Chapter 7
Emulsifiers in Dairy Products and Dairy Substitutes

Stephen R. Euston

7.1 Introduction

Bovine milk has been an important source of food for human beings for thousands of years. Not only is milk a very nutritious food in its own right, but it is also a very versatile starting point for many other dairy products.

Milk is a complex food emulsion and colloidal sol. Table 7.1 gives the composition of whole cow's milk. The emulsion is composed of fat droplets dispersed in an aqueous phase containing protein. The protein is in the form of both casein micelles, which are themselves colloidal particles, and free in solution as whey protein. A considerable reserve of knowledge has been assembled on the structure and properties of milk proteins (Swaisgood, 1992). The fat droplets are stabilized by an adsorbed layer of protein and phospholipid called the 'milk fat globule membrane' (MFGM), which is distinct from the aqueous phase protein (Walstra & Jenness, 1984). The average composition of the MFGM has been estimated to be about 48% protein, 33% phospholipid, and 11% water, with the remainder made up of other minor lipid components (Walstra & Jenness, 1984). The phospholipid fraction of the membrane is composed of lecithin, phosphatidyl ethanolamine, phosphatidyl serine, phosphatidyl inositide, plasmalogens and sphingomyelin. Phospholipids are important food emulsifiers in their own right. The contribution that they make to the stability of the milk fat globule is not well understood, but their use as food-grade emulsifiers has been the subject of extensive fundamental research (Courthaudon et al., 1991; Dickinson et al., 1993a; Dickinson & Iveson, 1993).

Because of its biological origin, milk is particularly susceptible to microbial and physical deterioration. This severely limits the shelf-life of raw milk. To overcome this milk can either be heat treated to kill bacteria or converted to other products that are more stable due to a decrease in pH, lowered water activity or the presence of salt. Until this century the conversion of milk to butter, cream, ice cream, and various types of cheese had been more of a craft than a science. It is only relatively recently that an albeit incomplete understanding of these processes has been available. It is now understood that the formation of these milk-based products is a consequence of either the destabilization of the dispersed-phase fat droplets (as in butter, ice cream and whipped cream) or of the dispersed aqueous-phase proteins (as in cheese).

G.L. Hasenhuettl and R.W. Hartel (eds.), *Food Emulsifiers and Their Applications*.

Table 7.1 Approximate composition of bovine milk

Component	Average content (wt%)	Range (wt%)	Average dry matter (%)
Water	87.3	85.5–88.7	–
Solids, non-fat	8.8	7.9–10.0	69.0
Fat in dry matter	32.0	21.0–38.0	–
Lactose	4.6	3.8–5.3	36.0
Fat	3.9	2.4–5.5	31.0
Protein	3.25	2.3–4.4	26.0
Casein	2.6	1.7–3.5	20.0
Mineral substances	0.65	0.53–0.80	5.1
Organic acids	0.18	0.13–0.22	1.4
Miscellaneous	0.14	–	1.1

From Walstra and Jenness (1984), Reprinted by permission of John Wiley & Sons, Inc.

To control the structure and stability of these products, the manufacturer can add a range of permitted additives that can be either naturally occurring or artificial. One of the most versatile of these additives are the low molecular weight emulsifiers.

In the following pages, the major emulsifier-containing dairy and imitation dairy products will be reviewed. A brief description of their production will be given where relevant, with emphasis on the role that emulsifiers play in the formation and stability of the product.

7.2 Ice Cream

Ice cream is probably the most complex food that we encounter. In addition to its scientific complexity, ice cream also has a complex history. Ancient texts confirm that ice has been used to cool beverages and foods for 4000 years. During this time several examples of cooled desserts have appeared. Production of a product closer to modern ice cream requires lower temperatures than possible by cooling with ice alone. In Europe this had to wait until the fifteenth or sixteenth centuries when the knowledge (long known to Arab scientists) that a mixture of ice and salt could be used to produce sub zero temperatures was acquired from the East. It wasn't until the nineteenth century that ice cream became available to all but the aristocracy in Europe, and until the twentieth century that mass production started.

Ice cream is both a foam and an emulsion, and it contains ice crystals and an unfrozen aqueous phase whose freezing point is depressed by freeze concentration of salts, sugars, and polysaccharide stabilizers (Clarke, 2005). Despite its obvious complexity, ice cream has been widely studied, and much is known about the formation of its structure and the role that low molecular weight emulsifiers play in this (Govin & Leeder, 1971; Lin & Leeder, 1974; Goff, 1988; Krog & Barfod, 1990; Barfod et al., 1991). A typical ice cream formulation is shown in Table 7.2.

Ice cream manufacture is a relatively simple process. The ingredients are mixed, heated to destroy pathogens, and then homogenized. The homogenization step is

Table 7.2 A representative composition of ice cream

Constituent	Weight percent in ice cream
Fat	10.0
Milk solid, non-fat	11.0
Sugar	13.0
Stabilizer	0.2
Emulsifier	0.5
Water	65.3

Based on Rosentahl (1991), Milk and Dairy Products, Properties and Processing

included to reduce the fat droplet size so that churning of the fat does not occur upon whipping. An in-line pasteurization step is then carried out prior to cooling to 4 °C and ageing of the mix at this temperature for at least 4 h. During this time milk proteins are able to redistribute between the fat surface and the aqueous phase and fat crystallization occurs. The ice cream mix is then aerated and froze in a continuous freezer. Freezing is completed by hardening the packed ice cream at minus 18 °C initially, and finally at minus 25 °C (Arbuckle, 1986; Rosentahl, 1991; Varnan & Sutherland, 1994; Clarke, 2005).

An acceptable ice cream product can be made without the addition of low molecular weight emulsifiers. Goff and co-workers (Segall & Goff, 1999, 2002a,b) have demonstrated that ice cream with acceptable physical properties can be made in the absence of emulsifiers if a 'two-phase process' is used. In this process the fat is emulsified with some of the protein and water, and then combined with the rest of the water and aqueous phase ingredients just before freezing (Segall & Goff, 2002b). In comparison to ice cream made by a conventional process with emulsifiers, the product made using the two-phase process had a comparable level of fat destabilization and meltdown rate, but the overrun (degree of air incorporation) was lower.

It has been known for several years, however, that incorporation of emulsifiers into ice cream results in a product that whips more easily, is drier (a necessary requirement in moulded products), has improved melt-down resistance, and has a smoother body and texture (Arbuckle, 1986). In addition to this, the ice cream has a higher overrun, the air is more finely dispersed, and the foam structure is more stable if emulsifiers are present (Keeney, 1982). An understanding of the mechanism by which emulsifiers change these properties has emerged over the past few years (Goff, 1988; Krog & Barfod, 1990; Barfod et al., 1991). Before describing the role of emulsifiers in ice cream structure formation, it is pertinent to consider the structure of the adsorbed layer formed around the fat droplet in the ice cream premix emulsion, since this plays a large role in determining emulsion droplet stability, and hence the stabilization of ice cream foam. During the homogenization stage the ice cream mix is subject to high shear. This results in the disruption of the fat phase into small droplets. Surface-active components of the mix will adsorb onto the nascent-oil/water interface, lowering the interfacial tension and thus stabilizing the emulsion droplets.

Recent research has thrown light on the competitive adsorption between different milk proteins (Dickinson, 1986; Dickinson et al., 1988b, 1989a,c; Euston, 1989;

Dickinson et al., 1990b; Dickinson, 1992), milk proteins and emulsifiers (Dickinson & Woskett, 1988a; Dickinson et al., 1990a; Dickinson, 1992; Euston et al., 1995a,b), and on the competitive adsorption between proteins and polysaccharide stabilizers (Dickinson & Euston, 1990; Dickinson, 1992, 1993). These studies have identified that, in general, the more surface-active protein in a mixture will dominate the adsorbed layer initially, low-molecular weight emulsifiers will, generally, displace protein from the surface with time, and under certain conditions polysaccharides can interact with proteins and/or emulsifiers to contribute to the structure of the adsorbed layer (Bergenstahl et al., 1992). The adsorbed layer of the ice cream emulsion will be a composite of all of these functional ingredients.

The key to the formation of ice cream structure is the formation of a stable foamed product. In ice cream this is achieved in two ways. The foam in ice cream is not a typical protein-stabilized foam, where air bubble stabilization is achieved by protein adsorption at the air/water interface. The initial stabilization of the foam network may indeed proceed by this mechanism, but prior to freezing the foam structure is stabilized primarily by the partial coalescence of emulsion droplets at the air bubble interface, in combination with an adsorbed layer of emulsifiers and protein. Figure 7.1 is a cryo-SEM micrograph of ice cream. Adsorption of fat

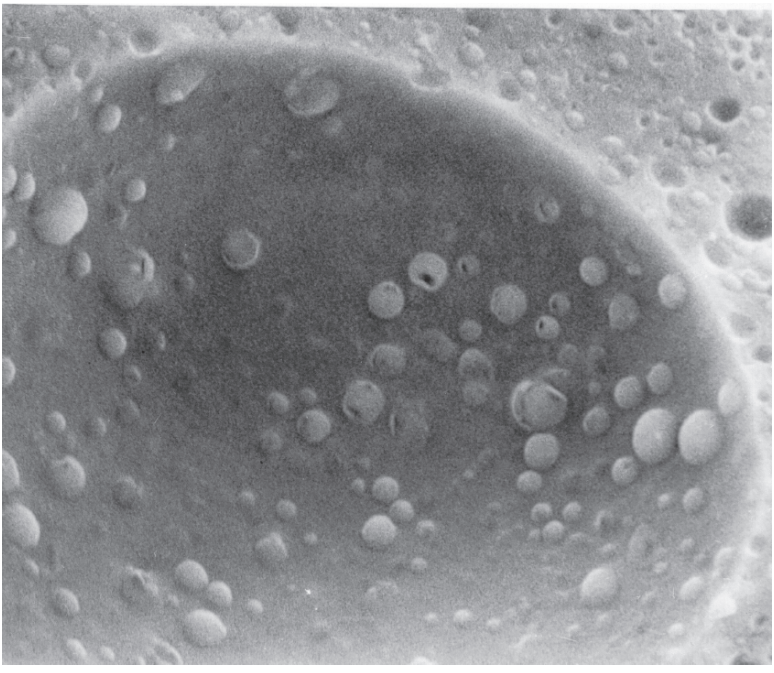

Fig. 7.1 Cryo scanning electron micrograph of a foam bubble in ice cream. Note the partial coverage of the air bubble surface by fat globules. Fat globules can also be seen in the foam lamellae outside of the droplet. (Reproduced by kind permission of Prof. D. Goff, Dept. of Food Science, University of Guelph.)

