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Particle-Stabilized Emulsions: A Brief Overview

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Since the 1980s there has been a trend towards surfactant-free emulsions[1-4] driven by products for sensitive skin and for improved sunscreens. In recent times there has been a flurry of research, development and intellectual property activity in the field of particle-stabilized emulsions. Tailored nanoparticles are desired for these applications. The purpose of this article is to briefly review the basic principles of the particle stabilization of emulsions.

Pickering Emulsions

Pickering reported the first recorded scientific study[5,6] of particle-stabilized emulsions in 1907 when he stabilized water and paraffin with basic copper and iron sulfates, in which the particles were precipitated in situ. He noted, "Many other precipitated substances act as emulsifiers but this property is destroyed as soon as they have been dried or have by any other means been deprived of their fine-grained structure." These emulsions are now known as Pickering emulsions. In Pickering emulsions, small particles position themselves at the oil-water interface and form a mechanical barrier to coalescence.[7] These emulsions were known as a problematic occurrence in the recovery of oil because stable water-in-oil emulsions were formed by minerals present in the system.[8] Other examples of Pickering emulsions are the stabilization of whipping cream by fat particles and the stabilization of ice cream by ice crystals.[9]

In order for particles to stabilize emulsions, they must be of an appropriate size, wettability[10-12] and concentration. Other factors contributing to the stability of the emulsion include the pH and presence of ions in the water phase as well as the presence of any other emulsifiers.[13] These three factors can lead to an inversion in the type of the emulsion.[8] The interactions of the particles with each other are also important.[14,15]

Particle size: The size of particles is very important because the particles must be small enough to form a film around the droplets of the dispersed phase. Obviously, the particles must be much smaller than the droplets.[7] Even when particles are smaller than the dispersed droplets, if they reach a critical size, they become too large to be held at the interface.[8] The ratio of droplet size to particle size is important in determining the ease in emulsion formation. The larger this ratio is, the more easily a stable emulsion is formed.[13] Generally the stability of an emulsion increases as particle size decreases.[13] However, when particles approach the size of surfactant molecules, which is less than half a nanometer, they become easily removed from the interface, which leads to increased instability.[9]

There are two mechanisms that are discussed in the stabilization of emulsions by particles. The first is that the particles adsorb at the interface and form a rigid film that acts as a barrier between the droplets of the dispersed phase. The second is that interactions of particles form a three-dimensional network in the continuous phase that surrounds the droplets.[13]

The size of the droplets of the dispersed phase is also noteworthy in determining the stability of the emulsion. Although millimeter-sized droplets have been successfully stabilized using particles,[9] in general it is advantageous to have very small droplets within the emulsion. As the concentration of par-

