



INFLUENCE OF HYDROCOLLOIDS IN OIL-IN-WATER EMULSIONS DURING STORAGE OF FOOD

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Abstract: *This paper describes the physico-chemical principles underlying the functional role of hydrocolloids in oil-in-water emulsions. Basic terms such as emulsifier and stabilizer are defined, and the origins of electrostatic and steric interaction potentials are explained. The paper discusses the main factors controlling flocculation, creaming, coalescence and Ostwald ripening, distinguishing between the differing effects of adsorbing and non adsorbing hydrocolloids. The attention is specifically paid to new understanding concerning the rheological and microstructural control of emulsion stability by non-adsorbing hydrocolloids, and the great potential of electrostatic protein-polysaccharide interactions at the oil-water interface to enhance emulsion properties.*

Keywords: *emulsion stability, depletion flocculation, rheology and microstructure, hydrocolloid emulsifiers*

1. Introduction

An emulsion is a dispersion of one liquid (the dispersed phase) as small spherical droplets in another immiscible liquid (the continuous phase). The two main types of emulsions are oil-in-water (O/W) and water-in-oil (W/O). Food emulsions of the oil-in-water type include, for example, milk, cream, salad dressings, sauces and beverages; examples of the water-in-oil type are butter and margarine. The oil phase is either a flavor oil (in soft drinks) or triglyceride oil (in dairy emulsions). In the latter case the oil phase is semi-solid at ambient temperatures due to the presence of dispersed fat crystals. Some emulsion products also contain other kinds of dispersed phases - gas bubbles (in whipped cream), starch granules (in cake batter) and ice crystals (in ice-cream). Despite the

wide diversity of structures, compositions and textures of food emulsions, there are some basic underlying principles that can be reliably used to understand and predict their general behavior. One generally important factor influencing their stability properties is the presence of hydrocolloids [1].

Emulsions are thermodynamically unstable. With time they tend to break down into their constituent oil and aqueous phases. The term 'emulsion stability' therefore refers to the ability of an emulsion to resist this breakdown, as indicated by growth in average size of droplets or change in their spatial distribution within the sample. The more slowly that these properties change, the more stable is the emulsion. In practice, stability is a relative term which depends on the context. For some food emulsions,

such as cake batters or cooked sauces, the required time-scale for stability is only a few minutes or hours. But for other products, such as soft drinks and cream liqueurs, emulsion stability must be maintained over a period of several months or years [2].

A hydrocolloid ingredient may act as an emulsifying agent, as a stabilizing agent, or in both of these roles. An emulsifying agent (emulsifier) is a surface-active ingredient which adsorbs at the newly formed oil-water interface during emulsion preparation, and it protects the newly formed droplets against immediate coalescence. Given that polysaccharides are predominantly hydrophilic in molecular character, and most hydrocolloids are not surface-active, they cannot act as primary emulsifying agents. There is really only one hydrocolloid - namely, gum arabic - which is commonly employed as an emulsifying agent. The main emulsifying agents used in food processing are the proteins, especially those derived from milk or eggs. A stabilizing agent (stabilizer) is an ingredient that confers long-term stability on an emulsion, possibly by a mechanism involving adsorption, but not necessarily so. In O/W emulsions, the stabilizing action of hydrocolloids, such as xanthan, carboxymethylcellulose, carrageenan etc., is traditionally attributed to the structuring, thickening and gelation of the aqueous continuous phase [3].

The expression 'emulsifying agent' is to be preferred over the more concise 'emulsifier'. This is because the latter term normally implies membership of the class of small-molecule surfactants, comprising lipid-based ingredients such as monoglycerides, phospho-lipids (lecithin) and polysorbates (Tweens). The functional role of these small-molecule emulsifiers in food technology is typically not for emulsion making, but for other reasons:

controlling fat morphology and crystallization; promoting shelf-life through interaction with starch; and destabilizing emulsions by competitive protein displacement from the oil-water interface [4, 6].

A stable emulsion is one where the droplets remain sufficiently small and well separated that Brownian motion alone keeps them evenly dispersed throughout the continuous phase. The physico-chemical principles of O/W emulsion stability are based on the classical colloid theories of electrostatic and steric stabilization. Electrostatic stabilization arises from the presence of electrical charge on the surface of the droplets, or more usually on the adsorbed stabilizer layer at the surface of the droplets. The greater the charge density at the surface, and the lower the ionic strength (electrolyte concentration) of the continuous phase, the more stable is the emulsion. Steric stabilization arises from the presence of a polymeric (steric) barrier at the droplet surface. To confer long-term stabilization, this polymer must be present at sufficient concentration to cover the oil-water interface completely, and it must remain permanently attached to the surface, with at least part of the molecule projecting away from the surface into the aqueous medium. Steric stabilization is increasingly supplemented by electrostatic stabilization in emulsions containing adsorbed proteins at pH values well away from the protein's isoelectric point (pI) [7].

