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Introduction to Food Emulsifiers and Colloidal System

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1.1 Introduction

This chapter provides a short introduction to the most important parameters involved in multiphase system. As an introduction, the forces that interact between individual molecules are briefly mentioned, followed by a short review of the factors responsible for formation of, and stability of, systems consisting of two or more incompatible phases, as illustrated by emulsions and cake batters. This illustrates how forces related to amphiphilic substances like food emulsifiers on a molecular level can be thought of as complex foods, or how models of food can be formulated and described to get an idea of how food emulsifiers can act in the complex food and benefit from the emulsifiers. For monographs dealing extensively with interface chemistry see, for example, Israelachivili [1] or McClements [2].

Food and food ingredients are made up of a huge number of different types of molecules, and most foods will be amalgamates of numerous different constituents, ranging from small-sized molecules to much bigger biopolymers, altogether forming the compounded food. This means a substance or individual component will be associated with a number of similar, as well as different, substances, and together they will give the food its texture, sensory and other characteristics. In the food or food ingredient, individual components can be
present in various forms – either in similar constituents, or as a mix of discrete components. Often, they will be organized into separate structural entities at the interface between different phases, or may be dispersed as separate accumulated bodies or aggregates in a bulk phase. The food components can also be elements of an internal three-dimensional lattice, forming an integrated structure and thus giving the food the characteristic physical and chemical properties recognized as texture and organoleptic profile.

This means that the properties of food originate from the substances present. Due to intermolecular interactions and forces combined with external factors like temperature, stress, etc. they combine into structural organizations like dispersions, foams, emulsions, gels and other composite systems.

At the molecular level, individual molecules will interact due to a number of attractive as well as repelling forces see Table 1.1 page 3 between the molecules. These forces are recognized as Van der Waal forces and, compared to intramolecular forces (i.e. covalent bonding), are approximately two decades weaker. However, although weak, they play and important role when considering interaction within neighbour compounds. The Van der Wall forces can be classified into three distinct groups: Orientation forces, Debye forces and London forces.

The first of these, i.e. the orientation forces, take their onset from electrostatic interaction arising from unsymmetrical charge distributions within electrically neutral molecules – a charge displacement causing a permanent dipole moment. The presence of a permanent dipole moment will induce an electrostatic interaction between the charged components or molecules possessing a dipole moment, and thus becomes a fundamental parameter in the orientation of substances and in molecular arrangements and organization.

The presence of a dipole moment in a substance can interact with other molecules by inducing a dipole moment in neighbouring substances, and in this way it can establish attractive or repulsive forces between the substances. In this case, the forces are recognized as Debye forces. A neighbour interaction can also take place when a dissolved ion, due to the presence of the electrical charge, induces an electronic distortion of a non-polar compound and, thus, turns the compound to a polarized species.

The third category is London forces, which originate in the movements of electrons within a molecule. The fluctuations of electrons generates an oscillation of a negative charge, forming dipole moments within the molecule, and the dipole moment will interact with neighbour molecules with a weak attraction or, in if the charge is similar, a repulsion.

An important force which can interact between molecules and have a power between the weak Van der Waal forces mentioned above and the forces of a covalent bond is hydrogen bonding. The hydrogen bond is a non-covalent bond formed from intra- as well as intermolecular interaction between a proton donor and a proton acceptor, the latter being an atom or
moiety of higher electronegativity than the donor. As mentioned above, the hydrogen bond can be an intramolecular bond but, more interesting in the case of colloidal and food systems, it can be an intermolecular attraction or bonding between individual compounds. The hydrogen bonding is formed by interaction between an electron donor and an electron-deficient centre, and the bond strength is determined from the length, with an exponential decay in relation to the distance between the species. In addition, the angle of bond has an influence on the bonding strength.

Hydrogen bonds are not simple bonds, but are considered to be partly electrostatic and partly covalent of nature (see Gabowski [3]). Hydrogen bonding can be shown by spectroscopic methods (e.g. IR, UV and NMR) and are the explanation for the extraordinary high boiling point of water and a number of organic solvents. Other interactions worth mentioning are the electron pair donor and acceptor interaction (C. Reichardt [4]), which originate in the presence of high energy electron occupied and low energy non-occupied molecular orbitals. Also, solvophobic interaction, which is the inclusion of a hydrophilic substance in water, has to be considered.

