

# Surfactants and Interfacial Phenomena in Cosmetics and Detergency

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Surfactants, one of the major ingredients of cosmetic products, are characterized by their tendency to concentrate at interfaces and to alter the free energy of the interfaces. Through interfacial processes such as wetting, emulsification, solubilization, dispersion and modification of interfacial viscosity and electrical charge, surfactants can mix various ingredients in cosmetics (oil phase, water phase, solids, pigments, dyes, perfumes, enzymes and other additives) into a stable and homogeneous system.

Surfactants possess unique physicochemical properties that give cosmetic products functionality. For example, anionic, nonionic and zwitterionic surfactants have excellent cleansing and foaming properties and are used widely as shampoos, shaving creams and laundry detergents. Cationic surfactants, on the other hand, find applications in conditioners due to their positive charge.

In this article, we will discuss the nature and classes of surfactants used in cosmetics. We'll also discuss their interfacial properties. An understanding of the behavior of surfactants and their related interfacial phenomena in cosmetics processes will help formulators design better cosmetics.

## Surfactants in Cosmetics

During the evolutionary process of human civilization, people's sense of cleanliness led to the adoption of soap-like materials from natural plant and animal sources. Those materials, which removed dirt and greasy substances, were the pioneering prototypes of an important class of chemicals called SURFace ACTive AgeNTS—surfactants.<sup>1</sup>

Surfactants as a class of compounds find application in numerous technologically, industrially and biologically relevant areas. They form a key ingredient in consumer products such as cosmetics, detergents and personal-care products (see sidebar on the following page).

**An amphiphilic molecule:** Surfactants are amphiphilic substances, meaning they contain two opposing parts: hydrophilic and hydrophobic. In general, the hydrophilic (water-loving) part is an ionic or polar group that prefers to be in water and the hydrophobic (water-hating) part is a hydrocarbon-

derived alkyl group that prefers to be in an oil phase. When dissolved in water, the former will be readily hydrated and the latter will try to avoid water.

In general, the molecules at a liquid surface possess higher energy than those in the bulk because the bulk molecules can interact with each other surrounding them on all sides more strongly than the ones at the surface with only the widely spaced gas molecules above the liquid. Work is therefore required to bring a molecule from the bulk to the surface.

When a surfactant is dissolved in water, the presence of the hydrophobic group in the bulk may cause distortion of the water structure, increasing the free energy of the system. This means less work is needed to bring a surfactant molecule to the surface than a water molecule. The surfactant concentrates (adsorbs) at the surface, leading to a reduction of the surface tension of the water with beneficial consequences in detergency. On the other hand, the presence of the hydrophilic group prevents the surfactant from being expelled completely from water as a separate phase since that would require dehydration of the hydrophilic group. Thus, the amphiphilic structure of the surfactant causes concentration of the surfactant at the surface and reduction of the surface energy of the water, as well as orientation of the molecule at the surface with its hydrophilic group in the aqueous phase and its hydrophobic group oriented away

## Key words

*Surfactants, surface tension, wetting, solubilization, emulsification*

## Abstract

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from it. This phenomenon is observed for both the air/liquid and liquid/liquid interfaces.

**Concentration-dependent properties:** The amount of surfactant adsorbed at the air/liquid or liquid/liquid interface is not easily measured because of the difficulty in isolating the interfacial region from the bulk phase when the

interfacial area is small. Instead, the amount of material adsorbed per unit area of interface is calculated indirectly from surface tension measurements. As a result, a plot of surface tension as a function of concentration of surfactant, shown in Figure 1, rather than an adsorption isotherm, is generally used to describe adsorption at interfaces. From such a plot the adsorption amount can readily be calculated by the use of the Gibbs adsorption equation.<sup>2</sup>

$$d\gamma = - \sum \Gamma_i d\mu_i$$

where  $d\gamma$  is the surface tension change,  $\Gamma_i$  is the surface excess concentration of any component of the system, and  $d\mu_i$  is the change in chemical potential of any component of the system. When the equilibrium is reached,

$$d\mu_i = RT \ln a_i$$

where  $a_i$  is the activity of any component in the bulk phase,  $R$  is the gas constant, and  $T$  is the absolute temperature.