globules at the air bubble surface is clearly visible, although these do not cover the whole surface of the air bubble. For fat globule adsorption to occur, the emulsion must be relatively unstable to the shearing forces exerted on the mix during air incorporation. Several workers have attempted to demonstrate the link between emulsion coalescence stability and the mechanical or viscoelastic properties of the adsorbed protein layer (Doxastakis & Sherman, 1984; Rivas & Sherman, 1984; Dickinson & Stainsby, 1988; Dickinson et al., 1988a). Dickinson et al., 1988a have shown a correlation between the surface shear viscosity of adsorbed layers of various proteins at the planar oil/water interface, and the coalescence stability of emulsions made with these proteins. The higher the interfacial viscosity, the more stable the resultant emulsions under perikinetic conditions. It has also been demonstrated that the orthokinetic stability of protein-stabilized emulsions (stability under turbulent or shearing conditions) is reduced by the presence of low molecular weight emulsifiers (Chen et al., 1993a; Dickinson et al., 1993; Dickinson & Williams, 1994). The explanation for this lies in the ability of the low molecular weight emulsifier to displace protein from the fat-droplet surface, thus reducing the mechanical strength of the adsorbed layer. Emulsifiers present at concentrations too low to cause significant protein displacement can interfere with inter-protein interactions within the adsorbed layer and reduce the interfacial viscosity in this way (Dickinson et al., 1990a).

Emulsifiers that have an improving effect on the structure of ice cream do so because they are able to aid in the destabilization of the milk protein-stabilized ice cream emulsion. Emulsifiers commonly used in ice cream mix such as glycerol monostearate (GMS) and polysorbates, destabilize the emulsion by displacing protein from the fat-droplet surface. This is a result of their greater surface activity than milk proteins. Zhang and Goff (2005) have studied the composition of the air bubble interface in ice cream in the presence of either saturated (GMS) or unsaturated (GMO) monoglycerides. They found that in ice cream emulsions made using skim milk powder as the protein source that both emulsifiers were able to displace protein from the surface. However, GMO appeared less able to displace the milk whey protein β-lactoglobulin than did GMS. Davies et al. (2000, 2001) have also highlighted the importance of emulsifier type in their study of the effect of glycerol monoleate (GMO), glycerol monopalmitate (GMP) and glycerol monostearate (GMS) on the shear stability of protein stabilized emulsions. They found that the order of coalescence of the sheared emulsions decreased in the order GMO > GMP > GMS. This affect was attributed to both differences in the ability of the emulsifiers to displace protein from the interface, and to differences in the morphology of fat crystals in the emulsions droplets. The latter effect, which occurs because emulsifiers can influence the crystal structure of the fat in the droplets, is discussed in more detail below. Davies et al. also found, however, that the emulsifier type that gave the highest degree of shear-induced destabilization was also relatively unstable under quiescent conditions. To achieve a balance between good quiescent stability and susceptibility to shear induced partial coalescence, they found that a combination of GMO and GMS, or GMO and GMP was required (Davies et al., 2001).

Several studies have shown that the surface activity of emulsifiers is strongly temperature-dependent. Studies on model systems (Dickinson & Tanai, 1992) and in ice cream mix (Krog & Barfod, 1990; Barfod et al., 1991) indicate that displacement of protein from the oil/water interface by emulsifiers is at a maximum at temperatures between 4 °C and 10 °C. This observation provides an explanation for the improvement in ice cream structure and stability imparted by the ageing process. It is during the ageing step at 4 °C in ice cream manufacture that the displacement of the majority of the protein occurs. Krog and Barfod and co-workers (Krog & Barfod, 1990; Barfod et al., 1991) have investigated the ageing effect in ice cream emulsions and have shown that whereas protein displacement does occur during ageing in the absence of emulsifiers, displacement is greater when GMS is present, and greater still when glycerol monooleate is added (Fig. 7.2).

The temperature dependence of emulsifier surface activity can be explained in terms of the phase behaviour in aqueous solution. In the bulk phase, emulsifiers exhibit a phase behaviour similar to that of triglycerides (Krog & Sparsø, 2005). That is, they can exist in two polymorphic forms, α and β forms, that differ in the way the molecules pack in the crystal structure. When cooled from a random molten state, a metastable crystalline structure termed the α-state is formed. Further cooling leads to a transition to the β state. The most stable β-crystalline structure will form if the α-state is stored at ambient temperature. Lutton et al. (1969) proposed that the temperature dependence of GMS surface activity can be explained by either the formation of a condensed crystalline monolayer at the oil/water interface

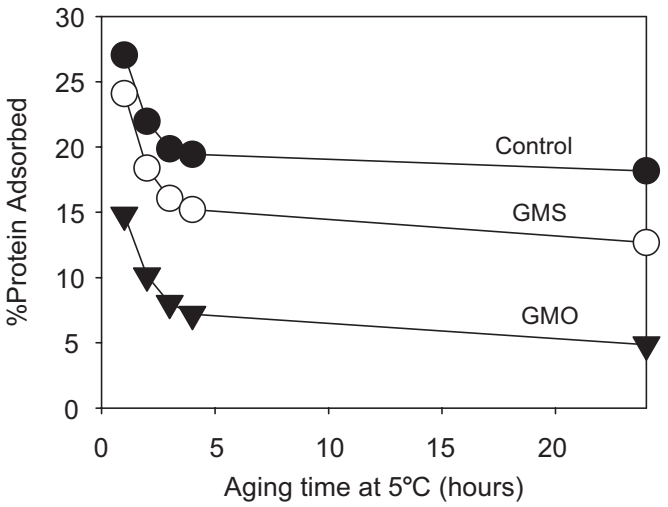

Fig. 7.2 Changes in amount of protein adsorbed to fat globules in an ice cream mix during the aging period at 5°C. The amount of protein bound in the fat phase is calculated relative to the total protein in the mix. (From Krog and Barfod, 1990. Reproduced with permission of the American Institute of Chemical Engineers, © AIChE. All rights reserved.)

at 5 °C or by micelle formation close to the surface. The possibility that both mechanisms contribute to the increased activity on cooling cannot be ruled out.

Monoglycerides, and indeed other emulsifiers, have also been shown to exhibit complex liquid crystalline phase behaviour in aqueous solution (Krog & Sparsø, 2005). Under certain conditions, the β-crystal form of a monoglyceride will interact with water to form a lamellar liquid crystal. On cooling this can transform to a so-called α-gel phase (Krog & Sparsø, 2005). It has been hypothesized that phase transitions between different crystalline and/or liquid crystalline forms of the adsorbed monoglyceride are important in protein displacement (Berger, 1990). During homogenization the temperature of the ice cream mix is high (80 °C). Protein and emulsifier will both occupy the surface, with the emulsifier having a relatively small effect on the protein surface coverage. As the mix is cooled for ageing, it is possible that a water-containing lamellar liquid crystalline phase of the emulsifier is formed, which subsequently transforms into the α-gel phase. This latter transformation is accompanied by the uptake of large quantities of water. At a later stage the more stable β–crystalline state may be formed. Berger (1990) believes that the two transformations, lamellar to α–gel, and α–gel to β-crystal, play a role in protein displacement. The change from a lamellar to a gel phase results in a decrease in surface area of about 30%, and formation of the β–crystal structure releases large amounts of water (Berger, 1990). On their own, each of these transitions will disrupt the adsorbed protein layer, and in combination they may be the cause of protein displacement. Darling and Birkett (1987), however, believe that in ice cream insufficient emulsifier is present in the system for liquid-crystalline phases to form. For this to occur the emulsifier must be adsorbed on the fat droplet surface at a concentration far greater than that required for monolayer surface coverage. This is not the case in ice cream emulsions (Darling & Birkett, 1987).

Once the emulsion has been destabilized in the freezer, partial coalescence of the fat droplets has to occur at the air/water interface to partially stabilize the foam structure prior to freezing. Research has indicated that the crystal structure of the fat in emulsion droplets is important in determining their susceptibility to partial coalescence (Boode, 1992; Boode & Walstra, 1993). Van Boekel (1980) has shown that when fat crystals form at the surface of emulsion droplets, and are large enough to penetrate the adsorbed layer, a lipid bridge can form between two droplets that are in contact with each other. The proportion of solid fat in emulsion droplets is important in determining instability (Walstra, 1987). If the majority of the fat is solid, coalescence, or partial coalescence will not occur, and the droplets will be stable. Similarly, if the droplets contain a very low proportion of solid fat, coalescence can occur, which leads to emulsion coarsening. If the solid fat content is in the approximate range 10–50%, partial coalescence is possible. A proportion of the emulsion droplet is required to be in the form of liquid fat for partial coalescence to occur. Walstra (1987) envisages a partial coagulum of fat droplets as being held together by necks of liquid oil.

Liquid fat is also considered to play a role in the adsorption of fat globules at the air bubble surface. The favoured view has been that during air incorporation, collisions between air bubbles and emulsion droplets lead to rupture of the fat globule,

which releases free fat that then spreads over the air bubble surface. This helps to anchor the droplets at the interface and helps to stabilize the bubble. Recent studies by Goff et al. (1999), however, have challenged this view. Using microscopy techniques, they studied the air bubble surface at differing degrees of fat destabilization onto the surface. This was achieved using differing levels and types of emulsifier, combined with different processing regimes. They found no evidence that free fat covers the whole air-bubble surface, even at the highest level of fat droplet destabilization which leads to the highest coverage of the air bubbles by fat droplets.

When fat crystallizes in dispersed emulsion droplets, considerable supercooling can be observed. Crystallization of fats occurs at nucleation points that already exist in the fat phase. These nucleation points occur relatively infrequently in emulsion droplets where the fat is dispersed into a large number of small droplets. Consequently, in dispersed systems the triglyceride needs to be cooled below its bulk phase freezing point before crystallization is initiated. Emulsifiers in adsorbed monolayers can act as templates for the surface crystallization of triglycerides. Emulsifiers containing saturated hydrocarbon chains have been shown to be good initiators of fat crystallization, whereas those with unsaturated hydrocarbon chains are not as good (Berger, 1990; Barfod et al., 1991). Figure 7.3 gives the solid fat content (SFC) as a function of time for model ice cream emulsions stored at 5 °C. Both saturated (GMS) and unsaturated (GMO) emulsifiers initiate crystallization compared to control emulsions with no emulsifier, but the SFC for GMS-containing emulsions is always greater than for those containing GMO.