Going from the interaction between two molecules to a system consisting of numerous molecules and where the materials are organized into structures or bodies formed from a high number of associated molecules, the interaction between the different colloid bodies can be simplified into attractive and repulsive forces between the individual colloid bodies. The interaction between colloid bodies originates from the molecular forces and will be an integration of the interaction between all the molecules of the colloid bodies, as well as interaction from molecules of the surrounding medium. This means that, in colloids, the interaction between the single colloid particles will originate from the same forces as those mentioned above. However, the overall interactions between the different colloid bodies are determined from the nature of the bodies and the surrounding solvent, both representing a huge number (and, often, a huge variety) of molecules.

In a multiphase system, the interaction between the discrete particles is related to two major forces, according to the DVLO theory of Derjaguin & Landau and Verweg & Overbeek. Here, the known Van der Waal interaction (i.e. the forces sourcing from the fluctuating dipole moments of neutral atoms) cause a polarizations of other atoms, and thus can establish an

Table 1.1  Some molecular and intermolecular forces.

<table>
<thead>
<tr>
<th>Type</th>
<th>Energy</th>
<th>Ratio vs distance</th>
<th>Type of forces</th>
</tr>
</thead>
<tbody>
<tr>
<td>Covalent</td>
<td>&lt;120 kJ</td>
<td>1/r (strong)</td>
<td>electrons are shared</td>
</tr>
<tr>
<td>Electrostatic</td>
<td>40–90 kJ</td>
<td>1/r (strong)</td>
<td>ion-ion, ion-dipole, dipole-dipole</td>
</tr>
<tr>
<td>Hydrogen bonds</td>
<td>6–25 kJ</td>
<td>1/r^6 (weak)</td>
<td>dipole-dipole + van der Waal</td>
</tr>
<tr>
<td>Van der Waal</td>
<td>2–10 kJ</td>
<td>1/r^6 (weak)</td>
<td>induction, rotation, dispersion</td>
</tr>
</tbody>
</table>
attraction between particles, thus acting as a driving force in flocculation into bigger bodies. The second force is the electrostatic repulsion between double layers, which is associated with an electrical charge, as in the case of ionic substances. The forces will counteract and equalize the Van der Waal interaction and will thus stabilize the colloid system (i.e. prevent the colloid from creaming and or flocculation). From a thermodynamic point of view, the system is unstable, but the counteracting forces between the particles bring the system into a metastable state which is, thus, kinetically stable. In addition to the two major forces of the DVLO theory, more detailed models include additional contribution from the steric repulsions and from hydrophobicity – interactions which also have to be taken into account when focusing on the overall interaction between colloid particles in a more complex picture of a colloid system.

In a colloid system, two or more individual phases are present, and the contact region of the two phases is known as the interface when the system is formed from two separate liquids or a liquid and a solid, or is described as a surface in a system formed from a liquid and a gas. Thermodynamically, such systems are unstable, and there will be a driving force favouring the energy of the system, which will divide the non-mixable substances into two separate bulk phases. Where a substance possesses an amphiphilic nature (i.e. having both hydrophilic as well as lipophilic moieties), the substance will migrate to, and organize, at the interphase. Thus, a migration takes place as long as the adsorption free energy can counteract opposite contributions from entropy and thermal energy. The adsorptions of molecules at the interface will increase the number of favourable thermodynamically interactions and, when equilibrium is reached, an optimum number of favourable interactions will have been formed.

The adsorption of a solutes such as an amphiphilic compound to the interface will also depend on the concentration of the solutes, as the adsorbed molecules will be in equilibrium with the molecules remaining in the bulk. This equilibrium has to be evaluated from a kinetic point of view, as the migration of small molecules takes place at different rates compared to big molecules like proteins. The small molecules are much faster in obtaining an equilibrium and can thus be an important parameter in forming and stabilizing an interface or a surface film. When the stabilizations come from polymers like proteins and or polysaccharides present in the system, the polymer will be associated to the surface of the colloidal particles, covering the interface/surface more or less.

Large biopolymers such as proteins often exhibit both lipophilic as well as hydrophilic segments and, when distributed in a multiphase system, the proteins will arrange themselves with the lipophilic moieties being in contact with the oil phase, while the hydrophilic region will be located within the aqueous phase. The ionic functionalities of the polymers imply repulsion between
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Particles of the same polarity, while another part of the polymers can be dissolved in the continuous phase. This increases the viscosity (especially the yield value) of the liquid phase, slowing down the movement of the dispersed particles and thus reducing the possibility of the dispersed bodies merging. At higher concentrations, polymers can also form cross-linking between particles, which results in a dramatic increase of viscosity, or gelling, of the system. On the other hand, addition of polymer material is sometimes seen to destabilize emulsions, the mechanism being a polymer cross-linking between two emulsion droplets, which starts coalescence.

