A Superficial Overview of Detergency

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Physical chemistry is easier to teach if we take into account that the conclusions drawn from its laws, theories, or mathematical equations can be used to explain everyday tasks and chores. In this regard, the study of daily tasks we are familiar with and are caused by reasons probably unknown to our students could be an interesting way of introducing a lecture on physical chemistry and a major contribution to its understanding.

One of these everyday tasks is detergency. We engage in it when we brush our teeth, wash our hands, do the laundry, or wash the dishes, and we are so familiar with its results that the analysis of the mechanisms causing it becomes a matter of particular interest. In this article, physicochemical principles will be useful to explain, among other things, why the activity of washing machines includes continuous movements, why it is easier to wash dirty dishes if they have been previously immersed in water, or why we use bath sponges.

Detergency Products

Commercial products such as glass cleaners, shampoos, toothpastes, or laundry detergents generally do not have similar textures, colors, or physical states, and so only with difficulty could they be grouped into the same product category. However, after analyzing the information on their labels, we see that, although they could include a great variety of ingredients in their manufacturing, they all have at least one or various components showing surface activity. These components are called surfactants and their main function is to ensure that the process of detergency, consisting of the removal of unwanted material from solid surfaces, is achieved.

The nonsurfactant composition of cleaners, such as those mentioned above, involves many different functions. We find anticorrosive additives that help prevent damage to the metal components of washing machines or abrasive substances with a physical role in the case of toothpastes. Chemicals known as *builders* play a key role in detergency by removing the ions that interfere with surfactants while others, such as Na_2SO_4, simply consist of a filling to provide powdered laundry detergents with volume. Although in a general study of detergency the interaction between these additives must be taken into account, in this overview, we only discuss the key role played by the surfactant composition.

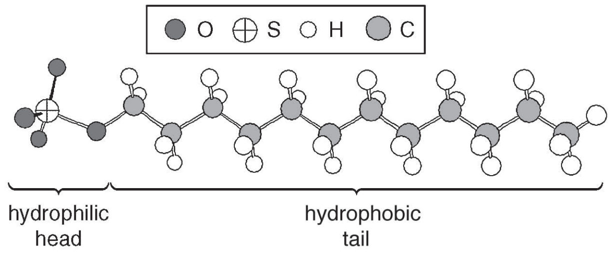

Figure 1. Structure of an anionic surfactant: sodium dodecyl sulfate.

It is necessary to review some of the concepts associated with detergency. Substrate is used to describe the solid surface to be cleaned and dirt describes the material to be removed. In this article we examine the physicochemical processes involved when the substrate is hydrophobic and the dirt, also hydrophobic, is liquid or particulate. By defining the nature of both substrate (S) and dirt (D) the complexity of the problem is reduced. However it is still necessary to consider a third element, the bath (B), which is the liquid added to keep substrate away from dirt. The range of baths used both at home and in industry is not as great as that of substrates and dirt. Moreover, water is the most frequently used substance.

Surfactants

Figure 1 shows the structure of sodium dodecyl sulfate (SDS), also known as sodium lauryl sulfate, a surfactant usually present in shampoos, toothpastes, hand soaps, body soaps, or hand dishwashing liquids. The structure of SDS can be used as an example to describe the structure of a typical surfactant. Two clearly differentiated regions are found in a surfactant, a lyophilic region (in those cases in which the bath is water it is called hydrophilic) and a lyophobic region (in this case it is called hydrophobic). In SDS, the hydrophobic section is represented by a hydrocarbon tail twelve carbon atoms long, whereas the hydrophilic part consists of a negatively charged sulfate group.

When a small quantity of SDS is added to water, the strongly attractive water–water interactions, in relation to the weak tail–water interactions, leave no space for the surfactant tails between the water molecules and as a consequence water molecules squeeze the surfactant molecules to the air (A)–water interface. In contrast, the interactions between hydrophilic heads and water molecules lessen the previous effect and reduce the extent of surfactant adsorption at the interface. This ability of surfactants to accumulate in interfacial regions entails an important consequence, namely, the decrease of the corresponding interface tension, which as we will see, plays a key role in detergency (see Appendix 1 in the Supplemental Material^{W}).

