Chapter 12

Application of Emulsifiers to Reduce Fat and Enhance Nutritional Quality

Matt Golding and Eddie Pelan

12.1 Introduction

At a time when both malnutrition and obesity are increasingly becoming global issues, it is perhaps unsurprising that health, nutrition and weight management are the current main consumer trends within the food industry. As a consequence of these trends, innovation within this sector is being driven by the need to reduce perceived ‘bad’ ingredients: (saturated/trans) fat, salt and sugar, whilst attempting at the same time to fortify foods with nutritional actives, such as minerals, vitamins and antioxidants, all in support of a healthier lifestyle. The market for reduced fat/reduced calorie products is highly lucrative. In the UK alone, this market segment was worth GBP 1,875 million in 2004, up from GBP 1,372 million in 2000. In 2005, sales are expected to reach GBP 1,975 million. However it should be stated that in moving towards healthier, more nutritious products, the demanding consumer still expects that the quality of the particular food in question is not compromised in terms of overall sensory performance (appearance, texture, flavour).

The use of emulsifiers as a structuring tool for fat reduction and/or nutritional enhancement is exemplified in many food product systems. Some examples of emulsifier applications for fat reduction, such as fat structuring in homogenised creams and ice creams, are not necessarily new innovations. However, there are also more recent developments, such as the use of emulsifier mesophase technology which have found application in products such as zero fat ice creams and spreads.

This chapter reviews some of these diverse applications, both old and new, aiming to show the versatility of emulsifiers when in food formulations for the purpose of fat reduction and nutritional enhancement. The term emulsifier in this instance refers specifically to (non-protein) molecules derived from fatty acids, such as lecithins, monoglycerides and their derivatives. It aims to examine the contribution of emulsifiers in improving product structural design as a means of reducing or eliminating (saturated) fat from food systems, whilst attempting to maintain the quality of the food product. It also aims to explore the use of emulsifiers as delivery mechanisms for nutritional enhancement of foods.

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

12.2 Homogenised Dairy and Non-Dairy Whipping Creams

Homogenised whipping creams have been produced commercially for over four decades. They are specifically designed to imitate the organoleptic properties of non-homogenised dairy creams for the main application properties of cooking, baking, pouring and whipping. In the particular case of whipping cream formulations, some of the main advantages presented by homogenised dairy and non-dairy creams compared to non-homogenised dairy analogues are improved shelf-life (through UHT treatment), more robust whipping properties (less chance of buttering), and especially reduced fat level (reduced from typically 30–40% in dairy systems to <20% in non-dairy systems). Whilst the natural composition of dairy cream lends itself to providing good whipping properties above a certain fat level, the challenge with homogenised dairy and non-dairy whipping creams is to design an emulsion systems with comparable whipping and sensory performance at these greatly reduced fat concentrations.

Dairy whipping cream is seen as an indulgent product, understandable considering the relatively high fat content. Homogenised non-dairy and dairy creams aim to target this high fat content offering lower calorie alternatives. A comparison between the caloric content of some dairy and non-dairy whipping creams is given in Fig. 12.1.

Whipping creams are aerated emulsions with overruns typically ranging from 100–300%. Whipped creams should also possess good stand-up properties (i.e. the foam structure should be self-supporting and not flow). Although foam lifetime of whipped creams is not intended to be more than a few days, there should not be any

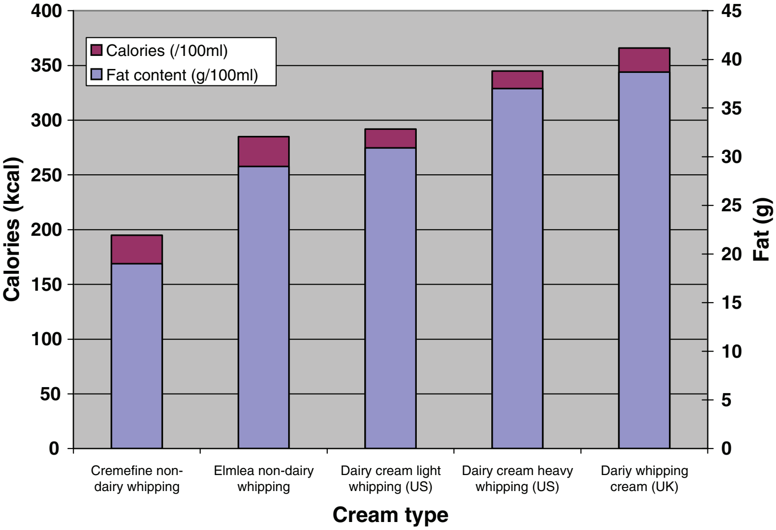

Fig. 12.1 Examples of caloric and fat contents of some non-dairy and dairy cream samples

visible ripening of the foam structure during the lifetime of the product. The mechanism by which a stable foam structure can be generated by whipping of dairy cream has been of considerable academic and commercial interest for a number of years (Flack, 1985; Bruhn and Bruhn, 1988; Goff, 1997; Leser and Michel, 1999; van Aken, 2001), and is discussed at greater length in chapter 7 of this book.

In order to demonstrate how the use of emulsifiers can contribute to the development of a low fat whipping cream, we need to review the mechanism by which whipped structures can be prepared. An elegant model for the development of the whipped cream structure is provided by Besner and Kessler (1998) who described the mechanism as occurring in three stages during the whipping process (Fig. 12.2):

a) Protein adsorption at the air water interface to provide initial foam stability. Milk proteins are generally present in both dairy and non-dairy cream formulations. In the specific case of dairy cream, most of the casein and whey protein is present in the continuous phase of the emulsion is not adsorbed at the oil-water interface (Needs and Huitson, 1991), forming a foam. At this stage, overrun is still low and the cream possesses no stand-up properties.
b) Adsorption of fat globules to the air-water interface. During the whipping process, the weak milk fat globule membrane allows fat droplets to adsorb to the surface of protein stabilised air-bubbles. This is possibly due to the rupture of the MFGM during the shearing process, which allows wetting and partial spreading of fat droplets on contact with the bubble surfaces. The formation of the globule-coated interface is more effective at preventing bubble coalescence than a milk-protein stabilised interface.
c) Fat globule adsorption to the bubble surfaces facilitates globule aggregation in the continuous phase. Droplet aggregation and subsequent formation of a fat globule network is required to prevent drainage of the stabilised foams and provide body/stand-up to the whipped cream. The shearing process leads to partial coalescence of fat droplets, an irreversible aggregation process in which fat wetting between two or more droplets can take place (Boode and Walstra, 1993;

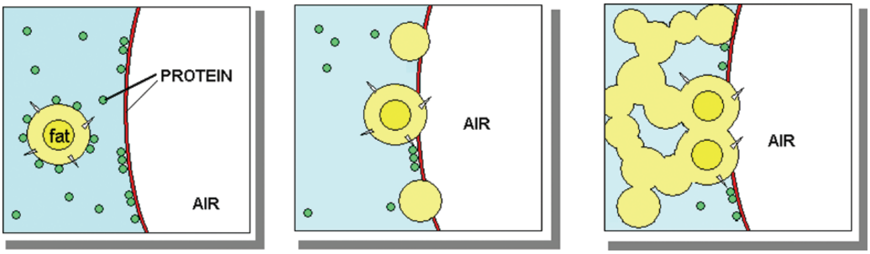

Fig. 12.2 Highly schematic representation of structure development in dairy whipping creams. **a** Initial stabilisation of air phase by adsorbed proteins. **b** Secondary stabilisation of air phase by adsorption of fat globules. **c** Development of partially coalesced fat network in the continuous phase

