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Coalescence Mechanisms in Protein-Stabilized Emulsions

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I. INTRODUCTION

A. Importance of Coalescence in Food Emulsions

Coalescence of emulsified oil may be defined as any physical process that leads to the merging of the oil droplets into a larger droplet. Coalescence is desired in some cases—for example, during butter manufacture, where churning of cream leads to the separation of butter granules through a phase-inversion process that involves coalescence of milk fat globules (1). Another example is during whipping of cream (2), where coalescence leads to the formation of a network of partially coalesced fat globules, which stabilizes the air bubbles in the cream (1,3). A final example is a limited amount of coalescence in the mouth, which may lead to the release of some oil that may coat the oral tissues and provide oily lubriciy (4) and enhance the release of fat-soluble flavours (5). However, usually coalescence is undesired, such as during emulsion formation by homogenisation, where the occurrence of coalescence of newly formed droplets reduces the efficiency of the homogenizer (6), and during storage, where coalescence leads to the formation of larger droplets with an increased creaming rate or even a visible oil layer on top of the emulsion.

B. Adsorbed Protein Layers

In food emulsions, stability against coalescence is obtained from an adsorbed layer at the surface of the oil droplets. The composition of this layer is usually complex, often consisting primarily of protein and protein aggregates, in combination with polar lipids, such as lecithin, and a wide range of low-molecular-weight surfactants, such as monoglycerides and diglycerides, polysorbates, Tweens, Spans, and sucrose esters (7,8). The most commonly used proteins in food applications are the caseins and whey proteins derived from milk. Caseins are a group of proline-rich proteins with relatively little secondary structure and low solubility at pH 4.6 (2,9). In solution, they are often present in the form of micelles that solubilize calcium phosphate. Whey proteins are a group of globular proteins (2,9) which have in common a much more compact and ordered molecular structure, organized in tight conformations, such as α-helices and β-sheets, and stabilized by physical bonds (e.g., hydrogen bonds, hydrophobic bonds) and covalent bonds (mainly disulfide bridges).

After proteins have adsorbed to the oil–water interface of the emulsion droplets, they slowly change their conformation (“unfold”), adapting their molecular structure to the changed environment at the interface (10–13). It has been suggested that on adsorption, globular protein molecules largely retain their secondary structure of α-helices and β-sheets but that the organization of these elements (tertiary structure) changes. This reorganizaiton leads to an increase of the binding energy of the protein to the interface and exposure of hydrophobic moieties and sulfhydryl groups at the aqueous side of the adsorbed protein layer (14,15). Intermolecular bonds are formed between the adsorbed molecules, largely hydrophobic bonds but, for many proteins, probably also intermolecular disulfide bonds (16). This leads to the formation of a cohesive layer of the adsorbed molecules, with strongly reduced lateral mobility of the molecules and the tendency of the adsorbed layer to fracture rather than flow when the adsorbed layer is deformed (17).

Some compounds bind to adsorbed protein layers. (e.g., polyphenols (tannins) and many polysaccharides, such as propylene glycol alginate, pectin and carrageenan). This was shown to enhance the elasticity of a mixed adsorbed layer of protein and low-molecular-weight surfactants and to reduce the rate of drainage of foams stabilized by such a mixed adsorbed layer (18).

The presence of coadsorbed surfactants and polar lipids often improves the overall performance of protein- or peptide-stabilized emulsions. These surfactants help to lower the surface tension during emulsification. Moreover, physical interactions occur between proteins and lipids and surfactants, forming molecular complexes (19). Investigation of mixed adsorbed layers of protein and surfactant has revealed that polar lipids and surfactants can displace proteins from the interface. If the protein is only partially displaced, the mixed adsorbed layer is often laterally

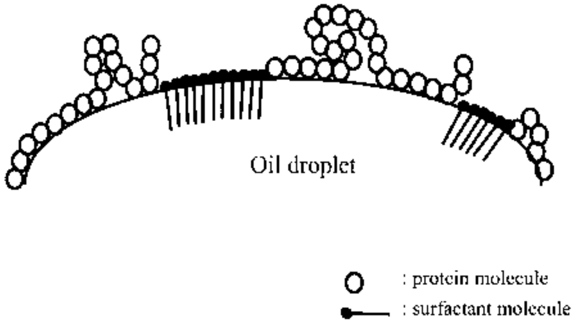

Figure 1 Sketch of an oil–water interface with an adsorbed layer of protein, to which a low-molecular-weight surfactant has been added, which displaces the adsorbed protein layer by the "orogenic" mechanism, leading to patchwise adsorption of protein and surfactant.

inhomgeneous, with a patchwise distribution of protein-rich and surfactant-rich regions. The displaced protein often remains attached to the interface as a wrinkled sheet in the protein-rich regions ("orogenic" displacement, illustrated in Fig. 1) (20,21).

Another important aspect is protein hydrolysis, which leads to the formation of protein fragments, peptides, and free amino acids. Protein hydrolysis usually occurs by proteolytic enzymes (e.g., during the preparation of fermented products such as yogurt and cheese). It may also be carried out to improve the solubility of the protein (e.g., in the preparation of soy protein isolates or for the formulation of low-allergenic infant food). The emulsifying and foaming properties of peptides obtained by hydryolysis are strongly dependent on the molecular mass and composition. Usually, the surface activity and the film-stabilizing properties become much lower with decreasing molecular masses. As a rule of thumb, good surface-active properties were obtained for amphipolar peptides with molecular masses exceeding 2000 Da and preferably containing disulfide-linked fragments (22,23).

C. Complexity of Processes Preceding Coalescence in Food Emulsions

In food emulsions, coalescence is usually not caused by a single process, but, instead, by a complex sequence of several processes preceding the final step of coalescence. These preceding processes strongly vary among different products and therefore cannot be generalized. However, some common tendencies can be distinguished.

An important aspect in the application of proteins as emulsion stabilizers is that the molecular structure and properties of the molecules in solution may change during processing. For example, the solubility is highly dependent on pH and, for most proteins, becomes very small in the vicinity of their isoelectric pH. In many food products, the pH is lowered to around 4–5 during manufacture, which is close to the isoelectric pH of many proteins. Another example is that microbial contamination is often reduced in the last stage of production by a heat treatment (sterilization or pasteurization). This may lead to irreversible denaturation of the proteins, which, as a result, often become insoluble. The denatured protein may precipitate as flocs and remain separate from the emulsion droplets or may precipitate onto the droplet surface, forming thick adsorbed layers or even encapsulating the droplets in the precipitate (2).