As the concentration of surfactant increases, a remarkable self-organization process occurs in aqueous solutions, resulting in the formation of aggregates called micelles. Micelles will have the hydrophilic part of the surfactant oriented toward the aqueous phase, and the hydrophobic part away from it, as shown in Figure 2. Thus a micelle in water has a

## Classes of Surfactants

Surfactants can be divided into four major classes based on the nature of the hydrophilic group: anionic, cationic, nonionic and zwitterionic.

Anionic surfactants with different structural makeup used in cosmetics are fatty acid soaps ( $\text{RCOO}^-\text{M}^+$ ), alkyl sulfates ( $\text{RSO}_3^-\text{M}^+$ ), benzyl sulfonates ( $\text{RC}_6\text{H}_5\text{SO}_3^-\text{M}^+$ ), monoglyceride sulfates ( $\text{RCOOCH}_2\text{CHOHCH}_2\text{SO}_3^-\text{M}^+$ ) and alkylether sulfates.  $R$  is the hydrocarbon chain that normally contains 10 to 18 carbon atoms and  $\text{M}^+$  represents a cation such as  $\text{K}^+$ ,  $\text{Na}^+$  or  $\text{Al}^{3+}$  or triethanol amine. Anionics have excellent cleansing and foaming properties and, therefore, are used widely in laundry detergents, shampoos, shaving creams and dentifrices.

Typical examples of cationic surfactants are alkyltrimethyl ammonium salts ( $\text{RN}(\text{CH}_3)_3^+\text{X}^-$ ), quarternary amide of ethylenediamine ( $\text{RCONHCH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3\text{X}^-$ ) and alkylpyridinium salts ( $\text{RNC}_5\text{H}_4^+\text{X}^-$ ).  $\text{X}^-$  represents an anion such as  $\text{Br}^-$ ,  $\text{Cl}^-$  or acetate. These surfactants, due to their positive charge, can adsorb on negatively charged surfaces such as hair and modify their behavior. They therefore find applications as hair conditioners. They also are reported to have germicidal properties and find use in anti-dandruff preparations.

Nonionic surfactants of interest include fatty acid alkanolamides ( $\text{RCONHCH}_2\text{CH}_2\text{OH}$ ), alkylpolyglycol ethers ( $\text{R}(\text{OCH}_2\text{CH}_2)_n\text{OH}$ ), polyethylene oxide alkyl phenols ( $\text{RC}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{OH}$ ) and alkyl polyethylenimine ( $\text{R}(\text{NHCH}_2\text{CH}_2)_n\text{NH}_2$ ) and alkyl polyglucosides. Nonionic surfactants can modify such properties as interfacial viscosity significantly in the presence of ionic surfactants, and are used, for example, as emulsion stabilizers in the manufacture of creams. Their solubility properties also enable them to be used as solubilizers for colorants and perfumes. Alkyl polyglucosides are of particular interest now because they are biodegradable and hence environmentally benign.

The zwitterionic (often referred to as amphoteric) surfactants can be illustrated with the typical example of betaines ( $\text{RN}^+(\text{CH}_2)_2\text{CH}_2\text{CO}_2^-$ ) or sulphobetaines ( $\text{RN}^+(\text{CH}_2)_2\text{CH}_2\text{CH}_2\text{SO}_3^-$ ). These compounds are milder on the skin than the anionics and have especially low eye-irritating effects, which lead to their use in toiletries and baby shampoos. Among the naturally occurring surfactants in this class are the important lecithins or phosphatidylcholines, which today are widely used in cosmetic formulations.

