

CHAPTER 20

Surface Tension

20.1 FLUID EFFECTS AT INTERFACES

20.1.1 Origin of Surface Tension

In all materials a certain amount of intermolecular forces keep the individual molecules together. If this force is not strong enough, the material will not exist as a solid bulk decompose but would into individual molecules. In the volume of the material, these intermolecular forces are balanced in all directions. Depending on the nature of the primary bonds, these forces may be directed and more strongly expressed in one specific direction, as is the case for covalent bonds.

However, on the surface of the material, those forces are not balanced (see Fig. 20.1). The last layer of molecules has no interacting neighbors on top of it, and therefore the forces pointing toward the inside of the bulk are not balanced. This is why surfaces always have a net force F_{net} pointing inward, *i.e.*, in the inward direction of the surface's normal vector. In liquids in which the molecules can move more freely as compared to a solid, this net force causes the formation of a meniscus. The smaller the diameter of the surface is, the more expressed this meniscus is, *i.e.*, the more strongly the surface is curved.

Now suppose the surface area of a system were to be increased. More molecules would have to be moved from the bulk to the surface. Consequently, more molecules would be left with unbalanced interaction forces. Obviously this is a thermodynamically less favorable state, and therefore increasing the surface requires energy. This state is the same for liquids and solids. A liquid will always try to minimize its surface area, which is why a water droplet will form a sphere. Similarly, solids will also try to minimize their surface, which is why energy is required to introduce, *e.g.*, cracks in a solid, which effectively increase, the surface. However, in order to reach a stable state, a system will always try to strive toward the state of lowest energy. This is why it is thermodynamically more favorable to reduce the surface area as much as possible.

20.1.2 Free Surface Energy

The energy required to increase the surface area is referred to as the *free surface energy* or *surface free energy* γ . Not surprisingly its unit is energy per area, *i.e.*, J m^{-2} , as it defines the amount of energy required in order to create a certain surface area. It can be thought of as the degree of imbalance of the intermolecular forces of a surface. Intuitively, this imbalance is dependent on the material that is on top of the surface. If a second layer that has a similar free surface energy covers the surface, the two imbalances are balanced, because the surfaces find respective neighbors with which to interact. This is why the surface free energy of a material is always given in reference to the surrounding material or fluid. Naturally, these values are often given for surfaces exposed to air. In Fig. 20.3 we will see an example of surface free energy balance if a solid is deposited on a liquid's surface.

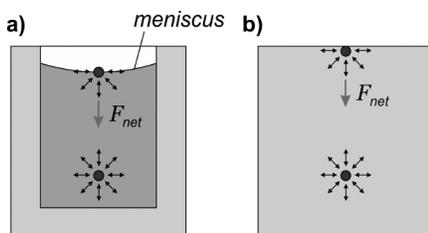


Fig. 20.1 Surface tension occurring at a liquid's (a) and a solid's (b) surface as a consequence of unbalanced intermolecular forces. In both cases, there is a net force directed in the inward normal direction of the surface. In liquids this causes the formation of a meniscus.

20.1.3 Low and High Free Surface Energy Surfaces

From the preceding discussion, we can also roughly classify surfaces according to their free surface energy. Usually, there is a distinction between *high free surface energy* surfaces and *low free surface energy* surfaces. As discussed, the free surface energy results from an imbalance of forces at the surface. As a result, this free surface energy must be higher for surfaces that are held together by strong bonds because strong intermolecular bonds in the bulk will lead to strong imbalanced forces at the surface.

This approximation is surprisingly correct. Metals and crystals, which are held together by primary bonds, have relatively high free surface energies. Tab. 20.1 lists the free surface energies of the elements. As can be seen, metals have very high values.

In polymers the individual chains of the polymer are held together by secondary forces, *i.e.*, van der Waals and hydrogen bonds. These bonds are significantly weaker, and consequently, these surfaces have very low free surface energies (see Tab. 22.2). Surfaces of materials with very low secondary interaction, *e.g.*, pure hydrocarbon and fluorinated polymers have the lowest free surface energies. Tab. 22.2 lists a selection of commonly encountered polymers. As shown the values are significantly lower than those in metals.

20.1.4 Estimating the Free Surface Energy

Several methods can be used to measure the surface free energy. Here we will use a simple model that allows us to derive values that actually are not too far away from the values measured. In the following we will consider a solid to consist of individual atoms that are interconnected (see Fig. 20.2a). In the plane, each atom has four neighbors. Additionally, it is connected to one neighbor in the layer on top of it and to one neighbor in the layer below. Therefore each atom in the volume has a total of six neighbors.

At the surface, each atom is bound to only five neighbors because the last layer misses the neighbors above (see Fig. 20.2b). We can therefore estimate that the free surface energy will be one-sixth of the bond strength divided by the surface area of an atom:

$$\gamma \approx \frac{1}{6} \frac{E_d}{d_{\text{atom}}}$$

The bond energy can often be precisely predicted by the enthalpy of vaporization ΔH_{vap} per atom, *i.e.*, by dividing ΔH_{vap} by the Avogadro constant N_A . This makes sense because transferring a liquid or a solid to the gaseous state is approximately equivalent to breaking all the intermolecular bonds. Therefore the energy required for this transfer should, with good precision, indicate the total bond energy. Therefore we find

$$E_d \approx \frac{\Delta H_{\text{vap}}}{N_A}$$

Tab. 20.1 Free surface energy values of the elements [1]

Substance	Surface tension γ mN m ⁻¹	Substance	Surface tension γ mN m ⁻¹
silver	1 086	sodium	234
aluminum	1 020	nickel	2 080
gold	1 333	lead	540
calcium	425	palladium	1 743
cobalt	2 218	platinum	2 203
chromium	2 006	tin	661
copper	1 566	titanium	1 749
iron	2 123	vanadium	2 301
potassium	129	tungsten	2 765
lithium	472	zinc	896
magnesium	688	zirconium	1 987
manganese	1 298		

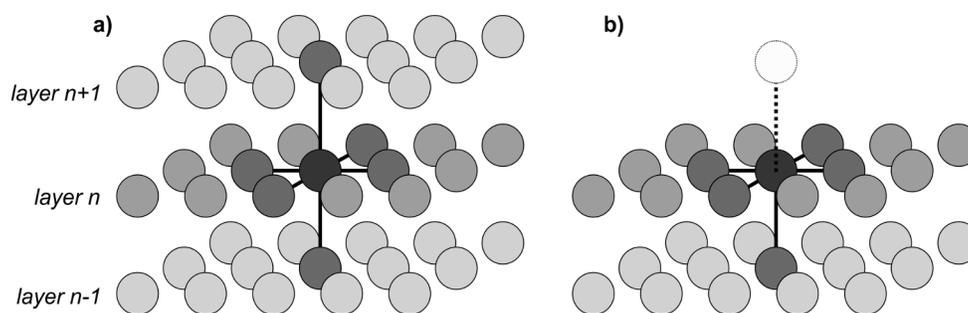


Fig. 20.2 Model for estimating the free surface energy. a) In the bulk, each atom has a total of six neighbors. b) At the surface, an atom has only five neighbors. The missing bond is the cause of the free surface energy.

Tab. 20.2 Surface tension of commonly used liquids, measured in air

Substance	Temp. °C	Surf. tens. γ mN m ⁻¹	Substance	Temp. °C	Surf. tens. γ mN m ⁻¹
Liquids [2]					
mercury	25	485.48	benzene	25	25.00
water	25	71.99	toluene	25	24.96
ethylene glycol	25	47.99	acetone	25	23.46
acetophenone	25	39.04	methanol	25	22.07
phenol	25	38.20	ethanol	25	21.97
cyclohexanol	25	30.50	cyclohexane	25	21.68
acetonitrile	25	28.66	isopropanol	25	20.93
dichloromethane	25	27.20	trifluoroacetic acid	25	13.53
tetradecane	25	26.13			
Influence of fluorination [3]					
<i>n</i> -pentane	20	13	perfluorinated <i>n</i> -pentane	20	9.90
<i>n</i> -heptane	20	20.30	perfluorinated <i>n</i> -heptane	20	13.20
<i>n</i> -octane	20	21.80	perfluorinated <i>n</i> -octane	20	13.60

which yields

$$\gamma \approx \frac{1}{6} \frac{\Delta H_{\text{vap}}}{N_{\text{A}} d_{\text{atom}}^2} \quad (\text{Eq. 20.1})$$

For water we find the following values: $\Delta H_{\text{vapH}_2\text{O}} = 43.990 \text{ kJ mol}^{-1}$ (see Tab. 6.5) and $d_{\text{atom}} = 0.31 \text{ nm}$ (see section 9.3.3). Using Eq. 20.1, we obtain an estimated surface free energy of $\gamma_{\text{H}_2\text{O}} \approx 126 \text{ mN m}^{-1}$. This value is definitely not correct (see Tab. 20.2); it should be around 72 mN m^{-1} , but it is surprisingly close.

20.1.5 Surface Tension

The term free surface energy is usually used only when talking about solid surfaces. When referring to liquids, the term *surface tension* γ is more commonly used. This term dates back to the work of English physicist Thomas Young¹. Please note that, despite the terminology, free surface energy and surface tension refer to the

¹ Thomas Young was an English physicist. Young initially studied medicine and worked as an eye surgeon. He is credited as being the first scientist to measure the wavelength of light using interference. In 1807 Young published accounts of an instrument that could be used to record sound on a sooth-covered cylinder, which essentially was the first sound recording instrument [4]. Young also made important contributions to the field of fluid physics and in 1805 was first to describe the curving of free surfaces in regard to a thin membrane under stress [5]. In this work, he first introduced the term *surface tension*.

same physical quantity and share the same symbol. The unit of the free surface energy is J m^{-2} , and the unit of surface tension is N m^{-1} , which is, once multiplied by m m^{-1} the same unit.

Tab. 20.2 lists surface tension values for commonly encountered liquids. As shown strongly polar liquids (such as alcohols and water) have very high surface tensions of around 50 mN m^{-1} to 80 mN m^{-1} . This is due to the strong cohesive forces originating from secondary bonds. Most organic solvents have surface tensions in the range of around 20 mN m^{-1} to 30 mN m^{-1} . Fluorinated substances have very low surface tensions approaching 15 mN m^{-1} . Fluorination leads to a significant reduction in surface tension as it reduces the amount of secondary interaction and therefore the cohesive forces. Tab. 20.2 lists examples of solvents in non-fluorinated and fluorinated form. As can be seen, the surface tension decreases significantly.

20.1.6 Temperature Dependency

In general heating a surface will cause the free surface energy to decrease. Following our rationale (see section 20.1.1), the free surface energy is due to the imbalance in the forces at the topmost atom layer of a surface. Heating increases the Brownian motion of the atoms thereby decreasing the interaction between the atoms. Eventually, heating will increase the motion such that the atoms can move freely in gaseous form (vaporization). This is due to the reduction of the interaction forces between the atoms. However, as surface tension is a consequence of the imbalance of the interaction force, it will decrease if the interaction forces decrease.

For example, heating a fluid will cause its surface tension to drop. Water has a surface tension of 74.23 mN m^{-1} at 10°C , 71.99 mN m^{-1} at 25°C , 67.94 mN m^{-1} at 50°C , 63.57 mN m^{-1} at 75°C , and 58.91 mN m^{-1} at 100°C [2].

20.1.7 Surface Tension Forces

Imagine that we want to immerse an object of a given size in a liquid (see Fig. 20.3). If the solid is placed on top of the liquid's surface, the liquid will align to the surface. There will be no curvature, as we can see, on the free liquid surface because the imbalance of forces is no longer there. The surface molecules now have neighbors, and interaction forces will occur. Therefore, there is no further contribution to the surface tension. The surface tension thus acts only in the outer contact line of the object. This is the point where the intermolecular forces are (again) imbalanced.