The sensitivity to coalescence often changes during storage due to ongoing chemical (e.g., oxidation), physical (e.g., creaming, crystallization of lactose or inorganic salts), and enzymatic (e.g., protease and lipase activity) transformations in the product. During handling, the emulsion is spread, stirred, mixed with other ingredients, acidified, heated, and exposed to air, all of which may lead to large structural and compositional changes in the emulsion, which may induce coalescence.

Finally, it is the complex behavior of the emulsion in the mouth that determines its perception by the consumer. Several processes change the structure of the emulsion and the release of flavor compounds (24), such as mixing with saliva, melting of the gelled continuous phase, hydrolysis of starch by amylases in saliva (25), and possibly also release of fat from the emulsion and its adherence to the mucosa (4).

D. Aim of This Work

The complexity of the composition and structure of food emulsions and foams complicates and understanding and adequate control the behavior of these systems. The final step of coalescence can be caused by several mechanisms and, as consequence, may reveal itself in many different ways, such as a coarsening of the droplet size distribution (dressings), formation of oil lenses on top of the emulsion (soups), and clumping of fat (cream). Because of the inherent complexity of food products and their application, predictive tests to determine the stability of an emulsion to coalescence are often not very reliable. These tests accelerate only one specific mechanism, which is not necessarily the most important in the situation considered. For example, a centrifugation test (26) is not suitable to predict coalescence mediated by the surface of expanding gas bubbles (Section IV. B). Clearly, there is a gap of knowledge in the realm of coalescence mechanisms in food emulsions. The aim of the present work is give a general overview of the multitude of physical mechanisms in food emulsions that are collectively referred to as ‘‘coalescence.’’

The organization of the main part of this chapter is as follows. The role of the adsorbed layer in coalescence processes is discussed Section II. The structure and stability of thin films are related to the properties of the constituent adsorbed layers, making a comparison between surfactant- and protein-stabilized thin films. Section III describes homogeneous coalescence. The main consecutive steps, droplet encounter and initiation of film rupture, are distinguished, and for each step, various mechanisms will be discussed. Finally, Section IV will focus on mechanisms of heterogeneous coalescence, which involves the interaction with a third phase. Distinction will be made among coalescence intermediated by a solid and liquid surfaces, coalescence induced by shearing in confined spaces, and coalescence caused by puncturing of thin films by small particles.

II. ROLE OF THE ADSORBED LAYER IN COALESCENCE

A. Thin Films

Stability against coalescence is directly related to the properties of the protective coating of adsorbed material at the droplet surface. This is because adsorbed layers on adjacent droplets repel each other (‘‘disjoining pressure’’), in this way keeping the internal phases of these droplets separated. This repulsion is usually of electrostatic steric origin. If the droplets attract each other (e.g., by van der Waals forces) or are pushed together by an external force, a thin film is formed. The thickness of this thin film is determined by a balance of attractive and repulsive forces and mainly depends on the range of the repulsive interactions (Fig. 2). For adsorbed layers consisting of uncharged polar lipids, the repulsion is the short-range Born repulsion. The thin film then consists of a bilayer of adsorbed material and hardly contains free water in between the adsorbed layers. Such a thin film is called a Newton black film (NBF). For charged adsorbed layers or adsorbed layers with hydrophilic chains extending into the continuous liquid [an example of the latter is an adsorbed layer of β-casein in which charged and hydrophilic N-terminal chain segment protrude into the water (27)], the distance between the adsorbed layers remains larger and the thin films contain free water. Such a film is called a common black film (CBF).

Over the last decade, the understanding of thin films stabilized by proteins has substantially increased. At pH remote from the isoelectric pH, adsorbed protein layers are charged. If two droplets of a protein-stabilized emulsion are pushed together, the electrostatic repulsion between

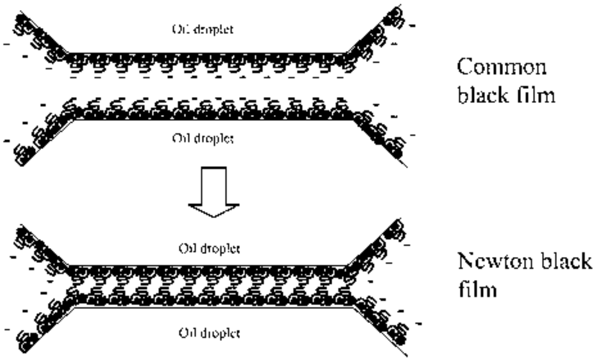

Figure 2 Transition between a common black film and a Newton black film, induced by increasing the normal pressure onto the thin film or by reducing the electrostatic repulsion between the films. Here, the thin films are stabilized by negatively charged layers of adsorbed protein molecules.

these layers keeps the adsorbed layers separated, thus forming a CBF. Increasing the concentration of 1 : 1 electrolytes reduces the Debye length, thereby decreasing the range of double-layer repulsion and the thickness of the CBF. This also increases the stability of the NBF state with respect to the CBF state and also reduces the energy barrier involved in the transition of CBF to NBF. High-valency cations (Ca^{2+}, Al^{3+}) are even more effective in this because they also lower the charge and surface potential by binding to the adsorbed protein molecules (28–30).

As described in Section I. A, proteins change their conformation after adsorption, leading to the formation of an elastic adsorbed film at the interface. At least for the whey proteins, this also leads to exposure of hydrophobic amino acid residues and free sulfydryl groups to the water phase. When adsorbed layers on adjacent droplets are in contact, corresponding to the NBF state, hydrophobic and disulfide bonds will then also be formed between these layers, strongly increasing the attractive interaction between the adsorbed layers. The binding may become so strong that it becomes effectively irreversible (15,30,31).

In dilute protein-stabilized emulsions at pH remote from the isoelectric pH, the electrostatic repulsion between the adsorbed layers keeps the droplets separated. Increasing the concentration of 1 : 1 electrolytes and especially high-valency cations promotes droplet flocculation and stabilizes the NBF state with respect to the CBF state. Because the NBF state allows the formation of intermolecular bonds between adsorbed layers in contact, the binding between the adsorbed layers becomes enforced and droplet flocculation becomes irreversible (often referred to as "coagulation").

In effect, on increasing the electrolyte concentration or approaching the isoelectric pH, the thin films between the flocculated droplets “jump” from the CBF state into an irreversible NBF state (32).

