Formulating Water-in-Oil Emulsions: A Scary Endeavor

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Formulating water-in-oil emulsions is inherently more difficult than oil-in-water emulsions. While there are several reasons for this, probably the most important one is that these emulsions (usually) do not have a clearly defined electrical double layer surrounding the emulsion droplets; thus there is a greater likelihood of coalescence. While water-in-oil emulsions have become more popular in the United States in recent years due to their rising popularity in the sunscreen arena, they have enjoyed widespread use in Europe for many years. I have never heard a good explanation for this geographical discrepancy.

I can't tell you how many times that chemists have told me that the emulsion they made must be water-in-oil since they'"added the water phase into the oil phase!" This, of course, is nonsense. Another comment I hear is that I have more oil than water in my emulsion, so oil must be the external/continuous phase. More nonsense.

One thing that I have noticed in recent years as we have developed more efficient W/O emulsifiers is that the ratio of oil to water is basically the same whether we have a W/O or O/W emulsion. As a general rule, the amount of water is approximately 60-80%. We should remember that if the internal phase ever exceeds 74%, we no longer have only spherical droplets. The type (O/W or W/O) of emulsion you wind up with is almost entirely dependent on the emulsifier.

Bancroft's Rule tells us that wherever the emulsifier is most soluble will become the external/continuous phase. One tried-and-true way to determine which type of emulsion you have is to add water to it with propeller mixing. If the water is readily incorporated and the viscosity drops, you can be quite certain that the emulsion is O/W. If, on the other hand, it required quite a bit of mixing to incorporate the water and the viscosity actually increases, then the emulsion is W/O. I find this test to be easy and generally reliable.

There are various things to consider when formulating W/O emulsions.

Manufacturing Procedures

When making O/W emulsions you have many options. You can:

- Add the oil phase to the water phase;
- Add the water phase to the oil phase (causing a phase inversion);
- Dump everything into one pot and heat to 80°C; or
- Make an emulsion concentrate and then dilute out the external (water) phase.

Unfortunately, these options are not open to you when making W/O emulsions. The water phase must be slowly added to the oil phase, making sure that the water does not pool up excessively on the surface. Some people claim they have made W/O emulsions in a one-pot procedure, or have even claimed to have added the oil phase to the water phase. However, I must admit that I have never successfully made W/O emulsions other than by adding the water phase *slowly* to the oil phase (which contains the emulsifiers).

Another issue that must be discussed is homogenization. As a general rule, I believe that W/O emulsions should be homogenized. In fact, it is more important to homogenize W/O emulsions than O/W emulsions since the reduction in interfacial tension is not as pronounced in these emulsions.

Emulsifiers

Choosing emulsifiers is always an arduous task. Generally, when formulating oil-in-water emulsions, never use a single emulsifier. By combining emulsifiers, the oil/water interface is enhanced/strengthened, and a more stable product results.

This same logic doesn't necessarily work for water-in-oil emulsions. Often adding a second emulsifier will destabilize the system. Unfortunately, it is difficult – if not

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impossible – to predict this. Sometimes we can add very low levels (0.1-0.25%) of hydrophilic emulsifiers (alkyl polyglucosides, cationic-monoalkyl materials, Gemini surfactants with two polar head groups each with a fatty tail separated by a spacer, etc.) and they will dramatically improve emulsion stability. The uncertainty can even be frustrating to an experienced formulator!

A good emulsion formulator can look at the structure of an oil-in-water emulsifier and have a good degree of certainty whether or not it will stabilize (or destabilize) the emulsion. The same, I'm sad to say, is not true for water-in-oil emulsifiers. Some emulsifier types include polyglyceryl esters, ethoxylated esters and ethers, polyvalent soaps (magnesium stearate, calcium stearate, aluminum stearate), dimethicone copolyol, alkyl dimethicone copolyol and sucrose esters.

Stabilizers

It is well known that the addition of electrolyte often destabilizes oil-in-water emulsions. A notable exception to this "well-known" phenomenon is cationic emulsions, where "salt" is often added to improve stability. Water-in-oil emulsions are stabilized, particularly the freeze-thaw stability, through the addition of electrolyte. Trial and error will tell you if sodium chloride or magnesium sulfate is more appropriate to your system. Sometimes the addition of a glycol (propylene glycol, glycerin, M,P diol, etc.) can also have a beneficial effect. However, be advised that adding both electrolyte and glycol (at high levels) can destabilize your emulsion.

Thickening Agents

We have come to rely on the addition of gums and polymers (natural and synthetic) to stabilize our oil-in-water emulsions (remember Stoke's Law). Unfortunately, the same type of materials are not available to us to thicken the external phase (oil-based) of water-in-oil emulsions. We must rely on the addition of waxes and other similar oil-soluble materials (polyethylene) to thicken/stabilize our emulsion.

The problem is that, generally, these materials do not impart viscosity at high (45˚C and higher) temperatures and, thus, high temperature stability can be a problem. Interestingly enough, the addition of typically used water phase thickeners (xanthan gum, carbomer, etc.) can reduce syneresis (water bleeding) and improve emulsion spreadability (play time).

Preservation

Water-in-oil emulsions are inherently less prone to bacterial contamination than are their oil-in-water cousins. This is due to the fact that the phase which permits (and encourages) bacterial growth is discontinuous and does not act as an easy medium for bacterial proliferation. Having said this, a potential problem still does indeed exist, and we must make sure to use adequate preservative systems that take into account materials such as gums, proteins, sugars, etc., that are tasty "food" for bacteria.

Water-in-Oil Applications

With all these difficulties, why should we persist in making these emulsions? There are several answers to this question. Water-in-oil emulsions are sometimes the best vehicle for a particular application.

Sunscreens: It is well known that water-in-oil sunscreen emulsions are more efficient with a higher SPF for the same percentage of sunscreen and will be inherently very water-resistant. In fact, I don't know how to make a water-in-oil sunscreen emulsion that isn't very water-resistant.

Makeup: Using a water-in-oil emulsion in makeup will insure smooth application because skin is hydrophobic. It also prevents smudging if a volatile solvent is used and gives great skin feel if the right "oils" are used.

Moisturizers: Very often we are asked to formulate a product designed for compromised skin, i.e., skin with an impaired barrier. The emulsifiers used to form water-in-oil emulsions are inherently mild and will not disturb the lipid bilayers between the skin cells. Thus, the TEWL (Trans Epidermal Water Loss) is minimized. Water-in-oil emulsions are perfect for dry skin.

As we can see, formulating this type of emulsion is not an easy task. But, rest assured, the performance of these systems makes the hard work worth it.

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