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CHEMISTRY AND TECHNOLOGY OF MILK FAT SPREADS

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6.1 INTRODUCTION

Butter, margarine and spreads are viscoelastic solids, i.e. plastic emulsions of the water-in-oil type. Butter and margarine must, by law, contain a minimum of 80% fat, but, according to recently published guidelines (Fédération Internationale de Laiterie-International Dairy Federation, 1993), spreads should contain either 62–80% fat, 41–60% fat (reduced fat), 39–41% fat (low-fat) or <39% fat. It is also possible to produce zero-calorie fat spreads in which either fat substitutes or enzyme-resistant zero-calorie lipid materials, such as sucrose polyesters, are used (Mattson *et al.*, 1971). The development of low-fat spreads was first stimulated in the USA by fat shortages during World War II. Oil-in-water spreads were the first to appear in the 1950s and 1960s but they had a number of technical disadvantages. Water-in-oil spreads were first reported in 1966 by Bullock but they did not gain a significant share of the edible fats market in the USA (Behrens, 1988).

Whereas recombined oil-in-water emulsion products, such as milk, cream and ice-cream, achieve stability by homogenization to reduce the mean fat globule size of the dispersed phase, water-in-oil emulsion spreads are stabilized by shearing to achieve water droplet size reduction and by simultaneous cooling to entrap the dispersed droplets in a continuous phase of plastic fat present mainly in the form of small β' crystals. This technology, called scraped-surface cooling, is used to produce margarine, reduced-fat and low-fat spreads. Dairy and blended spreads with more than 72% fat can be manufactured using either scraped-surface cooling or churning equipment. Efforts by equipment manufacturers to produce low-fat butter using continuous churning equipment with an additional shearing unit to incorporate

the extra aqueous phase have recently met with commercial success (Norgaard, Pedersen and Dueholm, 1990). High-fat products (>95% fat), such as baking fats, are also processed using scraped-surface or drum cooling but the primary aim in their manufacture is the production of small β' fat crystals for optimum functionality of these fats in baked goods (Joyner, 1953; Hoerr, 1960). The principal ingredients of fat spreads are fat, emulsifier, milk protein, stabilizer, sodium chloride and water, each of which affects the emulsion characteristics and processing of the final product. Other ingredients, such as preservatives, colours and flavours, do not affect product processability. In dairy spreads, the fat source is milk fat to which can be added hard (Keogh et al., 1988) or soft milk fat fractions (Verhagen and Warnaar, 1984). In margarine spreads, the fat source is usually either soyabean or sunflower oil blended with a hydrogenated oil, typically in the ratio 3 : 1. Blended spreads contain a mixture of milk, vegetable, animal or marine fats.

A number of economic (price, inadequate promotional expenditure, low retail margins, lack of both brand advertising and innovations in packaging), medical (COMA report, 1984; Surgeon General's report, 1988; Department of Health Ireland report, 1991) and social factors (more sedentary lifestyle, breakdown in traditional meal patterns, decline in the level of home cooking, decrease in bread consumption and increased refrigerator use, highlighting the poor spreadability of butter), have contributed to the decline in butter consumption. The development of spreads has been the response by manufacturers to these market forces.

Consumer pressures for a fridge-spreadable and more nutritionally acceptable spread were met in Sweden in 1970 by the introduction of Bregott, an 80 : 20 butterfat/soya oil blend, and the low-fat spread, Latt and Lagom (60 : 40 butterfat/soya oil), in 1974. It is possible to produce a product which is not subject to excessive softening or oiling-off at high ambient temperatures by using approximately 50% milkfat, 25% vegetable oil and 25% hydrogenated vegetable oil. Such a blended product, called Clover, was first marketed in the UK in 1983. This product had a monopoly in the UK until 1985 when Meadowcup and Golden Churn were launched by Kerrygold and Kraft, respectively. The Dairygold blended spread was launched on the Irish market in February 1985. The first low-fat margarine in the UK was Outline which was marketed by van den Berghs in the early 1970s. The first low-fat blend was Gold which was launched in 1979 by St. Ivel. This product initially consisted of a blend of milk fat and soya oil but soon after its introduction was changed to a full vegetable oil-based product (B. Edmunds, 1987, personal communication). The first low-fat product in Ireland was Dawn Light butter by Kerry Group plc. Reduced-fat butter (Golden Vale plc.), reduced-fat blend (Lifestyle, by Avonmore Foods plc.) and low-fat margarine (Low Low, by Kerry Group plc.) are also manufactured in Ireland. A 25% fat blended spread and a 5% fat oil-in-water spread which incorporates

Simplesse® fat replacer are also manufactured by Kerry Group plc., but these products are not marketed in Ireland.