B. Rupture of Thin Films

Film rupture occurs when a hole is formed in the thin film, with a diameter larger than a critical size, so that the hole will grow spontaneously. The hole can be formed spontaneously or by mechanical forces pulling at the film. Film rupture related to spontaneous formation of a hole will be called “spontaneous film rupture.” Film rupture induced by mechanical forces will be called “induced film rupture.” Various mechanisms may initiate film rupture and the most important ones will be treated in Section III. A. The way by which adsorbed layers protect the thin film against coalescence depends on the molecular properties of the adsorbed layer. Based on the properties of adsorbed protein layers discussed in the previous subsections, we may expect large differences between the ways proteins and low-molecular-weight surfactants to stabilize thin films.

Low-molecular-weight surfactants form mobile adsorption layers. Thin film stability is mainly due to a fast hole-repair mechanism (33), in combination with a preferred curvature of the adsorbed layer that opposes the mean curvature of a neck of liquid connecting the liquid volumes on both sides of the thin film (34). If the surfactant is charged or exposes a hydrophilic chain into the solution, a relatively large distance is maintained between the two sides of the thin film due to electrostatic or steric repulsion, respectively, which improves the stability of the thin film.

Proteins, on the other hand, form thick, cohesive, and elastic adsorbed layers and the molecules in the adsorbed layer are relatively immobile (35). These properties afford a strong barrier against film rupture under quiescent conditions (36). However, on large deformation, the adsorbed layers may fracture (Section I.B) and this may have important consequences for the stability of the thin films (see Section III. A. 1). As discussed in the previous section, on close contact between adsorbed layers, strong hydrophobic and covalent bonds can be formed between the adsorbed layers, leading to coagulation of the droplets. The presence of these bonds makes the emulsion sensitive to a specific mechanism of coalescence that will be discussion in Section III.A.3.

III. HOMOGENEOUS COALESCENCE

Commonly, coalescence involves the process of merging of two emulsion droplets, dispersed in a continuous liquid. This process of coalescence

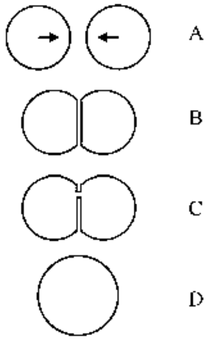

Figure 3 Basic coalescence process involving two droplets: (A) encounter of droplets; (B) thin-film formation; (C) thin-film rupture; (D) merging of droplets.

generally comprises two main consecutive steps: (1) encounter of droplet surfaces and the formation of a thin film and (2) initiation of thin-film rupture. The first step corresponds to the flocculation (reversible) and coagulation (irreversible) of the emulsion droplets (steps A and B in Fig. 3). The second step corresponds to the actual irreversible process of coalescence (steps C and D in Fig. 3). A detailed treatment on this subject in terms of the characteristic times for flocculation, coagulation, and film rupture has been given by Dukhin et al. (37). Which of the two main steps will be rate determining not only depends on the properties of the adsorbed layer but also on many other aspects, such as the droplet-size distribution, the volume fraction of droplets and the presence of liquid flow. These two main steps will be discussed in Sections III.A and III.B.

A. Initiation of Thin-Film Rupture

Film rupture is the final step of the coalescence process. It is initiated by the formation of a hole larger than a critical size in the thin film, leading to the merging of two droplets into one (Fig. 3, step C). Hole formation may have a number of causes, of which vacancies in the adsorbed layer, spontaneous passage formation and rupture by film stretching are the most important.

1. Rupture by the Presence of Vacancies

This mechanism prevails if the adsorption is below saturation adsorption, where part of the droplet surface remains uncovered by an adsorbed layer. If the adsorbed molecules attract each other, a two-dimensional phase separation between closed-packed molecules and empty regions (“vacancies”) will take place (Fig. 4). Film rupture is initiated if sufficiently large vacancies

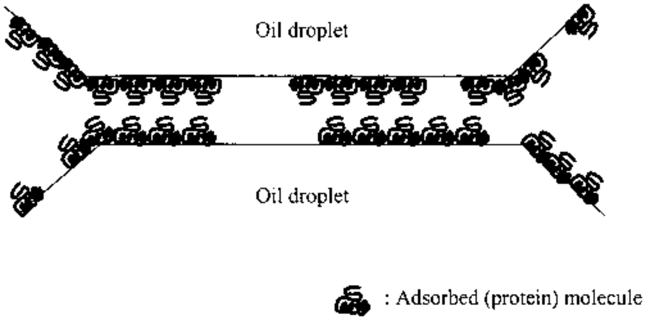

Figure 4 Sketch of a thin film between emulsion droplets, with vacancies in the adsorbed layer due to unsaturation of the adsorbed layers.

adjoin on both sides of the thin film. The lifetime of such a film then depends on nucleation and growth of these vacancies. This mechanism was modelled by Kashchiev and Exerova (38) and Exerova and Nikolova (39) to calculate the lifetime of surfactant bilayer films (which are equivalent to Newton black films).

Slighly below saturation adsorption of the surfactants in the adjacent monolayers, the model predicts a sharp transition toward very high stability of the bilayer. Also, for protein-stabilized films, a similar sharp transition in thin-film stability was found when the adsorption density reached saturation adsorption (40,41).

2. Rupture by Spontaneous Passage Formation

Here, a "passage" or "neck" is defined as a canal of the dispersed liquid passing through the sheet of thin film, in which the surface between the canal and the thin-film liquid is covered by an adsorbed layer. In this way, the surface of the passage forms a continuous bridge between the surfaces of the adjoining emulsion droplets (Fig. 5). Theories for the initiation of rupture by spontaneous passage formation have been developed mainly for surfactant-stabilized emulsions.

De Vries (42) described initiation of rupture of common black films by calculating the energy barrier related to the area increase needed to form a passage through the layer of liquid water. Related to this is a theoretical treatment by Harbich et al. (43) for the energy barrier involving passage formation in vesicles and lamellar phases. Later, Kozlov and Markin (44) extended this treatment by incorporating curvature components of the surface tension to describe the energy effect involved in the surface-topological transition of merging two droplets into one. Recently, Kabalnov and

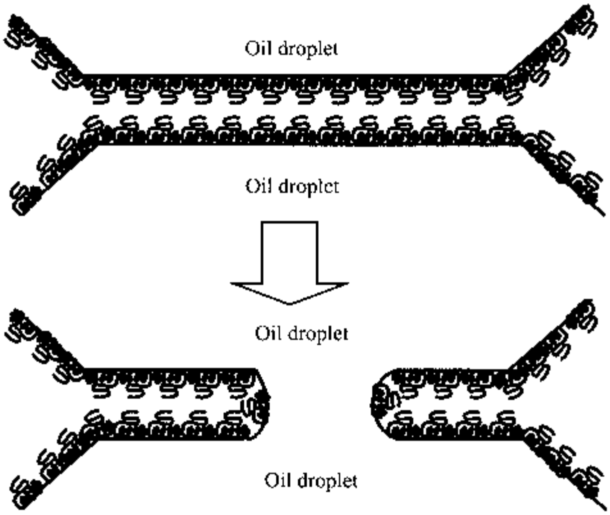

Figure 5 Sketch of rupture of a thin film between adjacent emulsion droplets, due to the formation of a passage through the thin film.