In the case of proteins present in a colloid system, the pH of the system also has an impact on the emulsifying and adsorbing properties of the molecules (e.g. proteins at the isoelectric point will exhibit less electrostatic interaction, compared to proteins at a pH value where the charged groups are present and the individual protein molecules exhibit electrostatic repulsion). Proteins often have quaternary structures, where the lipophilic parts of the proteins are located in the interior of the structure and the adsorption of the proteins to an interphase can unfold the proteins to gain a more energetically favourable state; due to the hydrophilic amino acids, moieties can come into closer contact with the aqueous phase. In the case of globular proteins, the presence of proteins adsorbed to the interphase can, according to Dickinson [5], be considered to be a two-dimensional network of cross-linked spherical particles.

In a system with both large emulsifying proteins and small amphiphilic molecules present, competing adsorptions will take place (Mackie [6]), but also a reorganization of the proteins takes place due to conformational changes. The latter interaction can be seen as a part of a dynamic process, running until equilibrium is obtained and a ‘stable’ multiphase system is obtained (Miller [7]).

The stability of such emulsified systems will also be influenced by other factors. For example, temperature will have a great impact on an interphase system, as high temperatures can be of an energetic level which can supersede the interfacial forces and, thus, destabilize the system. On the other hand, sub-zero temperatures will freeze part of the water present so that ice formation takes place. The latter is controlled by the temperature, but also by the presence of solutes, which implies a freeze-point depression of the water. The concentration of salts and other solutes will increase in the non-frozen water when ice is formed and will thus alter the solubility and intramolecular organization of the proteins (i.e. changes which will alter the emulsification properties of the protein-interface active materials).

Another important effect of the temperature of a colloid comes from the formation of lipid crystals, as oils and fat will crystallize more or less to solid fat crystals. The liquid–solid ratio is determined from the nature of the lipids and the temperature of the lipids. Lipids are well known to be of polymorphic nature, with different crystal forms and, thus, different melting
points. This means that fractions of an oil at certain temperature will change to solid state, and the compounded phase of the system will change from an all-liquid oil into a partly crystalline phase which encloses liquid oil. In case of small droplets, the lipid crystals on the surface of one particle can interact by penetration into the liquid region of a neighbour droplet. In this way, they can link or fuse two or more particles together – an energetically more favourable situation, due to the repulsive interaction that a lipid crystal will exhibit towards an aqueous phase. Furthermore, in cases where surface lipids crystallize and neighbour particles also are partly crystallized, the surface lipid still can be energetically favoured by forming inter-particle associations where, for example, the long hydrocarbon chains organize into crystalline lattice-like structures, where hydrocarbon chains are oriented in a parallel head and tail order. This linking of colloid particles will affect the system and have great impact on the physical properties, as well as the texture of a system.

1.2 Food emulsifiers

One important group of small molecules in relation to interfacial and surface physical chemistry are the food emulsifiers. These molecules belong to a group of chemical substances characterized by possessing amphiphilic properties (i.e. the compound exhibits a dichotomic nature). The amphiphilic properties are due to the coexistence of both lipophilic and hydrophilic functionality within the same molecule. This means that the emulsifier will be strongly polarized and will thus, at the same time, exhibit affinities to both polar and non-polar substances. The hydrophilic moiety will be oriented toward the polar solvents (typically water, together with solutes and compounds being able to form hydrogen bonding) and, at the same time, the lipophilic part of the emulsifier structure will be attracted to non-polar surroundings (e.g. the hydrocarbon chains of glycerides or other non-polar substances).

The basic raw materials for producing food emulsifiers are triglycerides (i.e. natural fats and oils). The latter substances are isolated from a number of suitable agricultural products and are afterwards processed to a refined quality, with a very low content of free fatty acids, phospholipids and colouring materials, as well as being free of flavours. Fats and oils are a characteristic of their botanical origin, and the fatty acid composition of the oil will be recognized within narrow limits to the specific type of oil (e.g. rapeseed oil, sunflower or palm oil), but can be modified by physical fractionation or hydrogenation to obtain a fatty acid profile to be built into an emulsifier. The choice of fatty acid source for an emulsifier is an important parameter, as the interphase properties, etc. of the emulsifier can be controlled by the lipophilic chain length (i.e. the carbon number of the fatty acid moiety) and also from the number of oleofinic bonds present in the fatty acid groups.
Other key raw materials for food emulsifiers are polyols like glycerol, sorbitol and sucrose. Glycerol and fatty acids are produced from fats and oils by hydrolysis of triglycerides and successive separation of the free acids and the glycerol. Both are purified using different techniques, e.g. decolourization, distillation or fractionation. Sorbitol is derived from starch hydrolysates.

