Emulsions: Emulsions and Surfactants in the Kitchen

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In the kitchen, emulsified systems and emulsions are frequently encountered, because most traditional food ingredients (as opposed to pure compounds used in note by note cooking; see Part III of this book), such as animal and plant tissues, contain both water and fat (Ciqual, 2018). When cooks are preparing dishes, these two non-miscible materials are often processed together, and, because energy is given (mechanical, thermal or chemical), they are frequently arranged in the form of fat “particles” dispersed in an aqueous solution; when the fat is liquid, or even when it is present as crystals, these particles are indeed droplets, and the systems are called “emulsions”, from a name created in 1560 by Ambroise Paré, surgeon of many French kings, who was considering drugs white and viscous as milk, in which he knew that there was fat and water; the word is based on the Latine *emulgere*, which means “to draw milk” (Paré, 1560).

More recently, the definition of an emulsion was standardized by the International Union for Pure and Applied Chemistry (IUPAC):

>A fluid colloidal system in which liquid droplets and/or liquid crystals are dispersed in a liquid. The droplets often exceed the usual limits for colloids in size. An emulsion is denoted by the symbol O/W if the continuous phase is an aqueous solution and by W/O if the continuous phase is an organic liquid (an “oil”). More complicated emulsions such as O/W/O (i.e. oil droplets contained within aqueous droplets dispersed in a continuous oil phase) are also possible.

(IUPAC, 1972)

In this definition, we observe that, contrary to what is frequently said or written, emulsions do not call for immiscible liquids, and this is fair, because physical chemistry is today discovering W/W emulsions, with only aqueous solutions (Bach *et al*., 2013).

Here, we want to discuss the question of emulsions from both physical and chemical points of view. What is given is not the result of personal research but rather, a collection of useful information about some common culinary systems.

**Oil Does Not Mix with Water; Surface Tension**

Let us start the discussion of emulsions and surfactants by the simple experiment of adding water and oil in a vessel (Figure 36.1). Oil poured over water from some height first sinks into the water before coming up to the surface at a velocity that can be calculated using the first principles of dynamics (see the chapter on decanting, in the Application part of this book). Of course, this phenomenon of “creaming” is due to the fact that the density of food oil is lower than that of water (Lide, 2005). But why do oil drops coalesce? This can be calculated as will be shown now, using free energy or free enthalpy, for transformations at constant pressure or at constant volume, respectively.

Let’s assume that the length of the cubic vessel is equal to 1 (arbitrary units, a.u.). Then, the surface where oil and water are in contact has an area $A$ equal to $1 \times 1 = 1$. In our world, matter, energy, electric charge and some other characteristics are always conserved; i.e., they are constant during the changes of the world. For our question, let us consider energy: any spontaneous evolution should take place as:

$$\Delta G = G_{\text{final}} - G_{\text{initial}} < 0$$  \hspace{1cm} (36.1)

![Figure 36.1](image)

**FIGURE 36.1** A system made of two layers of oil and water has less energy when oil is over water.
where the Gibbs function $G$ is equal to:

$$G = H - T. S. \quad (36.2)$$

where $H$ is the enthalpy, $T$ the absolute temperature and $S$ the entropy (McQuarrie, 2011). For example, let us imagine that oil made a layer at the bottom of the vessel, being covered with water. If $t_o$ is the thickness of the layer of oil and $t_w$ the thickness of the layer of water, then the potential energy would be (we decide that the bottom of the vessel is at zero potential energy and we consider the mass of each material at its centre of gravity):

$$W_i = W_o + W_w = m_o g \frac{t_o}{2} + m_w g \left(t_o + \frac{t_w}{2}\right)$$

$$= g \left[m_o \frac{t_o}{2} + m_w \left(t_o + \frac{t_w}{2}\right)\right]$$ \quad (36.3)

where $W_o$ and $W_w$ stand for the potential energy of oil and of water, respectively, and $m_o$ and $m_w$ are the mass of oil and the mass of water, respectively. Let us compare this energy with the one with oil on water:

$$W_f = g \left[m_o \left(t_w + \frac{t_o}{2}\right) + m_w \left(\frac{t_w}{2}\right)\right]$$ \quad (36.4)

The entropy being the same in both cases, the free enthalpy variation is:

$$\Delta G = G_f - G_i = g \left[ m_o \left(t_w + \frac{t_o}{2}\right) + m_w \left(\frac{t_w}{2}\right) \right] - m_o \frac{t_o}{2} - m_w \left(t_o + \frac{t_w}{2}\right)$$ \quad (36.5)