Whether emulsion droplets will remain dispersed or will tend to stick together depends on the nature of the antiparticle pair potential between the droplet surfaces. Generally speaking, colloidal stability requires that the antiparticle repulsion should be of sufficient range and strength to overcome the combined effects of gravity, convection. Brownian motion and the ubiquitous short-range attractive forces together drive the system towards its final

and inevitable phase-separated equilibrium condition. Figure 1 shows two possible forms of the interaction potential (measured in units of the thermal energy, kT) as a function of the surface-to-surface separation (measured in arbitrary units of the order of nanometers). The shape of the potential $U(d)$ at any separation d tells us about the nature and strength of the interaction force between the surfaces. That is, the force F is equal to the (negative) derivative of the potential, i.e., $F = -6U(d)/d$. Potential A in Fig. 2.2 corresponds to a stable system where the interaction force is repulsive or zero ($F > 0$) at all droplet separations. Potential B corresponds to a more complicated situation in which the interaction force is strongly attractive at close separations ($F < 0$, $d < 5$), repulsive at medium separations ($F > 0$), and weakly attractive or zero at larger separations ($F < 0$, $d > 12$). In this latter case, the system is stable with respect to coagulation (i.e., coalescence of emulsion droplets) but unstable with respect to reversible flocculation. In any particular emulsion, what determines whether the potential $U(d)$ is of type A or type B, or if it has some other functional form, is the delicate balance between the various types of molecular forces contributing to the overall interaction.

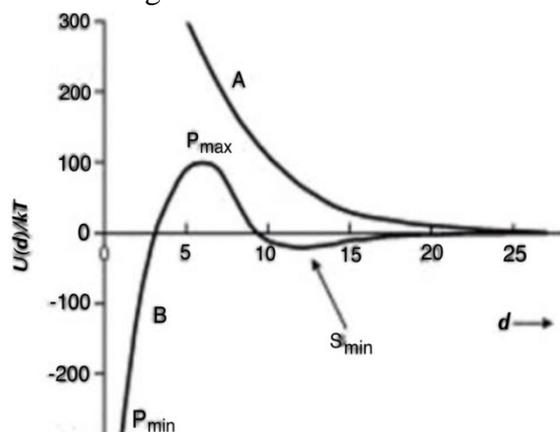


Fig. 1 Theoretical interaction potential between a pair of spherical emulsion droplets.

The energy $U(d)$ (in units of kT) is plotted as a function of surface-to-surface separation d (arbitrary units). Curve A corresponds to a pure repulsive interaction. Curve B corresponds to a DLVO-type potential having a potential energy barrier more than sufficient to confer colloidal stability (p_{min} = primary minimum, p_{max} = primary maximum, s_{min} = secondary minimum).

The aim is to study particle size effects on the stability of emulsions during storage and use in the manufacture of beverages and their stability during 180 days [5, 8].

2. Material and methods

As materials for research are prepared samples of drinks with emulsions (O/W) orange, lemon, peach, grapefruit in which use stabilizers (gum arabic, modified starch).

When consistency and stability of the emulsion in the beverage were verified by preparing drinks and placing them in direct sunlight, for at least 72 hours, an oily ring is formed. Then this emulsion is homogenized again for particles to 1 micron. Drink this emulsion based not put on stability during storage as oily ring will increase. If within 72 hours oily ring is formed in drinks, such drinks are investigated for stability following manner. For studies prepared samples of drinks with emulsions (O/W):

- non-alcoholic beverages orange (1), lemon (2), peach (3), grapefruit (4)(table 1)
- alcoholic beverages orange (5), lemon (6), peach (7), grapefruit(8) (table 2).

Preparation of drinks

Preparation of the sugar syrup.

- a. Weigh the required amount of water into a glass and heated to 50 -80° C.
- b. Attach the required amount of sugar and completely dissolve.

Dissolving citric acid and sodium benzoate in water (t=20 °C). Attach the required amount of sodium benzoate and completely dissolve. Add citric acid and dissolve completely.

Attach the required amount of emulsion and completely dissolve.

Weigh the required amount of ingredients of the drinks add in stirrer, mix at room temperature until ingredients completely dissolved in water with CO₂.