Fig. 20.3 shows that the total force resulting from the surface tension is

$$\begin{aligned} F_{\text{surface tensions}} &= \gamma_{\text{liquid}} l_c \\ &= \gamma_{\text{liquid}} 2(w + l) \end{aligned} \quad (\text{Eq. 20.2})$$

This is the maximum force that the surface tension will create. If the gravitational force of the object is higher than this value, it will immerse in the liquid. It is important to keep in mind that we need to calculate to circumference. For example, the legs of *gerridae*, small insects that can walk on water and are thus sometimes referred to as “water walkers” (see Fig. 20.4) have a contact area that can be approximated with a rectangle, similar to the one shown in Fig. 20.3. Usually, the width of the legs can be ignored, as $w \ll l$. Eq. 20.2 can be simplified to

$$\begin{aligned} F_{\text{surface tensions}} &= \gamma_{\text{liquid}} 2(w + l) \\ &\approx \gamma_{\text{liquid}} 2l \end{aligned}$$

The multiplier 2 is often forgotten when indicating the formula.

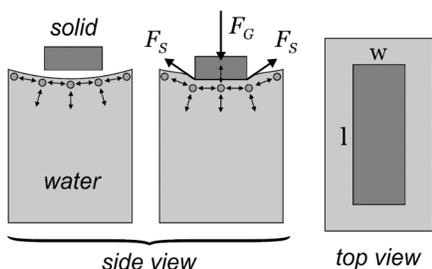


Fig. 20.3 Forces originating from surface tension when a solid is immersed in a liquid. The effective length to consider is the circumference.



Fig. 20.4 Photograph of a *gerridae* walking on a water surface. The visible bends in the surface of the water are due to the surface tension forces that sustain the animal's weight.

20.1.8 Contact Angle

Wetting. After discussing the origins and the effect of surface tension and free surface energies we will now turn to the study of its effects. If a fluid is brought into contact with a solid, the molecules in the surfaces of the two substances interact. Suddenly they have neighboring molecules with which they can interact thus potentially reducing the force imbalance in the surface layer. This reduces the free surface energy of both the surface and the fluid. Depending on whether or not this reduction in energy is significant, the fluid will tend to increase its surface area.

The behavior of the liquid on a surface is usually referred to as the liquid's *wetting* behavior on this specific surface. In general, the term wetting refers to the capability of a fluid, *e.g.*, a liquid, to keep contact with a surface. Wetting is governed by the balance of adhesive (in the boundary) and cohesive (within the volume of the fluid) forces. We will discuss the individual forces contributing to the wetting behavior in a moment.

Contact Angle. Once the liquid drop settles on top of the surface, it will form a characteristic *contact angle* Θ (see Fig. 20.5). This contact angle is the visible boundary between the fluid and the solid. There is, in fact, a third partner involved, which is the fluid surrounding the system. Usually, the fluid deposited will be a liquid, and the fluid surrounding this drop of liquid will be a gas. However, this does not necessarily have to be so, as the surrounding fluid could also be a liquid, *e.g.*, a silicone oil protecting the drop from evaporating. Please note that the contact angle is always measured "through the liquid".

For contact angles $\Theta < 90^\circ$ the liquid is said to be *wetting* or able to *wet the surface*. On the other hand, the solid is considered to be *wettable* or *wetting*. For water, the term *hydrophilic* is commonly used. A hydrophilic surface is a surface on which water will wet. For oils, the term *oleophilic* is used. Typical examples for hydrophilic

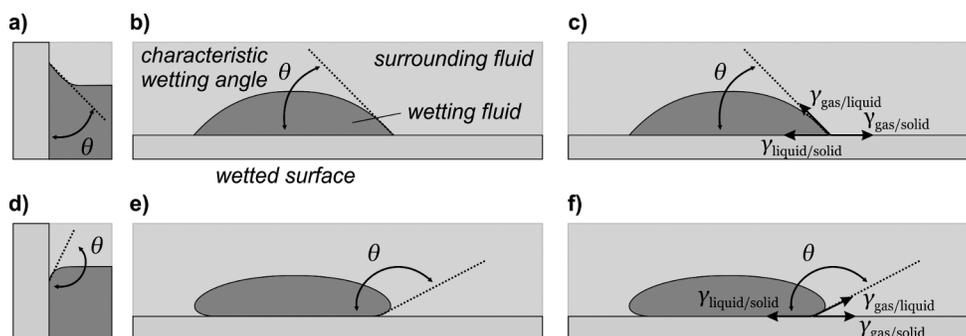


Fig. 20.5 a) Characteristic contact angles forming a (positive) meniscus. The liquid wets the solid. b) Three-phase interface that is formed between the wetted surface, the wetting liquid, and the surrounding liquid. c) Balance of forces at the three-phase interface. d-f) Negative meniscus forming at a liquid with bad wetting behavior on the solid.

surfaces are freshly cleaned glass surfaces. Examples for oleophilic surfaces include most polymer surfaces, *e.g.*, polyethylene.

For contact angles $\Theta > 90^\circ$, the liquid is said to be *non-wetting* or not able to wet the surface. On the other hand, the solid is considered to be *non-wettable* or *non-wetting*. For water, the term *hydrophobic* is commonly used. A hydrophobic surface is a surface on which water will not wet. For oils, the term *oleophobic* is used. Typical examples for hydrophobic surfaces include most polymers, *e.g.*, polyethylene. Examples for oleophobic surfaces include glass surfaces. As can be seen, hydrophilic surfaces are oleophobic and *v.v.* We will now turn to the intermolecular forces and their contribution to the formation of the contact angle.

Intermolecular Forces Between Wetting Fluid and Surface. Depending on their chemical composition, there will be a certain degree of adhesive forces between the wetting fluid and the wetted surface. These adhesive forces will force the wetting fluid to spread out as far as possible. On the other hand, the cohesive forces within the wetting fluid will try to counteract this spreading movement. So the degree of spreading is governed by the balance of adhesive forces between the wetted surface and the wetting fluid and the cohesive forces within the wetting fluid.

Intermolecular Forces Between Surrounding Fluid and Surface. The interaction between the surrounding liquid and the surface are likewise. If there are strong adhesive forces between the surrounding fluid and the surface, the fluid will spread as far as possible. On the other hand, the surrounding fluid will be retained by cohesive forces acting within its volume. Again, the wetting behavior is governed by the balance of these two forces.

Intermolecular Forces Between the Wetting and the Surrounding Fluid. The last of the three phase boundaries we need to discuss is the boundary between the wetting and the surrounding fluid. Likewise, there will be a tendency to increase the interaction area between the two fluids if there are adhesive forces between them. If this is the case, both fluids will form the largest possible contact area. On the other hand, cohesive forces within both fluids will try to counteract this spreading.

Rationale of the Balance of Forces. Returning to the concept of the free surface energy, we can now empirically balance the forces acting on the droplet. If the free surface energy of the solid is high, it will pull the droplet's boundaries trying to increase the size of the droplet. By doing so, the imbalance in intermolecular forces at the surface is reduced, similarly to the example of the solid being placed on top of the liquid's boundary (see Fig. 20.3). On the one hand, the droplet will try not to increase its surface area as this is energetically less favorable.

On the other hand, the droplet will form an interface with the surrounding fluid (usually air). As there is little interaction among gas molecules, the deficit in the balance of intermolecular forces is low in gases, which is why they tend to increase their surface area if the space is available. Therefore there is little gain for the free surface energy of the water droplet by forming a large contact area with air, which is why a drop of water will always try to decrease its size as a consequence of the cohesive forces.

As stated, if the surrounding fluid is a gas, it will have only a minor tendency to decrease or increase its surface as neither cohesive nor imbalance in intermolecular forces are critical in gases. However, if the surrounding fluid is a liquid, there will be a similar balance of cohesive forces versus reduction in free surface energy, as discussed for the wetting liquid.

Young's Equation. We will now introduce the analytical equation that balances the individual force distribution. This equation is the so-called *Young's equation*. It is given by

$$\gamma_{\text{gas/solid}} = \gamma_{\text{liquid/solid}} + \cos \Theta \gamma_{\text{gas/liquid}} \quad (\text{Eq. 20.3})$$

or

$$\cos \Theta = \frac{\gamma_{\text{gas/solid}} - \gamma_{\text{liquid/solid}}}{\gamma_{\text{gas/liquid}}} \quad (\text{Eq. 20.4})$$

From Eq. 20.4 we can derive a couple of important concepts. For $0 < \cos \Theta < 1$, the contact angle is $\Theta < 90^\circ$ and the liquid will wet the surface. This happens if the difference in the surface's free energy between the "gas-wetted" and the "liquid-wetted" state is high, *i.e.*, if there is a significant reduction in surface free energy gained by spreading of the liquid. In this case $\gamma_{\text{gas/solid}} - \gamma_{\text{liquid/solid}} \geq 0$. This will be facilitated if the liquid's surface tension is low, *i.e.*, it is easy to pull the liquid apart.

For $-1 < \cos \Theta < 0$, the contact angle is $\Theta > 90^\circ$, and the liquid will not wet the surface. This is the case if $\gamma_{\text{gas/solid}} - \gamma_{\text{liquid/solid}} < 0$, *i.e.*, there is no reduction in surface energy by spreading of the liquid.

We can also note that the surface tension of the liquid influences the spreading behavior. As this value is always positive and located in the denominator, it will not change the sign of the equation. However, it can be thought of as an amplification factor. If $\gamma_{\text{gas/liquid}} > |\gamma_{\text{gas/solid}} - \gamma_{\text{liquid/solid}}|$, it will merely "dampen" the reduction of surface energy by spreading, *i.e.*, reduce the value. However, if $\gamma_{\text{gas/liquid}} \approx |\gamma_{\text{gas/solid}} - \gamma_{\text{liquid/solid}}|$, the surface tension of the liquid may be able to "amplify" the factor, *i.e.*, the contact angle. A slightly negative nominator value would be amplified to -1 (perfectly non-wetting surface), a slightly positive nominator value would be amplified to almost 1 (perfectly wetting surface).

Spreading Parameter. As stated, the wetting of a liquid on a solid will decrease the solid's surface free energy. The surface free energy of the liquid will decrease when spread as the contact with both the surface and the wetting liquid will decrease its surface free energy. At the same time, the contact area between the surrounding fluid (usually air) and the surface will decrease as the surface area wetted with the liquid will "dewet" from the surrounding liquid. The latter term will increase the free surface. Wetting will take place only if the increase in the wetted area of the liquid will dominate the decrease of surface free energy compared to the increase brought by the dewetting from the surrounding liquid. Analytically this can be described as

$$\begin{aligned} d\gamma_{\text{total}} &= \gamma_{\text{gas/liquid}} dA + \gamma_{\text{liquid/solid}} dA - \gamma_{\text{gas/solid}} dA \\ &= (\gamma_{\text{gas/liquid}} + \gamma_{\text{liquid/solid}} - \gamma_{\text{gas/solid}}) dA = S dA \end{aligned}$$

where the change of surface area is denoted dA . Here we introduced the spreading parameter S

$$S = \gamma_{\text{gas/liquid}} + \gamma_{\text{gas/solid}} - \gamma_{\text{liquid/solid}} \quad (\text{Eq. 20.5})$$

Thermodynamically, this increase of surface will happen only if $d\gamma_{\text{total}} < 0$. Assuming $dA > 0$, it follows that the spreading parameter must be negative. Therefore for $S < 0$ the liquid will spontaneously wet the surface entirely. This wetting is driven entirely by surface tension forces. For $S > 0$, there will be partial wetting driven, *e.g.*, by gravitation. Eventually, these forces will be balanced by the increase in the free surface energy as the wetted area increases. Eq. 20.5 is sometimes referred to as the *Dupré¹ equation*. Eq. 20.5 can be combined with Eq. 20.3 to

$$\begin{aligned} S &= \gamma_{\text{gas/liquid}} + \gamma_{\text{liquid/solid}} + \cos \Theta \gamma_{\text{gas/liquid}} - \gamma_{\text{liquid/solid}} \\ &= \gamma_{\text{gas/liquid}} (1 + \cos \Theta) \end{aligned} \quad (\text{Eq. 20.6})$$

Eq. 20.6 is often referred to as the *Young-Dupré equation*. Please note that there is another notation of this equation that assumes spreading of $S > 0$. In this case, the signs in Eq. 20.6 must be reversed.