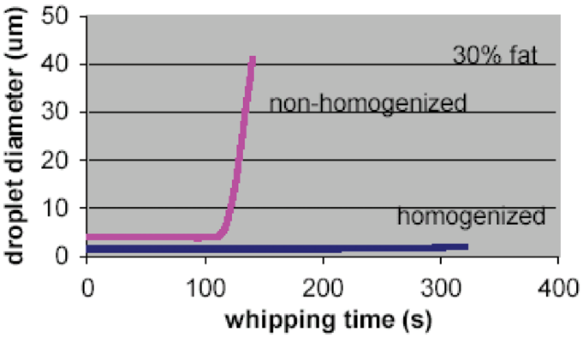

Fig. 12.3 Change in emulsion droplet diameter as a function of whipping time for 30% homogenised and non-homogenised whipping creams (Adapted from Besner H, Kessler HG, Milchwissenschaft 53 (12): 682–686 1998)

Table 12.1 Typical non-dairy whipped cream composition

Composition	Amount
Fat	20–30%
MSNF	3–6%
Added sugars	5%
Stabilisers	0.05–0.2%
Emulsifiers	0.05–0.6%

Vanapalli and Coupland, 2001). The presence of solid fat within the emulsion prevents full coalescence from taking place, so droplets partially maintain their integrity, hence the name (Boode et al., 1993) (Fig. 12.3)

A good whipped cream structure requires both fat globule adsorption to the surface of the bubbles in the foam, and the generation of an aggregated fat network in the bulk. This structure has been visualised by a number of authors (Buchheim, 1991; Brooker, 1993) and is described in more detail in chapter 7.

Non-dairy whipping creams and homogenised low-fat dairy whipping creams are formulated and processed to provide structuring according to this particular mechanism of whipping. A typical non-dairy whipping cream composition is given in Table 12.1.

For non-dairy creams butterfat is replaced by vegetable fat(s). These are commonly high lauric fats such as coconut or palm kernel oil, which provide the required solid fat content at whipping temperatures, but which melt at in-mouth temperatures (thus providing the desired oral response). As stated previously, non-dairy whipping creams can provide whipped structures with acceptable organoleptic properties at almost half the fat content of a conventional dairy whipping cream.

The milk solids non fat component (MSNF) is usually either skimmed or butter milk powder, which is added, in part, to provide a dairy flavour to the cream.

However, the MSNF also contains the milk proteins: casein and whey. Unlike dairy creams, non-dairy creams require a homogenisation step to form a stable emulsion. Milk proteins are important to the formulation, as they provide the initial stability to the emulsion on homogenisation. Droplet size for homogenised dairy and non-dairy creams is typically 1 µm or less, which is at least a quarter of that usually encountered for non-homogenised dairy creams. The reduction in droplet size also corresponds to a significant increase in specific fat surface area, which may account for the fact that less fat is required to provide a stable foam structure in the case of homogenised cream.

Protein is essential to provide a stable emulsion during preparation of the cream. However, the adsorbed protein layer prevents adsorption of globules to the air-water interface, and provides effective stability against partial coalescence during the whipping process. In order to achieve the functionality required to generate appropriate whipped structures, emulsifiers are included in the formulation. These have little or no effect on the stabilisation of the emulsion during homogenisation during processing, since at the temperatures applied during homogenisation (typically 80°C) there is less of a difference in interfacial tension between the emulsifier and the protein. However on cooling, an interfacial tension gradient opens between the protein and the emulsifier, with the result that the emulsifier displaces the protein from the interface. Displacement of adsorbed protein and replacement by emulsifier interfacial layers has a significant impact on the stability and functional properties of emulsion systems. Consequently, the displacement of protein by emulsifiers from interfaces has been the subject of considerable academic attention in recent years (Segall and Goff, 1999; Stanley et al., 1996; Tual et al., 2005, 2006).

In the particular case of non-dairy whipping creams, addition of emulsifiers has been shown to facilitate adsorption of fat globules to the air-water interface during whipping. This appears to be a common effect to most emulsifier systems, and therefore most emulsifier types will contribute to the interfacial stabilisation of the foam. There is some speculation as to why the presence of an emulsifier layer on the droplet interface should promote adsorption to the bubble surface. However, it may be related to the fact that regions on the fat globule surface where displacement has taken place are more interfacially-active than the protein layers adsorbed to the bubble surface during the beginning of the whipping process.

Consequently, during collisions with the bubble surfaces during shearing, fat globules become preferentially adsorbed to the air-water interface. Increasing emulsifier concentration will result in higher surface coverage of the emulsifier at the droplet interface and will therefore increasing the potential for a droplet to adsorb to a bubble surface during whipping. This particular aspect of the whipping process is used to great effect in the stabilisation of aerosol creams. Here, emulsifiers are used specifically to promote the adsorption of fat globules to the air-water interface where they provide excellent stability to the foam. Fat structuring in the bulk phase is not necessary since foam structure is derived from the high overrun produced by the aerosol.

For homogenised whipping creams addition of emulsifiers also promotes fat structuring during the whipping process, which is essential for providing rigidity to the cream. Type and concentration of emulsifier can have a significant impact on emulsion structuring properties. In short, it can be stated that displacement of protein from the oil-water interface by particular emulsifiers can create active sites on the droplet surface which can result in droplet aggregation under shear. The nature of the droplet aggregation is understood to be dependent on the type and concentration of the emulsifier systems used (Krog and Larsson, 1992).

Whilst it is certainly true that partial coalescence does take place for particular formulations of homogenised whipping creams, it is not necessarily the only type of aggregation observed during the whipping process. Under certain formulation conditions it is possible to design emulsions that form network structures through interfacial aggregation, as opposed to partial coalescence. In these circumstances, there is no rupturing of the interfacial layer. Both partial coalescence and interfacial aggregation result in the build-up of a fat network (similar to the processes taking place for dairy whipping cream), which increases the stand-up properties of the cream.

Whilst most food grade emulsifiers have the ability to displace protein from the interface of emulsion droplets, it is important to note that the composition and nature of the interface can vary significantly according to the specific emulsifier or emulsifiers used. Even emulsifiers with similar structures and HLB values can provide very different interfacial (and thus whipping) properties. As such, there are no definitive guidelines for which emulsifiers can provide acceptable whipping properties, although it is understood that particular emulsifiers are more effective at promoting fat adsorption to the air interface, whilst others are more effective at structuring the emulsion under shear. Often a combination of emulsifiers provides the most effective whipping properties in terms of aeration and fat structuring.

The composition of the oil-water interface is the main determining factor for how the emulsion behaves on whipping. Choosing the most appropriate emulsifier system for a non-dairy cream formulation and optimising its concentration and processing conditions will determine the functionality of the cream. Optimising emulsion droplet functionality is critical in determining whether a cream will be stable under storage conditions yet has acceptable whipping properties when aerated.

The current challenges facing the non-dairy creams industry are the ability to produce cream with acceptable structuring properties whilst continuing to lower the fat content of the cream. Whipping creams with less than 20% fat are now commercially available. Whilst there are a number of other structuring routes which can be used to provide whipped structures at even lower fat levels, the further reduction in fat will eventually lead to an unacceptable loss of sensory performance.