Wennerström (34) further developed this approach for the formation of a passage in thin films between emulsion droplets stabilized by low-molecular-weight surfactants for temperatures close to the phase-inversion temperature. In this ''oriented-wedge theory,'' the formation of a passage through a thin film of the continuous liquid is strongly inhibited if the surfactant tends to form micelles in the continuous phase (Fig. 6). This mechanism seems to be unimportant for emulsions stabilized by only protein, because of the thickness and hydrophilicity of the adsorbed layer (40).

3. Rupture by Film Stretching

Thin films may rupture when they are stretched at such a speed that the reduction of the adsorption density of the stabilizing surface-active material cannot be restored by adsorption from the bulk or by lateral mobility of adsorbed material. Stretching then leads to depletion of adsorbed material in the adsorbed layers, which may induce rupture by the presence of vacancies (Section III.A.1). This may occur for emulsion stabilizers that form relatively immobile films and are dissolved in the continuous liquid, which makes transport toward the middle of the thin film a slow process. These requirements are met for adsorbed protein layers (Section I.B). For thin films stabilized by cohesive layers of adsorbed

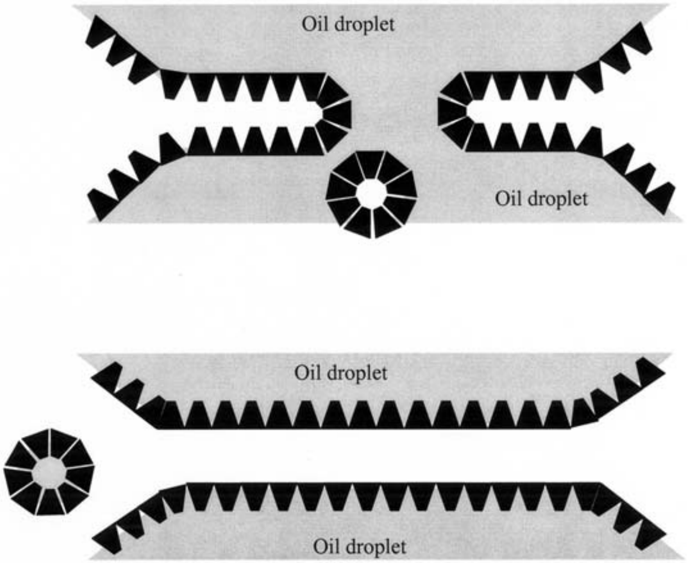

Figure 6 Oriented-wedge model for film-stabilizing properties of low-molecular–weight surfactants. The surfactant molecules are depicted as wedges, with the broader side oriented either to the oil phase (upper diagram) or the aqueous phase (lower diagram). The upper case corresponds to low-hydrophilic–lipophilic-balance (low-HLB) surfactants, which are able to form micelles in the oil phase and easily form a passage through an aqueous thin film, therefore not suited to stabilize oil-in-water emulsions. The lower diagram corresponds to high-HLB surfactants, which are able to form micelles in the aqueous phase and inhibit the formation of a passage through the aqueous film, therefore suited to stabilize oil-in-water emulsions.

protein molecules (Section I.B), we may also expect that initiation of rupture corresponds to fracturing of these adsorbed layers.

An additional requirement of this film rupturing mechanism is that external forces exerted on the emulsion lead to stretching of the thin films. This will only occur if external forces exerted on an emulsion are transferred onto the thin film in a direction parallel to the thin film. As a consequence, this mechanism will not be effective in relatively dilute, unaggregated emulsions under quiescent or gentle-flow conditions.

Rupture by film stretching was shown to occur in highly concentrated emulsions stabilized by protein (40,45–47). Emulsions are said to be highly concentrated whenever the volume fraction of the droplets exceeds the limit of close packing (Fig. 7). The starting point for explaining the experimental results is the hypothesis that film stretching occurs in these systems if externally applied stresses cannot relax sufficient by flow in the emulsion (46).

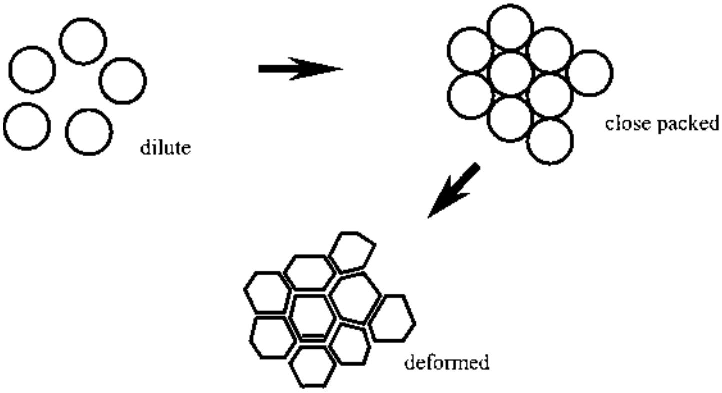

Figure 7 Formation of a highly concentrated emulsion by removal of the aqueous phase.

This occurs when slip between the droplet surfaces is inhibited by the presence of shear-resisting connections between the adsorbed layers of adjacent droplets (47). Van Aken et al. (46) suggested that the formation of shear-resisting connections is closely related to the transition of CBF to NBF that was discussed in the context of droplet aggregation in dilute emulsions stabilized by whey protein in Section II. B. Nuclear magnetic resonance (NMR) mobility measurements of water molecules pointed out that a state corresponding to a Newton black film (essentially no free water between the adsorbed layers forming the thin film) can indeed be obtained in a highly concentrated emulsion stabilized by β-lactoglobulin (48).

Similarly to the bonds formed in dilute emulsions stabilized by whey protein, the shear-resisting connections are probably formed by strongly attractive short-range forces such as hydrophobic interaction (47). They were shown to form between adsorbed protein layers of both β-lactoglobulin and β-casein when the droplet surfaces were pushed together with sufficiently large pressure (46). It was argued that this critical pressure is related to a pressure-induced jump over the kinetic barrier that is related to the transition of CBF to NBF. This was supported by kinetic measurements that showed that the rate of formation of shear-resisting connections increases as a function of the applied pressure and the ionic strength, and was strongly enhanced in the presence of calcium ions (47).