Darling and Birkett (1987) point out that in a mixed triglyceride system, such as is found in milk fat, single discrete crystals are unlikely to form under the rapid cooling conditions used in ice cream manufacture. They have shown that in a cooled vegetable oil emulsion, concentric layers of triglyceride crystals are formed at the

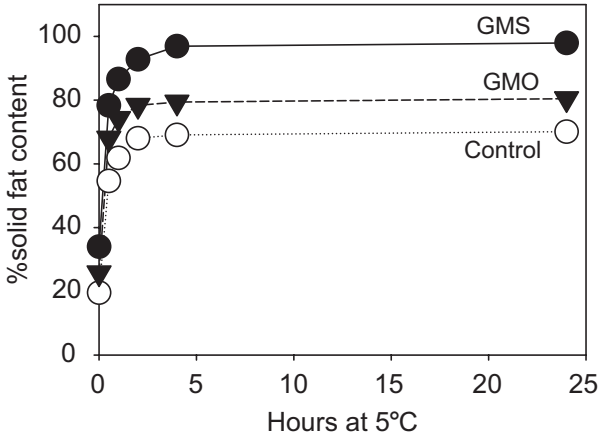

Fig. 7.3 Recrystallization of fat phase of ice cream emulsions without emulsifier (control) or with saturated (GMS) or unsaturated (GMO) monoglycerides after cooling to 5°C and aging. (From Barfod et al., 1991. Reproduced with permission.)

surface of droplets. These contain imperfections that may be due to dislocations or recrystallization processes, and these are likely to cause the destabilizing effect.

The ability of triglyceride crystals to penetrate the adsorbed layer depends on a number of factors. The surface tension between crystal and oil, crystal and water, and oil and water will determine how far into the oil phase the crystal will penetrate (i.e. if it is preferentially wetted by the oil or water phase). Emulsifiers, by way of their surface activity, will alter these surface tensions, and this may result in the crystals being able to penetrate further into the aqueous phase. This would lead to a decrease in emulsion stability. Desorption of protein by emulsifier also aids destabilization by reducing the thickness of the layer through which fat crystals have to penetrate. The polymorphic form of fat crystals will also play a role in fat-droplet instability. Triglycerides can exist in three general polymorphic forms, the α, β and β' polymorphs. When cooled from the melt, triglycerides will generally form α-type crystals. These are not stable (Larrson & Dejmek, 1990) and will transform into a β' polymorph and subsequently to the stable β polymorph. Having been formed at lower temperature, α crystals contain triglyceride in a more disordered liquid-like arrangement. The disordered crystals are softer and are able to deform and follow the contours of the fat droplet more easily. Consequently, they are less likely to penetrate the adsorbed layer. The β crystalline structure is more solid like, with the triglyceride molecules arranged in ordered arrays. The β crystals have a greater mechanical strength and are unable to deform to the shape of the fat droplets. This leads to their bursting out of the droplet into the aqueous phase (Darling, 1982).

In practice, two types of emulsifiers are commonly used in ice cream: mono- and diglycerides and polyoxyethylene derivatives of glycol or glycol esters, for example polysorbates (Keeney, 1982). Sucrose esters have also been evaluated and have been found to be suitable as ice cream emulsifiers (Buck et al., 1986). Mono- and diglycerides and polysorbates are usually all found in current ice cream emulsifier blends. The explanation for this lies in the relative abilities of polysorbates and mono- and diglycerides as emulsion destabilizers, or as foam-forming agents. Polysorbates are far more efficient at displacing protein from the oil/water interface than are mono- and diglycerides and thus are better emulsion destabilizers (Keeney, 1982). Mono- and diglycerides are better foaming agents and thus are able to aid the formation of the initial foam prior to fat-droplet agglomeration at the air/water interface (Keeney, 1982). A second factor is the differing abilities of emulsifiers to influence fat crystallization. Figures 7.2 and 7.3 show that whereas GMO is able to displace more protein from the fat globule surface during ageing than does GMS, GMS initiates more fat crystallization than GMO. Use of a mixed emulsifier system would also allow optimum protein displacement combined with optimum fat crystallization.

In summary, non-protein emulsifiers are important in ice cream in several respects:

1. They promote protein desorption from the surface of fat droplets, both by their higher relative surface activity and the possible formation of liquid crystal mesophases.
2. They can act as nucleation points for surface crystallization of triglycerides.

3. They may promote fat crystal penetration of the adsorbed layer by alteration of the surface tension between various phases.
4. They may help in the initial formation and stabilization of the ice cream foam prior to partial fat globule coalescence and freezing. Monoglycerides are particularly good at this function.

7.3 Whipped Cream and Whipping Cream

The terms whipping cream and whipped cream are often used interchangeably, although there are obvious differences between the two both in terms of structure and stability. Whipping cream is an oil-in-water emulsion stabilized by adsorbed milk protein and (where added) low molecular weight emulsifiers. Whipped cream is formed from whipping cream when air is incorporated into the emulsion to form a foam.

Whipping cream can be made by concentration of the milk fat globules found naturally in milk, or by a recombination process where amorphous milk fat is homogenized with milk proteins and low molecular weight emulsifiers. The fat content of whipping cream is about 35% by weight. Unlike ice cream emulsion, which only has to be stable long enough to be aged for a few hours before processing into ice cream, whipping cream emulsion has to be stable enough to allow storage for several weeks at ambient temperature, if UHT processed, without appreciable loss of stability.

The structure of whipped cream resembles that of ice cream in some ways. The foam is stabilized, initially by adsorbed protein and any added emulsifier. Prolonged whipping of the cream leads to partial agglomeration of fat globules at the air/water interface of foam bubbles. Whereas in ice cream the final structure is partially stabilized by fat globule adsorption at the air bubble surface, but mostly by freezing of the aqueous phase, in whipped cream the higher dispersed-fat phase content (35 wt% compared to about 10 wt% in ice cream) leads to a higher degree of fat-particle coalescence at the air/water interface. This greater fat adsorption leads to formation of a stable foam without the need for freezing. In addition, the fat globules aggregate in the aqueous phase of the cream to form a continuous, semi-solid gel-like network structure that traps the air bubbles and prevents them from coalescing. Figure 7.4 is a cryo-SEM micrograph showing fat-globule adsorption at the air/water interface in whipped cream, and the structure of the partially coalesced fat matrix in the foam lamellae. Comparing this to Fig. 7.1, a cryo-SEM of ice cream, it is apparent that the degree of fat-globule adsorption is less in ice cream. The adsorbed fat globules contribute to the rheological properties of the foam. By influencing drainage in the aqueous lamellae between air bubbles, the partially coalesced, adsorbed fat globules impart a small but finite yield stress on the whipped product (Dickinson & Stainsby, 1982). This allows whipped cream to ‘stand up’ under its own weight even at ambient temperature.

Non-homogenized cream separated from milk will whip satisfactorily without the addition of emulsifiers. If the cream is homogenized prior to whipping and the

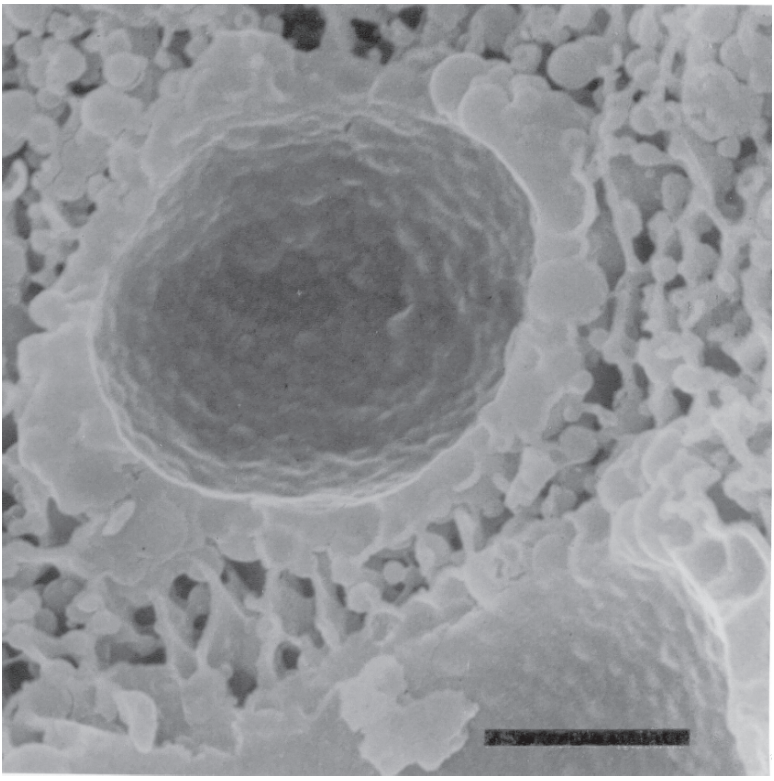

Fig. 7.4 Cryo-scanning electron micrograph of whipped cream. Note the greater coverage of the air bubble surface by fat globules than occurs in ice cream. The partially coalesced fat globule network that gives cream its semi-solid structure is also clearly visible. (Reproduced by kind permission of Prof. D. Goff, Dept. of Food Science, University of Guelph.)

mean fat globule size reduced, emulsifiers have to be added to aid destabilization. Anderson and Brooker (1988) have attributed the differences in whipping ability of homogenized and non-homogenized cream to the differences in interfacial composition of the emulsion droplets in these systems. Non-homogenized cream contains fat globules stabilized by native MFGM. The composition of this has been described earlier (see Sect. 7.1). After homogenization, the particle size is reduced, interfacial area is increased, and consequently, MFGM on its own is insufficient to stabilize the newly formed interface. A combination of increased interfacial area and competitive adsorption between MFGM and cream serum proteins means that proteins from the aqueous phase (caseins and whey proteins) contribute to the interfacial layer. The interfacial layer in homogenized cream has been found to consist mainly of caseins, with smaller amounts of β-lactoglobulin and α-lactalbumin (Anderson et al., 1977; Darling & Butcher, 1978; McPherson et al., 1984). This is consistent with the available data on competitive adsorption between casein and whey proteins

in model systems (Euston, 1989; Dickinson et al., 1990b). In the early stages of whipping, before fat-globule adsorption and partial coalescence occur to any great extent, the air bubbles are stabilized by adsorbed milk serum proteins. Since this air/water interface is composed of the same proteins that surround the fat/water interface in homogenized cream, the difference in interfacal tension between the two interfaces is not that great (Anderson & Brooker, 1988). The interfacial tension differences is a driving force for fat-globule adsorption at the air/water interface in both cream and ice cream, and if this is low or negligible, fat globule adsorption is reduced. In non-homogenized milk the interfacial tension differences between a fat globule stabilized by MFGM and an air bubble stabilized by cream serum proteins are sufficient to act as the driving force for fat-globule adsorption at the surface of air bubbles. Of course this is also aided by the presence of fat crystals at the fat-globule surface and by the shearing forces introduced during whipping.

