Science and Engineering of Emulsification

The only thing one can be certain about emulsion is: there is nothing certain.—
Anonymous

Arts and Science of Emulsion Making

Adel was an experienced product manager for skin care products with whom I had the pleasure of working frequently as a young chemical engineer while learning the art of formulating cosmetic emulsions. Adel was a perfectionist. The first project I worked on was a moisturizer, for which I developed an oil/water (o/w) emulsion. When I brought the first sample to her, she dipped her finger into the product, looked at the texture of the emulsion, smelled the product and then rubbed the product between her thumb and index finger and said, "It looks OK, but doesn't feel right." I was not sure what she meant by her fairly ambiguous description that the sample did not feel "right," so I asked for further explanation. She said, "Try it, this lotion doesn't have it!" leaving me no more clear about what she meant. I figured that she was referring to some physical properties of the sample, but, frankly, I was unable to divine the exact meaning of "it" even after I repeatedly rubbed the product between my fingers, using her method.

After several more submissions and frustrating rejections, I began to suspect that what Adel wanted was incorporation of certain rheological properties into the product. The emulsion I developed was a non-Newtonian, shear thinning type with yield value. I sensed that she liked the look of my emulsion because the yield value made the lotion look "rich" (viscous) and not runny (low viscosity). On rubbing (applying shear stress), the viscosity of this shear thinning emulsion would be reduced, making the product not sticky and easily absorbed into skin. Thinking in terms of rheology, I concluded that while she liked the shear thinning property of my lotion, she objected to it having too much shear thinning effect, making the product feel not "substantial" enough to her.

My rheological reasoning plus a significant amount of trial and error work in the laboratory finally yielded a formulation with just the right amount of shear thinning characteristic for Adel. I can still recall her expression—and my great relief—after she tested my revised formulation and declared, "This is it!" I learned a very valuable lesson from Adel in working on this product—skin feel can be strongly associated with quality by consumers of skin care products. I also learned the important art of using one's fingers to assess certain rheological properties of emulsions.

Like a good cook, a skillful cosmetic formulator must learn how to pick the right ingredients and blend them correctly to achieve an optimum result. In addition to its required functions, a cosmetic cream must look attractive, feel nice on the skin, smell pleasant, and above all, remain stable during its shelf life. Creating good formulations requires much skill, experience and patient trial and error laboratory work.

Likewise, manufacturing the emulsion in large scale production also requires a great deal of art and good engineering. Processing an emulsion requires correct control of key process conditions, as variables such as emulsification temperature, mixing speed and cooling rate can all significantly affect the quality of the end product. While acquiring the skill and understanding of the art necessary to formulate and manufacture high quality emulsions requires patience and time, it is worth the investment because this understanding is needed not only in formulating elegant and functional products, but in manufacturing them with consistent quality, as well.

Moreover, understanding of the related science can be crucial to solving many complex problems involving emulsions. Emulsion stability is often difficult to predict because the problem can be caused by so many factors, including use of defective or incorrect raw materials, unknown incompatibility or interactions of ingredients, or incorrect equipment or manufacturing procedures. When a manufacturing problem arises, it is easy to point fingers, pinning the blame on the compounder for not strictly following the specified procedures, for example. But ascertaining the correct procedure for a new product is not always easy because each emulsion can behave differently from others, making it often difficult to pinpoint the actual cause of the problem.

In some companies, manufacturing instructions are prepared by formulation chemists who have little or no production experience in the factory. I have worked with many experienced compounders at different cosmetic factories in the past and observed that they would, often, ignore certain manufacturing instructions prepared by the laboratory staff and use their own procedures (or "shortcuts") to make batches. Frequently, their experience and judgments proved correct, enabling them to simplify procedures and facilitate manufacturing process. However, other times their own version of revised procedures got them into trouble. I believe that a good understanding of the basic scientific principles in rheology, thermodynamics and surface chemistry can be very helpful in understanding problems and in shortening the time required to acquire various skills necessary to formulate and manufacture cosmetic emulsions.

Rheology and Cosmetic Formulations

Rheology is the science and study of flow properties of matter.[1,2] Understanding and controlling of the rheological properties is important in manufacturing cosmetic emulsions because many important product attributes, including appearance, skin feel, stability and even product performance can be strongly affected by any change in these properties. The smooth, fluffy look and luxurious feel of a night cream, as well as the ease of applying mascara on eyelashes or squeezing toothpaste out of tube, can be strongly affected by the product's rheological properties. As cosmeceutical skin care products gain popularity, cosmetics are becoming more like drugs and more attention is being given to the percutaneous absorption rate by which active ingredients are delivered into the skin. This rate can be strongly affected by the product's rheological properties. The degree of protection offered by a sunscreen, for example, is strongly affected by the thickness of the applied film, which is also dependent on the rheological properties of the product.

Viscosity is the measure of a fluid's resistance to flow. A force is needed to create flow of a liquid or semisolid, and depending on its internal friction (viscosity), the fluid can move rapidly, slowly or remain unmoved. Viscosity can be accurately measured with a viscometer, for example, by using the popular Brookfield viscometers or more sophisticated rheometers. But a quick way used by cosmetic formulators to gain a rough idea of viscosity is to stir the fluid with a spatula to see how "heavy" it feels, or how fast it runs down along a spatula. In the story I recounted above, Adel measured the viscosity by rubbing the product between her thumb and forefinger. All these methods of measuring viscosity have two things in common.

The first is that the fluid must be forced to move or flow during the measurement. This action may be achieved by rotating a spindle in the fluid, stirring the fluid with a spatula, allowing the fluid to flow by gravity, or rubbing the fluid between fingers. This forced movement then creates a shearing action on the fluid.

The second is a mechanism to register the response on the fluid while this shearing action is taking place. For a rotational viscometer, it is the torque measured by a spring and registered on a dial. In a spatula test, it is the force felt by one's hand during the agitation or the time it takes for the fluid to flow down the spatula. In Adel's finger rubbing test, it is the subtle friction force experienced by her trained fingers. This registered quantity may be mechanically, mathematically or mentally translated into some sort of viscosity scale, which is related to shear stress.

More precisely, shear stress is defined as the force (F) per unit area (A) or F/A. Shear rate and shear stress are the two fundamental parameters in rheology, and Isaac Newton defined viscosity (η) as:

Equation 4.1

$$\eta = \mathit{Viscosity} = \frac{\mathit{Shear\ Stress}}{\mathit{Shear\ Rate}}$$