In relation to the hydrophilic moiety of food emulsifiers (i.e. the polyols), the properties of an emulsifier play an important role and are determined from the number of free hydroxyl functionalities and ester groups present. Further ether linkages present in the emulsifier will play an important role as a polar contribution to the nature of the emulsifiers.

In addition to the abovementioned, important raw materials include organic hydroxyacids like lactic acid and citric acid, both obtained from fermentation processes, while tartaric acid is isolated as a natural component and by-product from wine production. All are acids which, by esterification with free hydroxyl groups (e.g. of glycerol) can change the degree of polarity of the emulsifiers by altering the ester, hydroxyl and carboxylic moieties of an emulsifier.

Propylene glycol and acetic anhydride are derived either from petrochemicals, though synthetic processes taking place in the C-3 pool and C-2 pool, respectively, or from the fermentation industry.

The food emulsifiers are made by reactions between selected raw materials. These reactions are mostly esterifications or interesterifications, but etherifications are also common within food emulsifier production. Often, the preparation is followed by successive purification and separation processes – operations that will create esters with the characteristic presence of amphiphilic properties and fulfilling the legislation concerning identity and purity in relation to food additives.

Food emulsifiers can be classified on basis of their fundamental nature as non-ionic, cationic, anionic and zwitterionic see Figure 1.1 page 9.

The non-ionics are the prevailing type of emulsifier used in food applications. Within the non-ionic food emulsifiers, the monoglycerides and the mono- and diglycerides are the most important representatives. These are substances with the hydrophilic part formed from the mono- or diesterified glycerol, while the lipophilic part can be assigned the hydrocarbon chain of the fatty acid radical. As the mono- and diglycerides possess free hydroxyl moieties, the emulsifiers are open for further esterification.

A non-ionic derivative of the monoglycerides is the lactic acid esters of the monoglycerides. Here, the esterified lactic acid will modify the hydrophilic group of the monoglyceride and change the application properties dramatically. Esters also derived from monoglycerides are acetic acid esters (i.e. in addition to a fatty acid ester linkage, the glycerol also has one or two acetylated hydroxyl groups). Other non-ionic emulsifiers include polysorbates,
which have a more hydrophilic nature in comparison with the monoglycerides, due to the long hydrophilic polyoxyethylene ether chain linked to the sorbitan moiety (dehydrated sorbitol) esterified to a fatty acid. The latter (i.e. esterified sorbitans) are an isolated compound considered as separate type of non-ionic emulsifiers. Polyglycerolesters are characterized from the hydrophilic backbone of oligomerized glycerol, which can be esterified with one or more fatty acids, while the propyleneglycol esters obtain their hydrophilicity from the free hydroxyl and esterified hydroxyl functionalities. Sucroseesters and sucroglycerides obtain the hydrophilic nature from the free and esterified hydroxygroups of the carbohydrate moiety. In the case of the sugar esters as well as the polyglycerolesters, the degree of esterification can vary from mono- to polyester, giving a spectrum of degrees of polarization of the emulsifiers and, thus, the interface properties.

Within the group of ionic emulsifiers, the food emulsifiers (the anionic type) are mostly used, and, due to the charge on the ionic moiety, they often exhibit a significant hydrophilic nature. These emulsifiers can be esterified derivatives of the monoglycerides, where hydroxyacids like tartaric or citric acids are esterified to a hydroxyl group of the monoglyceride. However, as both acids possess two or three carboxylic groups, respectively, one or two free carboxylic functionalities will be present in the resulting emulsifiers and will thus play an important role in the polarity of the emulsifiers. Another group of anionic food emulsifiers is the lactylates, which are a type of emulsifier where dimerized (oligomerized) lactic acids are esterified with a fatty acid, and the residual free carboxylic function of the terminal lactic group is neutralized to the corresponding sodium (SSL) or calcium (CSL) salt. Ammonium phosphatides are derived from mono-and diglycerides, the latter being esterified with a phosphate moiety to give an acid emulsifier, which is neutralized by addition of ammonia. Zwitterionic food emulsifiers, where both an anionic and a cationic moiety are present, can only be found as one or several materials in lecithin, a by-product of the fat and oil industry, consisting of a number of different phospholipids.

