Action of Emulsifers in Promoting Fat Destabilization During the Manufacture of Ice Cream

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ABSTRACT

Several emulsifiers have been examined in ice cream processing to determine their relative emulsion destabilizing power. The hydrophilic lipophilic balance value of the emulsifier did not account for all of the differences in destabilization; however, destabilizing power corresponded with the resulting interfacial tension between the serum and lipid phases of the mix. Fat destabilization results from the combination of ice crystallization and shear forces during ice cream manufacture. Neither shear nor ice crystallization alone were sufficient to cause the magnitude of destabilization encountered in a typical barrel freezer. It has also been shown that polyoxyethylene sorbitan monooleate, the most powerful destabilizing agent, reduced the amount of protein adsorbed to the fat globule surface. Thus, it is suggested that, based on their ability to lower the interfacial tension, emulsifiers control the adsorption of protein to the fat globule surface. The fat globules thus become more susceptible to coalescence induced by the shear forces of agitation and ice crystallization during ice cream manufacture.

INTRODUCTION

Destabilization of the fat emulsion during the whipping and concomitant freezing of ice cream is responsible in part for building into the frozen product an internal structure offering the beneficial properties of dryness upon extrusion during the manufacturing stages (aids in packaging and novelty molding, for ex-

ample), a smooth-eating texture in the frozen dessert, and resistance to meltdown or good stand-up properties (necessary for soft serve operations) (2, 4). The action of emulsifiers in promoting this fat destabilization and the mechanisms of the destabilization phenomenon occurring during the freezing process have not been fully explained and are the focus of this research.

In most dairy emulsions, the aqueous continuous phase consists of a sugar and salt solution and a colloidal casein suspension. The discrete, globular phase consists largely of the partially crystalline lipid components, including a complex mixture of triglycerides, diglycerides, and monoglycerides (31). The interface has both hydrophilic and hydrophobic components and consists of any amphiphilic molecules present. These include some of the milk proteins, the phospholipids or lipoprotein particles, and any added surfactant (31). The amphiphilic molecules have the ability to lower the interfacial tension between the two phases (1, 14).

In an ice cream system, classical theories of emulsion stability being enhanced by the surfactant may not sufficiently explain their complex action (18, 20). Kloser and Keeney (19) presented evidence that the desired smooth texture and dryness upon extrusion of ice cream was a result of an increase in nonglobular or free fat known as fat destabilization and was enhanced by some of the emulsifiers in common use. The mechanism whereby good stand-up qualities are obtained in the extruded ice cream is not unlike that occurring in whipped cream, a product that depends upon partial churning of the fat for its foam stability. In ice cream dryness studies, all those factors promoting dryness also favored partial destabilization of the fat emulsion (18).

Kloser and Keeney (19) reported that monoglycerides of short-chain fatty acids were powerful destabilizers, whereas monoglycerides

of longer chain fatty acids were not so effective. Also, glycerol monooleate [hydrophilic lipophilic balance (HLB) = 2.8] was a more effective destabilizer than glycerol monostearate (GMS) (HLB = 3.8). They also found that Spans (HLB = 4.3 to 8.6) did not give extensive destabilization, whereas Tweens (HLB = 15) were very effective. The HLB number represents the portion of the emulsifier molecule soluble in the aqueous phase on a scale of 20 (1, 14).

Govin and Leeder (16) and Lin and Leeder (21) reported a direct relationship between deemulsification and HLB of emulsifiers in the HLB range from 4 to 16. They speculated that emulsifiers of low HLB become firmly associated with the fat globule, minimizing deemulsification upon agitation due to the retention of the fat globule identify. However, emulsifiers of higher HLB are only loosely anchored to the fat globule and thus are swept off during agitation, removing the protection of the globule to stresses and thus promoting consequent coalescence. Berger and White (7) interpreted Leeder's results as being caused by concentration of Tween at the interface due to a preferential adsorption of Tween.

Oortwijn et al. (23, 24, 25) and Walstra and Oortwijn (30) studied the amount of milk protein adsorbed to the surface area of fat in an emulsion under various conditions. They reported that added chemical surfactants reduced the surface excess, a function defined as the amount of protein adsorbed per surface area of fat (mg/m^2). This was also found by Barfod and Krog (3) and Goff et al. (15).

In examining the state of the fat in ice cream, Berger et al. (5) and Berger and White (6, 7) reported that high melting triglycerides in the form of concentric crystalline layers are present on the innermost side of the membrane. A highly concentrated solution of fat crystals in liquid fat exists within these crystalline layers. The solid:liquid fat ratio is temperature dependent. Temperature changes may be responsible for fat globule distortion and contraction during fat crystallization. This distortion causes weaknesses in the high melting triglyceride shell, which can then fracture under stress, releasing liquid oil from the center of the globule which in turn can form a cementing layer around other fat globules. The clusters

thus formed actually hold the ice cream serum in their interstices, resulting in the observed dryness. These fat globule chains may also envelope the air cells, thus improving overrun.

Thomas (28) stated that ideal destabilization of fat should form networks of fat globules, which could strengthen the lamellae of air cells and prevent serum drainage. However, if excessive fat destabilization occurred too early in the freezing process, before a certain viscosity is reached, air cells could be ruptured, making it difficult to develop the desired overrun. Churning could lead to the development of a buttery, coarse texture, and a watery serum could be evident upon melting. The concomitant formation of ice crystals also helps to create a barrier to excessive fat chuning by mechanical obstruction (11, 12).