The importance of the fat phase manifests itself in two ways. As in ice cream (see Sect. 7.2), fat crystals are known to be important in the shear-induced coalescence of the fat globules (Darling, 1982), and the presence of a certain amount of liquid fat is a pre-requisite for good whipping properties. Bucheim (1986) put forward the idea that the interfacial layer surrounding the fat droplets ruptures when they collide during agitation. The subsequent spreading of liquid fat is the first stage in destabilization by aggregation of adjacent droplets. The importance of the solid fat content of the fat globules has been demonstrated by Darling (1982), who observes a direct correlation between the SFC and whipping time in natural cream.

Recombining technologies are becoming an increasingly important process for making whipping cream bases. These encounter the same problems as homogenized cream (i.e. the similarity in composition and interfacial tension between air/water and oil/water interfaces), if they are formulated with milk proteins as the only surface-active material. For this reason, recombined whipping creams, and indeed homogenized natural creams contain added low molecular weight emulsifiers. These adsorb at, and alter the composition of the fat-droplet surface, thus changing the interfacial tension. Addition of an optimum concentration of emulsifiers results in an oil/water interface composed of protein and emulsifier differing sufficiently from the air bubble interface for fat-globule adsorption to occur on whipping. For similar reasons to those proposed for ice cream (see Sect. 7.2), whipping cream emulsifiers are usually a combination of two types. There is often a lipophilic emulsifier such as GMS, or one of its derivatives, and a water-soluble polyoxyethylene derivative such as one of the Tweens. Thomé and Eriksson (1973) have shown that the amphoteric phospholipids are good emulsifiers in whippable emulsions when used in combination with monoglycerides. This is a significant observation when the trend toward natural, non-synthetic emulsifiers is considered. Phospholipids are a natural component of milk fat and can be produced as a by product when milk is processed into, for example, butter. This can explain the increasing use of buttermilk powders as combined emulsifier/protein systems in whipped emulsions (Vodickova & Forman, 1984).

The structure of the composite fat-globule surface layer in homogenized and recombined dairy whipping cream is not known for certain. Two theories have been

put forward. Krog (1977) maintains that a primary layer of emulsifier adsorbs at the fat-droplet surface, and that a secondary protein layer is attached to the primary layer through relatively weak co-operative hydrogen bonding. When the cream is whipped this protein layer is removed from the fat globule relatively easily, and the emulsion destabilized in this way. Doxastakis and Sherman (1984), however, have evidence that the protein and emulsifier form a mixed interface where both are adsorbed through hydrophobic interaction with the interface. It is speculated that this can lead to localized differences in the interfacial tension at the fat-droplet surface (i.e. between protein rich and emulsifier-rich regions of the adsorbed layer) which helps to drive fat-globule adsorption and partial coalescence. Whichever of these theories is correct, it is also likely to be relevant to the destabilization of ice cream emulsion when it is frozen and whipped.

A stable whipped cream can be formed from whipping cream that has been held at room temperature for some time. However, a superior product is obtained if the cream is aged for several hours at low temperature prior to whipping. This, as in ice cream, is a consequence of increased emulsifier surface activity a low temperature.

It would appear, therefore, that the functions of emulsifiers in whipping cream are essentially the same as for ice cream, i.e.

1. They destabilize the cream through their ability to displace protein from the oil/water interface. This changes the adsorbed layer composition and interfacial tension of the fat droplet.
2. They may destabilize the emulsion through their ability to form lyotropic liquid-crystalline mesophases and the subsequent phase transformations that occur to form stable crystalline forms.
3. They may participate in the initial foam stabilization.
4. They aid in the formation of fat crystals at the fat-droplet surface. These crystals are essential for fat-globule partial coalescence.

7.4 Whipped Toppings

Over the years, whipped toppings have become a popular alternative to dairy creams and ice cream. Table 7.3 gives a typical composition for whipped topping powder. In whipped toppings, as in dairy whipping creams, the emulsifiers appear to be

Table 7.3 Typical whipped topping powder composition

Ingredient	Composition (%)
Hardened coconut or palm kernel oil (melting point 31–36 °C)	32.0
Maltodextrin	32.0
Sodium caseinate	8.0
Emulsifiers	8.0

From Si (1991), Reprinted by permission of the Society of Dairy Technology

important in the destabilization of the emulsion, while the protein is important in giving initial stability to the oil-in-water emulsion. The mechanism by which emulsion destabilization is achieved, however, is different. Whereas whipped dairy creams and whipped imitation creams are stabilized by partially coalesced, relatively intact fat globules adsorbed at the air/water interface, whipped toppings are stabilized by crystalline fat at the air bubble surface. Krog and co-workers (Barfod & Krog, 1987; Bucheim et al., 1985; Krog et al., 1986) have carried out extensive studies of the factors that effect structure formation in whipped toppings. They have shown (Barfod & Krog, 1987) that part of the fat in spray-dried topping powders is in a supercooled state. When these topping powders are reconstituted in water at low temperatures, they show large structural changes that determine whipping characteristics and foam structure. The emulsion becomes unstable due to spontaneous recrystallization of the supercooled fat. The destabilization of the emulsion is probably promoted by the temperature-dependant desorption of protein from the surface, followed by coalescence. This makes crystallization of the supercooled fat more likely, due to the increased probability of nucleation sites (Bucheim et al., 1985).

Scanning electron microscopy studies (Bucheim et al., 1985) show that the final structure of the aerated whipped topping is stabilized by a layer of crystalline fat about 0.1 μm thickness. The aqueous phase lamellae between air bubbles also contain large proportions of crystalline fat, with smaller proportions of relatively intact fat globules.

The kinetics of fat crystallization and emulsion destabilization depend on the type of emulsifier used in the formulation. Si (1991) lists the type of emulsifier used in whipped toppings as propylene glycol esters of monoglycerides, acetic acid esters of monoglycerides, or lactic acid esters of monoglycerides. Bucheim et al. (1985) have investigated the effect of distilled propylene glycol monostearate (PGMS), distilled unsaturated monoglycerides (glycerol monooleate, GMO), and distilled saturated monoglycerides (glycerol monostearate, GMS) on the structure of whipped toppings. Only PGMS is typically used in commercial formulations. Figure 7.5 shows that all the emulsifiers promote fat crystallization when compared to toppings without added emulsifiers. The effect of PGMS and GMO, however, was greater than for GMS. The increased emulsion destabilization caused by the enhanced fat crystallization led to PGMS- and GMO-containing whipped toppings being more stable than those made from GMS-containing emulsions (Bucheim et al., 1985). The GMS-containing reconstituted topping emulsion is too stable to allow consequent stabilization of incorporated air (whipping).

The importance of protein desorption on whipped topping structure and stability has been demonstrated by Krog and co-workers (Krog et al., 1986; Barfod & Krog, 1987). Table 7.4 gives the percentage protein contents of the fat and aqueous phases of whipped topping powders reconstituted at 5 °C and 30 °C, and containing PGMS, GMS or no added emulsifier. At 5 °C in the absence of emulsifier almost one-quarter of the protein is associated with the fat phase. This falls to 1.7% when PGMS is present and 7.7% with GMS added. The temperature dependence of protein displacement is also evident. At 30 °C over 40% of the protein is in the fat phase when emulsifier is absent, but this drops to about 33.7% in the presence of PGMS and 12.35 when GMS is included in the formulation (Krog et al., 1986).

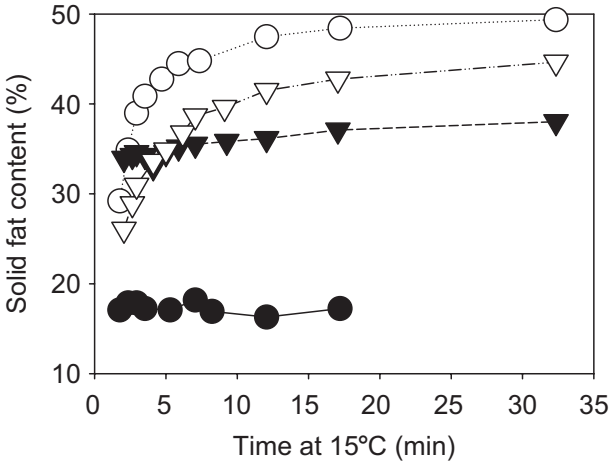

Fig. 7.5 Crystallization of supercooled lipid fractions in topping emulsions different surfactants, reconstituted (1:3) with deuterated water (D_2O), measured by pulsed-NMR at 15°C. ❍ GMO (Dimodan O), PGMS (Promodan SP), ∇ GMS (Dimodan PV), • no surfactant added. (From Bucheim et al., 1985. Reprinted by permission of Scanning Microscopy International.)

The GMS-containing reconstituted toppings have a significant proportion of protein still associated with the fat-droplet surface, even after ageing of the emulsions at 5 °C. Obviously this is enough to form an adsorbed layer strong enough, in combination with the lower degree of fat recrystallization, to prevent stabilization of the incorporated air bubbles. This is in contrast to the situation in ice cream and whipping cream, where GMS is capable of destabilizing the fat emulsion to a degree that partial coalescence can occur. Darling and Birkett (1987) point out that the level of emulsifiers in whipped toppings is sufficient to allow the formation of emulsifier adsorbed layers of far greater than monolayer coverage. They suggest that the formation of liquid-crystalline mesophases, and the α-gel phase of the adsorbed emulsifier, is a possibility. Westerbeek and Prins (1991) have shown that a common emulsifier used in whipped toppings, glycerol lactopalmitate (GLP), is capable of forming the α-gel phase at oil/water interfaces, and this may contribute to emulsion destabilization.