Additionally, removal of saturated triglycerides from formulations and replacing them with unsaturated triglycerides, whilst maintaining the textural and flavour properties associated with whipped cream is desired. Solid fat is a particular requirement for providing acceptable stand-up properties of whipped creams, both dairy and non-dairy. Manufacturing whipping creams with high levels of unsaturated oils which can be aerated and possess good structure is not a trivial exercise.

12.3 Reduced and Low Fat Ice Cream

Depending on which historical perspective is correct, ice cream has been consumed as an indulgent treat for between 300 and 700 years. At its most basic, ice cream can be described as an aerated frozen foam containing milk, cream, sugar with flavouring added (still most commonly vanilla). However, due to the consistent popularity of ice cream as a foodstuff (14.4 billion litres were sold globally in 2001), there are now many choices in today's ice cream market in order to suit a wide variety of consumer tastes. In order to provide some explanation as to the numerous ice cream formats available for purchase, the US FDA has set up standards of identity to characterise ice creams according to formulation. Whilst these are not necessarily applied globally, they can provide useful information regarding consumer trends in the consumption of ice cream. A summary of the FDA classification of ice cream is as follows:

- **Ice cream,** an aerated, frozen food made from a mixture of dairy products, containing at least 10% (milk) fat.

  Superpremium ice cream tends to have very low overrun and high fat content, and the manufacturer uses the best quality ingredients.

  Premium ice cream tends to have low overrun and higher fat content than regular ice cream, and the manufacturer uses higher quality ingredients.

  Regular ice cream meets the overrun required for the federal ice cream standard.

  Economy ice cream meets required overrun and generally sells for a lower price than regular ice cream.

- **Reduced fat** ice cream contains at least 25% less total fat than the referenced product (either an average of leading brands, or the company's own brand.)
- **Light** ice cream contains at least 50% less total fat or 33% fewer calories than the referenced product (the average of leading regional or national brands.)
- **Low-fat** ice cream contains a maximum of 3 g of total fat per serving (125 ml).
- **Non-fat** ice cream contains less than 0.5 g of total fat per serving.

The current consumer trends within ice cream present something of a paradox. Whilst consumers are generally becoming more health conscious about what they eat, the highest market segments in ice cream at the moment are the premium and super-premium brands of ice cream, which can contain anything between 10 and 20% fat (Fig. 12.4). At these high fat levels (usually in the absence of added emulsifiers), there is a dominant contribution of the fat phase to the sensory properties of the ice cream (creamy texture and flavour) as well as to the meltdown stability. Unfortunately, there is also a significant contribution to the caloric content as well!

To a degree this is accepted: ice cream has always been perceived as an indulgent product – with fat level as an indicator as to the quality of the product. Consequently, lowering of the fat content within the formulation is often accompanied by a perceived reduction in sensory quality of the ice cream. The relationship between calorific

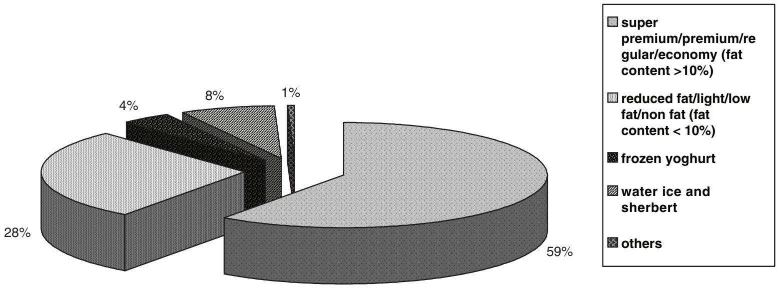

Fig. 12.4 Market segments for 2004 US Ice Cream market showing, amongst others, market share for high (>10%) and low (<10%) fat ice cream products. US Ice Cream market was estimated at 1.6 billion US gallons in 2004

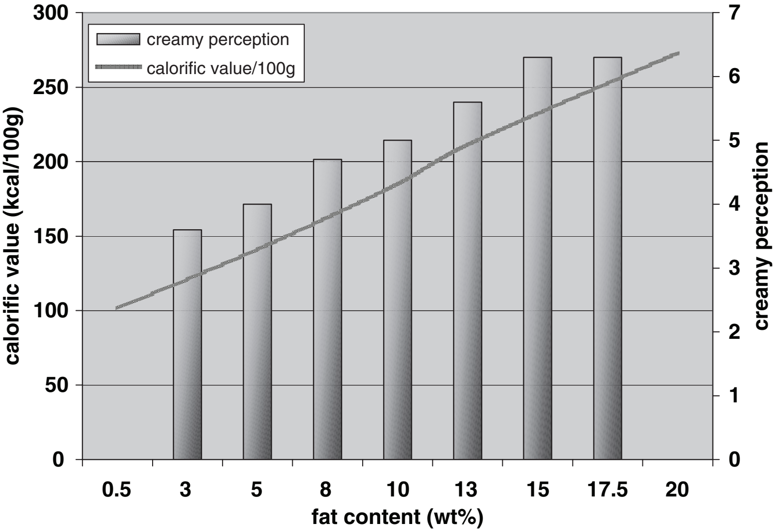

Fig. 12.5 Graph showing the relationship between fat content in ice cream, calorific content and perceived creamy texture. Ice creams were consistent in formulation and did not contain emulsifiers

content, as supplied by fat, and the perceived creaminess of the ice cream (in the absence of emulsifiers) is given in Fig. 12.5. However, it is possible to formulate ice creams with a lower fat content in which the sensory properties of the ice cream are not compromised by the reduction in fat.

One route by which the quality of lower fat ice creams can be improved is through the inclusion of low concentrations (0.1–0.5%) of emulsifiers to the ice cream mix. The use of emulsifiers in ice cream formulations is not particularly new, and its earliest application dates back to the 1940s. As with whipping creams, emulsifiers are added to improve the functionality of the fat, such that the fat becomes an active component in the development of the ice cream structure. This can lead to improved product attributes, such as dryness upon extrusion, improved air phase stability, improved meltdown resistance and improved sensory performance of the ice cream, especially for lower fat formulations.

A typical ice cream mix is given in Table 12.2 below.

Processing of ice cream requires the mix to be pasteurised, homogenised and aged prior to freezing. Prior to homogenisation, water soluble ingredients such as stabilisers, sugars and proteins are dispersed in the aqueous phase. Any oil soluble components are dispersed in the oil phase before the two phases are mixed. Emulsifiers used in the ice cream industry are limited by legislation and are predominantly monoglycerides, and to a lesser extent polysorbates. Monoglycerides, being of low HLB are generally dispersed in the oil phase, whilst the polysorbates being of higher HLB are placed in the aqueous phase.

