31 Moisturizing Cleansers

K.P. Ananthapadmanabhan, K. Subramanyan, and Greg Nole

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31.1 INTRODUCTION

The outermost layer of skin, the stratum corneum (SC), plays an important role in protecting against desiccation and environmental challenges. Optimal hydration of the SC is essential for maintenance and promotion of skin health. Water helps to plasticize SC making it more flexible and resilient to mechanical stress[1] and is also essential for the optimum biological functioning of the SC.[2–4] Various factors including cleansing can cause a loss of hydration of the SC leading to varying degrees of SC dysfunction. Cleansers contain surfactants that interact with the proteins and lipids in the SC, which reduces the water retention capacity and leads to short- and long-term deleterious effects on skin condition. Use of mild surfactants in cleansers provides a significant benefit by reducing the loss of hydration during cleansing and by preserving the integrity of the skin moisture

barrier. In addition to this, cleansers, especially in the liquid form, can incorporate significant amount of emollients/moisturizers that can be delivered and retained on skin during cleansing to provide significant boost in skin hydration, in a lotion like manner. These emollient cleansers, unlike common cleansers, provide significant benefit to the skin such as prevention of dry, tight skin, and in some instances even dryness relief. Moisturizing cleansers when used as part of everyday skin care routine help maintain the SC in a healthy state. In the sections below we examine the importance of moisturization, the science and technology underlying mild and moisturizing cleansers, and methods to evaluate their performance.

31.2 THE IMPORTANCE OF MOISTURIZATION

31.2.1 Hydration of the Stratum Corneum

Extensive research on the biology of the SC has shown that optimal levels of hydration are required for a number of key enzymatic processes leading to the development of a healthy SC.[2–4] SC processes that are influenced by hydration state include desquamation, barrier lipid formation, and natural moisturizing factor (NMF) synthesis. For example, the proteolysis of fillagrin, a critical process to maintaining flexibility and hydration of skin is itself initiated by changes in the water gradient in the SC.[5] It is becoming increasingly clear that normalizing hydration levels in the SC can significantly activate key processes in the living epidermis through an elegant feedback mechanism. Perturbation to the SC barrier leading to altered water flux sets in motion a cascade of events within the underlying epidermis to promote barrier repair and recovery.[6,7] The SC, which in the past was considered nothing but a dead protective tissue, is now recognized to be an enzymatically active biosensor that can regulate activities in the living epidermis.

There is a constant flux of water leaving the skin through the SC. A normal, healthy SC maintains its hydration by controlling the rate of water flux via the lipid barrier and NMF functions. This flux is affected mainly by the structural integrity of the moisture barrier and environmental temperature and humidity. A weakened or damaged barrier will lead to increased water loss from the skin, reducing water content of the SC. It is known that the SC barrier is compromised in several dry skin states such as atopic dermatitis, psoriasis, and winter xerosis.[8] Low humidity leads to an increased rate of water loss from the SC and less water retention in the SC leading to dry, rough, tight skin.

Consumers will alleviate these symptoms by "moisturizing" their skin. "Moisturization" refers to any process that restores the ability of the SC to bind and retain moisture. Typically this is achieved by the use of moisturizing creams and lotions that deliver water to skin along with humectants and emollients, that allow the skin to hold on to the moisture.

31.2.2 Impact of Cleansing on Skin Hydration

Frequent cleansing is known to reduce SC hydration and cause dry, scaly skin.[9,10] It is paradoxical that cleansing, a process that involves saturating skin with water, can actually lead to a net decrease in equilibrium SC hydration. Figure 31.1 shows a schematic of the typical change in skin hydration state during cleansing. There is an initial transient increase in water content of SC during cleansing, but the excess water is quickly lost and water content returns to below baseline values in a few minutes (10 to 15 min).

Although there is a transient increase in skin water content during cleansing, cleansing products can reduce water content of skin:

- In a short term, cleansing reduces water retention ability of SC by removing water soluble NMFs and superficial lipids.[11]
- In a long term, frequent cleansing with harsh surfactants can cause damage to the SC barrier and increase water loss.[12,13]

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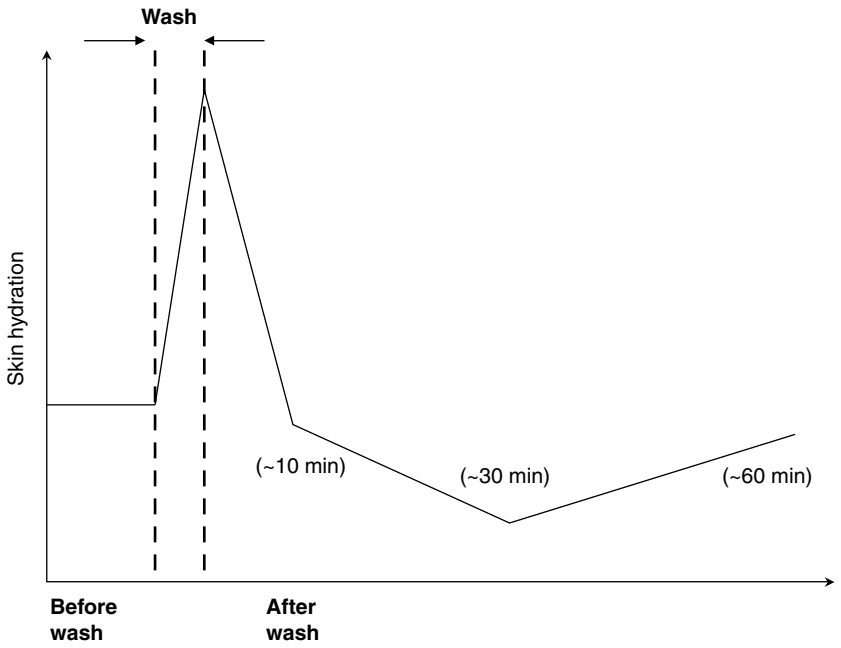

FIGURE 31.1 Schematic of the relative change in skin water content during typical cleansing routine.