Table 7.4 Distribution of protein between the fat cream phase and the water phase of centrifuged topping emulsion

	After 1 h at 5 °C		After 1 h at 30 °C	
Surfactant	% Protein in fat phase	% Protein in water phase	% Protein in fat phase	% Protein in water phase
10% PGMS	1.3	98.7	33.7	66.3
10% GMS	7.7	92.3	12.3	87.7
None	24.0	76.0	41.7	58.3

From Barfod and Krog (1987), Reprinted by permission of the American Oil Chemists Society

The present understanding of the formation of structure in whipped toppings suggests the following mechanism for emulsion destabilization and formation of the foam structure:

1. The powdered dried topping emulsion is stable.
2. When reconstituted at low temperature, protein displacement is initiated and is aided by added emulsifiers such as PGMS. The mechanism of protein desorption will be similar to that already described for ice cream. There is an almost total desorption of protein from the fat droplet surface.
3. Coalescence of fat droplets can occur during whipping, due to the presence of liquid fat produced by supercooling.
4. Coalescence leads to a recrystallization of the supercooled fat, which is again aided by the presence of emulsifiers.
5. A continuous phase of elongated fat crystals is formed, resulting in an increased viscosity of the whip, which is capable of stabilizing dispersed air bubbles.

As in ice cream, the functions of emulsifiers in whipped toppings are to promote protein desorption and fat crystallization.

7.5 Cream Liqueurs

Cream liqueurs are dairy emulsions of high added value. The combination of milk protein-stabilized cream emulsion and high alcohol content make cream liqueurs unique among dairy emulsions. Table 7.5 gives a typical range of compositions for cream liqueur. In practice many commercial formulations also have small amounts of GMS added. The production of cream liqueurs is governed by the relative poorness of the alcoholic aqueous phase as a solvent for proteins and sugars. Two commercial processes are in common use (Banks & Muir, 1988), namely, the single-stage process and the two-stage process. Figure 7.6 presents flow charts for both processes. The main difference between the two processes lies in the stage at which the alcohol is added. In the single-stage process this is prior to homogenization, whereas in the two-stage process it is after homogenization. Banks and Muir (1988) found that homogenization in the presence of alcohol leads to the formation of fewer large fat globules, and as such is preferable in terms of emulsion stability. A characteristic of cream

Table 7.5 Range of compositions of a standard cream liqueur

Component	Composition (wt%)
Milk fat	12–16
Added sugars	15–20
Sodium caseinate	2.6–3.5
Non-fat milk solids	1.0–3.5
Ethanol	14
Water	46–51

Reprinted from Banks and Wislon (1981), with permission

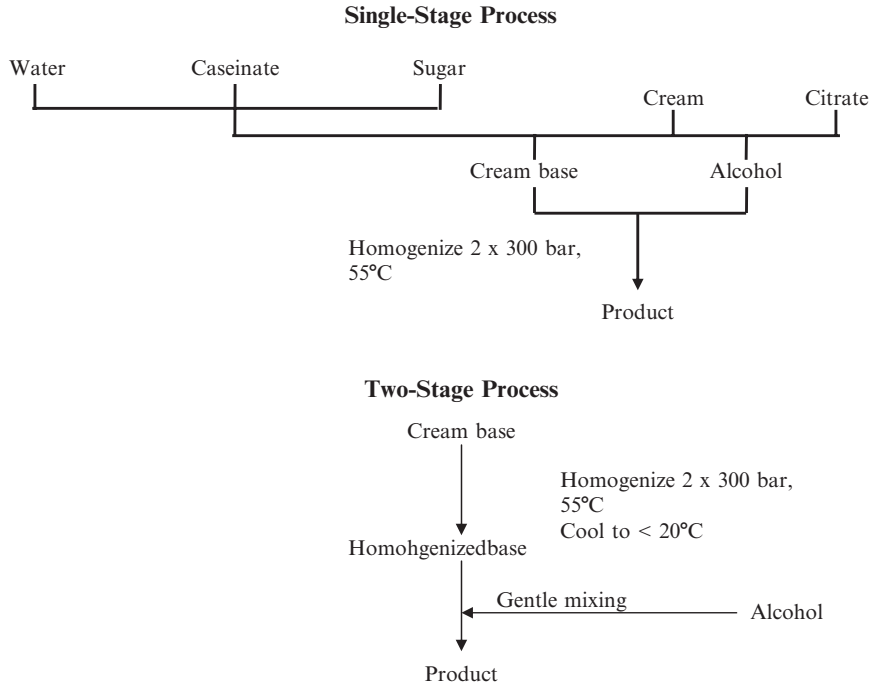

Fig. 7.6 Flow diagrams for the process of manufacture of a cream liqueur in **(a)** a single stage and **(b)** two stages. (From Banks and Muir, 1988. Reprinted by permission of Elsevier Applied Science Publishers.)

liqueur production is the harsh homogenization conditions used (two passes at 300 bar). This results in a product in which more than 97% of the fat droplets have a diameter less than 0.8 μm. A second factor favouring formation of smaller droplets is the significant lowering of interfacial tension observed at the oil/water interface when alcohol is added to the aqueous phase (Bullin et al., 1988; Dickinson & Woskett, 1988b; Burgaud & Dickinson, 1990). As a result of the very fine droplet size, the protein in the added cream has to be supplemented by sodium caseinate (to a fat-to-caseinate ratio of 5:1) to provide adequate coverage of the newly formed fat surface by protein (Banks & Wilson, 1981). The fine particle size of the dispersed phase fat droplets gives the product an excellent stability with respect to creaming. Banks and Wilson (1981) have noted no signs of creaming in liqueurs with a composition within the range quoted in Table 7.5 after 12 months storage. The high level of added sodium caseinate, however, leads to cream liqueur emulsions being unstable in acid environments. This means that they are not suitable for combination with acid beverage mixers such as lemonade. A cream liqueur that is stable in an acid environment can be made by replacing the sodium caseinate with GMS. The emulsifier replaces milk protein as the primary emulsion stabilizer at the oil/water interface, and the non-adsorbed protein is unable to aggregate the fat droplets when exposed to acidic

surrounding (Banks & Muir, 1988). Acid stability in this product is gained at the expense of emulsion stability and shelf life. In practice, legal limits in some countries set the concentration of GMS at no more than 0.4 wt%, and so total replacement of caseinate by GMS is not feasible. Many manufacturers add low concentrations of GMS as well as sodium caseinate to cream liqueur formulations. Dickinson et al. (1989b) have shown that, in addition to displacing some, but not all of the milk protein from the fat droplet surface, which presumably infers some acid stability on the product, GMS also improves the stability of a model cream liqueur. When model cream liqueurs were stored at room temperature for 12 weeks, no creaming was observed with added GMS concentrations above 0.5 wt%. Below this level of added GMS a reduced degree of creaming was observed compared to control samples with no emulsifier (Dickinson et al., 1989b). The increased stability was associated with rheological changes in the emulsifier aqueous phase. At low GMS concentrations the emulsions exhibit Newtonian behaviour, whereas above 0.5 wt% a yield stress is found. Dickinson et al. (1989b) postulate the formation of a weak gel-like network in the continuous phase formed by interaction of caseinate with GMS. It is also likely that interaction between caseinate and GMS at the oil/water interface plays a role in the creaming stability. Evidence for interactions between adsorbed caseinate layers and GMS has been reported by Doxastakis and Sherman (1984), who investigated the surface rheological properties of mixed caseinate GMS systems.

An apparent contradiction in the work of Dickinson et al. (1989b) is that although creaming stability is enhanced at GMS level above 0.5 wt%, the shelf life, as tested using an accelerated method at 45 °C, decreases in this region (Fig. 7.7). Dickinson et al. (1989b) point out that whereas weak gels are able to

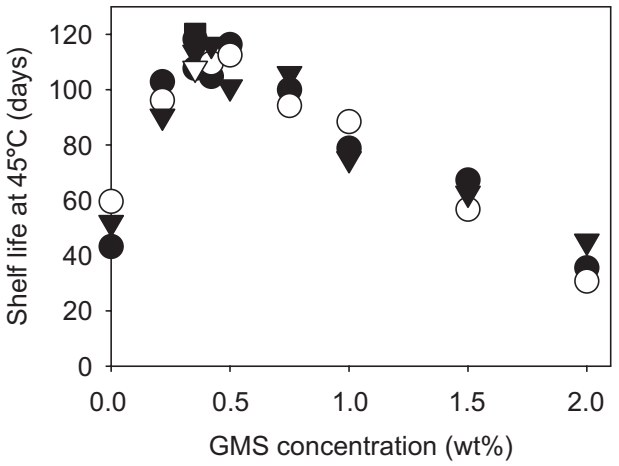

Fig. 7.7 Effect of GMS on the shelf life of simulated cream liqueurs on storage at 45°C. The time for serum separation to first become visible is plotted against the GMS concentration. Different symbols refer to separate experiments. (Based on Dickinson et al., 1989b. Reprinted by permission of the Institute of Food Technologists.)

prevent formation of a substantial cream layer, they are also prone to slow syneresis when stored for any length of time. This leads to separation of the aqueous phase and formation of a distinct, clear serum layer at the bottom of the sample container. Whether this syneresis will occur at room temperature is not certain, and Dickinson et al. (1989b) stress that a correlation between the shelf life at 45 °C and that at room temperature may not follow. Cream liqueurs stored under ambient conditions can have shelf lives of several years. Clearly these are likely to be consumed long before serum separation becomes evident. Since the legal limits on the amount of emulsifier are set at about 0.4 wt%, the problem of gel syneresis is unlikely to be encountered. At a level of 0.4 wt% added GMS, creaming under gravity would not be eliminated completely, but would be reduced to a level acceptable to the consumer (Dickinson et al., 1989b).

7.6 Creams and Coffee Whiteners

Cream products containing 10–20% fat have been popular as coffee creamers for over 50 years (Abrahamson et al., 1988). Coffee creamers and whiteners perform several functions: they give coffee a white colour, reduce bitter taste by complexation of the tannic acids with milk proteins, give the coffee a cream-like flavour, and give body to the coffee (Sims, 1989).

Traditionally, coffee cream is produced by simple concentration of milk up to the required fat content. The cream is usually heat treated using a UHT process, homogenized either before or after heating, and packed asceptically to give a long shelf life. Emulsifiers are not usually added to this product. More recently, with the advent of recombining technology and with the preference of some consumers for vegetable oil-based products over those that contain milk fat, new products have appeared that require the addition of emulsifiers if a stable formulation is to be manufactured. If a recombined coffee cream is produced, the formulation is more complex than for natural, concentrated coffee cream. Table 7.6 gives a typical formulation for recombined coffee cream containing 19% milk fat, as suggested by Zadow (1982).