It is generally accepted that air is necessary for rapid flocculation and coalescence of fat globules (31). When air is incorporated into an emulsion as in flotation churning, the large differences in interfacial tension between the air-serum interface and the fat-serum interface may cause some of the protein layer of the fat-serum interface to adsorb to the newly created air bubble. This desorption of membrane then causes a spreading of the liquid fat onto the surface of the air bubble. Because the system is dynamic, air bubbles collapse under shear forces, and the resulting layer of liquid fat coalesces into larger droplets or acts as a cementing layer in holding floccules or clumps together. As whipping proceeds, the constant formation and collapse of air bubbles and the continuous desorption of protein and spreading of fat at the air serum interface eventually leads to a complete churning of the emulsion (22, 26, 31). Fat destabilization in ice cream has been attributed to a similar process (2, 4). Liquid fat, either escaping from ruptured high melting glyceride (HMG) shells or expelled from the partially crystalline globules, acts as a cementing agent in tying together clumps or flocs which form during the whipping process in ice cream. If allowed to proceed too far, this creation and destruction of air cells can lead to excessive destabilization and formation of visible butter granules in ice cream.

A partially crystalline fat is necessary for clumping to occur (22, 31). van Boekel and Walstra (29) found emulsion stability of a

paraffin oil in water emulsion to be reduced by
six orders of magnitude when crystals were
present in the dispersed phase. This has been
attributed (10, 29) to the protrusion of crystals
into the aqueous phase causing a surface
distortion of the globule. The crystal pro-
trusions can then pierce the film between two
globules upon close approach. As the crystals
are preferentially wetted by the lipid phase,
clumping is inevitable. This phenomena may
account for partial clumping of globules under
a shear force.

Thus, emulsifier action may be related to
HLB numbers, interfacial tension values be-
tween the two phases in the presence of am-
phiphilic molecules, and to their effect on the
protein load at the fat surface. The fat de-
stabilization mechanism may be related to shear
forces or flotatation churning in the freezer and
to temperature changes affecting the fat and ice
crystallization processes. Hence, the objectives
of this research were to correlate the desta-
bilizing ability of the emulsifier to its HLB
number, since this concept has been explored
but with contradictory results; to correlate
the destabilizing power of the emulsifier with
the interfacial tension between the serum and
lipid phases of the emulsion in the presence of
the emulsifier; to examine the role of the shear
forces during whipping of ice cream, inde-
pendent of ice crystallization, in promoting
fat destabilization; to examine the role of ice
crystallization, independent of shear forces, in
promoting fat destabilization; and to examine
the influence of ice crystallization temper-
ature on the magnitude of fat destabilization so
as to elucidate any independent temperature
effects on fat crystallization or protein ad-
sorption.

MATERIALS AND METHODS

Destabilization Experiments

The destabilizing power of the following six
emulsifiers were compared: glycerol mono-
stearate (GMS, Dimodan PVK), glycerol mono-
oleate (GMO, Dimodan, LSQK, Grinsted
Products Inc., Industrial Airport, KA), sorbitan
monostearate (Span 60), sorbitan monooleate
(Span 80), polyoxyethylene sorbitan mono-
stearate (Tween 60), and polyoxyethylene
sorbitan monooleate (Tween 80, Polysorbate
80, ICI Americas, Wilmington, DE). Standard
ice cream mixes containing each of the emul-

sifiers were prepared and frozen. Four rep-
licates of each mix for each emulsifier were
performed. The basic formulation for all mixes
was 10% milk fat, 11% milk SNF, 10% sucrose,
5% corn syrup solids (Dri-Sweet 36, Hubinger
Co., Keokuk, IA), .1% stabilizer (Dariloid 100,
Kelco Div. of Merck, San Diego, CA, a proprie-
tary mixture of guar gum, xanthan gum, and
locust bean gum), and .08% emulsifier. The
sources of milk fat and serum solids for all
mixes prepared were fresh cream, 40% milk fat;
fresh skim milk, .04% milk fat, 9% milk solids;
and low heat spray process skim milk powder,
97% solids (Land O'Lakes).

All mixes were prepared by incorporating
the appropriate premixed dry ingredients into
the fluid milk and cream. Mixes were batch
pasteurized at 72°C for 30 min in a water
jacketed, air agitated vat. Following pasteuriza-
tion, all mixes were homogenized in a Mantin
Gaulin Type E two stage homogenizer (APV
Gaulin, Everett, MA) at 17.2 MPa, 3.4 MPa
on the second stage. Mixes were cooled in an
ice bath to approximately 4°C and aged 24
hours prior to freezing. Mix composition
was confirmed by checking milk fat (Bab-
cock) and total solids (oven drying) after
processing. A twofold vanilla-vanillin extract
(Virginia Dare Extract Co., Brooklyn, NY) was
incorporated at a rate of 3 ml/kg into all mixes
after aging. Mixes were frozen in a Taylor
batch freezer (Taylor Freezers, Rockton, IL).
Aliquots of aged mix (2 L) were whipped
and frozen to −5°C and held at this tem-
perature for the remainder of a total of 15
min in the freezer. It took approximately 6 min
for this temperature to be reached, at which
time the refrigeration was turned off and
whipping was continued. The temperature was
then maintained at −5 ± 1°C by toggling
the refrigeration as necessary.

Aliquots (40 ml) of mix were removed from
the barrel of the batch freezer every 2.5 min
starting at time zero and were analyzed for fat
destabilization by spectroturbidity (17). Sam-
ples were thawed, gently mixed, a sample was
removed with a 5 ml pipet, and 3 g were
weighed into a 50-ml Erlenmeyer flask, 27 ml
distilled water at room temperature were
added, 1 ml of the 1:10 dilution was placed in a
50-ml volumetric flask and diluted to the mark
with distilled water, and a sample of the 1:500
dilution was placed in a spectrophotometer

tube. The tube was centrifuged for 5 min at 1000 rpm (speed 6 on an IEC Clinical Centrifuge, Fisher Scientific, Fair Lawn, NJ), allowed to stand for 10 min, and absorbance was measured at 540 nm on a Bausch and Lomb Spectronic 21 Spectrophotometer (Fisher Scientific). Percent of fat destabilized was calculated as: $[(A_{unfrozen\ mix} - A_{sample})/A_{unfrozen\ mix}] \times 100\%$. Distilled water was used as a blank to zero the instrument. The percent of fat destabilized was then plotted against time in the barrel of the freezer.