This mechanism was shown to be relevant also is a more dilute emulsion of irreversibly aggregated droplets, where deformation of droplet aggregates by shear stresses may cause coalescence of droplets within the aggregate (Fig. 8) (47).

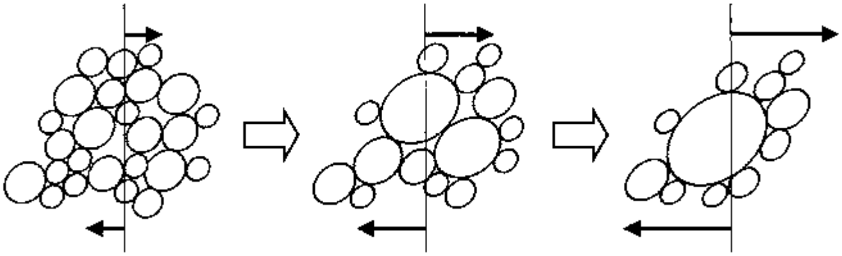

Figure 8 Deformation of a droplet aggregate by external forces, inducing coalescence by stretching of thin films between the droplets because slip between the adsorbed layers of the thin films is inhibited.

B. Encounter of Droplet Surfaces and the Formation of a Thin Film

Before a thin film is formed, two consecutive steps have to take place (Fig. 3). First, the emulsion droplets have to come close together on a colloidal scale-droplet encounter, step A in Fig. 3) and second, a thin film must be formed on a molecular scale (outflow of the continuous phase from the spacing between the droplet and thin-film formation, step B in Fig. 3).

1. Droplet Encounter Under Quiescent and Gentle-Flow Conditions

Droplet encounter may occur through diffusion (in analogy to fast perikinetic flocculation (49,50)) but is strongly accelerated by convection because this increases the encounter rate of the emulsion droplets (in analogy to fast orthokinetic flocculation (51)) and very weak repulsion between the droplet surfaces may be overcome by the shearing force.

The rate of droplet encounters is greatly increased by concentrating the emulsion either by an artificial procedure such as reverse osmosis or centrifugation or spontaneously by creaming (52). The ultimate situation is the previously discussed case of highly concentrated emulsions, in which the droplets are in continuous contact with each other (Fig. 7).

When the surfaces are sufficiently close together, they start to interact, first by hydrodynamic interaction, which retards the outflow of liquid (53–56), but at sufficiently short separation also by dispersion forces between the liquid interiors of the droplets and short-range forces between the adsorbed layers (57). The outflow of liquid becomes retarded if the hydrodynamic repulsion between the approaching droplets deforms the droplets, leading to the formation of a (dimpled) thin film (57). The retardation is enhanced by the elasticity of the adsorbed layers, because this resists the outflow of liquid by the coupling of liquid flow and surface flow (58).

This retardation is of importance mainly if the droplets are relatively large the surface tension is relatively low and under highly dynamic condition, such as during emulsification (58).

Finally, thin spots can form in the remaining liquid film by a spinodal thinning mechanism, described by Scheludko (59) and Vrij (60). This mechanism describes local thinning of a CBF caused by thermal undulations of the film thickness and is commonly accepted as one of the main steps in the process of spontaneous film rupture (61). This mechanism is retarded by increasing the viscosity of the continuous liquid and surface dilational elasticity of the adsorbed layers. Already at a very low surface elastic modulus ($\ll 1\,\mathrm{mN/m}$), the surface dilational elasticity strongly suppresses the spinodal thinning mechanism (62). This is the case for adsorbed protein layers, because the surface dilational elasticity is usually in the range 20–80 mN/m. Therefore, thinning of protein-stabilized films is strongly retarded and the spinodal thinning process is strongly damped, predicting that also the transition CBF to NBF is strongly retarded for protein-stabilized emulsions, as was indeed observed experimentally (35,63).

2. Droplet Encounter in Turbulent Flow

In turbulent flow, droplets bounce together by inertial forces, which may lead to large droplet deformation and to forces stretching the adsorbed layers and thin films between colliding droplets. Film rupture may then occur by similar mechanisms as described in Section III. A.3. As a first approach to describing homogeneous coalescence induced by turbulent flow, we will estimate the conditions needed for the occurrence of coalescence in highly turbulent flow. In turbulent flow, the outflow of the continuous phase from the spacing between the droplets may be greatly enhanced by the inertial between the droplets when they are bouncing against each other. Walstra and Smulders (64) estimated the magnitude of this pressure from Kolmogorov theory as

$$\Delta p = \varepsilon^{2/3} d^{2/3} \rho^{1/3} \tag{1}$$

where ε is the power density of the turbulent flow, d is the length-scale distance considered, for which we take the droplet diameter, and ρ is the density of the emulsion. The outflowing liquid exerts a shear force onto the adsorbed layers of the thin film, tending to stretch them. This may lead to film rupture by film stretching as described in Section III.A.3 (Fig. 9). This can be quantified by taking into account the surface tension gradient $\Delta\gamma$ along the surfaces of the thin film, which for immobile adsorbed layers

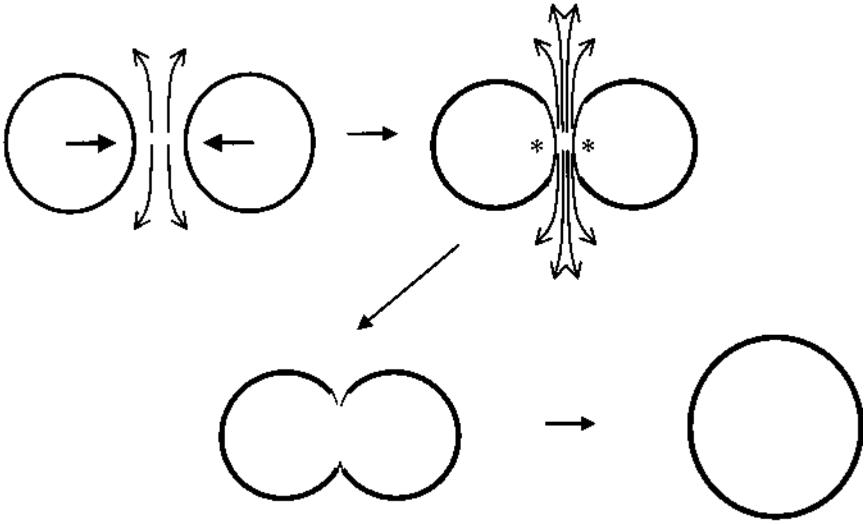

Figure 9 Coalescence induced by film stretching of droplets impacting in highly turbulent flow. The second drawing shows the outflow of continuous liquid from the spacing between the approaching droplets, as shown by flow lines, which drags along the adsorbed layers at the droplet interfaces. This produces a spot with high surface tension and low adsorption density in the thin film, as indicated by the asterisk, initiating film rupture and coalescence.