20.1.9 Young-Laplace Pressure at Curved Interfaces

One of the many applications where we see surface tension at work is the formation of curved interfaces, *e.g.*, in the case on a droplet deposited on the surface. Depending on the way the droplet was deposited, it will usually show an elongated shape that has an elliptical contact area with the underlying surface. If the two axes of the ellipse are identical, the surface area is a circle. We will consider the more general case of an ellipse in the following sections.

If the pressure inside of the droplet is greater than the pressure outside of the droplet, the droplet will tend to expand in order to decrease the pressure differences. This will increase the wetted surface area against the surface tension of the droplet. Expansion will proceed until the retaining forces of the surface tension are high enough to prevent further expansion. At this point, a static equilibrium is reached. In the following, we will derive the *Young-Laplace equation*, which is used to describe the two angles of the curved interfaces that result in equilibrium (see Fig. 20.6a).

¹ Athanase Dupré was a French scientist who used the Young-Laplace equation for the study of fluid adhesion effects.

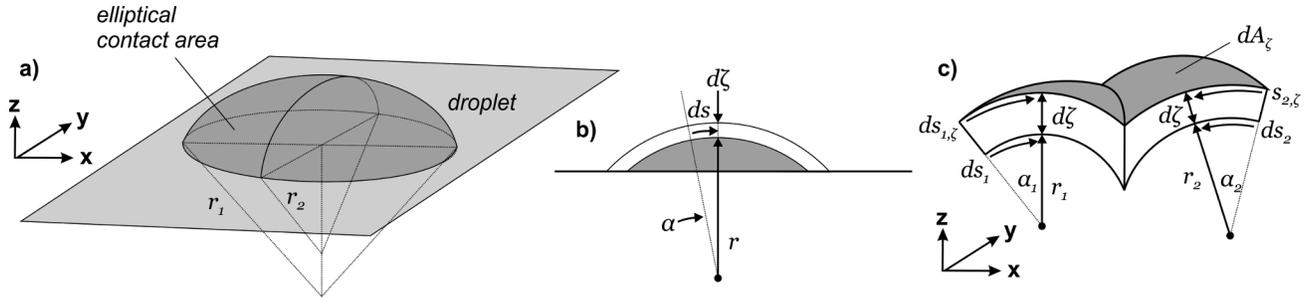


Fig. 20.6 Derivation of the Young-Laplace equation. a) Droplet on a solid forming an elongated ellipse as contact area. Please note that the droplet can be described by two circles with characteristic radii r_1 and r_2 . b) Cross-section of the droplet along one of the principal axes of the ellipses. The increase in diameter in this respective diameter is denoted $d\zeta$. The arc length of the surface ds can be calculated from the angle α and the radius r . c) View of the droplet with two radii r_1 and r_2 along the perpendicular axes of the ellipse. The increase in surface area dA can be expressed in terms of the increase in radius $d\zeta$.

The two forces acting are the forces resulting from the pressure difference and the surface tension. They act along the increase in diameters of the droplet and thus contribute energy. This contribution dE_p resulting from pressure differences and the contribution dE_w resulting from wetting are described by

$$dE_p = (p_{\text{inside}} - p_{\text{outside}}) dA d\zeta \quad (\text{Eq. 20.7})$$

$$dE_w = -\gamma (dA_\zeta - dA) \quad (\text{Eq. 20.8})$$

where dA is the surface area of the non-expanded droplet and dA_ζ the surface area of the expanded droplet. The linear increase in the respective diameters is denoted $d\zeta$. First, dA and dA_ζ have to be found. As we are considering a doubly curved surface, the surface area dA is given by the arc lengths $ds_1 \cdot ds_2$, which can be calculated as (see Fig. 20.6b)

$$ds = \alpha r \quad (\text{Eq. 20.9})$$

using the respective diameter of the circle. Eq. 20.9 is correct for small angles α , which, as we denote the infinitesimally small change in arc length ds , is a valid assumption. Using Eq. 20.9, dA can be calculated. dA_ζ can be derived from Fig. 20.6c. First we calculate the increase in length due to increase in diameter. As the angle α is not changed by the expansion of diameter, the increase in arc length is calculated using Eq. 20.9 as

$$\begin{aligned} ds_\zeta &= \alpha (r + d\zeta) \\ &= \frac{ds}{r} (r + d\zeta) \\ &= ds \left(1 + \frac{d\zeta}{r} \right) \end{aligned}$$

from which dA_ζ can be calculated as

$$\begin{aligned} dA_\zeta &= ds_{\zeta,1} ds_{\zeta,2} \\ &= ds_1 \left(1 + \frac{d\zeta}{r_1} \right) ds_2 \left(1 + \frac{d\zeta}{r_2} \right) \\ &= dA \left(1 + \frac{d\zeta}{r_1} \right) \left(1 + \frac{d\zeta}{r_2} \right) \approx dA \left(1 + \frac{d\zeta}{r_1} + \frac{d\zeta}{r_2} \right) \end{aligned} \quad (\text{Eq. 20.10})$$

where we used $dA = ds_1 \cdot ds_2$ and ignored the term containing $(d\zeta)^2$.

In order to reach equilibrium, the change of energy brought forth by Eq. 20.7 and Eq. 20.8 must be zero; therefore

$$\begin{aligned} dE_{\text{total}} &= dE_p + \gamma dA \\ &= ((p_{\text{inside}} - p_{\text{outside}}) d\zeta - \gamma) (dA_\zeta - dA) \end{aligned}$$

Using Eq. 20.10 results in

$$\begin{aligned} dE_{\text{total}} &= ((p_{\text{inside}} - p_{\text{outside}}) d\zeta + \gamma) \left(dA \left(1 + \frac{d\zeta}{r_1} + \frac{d\zeta}{r_2} \right) - dA \right) \\ &= ((p_{\text{inside}} - p_{\text{outside}}) d\zeta + \gamma) dA \left(\frac{d\zeta}{r_1} + \frac{d\zeta}{r_2} \right) \\ &= \left(p_{\text{inside}} - p_{\text{outside}} - \gamma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \right) dA d\zeta \end{aligned}$$

from which follows

$$\begin{aligned} p_{\text{inside}} - p_{\text{outside}} - \gamma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) &= 0 \\ p_{\text{inside}} - p_{\text{outside}} &= \gamma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \end{aligned} \quad (\text{Eq. 20.11})$$

Eq. 20.11 is the Young-Laplace equation. It describes pressure drops at curved interfaces and has a number of interesting applications.

Immiscible Flow. The Young-Laplace equation is valid for boundaries between two (largely) immiscible fluids in general. It is applicable for a liquid on a free surface in a gas atmosphere (*e.g.*, ambient air), but it can also be used for two immiscible fluids such as an oil and a water layer. This is because we have, during the derivation of the Young-Laplace equation, considered the energy associated with the displacement of the boundary in general. If the boundary is displaced against a second fluid, the interphase surface tension $\gamma_{\text{liquid A/liquid B}}$ has to be used instead of the surface tension of only one liquid.

Minimal Surfaces. A minimal surface is defined as a surface for which the right-hand side of the Young-Laplace equation, Eq. 20.11, is zero. As we can see from the equation, this needs to be the case for all surfaces that do not have a pressure drop across the surfaces, *i.e.*, which are open. A good example is a soap film that is suspended at open profiles, *e.g.*, rings. Fig. 20.7 shows an example of a soap film that is suspended between two open rings. There is no pressure difference between the inside and the outside of the film, thus $\frac{1}{r_1} + \frac{1}{r_2} = 0$ at all positions along x . As can be seen, r_1 decreases with increasing x and (by the same degree) r_2 increases in size. Interestingly, it may be very difficult to calculate these surfaces analytically. However, they will form readily when transferring the surface to models in a soap film experiment.

Surfaces Driven by Two Curved Interfaces. If a fluid plug is created inside a microfluidic channel that is slightly tapered, the plug will form two surfaces with different curvatures (see Fig. 20.8). This is because the contact angle is identical but the space restriction will squeeze a more strongly curved interface at the position with the smaller wall spacing. We know from Eq. 20.11 that the pressure drop across a surface increases if the radius decreases. In Fig. 20.8 the radius at the right side of the plug has a smaller radius; therefore the pressure drop on this side will be bigger. As a result, the plug will move toward the left. This mechanism can be used to drive fluid droplets or to extract air from microfluidic channels.

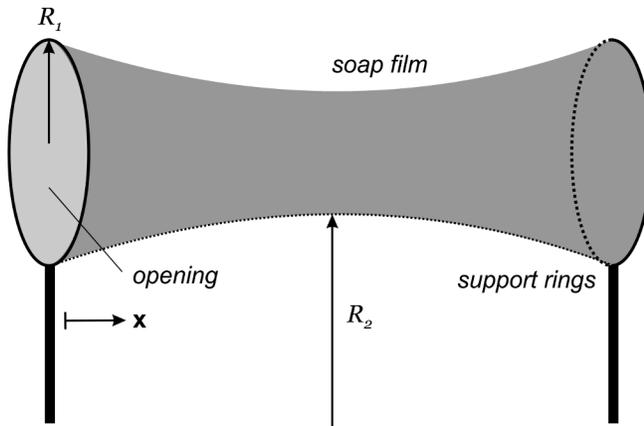


Fig. 20.7 Minimal surfaces demonstrated at a soap film. Because there is no pressure difference between the inside and the outside of the film, a characteristic minimal surface forms.

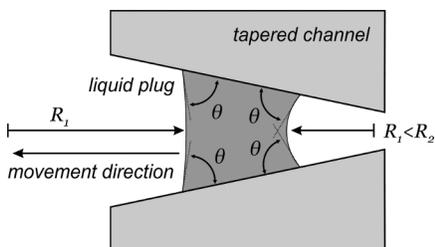


Fig. 20.8 Fluid flow in a tapered channel due to the formation of two surfaces with different radii. The pressure drop across the surface with the smaller radius (right) is larger. Therefore the plug will move toward the left side.

Pressure in Bubbles. The pressure inside of a bubble of radius r_0 is higher than the pressure outside of the bubble because of the curvature of the bubble. It is given by Eq. 20.11 as

$$p_{\text{inside}} - p_{\text{outside}} = \gamma \frac{2}{r_0}$$

The smaller the bubble, the higher the pressure difference. This is why smaller bubbles make significantly more noise when collapsing. This is the reason why champagne is “louder” than, *e.g.*, mineral water where the bubbles are significantly bigger.

In soap bubbles, the pressure difference is even higher as a soap bubble consists of a bilayer (see section 20.3.1). This bilayer consists of a layer of surfactant molecules arranged such that the unpolar tails are oriented inward and the polar head groups toward the outside (see Fig. 20.11g). This is why we have to account for a set of two doubly curved surfaces with approximately the same radius (if we assume the bubble to be spherical in shape). This is because the thickness of a surfactant bilayer is usually in the range of a few nm and can therefore be ignored, which results in

$$\begin{aligned} p_{\text{inside}} - p_{\text{outside}} &= \gamma \left(\frac{2}{r_0} + \frac{2}{r_0 + d_{\text{bilayer}}} \right) \\ &\approx \gamma \frac{4}{r_0} \end{aligned} \quad (\text{Eq. 20.12})$$

20.2 CONTACT ANGLE MEASUREMENT

20.2.1 Static Contact Angle

In general, there are two common methods of measuring the contact angle: static and dynamic. In static contact angle measurement, a droplet of a liquid is placed on top of a substrate, and the resulting contact angle is measured using a *contact angle microscope*. These instruments typically consist of a magnifying optical setup with attached camera that allows recording the contact angle, which is usually measured *via* software. Static contact angle measurement is important, *e.g.*, for the determination of the free surface energy of a substrate. Please refer to section 22.3 for further details on these methods. Fig. 24.10a shows an example of a contact angle measured for water on poly(methyl methacrylate), which was recorded using a contact angle microscope of type *DSA30 Drop Shape Analyzer* by Krüss (www.kruss.de).

