Book Chapter

The Colloidal State and the Micro-Science in the Beverage Industry: Emulsions, Foams, and Suspensions

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Abstract

Nowadays, the consumers ask for more than a drink, and in the market, it can be found a huge variety of beverages, where colloidal science is used for controlling flavor, color, presence of technological or nutritional value compounds, nutraceutical/bioactive compounds and, also, the beverage turbidity. Emulsions, foams, and suspensions are the basis of an extensive variety of use in the beverage industry. Beverage's emulsions are considerably diluted, contain little amounts of a dispersed oil phase in the finished product, and must remain physically stable for a long period of time. A beverage foam is a colloidal dispersion in which a gas is dispersed in a continuous liquid phase and foams are different from emulsions because it is the dispersion medium that has colloidal dimensions. Suspension drinks are dispersions of an insoluble substance (like lemon juice and pulp) in an aqueous or non-aqueous continuous phase. This chapter intends to make an overview of the modern advances in beverage-emulsions technology. Some examples are given, within the huge world of the beverages industry, from cream liqueurs, soft drinks, functional beverages to bottled water, fruit drinks, sparkling wine, and beer.

Keywords

Colloids; Cream Liqueurs; Soft Drinks; Milk-Coffee Beverages; Functional Beverages; Bottled Water; Fruit Drinks; Sparkling Wine; Beer.

Introduction

Colloidal systems appear nowadays in a wide variety of products including the food and beverage products, such as suspensions, foams, and emulsions [1-3]. Foams and emulsions are extensively used in food and beverage, for example, beer contains an edible foam, as also a chocolate mousse. Beverage emulsions are very dilute (20 mg/L of a dispersed oil phase in the finished product) and can remain physically stable for long periods (4 to 12 months) [4]. However, it is not always easy to keep the internal phase uniformly distributed during storage until consumption. This problem has led the food industry and the academicals community to investigate the ability of hydrocolloids and proteins to stabilize emulsions and foams against flocculation, coalescence, creaming, drainage, and coarsening, the phenomenon’s that can occur depending on their intended application [5]. Polysaccharides and proteins are natural macromolecules that are widely used as functional ingredients for various food colloids or emulsion formulations. They are essential for food colloid formulation mainly due to their ability to change product shelf life by changing food texture [6].

The use of a food emulsifier was first applied by the French chemist Hippolyte Mège-Mouriès aiming to produce Margarine, intended to be a substitute for butter, made by emulsifying milk with lipids [7]. This technique was soon employed by the beverage industry. For instance, in beverages, citrus flavor (essential oils extracted from the orange or lemon peel) is one of the most popular flavors used and could be found in soft drinks formulations. Due to its oily properties (insoluble in water), the beverages made with this flavor compound are diluted oil/water (O/W) emulsions.

Due to their intended use, food colloids need to be non-toxic, non-carcinogenic, and non-allergenic. Innovative ingredients and solutions are emerging to help formulators add flavors, colors, and healthy ingredients and keep up with consumer demands for innovative beverages [7,8].

The Colloidal State

Colloids are all around us: milk, butter, margarine, fruit jams, mayonnaise, creams, ice cream, and soft drinks. The word "Colloid" (Greek: kola – glue, as some of the original organic colloidal solutions were glues) has been used since 1862 to classify all the liquids that are colloidal dispersions. Indeed, Thomas Graham, in 1961, recognized two different classes of substances, defining them as Crystalloid: all substances that pass easily through animal and plant membranes; and Colloids: as substances that diffuse very slowly and cannot pass through membranes [9].

Fifty years later the colloidal state was described by Wolfgang Ostwald as a “world of neglected dimensions”, a reference to the world of systems in which the particles are extremely small [10]. So, a suspension of tiny particles in a continuous phase, the dispersion medium, is called a colloidal dispersion. The suspended particles are single large molecules or aggregates of molecules or ions ranging in size from 1 to 1000 nm [11]. Because a colloidal solution or substance is made up of scattered particles, light cannot pass straight through. This effect was observed and described by John Tyndall as the Tyndall Effect. This effect could be observed daily, for example when a light beam enters a room through the window and dust particles dispersed in the air, or when the light from car headlights passes through the water droplets of the fog [12]. The Tyndall effect is an easy way of determining whether a mixture is colloidal or not (Figure 1).

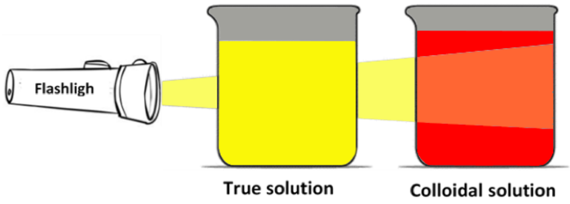

Figure 1: Tyndall effect. When light is shined through a true solution, the light passes cleanly through the solution, however, when the light is passed through a colloidal solution, the substance in the dispersed phases scatters the light in all directions, making it readily seen. (Adaped from Petrucci et al. [11]).

The Tyndall effect is one property of colloid systems that distinguish them from true solutions. Due to colloidal particles being so small, their motion changes continually because of a random collision with the molecules of the dispersion medium. This random, zig-zagging movement is called Brownian movement and was first discovered by Robert Brown, a botanist, in 1827, while studying the fertilization process of a newly discovered species, *Clarkia pulchella*, he noticed a "rapid oscillatory movement" of microscopic particles contained in the pollen grains suspended in the water. Initially Brown believed that this movement was a vital activity peculiar to male sex cells in plants, but later he observed that pollen from dead plants long ago showed the same movement [13]. Brownian movement is a phenomenon whereby small particles suspended in a liquid tend to move in pseudo-random paths through the liquid, even if the liquid has laminar movement. Brownian movement in colloidal sol arises due to the impact of the molecules of the dispersion medium with the colloidal particles. It has been postulated that the impact of the molecules of the dispersion medium on the colloidal particles is unequal [14] leading to the zigzag (random) movement of the colloidal particles, mathematically studied by Smoluchowski [15]. This movement helps to keep the particles in suspension, which is another property of the colloidal systems. Absorption is another colloidal characteristic since the finely divided colloidal particles have a large surface area. However, the presence of colloidal particles has little effect on the colligative properties (boiling point, freezing point, etc.) of a solution [16].