Liquid Dirt and Roll-Up

The origin of the problem that detergency tries to solve lies in the interactions established between substrate and dirt. In this section we will examine liquid dirt. These interactions are usually related to physical adsorption (van der Waals forces) or electrostatic forces *(1)*. The work, *W*, needed to keep

D away from S (Figure 2) is called *work of adhesion*. It is defined as the quantity of work required to increase BD and BS interfaces at the expense of the DS interface,

$$W_{\mathrm{ad}} = \gamma_{\mathrm{BD}} + \gamma_{\mathrm{BS}} - \gamma_{\mathrm{DS}} \qquad (1)$$

where γ is the interface tension. This equation introduces a key role of surfactants in detergency. As they accumulate in BD and BS interfaces, the corresponding interface tensions γ_{BD} and γ_{BS} decrease, resulting in a reduction in the value of W_{ad}. This conclusion is drawn from considering the interface tension concept as an energetic magnitude. However, in addition to this consideration, surface tensions can also be regarded as forces applied to a tangential disposition at the interfaces *(2)*.

The equilibrium established between the interface tensions in a three-phase system is shown in Figure 3. Here, Young´s equation is the result of an elementary equilibrium of forces:

$$\gamma_{\mathrm{BS}} - \gamma_{\mathrm{DS}} = \gamma_{\mathrm{BD}} \cos\theta \qquad (2)$$

Combining this with eq 1, the Dupré equation, we obtain the following result:

$$W_{\mathrm{ad}} = \gamma_{\mathrm{BD}}\left(1 + \cos\theta\right) \qquad (3)$$

This is the Young–Dupré equation, a relationship that allows the calculation of the quantity of work needed to separate dirt and substrate in terms of θ. The accumulation of the surfactant in the interface modifies the value of this angle, contributing to the appearance of one of the three cases shown in Figure 4.

- First case. The system reaches a limiting angle of 180°. This situation has an interesting implication, since the work of adhesion is interrupted (eq 3) and liquid dirt separates spontaneously from the substrate.
- Second case. The angle takes a value between 90° and 180°. W_{ad} decreases in relation to the value before adding the surfactant. However, the separation is not spontaneous and can not happen without the aid of some energy. This is the most general case and the one that explains why activities as different as brushing our teeth and washing our hands or the dishes require some mechanical work. Once this mechanical work has been provided, liquid dirt can be completely detached.
- Third case. The addition of surfactant has not been enough to modify the value of the angle over 90°. W_{ad} is still high, and because of this some external mechanical energy is needed. However, unlike the second case, this external work will not detach liquid dirt completely and a residue will continue to be adhered to the substrate.

The latter two cases require some degree of mechanical work to separate the liquid dirt from the substrate *(3)*. This mechanism is called roll-up *(4)*.

Emulsions

The roll-up mechanism would be of little use in detergency if, once detached, in a later stage the liquid dirt resettled on the substrate. Once more, the surfactant plays an essential role to avoid this problem, this time by forming an emulsion.

An emulsion consists of a dispersion of droplets (usually from 1 to 100 μm in diameter) in a liquid in which it is immiscible. An emulsion is a metastable system; that is, one that is not thermodynamically favored but lasts long enough (from a few minutes to a few years) to serve a purpose, in this case, to keep liquid dirt in suspension avoiding redeposition. Thermodynamic instability arises from the fact that an emulsion shows a lot of interfacial surface. As systems tend to spontaneously reduce their interfacial area,[W] an

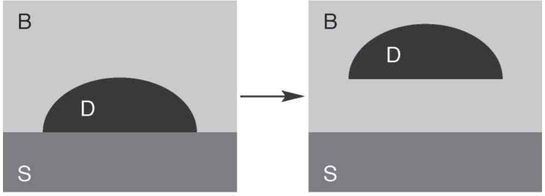

Figure 2. The work of adhesion between two immiscible phases (D and S) immersed in a bath (B) is equal to the work required to separate the unit area of the DS interface and form two separate interfaces BD and BS.

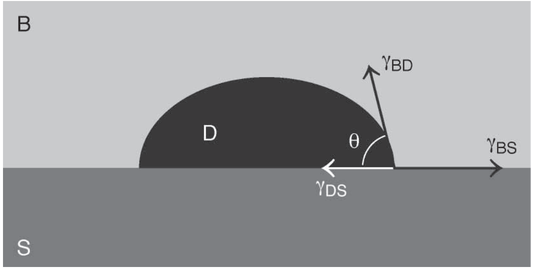

Figure 3. Young's equation can be considered the result of an elementary equilibrium of forces.

