

Paper 01: Food Chemistry

Module 14: EMULSIONS: PROPERTIES, TYPES AND EMULSIFYING AGENTS

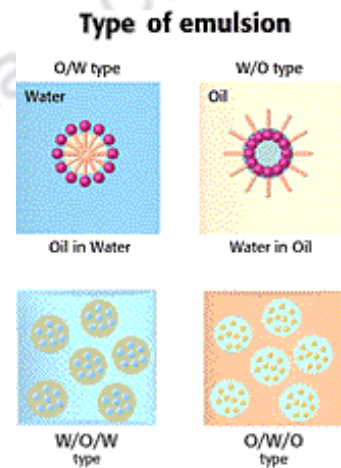
Among the structures and structure-forming units within foods, emulsions play a major part. They are known to impart desirable mouthfeel characteristics to the food, but, in addition, they are key ingredients in the formation of structures in certain products, such as whipped toppings and ice creams, and more complex products, such as processed cheeses. Therefore, the understanding of the formation, structures, and properties of emulsions is essential to the creation and stabilization of structures in foods. Food emulsions are widely used and are familiar to almost everyone. The formulation and creation of a food structure involving emulsions is always a compromise, depending on the desired qualities of the food and the materials which can be used to create these qualities.

B. Types of Emulsion

An emulsion is a suspension of one phase in another in which it is immiscible. One of the phases exists as discrete droplets suspended in the second, continuous, phase, and there is an interfacial layer between the two phases which is occupied by some necessary surfactant material.

There are four types of emulsions which are important, or potentially so, in foods.

- In oil-in-water (o/w) emulsions, droplets of oil are suspended in an aqueous continuous phase. These are the most versatile of the emulsion types; they exist in many forms (mayonnaises, cream liqueurs, creamers, whippable toppings, ice cream mixes), and their properties can be controlled by varying both the surfactants used and the components present in the aqueous phase.
- Water-in-oil (w/o) emulsions are typified by butter, margarine, and fat-based spreads in general. These depend for their stability more on the properties of the fat or oil and the surfactant used than in the properties of the aqueous phase, and because of this, there are fewer parameters which can be varied to control their stability.



- The third of the emulsion types is water-in-oil-in-water (w/o/w), which is, in effect, an o/w emulsion whose droplets themselves contain water droplets (i.e., are w/o emulsions). These are the most difficult emulsions to produce and control, because the water droplets contained in the oil droplets must be stable, as must the oil droplets contained in the continuous aqueous phase.
- The fourth type of the emulsion is oil-in-water-in-oil (o/w/o) emulsion which is a double emulsion system in which the dispersed phase is an oil-in-water (o/w) emulsion and the continuous phase is oil or plastic fat. Because of its limited application in food products, comparatively limited work has been done on the o/w/o emulsions.

