Emulsions and Emulsifiers

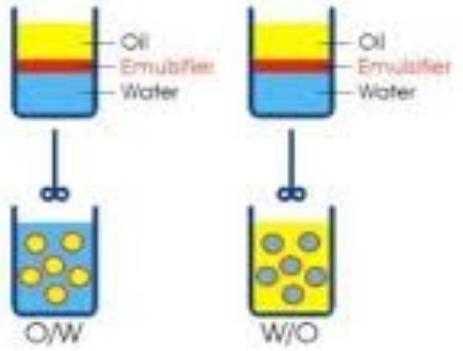
It is common knowledge that oil and water don't mix. If you try to mix them together they quickly separate, with the water sinking to the bottom and the oil floating on top. If you mix them very vigorously one of them will break up into droplets and disperse in the other. But even this dispersion won't last long and the two will soon separate as before.

Vigorously mixing oil and water has two possible outcomes: In one, droplets of oil are dispersed in a continuous phase of water. In the other, droplets of water are dispersed in a continuous phase of oil. The first form is called an oil-in-water emulsion (oil droplets dispersed in water, or O/W emulsion for short), while the second form is called a water-in-oil emulsion (water droplets dispersed in oil, or W/O emulsion).

Distinguishing between an O/W emulsion and a W/O emulsion is very important, because the mouth senses only the continuous phase rather than the dispersed phase. Mayonnaise is a perfect example. Mayonnaise contains about 80% oil and 20% vinegar, plus small amounts of egg and seasoning like mustard and salt. The surprising thing about mayo is that even with four times more oil than vinegar, the oil is dispersed as tiny droplets in a continuous phase of vinegar. As a result, mayo does not feel greasy in the mouth because the mouth senses only the continuous watery vinegar phase and not the dispersed oil droplets.

Now consider a simple vinaigrette made by vigorously mixing about 3-4 volumes of oil with one volume of vinegar. In this case the vinegar becomes dispersed as droplets in a continuous phase of oil. If the vinaigrette is prepared by slowly adding the oil to the vinegar with very vigorous mixing, the W/O emulsion will usually stay together long enough to taste, and even drizzle on some salad greens. A W/O vinaigrette "tastes" very oily compared with mayo. Another example is butter, which is also a W/O emulsion. Butter feels greasy in the mouth.

But why does mayo exist as an O/W emulsion while a vinaigrette, containing the same ratio of oil to vinegar, exists as a W/O emulsion? Confused? The answer is actually quite simple. The mayo contains egg and mustard which act as *emulsifiers* to stabilize the oil as droplets. Emulsifiers are substances that facilitate the dispersion of one phase (as tiny droplets) into another. A simple vinaigrette does not contain emulsifiers so the smaller volume of vinegar ends up being dispersed as droplets in a much larger continuous phase of oil. Without an emulsifier the liquid used in excess usually forms the continuous phase.



Egg yolks contain lipoproteins and phospholipids, like lecithin, that coat the surface of the oil droplets and prevent the droplets from coalescing and forming a continuous phase even though the volume of oil is four times greater than the volume of vinegar. But not all emulsifiers stabilize the oil as droplets. Some are better at stabilizing vinegar as droplets. It depends on the properties of the emulsifier.

As a general rule, the continuous phase is the one in which the emulsifier is soluble. If an emulsifier is more soluble in oil, then oil will form the continuous phase regardless of the proportions of oil and vinegar. Similarly, water-soluble emulsifiers stabilize vinegar as the continuous phase. In the home kitchen we have relatively few emulsifiers to pick from, namely egg yolks, mustard, and casein in milk. Both egg yolks and mustard tend to stabilize emulsions with oil droplets suspended in vinegar. That's why adding a little mayonnaise, which contains egg yolks, to a mixture of 3 parts oil to 1 part vinegar forms a fairly stable oil-in-water emulsion.

The food processing industry has many more emulsifiers to pick from (literally dozens). They range from water-soluble to oil-soluble. The solubility properties are expressed in terms of the emulsifier's *hydrophilic-lipophilic balance* (HLB). Hydrophilic substances are water loving, while lipophilic substances are fat (oil) loving. The HLB scale runs from 0-20. Emulsifiers with a high HLB value are hydrophilic and water-soluble (example: sodium stearoyl lactylate). Emulsifiers with a low HLB value are oil-soluble (example: glycerol monostearate). Emulsifiers with HLB values between 3-6 stabilize W/O emulsions, while emulsifiers with HLB values between 11-15 stabilize O/W emulsions. Emulsifiers with intermediate values (8-10) are good wetting agents (promote spreading of a liquid phase such as water onto a solid phase such as cocoa powder), but relatively poor emulsifiers.

So far I have discussed emulsions stabilized with emulsifiers. That is, the emulsifier prevents the oil and water from separating by forming a protective barrier around the droplets. But there is another way. Thickening agents like starch, flour, and gums also stabilize emulsions, but are not emulsifiers. They do not form a protective barrier around the dispersed droplets. These substances

increase the viscosity of water. When oil is dispersed in water that has been thickened with starch (the starch-water mixture must be heated first to thicken) the oil droplets will be stabilized because the high viscosity of the starch-water continuous phase prevents the oil droplets from moving around and coalescing. Can you think of any examples? Soups, sauces, and gravies thickened with cornstarch or flour form stable O/W emulsions with any fat that may be present. The O/W sauce will be creamy and smooth but not greasy because water is the continuous phase. Check the label of those super-stable creamy salad dressings in the supermarket and see if any of them contain starch.

When a stable emulsion is made it can be difficult to visually tell which is the continuous phase (oil or water). Taste can sometimes give an indication as described above. But the best way is to measure the electrical conductance. An emulsion with a continuous vinegar phase (plus a little salt) will readily conduct a low-voltage electric current, but an emulsion with an oil continuous phase will not. This method forms an interesting test using emulsions made with different ratios of oil and water stabilized with different emulsifiers, or none at all.