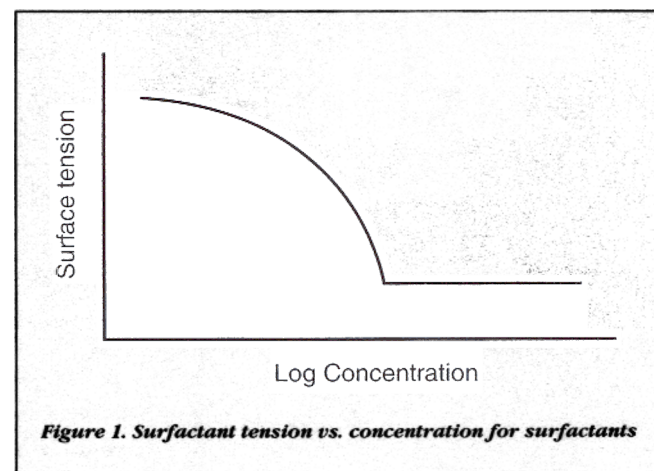


Figure 1. Surfactant tension vs. concentration for surfactants

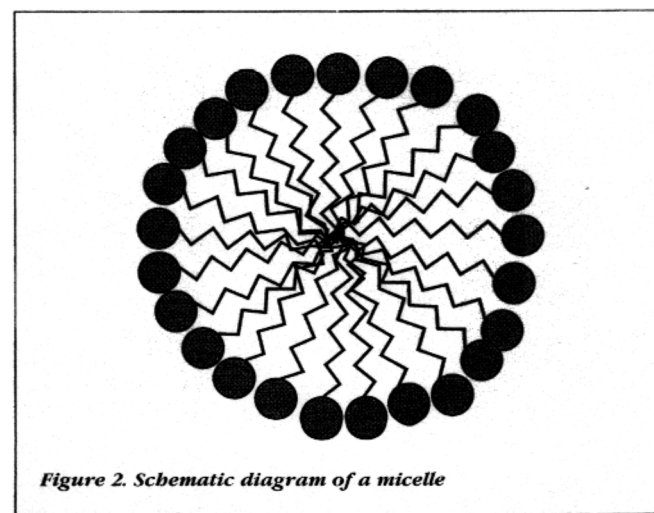


Figure 2. Schematic diagram of a micelle



hydrocarbon interior that can solubilize significant quantities of other hydrocarbon species, a phenomenon that is considered vital in detergency. Aggregation usually occurs above a temperature referred to as Krafft point, above which the ionic surfactant solubility enhances dramatically.

The concentration at which the micelle formation commences is called the Critical Micelle Concentration (CMC). Above the CMC, the physical properties of the aqueous surfactant solution undergo conspicuous changes at increasing concentrations. For example, properties such as osmotic pressure and surface tension remain constant; solubilization (ability of micelles to incorporate large amounts of insoluble substances) and magnetic resonance absorption continue to increase; equivalent conductivity steadily decreases, as shown in Figure 3.<sup>3</sup>

As at the liquid/air and liquid/liquid interfaces, surfactants can adsorb also on solids due to favorable energy of interactions between them and the solid. Surfactants can also self-associate at the solid/liquid interface to form what has been called solloids (Surface COLLOIDS)<sup>4</sup> or hemimicelles (half-micelles)<sup>5,6</sup> with the hydrocarbon tails pointing towards the bulk solution under certain conditions. Or, they can form a bilayer with hydrophilic parts turned toward both the solid and the bulk solution, as shown in Figure 4. Such adsorption can

