Technology

Understanding Surfactants And New Methods Of Dispersing Them

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Surface-active agents, or surfactants for short, are compounds that lower the surface tension of a liquid and lower the interfacial tension between two liquids. Surfactants are amphiphilic in nature, possessing both hydrophilic (affinity for water or aqueous phases) and lipophilic (affinity for oily or organic phases). The unique combination of these opposing properties in the same molecule is what enables a surfactant to reduce surface and interfacial tensions.

When present in high concentrations — above what is known as critical micelle concentration, or CMC — surfactant molecules will assemble in the bulk solution and form aggregates known as micelles. This tendency to orient at surfaces and form micelles allows surfactants to perform a number of basic functions.

Surfactants act as foaming agents, emulsifiers, and dispersants, suspending gases, immiscible liquids, or solids, respectively, in water or some other liquid. Solubilization, a function closely related to emulsification, is a condition where suspended droplets and surfactant micelles are of the same size. Finally, detergency is a complex combination of all the previous functions. Surfactants suspend, solubilize, dissolve, and separate soil from a surface being cleaned.

A surfactant accomplishes these functions as it absorbs at the surfaces of the suspended material and forms a protective layer around each particle. This ultimately decreases the overall free energy of the system and increases stability of the solution by discouraging separation of the phases. In addition to surfactant effects, the stability of suspensions is related to the particle size and density of the suspended material.

While all surfactants rely on their dual-affinity nature to deliver their functionality, the kind and level of surfactant vary widely depending on the application. Chemically synthesized surfactants are commonly used in the petroleum, food, and pharmaceutical industries. For medical applications, biosurfactants (produced by microorganisms) are useful as antimicrobial agents and immuno-modulatory molecules. Biosurfactants are also common ingredients in agrochemicals, food, cosmetics, pharmaceuticals, and personal products.

Surfactants And Droplet Sizes

As a generalization, droplet size is inversely proportional to emulsion stability. As demonstrated by numerous emulsification studies over the past few decades, the presence of surfactants decreases the equilibrium droplet size of emulsions. However, there are many different explanations for the specific role of the surfactant in droplet size reduction and the mechanisms, or combinations thereof, by which it accomplishes that role. The only common finding is that surfactants in a fluid system affect several of its properties, both in their equilibrium values and in their dynamic response to changes, as well as in the physical and rheological properties of the system's interfaces.

The following sections describe a simple experiment that was conducted to provide at least a practical understanding of the effect of surfactants on liquid-liquid dispersions. The specific objective of the study was to illustrate how surfactant levels affect the droplet sizes of emulsions prepared using different high-shear rotor/stator devices.

Test Equipment Used

Three Charles Ross & Son inline high-shear mixer models were used in this experiment: Model HSM-400DL with standard rotor slotted stator head, Model HSM-703 with X-Series rotor/stator, and Model HSM-703 with MegaShear rotor/stator.

Figure 1: X-Series rotor/stator heads (left) and MegaShear rotor/stators (right)

The HSM-400DL was equipped with a 1 3/8" diameter rotor turning at 2,758 ft/min, which developed a flowrate of 10 gpm. This type of device creates mechanical and hydraulic shear by continuously drawing product components into the rotor and expelling them radially through the openings in the stator.

The X-Series head (see *Figure 1*) on one HSM-703 is a rotor/stator generator composed of a matrix of interlocking channels. The rotor turns at a tip speed of 11,300 fpm, so the product being mixed is subjected to high levels of mechanical and hydraulic shear compared to conventional rotor/stator mixers or multi-stage heads. Gap settings can be adjusted from 0.010" to 0.060" by a set of shims. For water-like viscosities, the maximum flowrate produced by a 3" X-Series head is around 11 gpm.

The MegaShear rotor/stator (see *Figure 1*) used on the other HSM-703 operates at the same tip speed as the X-Series, but is more aggressive and shear-intensive. The generator assembly consists of parallel semicylindrical grooves in the rotor and stator toward which product is motivated by high-velocity pumping vanes. Different streams are induced within the grooves, and the resulting flow pattern causes these streams to collide several times. Flowrate based on water is 39 gpm on a 3" MegaShear rotor/stator.