6.2 TECHNICAL CHALLENGES IN PROCESSING FAT SPREADS

6.2.1 Rates of microbial growth

Fat spreads, whether of the high or low-fat type, are usually water-in-oil plastic solids (Bullock, 1966). Microorganisms that survive the heat treatment used before scraped-surface cooling are confined by the small water droplet size. Ideally, droplets should be less than 20 µm in diameter in low-fat spreads (Bullock and Kenney, 1969) and in butter, living bacteria were not observed in droplets less than 20 µm diameter (Muller, 1952). Poorly-worked spreads which supported bacterial growth had moisture droplets ranging from 50 to 100 µm in diameter. Some growth of microorganisms is expected to occur in droplets between 20 and 30 µm diameter, depending on the size and oxygen requirements of the organism but droplets should, in general, not exceed 30 µm and ideally be less than 20 µm in diameter. In contrast, microorganisms are relatively free to grow and multiply in oil-in-water spreads. Oil-in-water spreads also have a different texture and meltdown and lack freeze–thaw stability (Tobias and Tracy, 1958; Weckel, 1965; Seas and Spurgeon, 1968).

The lack of a defined relationship between bacterial growth rate and droplet size is partly due to the limitations of the light microscope method used (Dolby, 1965). Other influences are growth-promoting and inhibiting factors, such as nutrient level, salt and pH of the droplet contents. The light microscope method involves viewing a sample of the spread under a cover-glass which distorts to some extent the droplet appearance at the spread surface. More recent methods (Juriaanse and Heertje, 1988), using electron microscopy after the exposure of a fresh internal surface of the spread by freeze-fracturing, are more accurate. These latter methods have been coupled with image analysis counting techniques which give a true distribution of droplet sizes. However, because of the commercial value of these results, nothing has been published on the application of the combined techniques to fat products (B.E. Brooker, personal communication). The electron microscope technique has been used successfully to study the fat crystal shells surrounding the droplets (Heertje et al., 1987; Chawla et al., 1990) and to determine the ion content of the droplets using X-ray spectroscopy after electron bombardment of the spread surface (Brooker, 1990).

6.2.2 Phase inversion

It has been shown by light microscopy (Keogh et al., 1988) and by scanning

electron microscopy with freeze-etching (Brooker, 1990) that where droplets exceed 30 μm in diameter, some will join together to form channels or lakes and eventually the water phase may become continuous during processing, i.e. inversion of the emulsion may occur. At the other extreme, if the water droplets are too small or are over-stabilized, the required phase inversion in the mouth under the influence of shear and added aqueous phase (saliva) will not take place, or take place too slowly. Such spread products will have an unpleasant gummy mouthfeel. The cooling sensation due to the effect of melting fat will also be absent.

6.2.3 Spreadability and oiling-off

These properties will be discussed in Section 6.5.1.

6.3 TECHNOLOGY OF SPREAD MANUFACTURE

6.3.1 Processing

A scheme for the continuous processing of fat spreads is outlined in Figure 6.1. It comprises two steps, namely preparation by stirring of an aqueous phase-in-oil emulsion, followed by pumping the emulsion via a pump at a throughput (TP) through one or two scraped-surface coolers in series at a defined agitation rate (AR) and at a defined refrigerant temperature (RT) to form a plastic fat product with dispersed phase water droplets. Pin-working or crystallizing units are usually sited after each scraped-surface unit. In these units, the product is sheared without cooling by pins on the central rotating shaft and by static pins on the inner cylinder wall. The process variables, TP, AR and RT, have been studied (Keogh *et al.*, 1988). To produce a high-moisture spread of the water-in-oil type on a pilot-scale plant, the emulsions require more intensive working (850–1050 rpm) at higher refrigerant temperatures (−2°C to +4°C) and lower throughput rates (maximum 75 kg h^{-1}) than margarine. Under- or over-working causes inversion of the emulsion. When softer fats than milk fat are used for processing, optimum results are obtained at lower rates of throughput. A review of the role of the scraped-surface crystallizing units and resting tubes used for margarines and shortenings is given by Hoffmann (1989). A chapter on margarine and shortening technology by Bell (1991) deals especially with historical developments while those by Munro *et al.* (1992) and Lane (1992) specialize in milk fat products.

Information is also available from the three main suppliers of scraped-surface equipment in Europe, namely Gerstenberg & Agger (Denmark), Schröder (Germany) and Johnson (UK) who fabricate the Perfector, Kombinator and
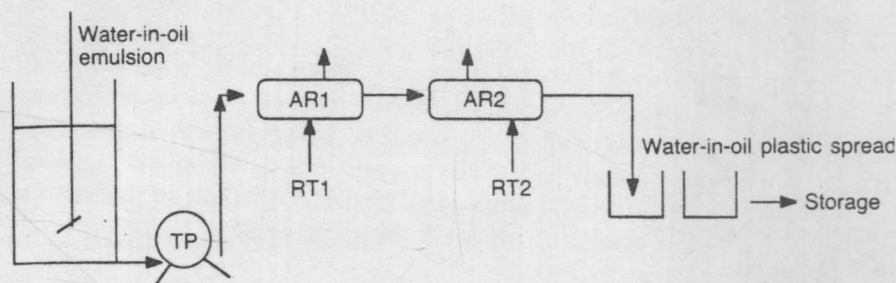
TP Pump throughput
AR1 Agitation rate, scraped-surface cooler no. 1
AR2 Agitation rate, scraped-surface cooler no. 2
RT1 Refrigerant temperature, scraped-surface cooler no. 1
RT2 Refrigerant temperature, scraped-surface cooler no. 2

Figure 6.1 Processing of fat spreads.