Classification of Colloidal Systems

The components of a colloidal dispersion are classified according to their relative amounts [10]. The particles in a colloidal dispersion are sufficiently large for definite surfaces of separation to exist between the particles and the medium in which they are dispersed. Simple colloidal dispersions are, therefore, two-phase systems. The phases are distinguished by the terms dispersed phase when the phase forming the particles are present in a relatively minor amount, and a dispersion medium for the medium in which the particles are distributed [17]. In a colloidal dispersion, either the dispersed phase or the dispersion medium can be in the gas, liquid, solid, or supercritical phase states [3]. Colloids are characterized according to the states of the dispersed phase and the dispersing medium [18]. Within this definition in addition to particles, droplets, and bubbles, thin films on large surfaces, such as the antiglare coating on glass, and thin liquid films such as foam films, which separate two vapor phases, emulsion films, used to separate two droplets, suspension films that separate two solid surfaces and wetting films that can separate a solid or liquid from vapor are also included [3]. Table 1 summarizes various types of colloidal systems.

Table 1: Types of colloidal systems. Adapted from Zumdahl and Zumdahl [18]; Moreno and Peinado [19].

Dispersing medium	Dispersed phase	Name	Examples
Gas Gas	Liquid Solid	Aerosol	Fog, sprays, clouds, mists Smoke, dust, airborne bacteria
Liquid	Gas	Foam	Whipped cream, soap suds, foam on beer, bubbles in sparkling
Liquid	Liquid	Emulsion	Milk, mayonnaise, vinaigrette
Liquid	Solid	Sol	Paint, ink, the starch in water, clays
Solid	Gas	Solid foam	Marshmallow, pumice, meringue, ice cream, bread, sponge cake
Solid	Liquid	Solid emulsion	Butter, cheese, gels
Solid	Solid	Solid sol	Pearl, opals, ruby glass

Although there are different types of colloidal dispersion sols and the emulsions are the most important according to Shaw [17]. The term sol or hydrosol (when the dispersion medium is aqueous) was used for distinguishing colloidal suspensions from macroscopic suspensions.

Colloids can be broadly classified as lyophobic or more specifically, in aqueous systems, hydrophobic and as lyophilic or hydrophilic [10]. However, according to Shaw [17], this description is not correct, because if there is no affinity between the particles and the dispersion medium no dispersion would be formed. Besides, in a lyophilic colloidal system, lyophobic regions are often present, for example in proteins which may be partly hydrophobic (hydrocarbon regions) and partly hydrophilic (peptide linkages, and amino and carboxyl groups).

Surfactant molecules, because of their affinity for water and oil and their consequent tendency to associate into micelles, form hydrophilic colloidal dispersions in water. Proteins, gums, gelatin, starch, and certain polymers (rubber) in organic solvents also form lyophilic colloidal systems [3]. So, while lyophilic dispersions (such as phospholipid vesicles and micelles) are inherently stable, lyophobic colloidal dispersions tend to coalesce because they are thermodynamically unstable as a result of their high surface energy in their native state [10].

Classification of Emulsions, Foams, and Suspensions

Emulsions

Emulsion products being familiar to our daily. Figure 2 shows some examples of drinks for ordinary consumption. Emulsions are colloidal dispersions in which a liquid is dispersed in a continuous liquid phase of different compositions [3,10]. The dispersed phase is sometimes referred to as the internal (disperse) phase and the continuous phase as the external phase [3]. The internal phase is determined by which component has higher surface tension [20].

Figure 2: Examples of beverage emulsions (O/W) - Oil and water are immiscible, but with the addition of stabilizing agents, an emulsion, can be achieved.

Several classes of emulsions may be distinguished (Figure 3): Oil-in-water (O/W), for oil droplets dispersed in water [3]; Water-in-oil (W/O), for water droplets dispersed in oil [3] and, Water-in-water (W/W), for two immiscible aqueous phases that are in thermodynamic equilibrium [21-23].

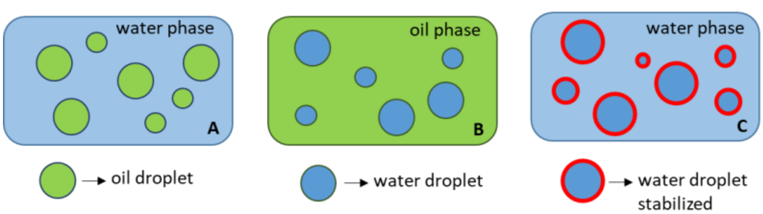

Figure 3: Types of emulsions. A|oil-in-water (O/W), B|water-in-oil (W/O), C|water-in-water (W/W) stabilized by particles, (not to scale).

The water-in-water (W/W) emulsions are remarkably interesting colloidal dispersions much less known than conventional oil-in-water (O/W) or water-in-oil (W/O) emulsions, even though phase separation in aqueous mixtures is highly common. This kind of emulsions could result from mixtures of hydrophilic polymers [21]. Dilution tests may be carried out to find out whether an emulsion is oil-in-water or water-in-oil. These consist of microscopic observation of a slide where a small amount of either oil or water is added to the emulsion sample [22]. It is also possible to formulate emulsions without water. Non-aqueous or anhydrous emulsions could be formulated as O_1/O_2 systems or oil in a polar solvent emulsion, as well as multiple oil-in-oil-in-oil systems or variants [10].

Most emulsions are not thermodynamically stable, they tend to separate into "oil" and "water" phases. Therefore, an emulsifying agent is usually required to form a stable emulsion [3,20].

Most meta-stable emulsions that will be encountered in practice contain oil, water, and an emulsifying agent (or stabilizing agents) which is usually a surfactant, a macromolecule, or finely divided solids. The emulsifying agent, or protective colloid, are surface-active, meaning that it reduces the surface tension of the liquid, and so tends to concentrate on boundary films [20]. Food emulsion needs stability against coalescence and stability against creaming.