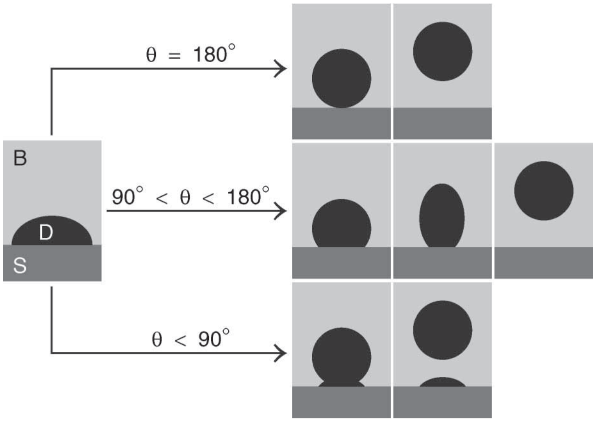

Figure 4. The sequences above illustrate how the liquid dirt (D) attached to the substrate (S) rearranges itself after the addition of the surfactant to the bath (B).

emulsion is unstable by comparison to a system that shows all its mass distributed in two single bulks (see Appendix 2 in the Supplemental Material^W^).

The life span of the emulsion depends on an establishing agent. This agent, called emulsifier, is just the surfactant adsorbed onto the BD interface. When adsorbed, the surfactant reduces the interfacial tension γ_{BD}, and therefore the work needed to enlarge the interfacial area ($dW = \gamma_{BD}dA$). This represents a thermodynamic support to form the emulsion. However, as some energy is still required, we find here another argumentation favoring the need for mechanical work in detergency.

Together with the thermodynamic role, surfactants have a kinetic function. As they adsorb in an orientated way both on BD and BS interfaces, they constitute steric barriers *(5)* (mainly when the surfactant is nonionic: Figure 5) or electric barriers (when surfactant is anionic: Figure 1), providing the system with mechanical resistance to coalescence and redeposition.

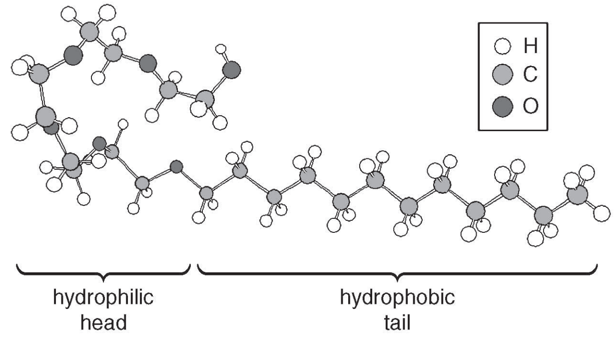

Figure 5. A linear polyoxyethylene alcohol is a good example of a nonionic surfactant being used in detergency. Here the hydrophilic region is a relatively bulky polyethoxylated chain.

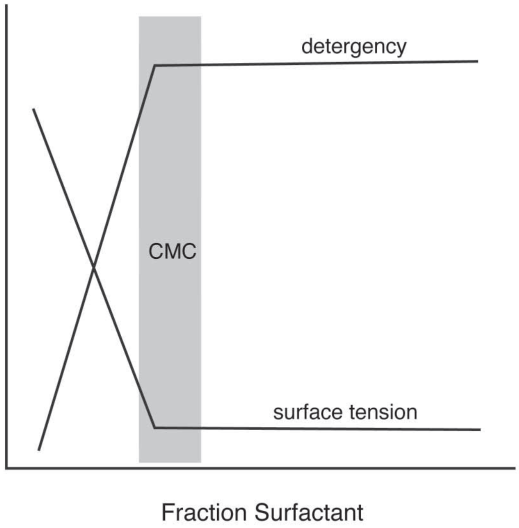

Figure 6. Surface tension and detergency versus surfactant concentration. The critical micelle concentration (CMC) is detected because of a sharp discontinuity in the physical properties of the solution.

Micelles

Mainly because of thermal agitation, the surfactant accumulated in the interface is in equilibrium with nonadsorbed molecules. Studies on solubility of nonpolar hydrocarbon solutes in water have shown that the hydrophobic part of the surfactant is surrounded by water, forming a solvent cage. This structure implies the creation of new hydrogen bonds among solvent molecules, which results in the adoption of a structural order *(6)*.

The presence of these structures is entropy-opposed, though the entropy of mixing counterbalances that. However, if the equilibrium favoring the presence of molecules in the bulk is altered (for instance by increasing the temperature or by adding more surfactant), the entropy of mixing will not make up for the increasing structural order. At this point, surfactant molecules associate to form an aggregate called micelle. A micelle is a structure that can adopt different shapes (spherical, cylindrical, laminar, etc.) with sizes less than 10 nm, in which the surrounding water is orientated by the hydrophilic region of each monomer, leaving an internal region where the hydrophobic tails interact with each other.

Micelle formation allows us to interpret the shape of the curves shown in Figure 6. The more surfactant is adsorbed, the less the surface tension will be, but once the concentration has reached a critical value (CMC), the formation of micelles yields an equilibrium between monomers and micelles. In this equilibrium, the chemical potential of the surfactant is constant and results in a constant activity that necessarily entails a constant surface tension, whereas the concentration varies in the micelle region.