An alternative way of classifying food emulsifiers is using the HLB number for the emulsifier. The HLB number is a numerical figure representing some information concerning fundamental properties of the substance (e.g. how it acts in water) and a simplified functionality by characterizing the balance between the hydrophilic and the lipophilic properties of the emulsifier. Thus, a low HLB number indicates a molecule with a high degree of hydrophobic character, while a high value expresses a structure with a strong hydrophilic nature. The number can be determined experimentally, but they are mostly calculated by using Davies estimate [8] or taken from reported tables in the literature, listing the HLB values of a number of pure and commercial substances. A few values of food emulsifiers are listed in Table 1.2.
Figure 1.1 Examples of food emulsifiers.
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Figure 1.1 (continued)
1.2 FOOD EMULSIFIERS

Table 1.2  Some values of food emulsifiers.

<table>
<thead>
<tr>
<th>Emulsifier type</th>
<th>HLB value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diglyceride</td>
<td>2–3</td>
</tr>
<tr>
<td>Monoglyceride</td>
<td>3–4</td>
</tr>
<tr>
<td>Data ester</td>
<td>8–10</td>
</tr>
<tr>
<td>Calcium lactylate</td>
<td>7–9</td>
</tr>
<tr>
<td>Sodium lactylate</td>
<td>18–21</td>
</tr>
<tr>
<td>Polyglycerolester</td>
<td>6–11</td>
</tr>
<tr>
<td>Propylene glycolester</td>
<td>2–3</td>
</tr>
</tbody>
</table>

In addition to characterizing a number of interface active substances, the HLB value can be used as a simple guideline to the selection of emulsifier for a colloidal system. Here, a rule of thumb is that values in the range of 2–6 shall be chosen for water in oil systems (i.e. emulsions with oil as the continuous phase), while emulsifiers with a value in the range 8–18 will be suited as an emulsifier for use in oil in water systems, where the continuous phase is aqueous. However, it must be remembered that food emulsions are complex systems and are mostly made up from many different substances in several liquid phases, as well as solid and gas phases. Consequently, the use of HLB in practice can only be used as a simple guide to the choice of emulsifier, as systematic testing has to be done to get the optimal solution for a given food system.

The polarized nature of food emulsifiers classifies them as a group of surface active compounds which do not need nucleation in dispersed systems. This means that the food emulsifiers in a dispersed system will spontaneously form structures, usually controlled by geometric and energetic parameters, and these aggregated structures are also known as association colloids. In addition to micelles (i.e. small globular spheres formed at low concentration of the emulsifier in water), self-assembled bodies like spherical bodies, hexagonal cylinders, spherical vesicles, laminar films and so on can be generated. The structures are recognized as mesophases and are highly dependent on concentrations, temperatures, and solutes, etc.

Classical studies have shown that, for example, monoglycerides in aqueous systems (Larsson et al. [9]) will interact with the water and form a number of different mesophases, depending on the concentration of the monoglyceride as well as the temperature of the system. Studies have also demonstrated that the carbonyl of the fatty acid moiety and the 3-hydroxyl group of a monoglyceride will exhibit strong hydrogen bonding (Holmgren [10]). Micelles, hexagonal bodies, cubic phases, lamellar sheets and reverse micelles are all structures where the hydrophilic moiety of the monoglyceride will associate with the aqueous medium through hydrogen bonds, while the
lipophilic hydrocarbon chains of the fatty acids groups, due to repellent forces in relation to the water, will organize to minimize the strain and the energy of the system. Diagrams showing the different mesophases related to the temperature versus the concentration in aqueous systems have been worked out (Qiu and Caffret [11]). It has also been demonstrated that the nature of the fatty acid chain plays a crucial role and, for example, significant differences will be seen between the diagrams of palmitic/stearic monoglycerides and the unsaturated glycerolmonooleate.

In an interesting study, Duynhoven et al. [12], using NMR and cryoSEM techniques, have reported a two-stage process of the monoglyceride-water gel state, where the emulsifier forms lamellar plates or sheets separated of aqueous layers known as the alpha-gel. It is suggested from the evidence of the work that the formation of the coagel follows a two-step mechanism, with a discrimination between L and D isomers in a rate-determined step organized in two dimensions. In the succeeding second stage, growth takes place in the third dimension.

Enantiomers of emulsifiers and lipids in general have to be considered as different stereo isomers, and mixes of these will have a fundamental influence on the molecular packing and crystallization. Blends of stereo isomers can crystallize as conglomerates of the different forms, or make up racemic compounds where, for example, the melting point will be related to the ratio between the two opposite isomers. It can also be as pseudo-racemic mixes, with a melting point independent of the ratio – circumstances which make lipid crystallization very complex.

Other types of food emulsifier in aqueous systems will also form mesophases, but in general they are not found to be as complex as in the case of monoglycerides. The nature of food emulsifiers to form liquid crystalline phases has been recognized as a fundamental parameter which can be utilized in forming and or preserving textures of food (Heertje et al. [13]).