Foams

Foams (Figure 4) are a colloidal dispersion in which small bubbles of gas are dispersed in a continuous liquid phase [3]. Foams are somewhat different from emulsions because, in foams, it is the dispersion medium which has colloidal dimensions [17]. However, some food emulsions, such as ice cream are also foams. There exists a wide range of food foams, including both solid and liquid foams.

Figure 4: Examples of foam suspension beverages.

Even though the bubbles in persistent foams are polyhedral and not spherical, it is nevertheless convenient to refer to the “diameter” of gas bubbles in foams as if they were spherical. Foam bubbles usually have diameters greater than 10 μm and may be larger than 1000 μm [3]. According to Calvert [20], in liquid foam, a colloidal adsorptive agent forms a film that bounds the gas bubbles. The colloidal dimension in the foam is the thickness of the film, not the size of the bubble. The bubble is lighter than its surroundings and will rise to the top, where it joins the foam. When carbon dioxide is released, it uses the adsorptive agent to make the foam. Meringue is a solid foam using egg albumin. Marshmallows use sugared gelatin for the same purpose. Bread, dispersions of gas in a solid, is a solid foam as well, the protein gluten makes the film that surrounds the dioxide carbon bubbles produced by the enzyme zymase secreted by the yeast [20]. The air content in food foams ranged also from 10% in a milkshake, about 50% in whipped cream, 70-80% in the risen dough and 90% in meringues, and over 90% in popcorn and rice cakes.

On the food industry foams are frequently prepared using aerator machines, gas is whipped into the liquid in batch systems a mixing head whips the gas into the liquid under pressure in continuous systems

Foams can also contain dispersed oil droplets and/or solid particles. Foam can also contain an emulsion in its liquid phase, such as whipped cream this is a foam emulsion because it consists of air bubbles dispersed in an emulsion, the cream. Foam emulsions can also be called aerated emulsions [3].

Foam stability is not necessarily a function of drop size, although there may be an optimum size for an individual foam type [3]. The stability of foam depends upon two principal factors: the tendency for liquid films to drain and become thinner, and their tendency to rupture because of random disturbances. Other factors which may significantly influence foam stability include evaporation and gas diffusion through the liquid films. All foams are unstable in the thermodynamic sense. However *unstable* and *metastable* foam structures are different. *Unstable* foams are formed from aqueous solutions of fatty acids or short-chain alcohols which delay drainage and rupture of the film, not preventing such processes from occurring continuously until the foam disappears. The *metastable* foams are formed from solutions of proteins, etc. The balance of forces is such that the drainage of the liquid stops when a certain thickness of the film is reached, and in the absence of disturbing influences (such as vibration, draughts, evaporation, diffusion of gas from small bubbles too large bubbles, heat, temperature gradients, dust, and other impurities), these foams would persist almost indefinitely [17].

Food foams can be stabilized by the natural surfactants present, such as proteins like casein or egg white albumin. The surface viscoelastic properties of proteins can increase foam stability.

Suspensions

A suspension is a colloidal dispersion in which a solid is dispersed in a continuous liquid phase [3]. On the other hand, Florence and Attwood [10] define suspensions as being dispersions of an insoluble substance in an aqueous or non-aqueous continuous phase.

Daily, the suspensions used consists mostly of solid particles in liquids (Figure 5). However, there are several examples of suspensions formed from two liquids or even from a solid or liquid in a gas.

Thus, suspensions may be either aqueous or non-aqueous. The particles in suspensions are greater than 1000 nm, according to Schramm [3] usually have diameters greater than 0.2 µm, a spherical shape, and may be visible to the naked eye or under a microscope.

If a suspension contains, in addition to solid particles and a continuous liquid phase, emulsified droplets and/or gas bubbles, two situations may occur:

- If the solid particles are adsorbed on the emulsion droplets, then it is an emulsion that also contains solids.
- If the particles and droplets are not mutually associated, then the system is at once a suspension and an emulsion.

In these situations, the term used should be the one that best fits the context. Frequently one or the other is the primary dispersion while the other phase is an additive or a contaminant [3].

Figure 5: Examples of suspension beverages.

Recent Developments in Beverage Emulsions
Cream Liqueurs

Alcoholic emulsion creams, or cream liqueurs (food oil-in-water emulsions containing ethyl alcohol), are sweet semi-liquid alcoholic drinks that contain over 400 g/L of total extract and often 17% (v/v) in alcohol or higher than 25% (v/v), produced with a wide range of spirit bases [24]. Most products contain several other added ingredients which may include sugar, full-fat milk powder, non-fat milk solids, flavorings, colorings, preservatives, and a thickening agent such as sodium caseinate, which also acts as a stabilizing agent to prevent the cream and alcohol from separating [3].

Cream liqueurs are beverage emulsions where very small droplet sizes are needed to form the emulsion, so, a coarse emulsion is usually passed through a high-pressure homogenizer [3]; which can produce small droplets (≈2 μm in diameter). Controlling the droplet size within an acceptable range is key to produce emulsion-based products with desired properties such as texture, appearance, and stability. High shear rates and high flow are needed for emulsification into small droplets and for good heat transfer or blending, respectively [3,25].