Key words

*particle, emulsions, Pickering emulsion*

Abstract

The fundamentals of particle-stabilized emulsions are outlined here, and comparison are made to surfactant-stabilized emulsions. Recent advances in Pickering emulsions for cosmetics are described in this survey article.
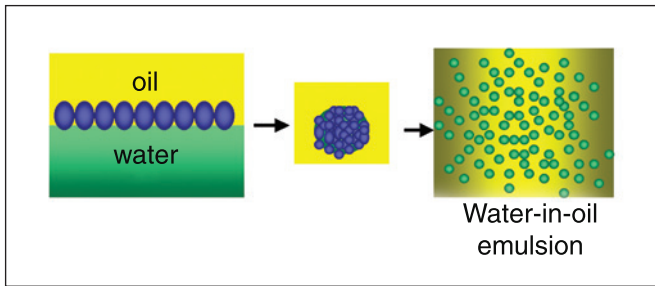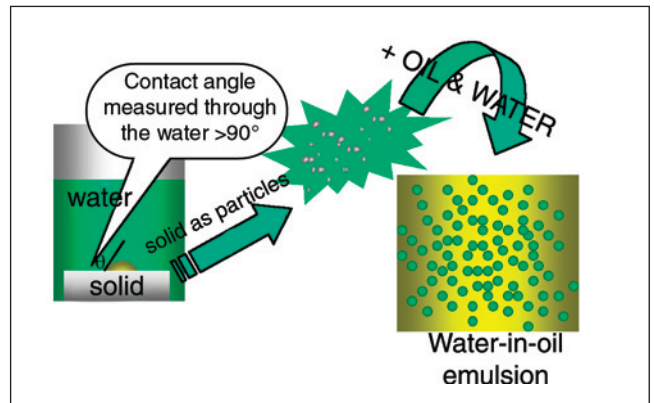
Figure 1. Emulsion stabilization with particles: if the particles are wetted more by water than by oil, then a water-in-oil emulsion will result.
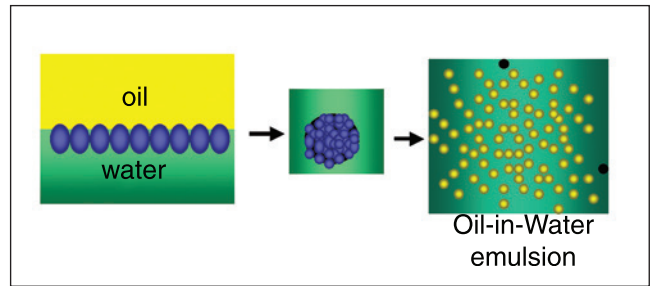
Figure 2. Emulsion stabilization with particles: if the particles are wetted more by oil than by water, then an oil-in-water emulsion will result.
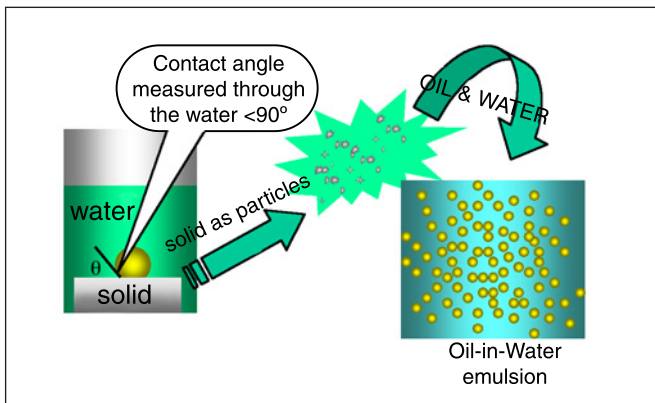
Figure 3. Particle wetting and emulsion stabilization: if the contact angle of the oil on the solid is greater than 90°, then an oil-in-water emulsion will result.

Figure 4. Particle wetting and emulsion stabilization: if the contact angle of the oil on the solid is less than 90°, then a water-in-oil emulsion will result.

ticles in the system increases, the size of the droplets decreases. When the droplet size decreases, more particles can be arranged at the interface, which imparts added stability to the emulsion.[13] However, particles that are too hydrophilic or hydrophobic create large, unstable droplets.[9]

Particle wettability: The wettability of the particles used to stabilize emulsions is of utmost importance. Because virtually all of these particles must lie at the interface between oil and water,[13] they must be amphipathic in nature. If they are wet too strongly by either water or oil, they will remain in the phase that they prefer instead of contributing to the stability of the emulsion.[16] However, it is expected that the particles will be more strongly wet by one of the liquids. This liquid will become the continuous phase of the emulsion.[9] (See Figures 1 and 2.)

The parameter used in determining particle wettability is the contact angle. For a particle to stabilize an emulsion, the contact angle of the liquid interface (measured through the water) at the particle surface must be near 90°. If a particle is slightly more hydrophilic,

the contact angle will be less than 90° and the particle will have the potential to stabilize oil-in-water emulsions. If the particle is slightly more hydrophobic, the contact angle will be greater than 90° and the particle will have the potential to stabilize water-in-oil emulsions.[9] (See Figures 3 and 4.)

If the particles are completely wetted by water, then they will reside in the aqueous phase and the emulsion will be unstable. Similarly, complete wetting by the oil phase will result in emulsion instability.[17]

There is a strong correlation between particle wettability and surface free energy. The interaction between particles and interfaces is strongest when the solid/liquid/oil contact angle is 90° from the interface. When the contact angle becomes less or greater than 90°, the interfacial interaction drops drastically. This extreme change in interaction is the reason that wettability is such an important factor in particle stabilization.[9] Emulsions cannot be stabilized by particles at all if the free energy change that occurs when the particles are transferred from the continuous phase to the interface is not negative.[8] However, the size of the particles allows Brownian motion to distribute the particles to the state with the lowest free energy. When the particles are of appropriate wettability, this state is between the two phases.[9]