Or:

$$\Delta G = g \left(m_o t_w - m_w t_o\right)$$ \quad (36.6)

But of course, there is a relationship between the thickness and the mass:

$$m_i = \rho_i t_i A$$ \quad (36.7)

where $i$ stands for $W$ or $O$. Thus:

$$\Delta G = g \left(A_t w t_o \rho_o - A_t o t_w \rho_w\right)$$ \quad (36.8)

Here, the sign of $\Delta G$ is given by $\rho_o - \rho_w$, and it is negative. Thus, the evolution from a layer of oil under of a layer of water is less stable than for a layer of oil over a layer of water.

This result explains why oil comes up, but it does not explain why droplets may coalesce. Here, we need to remember that interfaces separating two media are places where molecular forces are different than in the inside of the two separated media.

This can be shown experimentally for air and water, as when water is added to a glass up to more than the maximum level of the glass (Figure 36.2). If water can remain without flowing over the level of the upper edge of the glass, it means that forces are keeping it there in spite of the potential energy that would make it flow. In this particular case, hydrogen bonds between water molecules in the bulk of the liquid keep the water molecules from moving down. Let us analyse further. If forces “group” water molecules, it means that water molecules do not “like” (in terms of energy) to be at a surface. In other words, free enthalpy depends on the area of the interface. The simplest possibility would be:

$$G \propto A.$$ \quad (36.9)

Why such a proportionality? Because it is by the interface that hydrogen bonds can act; the bigger the area, the more bonds there are. However, instead of writing:

$$\Delta G = \gamma \Delta A$$

we write more correctly:

$$\gamma = \frac{\partial G}{\partial A}$$ \quad (36.10)

The parameter $\gamma$ is called surface tension (De Gennes et al., 2004).

Here, we started from the example of the air/water interface, but there are other values depending on the two phases that are in contact. Let us come back to oil floating over water, and imagine that the oil would be divided into two parts, which are in contact with water (interfacial energy $\gamma$) (Figure 36.3).

The area of the oil increases when it is divided, because of the surface created by a cut. How much?

Let us assume an initial sample of oil of volume $V$, whose side would be $n c$:

$$V = (n c)^3$$ \quad (36.11)

The area of its surface is:

$$A_i = 6 \times (n c)^2$$ \quad (36.12)
Let us divide this sample into small cubes of side $c$. The volume of one elementary cube is $c^3$, and their number is $n^3$. The area of their individual surface is:

$$a = 6c^2$$  

(36.13)

So that the total area of all small cubes is:

$$A_2 = n^3 6c^2$$  

(36.14)

The area has changed by:

$$\frac{A_2}{A_1} = \frac{6n^3c^2}{6n^2c^2} = n$$  

(36.15)

This means that one has to give energy to the system in order to disperse oil in water.

**Surfactants**

Having observed that emulsions need energy to be produced, let us now see how the required mechanical energy can be reduced. As a start, let us examine another experiment, often used in popularization environments: starting from the previous state, with water over the level of the glass, let us dip the tip of a clean needle into the water: the needle pierces the surface without any particular effect.

Now, let us first dip the needle in liquid soap and repeat the experiment of piercing the surface: the water above the upper level of the glass flows. We shall reach the conclusion that the “surface tension” of water was reduced, as this new surface energy is not enough to overcome the potential energy of water. Such a modification is helpful when one is dispersing oil in water; if the surface tension is reduced, this means that the amount of energy necessary to disperse oil in water is reduced.

Why is soap “surface active”? Soap has been produced for more than two millennia by heating fat and wood ashes (Konkol and Rasmussen, 2015). The French chemist Michel Eugène Chevreul explained the process chemically, showing in 1823 that potash (KOH, from ashes) could produce “saponification”, described by the chemical equation (Chevreul, 1823):

$$R-COO-R’ + OH^- \rightarrow RCOO^- + ROH$$

Oil, for example, is mainly (often more than 98%) a mixture of triglycerides (Pioch et al., 1998) (Figure 36.4). A glycerol residue is linked through ester links to residues $R_1$, $R_2$ and $R_3$, which are alkyl chains that may be saturated or unsaturated. In other words, saponification generates glycerol, on the one hand, and carboxylate ions, on the other hand. With such compounds, there is a negatively charged end (the “head”) and a hydrophobic end (“tail”). If one puts such molecules in a glass with water and oil, the head and tail molecules lower their energy by being more abundant at the interface, so that the hydrophilic heads are in water and the hydrophobic tails are in contact with the oil (Figure 36.5).