Votator, respectively. Numerous patents have also been published, but their review is outside the scope of this chapter.

6.4 FUNDAMENTAL ASPECTS OF EMULSIONS

6.4.1 Theory, rheology and stability to inversion of emulsions

An understanding of the mode of action of the component ingredients of fat spreads during processing requires a fundamental knowledge of the theory, rheology and stability of emulsions, especially to inversion.

(a) Emulsion theory
Liquid emulsions are inherently unstable to varying degrees. It is important to understand, therefore, the mechanisms that contribute to emulsion stability. Before the solidification step, instability of the emulsion can arise due to either phase separation or phase inversion (Mulder and Walstra, 1974). It is evident that the likelihood of phase inversion will increase as the fraction of added dispersed phase is increased. The vast majority of literature references is concerned with stability to phase separation as coalescence or creaming in oil-in-water emulsions (Halling, 1981; Jaynes, 1983). In addition, a method for the determination of stability to inversion in water-in-oil emulsions has not been reported. It is usually assumed that certain aspects of oil-in-water emulsion theory apply in reverse to water-in-oil emulsions.

Electrostatic or charge stabilization. This theory is based on the interactions between charged solid colloidal particles in an aqueous phase. The mechanism was first described by Derjaguin and Landau (1941) and Verwey and Overbeek (1948) and is named the DLVO mechanism after them. When charged particles are in suspension, they attract oppositely charged ions from the immediate environment to their charged surfaces to form a layer of counterions. This, in turn, leads to the formation of a further secondary layer of opposite charge to the first layer – the so-called electrical double layer. Thus, two charged particles give rise to a repulsion potential which depends on the distance between them and the height of the potential barrier. If the repulsion potential is greater than the attraction potential, the particles will be stable. The attraction potential is the van der Waals' interaction which has as its source the rapidly fluctuating dipole moment ($\sim 10^5$ s^{-1}) of a neutral atom which induces a polarized charge in neighbouring atoms resulting in an attraction. The extent of the attraction is proportional to the polarizability of the atoms, divided by the distance between them. A feature of the theory is the rapid increase in attraction potential at small distances. The sum of the repulsion and attraction potentials gives the total potential which determines the stability of the system. For very short distances, the attraction potential is always greater and an aggregation results. For intermediate distances, the repulsion potential, if large, results in a stable system. The most useful aspect of the DLVO theory is its ability to explain the destabilizing effect of added neutral salts which compress the double layer and reduce the repulsion potential, resulting in flocculation. According to the Schulze–Hardy rule, the ratio of critical flocculation concentrations for mono-, di- and trivalent ions is 100 : 1·6 : 0·13. Thus, divalent ions are over 50 times more efficient than monovalent ions in destabilizing a suspension (Friberg *et al.*, 1990).

It is important at this stage to recall that while the DLVO theory provides us with a useful starting theory, it applies to solid, charged particles in aqueous suspension. Thus, the theory does not apply accurately to emulsions, which are liquid. Also, the mechanism does not apply to water-in-oil emulsions where the repulsive layer is located on the concave side of the interface and, therefore, too distant from a neighbouring droplet to exert any repulsive force. Moreover, since the continuous phase of water-in-oil emulsions is non-ionizing, the development of an electrical double layer is not to be expected (Sherman, 1955*b*). In addition, the monoglyceride emulsifiers normally used in the manufacture of spreads are non-ionic. Conversely, the charge on protein molecules is quantifiable by the zeta potential and depends on the pH of the suspending medium as well as on other ions. However, proteins such as casein/sodium caseinate bind such ions, making the prediction of the emulsion behaviour very difficult in anything more than a qualitative way. Thus, oil-in-water emulsions stabilized by α_s-casein follow the DLVO theory and are reversibly flocculated by increasing ionic strength but similar emulsions containing β-casein do not behave in the same way (Dickinson *et al.*, 1987).

Steric stabilization. Flexible macromolecules, such as proteins, and small molecules, such as surfactants, are amphipathic and may form a layer at the oil and water interface. These molecules may also partly stabilize emulsions by forming a physical barrier to close contact, thereby reducing the attractive van der Waals' forces to ineffective levels (Dalgleish, 1989). The repulsion can arise in either of two ways and physicochemical calculations are available for both mechanisms in oil-in-water systems. Either the approaching protein-coated particles will tend to compress or alternatively interpenetrate the adsorbed proteins on the adjacent particle. The optimal structure of the stabilizing protein will be dealt with later in the section on protein as an ingredient.

Solid particle stabilization. In a few instances, emulsions can be stabilized by solid particles (Pickering, 1907). Examples are mustard seed in mayonnaise (Anon., 1968) or crystals of high-melting point triglycerides in margarine or butter (Precht and Buchheim, 1980; Heertje *et al.*, 1987). The solid particles are considered to act as a barrier which prevents coalescence of the droplets. Bancroft (1913) observed that the phase which wets the solid more easily will become the external phase.

