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Tiny Particles, Big Impact

The Art of Pickering Emulsions

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Many of the food products we regularly consume contain multiple phases that do not readily mix, such as oil and water. These result in small droplets of one liquid dispersed within the other, forming emulsions that are classified as either oil-in-water (O/W) or water-in-oil (W/O). Examples of O/W emulsions in food include milk, cream, dairy drinks, infant formula, soups, ice cream, salad dressings, mayonnaise and chocolate ganache. On the other hand, W/O emulsions encompass items like butter, margarine, and spreads. The key to the stability of these emulsions lies in emulsifiers, which play a vital role in preventing or delaying the thermodynamically favoured phase separation that could otherwise result in emulsion breakdown.

Emulsions represent a dispersion system comprising two incompatible liquids, typically a mixture of water and oil. The term “oil phase” is commonly used for organic liquids that are insoluble in water. Given the inherent thermodynamic instability of emulsions, the use of emulsifiers is essential to achieve the desired stability. Conventional emulsifiers typically fall into the categories of small molecule surfactants, including ionic and non-ionic surfactants, as well as amphiphilic biopolymers. However, emulsions stabilized by these conventional emulsifiers, such as surfactants or amphiphilic macromolecules with good solubility (e.g., proteins and polysaccharides), are often thermodynamically unstable and prone to breakdown due to coalescence, flocculation and Ostwald ripening over time. Moreover, some of these conventional emulsifiers pose health risks, limiting their applications in the food, cosmetics and pharmaceutical industries.

A Pickering emulsion is characterized by its stabilization through solid particles that adsorb onto the interface between two phases, forming a protective shell around oil or water droplets. The fundamental principle involves the binding of solid particles to the interface, preventing droplet coalescence and ensuring emulsion stability. Ramsden and Pickering were pioneers in identifying and describing Pickering emulsions in the early 20th century. Unlike classical emulsions, which rely on amphiphilic compounds for stability, Pickering emulsions exclusively use solid particles, earning them the alternative name of solid-stabilized emulsions.

Stability in conventional emulsions is obtained by the adsorption of amphiphilic chemicals, which change the interfacial characteristics of the two phases. However, in Pickering emulsions, solid particle adsorption at the liquid-liquid interface acts as a barrier, preventing droplet merging (coalescence). Solid particles can be adsorbed at the oil-water interface only if they are somewhat wet by both phases, indicating dual wettability. This adsorption reduces the surface area of the high-energy oil-water contact, which plays an important role in particle transport at the interface. Pickering emulsions are divided into two varieties depending on particle wettability: [1] oil-in-water (O/W) emulsions stabilised by hydrophilic particles and [2] water-in-oil (W/O) emulsions stabilised by hydrophobic particles. In addition, there is a version known as Double Pickering emulsion, which comprises [3a] W/O/W and [3b] O/W/O emulsions..

Despite the benefits, such as enhanced stability and reduced toxicity, offered by solid particles compared to surfactant-based emulsions, there has been a notable increase in research on Pickering emulsions in recent years. This heightened interest is driven by the potential value these emulsions bring to various novel applications, particularly in industries such as food technology, cosmetic products, oil recovery and more recently, drug delivery. Various types of organic and inorganic solid particles can serve as Pickering emulsifiers. The essential characteristics of a stabilizing particle include its dual wettability, morphology (size and shape), and concentration.

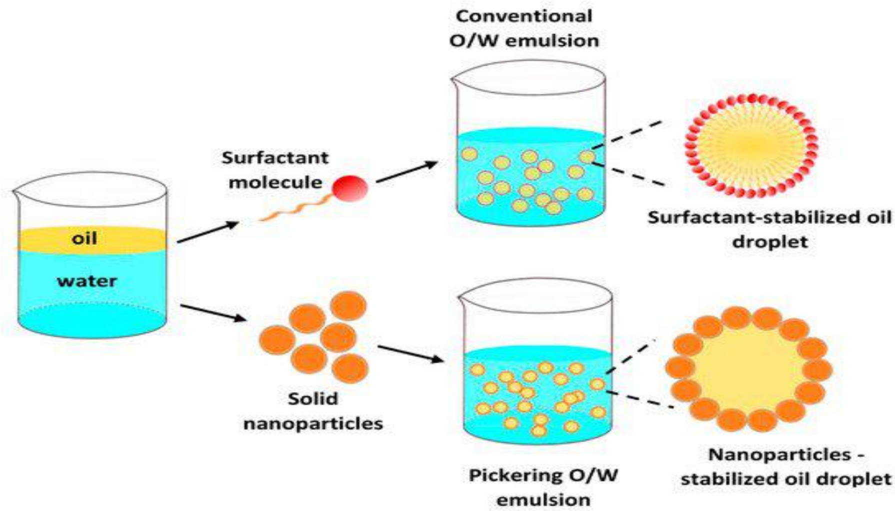

Fig. 1. Schematic of conventional emulsion and Pickering emulsion

The Pickering emulsions mainly consists of 3 parts

These emulsions are primarily composed of two phases: the continuous phase and the dispersed phase. The continuous phase, which prevents droplet aggregation, wets the particles more and is present in higher quantities. The phase forming the droplets is referred to as the dispersed phase.

- **Oil Phase:** This phase typically comprises water-insoluble organic liquids.
- **Aqueous Phase:** This phase generally consists of water or a water solution.
- **Solid Particles:** Pickering particles are solid micro or nanoparticles. Commonly used solid particles for stabilizing food-grade Pickering emulsions include polysaccharide particles, protein particles, lipid particles and inorganic particles. Examples of commonly used food-grade Pickering particles include:
  - **Polysaccharide Particles:** Starch particles, Chitosan particles.
  - **Protein Particles:** Quinoa protein.
  - **Flavonoid Particles:** Naringin particles, Rutin particles.

Conclusion

The Pickering emulsion is an innovative system utilizing solid particles as stabilizers to create a robust interfacial film. By enhancing steric hindrance, it effectively prevents droplet aggregation and precipitation, ultimately achieving emulsion stabilization. Pickering emulsions hold significant promise for diverse applications in the food industry, including dairy products, beverages, condiments and more. Furthermore, the growing focus on food safety and health has turned Pickering emulsion applications in functional foods into a key area of research interest. Despite numerous laboratory-scale experiments, the industrial-scale commercialization of Pickering emulsions is yet to be realized.