The Stability of Aerated Milk Protein Emulsions in the Presence of Small Molecule Surfactants

B.M.C. PELAN, K. M. WATTS, I. J. CAMPBELL, and A. LIPS
Unilever Research Colworth Laboratory, Sharnbrook MK44 1LQ, United Kingdom

ABSTRACT

The effects of milk proteins and small molecular surfactants on oil droplet surface coverage and emulsion stability were studied in model emulsions, and the results were related to the microstructure and physical properties of ice creams. Emulsions became increasingly more stable during partial coalescence at increased surface coverage as the protein concentration was increased. Model emulsions of 20% (wt/wt) 50:50 palm kernel oil and coconut oil, stabilized by skim milk powder emulsions, were more stable than sodium caseinate or whey protein emulsions, respectively. In ice cream premixes containing 12% butter oil and 13% skimmed milk powder, the water-soluble surfactant Tween 60 was much more effective in displacing protein from the interface than were oil-soluble surfactants, such as monoglycerides. Tween 60 destabilized the emulsions more than did unsaturated monoglyceride. Although saturated monoglyceride also displaced protein from the oil droplet interface, these emulsions were relatively stable at high surfactant concentrations under the shear conditions used in this study. The melting resistance of ice creams containing 12% butter oil was related not only to the amount of extractable fat, but also to the air cell stability, both of which were dependent on the type of surfactant. A better understanding of the functionality of surfactants in ice cream enables optimal ingredient selection, which should improve product properties.
(**Key words**: milk proteins, surfactants, emulsion stability, ice cream)

Abbreviation key: **MGP** = monoglycerol palmitate, **SMP** = skim milk powder.

INTRODUCTION

Interfacial aspects and competitive adsorption of caseins and whey proteins have been widely reported (5, 7, 15). Both caseins and whey proteins adsorb to a surface coverage of 2 to 3 mg/m^2 (3, 5, 7, 16), and this maximum amount of protein adsorbed per surface area of fat is assumed to be represented by a monolayer of proteins. The surface coverage in emulsions containing casein micelles, as present in milk, was found to be much higher at 10 mg/m^2 (12, 14). Electron micrographs have shown that casein micelles can adsorb and spread at the oil droplet interface (15). The stability of milk protein emulsions can be related to the adsorbed layer of proteins. In many food applications, though, the stability of the emulsion is not the only important consideration, because often a controlled destabilization of the emulsion is required to provide the desired texture and quality of the product (2). For example, in whipped cream and ice cream, fat droplets partially coalesce (clump) during the mechanical shear and air incorporation of the whipping process. In addition to milk proteins, food products such as ice cream often contain small molecule surfactants (often referred to as emulsifiers). The competition between proteins and emulsifiers at the interface is of importance to the final product structure (2, 6, 12). It has long been realized that these emulsifiers are not required to produce a stable emulsion, as sufficient protein is available (9, 11). Emulsifiers have been shown to displace virtually all milk proteins from the emulsion droplets (4, 6, 8). Both water-soluble surfactants, such as Polysorbate 80 (10), and oil-soluble surfactants, such as monoglycerides (1), can enhance the amount of fat destabilization during the freezing process. The mechanism is thought to be related to the displacement of milk proteins from the fat droplet interface, resulting in a lowering of the interfacial tension, thereby promoting the adsorption and coalescence of fat droplets at the interface of air and fat cells. (1). Fat aggregation is not only important to the stability of the air cells but also contributes to the structure formation in the ice cream via the formation of a fat droplet network, which can be noted, for example, from the improved melting resistance at increased amounts of destabilized fat (13). Although many publications have discussed either milk proteins and emulsifiers in model systems or the role of emulsifiers in products (e.g., ice cream), there are

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still gaps in the understanding of the relationship between interfacial aspects, emulsion destabilization, and the microstructure and physical stability of aerated food products such as ice cream.

This article describes some of the interesting features concerning the adsorption of milk protein in model oil-in-water emulsions, with or without emulsifiers present, and the relationship between protein surface coverage and the stability of the emulsion under shear conditions. First, this article discusses model emulsions, in which the oil phase consisted of an equal mixture of hardened palm kernel oil and coconut oil, stabilized by skimmed milk powder (**SMP**), sodium caseinate, or whey protein. Vegetable oil was used rather than butter oil to minimize the presence of impurities such as mono- or diglycerides. Second, this article describes the effects of small molecule surfactants such as Tween 60, monoglycerol palmitate (**MGP**), saturated and unsaturated monoglycerides on protein surface coverage, and emulsion stability in ice cream premixes. These ice cream premixes consisted of butter oil, SMP, sucrose, and water. These findings concerning protein surface coverage and emulsion stability are discussed in relation to the microstructure and melting resistance of ice creams made with butter oil and containing different concentrations of saturated or unsaturated monoglycerides.