Where emulsifiers are added to an oil (i.e. a triglyceride), the dichotomous nature of the emulsifier molecules will be a major factor, as the hydrophilic part of the emulsifier will associate due to the presence of relatively strong forces like dipoles or, in many cases, also due to hydrogen bonding. This will make a relatively strong intermolecular interaction between the hydrophilic moieties of the emulsifiers, while the acyl chain of the emulsifier will have an affinity for neighbouring acyl chains of the surrounding triglycerides and, thus, will minimize the energy of the system. This is the background of the report from Chen & Terentjev [14], where associative structures were observed when emulsifiers were present in triglycerides (e.g. monoglycerides in oil). In the study, it is described that, above the melting point, the monoglycerides in an oil will form an isotropic fluid and, when the temperature is allowed to decrease below the kraft point, inverse laminar phases are formed and organized into a hexagon in plane order.
Over the years, a number of studies and patents have dealt with emulsifiers in triglycerides as a structuring component in fats or as a possible alternative to partly hydrogenated triglycerides containing trans-fatty acids due to the ability of the emulsifiers to organize into structures and, in this way, exhibit properties more or less comparable to hydrogenated triglycerides used in food formulations like margarines, etc.

Depending on the hydrophilicity of an interface active substance, the emulsifier can be more or less miscible with liquid triglycerides. In the case of solid fats (i.e. crystallized triglycerides) and a limited solubility of the emulsifier, the latter can be more or less integrated into a crystal lattice of triglycerides (Aronhine et al. [15], Smith et al. [16]). The limited compatibility of the emulsifier can appear as imperfections in the crystals, while more hydrophilic emulsifiers will nucleate due to repulsive forces in the process and will thus occur as isolated heteronuclei seeds in the initial stages of a progressive crystallization of triglycerides. During the growth phase of the lipid crystals, the emulsifier can be adsorbed to the surface of the crystals and thereby shield the liquid triglycerides, thus inhibiting further development of the crystal growth. Besides the influence on the growth rate, the adsorption to the solid surface of a crystal can also have a great impact on the polymorphic nature of the fat. The emulsifier can form a barrier that will retard or inhibit not only interchange with the solute triglycerides, but also solid-solid interchanges and, in this way, will decrease the rate of polymorph transformations between the different crystal forms. The interaction of an emulsifier with solidifying triglycerides can thus alter or inhibit crystallization taking place, and emulsifiers are reported to find application as anticrystallization or anti-clouding agents in vegetable oils. In other cases, the presence of an emulsifier can be an accelerator and stabilizer in a crystallization process.

An opposite case can also occur with some types of emulsifiers, where the emulsifier can act synergistically in sintering fat crystals and can thereby increase the volume of solid triglycerides sediment (Johanson and Bergenstaal [17]). In the latter case, the emulsifier (i.e. glycerol-monooleate) is thought to adsorb to the crystal surface and enhance crystal sintering. A possible explanation is that the emulsifiers are adsorbed to triglyceride crystals such that the non-polar groups are incorporated into the crystal and the hydrophilic moiety into the liquid triglyceride. Here, the hydrophilicity causes an interaction with similar hydrophilic groups in neighbour crystals by dipolar forces and hydrogen bonding, which links the triglycerides into a lattice, experienced as an increase in solid fat. In addition, the adsorption of emulsifiers into the triglyceride crystal will have a stabilizing effect, because the emulsifier will retard Ostwald ripening as the rates of disintegrating and growth are decreased by the presence of an emulsifier film on the crystals.

Systems with two major different liquid phases are known as emulsions. In these systems, the oil, in the form of triglycerides and water, will be present
either as droplets or as surrounding liquid, depending on which phase includes the other. The surrounding phase is known as the continuous phase, and the emulsions are described as ‘oil-in-water’ or ‘water-in-oil’ emulsions. The separate phases can, in the simple form, comprise pure water and simple liquid triglycerides; however, in the case of food, the systems will be far more complex, as there will be solutes, as well as non-soluble materials like protein, salt and carbohydrates, present in the aqueous part. In the lipophile phase, triglycerides can be present as a liquid but also, to a large extent, as fat crystals, together with a range of different non-polar organic substances. The interphase of the water and oil will be formed by materials such as proteins and emulsifiers, together with phospholipids, but also solid materials such as lipid crystals and non-soluble salts can act in the form of a Pickering stabilization, and can thus take part of the interface (Gosh [18]).