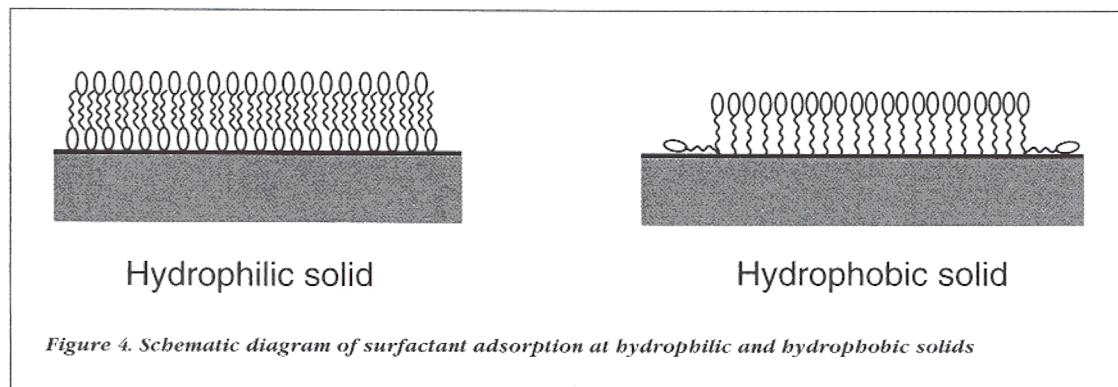
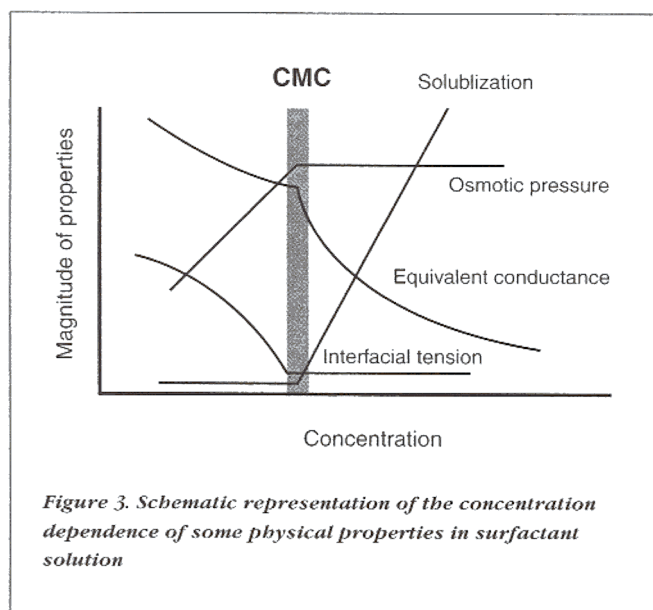
markedly alter the wetting of solids and, hence, their dispersion.

## Interfacial Phenomena

Knowledge of interfacial phenomena in cosmetics and the mechanisms by which interfacial properties can be modified by surfactants is essential for proper development of cosmetic products. An interface is a boundary between any two of three phases, namely solid, liquid or gas: solid/liquid, liquid/liquid, solid/solid, solid/gas and liquid/gas. Although an interface is often considered as a plane, it is actually a region at the boundary of phases where various physicochemical properties are different from that of the bulk. In addition, properties of the line contact (line of contact at the periphery of a drop or a bubble with the solid) between three phases (solid/liquid/liquid or solid/solid/liquid) are also important in determining system behavior.

As mentioned above, chemical species at the interface possess higher free energy than those in the bulk and this excess free energy (essentially due to the existence of an interface) is known as interfacial energy or surface energy. Indeed there is an increase in the total free energy of the system due to the existence of this interfacial energy, with the increase proportional to the total area of the interface.

A system always tries to reduce its total free energy. The tension that exists at the interface to reduce the total surface area, and thereby the increase in energy, is known as interfacial tension or surface tension. Minimization of this interfacial tension is important in the formulation of stable cosmetics, since many cosmetics



are emulsions made up of minute droplets of oil in water or water in oil and hence possess a large interfacial area.

A surfactant can adsorb at gas/liquid and liquid/liquid interfaces and reduce the interfacial tension, since it has a tendency, as mentioned earlier, to concentrate at the interface due to the affinity of one part of it to the oil phase and the other part to the water phase. The interfacial tension decreases with the addition of surfactant until the critical micelle concentration is reached.<sup>7-8</sup>

Surfactants can adsorb also at solid/liquid interfaces. Such adsorption can significantly alter the wetting and hence desoiling properties. The adsorbed surfactant layer can exist either as a loose gaseous film, liquefied films, or even as a rigid solidified film, depending on the nature of interactions between them. With a significant amount of cooperative interaction between the molecules, rigid films with relatively high interfacial viscosity can result. Such viscosities are often an essential requirement for cosmetic emulsions. It can help minimize the coalescence between the emulsion droplets, increasing its stability and life.

Adsorption of charged species results in a charged interface, the nature and magnitude of which will largely determine the extent of attractive and repulsive interactions between interfaces. Allowing a charged interface to form on the emulsion droplets can retard coagulation between emulsion droplets. The charge at the interface is balanced by ions of opposite charge, known as counter ions, which exist in solution. Addition of salts

causes crowding of counter ions in the interfacial region and effectively reduces the extent of interfacial repulsions between charged droplets and, for example, emulsion stability.