The recombining process involves a two-stage homogenization with an 18 MPa first stage and a 3–4 MPa second stage. Presumably the emulsifiers are added to aid

Table 7.6 Typical formulation for a recombined coffee cream

Ingredient	Composition (wt%)
Skim milk powder	3.0
Buttermilk powder	4.5
Anhydrous milk fat	19.0
Carrageenan	0.03
GMS	0.05
Tween 60	0.1
Water	73.32

From Zadow (1982), Reprinted by permission of the International Dairy Federation

in the homogenization process by reducing the energy required to form the fat/water interface. It may also be assumed that since in natural coffee creams the milk fat is already in a dispersed state, the energy required to reduce the particle size is less, and so emulsifiers are not needed. However, Zadow (1982) states that emulsifiers and stabilizers are required only if the product is to be given a high heat treatment (a UHT process or steam injection), which suggests a role for emulsifiers in product heat stability. Evidence exists to support this hypothesis and will be dealt with in more detail in Sect. 7.8.

Whereas coffee cream and recombined cream are used in a liquid form, coffee whiteners based on vegetable fat are also popular in dry powder form. Typical formulations for liquid and dry powder coffee whiteners are given in Table 7.7. Other water-soluble surfactants, such as Tween 60, are commonly used in place of the tartaric acid esters of monoglycerides listed in Table 7.7. Si (1991) states that the function of the emulsifiers in coffee whitener is to improve whitening ability and to aid powder dispersibility in coffee. Knightly (1969) has found that GMS is more effective in improving powder dispersibility, whereas Tween 60 is better at improving the rate of solution of the powder. Optimum whitening ability is attributed to small fat globules and a narrow particle-size range, and its attainment in coffee whitener has been attributed to the presence of GMS and its derivatives (Si, 1991). Whitening power in a dispersion is related to the surface area of the dispersed particles. The higher the surface area the greater the light reflectance from the dispersion and thus the greater the whitening effect. This is true for both dairy coffee creams and non-dairy coffee whiteners. Leo and Betscher (1971) have noted that there is an optimum particle size range for optimum optical density and whitening power of the dispersion. Over-homogenization of a coffee whitener formulation is known to result in a loss of whitening power.

The influence of emulsion droplet colloidal properties has been studied in detail by McClements and co-workers from both the theoretical and experimental perspective (Chanamai & McClements, 2001; Chantrapornchai et al., 1998, 1999a,b, 2001a,b; McClements, 2002a,b; McClements et al., 1998). There results have

Table 7.7 Typical formulations for liquid and powdered coffee whiteners

	Composition (wt%)	
Ingredient	liquid	powder
Fat	10.0	30.0
Sodium caseinate	1.0	4.0
Maltodextrin (DE28)	10.0	62.0
Monoglycerides	0.2	~1.5
Tartaric acid esters of monoglycerides	0.2	0.5
Carrageenan	0.05	–
Sodium alginate	–0.05	–
K_2HPO_4	0.2	1.5
Flavour	300 ppm	1000 ppm
Water	To 100%	–

From Si (1991), Reprinted by permission of The Society of Dairy Technology

shown that the whiteness of an emulsion is strongly related to both droplet size and droplet concentration. Emulsion lightness increases up to a maximum as the droplet size increases, and then starts to decrease if the droplet size increases above a critical radius (Chantrapornchai et al., 1998). This confirms the finding of Leo and Betscher (1971) that there is an optimum particle size range for optimum whitening power of a coffee whitener.

The emulsifiers added to powdered formulations prior to spray drying are capable of stabilizing the emulsion in the liquid form. Sodium caseinate is usually required to give stable fat droplets in the dried powder (Sims, 1989), since an adsorbed proteinaceous layer is better able to withstand the extreme conditions in the drier. Because sodium caseinate is required at high concentration (typically in the range 3–15%), ways of reducing the amount in coffee whitener have been sought as a cost saving exercise. One way of doing this is to use sodium (or calcium) stearyl lactylate or sodium stearyl fumarate as an emulsifier. Miller and Werstak (1983) have used 2.5% monoglycerides plus sodium-2-stearyl lactylate (SSL) in the approximate ratio 7.3:1. They claim a reduction of sodium caseinate to 60% of that required in normal formulations. The function of SSL appears to be through its ability to form a complex with sodium caseinate (Leo & Betscher, 1971). It is likely that this interaction results in improved fat encapsulation in the dried state through increased interfacial rigidity of the adsorbed layer. This is analogous to the increased emulsion coalescence stability observed when GMS complexes with protein adsorbed at the oil/water-emulsion interface (Doxastakis & Sherman, 1984; Rivas & Sherman, 1984).

7.7 Cheese, Processed Cheese and Cheese Products

The addition of emulsifiers to traditional cheese has been reported only a few times in the literature (Drake et al., 1994, 1996). In large part this is due to the regulations in many countries that prohibit the use of additives in traditional products. However, food manufacturers are always looking to manufacture new products with novel textures, tastes and functionality, and this has led to the development of cheese-based and dairy analogue products that are not required to adhere to the strict legislation for natural cheese.

One of the first cheese products was processed cheese, the manufacture of which dates back approximately 100 years. Originally it was used as a way of increasing the shelf life of cheese and improving the palatability of lower quality cheese (Caric et al., 1985). To manufacture processed cheese, the cheese raw material (a mixture of rennet and fresh cheeses) is first cleaned, chopped, and heated at 70–82°C with emulsifying salts and other additives. In this instance, the term emulsifying salt is a little misleading, as they are not low molecular weight (nor proteinaceous) emulsifiers, nor do they play a direct role in creating a fat droplet dispersion. Their main effect in this instance is to increase the solubility of the aggregated cheese proteins through sequestration of calcium, thus improving the emulsifying ability of the

caseins. Heating and water addition are often combined by using direct steam injection. The pH of the mix is lowered to 5.6 to 5.8 using organic acids and the product is then extruded into packages (Rosentahl, 1991). Alternatively, the correct pH can be obtained by careful selection of a blend of polyphosphate emulsifying salts, which have some buffering capacity in this application (Lee et al., 1996 personal communication). The final product can have 15–25% fat and up to 58% water.

Processed cheese is a dispersion of fat droplets in a concentrated, gelled protein network. This is in contrast to cheese itself, where the fat is not found as discrete droplets, but forms a semi-continuous phase throughout the protein gel. Emulsion stability in the fat droplets is controlled, primarily, by adsorbed caseins or hydrolyzed casein fractions. Some manufacturers add mono- and diglycerides as emulsifiers. The structure and texture of processed cheese is closely linked with the size and distribution of fat globules in the cheese (Thomas et al., 1980; Shimp, 1982). If the fat in a processed cheese is weakly homogenized and large fat droplets are formed, the cheese is soft and melts easily. If the fat droplets are small, the cheese is hard and non-melting.

To control the structure of processed cheese, so-called emulsifying salts such as polyphosphates are added. Although these are not surface-active they play an important role in modifying the emulsifying activity of the surface-active caseins. Caseins bind calcium, and this has the effect of reducing their solubility, and thus their emulsifying ability. Emulsifying salts have a higher affinity for calcium than do the caseins, and thus they are able to improve the solubility and emulsifying properties of the caseins. Emulsifying salts are of two types: those that bind calcium relatively weakly and those that bind calcium more strongly. Weak emulsifying salts have a modest effect on the emulsifying properties of the caseins and lead to the formation of a soft cheese with relatively large fat droplets. Strong emulsifying salts give a greater improvement in the emulsifying capacity and result in a hard cheese with smaller fat droplets.

The use of low molecular weight, surface-active emulsifiers in processed cheese (Tweens and Spans) was first investigated in the 1950s (Holtorff et al., 1951). They are not as good as emulsifying salts at promoting structure formation in processed cheese, and in some cases they act to destabilize the fat emulsion by protein displacement from the surface.

Concern has been expressed over the non-nutritional effect of forming a phosphorous/calcium complex in processed cheese, as the calcium is less easily adsorbed in this form. The supplementation of emulsifying salts by monoglycerides has been investigated as a way of reducing the concentration of emulsifying salts. Gavrilova (1976) produced processed cheese of improved rheology and shelf life using an emulsifying salt/monoglyceride mixture. Zakharova et al. (1979a,b) achieved a 50% reduction in the concentration of emulsifying salts required by adding 1% monoglyceride to the cheese. The processed cheese produced was reported to be of good quality and to have improved hydrophilic (water binding) properties.

Lee et al. (1996) have studied the effect of adding small concentrations of low molecular weight surfactants as co-emulsifiers in combination with emulsifying salts in a model processed cheese. The surfactants used were sodium dodecyl sulphate

(SDS, an anionic surfactants), cetyl-trimethyl ammonium bromide (CTAB, a cationic surfactant), lecithin (a zwitterionic surfactant), and GMS (a non-ionic lipophilic surfactant). Although the addition of surfactant was observed to result in a reduction in fat-droplet size, the degree of uniformity of the dispersion differed between emulsifiers. In contrast to previous reports that smaller more evenly dispersed fat droplets gave firmer cheeses (Thomas et al., 1980; Shimp, 1982), Lee et al. (1996) found no relationship between processed cheese hardness and emulsion structure in the presence of emulsifiers. They concluded that electrostatic interactions between the emulsifier and the protein played the major role in determining the rheological properties of the cheese. The anionic surfactant SDS gave the softest cheese, the cationic surfactant CTAB the hardest. GMS and lecithin gave cheeses with rheological properties little different from the control with no added emulsifier.

Vial et al. (2006a) have designed a formulation for a light-textured foamed fresh acid cheese product that has improved spoonability, spreadability and a more homogeneous texture than conventional fresh acid cheeses. The final product contained 15% air by volume, which contributed to the altered properties of the product. The structure, texture and properties were found to be sensitive to the level of addition and type of emulsifier added (Vial et al., 2006b). Mono di-glycerides were found to reduce the ease of foaming in the formulation, whilst phospholipids in combination with whey protein concentrate gave softer textures. Low molecular weight emulsifiers had little impact on the stability of the product, with this being improved by the addition of WPC.