This reduces the oil–water surface tension because the interface is changed, and this is why soaps are called “surface active agents” or “surfactants”. When more surfactants are added, some can be dissolved, in oil or in water (Figure 36.6). How much?

One way to characterize the distribution of a compound in a biphasic system is to use the partition coefficient, defined as follows (Leo et al., 1971). A compound distributes so that there

![FIGURE 36.3 The surface of oil is increased when oil is divided.](image-url)

![FIGURE 36.4 A triacylglycerol (tristearin) with a glycerol residue esterified by three residues of fatty acid.](image-url)
is a concentration $c_O$ in oil and a concentration $c_W$ in water. The partition coefficient $k$ is equal to:

$$k = \frac{c_O}{c_W} \quad (36.16)$$

Because “oils” are not well defined (for milk fat, the number of possible fatty acid residues on each of the three positions of the glycerol residue is estimated to be 400), the partition coefficient is often expressed for the distribution between octanol or n-octane in water (Bouteille et al., 2013).

However, the partition coefficient is difficult to use, because some compounds are very hydrophilic (ions, for example, and also saccharides, and more generally polyols, being able to establish a lot of hydrogen bonds with water molecules) and, on the other hand, other compounds (compounds with long hydrophobic chains) are very hydrophobic. This is why it is preferable to use the decimal logarithm of the partition coefficient, i.e., the “log $P$” for the distribution coefficient of compounds between n-octane and water, and the “log $K_{ow}$” for an octanol/water system (Table 36.1).

### TABLE 36.1

<table>
<thead>
<tr>
<th>Compound</th>
<th>log $K_{ow}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$-OH</td>
<td>−6.38</td>
</tr>
<tr>
<td>CH$_3$-CH$_2$-OH</td>
<td>−5.54</td>
</tr>
<tr>
<td>CH$_3$-CH$_2$-CH$_2$-OH</td>
<td>−4.7</td>
</tr>
<tr>
<td>CH$_3$-CH$_2$-CH$_2$-CH$_2$-OH</td>
<td>−3.86</td>
</tr>
<tr>
<td>CH$_3$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-OH</td>
<td>−3.0</td>
</tr>
<tr>
<td>CH$_3$-CH$_2$-CH$_3$</td>
<td>4.58</td>
</tr>
<tr>
<td>Phi-OH</td>
<td>−3.52</td>
</tr>
</tbody>
</table>

**HLB Values**

In the case of surfactants, such scales as log $P$ are not used in the industry. Instead, engineers have another scale, more like the pH scale: the HLB, or “Hydrophilic Lipophilic Balance”, in which surfactants are ranked between 0 and 14 (De Gennes et al., 2004). We consider now the way this is derived.

Let us move a surfactant molecule from water toward oil. If the work needed is $W$, the proportion of surfactant molecules can be expressed using the Maxwell–Boltzmann distribution:

$$k = \exp \left( \frac{-W}{k_B T} \right) \quad (36.17)$$

Let us calculate $W$, assuming an energy $E_H$ for transferring a hydrophilic group and the energy $E_L$ for transferring a lipophilic group. Let $n_H$ be the number of hydrophilic groups, and $n_L$ the number of lipophilic groups. Then, in this description:

$$W = n_H E_H - n_L E_L \quad (36.18)$$

And then:

$$k = \exp \left( \frac{-n_H E_H - n_L E_L}{k_B T} \right) \quad (36.19)$$

Taking the logarithm:

$$\log_{10}(k) = -p_H E_H + p_L E_L$$

The coefficients $p_H$ and $p_L$ can be measured.

In 1946, Griffin proposed defining HLB from a relationship of this kind, so that the scale would be between 0 and 14:

$$HLB = 7 + a(−p_H E_H + p_L E_L) = 7 + (−q_H E_H + q_L E_L) \quad (36.20)$$

Here, the constant $a$ is chosen so that the scale is similar to that for pH, i.e., between 0 and 14. Table 36.2 gives the $q$ parameters for some chemical groups.

Why do we use such a scale? This is because surfactants are now more easily chosen for particular applications (Table 36.3).

**Making Colloidal Systems**

Concerning surfactants, the simple distribution that was considered between oil and water is simplistic, as the surfactant...
molecules can self-associate when their concentration is high enough. In particular, they can make “micelles” (from Latin *mica*, part), with the polar heads being in water and the hydrophobic tails being far from water. This is frequently depicted as in Figure 36.7.