The ability of Tween 80 to destabilize the emulsion during freezing when added posthomogenization was determined. Tween 80, .08%, was added to a standard mix containing no emulsifier after aging and 30 min prior to freezing by sprinkling a 2:1 dilution (45°C distilled water) of emulsifier into the gently agitated mix at 4°C. Fat destabilization by spectroturbidity was determined as above and compared to mixes with no emulsifier and with Tween 80 added prehomogenization as usual. Four replicates of each mix were prepared and analyzed.

The influence of shear, independent of ice crystallization, was determined in the batch freezer by introducing mixes emulsified with either Span 60, Span 80, Tween 60, or Tween 80 to the barrel, whipping for 15 min as before, but in this case, the refrigeration was used only to maintain mix temperature at 4°C. Thus, no freezing occurred. Aliquots were removed and analyzed for fat destabilization. The experiment was replicated four times. Destabilization curves from these four trials were compared to the destabilization seen previously when the same four mixes were frozen. The influence of the degree of ice crystallization was also determined in a continuous freezer (Cherry Burrell Vogt Model 303, 240 gal/h maximum capacity). A mix of standard composition, 80 kg, emulsified with .08% Tween 80, was prepared. The mix was added to the flavor tank. The pumps were started and speed, mix back pressure, and overrun vacuum were set and held constant. Samples were taken every 15 s after equilibrium conditions were reached. After the 1st min of sample collection, the refrigeration was turned on and samples were collected until the temperature had stabilized at −4°C. Temperature was continuously monitored during this time. The sample collection period lasted 6 min, and the experiment was replicated three times. Fat destabilization was analyzed in all of the samples and a plot of percent fat destabilized versus temperature of extrusion was prepared.

The importance to the fat destabilization process of changes brought about by the temperature drop from 0 to −4°C other than ice crystallization, such as the solid to liquid fat ratio, emulsifier crystallization, or protein desorption, was examined. Mixes were made with 15% glucose to depress the freezing point such that the decrease in the freezer from 4 to −4°C would not cause ice crystallization. Mixes were prepared as described above except that the sweetener content was replaced by 15% D-glucose anhydrous. Emulsifiers used were Span 60 and Tween 80. Freezing was performed in the batch freezer by dropping the temperature to −4°C, holding for 15 min, and then lowering the temperature to −8°C and holding for an additional 15 min in the freezer. Samples were collected every 2.5 min and analyzed for fat destabilization by spectroturbidity. The experiment was replicated four times. The freezing points of the glucose mix and of a control mix sweetened with 10% sucrose and 5% corn syrup solids were determined using an Advanced Milk Cryoscope at three dilution levels, and the calculated freezing curves were then prepared for comparison (8, 9, 27).

Aged ice cream mixes emulsified with GMS, a commercial blend of monoglycerides and diglycerides (40% alpha mono, IV<5, Germantown Manufacturing Co., Broomall, PA), or Tween 80 were placed in a −20°C freezer, 24 h, for quiescent freezing. Following thawing, fat destabilization by spectroturbidity was analyzed and compared with unfrozen mix samples. This experiment was replicated four times.

Interfacial Tension Experiments

The interfacial tension between anhydrous butter oil (Mid American Dairymen, Inc., Springfield, MO) and 11% milk SNF in the presence of the following emulsifiers was measured with a Fisher Surface Tensiometer, Model 20, using a duNuoy ring (1): .08% of GMS, GMO, Span 60, Span 80, Tween 60, or Tween 80 dispersed in their appropriate soluble

phase (i.e., monoglycerides and Spans in oil and Tweens in milk SNF solution). It was necessary to limit the concentration of the emulsifier at the interface, and thus, the emulsifiers were placed in their appropriate soluble phase to prevent the formation of an emulsifier layer. The aqueous solution (50 ml) at 70°C was placed in a 100-ml jacketed beaker, heated with 74°C water, which was circulated with a paristaltic pump, and the platinum iridium ring was placed in the solution and assembled to the Tensiometer. Anhydrous butter oil at 70°C was carefully layered on the top of the solution and the interface was allowed to age for 10 min prior to measurement. At that time, the ring was drawn from one phase into the other and the interfacial tension (dynes/cm) was determined. Four replicates of each were performed. Analysis of variance and least significant difference tests were performed on the data.
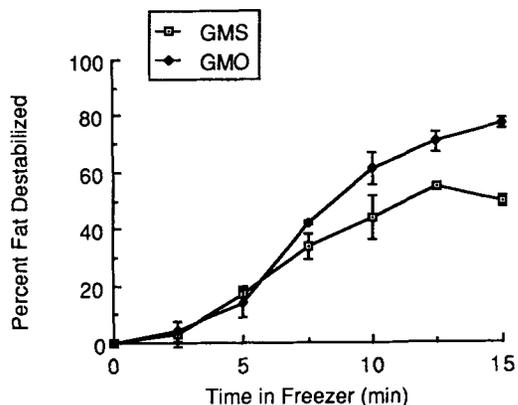

Figure 1. A comparison of glycerol monostearate (GMS) and glycerol monooleate (GMO) for the resulting fat destabilization when ice cream mixes emulsified with each were concomitantly whipped and frozen in the barrel of a batch freezer over the course of 15 min. Error bars represent 95% confidence limits of each value after four trials. Fat destabilization was determined by spectroturbidimetry.