will be magntitude (64)

$$\Delta\gamma \approx \tfrac{1}{4}(\Delta p)d \tag{2}$$

Combination with Eq. (1) yields

$$\Delta\gamma = \tfrac{1}{4}\varepsilon^{2/3}d^{5/3}\rho^{2/3} \tag{3}$$

For $\rho = 1000\,\mathrm{kg/m^3}$ and $d = 10^{-6}\,\mathrm{m}$, we find $\Delta\gamma = 2.5 \times 10^{-8}\varepsilon^{2/3}$. For adsorbed proteins, the maximum reduction of the equilibrium surface tension is limited to approximately 0.03 N/m, which is related to the occurrence of collapse of the adsorbed layer above this value. This value may therefore be taken as an estimate of $\Delta\gamma$, although for the very short time scale of droplet impact and the resulting film stretching, higher values may be attainable. Moreover, the actual rupture mechanism will probably be related to fracture of the adsorbed layer rather than collapse. Nevertheless, taking this estimate for $\Delta\gamma$, coalescence is expected if $\varepsilon > 1.3 \times 10^9\,\mathrm{W/m^3}$. This is much higher than highest value for the power density that can be obtained by a toothed colloid mill in highly viscous emulsions (for this situation, a maximum power density of approximately $10^7\,\mathrm{W/m^3}$ was reported by Karbstein and Schubert (65)). According to Walstra and Smulders, an Ultra-Turrax type of machine and high-pressure homogenisers can produce power densities up to 10^{10} and $10^{12}\,\mathrm{W/m^3}$, respectively (64), which should be sufficient for this coalescence mechanism.

Little experimental evidence on this coalescence mechanism can be found in the literature. One of the few studies on this subject was by Chen et al. (66), who showed an increased rate of coalescence under highly turbulent flow conditions. However, it cannot be excluded that coalescence was caused by the introduction of air (which may lead to air-intermediated coalescence, discussed in Section IV.B) or occurred at the surface of the impeller blade (which may lead to surface-intermediated coalescence, discussed in Section IV. A).

For surfactant-stabilized emulsions, surface-tension gradients may be suppressed by fast exchange of the surfactant from solution. However, in the thin-film region, supply of surfactant from the dispersed phase is much more efficient than from the continuous phase. Therefore, if the surfactant is preferentially dissolved in the dispersed phase, it is more difficult to induce surface-tension gradients and vacancies in the thin-film region, and film thinning will proceed faster than if the surfactant is preferentially dissolved in the continuous phase. However, if the preferential partitioning of the surfactant in the dispersed phase is caused by micelle formation in this phase, the oriented-wedge theory would predict fast film rupture by passage formation in this case (Section III. A. 2).

IV. SURFACE-INTERMEDIATED COALESCENCE

In some cases, a third phase intermediates in the coalescence of emulsion droplets. This class of coalescence mechanisms has received relatively little attention in the literature. Based on general considerations, the critical step must be the rupturing of a thin water film between the droplet and the third phase. The third phase may be solid (e.g., the wall of the processing equipment or the wall of the container in which the emulsion is stored, or a gas, such as the headspace in the container or air bubbles beaten in during pumping or whipping). A special, very important case is the situation where the third phase is formed by small solid particles. These cases will be treated in the following subsections.

A. Coalescence Intermediated by a Solid Surface

Although not much is known about this mechanism, we may expect that coalescence intermediated by a solid surface is related to spreading of the dispersed phase onto this surface (Fig. 10). A crucial requirement for this mechanism must be that the dispersed phase (partially) wets the surface; the contact angle should be lower than 90°or so. The kinetics of this mechanism will be determined by the rupture of the thin (aqueous) film between the droplet and the solid surface, which can be understood as the dewetting of the thin film of the continuous liquid at the solid surface. Dewetting has been described by spinodal dewetting (67) and by nucleation by nanoscale gas nuclei, as first suggested by Derjaguin and Gutop (68).

It has been suggested that coalescence intermediated by a solid surface may occur at the surface of the impeller blades in an agitated vessel, in the context of phase inversion of liquid dispersions (69). The process would be important if the dispersed liquid has a higher density than the continuous liquid, so that the drops are able to reach the impeller surface by inertial impaction, where they may spread at the impeller surface or not, depending on the wetting conditions. Also, for emulsification in a colloid mill, the spreading behavior of the dispersed phase onto the wall of the colloid mill was shown to be important for the efficiency of the emulsification process (70).

B. Coalescence Intermediated by a Liquid Interface

Coalescence intermediated by a liquid interface (the interface between a gas and a liquid or between two immiscible liquids) resembles that at a solid surface, but is different because interfacial flow and area dilations are possible (Fig. 11). A requirement is again that the dispersed phase must spread upon the liquid interface, which is the case for pure triglycerides at pure air–water interfaces. Under quiescent conditions, the liquid interface will be covered by an adsorbed layer of surface-active material supplied by the solution. Emulsion droplets that approach the interface will be repelled by this layer, and on close encounter, a thin film will be formed. The rate

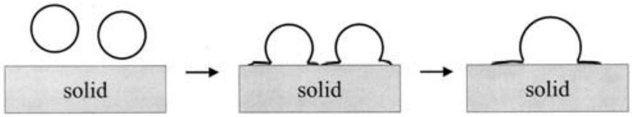

Figure 10 Coalescence intermediated by adsorption and (partial) wetting of droplets on the surface of a solid substrate.