Factors controlling the emulsion stability of cream liqueurs with high alcohol contents have been studied by several authors, since the properties, such as viscosity, surface tension, and density, for example, vary considerably with the addition of ethanol and, as a result, they have a significant impact on the preparation and stability of emulsions [26], so it is important to determine how these properties are affected by the presence of ethanol. Banks and Muir [27] found that, as the alcohol content of the cream liqueur increases, the emulsion becomes increasingly sensitive to the interaction between compositional parameters and processing conditions. The difficulties contributed by the alcohol content include making the aqueous phase a poorer solvent for proteins [3]. Banks and Muir [27] also found that the alcohol content of the liquid phase, rather than the total alcohol content, determines stability. However, as referred by Given [4], alcohol above 5% (v/v) is generally destructive to beverage flavor emulsions, especially for alcoholic beverages that need a hydrophobic flavor dispersion. By employing a polyglycerol fatty acid ester composed of at least 70% palmitic acid in conjunction with an anionic emulsifier, a stable acidified beverage containing a flavor emulsion and alcohol was achieved by the same author. Nonetheless, these problems have long been studied. For instance, the effect of adding low-molecular-weight surfactants, commercial glycerol monostearate, or sodium stearyl lactylate, on the stability of simulated cream liqueurs was investigated by Dickinson et al. [28]. The presence of 0.4–0.5% (w/v) of glycerol monostearate or sodium stearyl lactylate led to a substantial reduction in creaming at room temperature as well as a longer shelf-life at 45 °C. Improved stability concerning creaminess appeared to be associated with a change in emulsion rheological properties, probably arising from complex formation between low-molecular-weight emulsifier and caseinate, both in bulk aqueous solution and at the surface of the fat droplets [28].

Soft Drinks

Soft drinks are one of the most widely consumed beverages in the world. The ready-to-drink soft drinks are divided into carbonated and non-carbonated soft drinks. The non-carbonated drink has shown considerable growth because of aseptic packing, whereas carbonates beverages have an antimicrobial effect related to the presence of carbon dioxide. To give the natural appearance of fresh juice, artificial clouding agents are added to fruit-flavored beverages containing either low amounts of juice or highly processed and clarified juice. The turbidity is usually determined by spectrophotometry or nephelometry (in Nephelometric Turbidity Units, NTU). The desired level of turbidity depends on the product application: Carbonated soft drinks present lower turbidity (100–250 NTU), while juice-containing beverages are considerably more turbid (900–1500 NTU) [29]. A cloud gives turbidity, flavor, aroma, mouthfeel, and optionally color is typically added in concentrations of 0.01–0.2 wt % of the final product [30]. So, soft-drink beverages contain hydrophobic components, such as clouding agents, weighting agents, nutraceuticals, oil-soluble vitamins, and oil-soluble antimicrobials. Clouds are concentrated oil-in-water emulsions in which the turbidity results from the scattering of light by dispersed oil droplets with oil droplet size between 0.5 and 5µm [31]. Cloud composition is usually stabilized by amphiphilic polysaccharides, such as Arabic gum or hydrophobically modified starch, the oil phase consists frequently of vegetable oil, flavor oil, and a weighting agent [32]. The weighting agents increased the density of the oil phase and consequently contribute to the stabilization of the emulsion through the minimization of the difference in density between the different phases. A soft drink typically contains a sweetener and a flavoring. The sweetener may be fruit juice, sugar, high-fructose corn syrup, and sugar substitutes in the case of diet drinks. These drinks may also contain caffeine, colorings, preservatives, and other ingredients [33].

The consumption of sugar-sweetened beverages (SSBs) is associated with obesity [34], type 2 diabetes [35], dental caries, and low nutrient levels. It could also be associated with many weight-related diseases, including diabetes, metabolic syndrome and cardiovascular risk factors, and elevated blood pressure [36]. According to Sen [33], experimental studies support a causal role for sugar-sweetened soft drinks in these illnesses. "Sugar-sweetened" includes drinks that use high-fructose corn syrup, as well as those using sucrose.

Carbonated Soft Drinks

Carbonated drinks are made by injecting carbon dioxide into the drink at a pressure of several atmospheres. At high pressure, a high volume of gas could be dissolved into the beverage. As the pressure is released, carbon dioxide comes out of the solution forming numerous bubbles. The carbonated drinks containing flavorings, sweeteners, and other ingredients. Carbonated soft drinks are frequently prepared by diluting and carbonating "bottler's" soft drink syrups, which are O/W emulsions of flavoring oils (about 10%, v/v) in aqueous solutions of sugars, coloring, and preservatives [37]. They come in many forms, including regular, low-calorie, no-calorie, caffeinated and caffeine-free drinks [33].

Some flavors, like citrus oils, are prepared by formulation into an O/W emulsion [38], which must be stable to survive shipping and storage before bottling. Moreover, after purchasing by consumers, they must also be stable after dilution and storage. The emulsifying agents used are of low molar-mass when preparing these formulations, such as polysaccharides [37]. One important visual characteristic of fruit juices is their turbidity due to suspended fragments of cell walls. Turbidity has become a product requirement by consumers. When the juices are not naturally turbid, during their formulation, suspended particles, or even emulsion droplets, can be introduced to visually simulate the natural juice's turbidity.

Low-Calorie and Mid-Calorie Soft Drinks

Low or zero-calorie products are the beverages preferred by consumers since overconsumption of sugary drinks is associated with obesity, consumers tend to prefer low or zero-calorie products [39]. Low or zero-calorie drinks are not completely appreciated by consumers, due to their unpleasant taste. To overcome this issue the beverage industry has developed mid-calorie soft drinks by blending sugars (sucrose or high-fructose corn syrup) with high-potency sweeteners (acesulfame-potassium, aspartame, and sucralose). The number of calories is reduced, and the desired flavor profile of the drinks is maintained. Moreover, the tax may be imposed on sweetened beverages to discourage consumption of added sugar [40].

