

Pickering Emulsions using Food-Grade Non-Fat Particles

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Pickering stabilisation has long been recognised as a very useful and suitable method for producing emulsions with superior stability when compared to conventional surfactant stabilised emulsions. Pickering particles accumulate at the oil-water interface in the form of a densely packed layer. This layer then protects the emulsion system against droplet flocculation and coalescence via a steric mechanism. In comparison, surfactants stabilise emulsions via an electrostatic mechanism where surfactants, in constant dynamic equilibrium, lower the interfacial tension between the oil and water phases by adsorbing to the interface.

Several factors have been signalled as affecting Pickering emulsion stability. These include oil phase composition, particle concentration, emulsification technique and storage conditions. However, arguably, the two most important factors are the particle size and wettability. The relatively large size of Pickering particles, typically between 100nm and 5 μ m, when compared to surfactant molecules (approximately 0.4nm to 1nm) and protein molecules (normally between 1nm and 5nm) plays an important factor in determining the stability of the resulting emulsions^[1]. The larger size of the solid particles leads to slower kinetics of adsorption at the interface and higher energy barriers to particle adsorption, both of which can strongly affect the emulsification process. The slower kinetics of particle adsorption compared to surfactant adsorption means that as droplets are broken up during emulsification, there is much droplet surface area left uncovered. As the particles are slow to adsorb to these newly created areas of liquid interface, they are left exposed to approaching droplets and coalescence is imminent. However, the free energy of detachment ($-\Delta_{int}G$) for a particle from an oil-water interface is also dependent on the particle radius squared (Equation 1)

$$-\Delta_{int}G = \pi r^2 \gamma_{ow} (1 \pm \cos \theta_w)^2 \quad \text{Equation 1}$$

where γ_{ow} represents the interfacial tension between the oil and water phases, θ_w , particle contact angle through the water phase and r , particle radius^[2]. For particles of large sizes (i.e. < 10 μ m) much more energy is required to detach particles from the oil-water interface, whereas smaller particles will adsorb to the interface less strongly and produce emulsions with a reduced long-term stability. Therefore a balance in terms of the particle size must be struck.

Pickering emulsions do not depend on the HLB (hydrophilic lipophilic balance) system as simple emulsions primarily do, but on the contact angles of the particles at the interface. This important parameter can determine emulsion stability as well as whether water-in-oil or oil-in-water emulsions result and so the emulsion type produced is due to the wettability of the solid stabilising particles^[3].

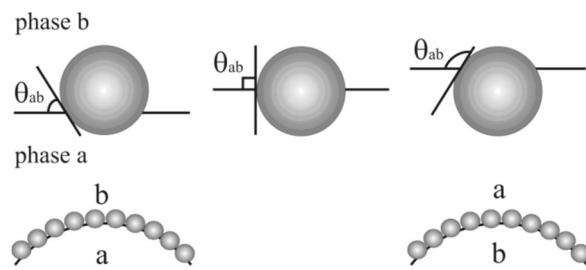


Figure 1. Contact angle schematic diagram at the liquid-liquid interface with regard to spherical Pickering particles^[3]

In Figure 1, if phase a is taken as the oil phase and phase b as the water phase in terms of a simple emulsion, particle wettability (i.e. degree of particle hydrophobicity) can be better understood. Where the contact angle, θ_{ab} , is $< 90^\circ$ (left hand diagram, Fig. 1), the majority of the Pickering particle surface resides mainly in the water phase and can be classified as being hydrophilic. If used solely to stabilise an emulsion, it will produce an oil-in-water emulsion. Adversely, if $\theta_{ab} > 90^\circ$, a larger fraction of the particle will remain in the oil phase (right hand diagram, Fig. 1) and thus water-in-oil emulsions will form. These Pickering particles are said to be lipophilic. Where $\theta_{ab} = 90^\circ$, (centre diagram, Fig. 1) there is no curvature of the interface and there is no preference for emulsion formation. It is also at around this contact angle that the particles possess the highest energy of detachment to the interface (Equation 1). However, when the contact angle approaches 0-20° or 160-180°, the $-\Delta_{int}G$ rapidly decreases and becomes comparable to that of surfactants. The particles can then easily become detached from the interface and stabilisation is severely reduced.

Modified starch, modified cellulose and flavonoids are three types of food-grade materials that can be used as Pickering particles. These particle groups have been selected for investigation as they are abundant in nature, edible as well as being relatively cheap. The particles employed were: two modified celluloses (colloidal microcrystalline cellulose and hydroxypropyl methylcellulose), two flavonoids (rutin and naringin) as well as a modified starch (octenyl succinic anhydride). It is the intention of this current work to investigate particle size and wettability of these food-grade particles and understand the effects these properties have on oil-in-water Pickering emulsions in terms of droplet size and stability.

References

- [1] Tcholakova, S., Denkov, N.D., and Lips, A., *Comparison of solid particles, globular proteins and surfactants as emulsifiers*. Phys. Chem. Chem. Phys., 2008, **10**, p. 1608
- [2] Binks, B.P., and Lumsdon, S.O., *Influence of particle wettability on the type and stability of surfactant-free emulsions*, Langmuir, 2000, **16**, p. 8622
- [3] Aveyard, R., Binks, B.P., and Clint, J.H., *Emulsions stabilised solely by colloidal particles*. Adv. Colloid and Interf. Sci., 2003, **100**, p. 503