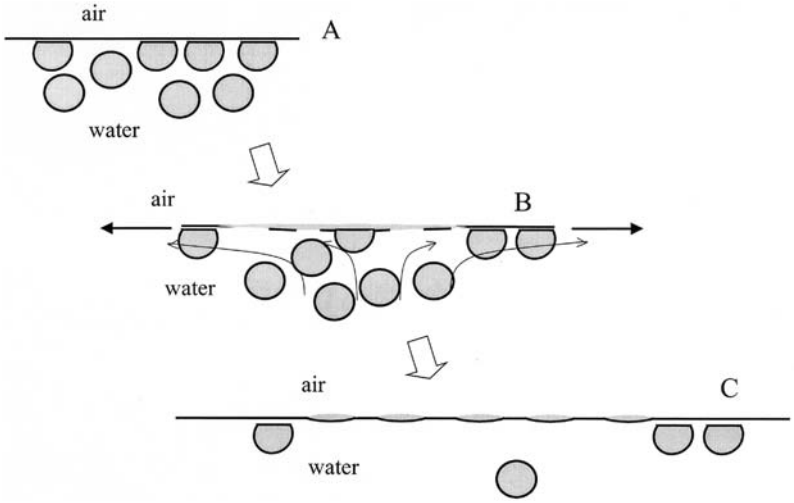

Figure 11 Coalescence intermediated by adsorption and spreading of the droplets at an expanding interface. (A) Droplets do not enter the air–water interface because of the kinetic stabilization by an air–water–oil thin film; (B) expansion of the air–water interface lowers the adsorption density at the air–water interface, leads to convective transport of droplets toward the air–water interface and increases the surface tension of the air–water interface to a value that enables spreading of the liquid oil onto this interface; (C) after spreading, the oil film contracts and breaks up into oil lenses.

of insertion and spreading of these droplets at the interface will then depend on the lifetime of this thin film. If the interface is expanded, the adsorption density at the interface will decrease by an amount that depends on the rate of adsorption of the surface-active material (Fig. 12). Higher expansion rates result in lower adsorption densities and higher surface tensions of the air–water interface. Moreover, if a cohesive adsorbed layer is formed, expansion of this layer may even result in the formation of bare cracks at the air–water interface by fracturing of this layer. In this way, expansion of the air–water interface will lower stability of the thin film between the expanding surface and the emulsion droplet, promoting droplet insertion.

Coalescence intermediated by air was studied at an expanding interface by Hotrum et al. (71) for emulsions stabilized by whey protein and β-lactoglobulin. It was shown that droplet spreading occurred if the air–water interface was expanded at such a rate that the surface tension of the interface exceeded a critical value. This critical value was shown to

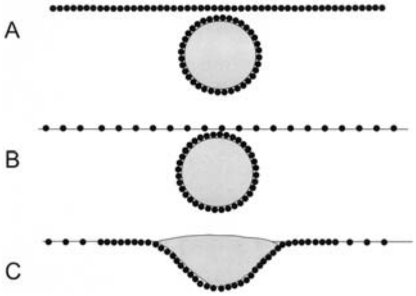

Figure 12 Coalescence intermediated by adsorption and spreading of the droplets at an expanding interface. Sketch showing how expansion of the air–water interface may reduce the stability of the air–water–oil thin film, promoting insertion of droplets at the air–water interface, which may initiate subsequent spreading of droplets. (A) quiescent air–water interface; (B) expanding air–water interface, with reduced adsorption density of surface-active material; (C) situation just after insertion: a lens is formed and surface-active material previously adsorbed on the droplet is transferred to the air–water interface.

correspond to the criterion of spreading of the oil at the air–water interface. Insertion of droplets without spreading should, in principle, be possible at lower expansion rates; however, this was not observed, probably because it is strongly suppressed by the high stability of the thin films between the emulsion droplets and the interface.

A self-amplifying mechanism for droplet spreading at the expanding interface was suggested by Hotrum et al (71). Spreading of oil at an air–water interface is a very fast process, with high expansion rates at the oil–water interface of the spreading emulsion droplet. The rapidly expanding oil–water interface may attract emulsion droplets from the underlying solution by convection, and if the spreading oil film is not sufficiently quickly covered by a protecting adsorbed layer, these droplets immediately coalesce with the spreading oil film. In this way, the spreading oil film is supplied with additional oil from emulsion droplets coalescing with the spreading film, amplifying the process.

After expansion, the spread oil film may be reintroduced into the emulsion in the form of droplets if the air–water interface disappears. In foamed emulsions, this may, for example, occur by coalescence or disproportionation of the gas bubbles. A well-known practical application of this process is the conventional process of butter manufacture by churning, where coalescence of milk fat globules and subsequent clumping to butter granules is intermediated by expanding and disappearing air–water interfaces (1).

Coalescence intermediated by a liquid interface may also be of great importance in several other situations. For example, during whipping of cream, dilating bubble surfaces may cause in insertion and (partial) spreading of milk fat globules. When an emulsion is poured, the air–water interface with area A will expand. The expansion rate ($d \ln A/dt$) depends on the pouring rate and presence of surface-active material and will be on the order of $0.1\ \mathrm{s}^{-1}$, similar to expansion rates measured in overflowing cylinders (72) or canals (73). During pumping, air bubbles may be beaten into the emulsion and be strongly deformed, leading to local high expansion rates of the bubble surfaces. On depressurizing or heating an emulsion, dissolved gas may be released as growing gas bubbles. The same may happen if gas is produced by (bio-)chemical reactions (e.g., the release of carbon dioxide during fermentation). In all cases, this may cause insertion and spreading of the emulsion droplets, by an extent that depends on the expansion rate of the interface and the rate of supply of film-stabilizing material from solution.

C. Coalescence by Shearing in Confined Spaces

Probably of great practical importance is the behavior of emulsions when confined to a thin layer between solid surfaces in relative motion to each other (Fig. 13). It is thought that such a situation occurs during oral processing, where the emulsion lubricates the movement between the tongue and palate (74). However, also during processing (e.g., homogenization in a colloid mill) and handling (e.g., spreading of a food emulsion with a knife), similar processes may occur. Obviously, conditions of high shear can easily be obtained in these configurations, but a special situation occurs when the distance between the shearing plates is the same order of magnitude as the droplet size or droplet size aggregates or is smaller than this. This is a largely unexplored field of thin-film tribological behavior, governed by large deformations and breakup of droplets and droplet

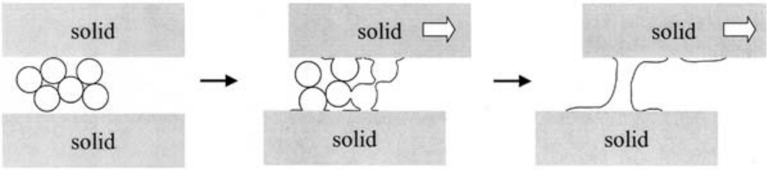

Figure 13 Coalescence induced by shearing in confined spaces. To illustrate possible processes, a combination of homogeneous and surface-intermediated coalescence is sketched for a droplet aggregate sheared between two closely spaced surfaces.

aggregates, droplet coalescence, and the interaction of the droplets with the solid surfaces (wetting, contact angles).