One particular type of particle that has been developed to stabilize emulsions is known as a Janus particle. These particles are round glass beads that have been chemically treated to have one hydrophobic hemisphere and one hydrophilic hemisphere. This is accomplished by protecting half of the glass sphere with varnish and coating the other half
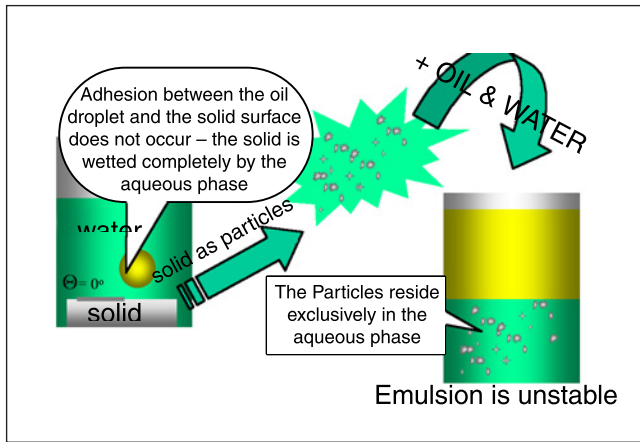
Figure 5. Particle wetting and emulsion stabilization: if the contact angle of the oil on the solid is 0°, then the particles will reside in the aqueous phase and the emulsion will be unstable.
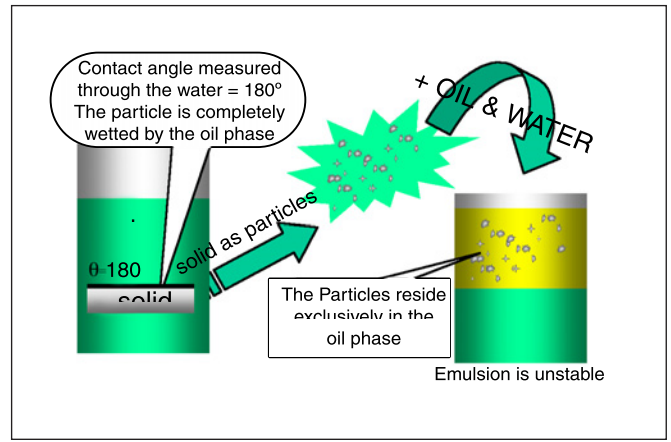
Figure 6. Particle wetting and emulsion stabilization: if the contact angle of the oil on the solid is 180°, then the particles will reside in the oil phase and the emulsion will be unstable.

with octadecyl trichlorosilane to impart a hydrophobic nature. The varnish is then removed to reveal the hydrophilic side of the bead. Janus particles range from 50 to 90 micrometers in size.[18] The advantage they have over particles of intermediate wettability is that they can be up to three times more surface active which leads to greater emulsion stability.[19]

Particle concentration: The concentration of particles in the emulsion, along with the wettability of the particles, determines the quantity of particles at the oil-water interface.[13] Closer packing of particles at the interface leads to an increase in the stability of the emulsion. (See Figures 5 and 6.)

Particle interactions: The interactions of particles at the interface also contribute to the stability or instability of the emulsion. In order to stabilize an emulsion, the particles at the interface may not form agglomerates.[5,7] However, the particles must be partially flocculated in order to form the film between the phases. If they are completely flocculated or deflocculated, stabilization will not occur.[13] In systems that are stabilized by clay particles, the particles actually form a three-dimensional network.[20] In other systems, where charged particles reside at the interface, the stability is enhanced because the particles create electrostatic repulsion between the droplets of the dispersed phase.[13] Finally, when a mixture of different particles is used, the interactions between these particles can greatly alter the character of the emulsion.

Comparison to Surfactant-Stabilized Emulsions

Although particles and surfactants are both able to stabilize emulsions, the characteristics of these emulsions are very different. To compare the two emulsifiers, it is important to see that for particle-stabilized emulsions, contact angle is an expression of wettability, just like HLB is an expression of surfactant hydrophobicity and hydrophilicity. Amphipathic particles can essentially be irreversibly adsorbed at the oil/water interface if they have appropriately constructed patterns of hydrophobicity and hydrophilicity on their surfaces.

Surfactants, on the other hand, tend to be more mobile at the interfaces and under appropriate conditions they can adsorb and desorb very quickly.[9] Surfactants and polymers tend to form aggregates in ways that particles do not. Because of this, solubilization phenomena that are important in surfactant-stabilized emulsions are not an issue for particle-stabilized emulsions. Another difference is that for surfactants, the type of oil used is important in determining whether the emulsion will be oil-in-water or water-in-oil. The choice of oil does not affect emulsion type for particle-stabilized emulsions. However, for particle-stabilized emulsions, the initial particle location has an effect on emulsion type and stability.