Types of Food Emulsions

Food	Emulsion type	Dispersed phase	Continuous phase	Stabilization factors, etc.
Milk, cream	O/W	Butterfat triglycerides partially crystalline and liquid oils. Droplet size: 1 – 10 μm . Volume fraction: Milk: 3-4% ; Cream: 10- 30%	Aqueous solution of milk proteins, salts, minerals, etc.	Lipoprotein membrane, phospholipids, and adsorbed casein.
Ice cream	O/W (aerated To foam)	Butterfat (cream) or vegetable, partially crystallized fat. Volume fraction of air phase: 50%	Water and ice crystals, milk proteins, carbohydrates (sucrose, corn syrup) Approx. 85% of the water content is frozen at -20°C .	The foam structure is stabilized by agglomerated fat globules forming the surface of air cells. Added surfactants act as “destabilizers” controlling fat agglomeration. Semisolid frozen phase.
Butter	W/O	Buttermilk: milk proteins, phospholipids, salts. Volume fraction: 16%	Butterfat triglycerides, partially crystallized and liquid oils; genuine milk fat globules are also present.	Water droplets distributed in semisolid, plastic continuous fat phase.
Imitation cream (to be aerated)	O/W	Vegetable oils and fats. Droplet size: 1 – 5 μm . Volume fraction: 10 – 30%	Aqueous solution of proteins (casein), sucrose, salts, hydrocolloids.	Before aeration: adsorbed protein film. After aeration: the foam structure is stabilized by aggregated fat globules, forming a network around air cells; added lipophilic surfactants promote the needed fat globule aggregation.
Coffee whiteners	O/W	Vegetable oils and fats. Droplet size: 1 – 5 μm . Volume fraction: 10 – 15 %	Aqueous solution of proteins (sodium caseinate), carbohydrates (maltodextrin, corn syrup, etc.), salts, and hydrocolloids.	Blends of nonionic and anionic surfactants together with adsorbed proteins.
Margarine and Related products (low calorie spread)	W/O	Water phase may contain cultured milk, salts, flavors. Droplet size: 1 – 20 μm Volume fraction: 16 – 50 %	Edible fats and oils, partially hydrogenated, of animal or vegetable origin. Colors, flavor, vitamins.	The dispersed water droplets are fixed in a semisolid matrix of fat crystals; surfactants added to reduce surface tension/promote emulsification during

				processing.
Mayonnaise	O/W	Vegetable oil. Droplet size: 1 – 5 μm . Volume fractions: Minimum 65%	Aqueous solution of egg yolk, salt flavors, seasonings, ingredients, etc. (pH: 4.0 – 4.5)	Egg yolk proteins and phosphatides.
Salad dressing	O/W	Vegetable oil. Droplet size: 1 – 5 μm . Volume fractions: Minimum 30%	Aqueous solutions of egg yolk, sugar, salt, starch, flavors, seasonings, hydrocolloids, and acidifying ingredients. (pH: 3.5 – 4.0)	Egg yolk proteins and phosphatides combined with hydrocolloids and surfactants, where permitted by local food law.

For convenience of description, we may divide o/w food emulsions into three classes, depending on how they are to be used. The first class contains emulsions which are end products in themselves. Coffee creamers and cream liqueurs are relatively simple emulsions whose only requirement is to remain stable toward creaming and coalescence during their shelf-life (which, however, may have to be considerable, so that sterility is also important). These emulsions present less of a challenge to the processor than do more complex emulsions; there are a few basic rules of formulation which allow successful products to be created. The second class of emulsions contains those which can be used as ingredients that participate in forming the structures of more complex products; that is, other components of the food (proteins, polysaccharides) form a matrix in which the fat globules are trapped or with which they interact. Examples are yogurts, processed cheeses, and other gelled systems containing emulsion droplets which must interact with other components in the food, but are not destabilized in the process. Their effect is to alter the rheological properties of the gel, thus creating texture and mouth feel. In the third class of emulsion, the droplets are required to create new structures during processing, such as in ice cream or whipped products, where the emulsion is destabilized and further interacts as a means of creating structure in the product. Some emulsions themselves may also form gels during heating, to create new structures within foods. The requirements for the compositions and properties of the emulsion droplets are different in these different cases. However, it is generally necessary for the emulsion droplets to interact with themselves and/or with the other food components to give the required structures.

EMULSIFYING AGENTS

Emulsifying agents are soluble in fat and water to allow uniform dispersion of fat in water. Emulsifying agents are also called emulsifiers and present in the food like butter, mayonnaise and salad dressing. These have one hydrophilic and one lipophilic part. These agents surround the oil droplets in water and reduce the tension between the two liquids thus impart stability.

Classification of Emulsifying agents

These can be classified on the basis of chemical structure and mechanism of action. Under chemical structure category are synthetic, natural, auxiliary agents and finely dispersed solids. In the category of mechanism of action comes the monomolecular, multimolecular and solid particle films.