RESULTS AND DISCUSSION

Destabilizing Power of the Surfactants

Three pairs of emulsifiers, two monoglycerides, two sorbitan esters, and two polyoxyethylene sorbitan esters, were chosen to examine the relationship between fat destabilization and properties of the emulsifier such as HLB, unsaturation, and polyoxyethylene groups (Table 1). The monoglycerides had similar HLB, as noted from Table 1. Stearic acid is a 18 carbon saturated fatty acid whereas oleic acid is an 18 carbon unsaturated fatty

TABLE 1. The three pairs of emulsifiers used in this study to examine the importance of hydrophilic lipophilic balance (HLB) or degree of unsaturation as a predictor of fat destabilization when ice cream mixes emulsified with these surfactants were frozen.

Common name	Chemical name	HLB
GMS	Glycerol monostearate	3.8
GMO	Glycerol monooleate	2.8
Span 60	Sorbitan monostearate	4.7
Span 80	Sorbitan monooleate	4.3
Tween 60	Polyoxyethylene sorbitan monostearate	14.9
Tween 80	Polyoxyethylene sorbitan monooleate	15.0

acid. It can be seen from Figure 1 that glycerol monooleate produced significantly more fat destabilization over the course of the 15 min in the barrel of the batch freezer than did glycerol monostearate. Span 60, sorbitan monostearate, produced significantly more fat destabilization than did Span 80, sorbitan monooleate (Figure 2). Similarly, Tween 60, polyoxyethylene sorbitan monostearate, produced significantly more fat destabilization than did Tween 80, polyoxyethylene sorbitan monooleate (Figure 2). It was also observed that Tween 60 produced significantly more fat destabilization than did Span 60. Likewise, the unsaturated polyoxyethylene emulsifier, Tween 80, produced significantly more fat destabilization than did Span 80 (Figure 2).

From these comparisons, it can be seen that the degree of fat destabilization was increased with the unsaturated emulsifiers and was increased with the polyoxyethylene derivatives. The HLB number did not account for the differences between the three pairs of surfactants (i.e., monoglycerides, Spans, Tweens), although the solubility of the emulsifier is probably one of the factors involved in interfacial action and fat destabilization. These results are in agreement with the early observations of Kloser and
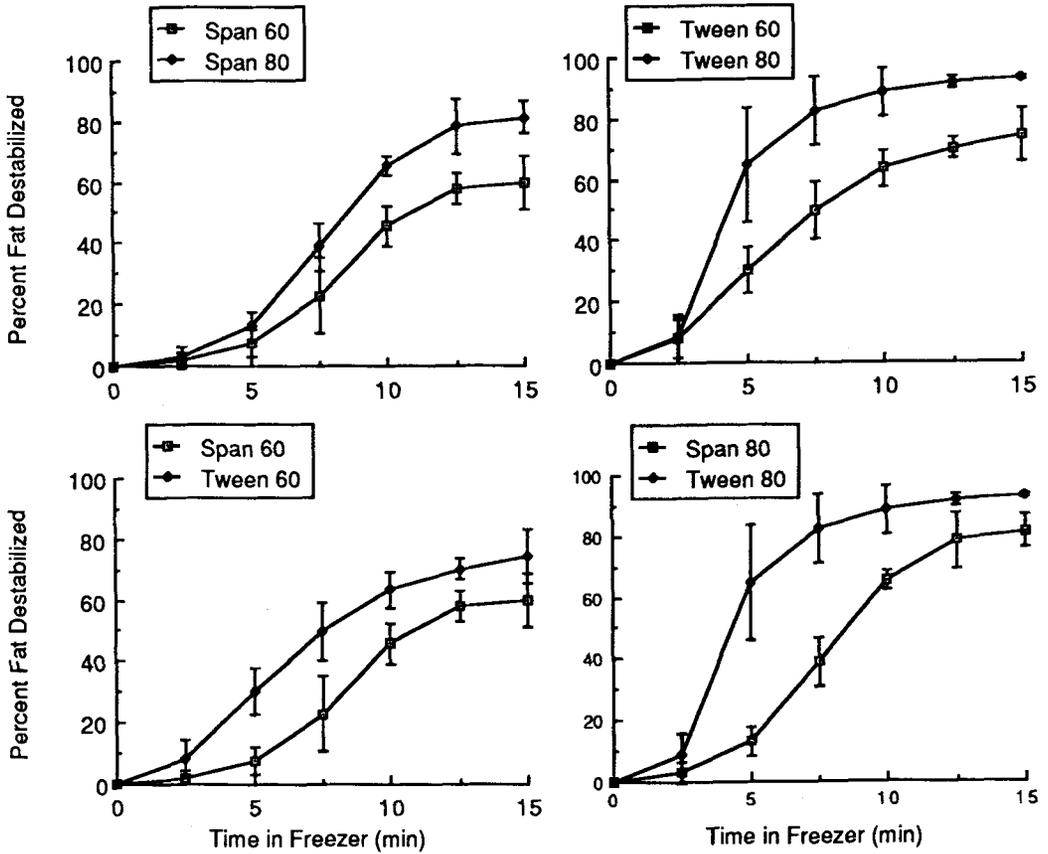
Figure 2. Fat destabilization of the various sorbitan esters as a function of time in the barrel of the batch freezer. The upper left plot compares ice cream mixes emulsified with sorbitan monostearate (Span 60) and sorbitan monooleate (Span 80). The upper right plot compares the polyoxyethylene sorbitan esters, Tween 60 and Tween 80. The lower left plot compares the saturated pairs, Span 60 and Tween 60. The lower right compares the unsaturated pairs, Span 80 and Tween 80. Fat destabilization was determined by spectroturbidimetry. Error bars represent 95% confidence limits on four replicates.