Mayonnaise is an 80% oil-in-water emulsion which relies on mustard seed for solid particle stabilization. Two constituents of egg yolk, lecithin and cholesterol, are surfactants which promote oil-in-water and water-in-oil emulsion formation, respectively. The ratio of lecithin to cholesterol in egg yolk favours the water-in-oil type. The final emulsion type formed is due to the action of mustard seed which favours an oil-in-water emulsion (Petrowski, 1976).

Stabilization by rheological methods. Increasing the viscosity of the continuous phase in oil-in-water emulsions increases the stability to flocculation, coalescence and creaming or oiling-off by reducing the frequency of collision between droplets. However, flocculation kinetic theory suggests (Friberg *et al.*, 1990) that the effect of continuous phase viscosity alone is less than expected without the concurrent energy barrier provided by electrostatic and/or steric effects. In non-food water-in-oil systems, the viscosity of the continuous phase can be adjusted by choice of hydrocarbon oil of varying molecular weight or by addition of oil-soluble compounds of high viscosity. However, in water-in-oil emulsions, there are no indications of the effects of the viscosity of the internal aqueous phase on the emulsion stability to oiling-off or inversion (Sherman, 1950). The view in the patent literature is that the higher the aqueous phase viscosity in multi-ingredient food systems containing protein and starch, the higher the stability (Platt, 1988). In this case, stability may be due to effects associated with the viscosity generated by the ingredients (which will be referred to again) rather than to the effect of viscosity *per se*. On the contrary, Sherman (1955a) showed that the viscosity of the aqueous phase had

no effect on the viscosity of water-in-oil emulsions and, therefore, should not affect emulsion stability.

In earlier work (Sherman, 1950), inversion of water-in-oil emulsions was achieved by increasing the proportion of the aqueous phase. Using 2–5% non-ionic emulsifier and up to 50% water, the resulting emulsions were Newtonian. Above this level of water, the rheological parameters increased significantly and inversion occurred at a water concentration of 75–80%. The higher the concentration of emulsifier, the higher the viscosity before inversion. A large decrease in viscosity accompanied inversion to the resulting 18–24% oil-in-water emulsion. The viscosity of the inverted oil-in-water emulsion should be of the same order but slightly less than that of a water-in-oil emulsion because the continuous phase dominates the viscosity at identical ratios of dispersed phase. Thus, since water has a viscosity of 1 mPas and that of hydrocarbon oils is of the order of 25 mPas, the oil-in-water emulsion at the same level of dispersed phase will have a slightly lower viscosity. Since there are few other relevant references devoted to water-in-oil emulsion theory (Sherman, 1955c, 1967a,b), one must return to the view (quoted in many reviews on emulsions) that oil-in-water emulsion theory applies in reverse to water-in-oil emulsions. References outside the patent literature on fat spreads are not available on multicomponent water-in-oil emulsions using food ingredients.

(b) Rheology of water-in-oil emulsions

According to Sherman (1955b), the factors that affect the rheological characteristics of a water-in-mineral oil emulsion are:

- *Volume of the disperse phase.* Below a concentration of 50% aqueous phase and with 2–5% non-ionic emulsifier, the emulsions behave as Newtonian fluids; above 50% aqueous phase, the emulsions become increasingly non-Newtonian (i.e. become shear rate dependent and develop a yield value).
- *Viscosity of the disperse phase.* The viscosity of the disperse phase, which ranged from 11 to 560 mPas in the experiments, did not alter the emulsion viscosity or yield value. The disperse phase fraction, ϕ, was 0.717 (Sherman, 1955a).
- *Viscosity of the continuous phase.* The viscosity of the continuous or oil phase is directly related to emulsion viscosity and yield value. Oil viscosity can be varied by choosing hydrocarbon oils of varying molecular weight or by the addition of viscous, oil-soluble compounds. In addition, as already mentioned, emulsion stability is increased by reducing the rate of globule flocculation in a higher-viscosity continuous phase.
- *Type and concentration of emulsifier.* The viscosity and yield value of emulsions ($\phi_{vol} = 0.66$) depends on the chemical nature of the emulsifier. Sherman (1955c) considered two possible reasons for this, namely interfacial viscosity and interfacial adsorption. Interfacial viscosity would affect

droplet resistance to deformation which would be reflected in the derived (emulsion) viscosity. A high level of interfacial adsorption would enlarge the size of the interfacial layer significantly and increase emulsion viscosity. Emulsifier adsorption at the interface should also increase with emulsifier concentration. The increase in the overall dimensions of the resulting droplets gives rise to an increase in viscosity and yield value.