Test Emulsions

The test emulsions for this experiment were as follows:

99.64–99.995%	1:10 canola oil in water
0.045–0.36%	Tagat TO (non-ionic surfactant)
100%	Total by weight

The emulsions were prepared using a laboratory mixer with 2" saw-tooth disperser blade operating at 4,000 rpm. The water and surfactant were agitated, and the oil phase was added over a 1-minute period. After 2 minutes of agitation, the emulsion batch was measured for particle size and split into three equal portions.

Test Procedure

Each emulsion batch was passed through the three inline high-shear mixers running at their maximum speeds. Samples were collected after a single pass. Particle size distributions were generated using a Malvern Instruments Mastersizer X laser particle size analyzer.

Test Results And Findings

No uniform trend was observed across surfactant levels, possibly indicating that the optimal concentration was not within the experiment's range. The expectation was that increasing the amount of surfactant in the solution would result in smaller droplet sizes, but only up to a certain level, at which point droplets would start to coalesce. The more consistent results come from droplet sizes produced by each high-shear mixer device (see *Figures 3* and *4*).

Test Conclusions

As shown in *Figures 3* and *4*, very similar distributions were detected by the laser particle size analyzer for each rotor/stator design, regardless of the variation in surfactant level. This indicates that for the dilute solutions prepared, shear input had a more significant effect on the resulting particle size than surfactant level.

More robust experimental matrices are needed to comprehensively quantify these relationships. The results of the study nonetheless important for anyone considering improving the particle size distribution of emulsions. Modifying emulsion formulations by adding more (or less) surfactant could lead to better results.

It should be noted that new high-shear mixers have a potential to redefine not only product standards through improved stability, but also production rates and maintenance requirements. A comparatively sized (horsepower-wise) ultra-high shear mixer generates lower throughputs that a standard rotor/stator, which has clearances that are not as tight. Temperature effects must also be taken into consideration, as some products could degrade or change properties with the elevated temperatures usually associated with ultra-high-shear mixers.

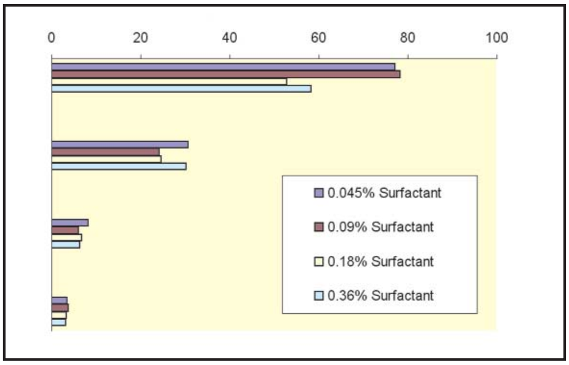

Figure 3: Median droplet size, in microns

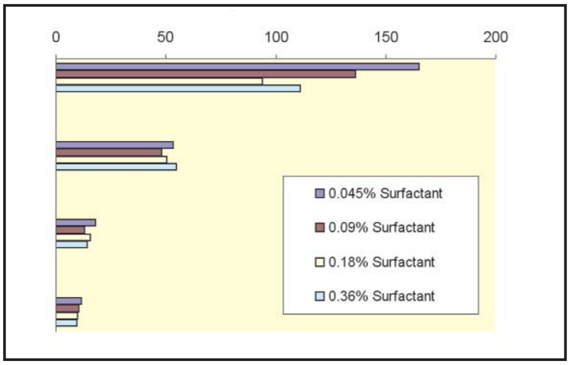

Figure 4: D90 droplet size, in microns

Why Is Mixer Choice Important?

Reevaluating the mixing process has the potential to fine-tune product formulation. The ability to reduce surfactant levels without compromising end product performance and quality provides a number of advantages related to biodegradability, cost, and foaming issues. In personal-care or medical products, this can reduce or eliminate irritating effects on the skin. In the manufacture of pressure-sensitive adhesive emulsions, minimizing the amount of surfactants cuts the need for defoaming agents. One problem associated with wetting agents and defoamers is that they can be adsorbed by the polymer particles, thereby altering the coating performance of the emulsion. This leads to product rework and/or scrap. ◆