Part one: The incredible shrinking Micelle
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By Steve Herman

Part One
The Incredible Shrinking Micelle

"The eyes see only what the mind is prepared to comprehend."
— Henri Bergson

Nothing is dearer to the cosmetic formulator than the amphiphilic molecule. The amphiphile, part water loving, part oil loving, bridges the gap that makes many cosmetics possible. The greatest gift of these molecules is the emulsion.

What strikes us first as we look at an emulsion? One common feature of creams and lotions in their native state is their white, milky appearance. This property is rooted in the science of optics. When light goes from one substance to another, its speed can change, bending its path. This can be observed in a straw immersed in a glass of water, which appears to change direction at the surface (assuming it isn't straight up and down). Air near a hot surface such as a road or sand can be warmer than air further from the surface, refracting light. The result is the appearance of a puddle on the road or a mirage in the desert.

In an emulsion, the difference in refractive index between the oil phase and the aqueous phase bends light in a multitude of random directions. The waves go in clear and emerge as a white jumble, since white is a mixture of all the visible wavelengths. For refraction to occur, the micelle size must be at least roughly comparable to the wavelength of light, so the light can "see it." Typical "macroemulsions" have micelle sizes ranging from 2000 to 100,000 Å (Å, an Angstrom is 10^{-10} m).

Microemulsions, on the other hand, are transparent. Their micelles are too small to deflect the incoming waves. White light has an average wavelength (λ) of 5600 Å. When micelles are smaller than around 1400 Å, white light passes directly through.

Like so many technological marvels, microemulsions were discovered by accident and used for years without a firm theoretical foundation. Their origin came in St. Louis, Missouri in 1928. George Rodawald was working on finishes for leather. He was impressed by the performance of a carnauba wax emulsion, and developed a formula similar to this (courtesy of Frank B. Ross Co):

Carnauba Wax	120
Oleic Acid	20
Triethanolamine	18
Caustic Soda (50%)	8
Water	834

Carnauba wax was uniquely suited to the emulsification process due to its abundant hydroxy groups.

A floor polish (Dri-Brite) based on this technology was launched. The small micelle size characteristic of microemulsions was the key to Dri-Brite's success. The small particle size left a uniform film on the floor that did not require manual buffing.

It was left to an academician to explain this new product development. Dr. Jack Schulman at Columbia University began his studies on what he then termed oleopathic hydro-micelles in the early 1940s, coining the more poetic microemulsion in 1958. Schulman alone, and later in collaboration with Leon Prince, laid the foundation of our current understanding of this area of surface chemistry.

Microemulsions can be viewed from at least two significantly different but equally valid perspectives. One approach is to consider them to be mini-versions of conventional emulsions. Garden variety emulsions are

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*Greek kosmEtikos, skilled in adornment or decorating.

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never truly stable, since coalescence will always decrease the Gibbs free energy, ΔG. If a microemulsion is just a normal emulsion with a very small micelle size, we must be concerned with thermodynamic instability. In this instance, the method of manufacture is important. A micelle of this sort is depicted in Figure 1. It is closely packed, and has a relatively limited internal phase.

Alternatively, if the microemulsion is a thermodynamically stable system, $\Delta G=0$. We can casually toss the right ingredients together and they will spontaneously form a microemulsion.

Figure 1 MICROEMULSION MICELLE

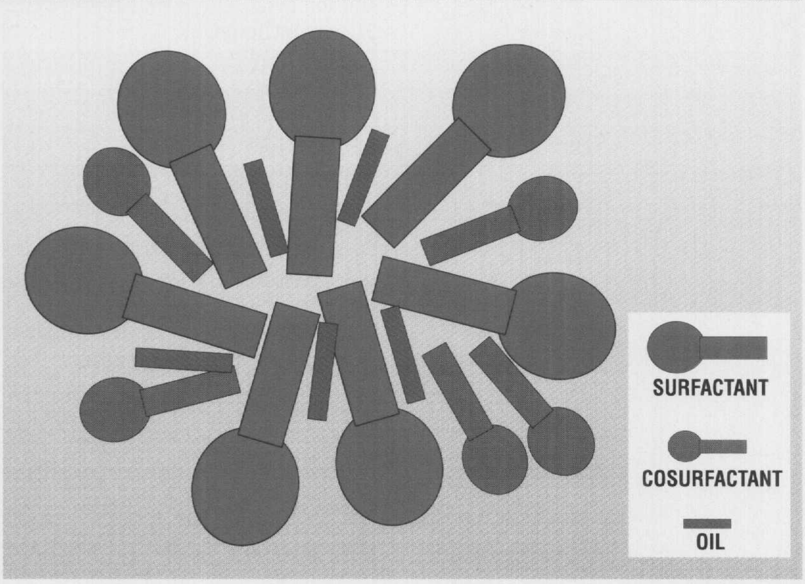
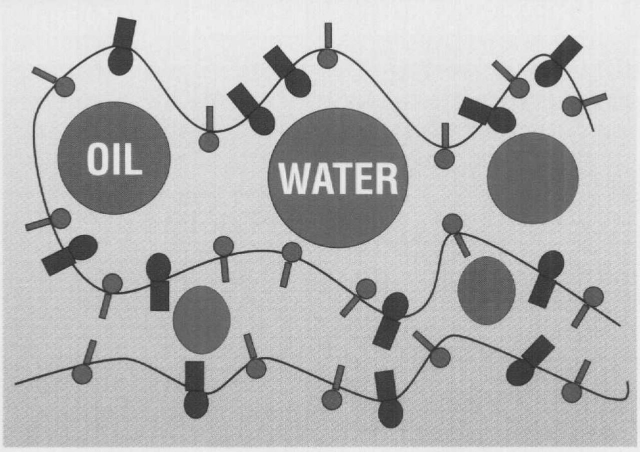


Figure 2 MICROEMULSION BICONTINUOUS STRUCTURE



The basic components of the formulation are oil, water, a surfactant, and a cosurfactant.

The distinction between a surfactant and cosurfactant is not precisely defined. They are both surface active, but not necessarily both traditional emulsifiers. In some systems, the surfactant is a high HLB amphiphile and the cosurfactant is a medium chain length fatty alcohol. Alternatively, a lower HLB ingredient can be considered the cosurfactant. It really doesnt matter—what is crucial is that the two surfactants can pack together well at the interface.

The thermodynamically stable system differs radically from the conventional view of emulsions with spatially defined and temporally fixed micelles as the characteristic feature. Instead, a loosely formed bicontinuous structure is present (Figure 2). The combination of properly chosen surfactant and cosurfactant profoundly reduces the rigidity of the interfacial film. Microareas of water and oil are separated by a flexible amphiphilic barrier. The emulsion is a dynamic rather than static system.

A reasonable rule of thumb for macroemulsions is to have 10-15 percent of the oil phase as emulsifiers. For a 20 percent oil O/W emulsion, that would translate into 2-3 percent emulsifier in the total product. By contrast, microemulsions typically contain 20-30 percent emulsifier. This is the most dramatic formulation difference between macro- and microemulsions.

We have set the stage. Next month we will examine some additional properties of microemulsions and their application to skin and hair care. ■

References

The classic text is:

Prince, Leon M., ed, Microemulsions Theory and Practice, Academic Press, 1977.

A good short account is found in:

Whitthamn, James H. et. al., Microemulsions: a new technology for the cosmetic industry, Cosmetic Technology, October 1979.