20.2.2 Dynamic Contact Angle Measurement

The term *dynamic contact angle measurements* refers to techniques that measure the contact angle during movement. This is usually accomplished by adding liquid to a static droplet on a surface and thus pushing the front of the liquid across the unwetted surface. The contact angle measured during droplet expansion is referred to as *advancing contact angle* Θ_a (see Fig. 20.9a). It is a measure of the dry-wetting behavior of a liquid or a surface, *i.e.*, of the fluid mechanics on a freshly wetted surface. On the other hand, continuously removing liquid from a droplet will decrease its size and thus cause dewetting of the surface. The contact angle that is formed during shrinking of the droplet is referred to as *receding contact angle* Θ_r (see Fig. 20.9b). The receding contact angle is a measure of the remaining interaction forces between the liquid and the solid. The difference between the advancing and receding contact angle is referred to as *contact angle hysteresis*. The contact angle hysteresis is a means of assessing the mean roughness of the sample. If the surface is chemically sufficiently homogeneous, advancing and receding contact angles are constant and do not depend on the size of the droplet.

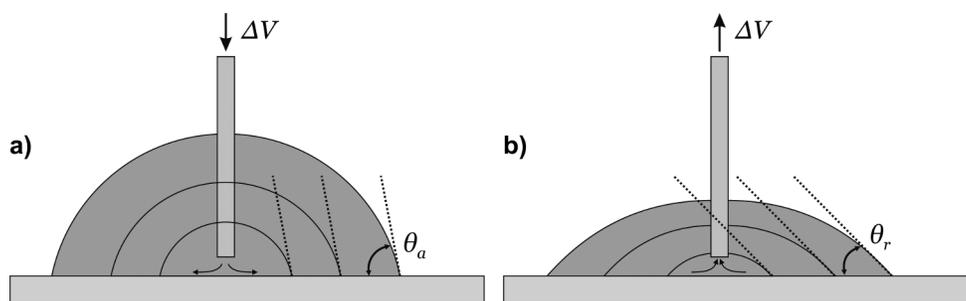


Fig. 20.9 Analysis of the advancing and the receding contact angle. The advancing contact angle is measured by increasing the amount of volume in a droplet. The liquid continuously wets uncovered surface area. The receding contact angle is a measure of the remaining liquid/solid interaction when continuously removing the volume of the droplet. The contact angle hysteresis, *i.e.*, the difference between advancing and receding contact angle, is a measure of the roughness of the surface.

20.3 SURFACTANTS

The word surfactant is a short form of *surface active agent*. It describes a class of substances that can assemble at fluid interfaces and change the property of the interface considerably. Surfactants are often used to change the interfacial surface tension or to increase or decrease the solubility of one fluid in another. Decreasing the solubility often leads to the formation of more stable fluid boundaries.

20.3.1 Chemical Structure of Surfactants

20.3.1.1 Classification

Potential surfactants are all molecules that have a polar head group and a long aliphatic tail. The charged head group gives the molecule its polar and hydrophilic character making it water-soluble. On the other hand, the aliphatic tail accounts for the molecules unpolar character that makes it oil-soluble. Usually, the charged head group carries a counterion to make the molecule a salt. Depending on the type of charge, we differentiate them as follows:

- *anionic surfactants* if the head group is negatively charged (see Fig. 20.10a)
- *cationic surfactants* if the head group is positively charged (see Fig. 20.10b)
- *zwitterionic* or *amphoteric surfactants* if the head group carries a positive and a negative charge (see Fig. 20.10c)
- *uncharged surfactants* if the head group carries no net charge (see Fig. 20.10d)

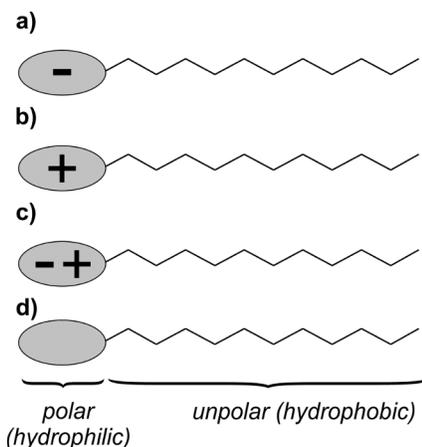


Fig. 20.10 Principle chemical structure of a surfactant consisting of a charged (polar) head group and an aliphatic (unpolar) tail. Some surfactants have more than one tail group. Depending on the charge nature we distinguish between anionic (a), cationic (b), zwitterionic or amphoteric (c), as well as uncharged surfactants (d).

Sometimes the first two categories are combined into one whose members are then referred to as *ionic surfactants*. There are many ways by which a polar head group and an aliphatic tail can be combined. The degree of hydrophobicity of a surfactant molecule is proportional to the length of the tail which can be varied. In contrast, the polar head group is not very variable, and only a small number of potential head groups are commonly used.

20.3.1.2 Micelle Formation

If mixed with a liquid, surfactants will, depending on the polarity of the liquid, form micelles. The minimum concentration at which a surfactant forms micelles is referred to as *critical micelle concentration (CMC)*. At concentrations below CMC, the surfactants are found only in detached form, whereas at concentrations above CMC, micelles will be formed in addition to the molecules in free form. Usually, surfactants will form micelles only above a given temperature, which is referred to as *critical micelle temperature (CMT)*. Depending on the nature of the surfactant, two primary structures are formed: *bilayers* and *micelles* (see Fig. 20.11).

20.3.1.3 Bilayers

Surfactants with two tail groups can be geometrically approximated as cylinders. They assemble in linear structures forming films as *bilayers (double-layers)*. Depending on the ambience, these layers will assemble such that they mimic the polarity of the ambience. In an unpolar environment, the surfactants will assemble in a bilayer with the polar heads inside of the layer and the unpolar tails oriented toward the outside (see Fig. 20.11c). In a polar environment, the surfactants will assemble such that the unpolar tails are oriented inward and the polar heads toward the ambience (see Fig. 20.11d).

Bilayers are encountered commonly, especially in biology. Cell membranes are nothing other than bilayer membranes formed from a specific type of surfactants, which are referred to as *phospholipids* (see section 20.3.2.3).

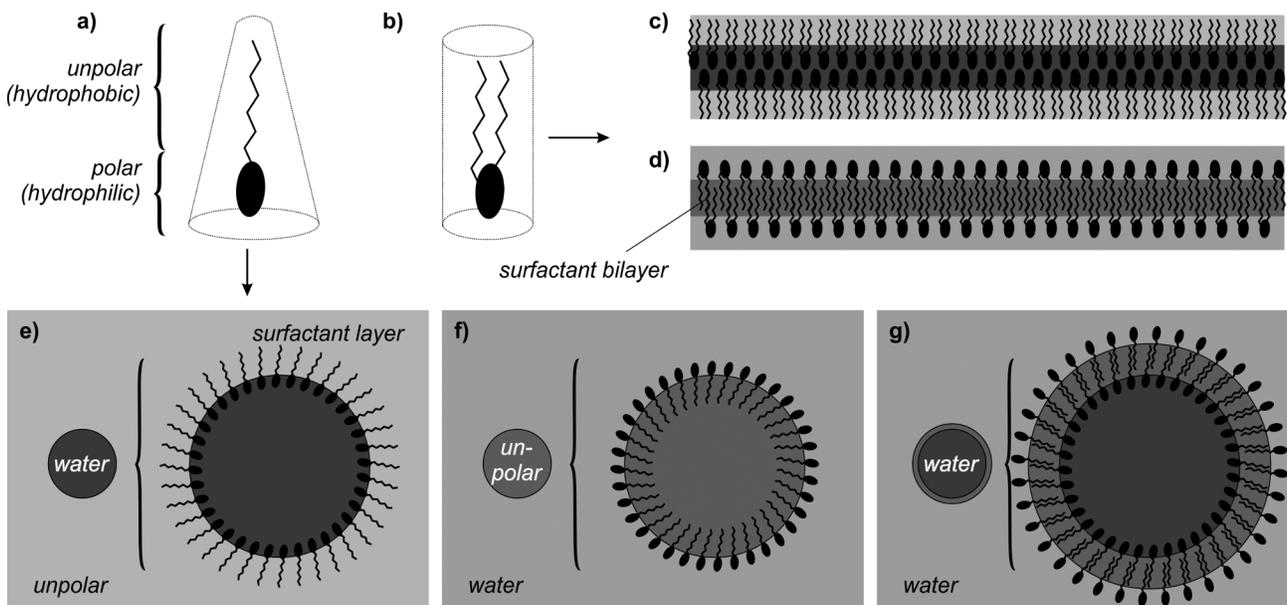


Fig. 20.11 Bilayer and micelle formation. Depending on the chemical structure of the surfactant different structures are formed. a) Surfactant with only one tail tends to form micelle structures. They can be approximated by cones, which is the reason for the formation of curved surfaces. b) Surfactants with two tail groups are better approximated as cylinders and thus form bilayers rather than micelles. c) Typical bilayer formation as seen in an unpolar environment. The surfactants will assemble such that the polar head groups are in close proximity. The exposed surface therefore mimics the unpolar character of the ambience. d) Typical bilayer formation in a polar environment. The surfactants will assemble such that the unpolar tails will be in close proximity. The exposed surface therefore mimics the polar character of the ambience. Cell membranes (which are lipid bilayers) are a good example for this behavior. e) Micelle formation in an unpolar environment. The formed bubble entraps polar liquid and may even contain similarly polar substances. f) Micelle formation in an aqueous environment. The polar head groups are oriented toward the surface keeping the unpolar head groups assembled. g) Example of a spherical bilayer structure. Examples include vesicles (lipid bilayer spheres), which occur in cells as well as soap bubbles in air.

