COLLOID ASPECTS OF MILK TECHNOLOGY

BY

W. L. DAVIES

(*Director of Dairy Research, New Delhi*)

MILK and cream are complex emulsions of amicronic butter-fat globules and micelles of a calcium caseinate-phosphate complex as the disperse phase, in an aqueous phase of sub-micronic protein molecules and lactose and salt solution. It is the purpose here to deal with the behaviour of such emulsions during the mechanical treatments involved in creaming, homogenising, whipping and churning, which are operations carried out in the manufacture of some milk products. Investigations of these processes in such natural and complex emulsions have added considerably to our knowledge of colloidal behaviour.

Milk fat globules.—The fat globules of milk vary in size from 0·2 to 22 μ in diameter; the average size is 3–4 μ, but size distribution curves show a major mode at 2 and a minor mode at 5 μ; the size distribution varies with age and breed of the cow and the stage of the lactation period. The process of homogenisation aims at reducing the size of the globules to 0·2–1·0 μ in diameter so as to obtain globules of uniformly small size within a confined small size-range. Whole milk contains $2\text{–}4 \times 10^{12}$ and homogenised milk $3\text{–}4 \times 10^{14}$ globules per ml.; homogenisation increases the fat surface area 100–120 times.

The fat globules in milk are stabilised by all the proteins of milk. The soluble proteins lower the surface tension and there is a considerable adsorption of all protein material on the fat globule surface. Most of this protein can be washed out of cream by repeated dilution with water and centrifuging. The ultimate protective colloid is a mixture of muco- and lecitho-protein, predominantly the latter. This protective scheme is the same as in other natural fat emulsions such as egg-yolk, crop milk of pigeons and in blood and lymph. The whole of the adsorbed protein layer may be looked on as the protective colloid in milk. This has been termed *slim membran* or haptogen membrane; it is the change in this layer by mechanical treatment which defines the behaviour of milk and cream in the manufacturing processes mentioned above.

Creaming of Milk.—When milk is allowed to stand, the fat globules rise against gravity to form a cream layer. Individual fat globules obey Stokes' law in this respect and the average rate of rise is 0·18 cm./hr. The fat has *d* 0·92 and the serum *d* 1·035 at room temperature. By raising the temperature, the difference between the *d* of fat and serum increases owing to the larger coefficient of thermal expansion of the fat. By using a cream separator, in operating which the force of gravity is multiplied × 1000, an almost instantaneous separation of cream can be brought about in milk at a temperature of 35–45° C. By adjustment, the fat content of the cream can be made to vary from 20–75 per cent.; that of the skim milk is about 0·05 per cent. and consists of globules less than 2 μ in diameter.

Of importance in the creaming of milk is the property of the fat globules to aggregate to form "clumps". In natural creaming these clumps rise as individual masses, thereby accelerating the process of creaming. The clumps are made up of thousands of fat globules and contain 50 per cent. of fat and have *d* 0·97. When creaming occurs with individual fat globules, a thin layer of cream of closely-packed globules with high fat content is formed; when this layer solidifies during storage it causes the defect known as "cream plug"; the layer is difficult to incorporate in the milk without first warming the milk. Creaming after clumping has occurred gives a thick cream layer of about 30–40 per cent. fat content. The clumps rise rapidly and their structure is such as to prevent packing, and the rigid condition of the semisolid fat globules prevents distortion of the clumps. A deep cream layer, or good "cream line" is important in the sale of bottled milk as it conveys the idea of richness to the purchaser. Since the heat treatment of milk tends to decrease clumping capacity, much attention has been paid to preserving the cream line in holder pasteurised milk. The best results have been obtained by not heating above 145° F., and cooling rapidly to 45–50° F. immediately after the heating period of 30 minutes, Short "flash" methods of pasteurisation do not influence creaming capacity or the depth of cream layer.

Clumping of fat globules.—The importance of clumping rests in the fact that the process diminishes the amount of adsorbed material on the surface of the globules, so that it is released into the serum, and is available for the stabilisation of a second disperse (gaseous) phase introduced into the emulsion in the process of whipping and churning. Clumping occurs when fat globules come into contact with one another, or when smaller clumps collide. The aggregation simulates that of the aggregation of individual gas bubbles on the surface of a liquid when they collide; such aggregates (foam) have common boundary areas between each bubble, each bubble is distorted and the radius of curvature at the outside layer of bubbles is much greater than for an individual bubble. The clumps in milk are stable to mild mechanical treatment and indeed agitation favours clump formation. The optimum temperature for clumping is 6–8° C. when the fat is in a semisolid condition. Heating milk breaks up the clumps especially when agitated and this treatment may have a small homogenising effect. If milk is heated above 63° C. the tendency to clump when cooled is diminished owing to the partial denaturation of adsorbable material (lactalbumin). The addition of a protective colloid such as gelatin, gum arabic or tragacanth or homogenised milk causes the property of clumping to be restored.

Homogenisation of milk.—This process is usually carried out in milk to prevent cream rising, and to prevent the layer of cream churning during milk transport, and to prevent processed cream in jar or tin from churning. The process is carried out by forcing milk or cream through small apertures under pressures of from 500 to 3,000 lb./in.^{2} The fat globules divide and are immediately stabilised by protein membranes. The efficiency of homogenisation increases with rise of temperature, that of the commercial process being at 63° C., at which also the ability of the globules to aggregate is nil. To prevent any creaming in milk, pressures from 2,500–3,000 lb./in.^{2} are necessary. This produces globules less than 2 μ in diameter and finer than those remaining in separated milk. The smaller globules are less susceptible to forces of agglutination and thus do not rise to form cream. The amount of adsorbed protein is enormously increased; there is thus not sufficient protective colloid in the serum to protect a second disperse phase such as a gas and homogenised products will neither whip nor churn.