Commercially used surfactants are invariably mixtures of different surface-active compounds. In most applications, surfactant mixtures perform significantly better than their components because mixed surfactants usually exhibit synergism or antagonism under different conditions, and these mixing effects can be used to control their behavior for desired formulations and properties. A full understanding of the interactions among surfactants and the manner in which these interactions affect the final product performance is necessary to effectively utilize the benefits of any synergistic effects.

Many polymers are used in personal-care products, markedly affecting the interfacial properties of the system. In most cases, polymers are used along with surfactants to obtain desirable effects. They can interact with individual species or with aggregates (micelles and hemimicelles), and can form polymer-surfactant complexes. These polymer-surfactant interactions in solution and at the interfaces can change the interfacial properties of the systems, and the resultant effects can be desirable or undesirable.

The properties described above comprise a set of fundamental criteria that are important in cosmetics. In addition, a number of other properties such as roughness and porosity of the substrate, hardness of the water, composition of soiling matter, and others, can have a governing role in the processes. With this background, we shall now briefly examine the major mechanisms involved in detergency and cosmetics.

Table 1. HLB values for selected surfactants<sup>10-11</sup>

Surfactant	HLB value
sodium lauryl sulfate	40
potassium oleate	20
triethanolamine oleate	12.0
sorbitan monolaurate	8.6
sorbitan monooleate	4.3
glycerol oleate	2.8
sorbitan trioleate	1.8

Table 2. Group number for selected surfactant functional groups<sup>12</sup>

Functional group	Group number
SO <sub>3</sub> Na	38.7
—COOK	21.1
—N (tertiary amine)	9.4
—COOH	2.1
—OH (Free)	1.9
—OH (sorbitan ring)	0.5
—CH <sup>+</sup> or —CH <sub>2</sub> <sup>+</sup> or CH <sub>2</sub> <sup>+</sup>	0.475
—(CH <sub>2</sub> —CH <sub>2</sub> —O) <sup>+</sup>	0.33
—(CH <sub>2</sub> —CH <sub>2</sub> (CH <sub>2</sub> )—O) <sup>+</sup>	0.15

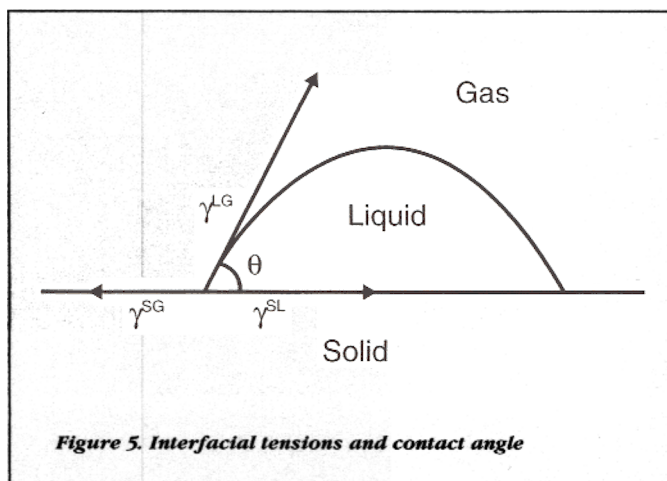


Figure 5. Interfacial tensions and contact angle



## Wetting

Wetting the substrate is the first step in enabling cosmetic products to be evenly applied to the skin or hair. Wetting involves displacement of air from the solid or the liquid surface by another liquid. In this process the degree of wetting is governed by the surface free energy of the substrate and the wetting solution. The surface that has a higher surface free energy tends to be replaced by a liquid that has a lower surface free energy, thus reducing the total free energy of the system.

Wetting is described in terms of spreading coefficient. For a liquid spreading on a solid in the air, the spreading coefficient,  $\sigma^{LG}$ , is defined as

$$\sigma^{LG} = \gamma^G - \gamma^L - \gamma^{LG}$$

where  $\gamma^G$ ,  $\gamma^L$ , and  $\gamma^{LG}$  are solid/gas, solid/liquid and liquid/gas interface tensions. When  $\sigma^{LG}$  is positive, spreading can occur spontaneously.

