

Stability of Pickering Emulsions

FIG. 31 exhibits optical microscopic images of water-in-decane Pickering emulsions stabilized by extensospheres in the case of (a) two isolated drops and (b) multiple drops. The diameters of the drops were within the range $d=659.3\pm 19.0$ μm . We note that these water-in-decane Pickering emulsions are very stable over long periods of time (more than a month) and that even drops which are very close to each other do not merge.

Change in Particle Distribution on the Surface of a Single Drop

In order to evaluate the influence of an externally applied uniform electric field on the particle distribution on a drop surface, we prepared first a single water drop immersed in decane and surrounded by extensospheres, and second a single silicone oil drop immersed in corn oil surrounded by the same particles. In order to make sure that we could clearly observe the particles on the drop surface, we sprinkled a sufficient number of particles while also making sure that particles would not cover the entire drop surfaces. In FIG. 32, the electrodes were located at the top and bottom of the photographs for FIGS. 32(a-c) and 32(g-i) while the electric field was normal to the sheet of paper for FIGS. 32(d-f) and 32(j-l). The maximum voltage applied was 2500V and the frequency of the AC field was 1 kHz for the two top rows and 100 Hz for the two bottom rows. In the first configuration (first and third rows), the particles were observed to migrate toward the poles of the drop (FIGS. 32(a-c) and 32(g-i)), and the particle density near the poles was seen to increase with the applied voltage. Notice that in this case the combined Clausius-Mossotti factor ($\beta\beta'$) is positive, thus leading to a motion of the particles toward the regions of maximal electric field strength, i.e. near the poles of the drop. Furthermore, particles which tend to form chains because of particle-particle interactions move together to the poles. Chains, however, are always more difficult to move than individual particles and it takes a higher voltage to bring chains to their final destinations. It is interesting to note that, as the electric field strength increases, chains which formed away from the poles and hardly moved at lower voltages also ended up migrating to the poles. This increased the uncovered areas away from the poles. In contrast, in the second configuration (second and fourth rows) the combined Clausius-Mossotti factor ($\beta\beta'$) is negative, which led to a motion of the particles toward the equator of the drop. There was no significant difference between the physical phenomena observed at the two different frequencies.

First and third row panels ((a-c) and (g-i)): A water drop is immersed in a decane solution (the combined Clausius-Mossotti factor is $\beta\beta'=0.2731>0$); it is clear that in this case particles cluster at the poles of the drop. Second and fourth row panels ((d-f) and (j-l)): A silicone oil drop is immersed in corn oil (the combined Clausius-Mossotti factor is $\beta\beta'=-0.0036<0$); it is clear that in this case particles cluster at the equator of the drop.

Destabilization of Pickering Emulsions Using an Electric Field

We now investigate the possibility of destabilizing Pickering emulsions in which drops are covered with particles. For this purpose, we first focus on the coalescing behavior of two drops subjected to an external uniform electric field. FIG. 33 shows time-sequences of two drops around the time of their coalescence for two different systems: water drops immersed in decane, or emulsion of type I, (top row) and silicone oil immersed in corn oil, or emulsion of type II, (bottom row). Recall that the combined Clausius-Mossotti factor $\beta\beta'$ is positive in the first case and negative in the second case. Note also that in both cases the axis joining the centers of the drops is inclined with respect to the direction of the electric field. When the electric field is turned off, the Pickering emulsion is

stable, and no coalescence takes place between adjacent drops even when the latter are in contact with one another (FIGS. 33a, d). However, shortly after the external electric field is applied, adjacent drops are seen to form bridges in between each other and subsequently merge (FIGS. 33b, c and FIGS. 33e, f). Here, we speculate that the motion of the particles and the subsequent uncovering of areas on the drop surfaces are at the origin of such mergers. For emulsions of type I (with a positive combined Clausius-Mossotti factor), particles are attracted to the poles of the drop, and for emulsions of type II (with a negative combined Clausius-Mossotti factor), particles are attracted to the equator of the drop. In both types of emulsion, as particles move they also leave other areas of the drop surface uncovered, thus breaking the particle barriers at those locations. Through these exposed areas, bridges can form in between drops and subsequently drops coalesce due to the tendency of the drops to minimize their surface energy.

If the previous scenario is correct, drops for which the line joining their centers is parallel to the external electric field in a type I emulsion should not merge. This was found to be the case, as demonstrated in FIG. 34a-c (top row). Likewise, drops whose line joining their centers is normal to the electric field in a type II emulsion do not merge, as shown in FIG. 34d-f (bottom row). Note that in both cases, the voltage applied (2500 V) exceeded the voltages used to induce drop coalescence in FIG. 33. On the other hand, drops for which the line joining their centers is aligned with the electric field are observed to merge in a type II solution, as displayed in FIG. 35. Recall that this was not the case in a type I solution (FIG. 34a-c). These observations indicate that the particle motion, rather than the elongation of the drops, is at the origin of the drop coalescence process. Finally, it is worth noting that while the position of the particles in a type II solution would allow drops whose line is normal to the electric field to merge, this scenario does not usually take place as in this case the drop-drop electrostatic interaction force is repelling and drops move away from each other.

An interesting drop arrangement is one in which three drops are next to each other in type I emulsion, two of the drops being on top of each other, and the other one being located on the side, in between the first two drops (see FIG. 36). In agreement with the scenario previously described, the drops on top of each other do not merge directly. Instead the bottom drop coalesces with the drop located on the side which, in turn, merges with the top drop. FIG. 37 shows a larger number of drops merging under a sufficiently large electric field.

It is noteworthy that merged drops are not spherical even after the electric field is turned off. These non-spherical drops are stable due to the fact that the surrounding particles are over-packed and trapped at the surface of the drops. A normal stress balance at the surface of a drop requires that

$$\Delta P = \frac{\sigma_1}{R_1} + \frac{\sigma_2}{R_2} \quad (8)$$

where ΔP is the pressure jump across the surface, R_1 and R_2 are the local principal radii of the curvature of the drop surface, and σ_1 and σ_2 are the corresponding principal surface stresses. In nature, unequal stresses ($\sigma_1 \neq \sigma_2$) are not supported for a normal fluid surface. However, the over-packed Pickering emulsions are capable of supporting such uneven stresses due to the jamming of the particles trapped on the surface after drop coalescence. Several experimental and theoretical studies have indeed shown that non-spherical Pickering emulsions can form when the surrounding particles are over-packed at the surface of drops (Aveyard, R., Clint, J. H.,