There are other possibilities, such as liposomes or bilayers, but one should remember that all such pictures have to be interpreted, because representing surfactant molecules with such heads and tails is simplistic; in general, the “size” of the head is only a few chemical bonds long, whereas the tails have a length of 10 to 20 covalent bonds. Moreover, at room temperature, molecules of liquid systems move; in particular, surfactant molecules exchange between the liquid environment and the structure that they form. At any time, a surfactant molecule can leave the structure in which it participates (e.g., a micelle), being replaced by a water molecule or another surfactant molecule, or by nothing. The picture is based on the fact that the residence time of water molecules is very low (Yamamoto *et al.*, 2014).

### Why Are Micelles Depicted as Spherical?

In the previous paragraph, it was observed that the heads of surfactant are sometimes much smaller than the tails. Why are they depicted as so big, and why are micelles spherical? The simple representation with bonds is not enough; instead, the “effect” on other molecules has to be taken into account. The heads are “big” because they are often electrically charged or have non-binding doublets (on oxygen atoms of phosphate groups, for example), leading to electric repulsion, whereas tails avoid contact only through steric effects, even being attracted by weak van der Waals forces.

One can calculate the structure of micelles, assuming that the “heads” of surfactant molecules have a projected area (“cross section”) $A$ and the “tails” a volume $V = n_q v_q$ ($n_q$ stands for the number of groups in the hydrophobic chain, and $v_q$ is the volume of one group); we assume micelles of radius $R$.

Let $N$ be the average number of molecules of surfactant per micelle. The total volume of the micelle is $N.V$. This volume can be put in relation with $R$:

$$\frac{4}{3} \pi R^3 = N.V = N n_q v_q$$

(36.21)

The surface, on the other hand, has an area:

$$4 \pi R^2 = N A$$

(36.22)

From these two equations, the radius can be calculated:

$$R = \frac{3 n_q v_q}{A_n}$$

(36.23)

And the average number of surfactant molecules per micelle:

$$N = \frac{36 \pi n_q^2 v_q^2}{A^3}$$

(36.24)

Experimentally, the order of magnitude of $N$ is measured to be 100.

### Micellar Concentration

Micelles form only when their concentration is higher than a particular concentration, which is called the “critical micellar concentration” (cmc). Can we calculate it? There are two principles involved here (the first and the second principles of thermodynamics), and we have to use the Gibbs function, or free enthalpy, in order to take these two principles into account. As concentrations are involved, we have to make a link with energy. We start from the concentration $c$, on one hand, and energy, $G$, on the other. The definition of chemical potential $\mu$ expresses the relationship between the two:

$$\mu_i = \frac{\partial G}{\partial n_i}$$

(36.25)
where \( i \) is a particular chemical species, and \( n_i \) is the number of moles of this species. Let us consider a surfactant molecule, which can either be isolated (\( \mu_i \)) or associated with others (\( \mu_a \)). For a charged surfactant:

\[
\mu_i = \mu_i^0 + 2k_B T \ln(c.V) \tag{36.26}
\]

The expression is given for a molecule (\( k_B \)) and not for a mole, as is more common. The factor 2 is because the surfactant is ionic, made from one ion and one counterion.

For the same molecule, in a micelle:

\[
\mu_a = \mu_a^0 + \frac{k_B T}{N} \ln \left( \frac{c.V}{N} \right) \tag{36.27}
\]

Here the entropic term is divided by \( N \), because micelles behave as unique structures with three degrees of freedom. As \( N \) is large, this term can be dropped, so that the equilibrium between isolated surfactants and associated surfactants can be written:

\[
2k_B T \ln(cmcV) = \mu_a^0 - \mu_i^0 \tag{36.28}
\]

The second term can be written \(-n_q U_q\) if we use the results obtained before for HLB values. Then:

\[
cmc = \frac{1}{V} \exp \left( -\frac{n_q U_q}{2k_B T} \right) \tag{36.29}
\]

### Surfactants in Emulsions

If surfactant molecules can associate in micelles, they can also migrate toward a hydrophobic–water interface, lower the surface tension, and stabilize oil in water emulsions (O/W). This is how clothes are washed in water, using soap, when organic matter such as fat is adhering to the fibres: soap molecules diffuse to the fat/water interface and cause it to curve, forming fat droplets entirely covered by soap molecules.