It is very difficult to determine  $\gamma^G$  directly, so an equation called Young's equation is employed by considering the equilibrium between force vectors at the S/L/G contact:

$$\gamma^G = \gamma^L + \gamma^{LG} \cos\theta$$

where  $\theta$  is angle of contact that the liquid/gas interface subtends with the solid/liquid interface (Figure 5).

From Young's equation, it can be seen that spreading will occur only if  $\theta = 0$ . Rearranging the equation yields:

$$\sigma^{LG} = \gamma^{LG} (\cos\theta - 1)$$

Since water has a higher surface tension, it does not spread on many solids that have a lower surface energy. Surfactants can reduce the surface tension of the water,  $\gamma^G$ , and the solid/liquid interfacial tension,  $\gamma^{LG}$ , and may cause the  $\sigma^{LG}$  to be positive and thus facilitate spreading.

## Solubilization

At concentrations higher than a certain critical value, characteristic of the chemical groups that make up the surfactant, micelles form in the solution. The micelles have a hydrophobic interior that can solubilize organic substances that are otherwise not soluble in water. This phenomenon is of major importance in cosmetics and detergency as it can incorporate water-insoluble substances into a thermodynamically stable solution. The location of the solu-

bilized organics in the micelle depends on the chemical nature of the compound. It can be on the surface of the micelle, between the hydrophilic groups, in the palisade layer of the micelle (between the hydrophilic groups and the hydrophobic groups) or in the core of the micelle. While a totally hydrophobic material will be in the core, a mostly hydrophilic one will be located on the surface. The latter will be more easily released/delivered than that in the core.<sup>9</sup>

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## Emulsification

Emulsification allows two immiscible liquid phases to be compounded into a macrophase mixture. When oil and water are mixed, the two phases will separate, but the separation can be delayed for years with the addition of emulsifying agents, usually surfactants.

The emulsifier acts by adsorbing at the interface and reducing the interfacial energy. It is the existence of this interfacial energy that is essentially responsible for the instability of an emulsion, since the large increase in interfacial area upon the formation of the emulsion droplets will cause an increase in the free energy of the system.

Adsorption of certain agents can momentarily produce a negative interfacial tension, a condition which is favorable for an increase in interfacial area and hence emulsification. In addition, certain emulsifying agents stabilize emulsions by causing the formation of a rather rigid interfacial film, and also by allowing the generation of electrical charge at the interface and hence repulsion between emulsion droplets.

The appearance of the emulsion is dependent essentially on the particle size of the droplets. The emulsion will be white if the particles are 1 micron in size or bigger, bluish white between 1 micron and 0.1 micron, semitransparent between 0.1 and 0.05 microns and transparent if smaller than 0.05 microns.

Emulsification in cosmetics is mostly the dispersion of oil globules in water (o/w) and, to a minor extent, of water droplets in oil (w/o). The type of emulsion obtained can be predicted usually with the help of what is known as hydrophile-lipophile balance (HLB). Surfactants contain both hydrophilic and hydrophobic groups and HLB values signify the balance of the forces due to these groups. HLB values of selected surfactants on this basis are shown in Table 1.

Many formulas have been developed for calculating the HLB value of surfactants. Among them, one formula that tries to obtain HLB values thermodynamically is based on surfactant functional groups:

$$\text{HLB} = \Sigma (\text{hydrophilic group numbers}) - \Sigma (\text{lipophilic group numbers}) + 7$$

where lipophilic group number is the number of  $\text{CH}_2$  groups and typical hydrophilic group numbers are given in Table 2.

Molecules that have a low HLB number (4 to 6) are soluble or dispersible in oil and usually give a water-in-oil emulsion. Those that have a high HLB value (8 to 18) on the other hand are soluble or dispersible in water and give rise to an oil-in-water emulsion. Surfactants with HLB values in the range 7 to 9 are commonly used as wetting agents and those with values in the range of 13 to 15 function as detergents.

Cosmetic creams are liquid or solid emulsions. Cold or cleansing creams made up of borax, beeswax and mineral oil are water-in-oil-in-water (w/o/w) emulsions. Here globules of oil containing minute droplets of water are dispersed in the water phase. Night or lubricating creams are obtained from this by introducing super fattening agents such as lanolin.