For traditional cheese products much of the research on emulsifier incorporation into the cheese structure has concentrated on improving the texture of reduced fat cheese (Drake et al., 1994, 1996). One of the nutritional criticisms of traditional cow's milk cheese is that it contains relatively large amounts of saturated fat. Thus, much effort has been put into either reducing the fat content of cheese or incorporating 'healthier' polyunsaturated fats into the cheese matrix. Early attempts at reduced fat cheese often led to products that had a poor texture, flavour and melting properties (Lobato-Calleros et al., 2001; Tunick et al., 1999). Swanson and co-workers (Drake et al., 1994, 1996; Drake et al., 1999) have found that emulsifiers can act in a similar way to fat-replacers by either improving water binding in the protein matrix, or by promoting the formation of mixed emulsifier-protein aggregates of a similar size to fat globules. These aggregates mimic the effect of fat in the cheese matrix and improve the texture properties of the cheese.

Other studies have looked at the effect of emulsifier blends on the properties of cheese containing canola oil as a functional food ingredient (Lobato-Calleros et al., 2003). One of the problems with fat replacement in cheese is that saturated fats are solid at storage (and eating) temperatures, whilst polyunsaturated fats are liquid. This has texture implications for the cheese, if it is desirable to mimic the texture of the saturated fat containing cheese. This has led to the investigation of the use of emulsifier blends to control the size of the polyunsaturated fat droplets in an attempt to modify the rheological properties of the product ingredient (Lobato-Calleros, et al., 2003). The rationale for this approach is the knowledge that low

molecular weight emulsifiers are known to alter the textural properties of protein gels and emulsion gels by changing the way in which the proteins interact with themselves and the way fat globules interact with the protein gel matrix.

Studies on, in particular, whey protein denaturation and gelation give some indication as to the mechanisms by which low-molecular emulsifiers affect the properties of protein gels. The situation is complex, with emulsifiers have differing effects depending on the emulsifier types and conditions of gelation. Lipids in whey protein concentrate (WPC) (derived from the original milk source) inhibit the gelation properties of the proteins by competing for hydrophobic binding sites in the protein (Mangino, 1992; Morr, 1992; Morr & Ha, 1993). In contrast, lecithin can enhance gelation or have no effect depending on the conditions (Ikeda & Foegeding, 1999a,b). The reason for this is the ability of whey proteins to form differing gel structures depending on the pH and salt concentration (Langton & Hermansson, 1992; Botcher & Foegeding, 1994; Bowland & Foegeding, 1995; Bowland et al., 1995). At low ionic strength, low pH well away from the iso-electric point aggregation occurs in a linear fashion to form a fine-stranded gel (Langton & Hermansson, 1992). At high ionic strength and/or pH close to the isoelectric point a particulate type gels are formed, and under intermediate conditions, between the two cases above, mixed gel structures form (Botcher & Foegeding, 1994; Bowland & Foegeding, 1995; Bowland et al., 1995). Foegeding and co-workers (Ikeda & Foegeding, 1999a,b) have shown that lecithin increases the gelation rate and gel strength for fine-stranded and mixed gels, but has no effect on particle gels. They hypothesise (Ikeda & Foegeding 1999a,b) that protein aggregation is facilitated by lecithin-protein interactions at low NaCl concentrations, because lecithin is iso-electric over a wide pH range. Consequently, there will be no electrostatic repulsion with the protein. As NaCl concentration is increased, charge screening will reduce the electrostatic repulsive barrier to protein aggregation, and the effect that lecithin has on promoting protein-protein interaction is reduced.

Emulsifiers can have a further effect on the mechanical properties of protein gels when fat droplets are present dispersed throughout the gel network. These so-called emulsion gels are formed when an oil-in-water emulsion is converted to a gel through the action of heat. A gel can be formed at lower protein concentrations than for a solution of the protein, since the fat droplets act as filler particles and increase the effective concentration of the proteins. The effect of lecithin on the mechanical properties of whey protein emulsion gels has been studied by Dickinson et al. (Dickinson & Yamamoto, 1996a,b; Dickinson et al., 1996). When lecithin is added before homogenisation (Dickinson et al., 1996) protein is displaced from the emulsion droplet surface. The droplets are not able to interact with the protein gel network through protein-protein interactions between the adsorbed and bulk phase protein, and they behave as inert filler particles that weaken the gel structure (Jost et al., 1989). Adding lecithin after homogenization does not cause protein displacement. Under these conditions an increase in the mechanical strength of the gel is seen (Dickinson & Yamamoto, 1996a,b), because the adsorbed proteins interact with the gel network, and strengthen it. Dickinson and Yamamoto (1996a) propose that lecithin is able to interact with adsorbed and non-adsorbed protein, thereby enhancing protein-protein cross-links and strengthening the gel.

Emulsifiers other than lecithin also have an effect on whey protein gel strength. The addition of glycerol monooleate (GMO) to WPC emulsion gels leads to a decreased elastic modulus at low additions of GMO, but this is recovered for higher levels of addition (Chen & Dickinson, 1999). Again it is believed that the decreased modulus results from protein displacement from the fat droplet surface, which does not allow them to participate in the gel network. At higher levels of GMO addition, the emulsifier aids the formation of a finer initial emulsion (smaller droplets), and when the emulsion gel is formed, even though the droplet do not crosslink with the gel structure, because they are smaller they perturb the protein gel network less (Chen & Dickinson, 1999).

The non-ionic emulsifier Tween-20 (T20) has a complex effect on emulsion gel strength (Dickinson & Hong, 1995; Dickinson et al., 1996), which is most likely due to its ability to bind with the major whey protein β-lactoglobulin to form a 1:1 complex. If the protein and T20 are present at a molar ratio (R) of protein:T20 of 1:1 (R = 1) there is a big increase in the gel elastic modulus for the heat set emulsion gel compared to gels made at lower R. As R is increased to 2, the modulus decreases sharply, and if R is increased above 4 the modulus increases again. The increase in modulus at R = 1 is attributed to the 1:1 complex formed between β-lac and T20 (Dickinson et al., 1996). As R is increased there is a displacement of protein is displaced from the emulsion droplet surface which amounts to about 90% displacement at R ≈ 2. This reduces extent of interaction of the emulsion droplets with the aggregated protein network and reduces the elastic modulus. When R exceeds 4 it is thought that mixed micelles of protein and T20 form, and these are able to reinforce the gel (Dickinson et al., 1996).

7.8 Recombined, Concentrated, and Evaporated Milks and Dairy Protein-Based Emulsions

Recombined and concentrated milk products are produced for economic reasons. The cost-effectiveness of transporting milk products that have been concentrated by removal of a proportion of the water phase, and the associated increases in shelf life, make milk concentration a viable process. Similarly, it is cost-effective to transport dehydrated ingredients for recombination into milk. The function of emulsifiers is, primarily, to aid in the formation and stabilization of the emulsions. A secondary function, which is claimed by many manufacturers of emulsifiers, is the effect that emulsifiers have on the heat stability of milks and milk products. This is of particular importance in enteral and parenteral emulsion products. These products are either tube-fed to seriously ill hospital patients (enteral formulations) or to new-born or young babies (parenteral formulations). In both cases microbial sterility of the product is very important, as it is undesirable to expose either of these two populations to high levels of bacteria since their immune systems may be suppressed or underdeveloped. As a consequence these types of emulsion are subjected to very intense heat treatments, and this can cause problems with emulsion fat droplet stability.

The effect of emulsifiers on milk and protein emulsion heat stability may be due to two effects. Low molecular weight emulsifiers are well known to compete for interfacial area with proteins and to displace them from the fat droplet surface (Dickinson & McClements, 1995). Displacement of protein depends on a number of factors such as the type (oil soluble or water soluble) and concentration of emulsifier (Dickinson et al., 1993a; Euston et al., 1995a) and environmental conditions such as the temperature (Dickinson & Tanai, 1992). The second effect of emulsifiers is that they are capable of binding to proteins and affect their heat stability and their adsorption at surfaces (Bos et al., 1997). The milk whey protein β-lactoglobulin is particularly susceptible to emulsifier-induced changes in heat stability since it has a hydrophobic cleft capable of binding amphiphilic and hydrophobic ligands (Hambling et al., 1992). Puyol et al. (1998) have reported that palmitic acid binding to β-lactoglobulin increases the temperature at which the protein denatures and gels, and Creamer (1995) has shown that binding of SDS or palmitic acid to β-lactoglobulin stabilizes it against denaturation in urea solutions.

In addition to reviewing the effect of emulsifiers on the properties of traditional milk emulsions, we will also summarize the relevant results on the heat stability of simple oil-in-water emulsions stabilized by dairy proteins. These studies have a direct relevance to the heat stability of commercial milks.

7.8.1 Recombined Milk

Recombination of dairy ingredients into milk products is a popular and viable alternative to the export/import of fresh dairy products. It is particularly important in countries where, for various reasons (e.g. transport delays, high temperatures), the shelf life of fresh products prohibits their importation or local production. In such cases, dried dairy ingredients are recombined close to the point of sale, so as to reduce these problems.

Two approaches to recombining of whole milk can be used;

1. Recombination of anhydrous milk fat (AMF), skim milk powder (SMP) and water.
2. Reconstitution of whole milk powder (WMP) with water.

In the past the latter process was, generally, less popular because of problems with the oxidative stability of the fat in the powder during storage. Advances in gas packing of powders, more regular shipping, and use of cooler storage facilities have removed this obstacle. Zadow (1982) noted that the choice of whether to recombine or reconstitute WMP depends on the export strategy of a particular manufacturer. The manufacture of different dairy products is often linked for practical reasons. If a particular manufacturer is making large quantities of butter, this requires separation of the cream (fat droplet) phase from the whole milk. This leaves a skimmed milk stream that is often dried to powdered SMP. Similarly, if cheese is the major product (which is made from whole milk), WMP is usually the major dried form of

milk manufactured by the processor. Thus, it makes economic sense for a butter-led industry to have a recombining strategy, whilst a cheese-led industry will have a reconstitution strategy. During the 1970s, an increase in the production of reconstituted WMP was seen. This corresponded to a change from a butter/SMP-oriented export industry to a cheese/WMP-oriented export strategy in countries such as New Zealand and Australia (Zadow, 1982).