The main contribution of micelles to detergency is their ability to spontaneously solubilize immiscible materials by means of a reversible interaction with their internal hydrophobic tails, a process called *solubilization (7)*. At low micelle concentration, solubilization is very limited so detergency is mainly based on the roll-up mechanism and the stabilization of the resulting emulsion. However, when micelle concentration is high enough (10 to 100 times higher than CMC), micelles can solubilize the entire immiscible material.

Roll-Up versus Solubilization

Although referred to as a critical concentration, the transition between monomers and micelles occurs over a range of concentrations. For this reason, CMC is represented by an interval of concentrations as can be seen from Figure 6. It is easy to conclude that the roll-up mechanism and the formation of an emulsion are the major processes involved in the detersive action. Detergency depends upon the concentration of monomeric surfactant and is practically unaffected by the presence of micelles, so the formation of micelles is secondary to the detersive process, and its main function appears to be providing a reservoir for replenishing unassociated surfactant adsorbed from the solution *(8)*. In relation to this, as micelle formation becomes the limit to the sharp decrease of interfacial tensions brought about by the adsorption of the surfactant, it represents a competing process that inhibits the progress of the roll-up mechanism.

From Figure 6, information related to the quantity of product needed to achieve detergency can be obtained. Maximum detersive efficiency is achieved when surfactant concentration reaches CMC and then maintains an almost constant level. Therefore, the addition of large quantities of surfactant does not improve detergency and represents just a waste of money.

Particulate Dirt: The Role of the Bath

Adsorption of surfactant at BD and BS interfaces influences detergency, as in the case of liquid dirt, because it decreases the energetic requirements represented by W_{ad} (eq 1). However, this adsorption results in a detersive mechanism different to the one previously described (roll-up). When dirt is particulate, the bath assumes an important role, simply because immersing dishes, clothing, or hands in water involves detersive action.

The water used to do the washing up, typically tap water, contains a variety of ions in solution. Cations are polarizing ions that are usually strongly solvated, and as a consequence they stay distributed in the bulk. On the other hand, anions are less solvated and, since they are more accessible, show a strong tendency to adsorb particularly onto the surface of particles and substrates. Because of this adsorption, these surfaces are usually negatively charged (see Appendix 3 in the Supplemental Material^{W}). As dirt and substrate have charges of the same sign (contributing to the formation of electrical double layer structures) repulsive forces arise, partially offsetting the attractive forces between them. This favors the removal of dirt and avoids particle aggregation.

This is the reason why the composition of many commercial detergents contains anionic surfactants. When an anionic surfactant, for example, SDS, adsorbs onto the interface of a substrate or a dirt particle, the adsorption is not caused by electrostatic attraction but by the ability of hydrocarbon tails to establish van der Waals interactions with the hydrophobic surfaces. This way, adsorption occurs in an orientated way, creating hydrophilic groups orientated towards the bath and hydrophobic tails orientated towards the surface.

Spreading

We have already seen the beneficial effects of using a bath for the removal of particulate dirt. To benefit from these advantages, the bath has to reach every single point on substrates where dirt could be adhered. However this is not always an easy task, since the extension of the bath entails energetic demands that can be expressed by means of the *spreading coefficient* (see Appendix 4 in the Supplemental Material^{W}) of the bath on the substrate, $S_{B/S}$, or on particulate dirt, $S_{B/D}$,

$$S_{B/S} = \gamma_{AS} - \gamma_{BS} - \gamma_{AB} \tag{4}$$

$$S_{B/D} = \gamma_{AD} - \gamma_{BD} - \gamma_{AB} \tag{5}$$

Equations 4 and 5 are useful tools to visualize another aspect of detersive action. As pointed out before, surfactants adsorb into BS, BD, and AB (air–bath) interfaces. This entails the decrease of interface tension values, which appear with a negative sign in these equations. Such decrease contributes to the spontaneous spreading of the bath on both substrate and dirt (the condition to be fulfilled for an initial spreading is, $S_{B/S}$ and $S_{B/D}$ should be positive or zero). On the other hand, since particulate dirt and substrates are usually hydrophobic, the corresponding interfacial tensions (γ_{AD} and γ_{AS}) are low enough to produce a nonspontaneous spreading. In short, in most cases a spontaneous spreading of the bath (i.e., wetting) is so unlikely that the contribution of external work is needed. This point leads us once more to the conclusion that devices such as washing machines, dish washers, and so forth need some kind of mechanical work.

