Miniemulsions: what we know, what we think we know, & what we do not know

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Miniemulsion technology can be applied to prepare a variety of unique materials from hybrid to encapsulated nanoparticles. Miniemulsions are often described as relatively stable submicron oil-in-water emulsions consisting of small droplets in the size range of 50 to 500 nm, whose stability is brought about by the presence of a stabilizer, such as a surfactant, adsorbed on the surface of the droplets and a costabilizer, a low molecular weight and low water solubility compound present inside the droplets. This description might be considered vague by some, too specific by others, and still too narrow or too broad. Not all miniemulsions have to be oil-in-water; water-in-oil miniemulsions are possible if uncommon. The size range is somewhat arbitrary and has been extended by some in either direction. However, this says nothing of the droplet size distribution except that it could be broad. In fact, relatively little is known about droplet size distributions owing to difficulties in reliably measuring them. Methods such as acoustic attenuation spectroscopy and capillary hydrodynamic fractionation are being investigated for this purpose.

Perhaps the most controversial part of the description of miniemulsions has to do with stability, its requirements, and its nature. Note that *relatively* qualifies *stability*. This is because miniemulsions seem to have stability lying between its neighbors, microemulsions and conventional emulsions. The former are thermodynamically (infinitely) stable while the latter usually separate within minutes of removing a source of mixing. Miniemulsions are not thermodynamically stable in that they do not have unlimited stability but they do rely on thermodynamics to provide for limited stability. Here it is the presence of the costabilizer that brings this about. Although most use costabilizers such as hexadecane which reside inside the droplets, not all are exclusively inside; cetyl alcohol (hexadecanol) resides chiefly on the surface of droplets and acts in concert with the surfactant to provide stability. Although high shear is commonly used to prepare miniemulsions, the early work did not require it. Recently some have claimed that the neither the costabilizer nor high shear is needed to make 'miniemulsion-like' dispersions. Others have claimed polymers as effective costabilizers taking away the low molecular weight requirement. This is thermodynamically unfavorable reducing the capacity of droplets to retain monomer. When a miniemulsion is first formed, monomer (provided it has a finite water solubility) shifts from small to large droplets (Ostwald ripening). This is expected to occur both during and after the emulsification process. As droplets are broken, coalesce, and are rebroken during sonification or with each pass through a high shear device such as the Microfluidizer, the distribution of the droplets evolves. So not only do the droplets have a distribution in size but they also have a compositional distribution. And these are seldom, described, reported, or even acknowledged to exist in the literature. Polymerization also brings some redistribution of monomer in response to the polymerization mechanism and thermodynamics. The so-called one-to-one copying of droplets to particles is a rarity in real systems.