- *pH*. In a study using one fatty acid ester emulsifier, water-in-oil emulsions were stable up to pH 9·0 (Sherman, 1955*c*). Above this value, inversion occurred either through interaction between ester and alkali or through soap formation between alkali and contaminating free fatty acid which would cause dispersion of the ester emulsifier.
- *Ionic conditions.* The influence of certain ions and metallic oxides used in printing fluids which affect the rheological properties of the aqueous phase and emulsions were studied by Sherman (1955*b*). As the conditions were not relevant to the food area, ionic conditions will be dealt with later under ingredient effects.

(c) Stability of water-in-oil emulsions to inversion

At this point, the effects of the concentration of disperse phase, emulsifier type and concentration on water-in-oil emulsion inversion have been outlined. However, since this chapter proposes to examine the effects of a multi-ingredient system on emulsion stability, consideration must be given to each of the following factors: emulsion formation, stability, instability, effects of shear and effects of ingredients (Becher, 1977).

Formation. The method of emulsion formation must be standardized and reproducible. The equipment used, the shear rate, time and temperature of emulsification are the main factors in emulsion formation.

Stability. Many methods are used to measure the stability of oil-in-water emulsions. In basic terms, coalescence is measured by the change in emulsion droplet size with time (Halling, 1981). However, since coalescence is slow in protein-stabilized emulsions (Tornberg and Ediriweera, 1987), an accelerated rate method is usually employed. The effects on coalescence of accelerated methods such as heating, freezing and shear stress were measured by turbidity (Pearce and Kinsella, 1978; Tornberg and Ediriweera, 1987; Melsen and Walstra, 1989). Other investigators have used measurements ranging from Coulter counter particle size (Hassander *et al.*, 1989), centrifugal photo-sedimentation (Boyd *et al.*, 1972) and an electronic imaging system (Klemaszewski *et al.*, 1989). Other indirect methods include creaming rate (Petrowski, 1974) and solvent extraction of free fat (Foley *et al.*, 1971; Tornberg and Ediriweera, 1987). Phase inversion temperature (Shinoda and Saito, 1969) and emulsifying capacity (Swift *et al.*, 1961) have been used to evaluate the effects of low molecular weight and protein emulsifiers, respectively. Unfortunately, it is not

possible to measure the size of the large droplets present in unhomogenized water-in-oil emulsions because the droplets coalesce very quickly. In addition, dilution of the continuous phase (with oil), as is done for oil-in-water emulsions (with water), would alter the most important factor so far identified affecting stability to inversion, namely the disperse phase fraction. The phase inversion temperature is not a relevant test as the temperature of inversion may not be directly related to the stability to inversion at the emulsification temperature. Furthermore, it has been stated that water-in-oil emulsions do not exhibit a true phase inversion temperature, unlike oil-in-water emulsions (Matsumoto and Sherman, 1970).

Instability. A new quantitative method for assessing stability to inversion and the extent of emulsion inversion has been developed recently (Keogh, 1993). The rheological method used was based on the observation that provided an aqueous phase with a viscosity greater than 300 mPas at 367 s^{-1} was used in a 25% fat emulsion, a stable water-in-oil emulsion is slightly thixotropic, a mixed emulsion is slightly rheopectic while an incompletely inverted water-in-oil emulsion is highly rheopectic. Thus, the change in viscosity over time (240 s) at a constant shear rate (291 s^{-1}) at 40°C varied from −49 to +449 mPas and was related to the stability of the emulsion to inversion as assessed visually after dispersion in cold water. The change in viscosity over time for a stable water-in-oil emulsion was negative or low (<100 mPas), that for a mixed emulsion was intermediate (100–200 mPas), and for an incompletely inverted emulsion was high (>200 mPas) (Keogh, 1993), as shown in Figure 6.2. The measurement of the electrical conductivity of the emulsions was considered as an alternative method since oil-in-water emulsions exhibit higher conductivity than water-in-oil emulsions (Röhl, 1972). However, this method, which has been used with some success to control water levels in butter (Prentice, 1953), has the disadvantage of being dependent on ion concentration. Therefore, certain added ions would increase conductivity but might not increase stability to inversion.