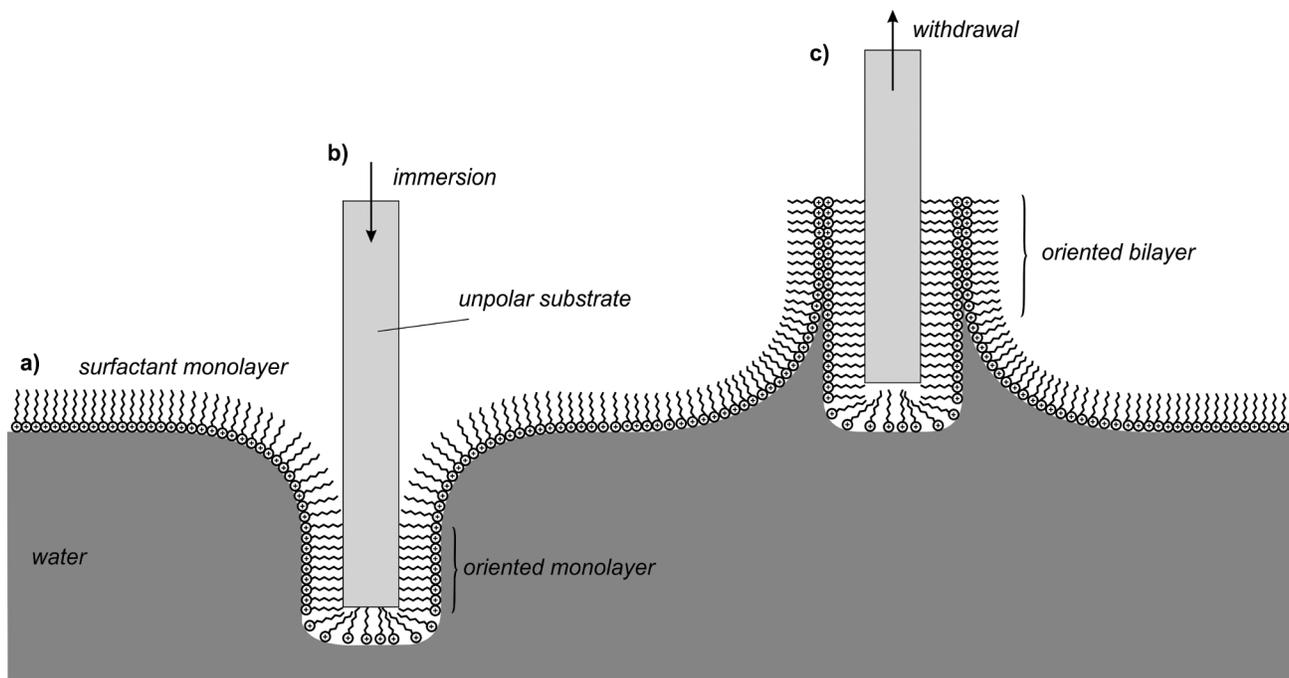


Fig. 20.12 Creation of a Langmuir-Blodgett film. An unpolar substrate (e.g., a polymer) is immersed in a solvent in which a surfactant was dissolved (a). The surfactant forms a monolayer at the surface of the liquid. During immersion, the surfactant molecules self-assemble on the surface of the substrate forming a monolayer. The substrate's surface is now polar (b). During retraction the substrate passes again through the surface layer, and a second layer of surfactant molecules will assemble inversely on the surface leaving the substrate (again) with an unpolar in surface (c). This process can be repeated multiple times.

20.3.1.4 Langmuir-Blodgett Films

The formation of surfactant layers at surfaces is a very stable process. This effect is exploited in the *Langmuir-Blodgett*^{1,2} method for thin film formation (see Fig. 20.12). For anyone interested in details about this method, a highly advisable resource is Langmuir and Blodgett's original paper, which contains many experimental details and potential pitfalls [9].

In this process, a substrate is immersed repeatedly in a solution of a surfactant. Depending on the polarity of the solvent, the surfactant molecules will be oriented at the interface, and once a substrate passes through this surface, the surfactant molecules will self-assemble at the substrate surface rendering it equivalently polar to the solvent. During withdrawal, the substrate passes the surfactant layer again, which results in the formation of a second, inversely oriented layer on top of the first. Therefore, after each immersion and withdrawal, a bilayer will be formed on the substrate surface, leaving it with the same polarity as before the first immersion. This process can be repeated multiple times. With each immersion and withdrawal, an additional bilayer will be deposited. The thickness of these layers is approximately twice the length of the surfactant.

In order to obtain smooth and even films, it is very important to immerse and withdraw the substrate at a very precise speed. For practical applications, high-precision linear stages are used for this purpose. Practically the same instrument is required for the *Wilhelmy plate method* for measuring the surface tension (see section 22.2.2).

20.3.1.5 Micelles

Micelles are spherical structures of surfactant layers. They are formed from surfactants with one tail group that can be best approximated by a cone. These molecules will assemble in curved layers that eventually lead to the

¹ Irving Langmuir was an American physicist who first introduced the method that we now refer to as *Langmuir-Blodgett films* [6].

² Katharine Blodgett was an American physicist who made significant improvements to the method of generating thin films originally developed by Irving Langmuir [7, 8]. Blodgett was a model scientist and the first woman to be appointed staff scientist at the research labs of General Electric in 1917.

formation of a sphere. Depending on the nature of the surroundings, the surfactant molecules will arrange such that the outside of the micelle mimics the polarity of the ambience. In a polar environment, the head groups will be oriented toward the inside and the unpolar tails toward the outside (see Fig. 20.11e). In unpolar environments, the polar head groups will be oriented toward the inside and the unpolar tails toward the outside (see Fig. 20.11f).

In both cases, the micelles are able to enclose molecules of matching polarity. This is the basic concept in *emulsion formation*: if an *emulsification reagent* is added to a two-phase system, this reagent (which effectively is a surfactant) will form micelles enclosing one of the phases. For example, numerous sauces in cooking are prepared using emulsification reagents in order to increase the amount of fat that can be dissolved in the aqueous sauce. Without an emulsification reagent, the sauce would show small fat droplets swimming on the surface. Milk is another prominent example. The color of milk is a result of the micelles. The micelles enclose the fat of the milk and scatter light, thereby causing milk to appear white.

In some cases, micelles can also be formed as double-layers, called *bilayers* (see Fig. 20.11g). Typical examples for this are soap bubbles, which is why the fluid mechanics of soap bubbles use a double layer when calculating the pressure drop across the surface (see Eq. 20.12). Micelles also occur in cells in the form of *vesicles*, although they are then usually formed using phospholipids, *i.e.*, surfactants with two tail groups.

20.3.2 Types of surfactants

20.3.2.1 Anionic Surfactants

Anionic surfactants are all surfactants that carry a negatively charged head group. In principle, any negatively charged functional group that can complex with a counterion may lend itself to be a cationic surfactant. This section lists the most commonly used ones.

Carboxylic Acids. The most commonly used anionic surfactants are based on aliphatic carboxylic acids, which can be derived from naturally occurring animal and plant fats (see Fig. 20.14). Fats as they occur in nature are usually triesters of carboxylic acids and glycerol. These fats can be hydrolyzed using potassium hydroxide or sodium hydroxide, a process that is commonly referred to as *saponification* (see Fig. 20.13). The term refers to

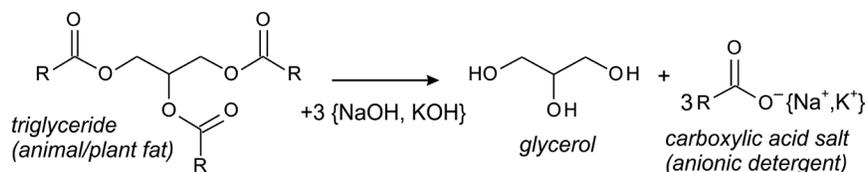


Fig. 20.13 Saponification reaction to obtain anionic surfactants (soap) by hydrolysis of naturally occurring triglycerides, which are animal or plant fats.

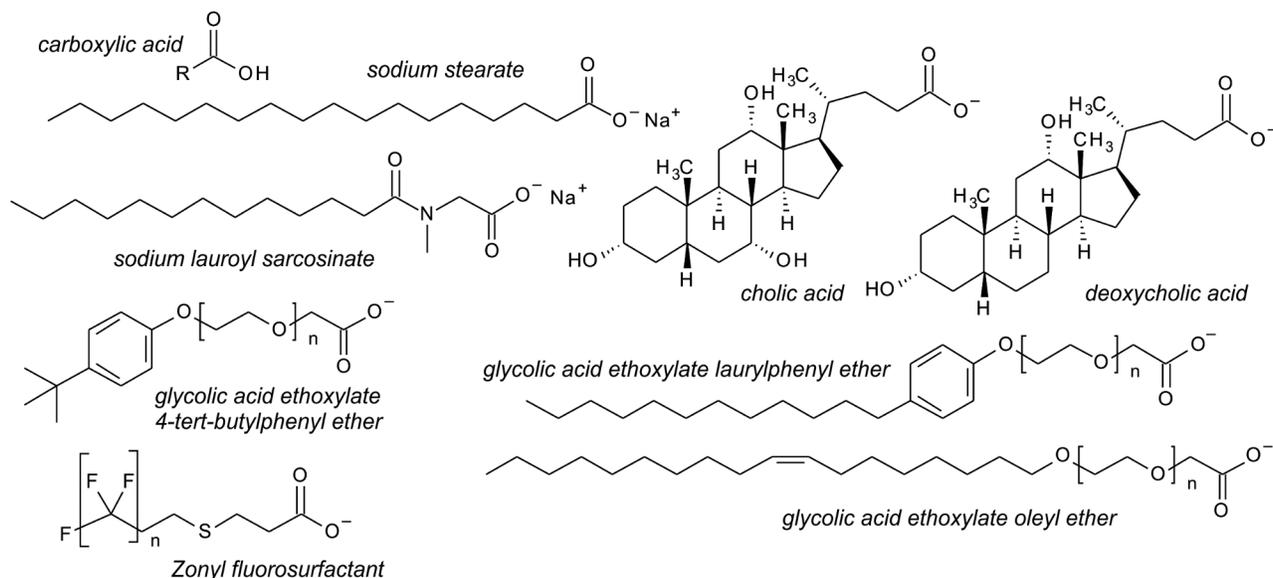


Fig. 20.14 Commonly used anionic surfactants based on carboxylic acids.

the fact that the resulting substances are what is generally referred to as *soap*. The carboxylic acids are retrieved as their sodium or potassium salts, which makes them anionic surfactants. They are the main ingredient of soap. Because they can be obtained from fats, these aliphatic carboxylic acids are often referred to as *fatty acids*.

Commercially, the most relevant surfactant is sodium stearate, which is the sodium salt of stearic acid. As stated, it is obtained by saponification of many animal fats. Several carboxylic surfactants are based on bile acid obtained from the bile of animals, among them cholic acid and its salt (usually the sodium salt) as well as deoxycholic acid, which has one less alcohol group. These surfactants are only weakly anionic, which makes them suitable for use in cell biology. Another commonly used substance for cell lysis is sodium lauroyl sarcosinate. It is also used in numerous cosmetics, shampoos, and soaps.

Several carboxylic poly(ethylene glycol) ethers can also be used as surfactants, *e.g.*, glycolic acid ethoxylate 4-*tert*-butylphenyl ether (with an aromatic hydrophobic tail) or glycolic acid ethoxylate laurylphenyl ether (with an alkylphenyl hydrophobic tail) as well as glycolic acid ethoxylate oleyl ether (with a purely alkyl tail).

You may come across a group of commonly used fluorinated surfactants called *Zonyl* FSA fluorosurfactants. These are usually used in form of their lithium salts.

Sulfonic Acids. The second important class of anionic surfactants is based on sulfonic acid. Fig. 20.15 shows a selection of the most important compounds of this class.

One of the most important surfactants of this class is sodium dodecyl sulfate, which is the sodium salt of dodecyl sulfonic acid. It is commonly used in biology and biochemistry for denaturing proteins, *i.e.*, for destroying the quaternary and tertiary structure. This is an important prerequisite for gel electrophoresis, which is often conducted after a denaturing step using sodium dodecyl sulfate. The gel is mostly made from polyacrylamide, which is why this type of gel electrophoresis is then referred to as sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE). It is also possible to combine dodecyl sulfonic acid with an ammonium ion, resulting in ammonium dodecyl sulfate. In order to increase water solubility, a polyether can be inserted into sodium dodecyl sulfate, resulting in sodium lauryl ether sulfate. Another commonly used anionic surfactant is dioctyl sodium sulfosuccinate. Besides aliphatic sulfonic acids, many aromatic sulfonic acid surfactant are in use, with sodium dodecylbenzenesulfonate being the most commonly used one.

In many applications, fluorinated anionic surfactants are being used, *e.g.*, as stain repellent additive in cloth and surface treatment. Fluorinated surfactants are usually environmentally critical as their half-life time is very high and they tend to accumulate in organism, which is why they are referred to as *bioaccumulating*. One of the most commonly used surfactants was perfluorooctane sulfonic acid, but it is being replaced by perfluorobutane sulfonic acid, which has a much shorter half-life time and does not seem to be bioaccumulating.