Milk-Coffee and Rich-Milk-Coffee Beverages

Milk coffee beverages contain about 1% milkfat, forming an oil-in-water emulsion. Milk coffee beverages are a protein-stabilized emulsion and consist of dispersed oil droplets in the aqueous phase. Casein, whey proteins, and mono- and diglycerides (MDGs) are surface-active agents that adsorb at the oil-water interface to form and stabilize emulsions. Protein is an important natural emulsifying agent in emulsion systems and interacts with MDGs at the oil-water interface to modify oil droplet size, zeta potential, flow behavior, physical stability, and oxidative stability. To emphasize the coffee flavor, many milk coffee beverages contain coffee extracts; these are the so-called ‘‘rich milk coffee’’ beverages. When the content of the coffee extracts increases, milk coffee beverages become unstable and since the storage period for these milk coffee beverages is 6 to 12 months, the milk fat gradually floats towards the air–emulsion interface. Aggregation or flocculation [41,42] follows, and a milk ring is formed at the air–emulsion interface. The milk ring formation, or “oiling off”, is accelerated in these drinks. Moreover, the average drop size distribution of the combined emulsifier system containing protein (in this case, milk proteins) increases because the protein induces an attractive depletion interaction between droplets, thereby inducing flocculation and coalescence [43]. This situation is aggravated by the fact that the plastic bottle is transparent: consumers can see that the milk fat has separated, so the product value depreciates. When flocculation happens, even if the milk coffee beverage is repeatedly shaken, the milk ring will not re-disperse, and some lumps of the milk fat will float on the surface. As explained by Ogawa and Cho [44], if the milk fat sticks to the can or plastic bottle, consumers will get the impression that these beverages are of low quality and will no longer purchase them. The authors Dickinson and Lorient [41] found that excessive roasted coffee beans will make the milk coffee unstable. The addition of emulsifiers like polyglycerol esters with long hydrophilic moieties are effective for ensuring emulsion's stability.

Beverage Concentrates

Beverage concentrates are products that are sold in liquid or powdered form, which consumers dilute with water before consumption. These formulations may contain ingredients such as flavors, sweeteners, color additives, or others, which all together form a drinkable beverage after dilution. According to Klein et al. [45], beverage concentrates, also known as “cloudy emulsions”, are usually prepared as concentrates and are diluted at a later stage to the final product. As consumers expected in these products the appearance of the juice of the named fruits, that are often opalescent, it will be necessary to add clouding agents to the fruit-flavored beverages to achieve a visual appearance similar to fresh juice, as cloud loss is considered a quality defect by the consumers. In natural fruit juices, the turbidity is caused by suspended proteins and pectins [46]. Most of the clouding agents are oil-in-water emulsions. They must also be stabilized by emulsifiers and/or amphiphilic polysaccharides such as whey protein isolate and Arabic gums which, in aqueous solution, interact via electrostatic force and improve the emulsion stability [45,47].

Functional Beverages

According to Gibson and Williams [48], functional foods are those foods or food components that are scientifically recognized as having physiological benefits beyond those of basic nutrition. Functional foods are also called nutraceuticals. This beverage category includes isotonic (beverages that rehydrate), lifestyle/wellness drinks, meal replacements, and medicinal teas. Nowadays, there is an increasing consumer demand for products beneficial to health and human wellness [47]. There is a high demand to fortify many beverage products with ingredients that are perceived by the consumers as giving added health benefits, such as vitamins, proteins, antioxidants, minerals, dietary fibers, and ω-3 fatty acids [47].

Dairy-based Beverages

In the case of functional dairy beverages, they can be categorized into two basic groups: (i) fortified dairy beverages (including probiotics, prebiotics/fibers, polyphenols, peptides, sterol/stanols, minerals, vitamins, and fish oil), and (ii) whey based beverages (both fruit juice type and dairy type).

Fresh milk, fermented milk, and yogurt drinks are the most common dairy-based beverages. They are vehicles for probiotics (main bioactive compounds of fermented functional dairy foods) [49]. According to FAO [50], probiotic is defined as live microorganisms which when administered in adequate amounts confer a health benefit to the host. There are several benefits related to the ingestion of probiotics, such as the alleviation of lactose-intolerance symptoms, treatment of diarrhea. Therefore, the consumption of probiotic bacteria via food products is an ideal way to re-establish the balance of intestinal microbiota

[51]. In children, they enhance the immune response and can be used to treat atopic dermatitis symptoms, alleviation of symptoms of inflammable bowel disease, and irritable bowel syndrome, among others [52]. Most dairy industries now add probiotic bacteria (*Lactobacillus* spp. and *Bifidobacterium* spp.) to some of their products [53].

There are also non-probiotic dairy beverages with bioactive/nutraceutical components that can be added such as ω-3 fatty acids (α-linoleic acid, eicosapentaenoic acid, and docosahexaenoic acid) [54]; plant sterols like phytosterols and phytosterols that, when added to foods, reduce the absorption of all sterols from the digestive tract, leading to the decrease of cholesterol levels in the blood [54,55]; proteins, like casein fractions, that may act as a precursor of biologically active peptides with different physiological effects [56]; conjugated linoleic acid that has been demonstrated to have anti-oxidative and anticancer effects and melatonin, a naturally occurring hormone, that controls the body's day-and-night rhythm and is effective for insomnia [54].

There are also functional dairy beverages with added minerals and vitamins. Some dairy and milk industries add vitamins and minerals, to compensate for vitamin and mineral losses during milk processing; added minerals typically include calcium, magnesium, and iron [54].
To promote the growth of favorable bacteria it is also often added to fermented milk prebiotics, including fructo-oligosaccharides, inulin, and galacto-oligosaccharides [57], while studies of other prebiotics such as oligofructose and polydextrose have also yielded positive results [58].

Milk-like Beverages

The probiotics market is currently dominated by fermented dairy products. However, there is a trend of increasing demand for probiotic vegetable products due to negative aspects of dairy consumption [56]. Lactose intolerance, allergy to milk proteins (casein), and cholesterol content are major disadvantages related to functional dairy products [56,59]. Therefore, the development of alternative solutions to dairy-based probiotic products and preference for non-dairy based probiotic products have been launched in the market, particularly, beverages based on fruits and/or vegetable juices, cereals, and soybeans [51]. Soybeans and “soybean-milk” are an interesting alternative due to some important characteristics. They are rich in fibers, vitamin K, riboflavin, thiamine, folic acid, minerals like magnesium and phosphorus, isoflavones, and other flavonoids, which present a strong antioxidant potential [60]. Some cereals could also be fermentable substrates for the growth of probiotic microorganisms [61] acting as vehicles for functional compounds [62]. Such as fermented oat beverages that are referred to as functional because of the symbiotic effect of probiotic starter cultures and the prebiotic fiber β–glucan [63].