Effects of shear. There is very little published information on the effect of shear or stirring conditions on the stability of water-in-oil emulsions to inversion. It has been established (Keogh *et al.*, 1988) that water-in-oil emulsions (7% sodium caseinate in 40% milk fat) are stable to inversion only within a narrow range of throughput rate, refrigerant temperature and agitation rate when processed in a single-unit Votator scraped-surface cooler. Until recently, such information was regarded as commercially valuable and therefore not published. Patents usually give wide ranges of processing conditions. Frequently, the conditions given, though suitable for one scraped-surface cooling system, are misleading for another system. Though guidelines can be given, processing conditions need to be optimized for each product and processing system.
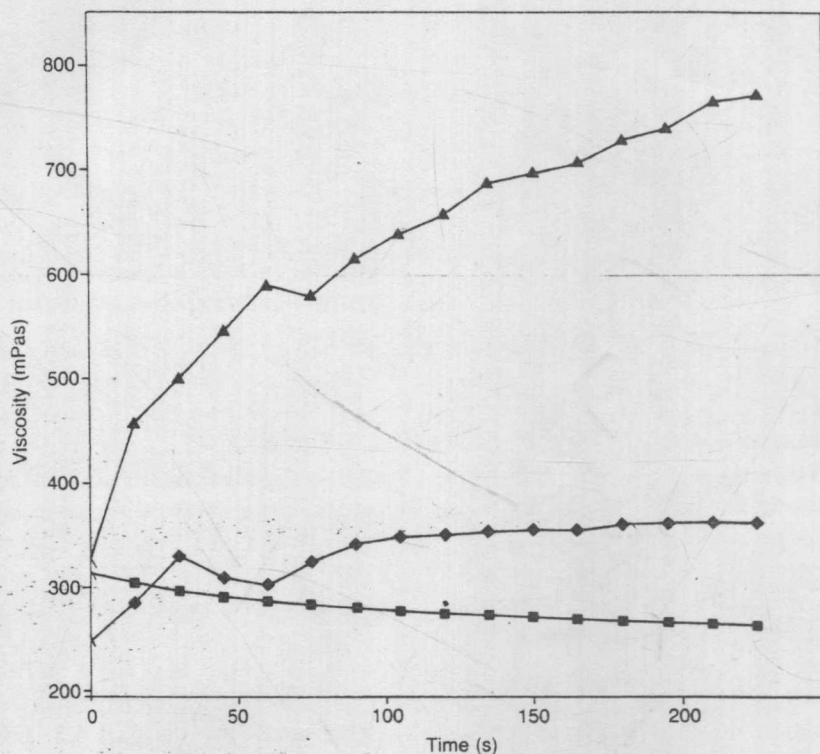
Figure 6.2 Time-dependence of water-in-oil (■), mixed (◆) and inverted (▲) emulsions.

6.5 EFFECTS OF INGREDIENTS ON EMULSIONS

6.5.1 Fat

As already outlined, the higher the viscosity of the continuous phase, the higher the viscosity of the emulsion. Oils of higher viscosity will therefore result in water-in-oil emulsions of higher viscosity. At higher emulsion viscosities, the stability to coalescence will be increased, which may result in increased stability to inversion. Fats of animal, vegetable or marine origin contain about 99% triglycerides and non-triglyceride materials can, for the most part, be ignored. The presence of small amounts of surfactants such as lecithins, monoglycerides and cholesterol should, however, be kept in mind. The functional behaviour of a fat or fat blend will depend on:

1. The melting point (determined as slip point or drop point) of the fat.
2. The content of solid or crystalline triglycerides present at any temperature but especially in the range of 4 to 37°C.

3. The crystal form which is determined by the degree of heterogeneity of the triglycerides, that is, of the fatty acids present in the molecule. The greater the diversity of fatty acids present, the more likely the fat is to form the less stable, but smaller (1×6 µm), β' crystals rather than the larger (20–30 µm-diameter), more stable β crystals, which result in a sandy mouthfeel (Mostafa *et al.*, 1985). Homogeneous fats, such as sunflower, lard, cocoa butter and coconut or palm kernel oils, tend to form β crystals during storage after cooling. Milk fat is a naturally heterogeneous fat. Palm oil, tallow and fish oils are also heterogeneous, as is lard after interesterification and partial hydrogenation. While heterogeneity can be increased by interesterification it is usually sufficient to increase the diversity of fatty acids by adding another fat or surfactant to prevent β crystal formation. It has been shown that the presence of palmitic (Wiedermann, 1978) or erucic acids (Hojerová *et al.*, 1992) are particularly effective in this regard. It is important to note, therefore, that crystal size and crystal form are interrelated (Hoerr, 1960).

The melting point of fats for spreads should not exceed mouth temperature (37°C) as an unpleasant waxy effect, termed 'palate-cling', starts to increase above this temperature.

The proportion of solid fat at any given temperature largely determines the behaviour of the fat at that temperature. The content of solid fat can be measured by dilatometry, by wide-line nuclear magnetic resonance (NMR) or by pulse NMR. The latter method is now in common use commercially to measure the solid fat index (SFI). It should be borne in mind that SFI values do not always represent precise values of the percent solid fat.

The behaviour of fats and fat blends during processing and storage of spreads can be related to the SFI *versus* temperature curve. The SFI/temperature profile of a fat is related to many of the product characteristics, including general appearance, packability (in foil wrap or tub), organoleptic properties (flavour release, coolness and thickness), firmness/spreadability and oil exudation. The firmness or yield value of a plastic material can be measured directly using a controlled stress rheometer or indirectly by cone penetrometer (Haighton, 1959), extruder (Prentice, 1954) or sectilometer (Knoop, 1972). Haighton provides a formula for relating the penetration depth to the yield value, but the latter two indirect methods measure the force required to extrude and cut the sample, respectively. It is important to note that the yield value is related to, but is not equivalent to, spreadability. The reason is that when the yield value is being measured in shear flow, the velocity gradient or rate of shear is perpendicular to the direction of the stress applied. In elongational flow, the rate of shear is in the direction of the stress applied. In manual spreading, the rate of shear lies variably between these two directions (van Vliet, 1991). The SFI at 4 and 10°C is related to the spreadability ex-refrigerator; an SFI of not greater than 32%

at 10°C should result in a butter which is spreadable at 4°C, i.e. having a yield value of maximum 1000 g cm^{-2} at 4°C. Packability can be determined by the yield value at 15°C. A minimum yield value in the region of 500 g cm^{-2} is desirable for foil wrapping. The SFI at 20°C determines the tendency towards oil exudation; a minimum value of 10% is essential to prevent oiling-off. This value represents the level of fat crystals required to adsorb the free oil present in the product at this temperature.

