Mixing Time, Inversion and Multiple Emulsion Formation in a Limonene and Water Pickering Emulsion

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1) Background

Surfactants, proteins or particles?

Phase inversion of oil and water happens as the system tries to reduce its energy. The interface between oil and water is energetically expensive, so the system tries to reduce its area.

It is possible to predict emulsion type from the contact angle of the stabilising particle.

2) Emulsification

The ingredients are just particles. Influencing the resulting emulsion type.

Three main ways of stabilising an emulsion exist: using surfactants, proteins or particles. We focus on the latter case.

Droplet shapes and sizes vary with mixing time. The times in the course of each panel reflect the mixing time for that sample. At low emulsification times, there are bare patches upon the interface, allowing arrested coalescence to occur. As such, there is a distribution of small droplets, and larger, coalesced droplets. At later times, the gap between small and large droplets reduces until the 20 minute panel, where a large, irregularly shaped droplet can be seen.

3) Phase inversion

Phase Inversion with mixing time

A set of five microscopy images are taken at the same concentration of silica at different mixing time. The water was dyed with Nile Red at a concentration of 2.5 μM.

4) Rheology

The rheology experiments were all done using a concentric cylinder geometry. The emulsions examined were not the same as above, showing phase inversion. Instead a simple system was examined with pre-dispersed silica. This allowed us to separate the effects of lumps of particles and droplet size on the resultant rheology. The aim was to see how different droplet sizes flow.

A range of water-in-oil emulsions were made up with different size droplets. By controlling the silica concentration, we were able to emulate a stock dispersion of silica-in-oil. These emulsions had the advantage of no particle clusters present.

Oscillatory rheology showed that the storage modulus (G’) is dominant, particularly for small droplets. This tells us that they are elastic, and as such is not to deform and flow.

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5) Microscopy

Confocal fluorescence allows the water (black), limonene (pink) and silica (bright yellow) to be visualised. The arrows point to silica clusters, an emulsified silica structure and a multiple emulsion droplet respectively.

6) Statistics

Left, Matlab was used to segment the microscopy to get quantitative data from analysis. Large and small droplets were separated by a 20 μm interface threshold.

The size normalisation of silica clusters matters. On average clusters are broken up. However, a small number of large, dense clusters are seen in the interface of flabby, large droplets身旁. This is reflected by the silica clusters. After breaking off from the interface, small droplets disappear when weighting the average by cluster volume.

7) Conclusion

Unifying emulsification experiments with rheology

Where you put the particles to begin with is important!

Mixing the same composition for different times lead to completely different emulsions with different flow properties. This emulsion is made up of hard particles so we see that the droplets undergoing this transformation are water-in-oil.