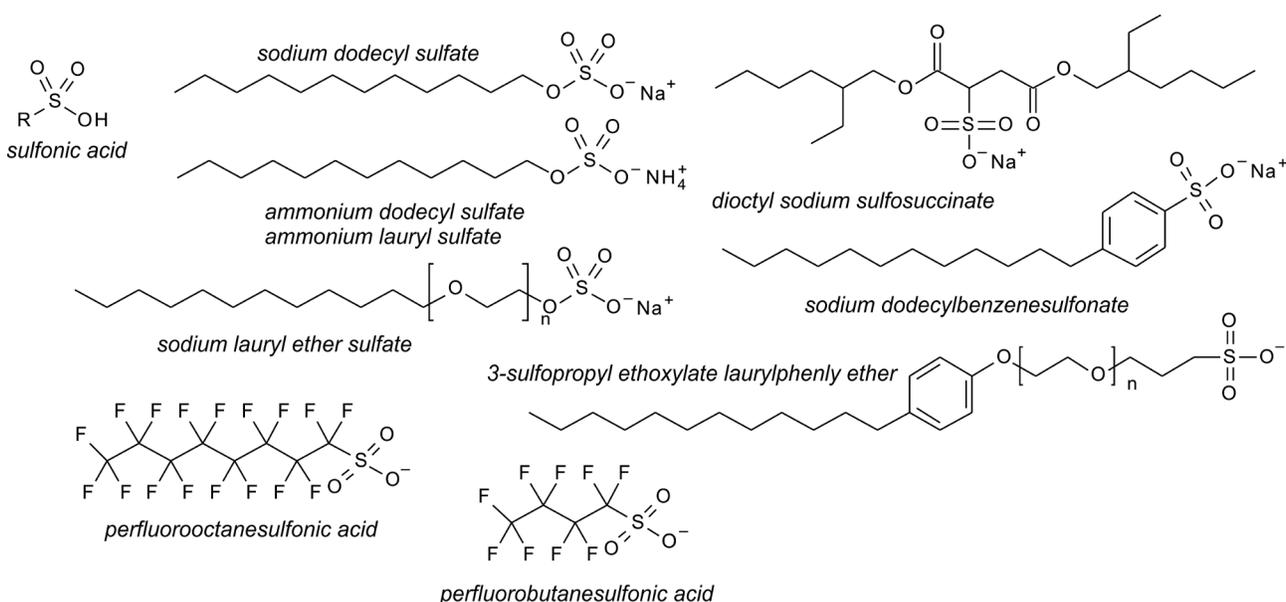


Fig. 20.15 Commonly used anionic surfactants based on sulfonic acids.

As for the carboxylic acids, several sulfonic acid ethers can also be used, *e.g.*, 3-sulfopropyl ethoxylate laurylphenyl ether (with an alkylphenyl hydrophobic tail); it is mostly used as its potassium or sodium salt.

20.3.2.2 Cationic Surfactants

Cationic surfactants are all substances that carry a positive charge. This charge may be either permanent or only exist in certain pH value ranges. The most important classes of cationic surfactants will be discussed in the following section. Fig. 20.16 lists a selection of the most commonly encountered substances.

Amine-Based. Primary, secondary, and tertiary amines can be positively charged, depending on the ambient pH value. Typical substances used may include triethylamine, which is commonly used as triethylamine hydrochloride or octenidine dihydrochloride.

Quaternary Ammonium. Quaternary ammonium compounds are an important class of zwitterionic surfactants. A quaternary ammonium is an amine with four rest groups, which renders it permanently positively charged. These substances are often referred to as *quaternary ammonium salts*, and they only occur as complex with an anion. Commonly used aliphatic quaternary ammonium compounds include cetrimonium bromide, cetylpyridinium chloride, dimethyldioctadecylammonium chloride, and *Adogen*. Aromatic examples include pyridine derivatives and alkylbenzene derivatives, *e.g.*, benzethonium chloride.

20.3.2.3 Zwitterionic Surfactants

Zwitterionic or amphoteric surfactants are surfactants that carry both a positive and a negative charge. As stated, these charges can either be permanent or dependent on the pH value. Often the cationic compound is either an amine or a quaternary ammonium cation, whereas the anionic part is mostly a carboxylic, sulfuric, or phosphoric acid (or esters thereof). Fig. 20.17 lists the most commonly encountered zwitterionic surfactants.

Carboxylic Acid/Quaternary Ammonium. An example of a combination of a carboxylic acid and a quaternary ammonium ion is cocamidopropyl betaine or amidosulfobetaine-16 which has a longer hydrophobic tail, or the C80 detergent, which has an alkylphenyl hydrophobic tail. Several other carboxylic acid/quaternary ammonium surfactants are in use, *e.g.*, lauryl-*N,N*-(dimethylammonio)butyrate and lauryl-*N,N*-(dimethyl)glycinebetaine.

Sulfuric Acid/Quaternary Ammonium. A typical example of a combination of sulfuric acid and a quaternary ammonium ion is 3-[(3-cholamidopropyl)dimethylammonio]-1-propanesulfonate, which belongs

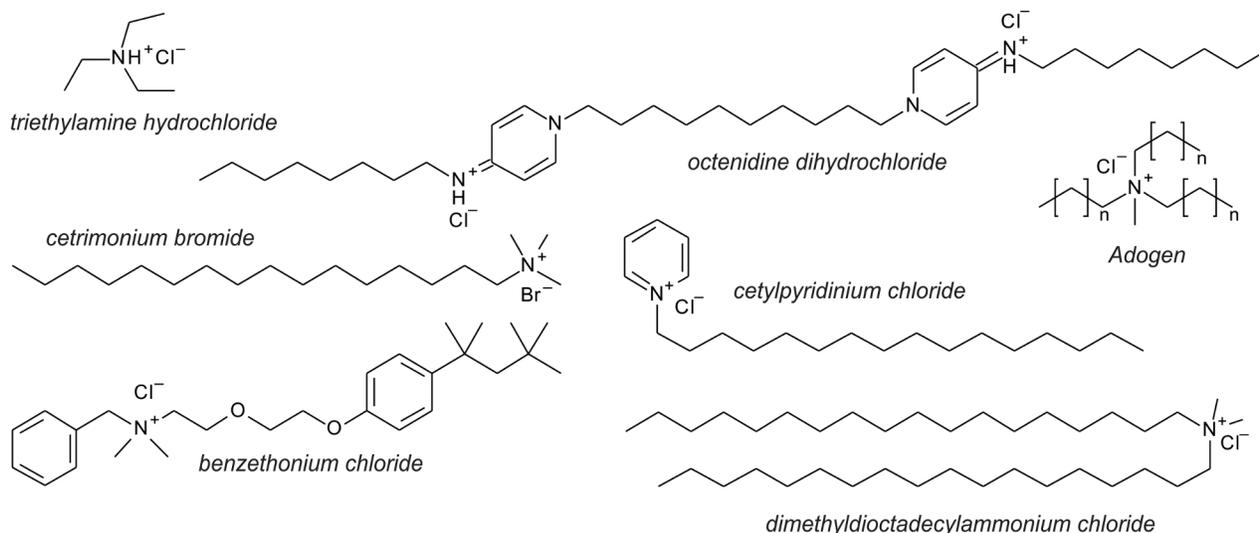


Fig. 20.16 A selection of commonly encountered cationic surfactants.

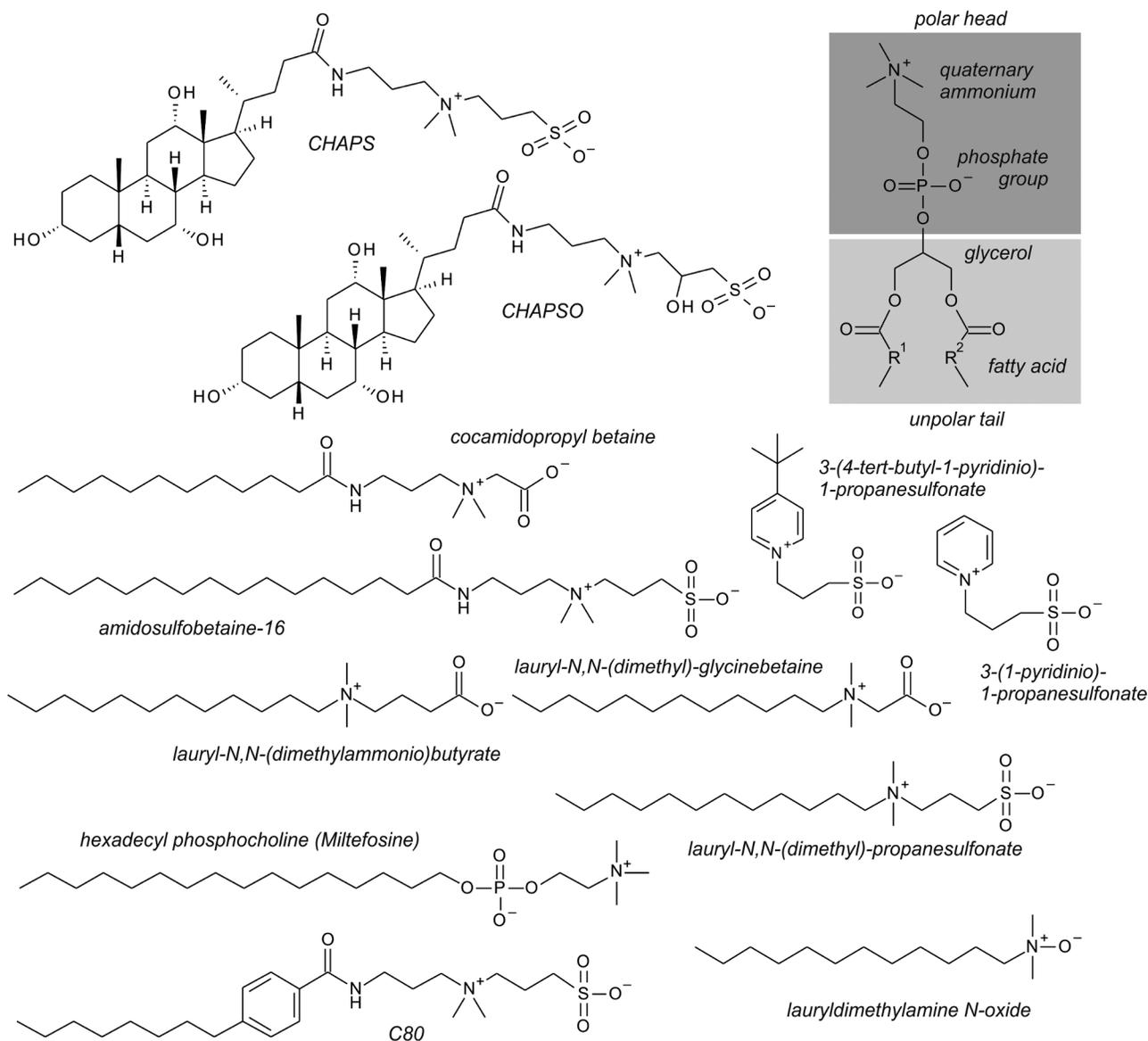


Fig. 20.17 A selection of commonly encountered zwitterionic surfactants.

to the *hydroxysultaines* class. A slightly modified version is 3-([3-cholamidopropyl]dimethylammonio)-2-hydroxy-1-propanesulfonate, which is slightly more hydrophilic than 3-[(3-cholamidopropyl)dimethylammonio]-1-propanesulfonate. There is also a sulfuric acid equivalent of lauryl-*N,N*-(dimethylammonio)butyrate, lauryl-*N,N*-(dimethyl)-propanesulfonate. Several aromatic quaternary ammonium surfactants are being used, *e.g.*, 3-(4-*tert*-butyl-1-pyridinio)-1-propanesulfonate, 3-(1-pyridinio)-1-propanesulfonate, and 3-(benzyl-dimethylammonio)propanesulfonate. Several zwitterionic surfactants are derived from bacteria, *e.g.*, surfactin, exist.