Keeney (19), and with Berger (4), as discussed in the introduction; however, the direct increasing relationship between HLB and fat destabilization as reported by Govin and Leeder (16) and Lin and Leeder (21) may be due to an increasing concentration of Tween at the fat surface in their experiments.

**Posthomogenization Addition
of Emulsifier**

Tween 80 (Polysorbate 80) is widely used in the ice cream industry to aid in drying a product that is normally quite wet or sloppy on extrusion, for example, a strawberry ice cream. In this regard, it is often added just prior to freezing. The ability of Tween 80 to destabilize the emulsion if added posthomogenization needs to be accounted for in developing an explanation of emulsifier action and fat destabilization. Therefore, the resulting fat destabilization when Tween 80 was added prior to homogenization and prior to freezing was examined. Tween 80 has the ability to promote fat destabilization when added just prior to freezing (Figure 3); however, the extent of fat destabilized is not as great as when the surfactant is present at homogenization.
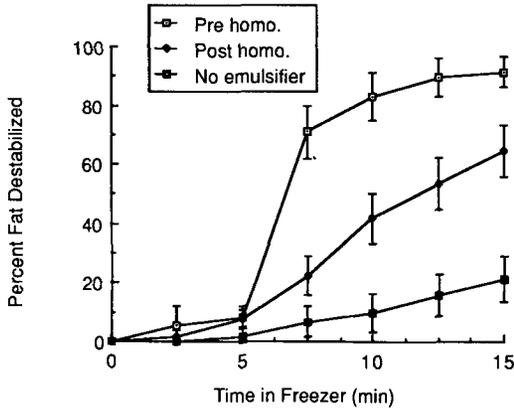
Figure 3. Fat destabilization resulting from the addition of Tween 80 to the ice cream mix either prior to homogenization (pre homo) or immediately prior to freezing (post homo) as determined by spectroturbidity, plotted as a function of time in the barrel of the batch freezer.

TABLE 2. Interfacial tension values (dynes/cm) between 11% milk solids-not-fat solutions and anhydrous butter oil in the presence of various emulsifiers dispersed in their appropriate soluble phase (.08%) at 70°C as measured by a duNuoy ring.[1]

Emulsifier	Interfacial tension
	(dynes/cm)
No emulsifier	6.16
GMS	5.52[a]
GMO	5.09[b]
Span 60	5.64[a]
Span 80	5.02[b]
Tween 60	2.42
Tween 80	2.24

[a,b]Values followed by the same letter are not significant ($P<.05$).

[1]n = 4.

Interfacial Tension as a Predictor

The interfacial tension between anhydrous milk fat and a milk SNF solution in the presence of the surfactants was measured. A difficulty encountered was the solubility of each emulsifier in the two phases. In cases where the emulsifier was more oil soluble and dispersed in the aqueous phase, it formed a layer at the interface after the 10-min equilibration time. It was thus decided to disperse the emulsifier in the phase in which it was most soluble so as to maintain a relative concentration at the interface. The results are given in Table 2. The interfacial tension associated with the unsaturated emulsifiers was significantly lower than with the saturated emulsifiers when the monoglyceride, Span, and Tween pairs are compared. Also, the Tweens produced the lowest values, whereas the Spans and monoglycerides produced significantly higher values when oleate pairs are compared with the stearates. Thus, an inverse relationship exists between the interfacial tension at the two phases and the fat destabilization that results when ice cream mixes with these surfactants are frozen. Tween 80 produced the highest degree of fat destabilization and the lowest interfacial tension, various other surfactants fell in between, and a mix with no emulsifier produced

the highest interfacial tension and least fat destabilization.

An assumption made is that the interfacial layer in this system is representative of the interface in an emulsion. This serves as a good approximation for the examination of relative trends and methods for the measurement of interfacial tension at the interface in an emulsion are extremely complex. Also, although the emulsifier would be added to the aqueous phase during ice cream manufacture, regardless of its relative solubility in each phase, it was thought that concentration at the interface in this experiment due to creaming would not be representative of surface concentration of the surfactant in an emulsion.

Influence of Shear on Fat Destabilization

If flotation churning was principally responsible for the destabilization of the fat emulsion during ice cream manufacture, or if the membrane was ruptured and swept off, thus exposing the fat and making subsequent coalescence possible due to mechanical action, then it was hypothesized that fat destabilization would occur when mix was subjected to the shearing action of the dashers and the blades independent of a temperature drop or ice crystallization in the mix. This hypothesis was tested by introducing ice cream mixes to

the batch freezer, starting the whipping process, but using refrigeration only to maintain the mix temperature of 4°C and not to induce freezing. Destabilization curves for each emulsifier obtained when the mixes were whipped in the absence of freezing are compared with the destabilization curves obtained when the ice cream mixes were conventionally whipped and frozen, as presented earlier (Figure 4). It is evident that a limited amount of fat destabilization is occurring from the mechanical action, that the same relative trends were seen in terms of the destabilizing power of each of the four emulsifiers, and that a significant reduction in the extent of fat destabilized was realized by removing the presence of the temperature drop and ice crystallization. The importance of ice crystallization can also be

noted in Figure 2 and 3 at the 5 to 7-min range. When the temperature of −5°C was obtained, fat destabilization increased rapidly.