MATERIALS AND METHODS

First discussed are model milk protein emulsions in which the oil phase consisted of an equal mixture of hardened palm kernel oil and coconut oil, at a total phase volume of 20% (wt/wt). This mixture of vegetable oils was chosen to minimize the presence of impurities such as mono- or diglycerides, which are usually present in butter oil. The protein concentrates studied include SMP (Eden Vale Food Ingredients, Northallerton, United Kingdom) containing 36% protein, sodium caseinate (DMV Spray Bland, Veghel, The Netherlands) containing 90% protein, and whey protein (Lactalbumin 70; Food Ingredients Specialists, Hayes, United Kingdom) containing 70% protein. These model emulsions, which were used to study the effect of milk protein concentration and type on emulsion stability, contained protein concentrations within a range of 0.5% to 7.5% (wt/wt). Throughout this article, the amounts of milk protein in the emulsions are expressed in terms of the intrinsic protein concentrations of the SMP, caseinate, and whey protein concentrates, represented as the percentage of protein in the total emulsion. In the preparation of these emulsions, the milk proteins were dissolved in deionized water at 60°C. The fat phase was melted in a 60°C water bath and added to the water phase; then, this pre-emulsion was heated to 65°C. The emulsions were homogenized (Crepaco, Chicago, IL) at an operating pressure of 140 bar and a temperature of 65°C. After the emulsions were cooled to 5°C, they were stored at this temperature for 3 d before tests were carried out.

Second, the article discusses ice cream premix emulsions, which contained 12% butter oil (Eden Vale Foods Ingredients), 13% SMP, 15% sucrose, and deionized water. The water-soluble surfactant Tween 60 (polyoxyethylene sorbitan monostearate) was obtained from Sigma Chemical Co. (St. Louis, MO). The oil-soluble emulsifiers studied included MGP (50% saturated monoglyceride and 40% diglyceride), Hymono 8903 (99% pure saturated monoglyceride), and Hymono 7804 (70% unsaturated monoglyceride and 30% saturated monoglyceride), which were all obtained from Quest International (Naarden, The Netherlands). Emulsifier concentrations ranged between 0.05 and 1.0% (wt/wt total emulsion). Throughout the article, Hymono 8903 is described as saturated monoglyceride and Hymono 7804 as unsaturated monoglyceride. In the preparation of these ice cream premix emulsions, Tween 60 was added to the water phase together with the SMP, and the oil-soluble surfactants were added to the fat phase prior to melting. These ice cream premixes were prepared exactly as the model emulsions were.

Measurements of protein loading involved centrifugation of the premix emulsions at $48{,}500 \times g$ for 2 h at 5°C (Beckman Instruments, Inc., Palo Alto, CA) to separate the oil from the aqueous phase. Surface coverage was then calculated from the specific surface area, as determined by small-angle light scattering (Malvern Mastersizer, Great Malvern, United Kingdom), and the difference between the total protein content and the protein concentration in the aqueous phase (14), as measured by nitrogen analysis (Foss-Heraeus Macro Nitrogen Analyzer, York, United Kingdom). The orthokinetic stability of the premixes was determined by shearing the emulsions (200 ml) at a constant speed (900 rpm) and at a fixed temperature (15°C) in the presence of air, using an experimental design, which has been described previously (17). The relative destabilization after 50 min of shear was determined by a solvent extraction technique using petroleum spirit (Fischer Scientific, Loghborough, United Kingdom). A higher amount of extractable (or destabilized) fat indicates a less stable emulsion, because more fat has coalesced. The

data for surface coverage and emulsion stability presented in this paper are the means of three measurements. The solid fat content in the emulsions was measured by ^{13}C-labeled nuclear magnetic resonance (Bruker AMX400; Karlsruhe, Germany) at a temperature of 5°C.