Table 1
Formulations of non-alcoholic beverages orange (1), lemon (2), peach(3), grapefruit (4)

The ingredients of the drinks	Content. g/100g			
	Number of drinks			
	1	2	3	4
Emulsion	1	1	1	1
Sugar	100	100	100	100
Juice Bx 70%				
Vodka 40%	3.5	3.5	3.5	3.5
Citric acid (E330)	0.15	0.15	0.15	0.15
Water	895.4	895.4	895.4	895.4
Total	1000	1000	1000	1000

Table 2
Formulations of alcoholic beverages orange (5), lemon (6), peach (7), grape fruit(8)

The ingredients of the drinks	Content. g/100g			
	Number of drinks			
	5	6	7	8
Emulsion	2	2	2	2
ugar	180	180	180	180
Juice Bx 70%	23	23	23	23
Vodka 40%	450	450	450	450
Citric acid (E330)	2.5	2.5	2.5	2.5
Water	342.5	342.5	342.5	342.5
Total	1000	1000	1000	1000

For alcoholic beverages add required amount of vodka 40%.Measure density, pH of the drinks. The results of measurement of each emulsion: density- lab density meter, pH- lab pH meter.

3. Results and discussion

Figure 2 illustrates the four main kinds of instability processes exhibited by O/W emulsions: creaming, flocculation, coalescence and Ostwald ripening. (For W/O emulsions, the processes are the same, except that sedimentation replaces creaming). Flocculation is probably the most subtle and complicated phenomenon to control, because it can be triggered by so many different factors, and the resulting emulsion properties can be quite different depending upon whether the flocculation is weak or strong. In dairy-type O/W emulsions, at or below ambient temperature, instead of the full coalescence of liquid droplets, we have so-called 'partial coalescence' ('clumping') of semi-crystalline globules. In practice, two or more of the phenomena shown in Fig. 1 may happen at the same time, and the presence of one mechanism (flocculation) may trigger or enhance another (creaming or partial coalescence). Emulsion phase inversion, as in the shear-induced transformation of cream (O/W) into butter (W/O), is a multi-mechanism process. If the particle size is less than 1 micron, the emulsion is highly robust stability and gives some turbidity but less than 1 micron particle size, the less turbidity, if the particle size is not greater than 0.3 micron. The principle of leverage ratio of water and oil phase of emulsions with different stabilizers is the same. In the obtained parameters also affects the nature of emulsions stabilizer.

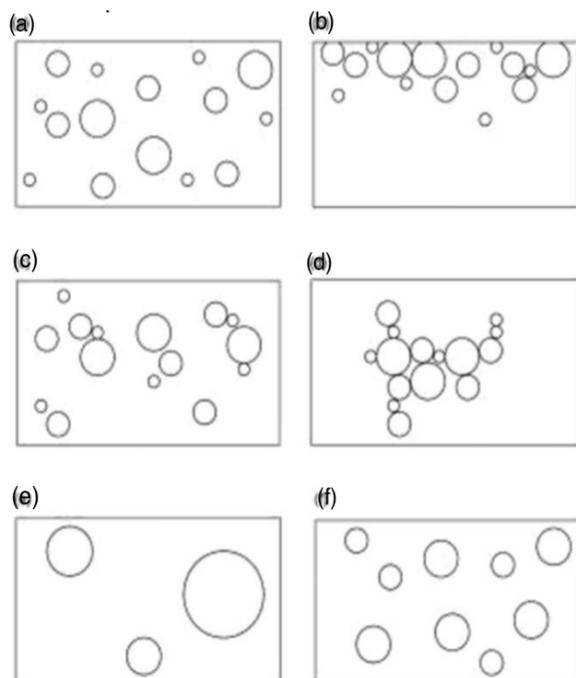


Fig. 2 Schematic representation of the key mechanisms of O/W emulsion instability: (a) stable dispersion of droplets; (b) creaming; (c) flocculation (weak); (d) flocculation (strong); (e) coalescence; (f) Ostwald ripening.

Investigation of the stability of emulsions was carried out by determining the size of the diameter of the particles by laser granulometry and placement on the stability of soft drink, which was used emulsion for 180 days. During storage of beverages prepared from emulsions studied, there was no formation of oil ring or “creaming” bottled, indicating the stability of emulsion systems.

4. Conclusion

The use of aromatic emulsions in the manufacture of soft drinks has several benefits, including: reduced duration blending, as there is no need to pick up the flavor, color and taste.

The process of storing drinks not observed the emergence of oil rings on the surface of

the drink, there was no change in color, taste and aroma of the drink.

Complete the emulsion must have the following parameters: the size of the oil particles (up to a micron); organoleptic - appearance, color, smell (aroma) and taste according to recipes; density (1,030-1,100), g/cm³; pH (3, 3 ± 0, 7); stability in the drinks.

The best result of research in emulsions - is to obtain the maximum number of particles of about 1 micron.

Creating a stable emulsion system is a pressing issue in the food industry, so these studies are useful and important for the development of new food products.

5. References

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