The influence of ice crystallization on the fat destabilization process was also examined in the continuous freezer. The results are presented in Figure 5. As the temperature decreased through the freezing range from 0 to −4°C, fat destabilization increased from 10 to 60%. The mechanical action of the freezer from the pump, dasher, and blades was held constant across this range. It is evident, therefore, that some fat destabilization occurred as a result of this mechanical action. However, the magnitude of fat destabilization normally associated with optimal ice cream structure and texture, around the 60% range, was not developed until the temperature had fallen well below the freezing
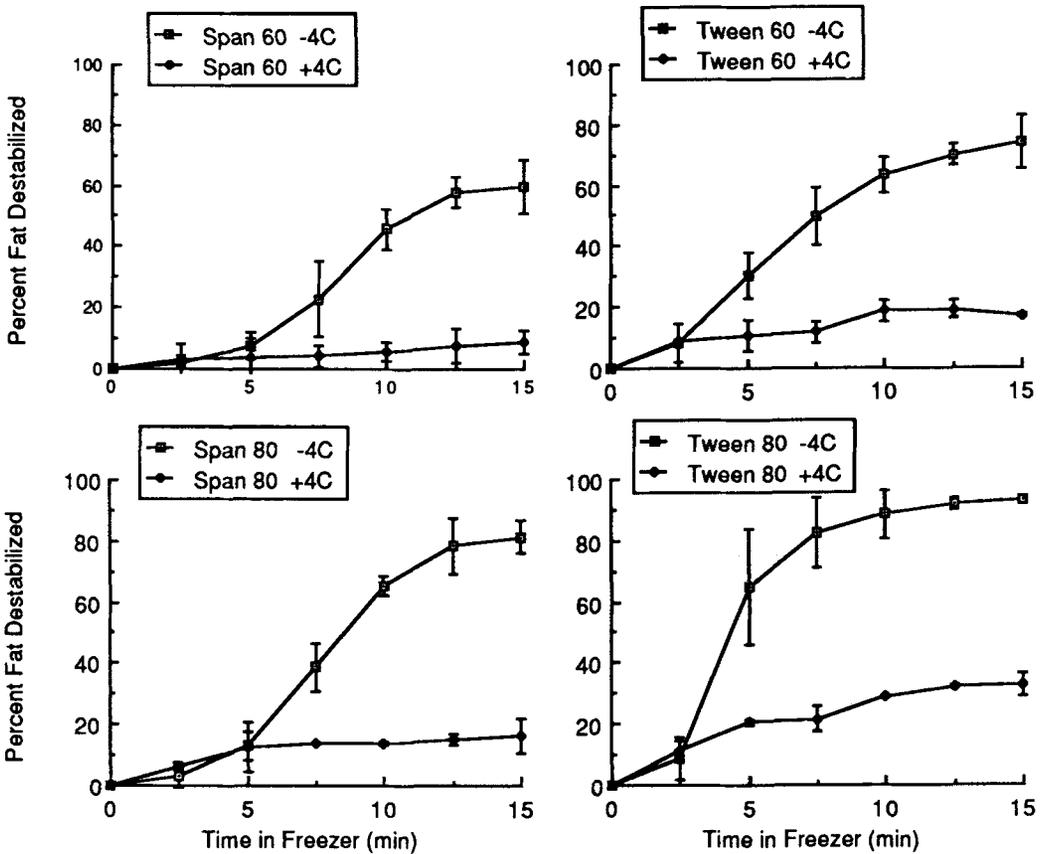

Figure 4. The influence of ice crystallization on the fat destabilization process in the batch freezer. The four pairs of emulsifiers are compared at −4°C, as in Figure 2, and at 4°C, in which case no freezing was involved. Error bars represent 95% confidence limits on four replicates.
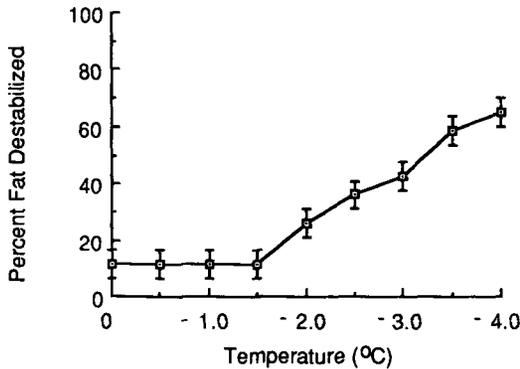
Figure 5. The influence of ice crystallization on the fat destabilization process in the continuous freezer as demonstrated by a reduction in the draw temperature.

TABLE 3. The effect of quiescent freezing of ice cream mixes on fat destabilization as measured by spectroturibidity (absorbance at 540 nm).[1]

Emulsifier in Mix (.08%)	Absorbance	
	Not frozen	Frozen
Glycerol monostearate	.79[a]	.79[a]
40% mono/60% diglyceride IV<2.5	.78[a]	.78[a]
Tween 80	.75[b]	.75[b]

[a,b]Values followed by the same letter are not significant (P<.05).

[1] n = 4.

range. Fat destabilization was still developing as the temperature reached steady state at $-4°C$. This confirms the results of the experiment run in the batch freezer. It also confirms reports that freezing ice cream at temperatures below the normal freezing range, as is the case in some commercial freezers that operate at -6 to $-8°C$, also enhances fat destabilization (4, 13).

The presence of ice crystals and the increased viscosity would contribute to the shear force exerted on the mix. However, the temperature drop would also potentially account for other changes in the chemistry of the mix, including a concentration of mineral salts and ions influencing electrostatic barriers of repulsion between the fat globules as water was frozen out of solution, a dehydration of membrane proteins causing disruption of the membrane, and a shift in the solid:liquid fat ratio as the temperature drop induced further fat crystallization. Thus, it was evident that either the ice crystallization process or the temperature drop and its associated effects were of prime importance to the destabilization phenomena. To elucidate fully the interaction between shear and ice crystallization, it was decided to freeze quiescently a number of ice cream mixes prepared with various emulsifiers and to examine the extent of fat destabilized upon thawing: in essence, to examine the influence of ice crystallization independent of any shearing action. No fat destabilization occurred as a result of this quiescent freezing

(Table 3). Mean absorbance values prior to and subsequent to quiescent freezing did not change, resulting in 0% destabilized fat according to the spectroturbidity method used in this project. Dynamic conditions were necessary to develop any partial coalescence in the mix.