Ice creams were prepared with 12% butter oil, 13% SMP, 15% sucrose, and deionized water. Saturated or unsaturated monoglycerides were added at concentrations between 0.2 and 0.5% (wt/wt, total emulsion) at the expense of water. The premixes were mixed and homogenized as just described, but were pasteurized at 85°C for 15 s before cooling to 5°C. The premixes were subsequently stored for 2 h before being frozen in a Crepaco C freezer at an overrun of 100% and an extrusion temperature of –5.5°C. Ice creams were hardened at –35°C for 24 h and stored at –20°C for 3 d before further testing. No stabilizers were added to the ice cream emulsions to enable emulsifier effects to be studied more fully.

The microstructure of the ice creams was observed by low temperature scanning electron microscopy to obtain a qualitative image of the air phase state in the ice creams because quantitative measurement of air cell sizes is difficult. The stability of ice creams upon melting was determined by placing the samples from the –20°C freezer on a meshed grid in a temperature controlled cabinet (20°C) and weighing the material that leaked through the grid over 4 h.

RESULTS AND DISCUSSION

Surface Coverage and Emulsion Stability in Model Milk Protein Emulsions

Figure 1 shows the surface coverage of the fat droplets as a function of the protein solution concentration for the three protein concentrates. The percentage of solid fat in these model emulsions containing palm kernel oil and coconut oil was 60 ± 5% at 5°C, which is very similar to the concentration of solid fat in butter oil at this temperature. All emulsions presented in Figure 1 had a mean droplet diameter (d_{32}) of 0.55 ± 0.10 μm. Below 1.1% (wt/wt) protein, homogenization-induced clustering occurred in the SMP emulsions, which was noted from the increase in the mean droplet diameter and was verified by light microscopy. Oortwijn and Walstra (14) reported the appearance of homogenization clustering in reconstituted creams and attributed this effect to the bridging of casein micelles between fat droplets at low protein concentrations. Because the surface areas for these clustered samples could not be measured reliably, the surface coverage for these emulsions was not calculated. For whey protein emulsions, a maximum

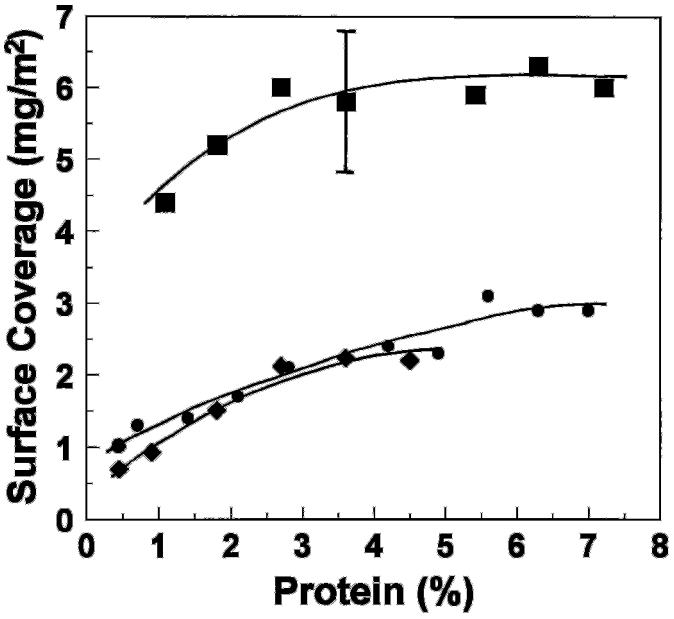

Figure 1. Surface coverage as a function of the protein concentration for whey protein (●), caseinate (♦), and skim milk powder (■) in emulsions containing 20% (wt/wt) 50:50 palm kernel oil and coconut oil.

surface coverage of 2.5 to 3 mg/m^2 was measured for protein concentrations above 5% (wt/wt), and, for sodium caseinate emulsions, surface coverage was 2 to 2.5 mg/m^2 for more than 2.5% (wt/wt) protein; in both systems, the measured amounts of surface coverage agreed very well with literature values found for β-LG (3, 7) and β-CN (5, 16), respectively. The plateau surface coverage in the SMP emulsions was much higher at 6 ± 1 mg/m^2. The higher value for surface coverage (10 mg/m^2) that was found in previous experiments (12, 14) was possibly caused by differences in emulsification conditions (e.g., temperature, pressure during homogenization, and number of passes) and source of material. The higher surface coverage in emulsions with SMP than in emulsions with sodium caseinate and whey suggest that casein micelles are adsorbed at the fat-droplet interface, which agrees with the reported findings of Oortwijn and Walstra (14) and Krog et al. (12).