Natural emulsifying agents are derived from plant and animal tissues and mostly in the form of hydrated lipophilic colloids. These emulsifiers make the protective sheath around the droplets, give droplets a charge so that they repel each other and swell to step-up the viscosity of the liquid. Natural ones are derived from vegetables, animals, semi synthetic and synthetic agents. Although natural agents are inexpensive, safe and non toxic but these are slow in action. So large quantity of emulsifier is required for proper action. Also the natural emulsifiers need preservatives as these are subjected to microbial growth. The animal derivatives are stronger than the plant ones. The best example of this is lecithin and cholesterol. Some people are allergic to these so must be consumed after knowing the derivatives. Both semi-synthetic and synthetic emulsifying agents are strong and require no preservative as these are not prone to microbial growth.

Properties of emulsifying agents

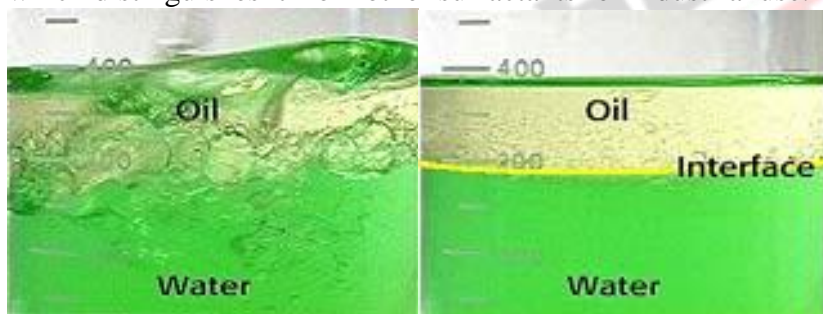
An emulsifier consists of water soluble hydrophilic parts and water-insoluble, oil-soluble lipophilic parts within its. When an emulsifier is added to a mixture of water and oil, the emulsifier is arranged on the interface, anchoring its hydrophilic part into water and its lipophilic part into oil.



On the interface surface of water and air and of oil and air, the hydrophilic part and the lipophilic part are adsorbed and arranged around the interface. The interfacial tension is reduced by the emulsifier. That is, the force to separate the oil and water is thus weakened, resulting in the easily mixing of oil and water. There are many important properties of emulsifiers which are applicable in many foods.

1. Surface Active Agent

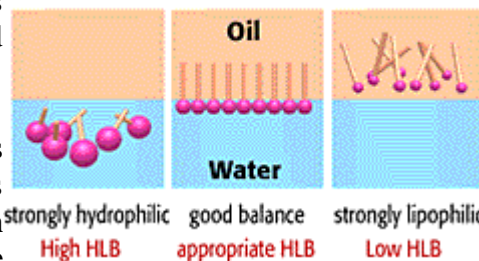
When a water droplet is in the air, surface tension, a force to reduce the surface area acts on the surface of the water, resulting in spherical water droplets. When water and oil are present in a container, they do not mix together even after stirring and separate into two layers. When two immiscible substances are in contact, the contact surface is called interface. Interfacial tension, a kind of surface tension acts on the interface so that the two substances separate from each other. As interfacial tension increases, the force to separate two substances becomes stronger. Surfactant weaken interfacial tension and changes the properties of an interface. Events almost impossible under ordinary conditions are made possible by these effects. Interface is not only present between water and oil, but also in the boundary among various immiscible substances, and as foods are generally composed of carbohydrates, protein, fats and oils, water and air, they include many interfaces. Surfactant for food is called food emulsifier which distinguishes it from other surfactants for industrial use.



2. HLB

The hydrophilicity and lipophilicity are different among emulsifiers, and the balance between the two is called HLB value. The value ranges from 0 to 20. An emulsifier with higher lipophilicity shows a lower HLB whereas higher hydrophilicity has high HLB, and the behaviors and functions to water depend on this HLB.