Butter which is fridge-spreadable, but with poor stand-up qualities at 21°C, was made from combinations of mainly low-melting liquid butteroil fraction and some high-melting solid fraction. The additional use of very high-melting solid fractions, obtained by acetone fractionation, enabled production of butter which was also physically stable at 21°C. In addition to their illegal status, the acetone fractions were also more susceptible to oxidation (Kaylegian and Lindsay, 1992). Other means of obtaining very high-melting fractions are therefore necessary.

In low-fat spreads, margarines and shortenings, a proportion of high-melting point fats is necessary for the formation of the fat crystal network (Haighton, 1976). Aggregation of the crystals occurs to form platelets and eventually shells which surround the water droplets (Precht and Buchheim, 1980; Heertje et al., 1987, 1988; Juriaanse and Heertje, 1988; Chawla et al., 1990). As already mentioned, the crystals should preferably be in the small β' form. The absence of β' crystals would lead to a lack of plasticity and possibly to inversion during the cooling process but has no direct effect on the emulsion at 40°C. However, during preparation of emulsions, care must always be taken to melt completely crystals of fats and emulsifiers. The presence of large crystals could lead to the rupture of droplets during both stirring and cooling of the emulsion and thereby cause inversion.

6.5.2 Emulsifiers

Emulsifiers lower the interfacial tension between two mutually immiscible liquids because they have an affinity for both phases. Ford and Furmidge (1966) indicated three essential properties of an emulsifier for concentrated water-in-oil emulsions:

1. The emulsifier should lower the interfacial tension to a fraction of a mN m^{-1}.
2. It should form a relatively rigid, uncharged interfacial film, through either electrostatic or hydrogen bonding between the emulsifier molecules, which will prevent the coalescence of water droplets while facilitating the coalescence of oil droplets.
3. It should adsorb rapidly at the oil/water interface.

Sherman (1973) also suggested that a strong interfacial film of emulsifier is necessary to prevent coalescence of water droplets in oil-continuous emulsions.

The emulsifier should always be more soluble in the continuous than in the dispersed phase (Bancroft, 1913). Solubility, as determined by polarity, has been rated hydrophilic to hydrophobic on a scale of 20 to 1 by Griffin (1949, 1954). Ford and Furmidge (1966) noted that their water-in-oil emulsifiers had hydrophilic–lipophilic ratios (the so-called HLB) of 3·5 to 6·0 but interfacial viscoelasticities were not quantified. These emulsifiers were fatty acid monoesters of either sorbitol or glycerol. Later, it was shown empirically that monoglycerides with HLB values in the region of 3–4 and a degree of unsaturation corresponding to an iodine value of 40–55 give good stability in water-in-oil emulsions (de Feijter and Benjamins, 1978). The properties of a range of monoglyceride emulsifiers of different iodine value, fatty acid profile, HLB and slip point are outlined in Table 6.1. Monoglycerides with an iodine value 40–55 and a melting point in the region of 55°C were found to be optimal (Grindsted, personal communication) because this level of unsaturation conferred an ideal level of flexibility/rigidity to the molecule (Garti and Remon, 1984). Variations in fatty acid composition have only a slight effect on HLB but quite a marked effect on emulsion stability (Quest International, personal communication). In water-in-oil emulsions, a positive correlation was established between emulsion stability and fatty acid chain length and a negative correlation with the dielectric constant of the emulsifier. Increasing molecular weight and decreasing dielectric constant indicate greater hydrophobicity, leading to better impregnation of the interface and to a more stable emulsion (Goubran and Garti, 1988).

6.5.3 Proteins

Proteins can affect the stability of emulsions by electrostatic, steric or rheological means, as already outlined. The mechanisms involved are highly complex, interactive and, as a result, are very difficult to quantify. However, valuable insights into their mode of action have been obtained in recent years (Dalgleish, 1989; Dickinson, 1989; Leman and Kinsella, 1989).