Influence of Crystallization Temperature

The temperature drop from 0 to $-4°C$ is not only the range of ice crystallization but also when other phenomena, such as a shift in the solid to liquid fat ratio, occur (22, 30). This may partially account for fat destabilization. To test this hypothesis, a mix was made in which sugar content was totally replaced with glucose to lower the initial freezing point to $-4°C$. The freezing point depression of an ice cream mix is a function of the number of molecules in solution. Because glucose has half the molecular weight of sucrose and is also less than that of 36 dextrose equivalent (DE) corn syrup solids, the number of molecules in the 15% glucose mix was at least double that of the conventional mix, which was sweetened with a mixture of 10% sucrose and 5% 36DE corn syrup solids. Hence, the initial freezing point was reduced. The freezing curves of the glucose mix and the standard ice cream mix are plotted in Figure 6. The initial freezing points are on the y intercept. The standard mix began freezing at $-2°C$ and the freezing point of the glucose mix was $-4°C$. At $-4°C$, approximately 40% of the water in the conventional mix was frozen. To freeze approximately 40%
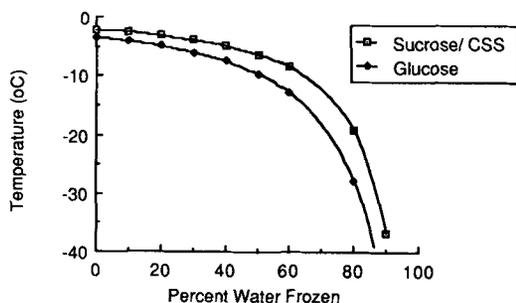
Figure 6. The freezing curves of the standard ice cream mix and of the ice cream mix sweetened with glucose showing the initial freezing point (at 0% water frozen) and the percent of water frozen as a function of temperature.

of the water in the glucose mix, a temperature of $-8°$C was necessary.

Glucose mixes emulsified with each of sorbitan monostearate (Span 60) and polyoxyethylene sorbitan monooleate (Tween 80) were then placed in the batch freezer and the temperature was reduced to $-4°$C and held for 15 min as before. The results are shown in Figure 7. In this case, where no ice crystallization occurred, the fat destabilization, shown on the left axis, was greatly reduced and equalled the destabilization seen previously when the mix was held at $4°$C. However, when
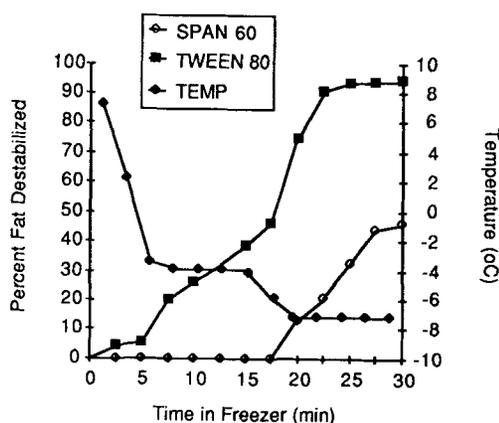

Figure 7. The extent of fat destabilized during the freezing time in the batch freezer (left axis) and the plot of temperature during that same time (right axis) for the mixes sweetened with glucose and emulsified with either Span 60 or Tween 80.

ice crystallization was induced by dropping the temperature in the freezer from -4 to $-8°$C at the 15 to 20-min interval, the rate of fat destabilization increased dramatically to approximately the same levels seen at $-4°$C in the conventional mix (Figure 4). The temperature is plotted on the right axis of Figure 7.

Changes in temperature from 0 to -4 to $-8°$C do affect the solid:liquid fat ratio in milk fat (31). Temperature changes in this range no doubt have other subtle effects on the chemistry of these emulsions. However, these temperature changes had little effect on the extent of fat destabilized in the ice cream mix as opposed to the dramatic impacts of the ice crystallization process. If the temperature drop from 0 to $-4°$C had a major impact on fat destabilization through fat crystallization, for example, then the glucose mix would have exhibited more destabilized fat at $-4°$C than it did. The ice crystallization process in the glucose mix from -4 to $-8°$C was similar to the freezing process in the conventional mix from 0 to $-4°$C. It also had very similar effects in terms of fat destabilization. Thus, it becomes clear that the overriding factor involved in the partial coalescence of the fat emulsion is ice crystallization in the dynamic conditions of the barrel freezer.

CONCLUSIONS

An inverse relationship was found to exist between the destabilizing power of the emulsifier and the resulting interfacial tension between the serum and lipid phases of the mix in the presence of that emulsifier. Emulsifier action may thus be summarized as follows. Added emulsifiers reduce the interfacial tension between the serum and lipid (fat globule) phases of the mix. It is thus more favorable for the emulsifiers, rather than caseins, to adsorb to the fat surface at homogenization, as this leads to a lowering of the net free energy of the system. It has been reported elsewhere that these small molecule surfactants can reduce the amount of casein adsorbed onto the surface of the fat globule (3, 15, 23). This reduction in the amount of casein, however, produces an emulsion that is less stable to the shear forces applied during ice cream freezing. As a result, the fat emulsion is destabilized to a greater extent in the presence of the emulsifiers.

Destabilization leads to the production of a smoother ice cream with good melt resistance due to the enhanced structure of the foam caused by the fat network.