## Dispersion

Suspensions of insoluble solid particles are also important for certain cosmetic formulations. In this process, surfactants can reduce the solid/liquid interfacial tension and facilitate the formation of a new solid/liquid interface, enhancing the dispersion. Adsorption of surfactants on solids also changes the surface charge of the particles and makes them repel each other, achieving stabilization and dispersion.<sup>13</sup>

## Detergency

Detergency is one of the most important applications of surfactants. Wetting, adsorption, dispersion, solubilization and emulsification all play an important role in detergency. When a soiled fabric or any other substrate comes in contact with a detergent solution, air is first displaced from the surface by a wetting process and then oily dirt is removed by the detergent solution spread on the fabric surface. Here the detergent, with its strong tendency to adsorb on the substrate, is able to remove the oily dirt, which rolls up to form beads and gets detached from the surface.<sup>14-15</sup>

Solubilization of oily matter into the detergent micelle is also possible above the critical micelle concentration, which is invariably achieved under most laundering conditions. A similar possibility is penetration of oily dirt by detergent species, leading to the formation of a liquid crystalline phase that is often followed by dispersion or dissolution of it into water. If the dirt contains any water-soluble matter, the condition is also favorable for the osmotic flow of water into the soil. Such seepage of water can cause swelling of the dirt matter and its eventual dispersion or detachment.

Once the dirt is removed, it should not redeposit on the surface. To prevent redeposition of the oil droplets, dissolved oily matter and dispersed particulates, one can control the surface charge of the substrates involved in such a way that they will be repelled from it. Most surfaces have a negative charge. Dirt dispersed in water will also normally have such a charge due to the anionic surfactant adsorbed on its surface.

A severe problem in detergency is the presence of calcium and magnesium in the water used. Such

divalent-species present in hard water can strongly bind dirt to fiber, making it difficult to clean and cause soil redeposition. In order to overcome these problems, reagents known as builders are normally used to complex the calcium-type species and thus reduce the effect of their presence. Commonly used builders are phosphates, silicates, carbonates and zeolites.<sup>16</sup>

## Foaming

Foam is a two-phase system of gas bubbles in liquid that is thermodynamically unstable and is generated by introducing air or other gas into the liquid. Since the formation of foam causes an increase in surface area, and surface tension is the work needed to generate a new surface, the lower the surface tension of the liquid, the greater the surface area that will be generated. Surfactants enhance the foam formation by reducing the surface tension of the liquid. Foam is unstable. When the liquid drains out from the lamellar layer, the layer becomes thinner and eventually breaks.

Surfactants also play an important role in foam stability through their electrostatic and interfacial viscosity effects in the lamellae between the bubbles.

Foaming, in addition to being a necessary requisite in the eyes of consumers, can assist removal of oil during laundering due to pressure waves generated on the oily surface by the moving foam. The pressure waves have their origin in the pressure differential that normally exists at curved film interfaces.<sup>17</sup>

## Summary

In general, cosmetics are essentially an ensemble of interfacial phenomena critically dependent on the successful application of surfactants. For different applications, the surfactants must possess different desirable interfacial properties. Some should have good wetting properties, whereas others should possess emulsifying or foaming properties to different extents. For example, creams such as sun tan creams that are meant to remain on the skin for longer intervals have to be formulated so that they will

not penetrate the skin, whereas medical creams will have to be formulated for penetration through the skin.

It is evident that a wide variety of requirements are placed on surfactants for use in cosmetics and detergency. For detergents, the surfactants should have higher cleansing efficiency, good foaming ability, no precipitation in hard water and less drying or irritation on the skin. For personal-care products, the major concerns are that the surfactant be nontoxic, have no odor and low irritation, and that it improve product stabilization.

With increasing concerns for the environment, development of environmentally benign formulations is the current trend. Generally, the cosmetics industry is looking for surfactants that are highly efficient, multi-functional, non-irritating and biodegradable. Knowledge of the interfacial phenomena relevant to the processes discussed above is essential for the efficient development of future cosmetic products.

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