Figure 2 confirms the expected increase in the stability under shear of the emulsions with increased surface coverage. Although the results presented here are for emulsions with 20% fat, the same relative trends were found for other fat percentages. Emulsions containing SMP appeared to be relatively more stable than sodium caseinate and whey emulsions, which can be related to the larger amount of protein adsorbed at the interface, thus providing a more effective steric barrier against coalescence. Caseinate

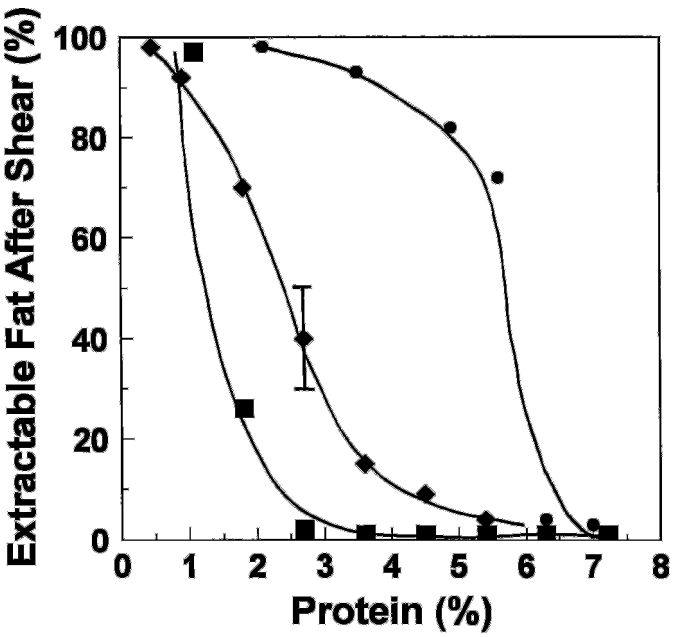

Figure 2. Extractable fat after shear as a function of the protein concentration for whey protein (●), caseinate (♦), and skim milk powder (■) in emulsions containing 20% (wt/wt) 50:50 palm kernel oil and coconut oil.

emulsions become increasingly less stable at surface coverage below the plateau level, indicating that maximum stability against partial coalescence or clumping is provided only at adsorption levels close to saturation. Whey protein emulsions seem to be the least stable of the three protein mixtures tested. Goff and Jordan (9) also noticed, in ice creams made with various milk protein concentrates in the absence of emulsifiers, that whey protein was less effective in fat stabilization in ice cream than, for example, sodium caseinate. It should be noted that the effects described here are found for model emulsions that were processed at temperatures below 65°C, without pasteurization. It has been reported previously (3) that whey protein emulsions become very stable against coalescence under shear after heating to temperatures above the denaturation temperature of the whey protein. The heating also caused an increase in the surface coverage. The effect of heat on whey emulsions before homogenization was not studied here.

Effects of Emulsifiers on Surface Coverage and Emulsion Stability in Ice Cream Premix Emulsions

All ice cream emulsions containing surfactants were found to have monomodal droplet distributions and a mean droplet diameter (d_{32}) of 0.50 ± 0.10 μm. The solid fat concentration in the premixes reached an equilibrium value of 50 ± 5% after 2 h at 5°C that was independent of the presence of emulsifiers and equivalent to the expected solid fat concentration in bulk butter oil at that temperature. It was therefore assumed that differences in emulsion stability were not related to fat crystallization but mainly to changes in interfacial properties.

Figure 3 shows the effect of the presence of Tween 60, MGP, and unsaturated and saturated monoglycerides on the surface coverage in the emulsions. Without emulsifier, the surface coverage was 11 ± 2 mg/m^2, which was much higher than that shown for SMP emulsions in Figure 1 (6 ± 1 mg/m^2). It is thought that the higher surface coverage found in these ice cream premixes than in the model emulsions in the previous section is related to the presence of sucrose, which possibly changes the solvent conditions and thereby the size distribution of the (adsorbed) casein micelles. The water-soluble surfactant Tween 60 strongly displaced the protein from the interface, resulting in a surface coverage of 0.5 ± 0.5 mg/m^2 at a concentration of 0.4%, which is in agreement with other results (4, 8, 14). Even at the highest emulsifier concentrations, the oil-soluble monoglycerides only partially displaced the protein from the interface. Although the emulsifiers displaced protein from the interface, the scatter in the data did