In order to adsorb at the interface and be surface-active, proteins must be

TABLE 6.1
Properties of partially hydrogenated monoglyceride emulsifiers

Commercial name	Iodine value	Saturated fatty acids (wt %)	Unsaturated fatty acids (wt %)	HLB	Slip point (°C)	Source
Dimodan S	40–50	50·4	47·7	4·3	61	Lard
Dimodan OT	55	22·2	76·8	4·3	55	Tallow olein
Dimodan CP	80	28·9	70·3	4·3	48	Vegetable oils
Dimodan LS	105	–	–	4·3	44	Sunflower oil

HLB, = hydrophilic–lipophilic ratio

flexible and amphipathic, i.e. have some affinity for both phases. The hydrophobic side-chains will adsorb on the oil side of the interface while the hydrophilic side-chains will interact favourably with the aqueous phase. Three aspects of the side-chains of a protein are important:

- content, location and grouping of the hydrophilic and hydrophobic amino acids;
- surface polarity or charge which is relatively more important for emulsions than the overall charge;
- protein structure and ability to unfold which is determined by the amino acid sequence.

Proteins are dynamic molecules with respect to structure. The preferred 'folded' structure for a given set of environmental conditions is that which displays the minimum free energy. The driving force to assume a given folded structure is a thermodynamic force. In aqueous systems, the hydrophobic side-chains will endeavour to orient away from the surrounding water and towards the core of the molecule. However, for high surface activity it is essential that the protein molecule should unfold and orient its hydrophobic side-chains to the oil phase. A lack of hydrophilic residues normally does not restrict protein functionality at interfaces. Thus, flexible proteins can create a highly hydrated, mobile layer to stabilize an emulsion particle.

One way of increasing the flexibility of a protein is to denature it, e.g. by heating or urea treatment. Denaturation will also occur after adsorption of the protein at the interface (Graham and Phillips, 1979), a process which may be slow. Emulsion properties are, therefore, time dependent.

(a) Rheology

The third mechanism by which proteins affect the stability of emulsions is rheological. This mechanism derives fundamentally from electrostatic and steric effects. The importance of viscosity has been referred to already. The viscosity of a caseinate solution is, *inter alia*, an indicator of the degree of bound water absorbed by the hydrophilic groups as well as the water trapped inside the molecule aggregates (Korolczuk, 1982).

The viscosity parameters (K, apparent viscosity at zero shear stress; n, the power law factor and σy, the yield stress) of sodium caseinate have been studied and found to be affected by concentration (Hermansson, 1975), precipitation and solution pH of casein (Hayes and Muller, 1961; Korolczuk, 1982), denaturation (Hayes and Muller, 1961; Canton and Mulvihill, 1982), sodium chloride (Hermansson, 1975; Creamer, 1985), calcium chloride (Hayes and Muller, 1961) and temperature (Korolczuk, 1982).

6.5.4 Hydrocolloid stabilizers

From a rheological and stability standpoint, hydrocolloid stabilizers may be

used to increase the viscosity of the aqueous phase of a low-fat spread by water binding. Gelatin is of special interest as it is a protein. However, gelatin is very hydrophilic. Its lack of hydrophobicity gives it a low rating in terms of interfacial activity and consequent emulsion stability (Chesworth et al., 1985). It has been shown that caseinate displaces gelatin at the oil–water interface. At higher concentrations of caseinate, gelatin is entirely desorbed and is found only in the aqueous phase (Musselwhite, 1966). Thus, gelatin would have no electrostatic or steric role at the interface in a water-in-oil emulsion but would have a role in increasing viscosity through water binding.

Other hydrocolloids which increase the viscosity of aqueous systems are also potentially useful. These include carrageenans and starch. κ-Carrageenan is an anionic polysaccharide which reacts with positive sites on κ-caseinate (Snoeren et al., 1976). This interaction can occur even when the pH of the solution is above the isoelectric point of the protein (Bettelheim et al., 1966) and has been attributed to the uneven distribution of charged residues on the protein. The interaction seems to be electrostatic because it is eliminated by chemical modification of the caseinate to remove all positive sites (Day et al., 1970). Maximum effect of κ-carrageenan occurs at lower concentrations. The ratio to caseinate should not exceed 1 : 4 as some precipitation of the aggregates occurs (Elfak et al., 1979). Interaction between other carrageenans (λ and ι) and α_s- and β-casein fractions via Ca^{++} bridging also seems to occur, since these proteins bind carrageenans in the presence of Ca^{++} (Hansen, 1968), and the casein–carrageenan interaction is minimized in the absence of Ca^{++} (Lin and Hansen, 1970).

Starch is also of interest because it is reported to increase the viscosity of caseinate solutions in some synergistic manner, especially at caseinate concentrations >10% (Platt, 1988). The increase in viscosity was thought not to be due to any chemical interaction (Jones and Wilson, 1976) but rather to the increase in the swelling volume of the starch (Lelièvre and Husbands, 1989).

6.5.5 Sodium chloride

The effect of sodium on the stability of water-in-oil emulsions is expected to be exercised mainly through its influence on sodium caseinate. It has been shown that as the surface casein concentration on oil droplets increased, oil-in-water emulsions became less susceptible to flocculation/coalescence in the presence of electrolyte. However, the additional sodium chloride broadened the droplet size distribution at low casein content (0·25%) but caused this effect at a high casein content (0·5%) only when calcium chloride was added (Dickinson et al., 1984).

6.5.6 Disodium phosphate and tri-sodium citrate

These salts probably have little effect on the water-binding capacity and