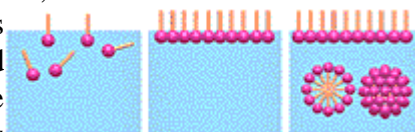
HLB and emulsifiers in water/oil



All compounds that have hydrophilic parts and lipophilic parts are not always useable as an emulsifier. when hydrophilicity is too great, such compounds disperse into water and the ones with great lipophilicity would disperse into oil. When the hydrophilicity and lipophilicity are well-balanced, the emulsifier exhibits sufficient effects.

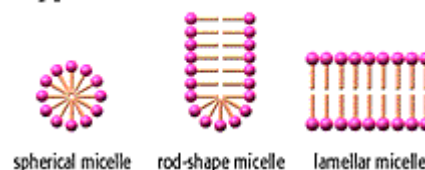
3. Micelle

Because an emulsifier has opposite properties; hydrophilic and lipophilic, its solution does not become a simple aqueous solution but a colloidal solution, of which properties greatly vary depending on its concentration. In an extremely-diluted solution, there is no special change, but the emulsifier gathers on the interface and the surface tension is reduced as an increase of its concentration.



As further increase of the concentration, a uniform mono molecular layer is made on the surface and the surface tension drops to the minimum. A further increase of the concentration causes micelle formation, micelles formation occurs when the excess molecules, in which the lipophilic groups are positioned face to face gather and there is no change in the surface tension. The concentration to start micelle formation is called critical micelle concentration (cmc) and the properties of the solution change greatly with a change of this concentration. Similar changes appears on the interface of oil and water , when the interfacial tension reaches the cmc point. When the concentration exceeds cmc, spherical micelles appear at first and disperse into water. A further increase in the concentration causes rod-shape micelles. Finally, lamellar micelles with higher structures called liquid crystal are produced.

Types of micelle

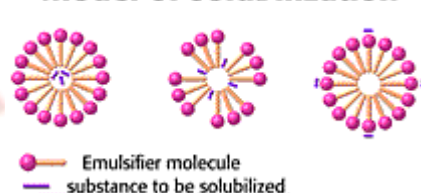


4. Solubilization

When a small amount of insoluble substance is incorporated in an emulsifier micelle, semi-transparent solution is produced. This phenomenon is called solubilization.

Solid monoglyceride has a large capacity of crystallization which affects its performance. It also makes a liquid crystal which has intermediate characteristics between solid crystal and liquid. The form varies with the kind of emulsifier, temperature and its concentration. In practical use, it is-necessary to select a suitable emulsifier with consideration to conditions, including temperature and food constituents.

Model of solubilization



Functions of Emulsifying Agents

The use of food emulsifier began with the production of margarine as monoglyceride and lecithin. These compounds were commonly called emulsifiers. After that quite different functions were found and emulsifiers have since been used in starchy foods such as breads, and dairy products like ice cream. Nowadays, emulsifiers are also used in Japanese-foods like Tofu and minced fish products.

Generally speaking, an emulsifier is as a compound with emulsifying effects, however, actually it has various functions. For example: To modify oil crystal and prevent water spattering in cooking. In ice cream, an emulsifier does not promote emulsification, but rather destroys emulsion to stabilize foam and to make a product with smooth texture and shape keeping property. In bread, an emulsifier reacts with proteins to make a smooth easy-rising dough with no relation to emulsification. It also acts on starch to make bread soft.

Functions of emulsifiers		application examples	
Surface active ability	Emulsification	W/O	margarine, butter, butter cream
		O/W	ice cream, cream, milk drink
	Dispersion	chocolate, cocoa, peanut butter	
	Foaming	cake, desserts	
	Anti-foaming	tofu, fermentation industry, jam	
Wetting	powdered foods, chewing gum		