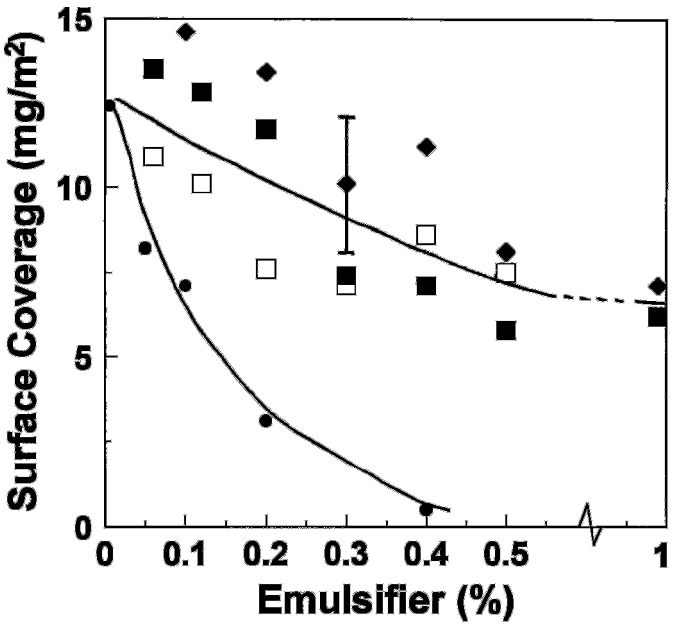

Figure 3. Surface coverage as a function of emulsifier concentration for Tween 60 (●), unsaturated monoglyceride (□), saturated monoglyceride (■), and monoglycerol palmitate (♦) in ice cream premix emulsions containing 12% butter oil, 13% skim milk powder, and 15% sucrose.

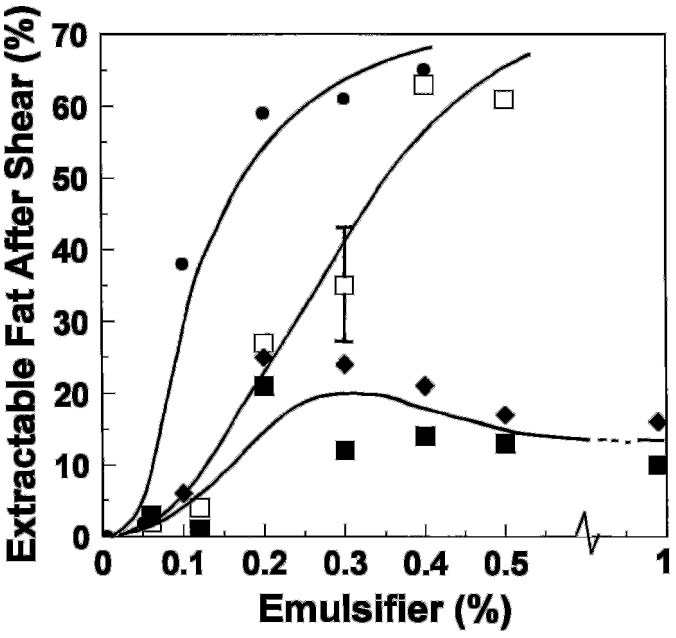

Figure 4. Extractable fat after shear as a function of emulsifier concentration for Tween 60 (●), unsaturated monoglyceride (□), saturated monoglyceride (■), and monoglycerol palmitate (♦) in ice cream premix emulsions containing 12% butter oil, 13% skim milk powder, and 15% sucrose.

not enable the confirmation of previously reported findings by Barford et al. (1), which suggested that unsaturated monoglycerides were more effective at displacing milk proteins than were saturated monoglycerides.

The stability of the emulsions in the model shearing experiment is indicated by the amounts of extractable fat in the premixes after shear in Figure 4. The water-soluble surfactant Tween 60 appeared to be most effective in destabilizing the emulsions, as indicated by the high percentages of extractable fat after shear at low surfactant concentrations. Increased concentrations of unsaturated monoglyceride also led to increasingly less stable emulsions. The lower stability of these emulsions is thought to be caused by the decrease in adsorbed protein. The surface coverage data presented here, however, do not completely describe the effects of the emulsifiers on the emulsion stability. Destabilized fat increases greatly after shear when the concentration of unsaturated monoglyceride is increased from 0.2 to 0.5%, but the decrease in surface coverage is small. Barford et al. (1) found that protein desorption was more pronounced when observed in transmission electron micrographs compared with desorption observed in protein surface coverage measurements when very similar emulsion systems were evaluated. Those researchers suggested that the apparent discrepancy might be because protein analysis does not measure the binding strength of protein to fat, but electron microscopy visualizes the protein-fat interaction directly. Transmission electron microscopy was not carried out on the emulsions in this study. The effect of pure saturated monoglyceride and MGP seems surprising. At 0.2%, these emulsifiers produced the expected decrease in stability. However, at higher concentrations, the emulsions appeared to become more stable, although protein coverage decreased slightly (Figure 3). Therefore, in the presence of saturated monoglyceride, protein coverage apparently is not the only important factor controlling orthokinetic stability. The presence of monoglyceride crystals at the interface, giving rise to Pickering stabilization, could be considered to be a possible explanation for the lack of instability of the emulsions at high concentrations of saturated monoglyceride.