Finally, fruit juices made with cranberry, blueberry, pomegranate, apple, blackcurrant, acai, acerola, guarana, mango, bilberries, grapes, cherries, kiwifruits, strawberries, feijoa, peach, and plums, could also be ideal media for probiotic, due to their content of essential nutrients [60]. Moreover, Gaanappriya et al. [61], also studied juices from watermelon, sapodilla, and orange as suitable carriers for lactobacilli for preparing beverage for consumers who are allergic to dairy products.

Sport and Energy Drinks

Sport drinks prevent dehydration (provides water), supply carbohydrates (energy), and electrolytes (sodium, potassium, calcium, magnesium) in a palatable and readily assimilable form [65]. They are usually consumed before or during exercise and training and they typically do not contain caffeine [66]. Due to their high sugar content (glucose, fructose, sucrose, and maltodextrin/glucose polymers), they could be perceived “as extremely sweet”. Thus, the addition of maltodextrins and glucose polymers, as alternatives for sucrose or glucose, is recommended [61]. However, sport drinks must be consumed with moderation, once excessive consumption of carbohydrates increases overall daily caloric intake that could lead to weight gain, and poor diet quality [61].

Energy drinks are non-alcoholic beverages refer to contain, besides calories, caffeine in combination with other presumed energy-enhancing ingredients such as taurine, herbal extracts, glucuronolactone, guarana, and B vitamins [67]. They have become popular among young people, athletes, and active individuals between the ages of 21 and 35 years [68]. Their objective is to provide sustenance and improved performance, concentration, and endurance [69]. However, serious concerns have arisen about the safety of these drinks or some of their major components (caffeine, guarana, and ginseng). Interestingly guarana also contains significant amounts of caffeine [66], thus its presence in an energy drink is a cause of concern because it increases the total caffeine level in the beverage. Ginseng has multiple and important drug interactions [69]. In young people, of concern is the increasing use of alcohol mixed with energy drinks, which may increase alcohol dependence and the likelihood of alcohol-related accidents and injuries [70].

Bottled Water

Recently, there has been an increase in the global sales of flavored bottled waters, and fruit-flavored waters. Flavored waters are a kind of soft drinks formulated with mineral or bottled water, flavorings (extracts, juices, or aromas), and additives which mainly are acidifying agents and sweeteners. The utilization of conventional emulsions in bottled waters to deliver oil-soluble flavors and nutraceuticals is limited due to the increase in turbidity caused by light scattering from the oil droplets [62]. However, microemulsions and nano-emulsions that contain exceptionally fine droplets that do not scatter light strongly may be used for this purpose [71] (Figure 6). Microemulsions are potentially excellent carriers for bioactive molecules. They offer the advantage of spontaneous formation, ease of manufacture, thermodynamic stability, and improved solubilization of bioactive materials. Spernath and Aserin [72] found that even W/O microemulsions, which are expected to break upon dilution in the digestive tract, increase the permeability and bioavailability of drugs.

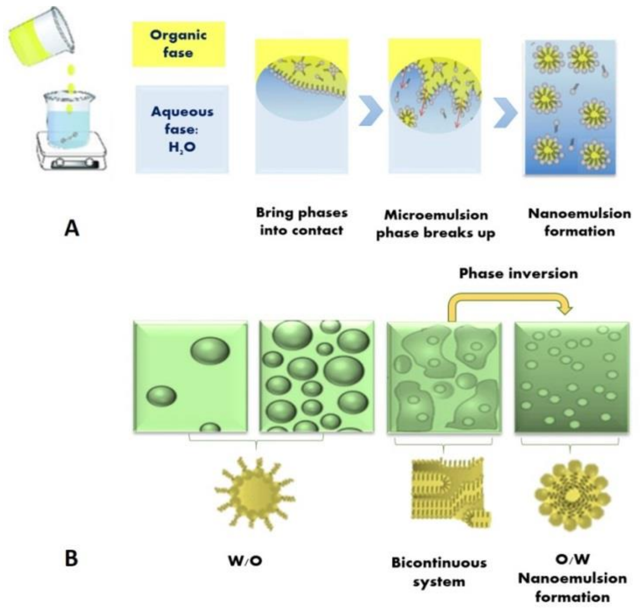

Figure 6: Schematic diagram of a potential mechanism for the formation of nanoemulsions: **A** - by the spontaneous emulsification method. When the organic phase (oil + hydrophilic surfactant) and the aqueous phase (water) are brought into contact a bicontinuous microemulsion is formed at the boundary, which breaks up and forms tiny oil droplets. **B** - by the emulsion phase inversion method. In this case, water is titrated into a surfactant–oil mixture with constant stirring.

Fruit Drinks

Today's consumer’s demand for beverages with added health benefits is adding another level of complexity in the process of beverage formulation and development. The beverage industry is responding to these requests by reducing calories and minimizing ingredient lists. For the consumer, a beverage communicates functionality by its cloudy appearance and thickness in the mouth [73]. To invoke the idea of freshly squeezed juice, fruit juices, incorporate specific cloud emulsions in product formulations, suggesting that the juice is made of ripe, real fruit and vegetable ingredients [73]. There is a large range of substances that can be used as emulsifiers such as, small-molecule surfactants that are used to stabilize beverage products, as they adsorb rapidly at the oil/water interface due to the presence of fatty acid in their molecular structure. However, other molecules such as proteins, polysaccharides or other biopolymers may also be used to their emulsion formation capacity even in the absence of fatty acid groups in their structure, since they present other functional groups capable of adsorption at the interface. Emulsifiers used for emulsion stabilization are food-grade and are safe food additives, and their use and maximum permitted doses are regulated by current legislation (EU 1333/2008). To produce fruit juice with a high content of pulp, there are difficulties to stabilize the pulp suspension for long periods. To overcome this problem, the food industry used hydrocolloids, such as xanthan, alginate, carboxymethylcellulose, as stabilizing agents of emulsion, yielding products with low viscosity and good taste, these gums increase the stability of the turbidity of fruit juice stored in bottles [74].