Phosphoric Acid/Quaternary Ammonium. In addition to carboxylic acids and sulfuric acids, numerous phosphoric acid/quaternary ammonium surfactants are being used, with hexadecyl phosphocholine (also referred to as *miltefosine*) being a typical example.

Miscellaneous. Zwitterionic surfactants can also be obtained if a quaternary ammonium with an attached hydroxy group is used. The hydroxy group is usually only weakly acidic but is rendered significantly more prone to deprotonation if attached directly to a nitrogen atom. A typical example of this class of surfactants is lauryldimethylamine *N*-oxide.

Phospholipids. A very important group of zwitterionic surfactants are *phospholipids*, which consist of a quaternary ammonium head coupled *via* a phosphate group and glycerol to two hydrophobic fatty acids. These specific types of surfactants make up the membrane of cells and are therefore among the most important surfactants for cell biology.

20.3.2.4 Non-Ionic Surfactants

Non-ionic surfactants are surfactants that have polar head groups that are not electrically charged (see Fig. 20.18). They usually rely on a functional group able to deprotonate but only to a very low degree. Thus the substance does not act as a good Brønsted acid but provides decent solubility in polar solvents, *e.g.*, water. In general, the solubility of non-ionic surfactants is not as good as the solubility of ionic surfactants, but they do not change the pH of the solution. Their CMC is usually higher than those encountered in ionic surfactants, which may be an advantage as it allows more surfactant to be mixed into a solution without running the risk of (potentially) undesired micelle formation.

In general, alcohols are good candidates for such head groups. Alcohols are weak acids with decent solubility in aqueous solutions. Primary alcohol groups bound to unpolar aliphatic tails or cyclic or aromatic structures are generally good candidates for non-ionic surfactants. Non-ionic surfactants are important substances for cell biology as they are mild and do not break protein/protein interaction while still providing the potential to dissolve unpolar compounds, *e.g.*, bilayer membranes. This makes them suitable, *e.g.*, for disrupting cell membranes, a process referred to as (*cell*) *lysis*.

Alkylphenyl Ethers of poly(ethylene glycol). Alkylphenyl ethers of poly(ethylene glycol) are a very common group of non-ionic surfactants. One of the most prominent members of this surfactant family is *Triton*, which is a polar oligo(ethylene glycol) tail bound to an alkylphenol that acts as the hydrophobic head. The number following the name indicates the length of the polar tail. There are also reduced forms of *Triton* based on a cycloalkane. These are referred to as *Triton (reduced)*.

Several other alkylphenyl ethers are used as surfactants that mainly differ by the side groups of the benzene ring. For example, nonoxynol-9 uses a *n*-nonane hydrophobic tail and has been used as an ingredient for shampoos and creams.

Alkylethers of poly(ethylene glycol). Besides alkylphenyl ether, alkylethers of poly(ethylene glycol) are also commonly used non-ionic surfactants. They consist of a poly(ethylene glycol) chain with varying lengths to which an aliphatic hydrocarbon chain is attached (often *n*-dodecane). Typical examples of this surfactant family include octaethylene glycol monododecyl ether and pentaethylene glycol monododecyl ether.

Alkylethers of poly(propylene glycol). Another alternative to using poly(ethylene glycol) is poly(propylene glycol). Its alkylethers are also commonly used non-ionic surfactants. For example, poly(propylene glycol) is less hydrophilic than poly(ethylene glycol) and can often be combined with poly(ethylene glycol) to form surfactants as well. The group of polymers referred to as *poloxamer*, poly(ethylene glycol)/poly(propylene glycol)/poly(ethylene glycol) block copolymers, can also be used as surfactants of this family.

Alkylethers of glycerol. Likewise, glycerol can be used as hydrophilic head in non-ionic surfactants. Usually, it is partly esterified with long-chained fatty acids, *e.g.*, lauric acid, resulting in glycerol monolaurate.

Derivatives of ethanolamine. Several derivatives of ethanolamine can be used as surfactants. These are usually amids obtained by reacting ethanolamine with long-chained fatty acids, *e.g.*, lauric acid. The resulting surfactant is a secondary amine. These surfactants are often referred to as *cocamide surfactants* because mostly fatty acids from coconut oil are used. A typical example is lauramide monoethylamine. An alternative to ethanolamine is diethanolamine, which is also reacted with a fatty acid to obtain a tertiary amine. Typical examples of such surfactants are 2-dimethylaminoethanol and polyethoxylated tallow amine.

Sugar-Based Surfactants. This group of non-ionic surfactants uses hydrophilic sugars to which hydrophobic tails are bound. One common substance of this class is *n*-dodecyl- β -D-maltoside, a member of the *maltoside*

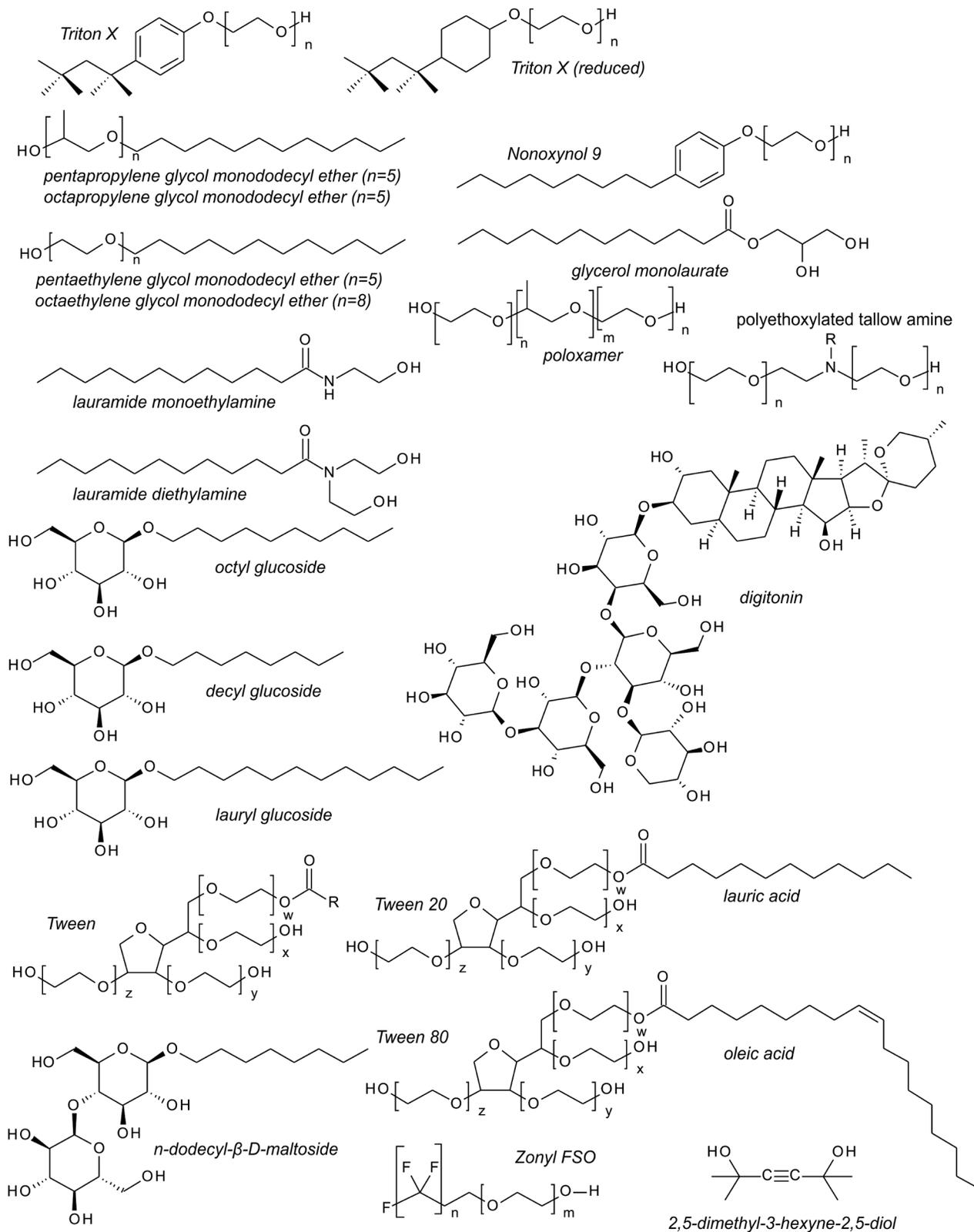


Fig. 20.18 A selection of commonly encountered non-ionic surfactants.

surfactants so named because the sugar unit used is maltose. An example of a *pyranoside* surfactant is *n*-octyl- β -D-thioglucopyranoside. This class uses pyranose as the sugar unit. Examples of the *glycoside* surfactants are octyl glucoside, decyl glucoside, and lauryl glucoside. An example of a polysugar surfactant is digitonin.

Another very important group of sugar-based surfactants are the *Tween surfactants*, most notable Tween 20 and Tween 80. These surfactants are based on a sorbitan sugar, which is why they are commonly referred to as *polysorbate surfactants*. Three oligo(ethylene glycol) side groups of varying lengths are bound to the sugar increasing the hydrophilicity of the head group. This structure forms the core of all Tween surfactants. They deviate in the hydrophobic tail, which is a fatty acid coupled *via* an ester to four oligo(ethylene glycol) tail. In Tween 20 this fatty acid is lauric acid; in Tween 80 it is oleic acid.

Miscellaneous. Several hydrophobic substances to which several hydroxy groups are appended can also be used as surfactants. If these compounds are of lower molecular weight, they are usually unsaturated in order to ensure sufficient hydrophobicity. A typical example is 2,5-dimethyl-3-hexyne-2,5-diol. There is also a class of fluorinated surfactant based on perfluorinated alcohols. The most common representatives of this class are the *Zonyl* FSO surfactants.

Another important point to consider is the choice of counterions. As stated, for numerous surfactants, the counterions are defined by their method of making. Good examples are the carboxylic acid surfactants created by saponification (see section 20.3.2.1). These usually carry an alkaline metal counterion, mostly Na^+ or K^+ . These are the most common counterions for anionic surfactants.

Cationic surfactants often occur with halide counterions, most commonly Cl^- , Br^- , and I^- .

The counterion can also be the ammonium cation NH_4^+ (the protonated form of ammonia) or a protonated tertiary amine, *e.g.*, $\text{NR}_3\text{H}^+\text{Cl}^-$.

20.3.3 Applications of Surfactants

There are numerous applications for surfactants, the most important ones will be discussed in this section.

Emulsification. Surfactants are used for numerous applications in everyday life. From shampoos to soaps, cleaning agents, fat remover, and laundry detergents, all of these products use surfactants. They are also used in order to form emulsions, *i.e.*, in order to increase the solubility of two substances that would normally not mix. Soap is a very good example. During hand washing, the water will dissolve all water-soluble substances on our hands leaving behind all substances that are not water-soluble. Using soap as surfactant, these substances can be encapsulated in small micelles and thus rendered water-soluble, which allows them to be washed off our hands. Usually surfactants with cleaning properties or surfactants that are used for cleaning are referred to as *detergents*.

Stabilization of Suspensions. Many suspensions use surfactants in order to increase the liquid's capability to keep solids suspended and to avoid aggregation by forming repulsion layers around the objects (see Fig. 20.19). These layers rely on the repulsive action of equally charged surfaces that can be introduced using surfactants. Especially if an unpolar particle (such as a polymer bead) is suspended in a polar liquid (such as water), the particles tend to aggregate quickly. This is because the polarity of the solvent and the particles is different, and therefore the particles tend to cluster more easily. After adding a surfactant, the surface of the particles will be masked, thus exposing the same polarity as the solvent. Furthermore, if ionic surfactants are used, the particles will be equally charged and thus repel each other. Many synthesis protocols for nanoparticles rely on surfactants in order to keep the particles stable in solution.