The same occurs when making a mayonnaise or a “geoffroy” (an O/W emulsion obtained by whipping oil in an aqueous solution of proteins) (This, 2009), or a “kientzheim sauce” (the same as a mayonnaise, but with melted – possibly brown – butter instead of oil), for example. When the oil fraction remains below the close packing coefficient, the oil droplets are spherical, but, when this ratio increases, the droplets deform (Figure 36.8a and b).

Of course, this description is classic, and nowadays new kinds of emulsions are being studied. In the kitchen, systems such as mayonnaise (made from egg yolk, vinegar, oil, salt and pepper) are called emulsions (IUPAC, 2018), but for some systems, such as when water is added to Pastis or Ouzo, i.e., solutions of anethole in water–ethanol systems (Scholten et al., 2008), very different properties can be produced. Other culinary emulsions will be recognized as Ramsden emulsions, sometimes called Pickering emulsions, i.e., emulsions for which the oil/water interface is covered by solid particles (Rayner et al., 2014; Ramsden, 1904). This is also discussed in the chapter by Fameau in this book.

Nowadays, one important kind of emulsions is “microemulsions”, because they are much more stable than the usual type. There is some confusion about them because they are poorly named.

In culinary emulsions, such as mayonnaise made with a fork or a kitchen whisk, the diameter of oil droplets is between 1 and 100 \( \mu m \), in the micrometre range, so that the term “microemulsions” could have been given to them. However, this name is used, rather, to refer to thermodynamically stable isotropic liquids formed by mixing oil, water and surfactants together (Jonsson et al., 1998; Fanun, 2008). Such mixtures can form many different systems depending on the composition and on the physical conditions, such as temperature. In particular, they may contain a certain number of phases (1, 2, 3 or more) that are in equilibrium with each other. These phases may or may not be continuous, and, as shown for micelles, the structures can be diverse: one-dimensional (spheroids or cylinders), two-dimensional

![FIGURE 36.8](image-url)
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(lamellar structures) or even intricate three-dimensional (sponge-like) forms (Roux, 1995). On the other hand, “nanoemulsions” can be considered as conventional emulsions made of very small particles (Tadros et al., 2004; Mason et al., 2006).

One reason for the confusion between these two kinds of systems is that “micro” refers to sizes of $10^{-6}$ m, whereas “nano” applies to sizes of about $10^{-9}$ m; according to this rule, nanoemulsions would be made of particles that are smaller than those in microemulsions. However, this terminological rule does not apply: the first article appearing with the word “microemulsion” was published in 1961 (Schulman and Montagne, 1961), whereas the word “nanoemulsion” appeared in 1971 in relation to the development of nanotechnology. Of course, there are other debates about the upper limit for “nano” particles: 500 nm (Anton et al., 2008), 200 nm (Huang et al., 2010) or even 100 nm (Rao and McClements, 2012). Indeed, the main change in physicochemical properties when the size of the dispersed structures is reduced occurs when their potential energy ($m g h$) is of the same order of magnitude as the thermal energy of the dispersing medium ($k_B T$).

Concerning Ramsden emulsions, they are stabilized by very small particles. They have attracted much research in the past decade due to their properties, such as high stability with respect to coalescence and Ostwald ripening (see the chapter on this subject in this book). In particular, they can be made with biomass-based particles in the context of foods and topical creams (Rayner et al., 2014), such as starch granules or egg yolk granules. The particle stabilization of oil droplets is possible due to partial dual wettability of particles at the oil–water interface. Native starch is not intrinsically hydrophobic; however, its hydrophobicity can be increased by chemical modification with octenyl succinic anhydride. Heat can be applied to induce a partial gelatinization of the starch granules, forming a cohesive layer at the oil–water interface and increasing barrier properties. Egg granules, on the other hand, are hydrophobic and, at low ionic strength (<0.3 M NaCl), are insoluble with a compact structure; size decrease with increasing concentration can be controlled by the granule-to-oil ratio.

**Conclusions**

It is interesting to have a historical perspective on the theory of food emulsions. As late as the 1950s, it was said, even in scientific circles, that emulsions such as mayonnaise had to be prepared with an iron whisk and a copper bowl because of a “battery effect”. As late as the 1980s, mayonnaise sauces were said to be stabilized by phospholipids (rather than proteins). Until recently, Ramsden emulsions were absent from courses on the physical chemistry of food (there is nothing about them in the well-known *Food Chemistry* by Belitz et al. (2009)). What will be the next steps?

**REFERENCES**