The most important components of the interface are the proteins and the small-size molecule emulsifiers. Both types have significant affinity for the polar as well as the non-polar phases. At the boundary, an equilibrium between proteins and emulsifiers will take place as the food emulsifiers will compete and displace the proteins. Furthermore, some types of emulsifiers can exhibit an affinity to the proteins and can thus bind to the latter through hydrogen bonds or dipolar forces – an association that will implement changes in the proteins and the interphase properties of the proteins (Dalgleish [19], Dalgleish et al. [20] and Wilde et al. [21]). This means that the interphase will be formed from proteins and small molecule emulsifiers.

In studies, Gunning et al. [22] point out that the interface does not represent a uniform mix of the two types of materials, but there seem to be zones at the interface formed by proteins, separated by other zones consisting of emulsifiers. The formation have been described as an orogenic mechanism (Wilde et al. [21]), where a protein film is initially formed at the interface and successively small-molecule emulsifiers penetrate into the protein network at imperfect spots. As the emulsifiers continue to build up, the proteins will undergo an increasing stress until a displacement from the interface happens. A consequence of the extrusion of the proteins by food emulsifiers is a weakening of the interface film, with more elastic barrier properties as a result. The orogenic mechanism, based on atomic force microscopy, has been discussed by Morris and Gunning [23] in relation to food and digestion.

The orogenic mechanism builds on studies done on highly hydrophilic emulsifiers present in the aqueous phase. It describes the process as singular small emulsifier molecules starting to penetrate the protein and then build up. However, most food emulsifiers have an affinity for both the water phase as well as the lipophilic phase, and they will be present in both phases. Furthermore, the emulsifiers will organize in mesophases, as mentioned above, and it is most likely that the emulsifier will be present as small lyotropic
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bodies in the respective phases. These structures will expose a hydrophilic sheet, composed of multiple hydrophilic moieties of the emulsifier and, thus, will amplify the force or the hydrophilic potential. They thus represent a far stronger force in the replacement of high molecular weight proteins bound by affinity to the interface, as illustrated in Figure 1.2 below. The presence of liquid crystals at the interface can also act on the crystallization of the

Figure 1.2 Low molecular weight emulsifier (L) displacement of protein at the interphase of an oil droplet.
triglycerides by acting as a nucleus for, and promoting the formation of, triglyceride crystals at the interface.

Kalnin et al. [24] see the lyotropic crystallization of the food emulsifiers as an important parameter at the interface in food emulsions. In the case of water in oil systems, the lipid crystals network, as well as food emulsifiers, play a significant role in the stabilization of the emulsion, as the emulsifier crystals will be at the interface and form of Pickering stabilization of the system.

Other systems of great interest and relevance in foods are foams, where a gas is enclosed in a liquid, which can include suspended solids as well as one or more liquid phases and thus can be complex systems. Foams are often aerated emulsions, as in the case of whipped dairy creams and whipped cake batters, etc. In a foam, the air cells will be separated from each other by a liquid film. Depending on the thickness of the film, the systems can been considered as a dispersion of air into a liquid in cases where film thickness is larger or of the same size as the air cells. Where the film is thin, the latter is called lamellae. Under a low stress, the foam will act as a solid but, beyond a certain yield stress, a flow is obtained. The liquid phase forming the barrier between the air cells (i.e. the lamellae) includes the surface, which provides the stability of the foam towards coalescence. Thus, the interface will consist of amphiphilic compounds like proteins and food emulsifiers but, in many cases, will also include solid materials such as fat crystals, etc. These will be adsorbed at, and thus be part of, the interface film, and will stabilize the aerated system. This is not stable, as rupture of the exposed barrier can lead to coalescence, ending in collapse of the foam. Instability from drainage of the film must also be considered, as drainage can lead to a point where the thickness of the barrier becomes so small that thermal fluctuation can burst the lamellae (Weaire and Hutzler [25]).

Stabilization of foam is a combination of several different mechanisms, and depends on the nature of the compounds present in the system. Inter- and surface-active proteins, with or without food emulsifiers present, are often found to play a substantial role in the formation and stabilization of a foam. Many studies (e.g. Rodriguez Patino et al. [26]) have dealt with the mechanism and the interface chemistry of such foams. As in the case of emulsions, there will be competition between the proteins and the food emulsifiers adsorbed to the surface film. Here, proteins will unfold and form a network at the surface, while emulsifiers will migrate to the surface at non-covered spots and, by successive adsorption, will expand and displace the proteins until the heterogeneity of the protein filament leaves the protein as isolated spots (Mackie et al. [27], Sánchez et al. [28], Woodward et al. [29] and Morris and Cunning [23]).