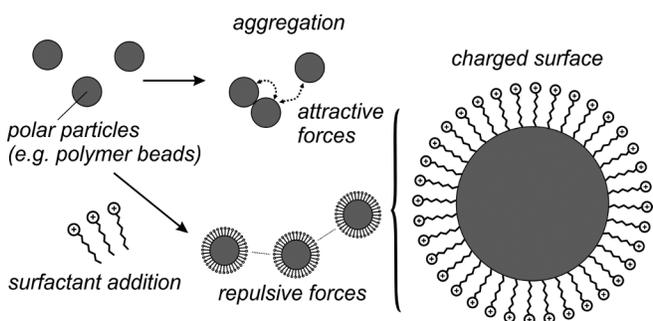


Fig. 20.19 Stabilization of suspensions, *e.g.*, of polymer beads in solution. The surfactants form layers around the particles that repulse because of the equal charging of the surface, thus avoiding aggregation of the particles.

Micelle Reaction Compartments. In many synthesis applications, micelles are formed inside of a solvent and act as small reaction compartments. These *emulsion reactions* use the local confinement of reactions partners, *e.g.*, to synthesize components of only a given size. Again, the synthesis of nanoparticles is a good example. Here small micelles act as the boundary of the reaction and limit the growth of the nanoparticles. If the micelle size is varied, the size of the nanoparticles can be optimized.

Changing the Surface Tension. One of the main applications of surfactants is changing the surface tension of liquids. In many applications, liquids that need to be handled by a given technical system may not have sufficiently high surface tension. This may be critical, *e.g.*, if a liquid is to be transported from a reservoir onto a given substrate *via* a stamping method or by pin transfer. If the liquid's surface tension is too low, it may not be possible to transport a sufficient amount of liquid. In this case, a surfactant can be added that will migrate to the liquid's interface and increase the surface tension. For example, a low surface tension oil (*e.g.*, a silicon oil) can be blended with an ionic surfactant that has a polysiloxane tail. After migrating to the surface, the charged head groups of the surfactant will lead to a stronger interaction in the interface layer and lead to stronger unbalance forces and thus increasing the surface tension. This allows transporting larger quantities of the liquid *via* a liquid transfer method as the liquid/gas interface can sustain higher forces and thus retain larger quantities of liquid.

Another common example of optimization of the surface tension are inks used for inkjet printing. These are usually mixed with surfactants in order to optimize their ability to be spotted without the formation of satellite drops. Also, the wetting behavior on the paper onto which the ink is spotted can be altered by adding suitable surfactants.

Interface Stabilization. Many applications in microfluidics would not be possible without the use of surfactants in order to stabilize liquid/liquid interfaces. Whenever discrete droplets of liquids are to be handled, surfactants are used in order to stabilize the liquid/gas or liquid/liquid interface.

Digital microfluidics is a good example for this. Here the droplets to be moved are usually immersed in an inert oil phase. Because the electrowetting induces substantial shear stress on the boundaries, it is usually advisable to stabilize the boundary using a suitable surfactant. Also because the contact area between the droplet and the top and bottom substrates carrying the electrodes is usually large (the reason being that the droplet is squeezed in-between them), it is advisable to use a surfactant, which will reduce the unspecific interaction between the droplet and the substrates. This is especially true if the setup is being used for an analytical assay where the loss of analyte (*e.g.*, a protein) must be avoided.

A second common example is droplet microfluidics. Here the droplets are dispersed in an oil phase exposing a significant surface area. Stabilization of the droplets is not only critical to maintain the droplet intact during formation but also to avoid droplets sticking to the channel walls and to reduce the risk of (undesired) droplet merging. By introducing a surfactant (either into the droplet itself or into the oil phase), the interface of the droplet is stabilized, inducing a certain repulsion between the individual droplets. This significantly reduces the risk of droplet coagulation and merging.

Passivation. Numerous applications in bioanalytics require biochemical passivation of channel walls and substrates in order to reduce the unspecific adsorption of, *e.g.*, proteins. This can be accomplished using suitable surfactants which render the surfaces of the microfluidic system more hydrophilic, thus inhibiting hydrophobic interaction of the proteins and the (mostly) hydrophobic substrate. In many applications, the *Triton* surfactants are the first substance of choice here. Depending on the native polarity of the substrate, surfactants with a higher unipolar character may have to be used especially when working with polymers. In general, non-ionic surfactants are preferred in order to decrease the risk of altering and/or degenerating the proteins of interest.

Surface Coatings. Just as surfactants can change the surface tension of liquids, they can also alter the surface free energy of a substrate, thereby allowing or preventing the wetting of a given liquid. A typical example includes anti-icing coatings where, *e.g.*, a glass window is coated with a layer of a surfactant that lowers the surface free energy. As a result, water will not wet the surface, and therefore the surface will not show icing.

Detergents. The term *detergents* in biochemistry usually refers to surfactants used for cell lysis. Detergents usually have to be very mild surfactant and biocompatible substances in order to ensure that they only disrupt the cell membranes and do not significantly alter any other compound of interest. Detergents are also used to break interactions between proteins or to destroy their quaternary and tertiary structure.

In general, ionic surfactants are not a good choice as detergents with a few exceptions. As stated, sodium dodecyl sulfate is commonly used for protein denaturing during gel electrophoresis. It adds a negative charge to all proteins irrespective of their pI, which allows a subsequent separation by size and weight only. Also, cholic acid and deoxycholic acid (both being very weak anionic surfactants) can be used to dissolve membranes. Sometimes sodium lauroyl sarcosinate can also be used.

Other detergents of choice are usually glycoside surfactants, *e.g.*, *n*-dodecyl- β -D-maltoside or *n*-octyl- β -D-thioglucopyranoside, both of which are very mild reagents that maintain protein activity during cell lysis. *Tween* surfactants are often used as surfactants in washing buffers.

Environmental and Health Risks. Depending on their chemical nature, surfactants may have a significant half-life, and their effects on the environment must be considered. As surfactants allow such a wide variety of processes, they also act after being used if not properly disposed. Surfactants may significantly alter an ecosystem if probed in sufficient quantity. Another important aspect is their bioaccumulating capability, *i.e.*, their potential to accumulate in animals or humans. This is especially critical for halogenated surfactants, with fluorinated and chlorinated surfactants being considered the major risk. For most surfactants, biotoxicity assays must be performed prior to use in order to assess these risks. Some surfactants (most prominently the halogenated ones) must be disposed of properly, whereas others (such as soap) may be disposed simply as waste water.

20.4 MARANGONI EFFECT

The *Marangoni*¹ effect refers to forces that occur as a consequence of inhomogeneities in free surface energy of a solid or liquid surface. In the latter case, we usually refer to the gradient in the surface tension (because the term free surface energy is not commonly used with liquids). As discussed in section 20.1.3, surfaces with high free surface energy are significantly easier to wet than surfaces with high surface energy. As a result, a liquid on a surface will flow toward areas of low surface energy (see Fig. 20.20). This gradients in free surface energy can either be static, *e.g.*, by selectively modifying fractions of the surface with the aim of reducing the free surface energy, or temporally induced. The latter can be accomplished, *e.g.*, by applying electric fields or temperature gradients.

20.4.1 Temperature

Local heating or cooling causes changes in the free surface energy and can thus be used to drive fluids in a suitable technical system. As stated in section 20.1.6, heating a surface (or a liquid) will cause its surface tension to drop. Therefore applying a temperature gradient to a surface can be used to drive liquid flow. This is sometimes referred to as *thermal creep*. The dimensionless number often used when characterizing flows because of temperature gradient is the Marangoni number (see section 9.9.14).

20.4.2 Surfactants

A very good demonstration of the Marangoni effect is obtained by dropping a small amount of a surfactant (usually a drop of soap) to a static water reservoir (see Fig. 20.21). The surfactant will locally decrease the surface tension, thus inducing a fluid flow away from the region of lower surface tension. This flow can be

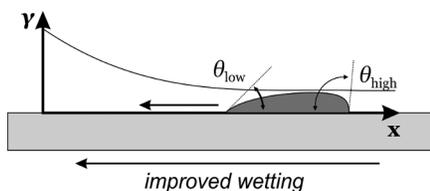


Fig. 20.20 Marangoni effect as observed on surfaces with a gradient in surface tension. The liquid will move into regions of higher surface tension.

¹ Carlo Marangoni was an Italian physicist who studied the interaction of liquids, *i.e.*, the spreading of one liquid on top of a surface or a second liquid [10]. The forces involved in these effects are therefore commonly referred to as *Marangoni forces*. However, these effects were also reported earlier, *e.g.*, by Irish engineer James Thomson [11], in form of the so-called “tears of wine” effect. Thomson was the younger brother of William Thomson who is generally referred to as “Lord Kelvin”.

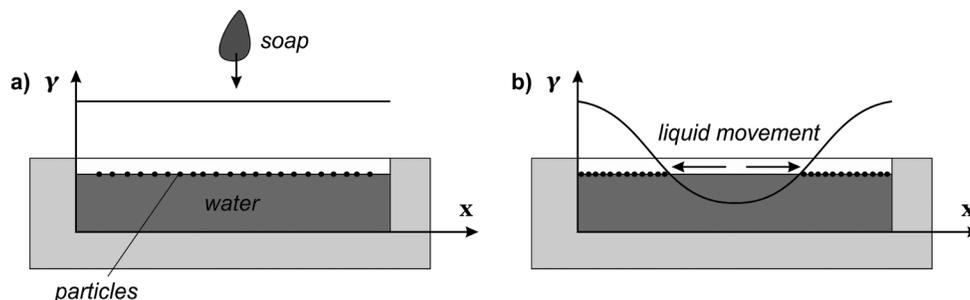


Fig. 20.21 Demonstration of the Marangoni effect using a surfactant to modify the surface tension. After adding a small amount of surfactant to the water (a) fluid will move toward regions of higher surface tension (b). This can be seen by adding particles to the fluid's surface.

observed by adding a small number of particles (dust or carbon black) to the water, in which case one can see that the particles completely vacate the region into which the surfactant was dropped.

20.4.3 Tears of Wine

Similar effects can also be observed for other liquids that have a lower surface tension than water. Dropping ethanol into water will result in a similar effect because of the lower surface tension (see Tab. 20.2). This results in the “tears in wine” phenomenon. It can be observed in wine glasses. Wine (which is roughly speaking a mixture of water and ethanol) wets the surface of the glass and forms a meniscus because of capillary action (see section 21). Because of the increased surface area, the evaporation is increased, and, as ethanol has a lower boiling point and a higher vapor pressure compared to water, ethanol will evaporate quicker leaving the liquid in the meniscus with a higher overall content of water. Because water has a higher surface tension, the surface tension gradient in the glass will increase toward to outside, *i.e.*, toward the meniscus. This effectively pulls more and more liquid into the meniscus, which will eventually collapse into small droplets of water that flow back from the side of the glass forming the characteristic “tears of wine”.

20.5 SUMMARY

In this section we introduced the concept of free surface energy, which in liquids is usually referred to as surface tension. Surface tension is inherent to all liquids. As stated, surface tension is the term used to refer to the free surface energy of a liquid. Surface tension gives rise to forces that are used, *e.g.*, by insects that can walk on water because their gravitational weight is balanced by the surface tension forces. We also introduced the Young-Laplace equation, which describes the forces acting on curved liquid surfaces. As we will see, this equation is very important for describing effects such as the formation of droplets and the wetting dynamics of surfaces. As we have seen, the surface tension of liquids can be changed by adding surfactants. Surfactants are used in everyday life, *e.g.*, in the form of soaps, and a wide variety of substances can be used to adapt the surface tension of liquids.

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