In the recombination process, AMF, SMP and water are recombined to give a product with the same fat and protein content as whole milk (Kieseker, 1983). The skim milk powder is dissolved in the water at 40 to 55°C. The fat is added in a molten state, and the mixture is homogenized 14.0 to 17.5 MPa for the first stage and at 3.5 MPa at 55 to 60°C in the second stage. The milk is then subjected to one of three heat treatments: pasteurization at 72.2°C for 15seconds; UHT processing at 135 to 150°C for 2 to 5 seconds; or in-can sterilization (e.g. 120°C for 20 min). UHT processing can be by either direct steam injection or indirect heating in a plate or tubular heat exchanger.

Many manufacturers add low molecular weight emulsifiers to the formulation, particularly mono- and diglycerides (Zadow, 1982; Kieseker, 1983; Sjollema, 1987). Emulsifiers in the form of phospholipids can also be added through the practice of replacing up to 20% of the SMP with buttermilk powder (BMP) (Zadow, 1982; Kieseker, 1983; Sjollema, 1987) to give an improved taste.

It is claimed that emulsifiers aid in the formation of the milk fat emulsion during homogenization. Recent research by Mayhill and Newstead (1992), however, suggests that little benefit in terms of emulsion formation and stability is gained by their addition. In the case of mono-/diglyceride emulsifiers, it appears that tradition dictates their presence in the formulation. It is possible that any reduction in creaming due to reduced fat-droplet size in the presence of emulsifier is cancelled out by reduced emulsion stability caused by protein displacement.

7.8.2 Evaporated and Concentrated Milks

Evaporated and concentrated milks are made by removal of water from natural or recombined milks. The technology used to make these products includes evaporation under reduced pressure, reverse osmosis, ultrafiltration, and freeze concentration (Knipschildt & Andersen, 1994; Varnan & Sutherland, 1994). These concentrated milk products are more susceptible to heat coagulation when UHT processed or sterilized, than are normal concentration milks.

It has been known for some time that the heat stability of skim milk can be altered by surfactant molecules (Singh & Creamer, 1992). Anionic surfactants such as SDS have been shown to shift the maximum in the heat stability/pH profile of skim milk to more acidic values and to give a marked increase in maximum heat stability (Fox & Hearn, 1978). Cationic surfactants such as CTAB move the maximum heat stability to more alkaline values and give only a slight improvement in the heat stability at the maximum (Pearce, 1978; Shalabi & Fox, 1982). The mechanism

by which these changes occur is not known for certain. It has been suggested that binding of the surfactant to casein micelles alters the surface charge, which leads to changes in heat stability (Fox & Hearn, 1978; Pearce, 1978; Shalabi & Fox, 1982). This view is supported by the fact that non-ionic surfactants such as Triton X and Tween 80 have no effect on the heat stability of skim milk (Fox & Hearn, 1978). Research into the effect of addition of SDS and CTAB on the heat stability of milk proteins is useful only in helping to understand the process of heat coagulation. These surfactants cannot be added to milk products. In addition to this, in most concentrated milk products and in whole milk, the fat globules play a role in heat stability. Surfactants would interact with both the fat-droplet surface and the milk proteins. This makes the process of heat coagulation in fat-containing milks more complicated than in skim milk.

The milk fat globule membrane is known to play a role in the heat stability of milk. In non-homogenized whole milk the fat globules have little effect on heat stability (Singh & Creamer, 1992). However, after homogenization the heat coagulation time decreases with increasing homogenization pressure (Singh & Creamer, 1992). Obviously, this is an important observation since homogenization of milk is often essential so as to give adequate creaming stability.

It has been known for some time that lecithin can be used to increase the heat stability of homogenized and concentrated milks (Maxcy & Sommer, 1954; Leviton & Pallansch, 1962; Hardy et al., 1985; Singh & Tokley, 1990; Singh et al., 1992). The mechanism of lecithin action has as yet not been elucidated. Lecithin is known to displace protein from the fat-droplet surface (Courthaudon et al., 1991; Dickinson et al., 1993a; Dickinson & Iveson, 1993) and to complex with milk proteins (Barratt & Rayner, 1972; Korver & Meder, 1974; Hanssens & van Cauwelaert, 1978). Hardy et al. (1985) and McRae and Muir (1992) also believe that lecithin/protein interactions play a role in heat stability of concentrated milks. Singh et al. (1992) have put forward the view that lecithin may promote the formation of a complex between κ-casein in the micelles and β-lactoglobulin. The formation of the same complex can be promoted by pre-heating concentrated milks prior to the main heat treatment. This has been shown by Newstead et al. (1977) to have a stabilizing effect on the heat stability of recombined evaporated milk. It is interesting to note that, despite evidence of lecithin/protein interactions, Singh et al. (1992) have shown that the heat stability of skim milk is unaffected by lecithin addition. This is powerful evidence for the main stabilizing effect being fat-droplet based.

7.8.3 Dairy Protein-Based Emulsions

Dairy emulsions are formed by homogenizing fat or oil in the presence of an emulsifying agent, usually a protein. In dairy systems the common protein emulsifiers are the milk caseins and the whey proteins. Of these the caseins are very heat stable (Cruijsen et al., 1994) and casein stabilized emulsions must be heated at high temperature for long times before they become unstable. The whey proteins, on the

other hand are globular proteins, and as such they will denature and aggregate on heating. The fact that milk whey protein denaturation only occurs above the temperature range 70–80°C only exacerbates the problem since common processing temperatures are in this range or above. The obvious response to this would be to remove whey proteins from milk protein based emulsions and to use only the caseins. However, whey proteins are added for their nutritional value, especially in infant formulations based on cow's milk which are designed to have a composition that mimics human breast milk, and also because they are stable at acid pH whereas caseins are not. In paediatric formulae, milk protein based formulations are made with an increased level of whey protein compared to normal milk (Emmett & Rogers, 1997). The reason for this is that human milk has a higher whey protein: casein ratio (60:40) than cows milk (Emmett & Rogers, 1997). The sterility of these infant formulae is of critical importance since they are fed to premature or newborn infants who may not have an immune system that is resistant to common bacterial contaminants. As a consequence these are usually given an intense heat-treatment, such as in-container sterilization (e.g. 120°C for 20 min) which can lead to instability of the emulsion. To avoid this, the milk proteins in these formulations are usually hydrolyzed, i.e. they have undergone enzymatic hydrolysis to break up their native structure and release peptides and amino acids. Hydrolysis can be beneficial for two reasons. The whey protein β-lactoglobulin has been linked with allergy to cow's milk (Cordle, 1994; Tormo et al., 1998), and its hydrolysis can remove this by produces small peptide fragments and/or free amino acids, that are more easily digested and absorbed in the gut (Frøkjaer, 1994). Secondly, hydrolysis of whey proteins can reduce its susceptibility to heat denaturation. Unfortunately, this does not necessarily mean that dairy emulsions made with whey hydrolyzed proteins are more heat stable. Hydrolyzed protein form emulsions that are less stable to coalescence, and this is accelerated by heating (Euston & Finnigan, 2001). As a consequence, research has focused on how other ingredients affect the heat stability of food emulsions (Euston et al., 2001; Euston et al., 2002). In particular, low molecular weight emulsifiers have been shown to either increase or a decrease the aggregation rate in heated whey protein emulsions depending on the surfactant type (oil or water-soluble) and the concentration (Euston et al., 2001). This was explained in terms of either the ability of surfactants to displace protein from the droplet surface, or their ability to bind to whey proteins (particularly β-lactoglobulin, β-lac) and thus to influence denaturation and aggregation (Euston et al., 2001).

7.9 Other Dairy Applications of Emulsifiers

Emulsifiers have been added to other dairy products to exploit functional properties not normally associated with such emulsifiers. In recombined butter, phospholipids are added as anti-spitting agents, to prevent fat spitting during heating, and monoglycerides have been claimed to provide better 'stand-up' properties during storage (Kieseker, 1983).

Both sucrose esters and glycerol esters of fatty acids (monoglycerides) are finding a wide range of novel uses. In addition to being good emulsifiers for use in ice cream (Buck et al., 1986), they are known to improve the mouthfeel in yoghurt (Farooq & Haque, 1992), inhibit microbial growth (Conley & Kabara, 1973; Kato & Shibasaki, 1975; Shibasaki, 1979; Beuchat, 1980; Kabara, 1983; Tsuchido et al., 1981; 1987), enhance the thermal death rate of bacteria and bacterial spores (Tsuchido et al., 1983), and increase the heat stability of bovine serum albumin (Makino & Moriyama, 1991). It appears that these functions are a result of their ability to bind to proteins (Clark et al., 1992; Fontecha & Swaisgood, 1994).

7.10 Summary

Emulsifiers are very versatile food additives that can be used as aids to emulsion formation (e.g. in coffee whiteners/creamers and recombined products), or in contrast, as emulsion destabilizers in ice cream, whipping cream and whipped toppings. These two functions rely on the classical ability of emulsifiers to act as surface-active agents. In this way they can influence the formation and stabilization of the fat-droplet adsorbed layer and the composition of this layer. This ability of emulsifiers to displace protein from the droplet surface also, probably, accounts for the increase in heat stability of concentrated milks when phospholipids are added.

In a similar vein, displacement of adsorbed caseinate by GMS in cream liqueurs can be used to give increased acid stability to these products. A secondary function of the GMS in cream liqueurs is its ability to interact with proteins, thereby forming a weak gel in the aqueous phase. The associated increase in viscosity gives increased creaming stability. The ability of the emulsifier SSL to interact with caseinate is also exploited in coffee whiteners. The replacement of sodium caseinate in coffee whitener is achieved using SSL. It has been hypothesized (Leo & Betscher, 1971) that this is possible because of the increased mechanical strength of a protein/SSL adsorbed layer caused by emulsifier/protein interactions.

In processed cheese and cheese substitutes, the ability of charged emulsifiers to interact with proteins in the cheese matrix may prove a useful way of controlling cheese texture. This would introduce a way of reducing emulsifying salts such as mono- and polyphosphates. The final, but very important, function of some emulsifiers is their ability to act as initiators of fat crystallization. This is a particularly important function in whipped products, and in combination with protein displacement forms the basis of the formation of the whipped foam structure.

A wide range of emulsifiers allowed for food use can be added to achieve the above effects. Of late, consumer opinion has been focused on the ‘unnatural’ nature of synthetic emulsifiers. There is a slow push toward the replacement of synthetic emulsifiers with natural emulsifiers such as milk and soy phospholipid, and milk fat-derived mono- and diglycerides. The future may see a large increase in products such as BMP, which is rich in natural milk phospholipid as well as protein, and milk fat that has been enriched in mono- and diglycerides by processes such as controlled glycerolysis of triglycerides.

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