A process following the orogenic principle, such as the case of a liquid-liquid interface, also has its onset in highly hydrophilic emulsifiers like polysorbates, while emulsifiers like aerating monoglycerides, whose nature is to form
mesophases composed of numerous molecules in aqueous environment, have not been taken into the model. In a study of monoglyceride and protein at a water-air interface, Cejudo et al. [30] conclude that protein displacement is more easy for spread than adsorbed films, and the latter have a higher degree of segregation, etc. The same study also reports that at low concentration, glycerol monooleate more easily displaces proteins adsorbed in air at the water interface than glycerol monopalmitate, while at higher concentration of the emulsifier, the opposite is observed. This, combined with the fact that this type of monoglycerides have quite different mesophase behaviours in aqueous systems, suggests that the lyotropic nature of the food emulsifiers in an aqueous regime has a great impact on the emulsifier-protein film.

The effect of the addition of food emulsifiers to a whipping has been found to result in a higher ratio of liquid, as the foam is more dense due to the generally smaller size of the air cells (Gomez and Patino [31]).

In the same study, it is stated that the surface shear properties seem to be important with respect to the stability of the foam, as a higher concentration of the emulsifiers at the interface increases the viscosity of the film, which implies increased stability of the film. The latter can be combined with the fact that liquid crystalline phases were already connected to stability of foamed systems by the early 1970s (Jederström et al. [32]).

Another aspect of emulsifiers at air-water interface is in foamed systems without proteins present. In this kind of system, the mesophase behaviour of food emulsifiers is recognized by Shrestha et al. [33] in a study of the foam ability and stability of an aqueous foam made in presence of a polyglycerolester. The foam ability has been found to increase exponentially with the emulsifier content. The stability demands a certain level before the lifespan becomes stable. In addition, it has been found that unsaturated emulsifiers, or mixes with unsaturated fatty acid moieties, make the foam more labile. The stability of the foam has been attributed to small particles formed from the emulsifier in a sort of Pickering stabilization, while the laminar mesophases of the polyglycerolester are thought to play a minor role.

Duerr-Auster et al. [34] have reported that the emulsifier, a polycerol ester, forms a monomolecular film at the air-water interface, combined with a number of bilayers in the subsurface bulk. Emulsifiers like monoglycerides are adsorbed to the surface from laminar liquid crystals in the bulk phase, and part of the lamellar structures can reach from the surface into the aqueous bulk, thereby stabilizing the foam, as shown in Figure 1.2, where the oil is substituted by air. The mechanical properties of the film are assigned to the interaction of the alkyl moieties of the emulsifier which, in the solid state, makes the film less flexible. In a study using scanning force microscopy on polyglycerolester foam, Curchellas et al. [35] confirm the presence of a monolayer, combined with emulsifier vesicles forming multiple layers in the bulk phase, but the emulsifier vesicles are also seen as stabilizing part of the bulk
phase, retarding a drainage of the film, which can be attributed to the formation of strain in the aqueous phase.

Turning from studies of relatively simple model systems to complex food systems, including numerous different ingredients of soluble and non-soluble origin such as in a sponge cake, Sahi and Alava [36] have demonstrated that monoglycerides, as well as polyglycerol esters, will both compete with and displace proteins from egg and flour. The displacement weakens the strength of the surface film between batter serum and gas, and thus makes the film more flexible and the gas cell easier to disrupt into multiple smaller cells (i.e. a more stable system). In addition, the food emulsifiers will form mesophases with the water and build up lattice-like structures that will increase the viscosity of the batter and, thus, prevent movement and coalescence of gas bubbles during processing and baking of the batter.

In high-ratio cakes with a high content of fat, the whipped batter will be formed from the proteins present in an ‘all-in-one batter’. The protein film will only be intermediate, as fat in the form of small globules or, rather, triglyceride crystals, with the tip attached to the gas phase, will interact. The fat crystals – or more precisely the tips of the crystals – are adsorbed to the gas serum interface, stabilizing the foam according to Brooker [37], who also considers food emulsifiers to take part of the film formed. Small molecular emulsifiers will, in this case, complex to and interact with the fat particles, and it is very likely that the hydrophilic moieties of an emulsifier, linked though the lipophilic moiety to a fat crystal or globule, can make hydrogen bonds with similar groups connected to neighbouring fat particles, and thus form conglomerates or lattices including confining solids as well as gas cells.

The text above has provided a short review of how food emulsifiers can interact, and which processes and mechanisms operate. The studies mentioned have been done on more or less simple systems, but the mechanism can recur in food and can thus be used in explaining the effects of an emulsifier in a food formulation. The mechanisms can also be used to help in selecting the right emulsifier or combination of interface active ingredients when working with food.

References

REFERENCES