The addition of Tween 80 posthomogenization also led to an increase in the percent of fat destabilized. It can be hypothesized that the proteins adsorbed to the fat globule, particularly the casein micelles, which remain largely intact and exhibit only limited spreading, do not form a cohesive network but can be displaced even after adsorption by small molecule surfactants, which lower the surface excess.

It appears that ice crystallization in the dynamic conditions of the barrel freezer is necessary for fat destabilization to occur. The concepts of flotation churning through the incorporation of air, or shear sensitivity involving the rupturing or stripping of the fat globule membrane, are not sufficient to explain the magnitude of fat destabilization that has been demonstrated in the presence of ice crystallization. These effects might be accounted for by the physical presence of the ice crystals contributing to the shear forces on the globule or to increases in viscosity that occur as ice crystallizes.

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REFERENCES

1 Adamson, A. W. 1982. Physical chemistry of surfaces. 4th ed. John Wiley and Sons, New York, NY.
2 Arbuckle, W. S. 1986. Ice cream. 4th ed. AVI Publ. Co., Westport, CT.
3 Barfod, N. M., and N. Krog. 1987. Destabilization and fat crystallization of whippable emulsions (toppings) studied by pulsed NMR. J. Am. Oil Chem. Soc. 64(1):112.
4 Berger, K. G. 1976. Ice cream Page 141 *in* Food emulsions. S. Friberg, ed. Marcel Dekker Inc., New York, NY.
5 Berger, K. G., B. K. Bullimore, G. W. White, and W. B. Wright. 1972. The structure of ice cream. Dairy Ind. 37:419, 493.
6 Berger, K. G., and G. W. White. 1971. An electron microscopical investigation of fat destabilization in ice cream. J. Food Technol. 6:285.

7 Berger, K. G., and G. W. White. 1976. The fat globule membrane in ice cream. Dairy Ind. Int. 41:199.
8 Bradley, R., and K. Smith. 1983. Finding the freezing point of frozen desserts. Dairy Rec. 84(6):114.
9 Bradley, R. 1984. Plotting freezing curves for frozen desserts. Dairy Rec. 85(7):86.
10 Darling, D. F. 1982. Recent advances in the destabilization of dairy emulsions. J. Dairy Res. 49:695.
11 Durham, K. 1963. Physical chemistry of ice cream. Chem. Ind. 8:681.
12 Durham, K., T. G. Jones, D. J. Shaw, and D. A. Walker. 1962. Factors affecting the structure of ice cream. 1st Int. Congr. Food Sci. Technol., Vol. 1:769.
13 Frazeur, D. R., and R. B. Harrington. 1968. Low temperature and conventionally frozen ice cream. 1. The effect of storage conditions and heat shocks on body and texture. Food Technol. 22:910. 2. Interrelationships associated with selected factors affecting body and texture. Food Technol. 22:912.
14 Friberg, S. 1976. Emulsion stability. Ch. 1 *in* Food emulsions, S. Friberg, ed. Marcel Dekker, New York, NY.
15 Goff, H. D., M. Liboff, W. K. Jordan, and J. E. Kinsella. 1987. The effects of polysorbate 80 on the fat emulsion in ice cream mix: evidence from transmission electron microscopy studies. Food Microstruct. 6:193.
16 Govin, R., and J. G. Leeder. 1971. Action of emulsifiers in ice cream utilizing the HLB concept. J. Food Sci. 36:718.
17 Keeney, P. G., and D. V. Josephson. 1958. A measure of fat stability in ice cream. Ice Cream Trade J. 54(5):32.
18 Keeney, P. G., and D. V. Josephson. 1962. Newer concepts on the mode of action of emulsifiers. 16th Int. Dairy Congr. Sect. VI, 53.
19 Kloser, J. J., and P. G. Keeney. 1959. A study of some variables that affect fat stability and dryness in ice cream. Ice Cream Trade J. 55(5):26.
20 Knightly, W. H. 1959. The role of the liquid emulsifier in relation to recent research on ice cream emulsification. Ice Cream Trade J. 55(6):24.
21 Lin, P. M., and J. G. Leeder. 1974. Mechanism of emulsifier action in an ice cream system. J. Food Sci. 39:108.
22 Mulder, H., and P. Walstra. 1974. The milk fat globule. Commonw. Agric. Bur. Farnham Royal, Bucks., Engl.
23 Oortwijn, H., and P. Walstra. 1979. The membranes of recombined fat globules. 2. Composition. Neth. Milk Dairy J. 33:134.
24 Oortwijn, H., and P. Walstra. 1982. The membranes of recombined fat globules. 4. Effects on properties of the recombined milks. Neth. Milk Dairy J. 36:279.
25 Oortwijn, H., P. Walstra, and H. Mulder. 1977. The membranes of recombined fat globules. 1. Electron microscopy. Neth. Milk Dairy J. 31:134.
26 Schmidt, D. G., and A.C.M. vanHooydonk. 1980.

A scanning electron microscopal investigation of the whipping of cream. Scanning Electron Microsc. 3:653.

27 Smith, D. E., Bakshi, A. S., and C. J. Lomauro. 1984. Changes in freezing point and rheological properties of ice cream mix as a function of sweetener system and whey substitution. Milchwissenschaft 39(8):455.

28 Thomas, E. L. 1981. Structure and properties of ice cream emulsions. Food Technol. 35(1):41.

29 van Boekel, M.A.J.S., and P. Walstra. 1981. Stability of oil-in-water emulsions with crystals in the disperse phase. Colloids and Surfaces 3:109.

30 Walstra, P., and H. Oortwijn. 1982. The membranes of recombined fat globules. 3. Mode of formation. Neth. Milk Dairy J. 36:103.

31 Walstra, P., and R. Jenness. 1984. Dairy chemistry and physics. John Wiley and Sons, New York, NY.