After homogenisation and ageing the mix is transferred to the ice cream freezer. An ice cream freezer is essentially a scraped surface heat exchanger, operating at –20 °C into which air is channelled at a pressure of 2 bar. The low temperatures on the surface of the heat exchanger barrel form ice crystals, which are scraped into the ice cream mix. In addition, the high shear forces applied within the freezer assists in aeration of the ice cream. This combination of high shear and low temperature creates the frozen foam ice cream microstructure. The ice cream is then extruded from the freezer before being hardened to at least −30 °C. Storage of ice cream is generally maintained at −18 °C, although some formulations are designed to be stored at temperatures as warm as −10 °C. Volume fractions of the various phases are given in Table 12.3 for different ice cream formats, whilst the distribution

Table 12.2 Ingredient breakdown of a typical regular ice-cream

Ingredient	Amount (wt%)
Fat	5–15
Milk protein	4–5
Lactose	5–7
Other sugars	12–16
Stabilisers	0–0.5
Emulsifiers	0–0.5
Total solids	28–40
Water	60–72

Table 12.3 Typical phase volumes of ice cream components

Phase	Low fat ice cream (%)	Regular ice cream (%)	Premium ice cream (%)
Fat	1	5	10
Air	48	50	35
Ice	31	30	25
Matrix	20	15	30

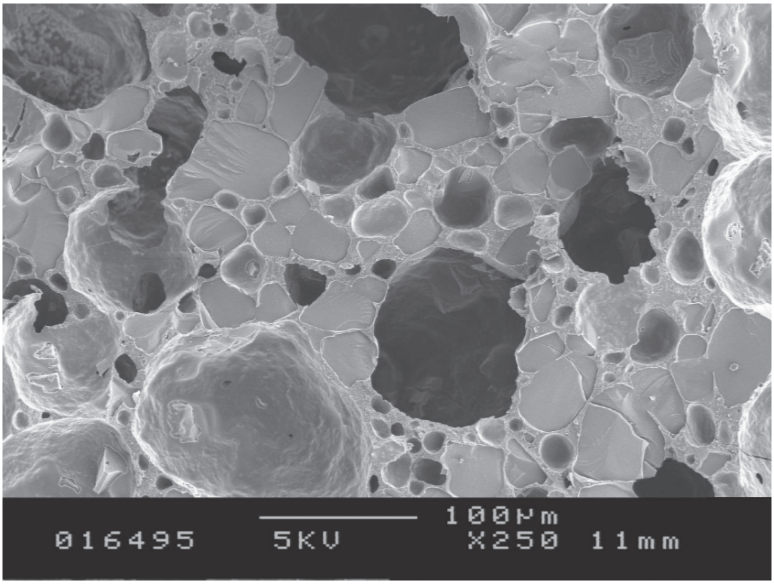

Fig. 12.6 Scanning electron micrograph of ice cream microstructure showing air bubbles, ice crystals and surrounding matrix

of these phases in a typical ice cream microstructure is shown by scanning electron microscopy in Fig. 12.6.

The mechanism by which addition of emulsifiers can influence the microstructural properties is in some respects similar to the effects observed for homogenised whipping creams. As with whipping creams, emulsifiers are added in order to displace protein from the interface of the fat droplets. This takes place during the ageing process after homogenisation. The presence of the emulsifier on the surface of the emulsion droplets facilitates the adsorption of the droplets to the air-water interface during freezing (again the analogy with whipping cream systems can be drawn, since droplets stabilised purely by protein do not undergo adsorption to the surface of bubbles).

Several studies have been carried out to better understand the mechanism by which fat globules containing emulsifiers can adhere to the air-water interface. Whilst the exact mechanism is still the subject of some speculation, it has been recently shown by Zhang and Goff (2005) that the process is sensitive to both the type and concentration of both emulsifier and protein present during the freezing process. In the case of the emulsifier, this is in part influenced by the efficacy by which specific emulsifiers can displace protein from the interface – the more droplet surface coverage by the emulsifier, the greater the potential for adsorption to the surface of a bubble.

Pelan et al. (1997) showed that displacement from the interface varied according to the emulsifier used (Fig. 12.7), and that for the commonly used ice cream emulsifiers, displacement increased in the order:

Saturated monoglycerides < unsaturated monoglycerides < polysorbates

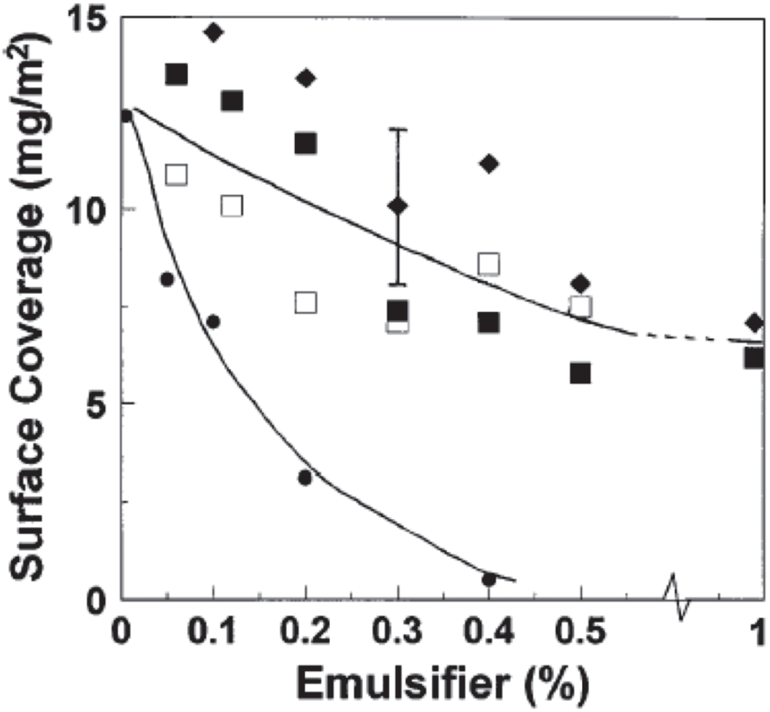

Fig. 12.7 Change in protein loading for ice cream mixes (12% fat, 13% SMP, 15% sucrose) as a function of emulsifier type and concentration. • Tween 60; ❑ Unsaturated monoglyceride; ■ Saturated monoglycerides; ♦ Glycerol monopalmitate

Differences in displacement between the two types of monoglyceride have in the past been attributed to the structural arrangement of the two emulsifiers at the oil-water interface. However, it may also be due to the fact that saturated monoglycerides are able to nucleate fat crystals on cooling and may therefore become trapped within the bulk of the oil droplet, rather than adsorbing to the interface. Unsaturated monoglycerides have a lower melting temperature than saturated monoglycerides and do not tend to act as nucleators. The fact that emulsion droplets containing unsaturated emulsifiers crystallise at a slower rate than those containing saturated emulsifiers may allow the unsaturated emulsifiers longer to adsorb to the oil-water interface, thereby displacing more protein at equivalent concentrations. Polysorbates are even more effective, since they are water-soluble and adsorb to the oil-water interface independently of the internal state of the oil droplets.

The ability for oil droplets containing emulsifiers to adsorb to the air-water interface has been shown to reduce bubble size during processing and improve bubble stability on storage (e.g. Fig. 12.8 for zero fat ice cream). As with whipped cream systems this is attributed to a Pickering type stabilisation mechanism, which

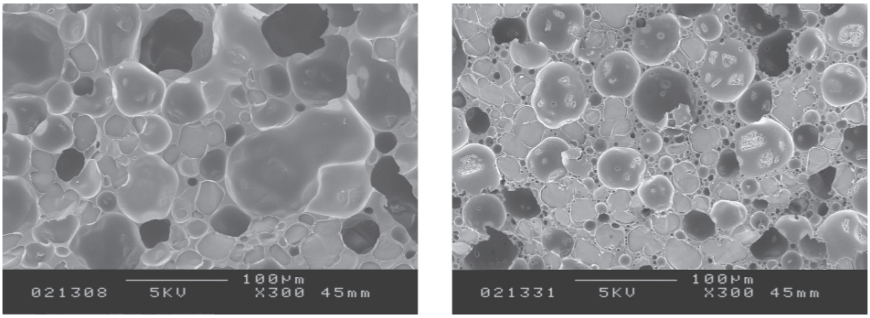

Fig. 12.8 Scanning electron micrographs of zero fat ice creams. In the left hand image the air phase is stabilised purely by milk proteins present in the formulation. In the right hand image, 0.5% saturated monoglyceride has been added to the formulation prior to freezing

prevents coalescence from taking place. Improvement to the fineness of structure and the stability of the air phase are partly responsible for the improved textural attributes of ice cream containing emulsifiers compared to those without. Certainly addition of emulsifiers and the adsorption of fat to the air interface helps inhibit loss of quality through air phase coarsening as a result of temperature cycling.