The initial location of the particle determines which phase will be continuous. This is an advantage over surfactants because it allows both water-in-oil and oil-in-water emulsions to be formed depending on the oil-to-water ratio.[9] In these systems, maximum stability can be achieved by changing the initial location of the particles. Any one surfactant or surfactant system is less versatile in this respect due to the speed at which surfactants are distributed and redistributed throughout the emulsion. A final difference between the two types of emulsifiers is that surfactant-stabilized emulsions are least stable at conditions near inversion, while particle-stabilized emulsions are most stable at those conditions.[9]

Recent Advances in Pickering Emulsions for Cosmetics

It has been revealed that "emulsifier free" oil-in-water Pickering emulsions can be formed in which the stabilizing particles are zinc oxide or titanium dioxide that has been coated with aluminum stearate or dimethicone, and aluminum hydroxide or silicon dioxide[a,b,21-23].

The ultrafine amphiphilic particles are defined as having particle sizes less than 200 nm. The specifications of these patents disclose that these formulated emulsions are characterized by excellent skin tolerability and exhibit higher effectiveness in sunscreen formulations.

It is interesting that these emulsifiers follow a modification of Bancroft's rule. Bancroft states that the phase in which the emulsifier is soluble becomes the continuous phase of the emulsion. Gers-Barlag et al reveal that if the particles are first dissolved in the aqueous phase, then an oil-in-water emulsion results. On the other hand, if they are first dispersed in the oil phase, then a water-in-oil emulsion results. Water-in-oil emulsions preferably contain magnesium silicate particles as stabilizers.

The inventors also reveal that these particle-stabilized emulsions are remarkably stable in the presence of electrolytes[24] and this makes it possible to design systems containing both astringents and antimicrobials[21]. One type of amphiphilic particle that is disclosed is hydrophobic latex rendered hydrophilic by saponification or by polymerizing acrylic acid on the particle surfaces[25]. Hydrocolloids may be added to the water-in-oil emulsions; a particularly advantageous hydrocolloid is hydroxypropylmethylcellulose[c,26].

In one manifestation, water-in-oil emulsions are claimed for relatively non-viscous oils[27] and in another, waxes and oil thickeners may be included. These include natural waxes[d], chemically modified waxes[e] and synthetic waxes[f]. The preferred thickeners are aluminum stearate and magnesium stearate and stearalkonium hectorite[28]. In one invention the modified phyllosilicate, stearalkonium hectorite[g] is combined with ultrafine boron nitride particles as the emulsion stabilizer[29].

In addition to the amphiphilic particles, it has been claimed that stable compositions can also contain non-amphiphilic pigments such as hydrophobically-modified titanium dioxide[h,30-31].

Polymeric moisturizers (such as chitosan and hyaluronic acid) can be included[32]. The optional addition of cosmetic ingredients or pharmaceutical additives has been claimed[33-35]. One drawback of particle-containing emulsions is that they can give a dry or dull impression on the skin. This is overcome in particle-stabilized emulsions containing cyclodextrin[36], preferably beta-cyclodextrin and gamma-cyclodextrin[j,37,38].

Cyclodextrin functions as a molecular sheath on exposed hydrophobic groups. Once "sheathed" the moieties become hydrophilic but the cyclodextrin partitions away from the original hydrophobe when sufficiently high concentrations of surfactants or oils are introduced into the composition, and the original hydrophobes can be exposed for hydrophobic association.

It has been claimed that emulsifier-free cosmetic or dermatological emulsions can be obtained from compositions comprising an oil phase, an aqueous phase and an amphiphilic polysaccharide[39]. The amphiphilic polysaccharide is non-thickening[k].

It is interesting that it is claimed that these emulsions are characterized as being free of hydrocolloids, particularly carbomers[40].

Conclusion

Pickering emulsions have been somewhat of a laboratory curiosity since their discovery almost a century ago. Recent technological advances have resulted in the introduction of amphipathic nanoparticles that are enabling the production of surfactant-free particle-stabilized emulsions. Hydrophobic/ hydrophilic tailoring of nanoparticles holds the promise for formulators of novel stimuli/responsive surfactant free emulsions.

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