Lather

Lather results when the air–bath interface is enlarged owing to the decrease of surface tension, γ_{AB}. It can be seen from eq 1 that none of the interfacial tensions in this expression is related to the ability of a detergent to form lather, and so its presence does not affect the energetic demand to detach dirt from substrates. However, our analysis does not finish here, since γ_{AB} appears in eqs 4 and 5. The decrease of γ_{AB} contributes to the spreading of the bath and at the same time contributes to the detersive action. This is the reason why we use bath sponges, because they maximize the air–bath interface area, favoring lather formation and decreasing the energetic demands of water to reach both dirt and substrate.

In any case, if we take into account that an excessive production of lather might easily lead to the loss of the minimal volume of bath needed to achieve detergency, we come to the conclusion that the production of lather is a complex matter that should always be under control. This is why its formation is avoided in detergents for dishwashing and washing machines, although it is only partially controlled in hand dishwashing detergents. In the latter case people's belief about the benefits of lather has made manufacturers create products that satisfy such demand.

Types of Surfactants

The composition of both dishwashing and laundry detergents contains anionic surfactants. Since they have a negative charge, they are the most effective surfactants for particulate dirt. SDS and sodium dodecyl benzene sulfonate (Figure 7) are among those most frequently used.

Nonionic surfactants are also components of cleaners, but they are less numerous than anionics. This is because nonionic surfactants usually have smaller values of CMC and, as previously mentioned, concentrations over CMC rarely improve detergency. The nonionic surfactants seem to be effective for the production of steric barriers for the prevention of soil redeposition. In this sense, polyoxyethylene alcohols (POE) are the most frequently used surfactants in commercial products (Figure 5). It has been found that, probably owing to their greater surface coverage per molecule when adsorbed on substrates and soils, nonionic POEs can remove

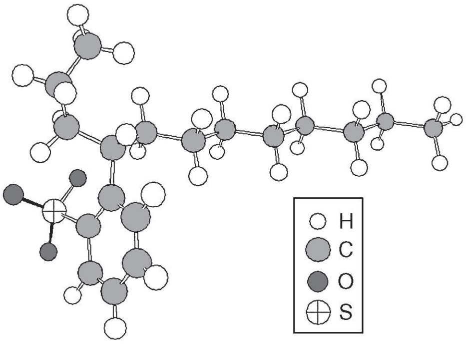

Figure 7. Predominant isomer of sodium dodecyl benzene sulfonate.

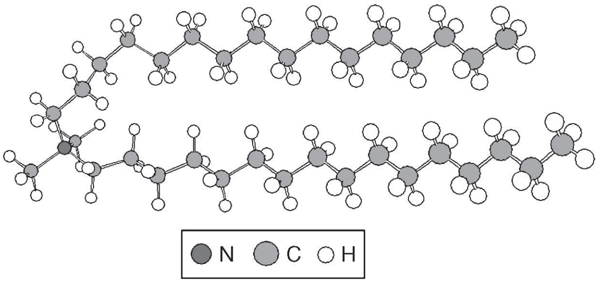

Figure 8. The di-*n*-alkyldimethylammonium chloride is a cationic surfactant traditionally used as fabric softener.

nonpolar soil from hydrophobic substrates more effectively than anionics. However, these surfactants lose efficiency in relation to anionics when substrates are relatively hydrophilic (e.g., cotton). This is probably due to an inverted adsorption of the surfactant caused by the formation of hydrogen bonds between polyoxyethylene groups and the substrates, which results in sites for soil redeposition *(1).*

This problem, occasionally shown by nonionic surfactants with relatively hydrophilic substrates, is permanent in a system based on a cationic surfactant, whatever the substrate is. As it has already been mentioned, substrates immersed in aqueous media acquire a negative charge. If a cationic surfactant is added, it adsorbs onto substrate and soil, orienting the hydrophobic tails toward the bath and decreasing the negative electrical potentials of both. Not only does this makes the removal of dirt difficult, but it also favors its redeposition. As a result, cationic surfactants show very poor detergency and are not considered for the composition of commercial detergents. But the situation turns out to be beneficial if a cationic surfactant (e.g., quaternary ammonium salts shown in Figure 8) is added in a later stage, once the detersive action has taken place. This is what happens when we use hair conditioners or fabric softeners. Once the substrate (e.g., hair or fabric) is clean, a cationic surfactant adsorbs orienting the hydrophobic tail towards the bath producing a “greasy” monolayer that provides the substrate with a soft feel and prevents the damage caused by friction.

^{W}Supplemental Material

Details of mathematical concepts used in this article are available in this issue of *JCE Online*.

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