Inclusion of emulsifiers in the formulation also helps to promote structuring of the fat through partial coalescence, which takes place during the freezing process. Again, the displacement of protein from the oil-water interface weakens the fat droplets. Consequently, droplet collisions driven by the high shear forces in the ice cream freezer allow penetration of droplet interfaces by fat crystals leading to partial coalescence. Again, there are differences between emulsifier types in terms of the amount of aggregated fat generated in the freezer such that, for equivalent concentrations:

polysorbate 60 > unsaturated monoglyceride > saturated monoglyceride

Again, this is in part due to the relative amount of protein displaced by each type of emulsifier at the oil-water interface. However, in the specific case of saturated monoglycerides there is an optimum emulsifier concentration at which maximum fat aggregation can be achieved. If the saturated emulsifier level increases too much, droplets become more stable to aggregation. This is possibly due to the formation of a crystalline emulsifier layer on the surface of the droplets which is thick enough to prevent fat penetration and wetting from taking place.

Whilst fat aggregation is unlikely to lead to the formation of extended fat networks in the same way as whipping cream (due to the lower fat content and presence of ice which disrupts the formation of network structures), localised fat structure formation does improve the meltdown resistance of ice cream. In this case, it is likely that small aggregates of fat inhibit drainage of liquid from the foam structure as the ice melts, holding the foam together for longer.

Partial coalescence has been an accepted model for emulsifier-facilitated fat structuring in ice cream for many years now. However, it has been recently been demonstrated that addition of emulsifiers can lead to other forms of fat droplet functionality which can provide additional benefits in terms of quality improvements for reduced and low fat ice cream.

Continued understanding of how emulsifiers add functionality to ice cream systems is necessary if the ice cream industry is to follow in the current trend of health and vitality. There is a constant need to improve the quality of low fat systems, and new challenges such as the replacement of saturated fat in formulations will require development of new approaches for how emulsifiers can continue to contribute to the improved structuring of ice creams.

12.4 Zero Fat Ice Cream

The use of saturated monoglyceride emulsifiers has also been shown to provide a specific role in improving the sensorial attributes of ice cream systems in the absence of fat. Zero fat ice cream is something of a niche market. Whilst it might be considered desirable that the overall calorific content of the ice cream is greatly reduced relative to ice cream containing fat, there is unfortunately a corresponding significant drop in product quality which is generally not acceptable for most consumers.

There are two potential routes for improving the sensory properties of zero fat ice cream. The first route uses direct replacement of fat with a non-fat substitute. Fat mimetics, such as microparticulated proteins, can provide limited sensory improvements, but these are expensive and quality enhancement is not particularly noticeable.

An alternative route is provide sensory benefits through optimisation of the microstructure of the ice cream. It is known that ice cream quality is as much dependent on optimising microstructure, as it is about using high quality ingredients. It has been shown that even with the removal of fat from the composition, there are alternative, indirect formulation routes for improving the microstructure, and thus the organoleptic properties of the ice cream.

One particular formulation route that has been patented by Unilever and is currently used in zero fat formulations is the inclusion of a small amount of saturated monoglyceride into the ice cream mix. Although monoglyceride is classified as a fat/lipid on ingredients lists, the amounts used (typically 0.1–0.5%) are within legislation requirements for the ice cream to be labelled as zero fat.

The addition of monoglyceride in a fat-free ice cream mix has been shown to result in the formation of a considerably finer air phase structure compared with protein alone. Figure 12.8 compares micrographs of zero fat ice creams containing no added monoglyceride or 0.5% added saturated monoglyceride. The protein stabilised air phase shows bubbles typically 100 μm or larger, with some signs of coalescence also having taken place. In comparison, the ice cream containing the added emulsifier shows a bimodal distribution of stable air bubbles with a larger phase of typically 50 μm or less, and a high number of very small bubbles of<10 μm.

The observed bimodal distribution is suggestive that partial disproportion has taken place. The fact that bubbles of <10 μm can still be observed implies that this smaller fraction is resistant to complete disproportionation. These small, stable air bubbles are understood to provide a positive contribution to the organoleptic properties of the ice cream. They are stable melting at ambient temperatures, and may retain stability in the mouth, giving the perception of enhanced creaminess and reduced iciness.

Figure 12.8 indicates that the inclusion of a low concentration of monoglyceride can greatly improve the stability of the aerated structure within ice cream. Saturated monoglycerides display particular mesophase behaviour in aqueous media. At temperatures below the Krafft point, and for low concentrations they form β-crystals in water which do not have foaming capacity. However, in ice cream mixes the monoglyceride forms surface-active particulates. This is understood to be due to the formation of milk protein-monoglyceride liposome structures as a result of the homogenisation process. These are able to adsorb to the air-water interface during the freezing process. These particulates are able to provide considerably greater surface elasticity to the bubbles than protein alone (Fig. 12.9), providing effective resistance to coalescence and preventing complete disproportionation from taking place.

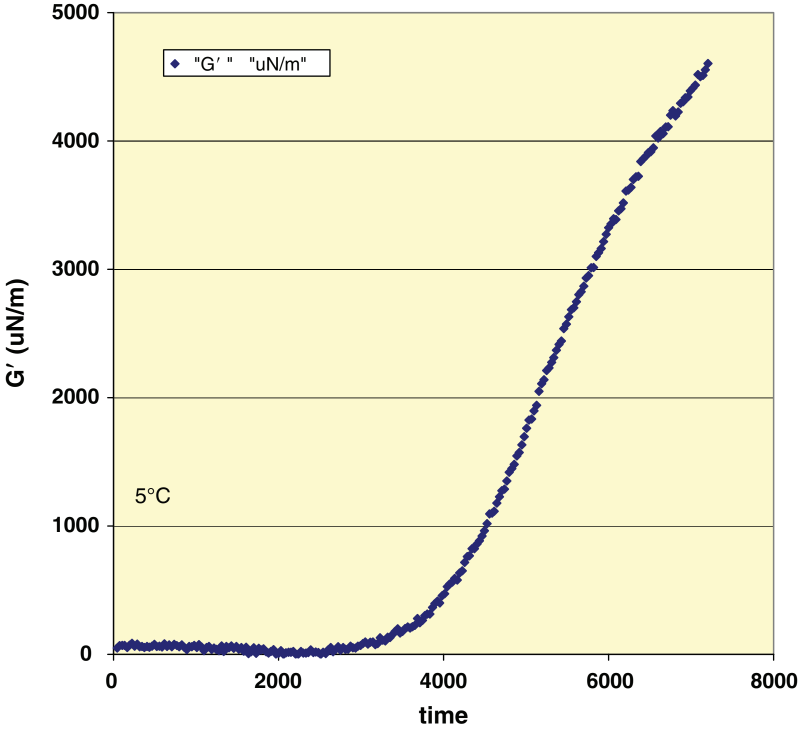

Fig. 12.9 Surface shear rheology (Camtel CIR-100 rheometer) of homogenised mixture of 2.5% sodium caseinate and 0.1% saturated monoglyceride at 5 °C (torque = 10,000 μ rad, frequency = 3 Hz)