Ice Cream Microstructure

The functionality of emulsifiers in ice cream is illustrated by the microstructure of ice creams containing either no emulsifier or saturated or unsaturated monoglyceride. It should be noted that the effect of Tween 60 was comparable with that of unsaturated monoglyceride in ice cream microstructure and melting resistance; MGP was similar to saturated monoglyceride. The amounts of destabilized fat that are mentioned in the following paragraphs are measured in the ice creams and not from shear experiments using the premix emulsions, as was done in the previous part of the article.

Ice creams without emulsifiers were characterized by the presence of large air cells (greater than 100 μm), some of which had coalesced, (Figure 5). The coalescence indicates poor air cell stability, which was probably related to the lack of fat droplets at the air cell interface. The amount of extractable fat in this product was very low (2%).

Increased concentrations of unsaturated monoglyceride in the ice creams resulted in an increase in extractable fat to 93% at 0.5% emulsifier. Some small air cells were observed in the microstructure of this ice cream, as shown in Figure 6, but extended air cell coalescence was also apparent. The smaller air cells were probably an indication of improved air cell stability by the adsorption of fat droplets at the air-cell interface because the fat droplets became more hydrophobic when protein was displaced by the unsaturated monoglyceride. The air cell coalescence observed in these highly destabilized fat samples is

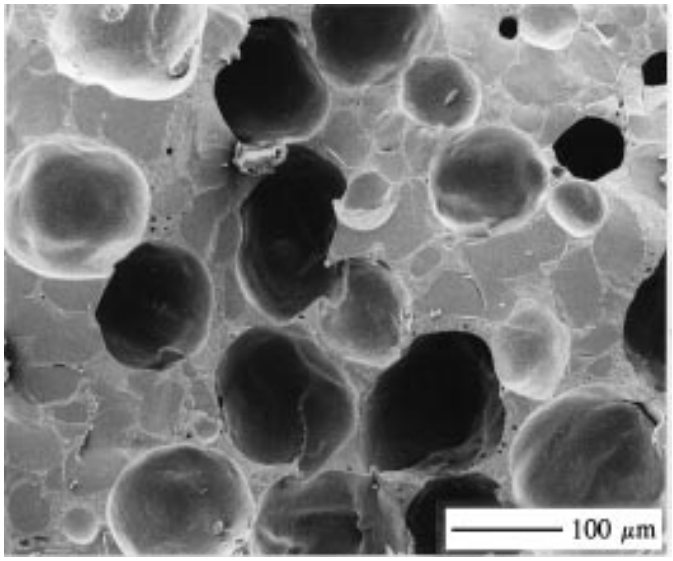

Figure 5. Microstructure of ice cream without emulsifiers, as shown by scanning electron microscopy. Ice cream contain 12% butter oil, 13% skim milk powder, and 15% sucrose; extractable fat was 2%. Black areas are air cells.

presumably similar to events during the later stages of whipping cream, in which overrun increased initially, followed by loss of air just before the emulsion finally churns because of excessive fat destabilization.

Ice creams containing saturated monoglyceride contained very little extractable fat (13% at 0.5% saturated monoglyceride). An increasing in the concentrations of saturated monoglyceride led to increasingly smaller air cells in the ice cream, as shown in Figure 7 for 0.5% saturated monoglyceride. It is not clear why saturated monoglyceride reduced the air cell size more than unsaturated monoglyceride did, but unsaturated monoglyceride may have caused too much fat destabilization and ultimately air cell coalescence. Saturated monoglycerides, however, could promote adsorption of fat droplets at the air cell interface, thereby stabilizing air cells but not leading to extensive fat aggregation.

Melting Resistance of Ice Creams

Increased fat destabilization in products is usually accompanied by drier appearance of the ice cream upon extrusion (at –5°C from the freezer) and improved melting resistance of the products, both of which are desirable characteristics (11, 13). Studying the melting behavior as a function of emulsifier is useful, because, in the absence of stabilizers, only fat and air can contribute to the shape resistance of the product once the ice has melted.