D. Rupture by Penetration of Particles

Film rupture by penetration of particles can be viewed as a special case of surface-intermediated coalescence (Fig. 14). It is a very commonly encountered mechanism. Particles that are fully wetted by either the dispersed liquid or the continuous liquid may puncture the thin film due to mechanical forces. However, often the particles are partially wetted by the other phase (finite contact angle at the oil–water interface), in which case the crystals have the tendency to reside at the oil–water interface and bridge the thin film. The particles may originate from the aqueous phase (e.g., calcium phosphate, lactose) or the oil phase (fat crystals).

Rupture by particles dispersed in the continuous liquid has been studied for foams in relation to antifoam agents (75), but much less for emulsions. De Gennes (76) has described a mechanism for coalescence caused by film rupture by penetration of particles. In this model, a single particle that remains emerged in the continuous phase may lead to a sequence of film ruptures that finally results in a few large droplets embedded in remaining uncoalesced droplets. An example of coalescence caused by penetration of thin films by water-soluble sodium nitrate crystals is shown in Fig. 15. Here, a highly concentrated emulsion, stabilized by whey protein isolate, was dried by exposure to the air. The emulsion was quickly destabilized and separated oil as soon as sodium nitrate, dissolved in the aqueous phase, started to crystallize.

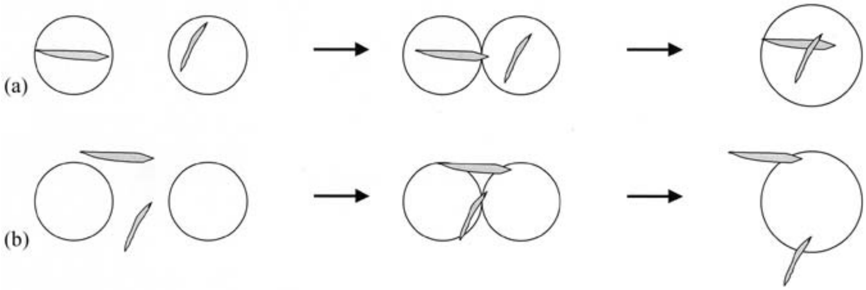

Figure 14 Coalescence intermediated by film penetration by particles suspended in (a) the dispersed oil and (b) the continuous water. The particles may or may not reside at the oil–water interface because of partial wetting by both liquids (as explained in the text).

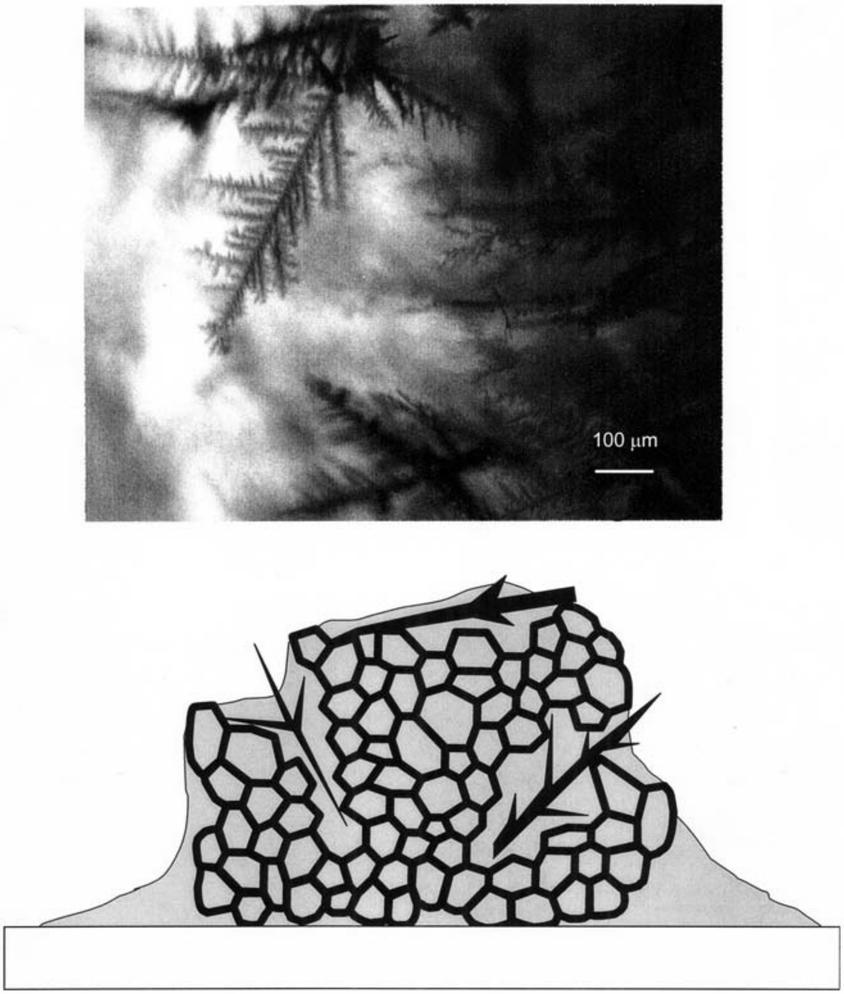

Figure 15 A highly concentrated oil-in-water emulsion (droplet diameter = 1 µm, volume fraction of oil = 0.9), stabilized by whey protein isolate and containing 0.1 *M* sodium nitrate dissolved in the aqueous phase. Visible are sodium nitrate crystals that were formed when the emulsion was dried by exposure to the air. The formation of these crystals lead to rapid separation of oil from the highly concentrated emulsion, which did not occur if a similar highly concentrated emulsion without sodium nitrate was dried. Individual emulsion droplets or separated oil cannot be observed because of the low optical contrast. The drawing shows a sketch of the situation.

An important example of rupture by particles embedded in the dispersed phase is the phenomenon of "partial coalescence," which has been studied extensively for dairy-related emulsions (77,78). Here, the particles are fat crystals that are present in the oil droplets at the temperature of application. Dependent on the presence of surfactants or polar lipids and on the mobility of the fat crystals inside the droplet, these fat crystals may move to and reside at the oil–water interface, finally leading to rupture of the thin films. Partial coalescence of emulsions of partially crystallized fat leads to the formation of clumps of fat globules, which retain part of their original droplet structure because the fat crystals inhibit the flow of two spherical droplets into one (step D in Fig. 3). In this way, networks of clumped fat globules can be formed, which are important for structuring products such as whipped cream and ice cream.

V. CONCLUSIONS AND PERSPECTIVE

A large number of coalescence processes may be responsible for the coarsening of the droplets in a food emulsions. Fundamental knowledge of these processes is needed in order to distinguish them and to take adequate action to control them. The intention of this work was to give an overview of possible mechanisms, some of which are already known in the literature, but most of them are hardly studied. The present overview may initiate new research in this complex field of coalescence in food emulsions.

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