Saturated monoglycerides appear to be the most effective emulsifier for improving the stability of the air phase in zero fat ice cream. Unsaturated monoglycerides, for example, can also form particulates in the presence of milk proteins. These are known as cubosomes. However, it has been shown that whilst these are also surface active and can readily adsorb to the air-water interface, the surface elasticity of an interface stabilised by cubosomes is considerably lower than that of saturated liposomes. This may, in part, explain why unsaturated emulsifiers are less effective at providing foam stability in the absence of fat. Specific choice of emulsifier is ultimately limited by legislation. Whilst some alternative emulsifiers, such as polyglycerol esters of monoglycerides also show excellent foams stabilising properties in the absence of fat in a manner similar to that of saturated monoglycerides, these do not currently have clearance with the US and EU markets for application within ice cream formulations.

The use of monoglycerides to improve the sensory properties of zero-fat ice cream provides an effective example of how the relationship between ingredients processing and product microstructure can be manipulated to give improvements in the quality of low and zero fat foods.

12.5 Margarine

12.5.1 Historical perspective

Margarine was invented and patented by Mège Mouriès in 1869 as the result of a national competition from Emperor Napoleon during the economic crisis leading up to the Franco-Prussian war. Napoleon III needed a cheap butter substitute, which would feed his armies and remain edible after long journeys. Thus the original advantage of margarine was that it offered a *high* calorific energy source that would be microbiologically stable for several months. Since then consumer demand and a changing world over the last 120 or so years have spurred margarine (spread) development to become one of the healthier (low fat) food types available today.

Mouriès theory was that butter fat was formed in the udder of the cow from it's own fat and milk, so he mixed oleo (beef tallow) and skimmed milk and added a strip of udder to mimic the way in which milk is curdled. He found that if he chilled, stirred and worked the mixture, it formed a white buttery mass with a pearly sheen, which he named after *margos*: Greek for pearl (Davidson, 1999). This biological reasoning was completely wrong, but Mouriès had succeeded in producing a butter-like substance that has now become an indispensable staple on bread or as a cooking aid in large areas of the world.

The real microstructure and a schematic diagram of a typical margarine are shown together in Fig. 12.10. What is clear from the Cryo-TEM inset photo is that the margarine is inhomogeneous at a microscopic level, consisting of a finely divided water phase in a continuous phase comprising fat crystals and liquid oil.

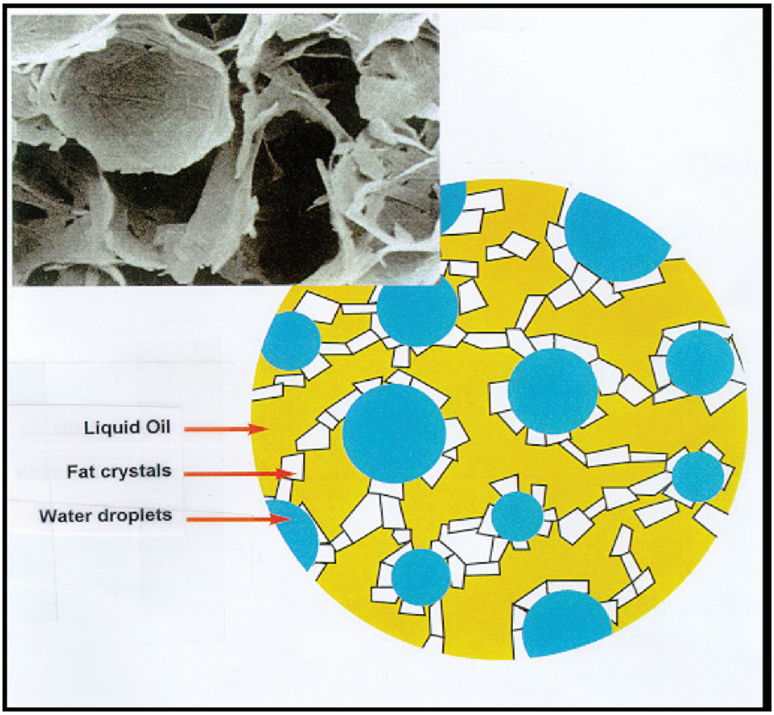

Fig. 12.10 Upper left corner: Cryo-SEM image of a fat crystal network in a 60% fat-continuous spread; oil and water have been removed from the sample for clarification

Conceptually we can think of margarine as a particle-filled gel in a plastic network as shown schematically beside the physical microstructure.

Margarine is technically an oil-in-water emulsion. Depending on legislation, full fat margarine has between 80 and 82% fat as this was the original benchmark definition of full fat butter which it had to mimic.

As is well known, oil and water don't readily mix or stay mixed, but for full fat margarine it is almost impossible *not* to make a stable emulsion. This is due to the solid fat crystals present in the overwhelming continuous phase rapidly adsorb to the oil-water interface during the manufacture of the pre-emulsion and crystallise out upon cooling during processing: classical Pickering stabilisation.

The product has to be microbiologically safe, both in transit to the shops and afterwards during repeated use (open shelf-life). Additionally, it has to function as a heat transfer medium in the kitchen during cooking or baking, it functions as an ideal carrier of fat soluble flavours, and it improves the 'mouthfeel' of bread by acting as a lubricant. It should also spread directly from the fridge without tearing the bread. It should be healthy by providing essential fatty acids, fat-soluble vitamins and aid in the uptake of other fat-soluble ingredients. Recent developments now offer cholesterol reduction with regular intake and margarine is an excellent vehicle to provide a delivery platform for functional ingredients in many parts of the world (e.g. Nestel et al., 2001)

Margarine quality has come a long way since the first crude products from 130 years ago. The first technological improvements were in the refinement of the triglyceride processing (hardening and fractionation) in the early twentieth century. This led to better tasting fat (less rancidity as metals were removed to reduce oxidation) and also allowed the 'design tools' to manipulate melting curves for *blends* of fats to tailor margarine to different applications e.g. frying, baking or spreading on bread. (e.g. Bockisch, 1993).

12.5.2 Low and Very Low Fat Spreads

Around the mid 1970s, as consumers became more health conscious, the drive to lower fat levels in the edible fats sector began. Fat levels were reduced from the traditional 80% levels to 60% (reduced fat spread) and then through further development to 40% fat (low fat spread) in the 1980s. Processing of these so-called reduced fat spreads was still the same as full fat, namely a fat-continuous process, but when the dispersed water phase volume reached 60% in the low fat spreads, novel water phase control through process and emulsifiers was needed. Using the traditional process route at 40% fat resulted in water continuous systems so a new 'inversion' process was developed. The choice of emulsifier was now crucial in controlling the balance between break-up and coalescence in the product to effectively force the equilibrium towards coalescence to drive phase inversion from a water continuous pre-mix to a fat continuous product. This is a non-trivial challenge for the emulsion scientist. The product begins as a thin water continuous liquid pre-mix which is cooled under controlled shear until it phase inverts to become the thick spreadable plastic structure we know as margarine. However if there is a problem during manufacture the cooled product has to be re-heated and re-worked back to a water continuous state where it is re-processed in the pre-mix tank. When the margarine is consumed it should also re-invert quickly in the mouth to provide salt release. Thus there is a delicate interplay between small molecular weight monoglycerides and lecithins (fat continuous) and milk proteins (water continuous) to get the required emulsion stability during pre-mix, inversion, storage and in-use.