Xanthan gum (Figure 7), is a polysaccharide used in drinks made with citrus and in fruit-flavored drinks to create a satisfactory texture and as an odor and flavor stabilizer. Since it dissolves completely and quickly at low pH, it will help the suspension of insoluble compounds. According to Zecher and Van Coillie [75], xanthan gum helps also to create texture in fruit-flavored drinks. Also, carboxymethylcellulose (CMC – Figure 7) or mixed hydrocolloids, are added to maintain turbidity and suspension [75,76]. CMC, also called cellulose gum, is a cellulose derivative with carboxymethyl groups (-CH2-COOH) bound to some of the hydroxyl groups of the glucopyranose monomers that make up the cellulose backbone and it is often used as its sodium salt derivative (sodium carboxymethylcellulose) [77]. The amount of CMC added depends on the soluble solid content of the drink and the level of dilution before consumption. Large amounts of CMC can be used to improve texture and as a stabilizing agent. CMC reduces/prevents the formation of oil rings around the neck of the bottle. CMC is usually added after the addition of preservatives, coloring, or flavoring agents. The concentration of CMC that is typically used is in the range of 0.1–0.4% [75]. In some cases, CMC is used together with other types of gum [76].

Figure 7: Powdery form of Xanthan gum and CMC.

Sparkling Wine and Beer

Sparkling wines are a beverage that undergoes a second alcoholic fermentation in closed bottles or in hermetically sealed tanks, by which yeast produces carbon dioxide that becomes dissolved in the liquid, and consequently, the formation of bubbles occurs. The level of dissolved carbon dioxide in the liquid phase is of high importance since carbon dioxide is responsible for the visually appealing, the so-called effervescence. The formation of foam, its stability, and the size of the bubbles in sparkling wines are causally related to the surface tension. This can be defined as the force per unit area that maintains the bond between the molecules at the surface of the liquid. These bubbles (foam) are evanescent and not very stable, but the presence of surfactants reduces the surface tension of the liquid and allows the formation and persistence of bubbles. However, it is thought that proteins, due to their surfactant properties, and polysaccharides from the grapes and form the yeast cell wall (mannoproteins) used for winemaking are important factors in foam formation and stability [78-80].

The foam formation and foamability parameters seem to be dependent on: (1) the grape variety used in the production of the base wine due to differences in the concentrations and types of proteins as well as on grape polysaccharides; (2) aging time on yeast lees after the second fermentation for at least 9 months (EC Regulation N° 606/2009), the autolysis of the yeast occurs during this contact time and involves hydrolytic enzymes that act to release cytoplasmic (peptides, fatty acids, nucleotides, amino acids) and cell wall (mannoproteins) compounds into the wine that have been described as the major foam promoters due to their structure, which favors adsorption to the foam bubbles gas/liquid interface [79,81,82]; (3) concentration of iron in the wine, due to the ability of iron cations to complex with the proteins [83]; (4) wine anthocyanins (mainly different forms of malvidin) and amino acids (mainly β-alanine that confer hydrophobicity to the peptides and improve the quality of the foam) [80]. Therefore, both foam formation and duration are related to the chemical composition of sparkling wines [80].

Within the fermented beverages, beer is one of the most relevant as it is the alcoholic beverage most consumed. The consumer preferences for beer foams differ but can be characterized in terms of foam stability, quantity, lacing (adhesion to a glass surface), whiteness, "creaminess" (bubble texture), and concentration. The foam "head" created when the beer is poured or dispensed, is also an important aspect of consumer approval of a beer product. Also, unlike for champagne, whose foam film lifetimes are short (hydrodynamic control), beer foam has a slower drainage rate due to the adsorption of proteins at the interfaces and the generation of a significant disjoining pressure between bubbles [3]. Concerning the importance of the beer foam for the beer consumers acceptance, several parameters are defined to evaluate the beer foam quality including foam stability or head retention, foam texture (related to the bubble size – fine-textured foam consists of small bubbles; coarse foam contains larger bubbles), and foam adhesion (considered to be related to the formation of foam lace to the glass) or foam cling [84]. In general, a superior foam can be defined as foam with uniform, small, spherical bubbles that persist for a desirably long period and leave a pleasant adherence to glass [85].

Beer foam formation and stability are influenced by both raw materials, namely malt, and brewing process. Evans et al. [86] established that foam stability depends on the malt source. But the “head” character cannot be predicted. According to several authors, the beer foam stability is determined by the interaction of several components present in beer, mainly barley malts proteins/polypeptides and bittering agents derived from hops, iso-α-acids, to form a matrix, which increases the viscosity of the liquid regions in the foam, reduces drainage, and improves foam stability [87–90].

According to Kordialik-Bogacka and Antczak [91], a more stable beer foam is the one that presents smaller bubbles of uniform size. There are multiple variables for brewers to manipulate to achieve this type of foam. By increasing concentrations of barley malt proteins, foam stability could increase. The same phenomenon occurs when adding propylene glycol alginate (PGA -heterogeneous substance formed by the partial esterification of alginic acid with propylene oxide) as a foam additive [84], metal cations (e.g., Mn^{+2}, Al^{+3}, Ni^{+2}), and hop iso-α-acids. Increasing the number of lipids, protein modification, and alcohol content will lead to the opposite effect – decrease foam stability. Moreover, according to Evans and Sheehan [84], in unpasteurized beer, proteinase A also reduces beer foam stability.

Another consumer-driven objective, in addition to stable foam, is the so-called "lace curtains" on the wall of glass and cling patterns (adherence to glass) (Figure 8). The adhesiveness needed by the foam to produce this effect appears to be derived from the hops [90].