The ice cream without emulsifier, having large air cells and a low percentage of extractable fat (2%), has very poor melting resistance, as shown in Figure 8 (curve a). The complete sample had collapsed within 2 h, and the original premix remained. Increased amounts of unsaturated monoglyceride, which led to increased percentages of extractable fat, improved the melting resistance (Figure 8, curves b and c). The fat aggregation in this system is thought to hold the structure once the ice has melted; the material that remained on the grid was analyzed as containing a high concentration of fat, but the material leaking through the grid contained hardly any fat. The melting resistance of these ice creams did not appear to be correlated to the air phase stability, because, at high concentrations of unsaturated monoglyceride, the melting resistance was optimal, despite large coalesced air cells in the microstructure (Figure 6).

The melting behavior of ice creams containing saturated monoglyceride cannot be explained by fat aggregation; the amount of extractable fat was very low and independent of the emulsifier concentration. The structure remaining on the grid seemed to be related to the degradation of the foam structure in these ice creams. At 0.2% saturated monoglyceride (Figure 8, curve d), the melting resistance was comparable with that of the ice cream containing 0.2% unsaturated monoglyceride. When the ice in this ice

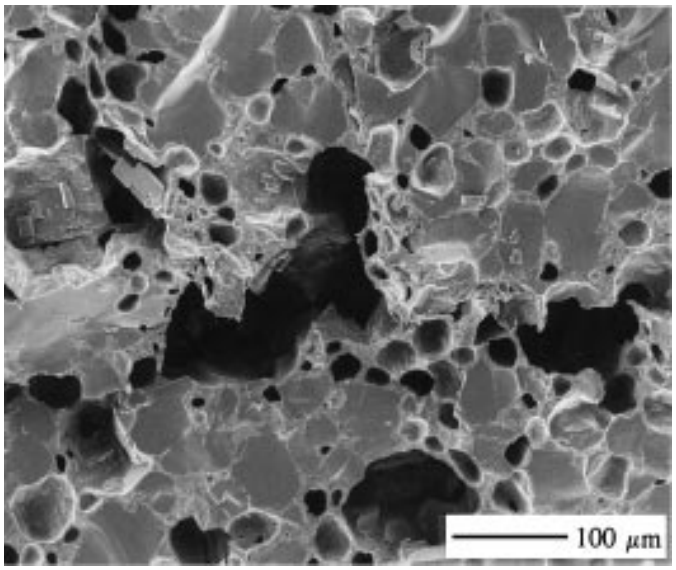

Figure 6. Microstructure of ice cream with 0.5% unsaturated monoglyceride, as shown by scanning electron microscopy. Ice cream contained 12% butter oil, 13% skim milk powder, and 15% sucrose; extractable fat was 95%.

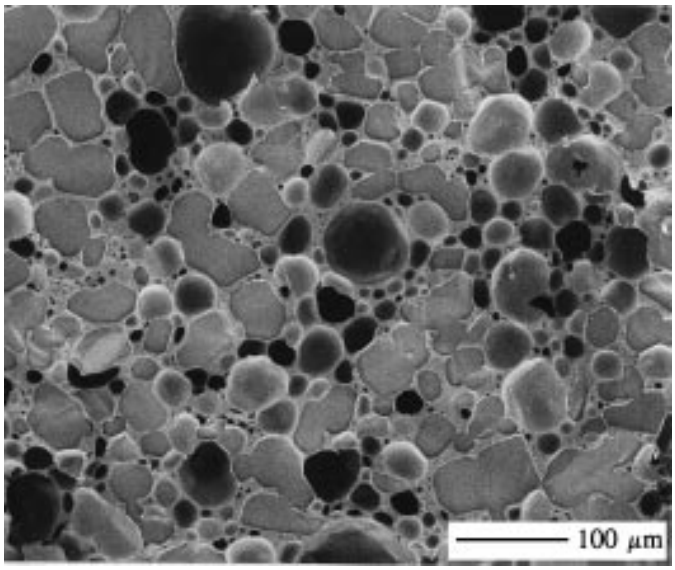

Figure 7. Microstructure of ice cream with 0.5% saturated monoglyceride, as shown by scanning electron microscopy. Ice cream contained 12% butter oil, 13% skim milk powder, and 15% sucrose; extractable fat was 13%.