The trend in fat reduction has continued into the 1990s where the technical limit based on conventional processing is around 20% fat. Holding 80% water in 20% fat is a challenge in collodial packing and can only be accomplished by using powerful water-in-oil promoting emulsifiers such as Admul wol (Polyglycerol polyricinolate). Effectively the emulsion is beyond the close-packed limit for random spheres and as such exists as a polyhedral mass, where the internal pressure to re-coalesce and phase separate is high.

Fortunately, as little as 0.5% Admul Wol will emulsify and stabilise 80% water in 20% oil. Additional product stability can be gained by thickening the aqueous phase by biopolymers. However the problem now shifts to making the spread de-stabilise in the mouth during mastication to allow salt release and to reduce unnecessarily thick mouthfeel. This is a difficult compromise to make; stable during processing, storage and spreading, becoming physically unstable during the transit time (mastication) in the mouth. A replacement for Admul Wol having the same physical stability but better mouthfeel is a Holy Grail in low or very low fat spreads.

Another low fat challenge is to obtain the same product functionality (cake baking, shallow frying, and on bread). For kitchen applications, fat is *the* perfect medium to transfer heat during the cooking process as it as a much higher boiling point than water. In particular for baking, the fat phase is crucial during the early steps of air incorporation and stabilising when whipping the cake batter. If the batter doesn't have enough entrained air, or the bubble size distribution is not optimal, then the final cake texture and crumb structure is not good. Solid (saturated) fat (SAFA) plays an important role here traditionally, so when one goes from 80% fat to say 40% fat the baking functionality is quickly lost. To restore this to the high fat standard required a change in emulsifier type and level. The supplementary use of alpha-tending emulsifiers (monoglyceride derivatives) or anionics (SSL, CSL) were found to compensate for the loss of SAFA upon reduction of fat level. In addition, the use of mono-glycerides has a beneficial effect on the anti-staling of the starch allowing a longer shelf-life of the baked product. (Wootton et al., 1967; Mizukoshi, 1997)

At 60% fat emulsifiers alone can compensate for reduced kitchen functionality, but when the fat level is reduced to 40%, processing necessitates that the water phase is thickened, typically by biopolymers such as starch or alginate. Then the kitchen performance is severely hampered as the biopolymers tend to burn or discolour during heating. In addition spattering (explosive loss) of the water phase during frying becomes a bigger issue as the fat level is reduced. To combat spattering, lecithin is added to promote the flotation of water droplets to the air/oil interface during frying where they can harmlessly evaporate. Salt also has a positive effect on reducing spattering by functioning as anti-bump crystals during frying. In practice the limit for general kitchen functionality is thus 60% fat where a viscous water phase is not needed for processing.

Duplex emulsions (O/W/O) have also been considered as a theoretically attractive route to lowering fat level as the internal water phase under some circumstances can 'hide' some of the external fat phase. In practise there are two main problems: processing is not perfect as the first emulsion W/O has to be carefully emulsified into the bulk fat/oil to make the O/W/O. Since emulsification requires shear it is inevitable that the duplex emulsion is broken and thus yields are low. The second problem is coalescence of internal phase during storage, which again leads to loss of overall emulsion stability. Recent successes have been made with duplex emulsion manufacture using microfluidic devices (e.g. Nisisako et al., 2005). However these currently manufacture at single drop rates so are many orders of magnitude too slow to be commercialised. Membrane emulsification has also shown promise in duplex manufacture, but with systems containing protein as one emulsifier, fouling and blocking of pores is a difficult problem here (Hitchon et al., 1999).

12.5.3 Zero-Fat Spreads (Lipogel Technology)

It is the ambition of many product developers to successfully replace all the fat in a product whilst maintaining acceptable sensory properties of the food product. In the case of spreads, which are generally a high fat food, this presents an incredibly challenging technical problem. A number of approaches have been tried including gelling bio-polymers, shear-gelled systems and the use of microparticulated proteins. One particular approach to this problem is to use the mesophase properties of monoglycerides and other emulsifiers in solution to design structures with acceptable material and sensory properties.

Figure 12.11 shows a typical phase diagram of a monoglyceride system. Given the relative simplicity of the chemistry of this system it is surprising how rich the microstructural possibilities are as witnesses by the different mesophase possibilities. A summary of this approach is that emulsifiers, due to their amphiphilic nature, display particular phase behaviour in solution in the absence of fat. For example, through control of formulation and process, monoglyceride lamellar structures can be crystallised into water-swollen α-gel crystal structures which can provide spread-like textures, even for relatively low concentrations of emulsifier. Typical levels of emulsifier are 4–10% which when processed properly can hold 96–90% water in a plastic, spread like rheology. These liquid crystal lamellar phases are sometimes called lipogels. Small amounts (5%) of fat can also be included but processing becomes critical.

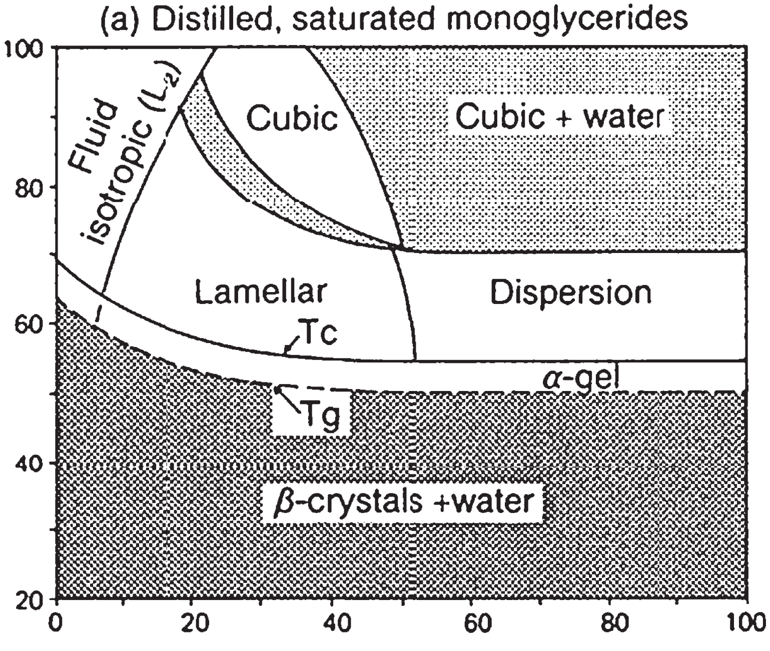

Fig. 12.11 Phase diagram showing possibilities of (edible) structured mesophases (Krog, 1997, with permission)

Nutritionally 1 g fat (SAFA) is comparable to around 20 g of lipogel which offers a spreadable product at low nutritional load. This structuring/nutritional ratio would not be possible with conventional fat –continuous technology.