	Solubilization	flavors
	Cleaning	cleaning agent for food industry
starch complex forming ability	protection of starch granule	instant mashed potato
	Anti staling	bread, cakes
	Prevention of sticking	spaghetti, noodles, rice
	Prevention of gelatinization	flour paste, desserts
Modifying ability for oils and fats	Crystal modification	margarine, shortening, chocolate
	Creaming ability	margarine, shortening
	water-holding ability	margarine, shortening
	others	coating agent, lubricant agent
Protein modifying ability	Gluten modification	dough conditioner
	Others	tofu, frozen surimi
Others	Antibacterial and anti-fungal	
	plasticizing	
	anti-oxidation	

1. Emulsification

Oil and water produce emulsion by stirring, however, the emulsion starts to break down immediately after stirring is stopped. The aim of emulsification is to stabilize emulsion by preventing break down. The break down of emulsion occurs due to creaming, aggregation and coalescence. To solve this, several measures have been taken, to decrease the size of dispersed particles, to reduce the density difference of dispersion and to protect the surface of oil droplets. There are two types of emulsion, O/W emulsion or oil droplets in water, which can be found in ice cream and or milk, and W/O emulsion or water droplets in oil, found in butter and margarine. Recently, developments of W/O/W type emulsion or water dispersed within oil droplets of O/W type emulsion and O/W/O type, an opposite type emulsion have been progressing. These multiple type emulsions not only make low calorie items such as cream which contain less oil, but also stabilize the emulsion by dissolving the unstable substance present in the deepest region of water droplets. Taste can also be enhanced by injecting seasonings and flavors into the water droplets.

2. Dispersion



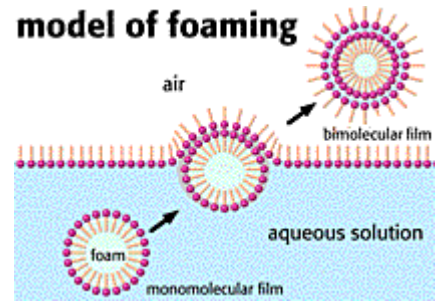
Water-insoluble fine powder like cocoa is difficult to disperse as small lumps tends form on the surface interface. Powders gradually aggregate and precipitate even if dispersed by shaking. Maintaining suspension of such water insoluble fine powder is called dispersion. When the dispersing material is liquid, we call it emulsion. Cocoa drinks are produced by dispersing cocoa powder in water, and chocolate is made by dispersing it in oil. Emulsifier adsorbed on the surface of insoluble fine powder changes the particle surface to be

hydrophilic or lipophilic. The results of which produce stable water or fats and oils at the outer layer and stabilize suspension, by increasing the affinity to water or oil in the outer phase.

3. Foaming

Foaming ability is one of the major characteristics of emulsifiers. When a solution containing an emulsifier is stirred, the emulsifier is adsorbed on the surface of the produced foam to make a monomolecular layer and the foam outside of the solution makes a bimolecular layer of the emulsifier.

The film surrounding a soap bubble is about 100 times thicker than a bimolecular layer, but a bubble breaks as soon as the migration of the liquid trapped between bimolecular films occurs. Foaming ability and stability, are important factors in the effects of an emulsifier. The foaming effects are utilized for the production of such items as cream. The addition of an emulsifier enables forming ability and stabilization action. Thus, smooth texture can be obtained as well as expanded volume. Typical cases of use are cakes, ice cream, moose, whipped topping, etc.



4. Defoaming

Emulsifier also has foam extinguishers, one is called anti-foaming and the other de-foaming. During food production, foaming may occur in the presence of protein, starch, etc. and an emulsifier with foam extinguishing action is used. Foam extinguishers have the following properties;

- water insoluble
- floatable on the surface because of its small specific gravity
- small surface tension and easy spreading on liquid surface

These properties easily lower the surface tension and so, the foam becomes thinner. As these agents spread easily on the liquid surface, all foam can be diminished. These are used in the productions of tofu, jam, and sugar as well as in the fermentation industry.