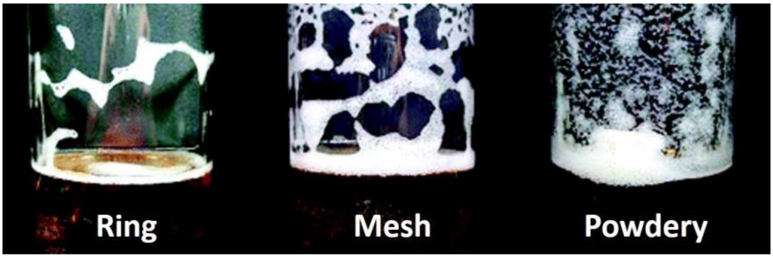

Figure 8: Three major types of cling that can be created by hop acids in lager beer. Foam-stabilizing properties and cling formation patterns of iso-α-acids and reduced iso-α-acids, investigated by Kunimune and Shellhammer [89], using an unhopped lager beer. The unhopped beer was dosed with iso-α-acid (Iso), rho-iso-α-acid (Rho), tetrahydro-iso-α-acid (Tetra), and hexahydro-iso-α-acid (Hexa), separately, over a range of concentrations from 2 to 10 ppm. Cling formation patterns could be categorized into three groups: "ring", "mesh", and "powdery". The control beer had the lowest foam stability and did not yield any foam cling [90].

Final product quality is critical to producing sparkling wine and beer. The visual attributes linked to bubbles are causally related to their quality. This is due to the relationship between bubbles, and other sensory characteristics, such as mouthfeel, the release of aromas, and changes in tastes and flavors [92,93]. The main components that determine bubble characteristics, foam formation, and stability are the dioxide carbon content, as well as some tensioactive or surfactant substances such as proteins and sugars. All these components and compounds have a direct influence on beverage quality, hence the importance of their assessment and control [94]. The most representative parameters of the foam behavior are the foamability (capacity of foam formation) and foam stability. For sparkling wine there are specific methods for the foam assessment, such as the Mosalux method [95], this method can measure three parameters (i) maximum foam height, (ii) foam stability height and (iii) foam stability in time [96].

Final Remarks

There are many challenges associated with the development of beverage emulsions. They are prepared from various ingredients with different formulations and processing operations, thus subjected to undesirable changes in their physical and sensory properties. To reduce risks and maintain product overall quality it is mandatory to develop a robust initial formulation and manufacturing processes.

In some drinks, consumer appreciates the foam that appears in the glass, which is the case of beer and sparkling wine. The foams could be characterized by stability, quantity, lacing, whiteness, "creaminess" and concentration. These parameters are influenced by both raw materials, namely malt and iso-α-acids from hop (in beer) and yeast fermentation process and yeast proteins (in sparkling wine).

To meet changing market and consumer demands, the beverage industry needs to seek new product formulation that may include constituents of technological, nutritional, and nutraceutical/bioactive characteristics and at the same time, remove ingredients that are undesirable from the consumer's perspective. For completion, a list with the permitted emulsifying, gelling, stabilizing, or thickening agents, last revised on 25 September 2017, and approved by the Government of Canada was included (Table 2) [97].

Table 2: List of Permitted Emulsifying, Gelling, Stabilizing, or Thickening Agents [97].

Additive	Permitted in or Upon
Acacia Gum / Arabic Gum	Flavored skim milk; ice milk mix.
Acacia Gum modified with octenyl succinic anhydride (OSA)	Unstandardized beverages.
Agar	Partly skimmed milk; partly skimmed milk with added milk solids; flavored skim milk.
Algin / Potassium Alginate	Ale; beer; flavored skim milk.
Ammonium Carrageenan	Ale; beer; light beer; malt liquor; flavored milk; flavored skim milk.
Ammonium Salt of Phosphorylated Glyceride	Flavored milk; flavored skim milk.
Arabinogalactan	Unstandardized beverage bases; Unstandardized beverage mixes.
Calcium Alginate	Ale; beer; flavored skim milk.
Calcium Carrageenan	Ale; beer; light beer; malt liquor; flavored milk; flavored skim milk; stout
Carboxymethyl Cellulose/ Sodium Carboxymethyl Cellulose/ Cellulose Gum/ Sodium Cellulose Glycolate	Flavored milk; flavored skim milk.
Carob Bean Gum	Flavored milk; flavored skim milk.
Carrageenan	Ale; beer; light beer; malt liquor; flavored milk; flavored skim milk.
Furcelleran / Potassium Furcelleran/ Sodium Furcelleran	Ale; beer; light beer; malt liquor; porter; stout
Gelatin	Flavored milk; flavored skim milk.
Gellan Gum	Unstandardized beverages
Guar Gum	Flavored milk; flavored skim milk
Hydroxypropyl Methylcellulose/ Propylene Glycol Ether of Methylcellulose	Flavored milk; flavored skim milk.
Irish Moss Gelose	Ale; beer; flavored milk; flavored skim milk; Stout.
Karaya Gum	Flavored milk; flavored skim milk.
Lecithin	Flavored milk; flavored skim milk.
Methylcellulose	Ale; beer; light beer; malt liquor; porter; Stout
Pectin	Flavored milk; flavored skim milk.
Polyoxyethylene (20) Sorbitan Monooleate (Polysorbate 80)/ Polyoxyethylene (20) Sorbitan Monostearate (Polysorbate 60)	Unstandardized beverage bases; Unstandardized beverage mixes
Polyoxyethylene (20) Sorbitan Tristearate (Polysorbate 65)	Flavored milk; flavored skim milk.
Potassium Carrageenan	Ale; beer; light beer; malt liquor; flavored milk.
Propylene Glycol Alginate	Ale; beer; light beer; malt liquor; porter; Stout.
Quillaia extract (Type 2)	Oil-based coloring formulations or unstandardized oil-based ingredients for use in non-carbonated water-based flavored and sweetened beverages, or in unstandardized flavored alcoholic beverages or caffeinated energy drinks, sports drinks or beverages with vitamin and mineral nutrients added, except beverages with vitamins added following Part D of the *Food and Drug Regulations*
Sodium Carrageenan	Ale; beer; light beer; malt liquor; flavored milk; flavored skim milk; Stout.
Sodium Phosphate, dibasic	Flavored milk; flavored skim milk.
Sorbitan Monostearate	Unstandardized beverage bases; Unstandardized beverage mixes
Sucrose Monoesters of Lauric, Palmitic or Stearic Acid	Unstandardized beverages; Unstandardized beverage concentrates; Unstandardized beverage mixes
Xanthan Gum	Fruit-flavored drinks

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