cream melted, at 0.2% saturated monoglyceride and only 20% destabilized fat, some air cell coalescence was thought to occur, and some of the mix drained from the foam, but the material remaining on the grid was effectively higher in volume of the air phase and viscous enough not to flow through the grid. The material collected had the same composition as the initial premix. Although the melting resistance of ice cream containing 0.5% monoglycerides (13% extractable fat) seemed to be very poor, the material flowing through the grid had retained most of the air, indicating a very stable air phase, as had already been demonstrated by the small air cells observed in the microstructure (Figure 7). Because no fat aggregation occurred in the structure, this foam (at 50% volume of the air phase) was very fluid, and shape retention was poor. Although fat aggregation is the major contributor to the melting resistance of ice creams, the stability of the air phase can influence the degradation of the structure as well.

CONCLUSIONS

The shear stability of emulsions increased when amounts of protein added to the emulsions increased and more protein was adsorbed at the fat droplet interface. For whey protein emulsions, a maximum surface coverage of 2.5 to 3 mg/m^2 was measured for protein concentrations above 5%, and, for sodium caseinate emulsions, coverage was 2 to 2.5 mg/m^2 for more than 2.5% protein (independent of fat phase volume). The plateau in SMP emulsions was much higher, at 6 ± 1 mg/m^2. The SMP-stabilized emulsions were more stable against partial coalescence under shear conditions than were caseinate emulsions, presumably because of the higher percentage of adsorbed protein. Whey protein emulsions were less stable than either SMP or caseinate emulsions.

The water-soluble surfactant Tween 60 was much more effective in displacing protein from the fat droplet interface than were oil-soluble surfactants (such as monoglycerides). For most systems studied, orthokinetic stability decreased for lower protein loadings, as it did for emulsions made with milk proteins alone. The functionality of saturated monoglyceride and MGP was more complicated because no strong decrease in emulsion stability occurred during protein displacement from the interface. Although the mechanism by which monoglyceride stabilized the emulsion at high concentrations is still not understood fully, the mechanism is thought to be related to the crystallization of the monoglyceride in the fat droplets.

For ice cream, emulsifiers displaced and destabilized fat, resulting in the appearance of smaller air cells and improved resistance to melting, although, if

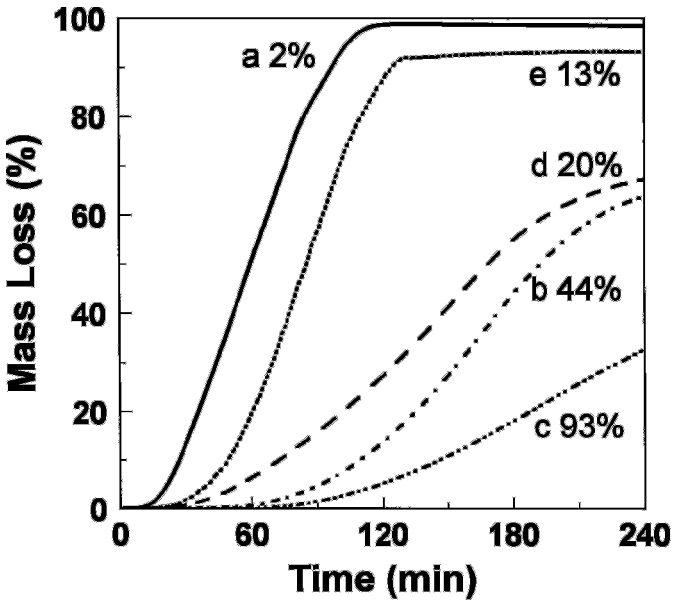

Figure 8. Melting resistance at 20°C of ice creams containing 12% butter oil, 13% skim milk powder, and 15% sucrose. Melting resistance is represented by the mass loss as a function of time (a: no emulsifier, b: 0.2% unsaturated monoglyceride, c: 0.5% unsaturated monoglyceride, d: 0.2% saturated monoglyceride, and e: 0.5% saturated monoglyceride). Percentages indicate amount of extractable fat in ice creams.

extractable fat concentrations were too high, air cell coalescence was extensive. With increased concentrations of saturated monoglycerides or MGP, however, the air cells in the ice creams were reduced in the absence of significant fat destabilization. In these products, the melting resistance appeared to be related more to the degradation of the foam structure. A better understanding of the functionality of small molecule surfactants in stabilizing fat droplets and air cells is required to explain the functionality of saturated monoglyceride in a complex food system such as ice cream.

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