5. Wetting

Wetting effects of emulsifier moisten the solid surfaces. Solid material is mixed with an emulsifier or its surface is spread with it, the surface then becomes hydrophilic. For example, chewing gum is apt to stick to teeth. Adhesion to natural teeth does not occur easily because the enamel is hydrophilic and always wet, whereas the adhesion to artificial teeth, occurs easily. We can prevent adhesion by wetting the surface of chewing gum by adding emulsifier.

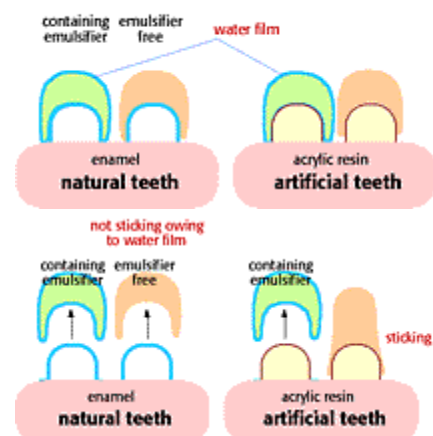
6. Bacteriostatic effects

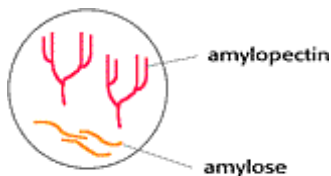
Monoglycerides, polyglycerol esters of low molecular fatty acid have specific bacteriostatic effects, which can be used as a bacteriostatic agent. It is used in hot vendor drinks, flour paste, etc.

7. Action on starch

Fresh bread is soft, elastic hardens over time. Starch particles consist of spherical shaped amylopectin and amylose. Raw starch called beta-starch is insoluble in water.

Anti sticking effect on Gum





β -starch

But when heated to a certain temperature, the starch absorbs water and change into the crystalline form of alpha-starch. Amylose gets hard easily with cooling and amylopectin becomes hard gradually with time. The immediate hardening of bread by cooling is mainly due to the change of amylose.

Baking

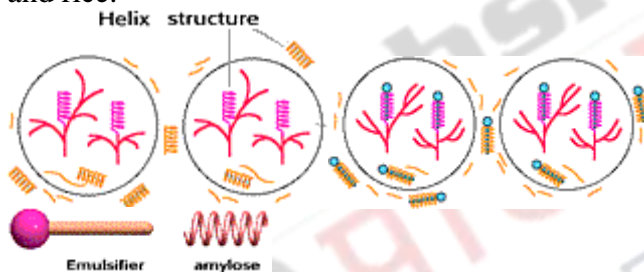
Cooling



α -starch

β -starch

Amylose changes to a helix structure, a kind of spiral structure by heating. If monoglycerides are introduced, they can be anchored into the helix structure. Since the anchoring does not change even after cooling, softness is maintained. This function is also utilized for instant mashed potatoes, noodles and rice.



8. Action on protein

Wheat flour contains protein called gluten which takes the shape of a mesh-like structured when mixed with water. This wheat flour & water based dough is filled with carbon dioxide produced by fermentation and steam generated during baking, which produces raised bread. When the gluten content is small, the dough rises little. An emulsifier modifies gluten molecules and enhances its film-forming power resulting in good spreadability and improvement of working efficiency. Thus, easy-rising bread can be obtained.

9. Action on oils and fats

When fats and oils form into crystal, an emulsifier promotes and inhibits the growth preventing the formation of abnormally crystal. This function is utilized for margarine, shortening and chocolate.

Conclusion

The object of making food emulsions is to provide a stable and controllable source of food, whose texture, taste, and nutritional and storage properties are acceptable to the consumer. Although the number of possible ingredients is limited by the constraints of healthy nutrition, it is nevertheless evident that within the available range, there is a great deal of opportunity for variation in the properties of the emulsions—for instance, the particle size and the composition of the stabilizing layer of the interface, which, in turn, influence the stability and functional behavior of the emulsion. On the

other hand, many emulsions used in foods have their roots in established formulations, and an understanding of why certain emulsions behave as they do is still not established in a number of cases.

