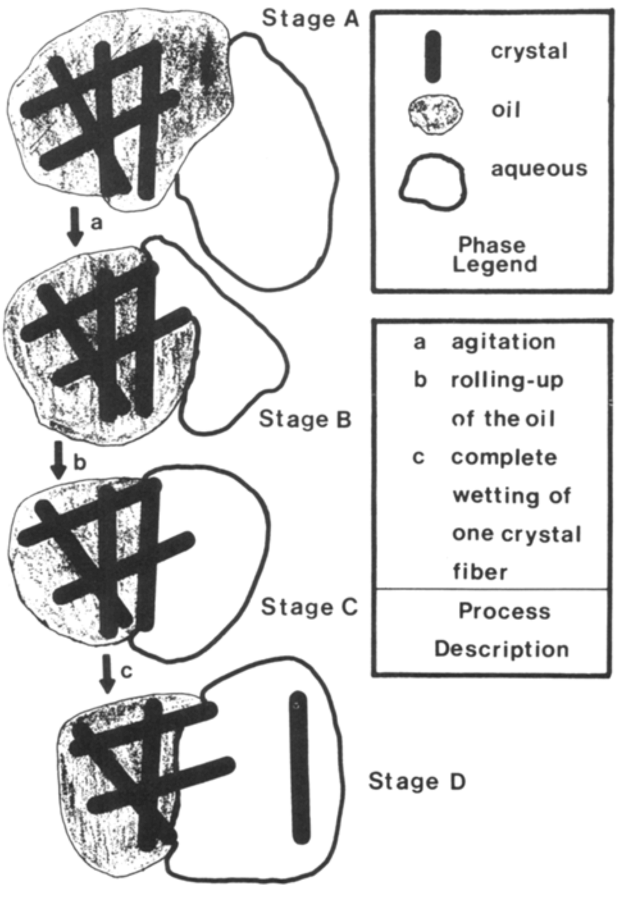

FIG. 5. Crystal agglomerate wetting mechanism. After mixing of the partially crystallized oil and the aqueous solution creates 3 phase contact points, the wetting of the agglomerates begins. The surfactant solution penetrates the boundaries between individual crystals and one by one they are all wetted.

aqueous phases. When the 3-phase contact is created, the high concentration of surfactant in the aqueous solution rolls-up the oil from the crystal surface almost immediately.

Figure 4 shows the process for the small single crystals generated by the partial crystallization procedure. Microscopic observation of the components of the process provided the basis for the mechanism diagrammed in Figure 4. Stages A and D were observed directly. Stages B and C are proposed based on detergency theory. It is believed that the intermediate steps occur rapidly enough that they cannot be observed by normal microscopic techniques.

The spherulitic crystals, as shown in Figure 5, are wetted in a similar way with the same end result except for the size of the olein droplets formed. The detergent wetting of the polycrystalline spherulites into the aqueous phase is attributed to the breaking up of the individual crystals from the spherulites. The surfactant solution penetrates the boundaries between the individual crystal fibers, and they are then separated from the large aggregate (16,17,18). The oil rolled-off each individual crystal remains in contact with oil surrounding the rest of the crystal agglomerate. When the last individual crystal is wetted the oil becomes an emulsified oil droplet that is much larger than the droplet from a small single crystal. Stage A was observed directly by microscope. After stage D is formed the rest of the crystal agglomerate is wetted quickly. A large number of single crystals in the aqueous solution have been observed by light microscopy after wetting a spherulite. No crystal agglomerates were observed after the separation.

Increasing the surfactant concentration with no change in oil droplet size is known to stabilize emulsions, especially with sodium dodecyl sulfate as the surfactant. If the oil droplet size is increased, with the surfactant concentration remaining the same, less force is required to coalesce the larger droplet with other oil droplets.

Poot et al. (3) found that when using a 5% sodium dioctylsulfosuccinate solution, the oil droplets must be greater than 12 m in diameter for them to coalesce during centrifugation. The final surfactant concentration was 1 to 3% by weight of the aqueous solution, or 2.0 to 7.5% by weight of the fat. Certainly the allowable low range of oil droplet size depends on the surfactant type and concentration.

Since smaller emulsified oil droplets are formed from the wetting of small crystals, increased emulsified olein product is expected when compared to the wetting of larger crystals. Increased surfactant concentration caused more emulsified olein product also. The principles of detergency applied to the fractionation process provided a mechanism to explain fractionation results. The authors are continuing to research the detergent fractionation of tallow in order to develop a quantitative model of the process and define the morphology of the crystals.

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