The main challenge of lipogel technology is to manipulate the phase behaviour of the emulsifier systems to provide the most appropriate crystalline structure for the particular application, thus optimising the rheological properties of the lipogel. Often co-emulsifiers are needed (depending on pH); however, salt is known to interfere with mesophase formation. However, through appropriate use of emulsifier blending and processing it is possible to create lipogel structures for a wide range of applications, not just for use in zero-fat spread systems. In addition because monoglygerides are lipid based, they can incorporate the same fat soluble flavours and colorants normally used in high fat margarine which is a distinct advantage above water-continuous products as zero fat alternatives. Since lipogel contains high levels of surfactant it performs surprisingly well as a baking margarine because the monoglycerides aid the aeration step during batter preparation.

Other applications of the lipogel technology have now been extended to include zero fat dressings, mayonnaise, ice cream, whipping cream, and frozen desserts but the sensory properties of this class of products often differs from the high fat version.

12.5.4 Nutritional Enhancements

The food industry has come a long way in the last few decades. Particularly now that most developed countries have the luxury of eating (often more than) enough calories per day the emphasis has shifted away from absolute level of fat or oil to *quality* of fat or oil. Thus for example most spreads now sold typically contain 40% fat and less high fat margarine or zero fat spreads are sold today. In addition the consumer is constantly looking for more functionality in the products. This can take many physical or nutritional forms such as easier spreadablilty or spoonability from the packaging, fortification (vitamins and minerals) and more recently to complex functional claims such as reduced cholesterol, blood pressure, improved satiety at reduced calories, or even improved mental performance (e.g. Upritchard et al., 2005).

For each of these functional claims there will typically be a preferred product format depending on functional active and even a preferred targeted part of the body to deliver the functional ingredient to. Manufacturers will have to use clever emulsion design rules to take account of break-down under physiological conditions to be able to make verifiable functional claims. For example fast breakdown in the mouth boosts flavour release and salt perception; however it may be necessary to get an intact emulsion into the stomach or even small intestine to claim proper (improved) bioavailability of a fortified product.

Such challenges between emulsion science, processing and nutritional demands will take functional food claims (and thus emulsion science) to a new level in the next decades in response to ever increasing consumer demand for healthy, nutritious and good tasting food.

References

Besner H. and Kessler H.G. (1998). Interfacial interaction during the foaming of nonhomogenized cream. *Milchwissenschaft* **53** (12): 682–686.

Bockisch M. (1993). Nahrungsfette und Öle. *Handbuch der Lebensmitteltechnologie*, Ulmer Verlag, Stuttgart, Germany.

Boode K. and Walstra P. (1993). Partial coalescence in oil-in-water emulsions.1. Nature of the aggregation. *Colloid Surface* A **81**: 121–137.

Boode K., Walstra P. and DeGroot-Mostert A.E.A. (1993). Partial coalescence in oil-in-water emulsions.2. Influence of the properties of the fat. *Colloid Surface* A **81**: 139–151.

Brooker B.E. (1993). The Stabilization of air in foods containing fat—a review. *Food Structures* **12** (1): 115–122.

Bruhn C.M. and Bruhn J.C. (1988). Observations on the whipping characteristics of cream. *Journal of Dairy Science* **71** (3): 857–862.

Buchheim W. (1991). Microstructure of whippable emulsions. *Kieler Milchw Forsch* **43** (4): 247–272.

Davidson A. (1999). *The Oxford Companion to Food*, p. 479, OUP.

Flack E. (1985). Foam Stabilization of dairy whipping cream. *Dairy Industries International* **50** (6): 35–37.

Goff H.D. (1997). Instability and partial coalescence in whippable dairy emulsions. *Journal of Dairy Science* **80** (10): 2620–2630.

Hitchon B., Gunter W.D., Gentzis T., Bailey R.T., Joscelyne S.M. and Tragardh G. (1999). Food emulsions using membrane emulsification: conditions for producing small droplets. *Journal of Food Engineering* **39**(1) 59–64(6).

Krog N. and Larsson K. (1992). Crystallisation at interfaces in food emulsions—A general phenomenon. *Fett Wissenschaft Technologie-Fat Science Technology* **94** (2): 55–57.

Krog N. (1997). Food emulsifiers and their chemical and physical properties in food emulsions, 3rd Ed. (SE Friberg and K Larsson), Marcel Dekker, NY, pp 141–188.

Leser M.E. and Michel M. (1999). Aerated milk protein emulsions—New microstructural aspects. *Current Opinion in Colloid & Interface Science* **4** (3): 239–244.

Mizukoshi M. (1997). Baking mechanism in cake production. *Journal of Food Engineering* **41**: 97–100.

Needs E.C. and Huitson A. (1991). The contribution of milk serum-proteins to the development of whipped cream structure. *Food Structures* **10** (4): 353–360.

Nestel P., Cehun M., Pomeroy S., Abbey M. and Weldon G. (2001). Cholesterol-lowering effects of plant sterol esters and non-esterified stanols in margarine, butter and low-fat foods. *European Journal of Clinical Medicine* **55**: P1084–P1090.

Nisisako T., Okushima S. and Torii T. (2005). Controlled formulation of monodisperse double emulsions in a multiple-phase microfluidic system. *Soft Matter* **1:** 23–27.

Pelan B.M.C., Watts K.M., Campbell I.J. and Lips A. (1997). The Stability of Aerated Milk Protein Emulsions in the Presence of Small Molecule Surfactants. *Journal of Dairy Science* **80**: 1010, 2631–2638.

Segall K.I. and Goff H.D. (1999). Influence of adsorbed milk protein type and surface concentration on the quiescent and shear stability of butteroil emulsions. *International Dairy Journal* **9** (10): 683–691.

Stanley D.W., Goff H.D. and Smith A.K. (1996). Texture-structure relationships in foamed dairy emulsions. *Food Research International* **29** (1): 1–13.

Tual A., Bourles E., Barey P., Houdoux A., Desprairies M. and Courthaudon J.L. (2005). Effect of surfactant sucrose ester on physico-chemical properties of dairy whipped emulsions. *Sciences Des Aliments* **25** (5–6): 455–466.

Tual A., Bourles E., Barey P., Houdoux A., Desprairies M. and Courthaudon J.L. (2006). Effect of surfactant sucrose ester on physical properties of dairy whipped emulsions in relation to those of O/W interfacial layers. *Journal of Colloid Interface Sciences* **295** (2): 495–503.

Upritchard J.E., Zeelenberg M.J., Huizinga H., Verschuren P.M. and Trautwein E.A. (2005). Modern fat technology: what is the potential for heart health? *Proceedings of the Nutrition Society* **64** (3): 379–386.

van Aken G.A. (2001). Aeration of emulsions by whipping. *Colloids and Surfaces A-physicochemical and Engineering Aspects* **190** (3): 333–354.

Vanapalli S.A. and Coupland J.N. (2001). Emulsions under shear—The formation and properties of partially coalesced lipid structures. *Food Hydrocolloids* **15** (4–6): 507–512.

Weitzlab. (http://www.deas.harvard.edu/projects/weitzlab/research/Microfluidics/Microfluidic.html)

Wootton J.C., Howard N.B., Martin J.B., McOsker D.E. and Holmes J. (1967). The role of emulsifiers in the incorporation of air into layer cake batter systems. *Journal Cereal Chemistry* **44**: 333–345.

Zhang Z. and Goff H.D. (2005). On fat destabilization and composition of the air interface in ice cream containing saturated and unsaturated monoglyceride. *International Dairy Journal* **15**: 495–500.