Whipping of cream.—Milk and cream foam readily when air is beaten into them. Cream can be whisked into a stiff foam by incorporating into it a second (gaseous) disperse phase in a fine state of division. A whipped white of egg is a simple picture of the conditions reached in whipped cream. By continuous whisking, air is broken up into small bubbles which are immediately stabilised by albumin adsorbed at the air/liquid interface; continued whipping breaks up the air globules to a finer state of division so that the degree of protein adsorption is such as to cause the albumin to precipitate as a solid at the interface (Ramsden phenomenon) which gives the foam rigidity and stiffness. In cream, the compositions of the phases are more complex. There must be sufficient adsorbable material to stabilise the gaseous phase and since this is not so concentrated as in egg-white the semisolid fat globules confer most of the rigidity on the whipped product. The variations in rigidity of whipped cream, such as a "soggy", partly whipped or product giving a drainage of serum, are due to incorrect fat content, incorrect temperature of conditioning the cream before whipping and lack of protective colloid. Cream of 35 per cent. fat conditioned at 8° for 16 to 24 hours is best for whipping.

Much confectionery cream is now made from cream reconstituted from butter and dried or whole milk. With dried milk, inferior whipping properties are given if the protein has been denatured by heat; spray-dried milk gives cream of good whipping properties. A small amount of gelatin as stabiliser enables all creams including homogenised cream to be whipped successfully. Reconstituted creams for whipping require low pressures only in the homogenising (or reconstituting) process and to be held at 8° C. for 16–24 hours for conditioning. In the holding period, the fat globules must attain a semisolid condition and aggregate into clumps; both conditions assist in giving rigidity and stability to the whipped product.

Ice cream manufacture.—Ice cream mixes are pasteurised before freezing. They contain added stabilisers such as gelatin or dextrinised starches (up to 0·5 per cent.) to assist in the whipping process which is carried out early in the freezing of the mix. The homogenised mix thus incorporates in the freezing process an air phase equal to 80 to 120 per cent. of the volume of the mix (overrun); the gaseous phase is stabilised partly by milk proteins and partly by the added stabilisers.

Churning.—The churning of cream into butter is a mechanical process which proceeds beyond the whipped stage of cream described above until the aggregating of the fat globules is so intense and the demand of protective colloid by the gaseous phase so large that the emulsion breaks. In the churning process, the whipped condition is marked by the cream "going to sleep" in the churn; the breaking of the emulsion is marked by a dramatic change in the fluidity of the churn contents from a viscous mass to a mobile liquid.

Two theories have been advanced to explain the churning process. The *foam theory* (Rahn) takes into account the close-packing of the fat globules in the foam leading to fat clumps. The protein in the lamellæ of the foam gradually assumes a solid character until further churning destroys the structure and the foam collapses; this is followed by coalescence of the fat globules.

The *phase inversion theory* takes into account the gradual dehydration of protein at the fat/water interface which enhances the tendency to the formation of butter, and that the process reverses the type of emulsion.

A gaseous phase is essential to churning. A full churn with no air-space will not yield butter. The above two theories are related in that, in the foam theory, what happens in the destruction of the protective properties of the colloid is the dehydration of protein to such an extent that protein is precipitated so that its protective power in the emulsion is lost. When butter is formed as granules, the protective colloids appear in the serum (buttermilk). If synthetic creams are made by homogenising fat in separated milk, whey or buttermilk, only cream from buttermilk will churn completely. The stabilising factor and that taking part in churning are thus removed from milk in the cream but are liberated into buttermilk when the foam formed during churning breaks.

Methods of obtaining butter other than by churning support the foam theory. Converting milk into froth by means of streams of gas concentrates the fat in the foam from which butter may be obtained by collecting in a fine sieve. Boiling cream *in vacuo* at low temperature is a modification of the same process. The passing of cream and air through long tubes of fine bore and separating butter by sieving the liquid is another modification.

The structure of butter.—Butter is not strictly a water-in-oil emulsion; it is more complicated in structure and different types of butter vary in structure. The continuous phase is butter-fat in which are dispersed globules of fat, water and air, surrounded by the same protective colloid as the fat globules in cream. Of importance is the water content and the distribution of water in butter. Most countries have set a maximum legal standard of 16 per cent. of water in butter. By churning cream at temperatures higher than those usually used (9–12° C. in summer, 13–15° C. in winter) more moisture is incorporated in the butter and this cannot be reduced by working the butter. An inefficient conditioning of the cream has the same effect, while butter from cream in which the fat globules are still liquid is of high moisture and curd content and cannot be "worked" like ordinary butter. There are three phases of water in butter, (*a*) the water globules, which are buttermilk emulsified in fat, (*b*) films of water separating the butter granules and (*c*) small pockets of wash water. Butter from which water can be squeezed by pressure contains too much wash water.

The "working" of butter by corrugated rollers after churning has two effects, namely, pressing out wash water and increasing the amount of fat as the continuous fat phase. Overworking has the effect of increasing the amount of fat phase to such an extent as to give a greasy or "salvy" texture; the same effect can be produced by churning the butter to lumps in the churn instead of into granules of the size of lead-shot. The moisture incorporated into such butter is less (10–12 per cent.) than in properly-made butter, while leaky butter does not necessarily contain more moisture than well-made "dry" butter.