The basic function of a cleanser is to promote health and hygiene of skin by removing excess dirt, sebum, and bacteria from skin and promoting exfoliation. However, as explained earlier, cleanser surfactants also interact with SC proteins and lipids, causing damage to the SC barrier, leading to a net loss in SC hydration.

Use of mild surfactant cleansers (as described in Section 31.3) helps mitigate this problem to a large extent. For example, mild cleansing bars, based on synthetic detergents (syndet) are known to be inherently mild and moisturizing to skin as compared to basic soap-based cleansers.[14] A complementary approach to enhance skin hydration after cleansing is to help skin retain some of the moisture it absorbs during cleansing. This can be achieved by depositing emollients, occlusives, and humectants on to the skin that slow down the rate of water loss after a shower and improve SC hydration.

31.2.3 Consumer Perception

In consumer parlance, "moisturization" is a highly desired skin state and expressed in a variety of ways such as soft, smooth, healthy, nourished skin. In the context of moisturizing creams and lotions, it refers largely to the alleviation of the dry skin symptoms and the efficacy is measured by the extent and duration of the relief.

Cleansers induce a perception of tightness, roughness, itch in a short term, resulting from a high rate of dehydration following a wash. Figure 31.2 depicts a typical onset of after-wash tightness on the face immediately after cleansing, as measured by consumer self-perception. Therefore, moisturization from a cleanser mainly connotes an absence of the dehydrating effects of cleansing. This translates to an absence of tightness, roughness, itch immediately after wash and a lack of drying and scaling in the long term. All of this can further translate to a reduced need to apply a moisturizer (especially after showering) in order to maintain a perceivably "moisturized" skin state.

Table 31.1 indicates differences in consumer expectations from a moisturizing lotion versus a moisturizing cleanser.[15] It is interesting to note that for the cleanser, the consumer desire for

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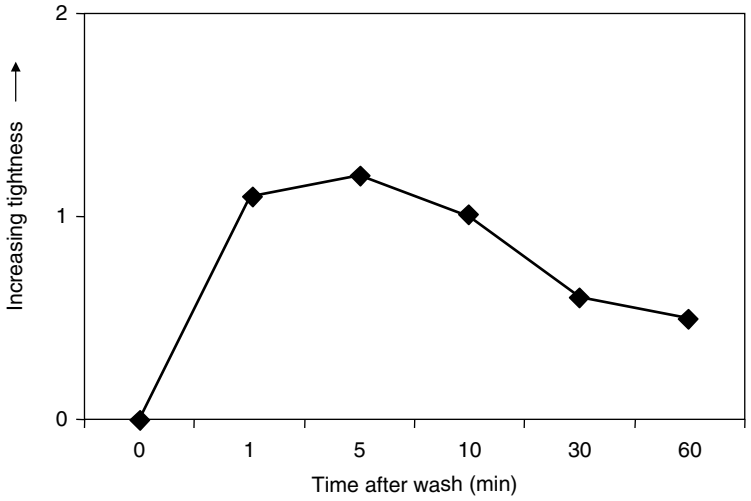

FIGURE 31.2 Profile of the consumer perception of tightness after wash.

TABLE 31.1
Top 5 Consumer Desired Qualities in Lotions and Cleansers

Lotion	Cleanser
Nongreasy feel	Nongreasy feel
Nonsticky feel	Rinses off well
Dry skin relief	Does not dry skin
Softens skin	Smoothes skin
Heals dry skin	Cleans thoroughly

"moisturization" (expressed as "does not dry out skin") is ranked ahead of its primary cleansing function.

As summarized in Table 31.2, consumer perception and manifestation of dryness through cleansing can be described in terms of their technical mechanism. In doing so, routes to ameliorate these negative attributes can be identified, which forms the basis for moisturizing cleanser technologies. This requires an understanding of the complex interaction of surfactants, water, and skin during the cleansing process.

31.3 EFFECT OF SURFACTANTS ON SC

During cleansing, SC is exposed to a relatively high concentration of surfactants (5 to 20%). At these concentrations surfactants have the ability to damage the SC proteins and lipids, and increase the leaching and removal of water-soluble aminoacids, often referred to as skin's natural moisturizing factors (NMFs). The extent of damage will depend upon the nature of the surfactant and the cleansing conditions such as water temperature and hardness.

While it would appear that there is a distinct difference in the mechanisms driving the immediate and longer term consumer perception of cleansing, for the most part it is a matter of degree, related to the increasing interaction of surfactants and skin. For example, superficial dryness seen as an

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TABLE 31.2
Short-Term and Long-Term Effects of Cleansing

Symptoms	Technical mechanism	How to measure	Technical solution
Immediate effect of cleansing (short term)			
Tightness and itch	Loss of NMF Protein swelling Differential stress due to rapid dehydration Changes in lipid fluidity	Consumer perception Expert panel Naïve consumer panel Bioinstrumental elasticity	Milder surfactant to remove less NMF and reduce protein swelling Replenish NMF during wash Deposition of emollients and occlusives to moderate rapid water evaporation
Superficial visual dryness	Alteration of the optical properties of the surface cells Loss of surface lipids	Visual expert grading Consumer perception Photography	Milder surfactant to remove less surface lipid and extract less NMF from surface cells Replenish surface lipids Deposit emollients and occlusives
Cumulative effect of cleansing (long term)			
Visual dryness	Aberrant surface desquamation Debonding of cells Loss of flexibility leading to the formation of cracks	Visual expert grading Photography Microscopy	Milder surfactant to extract less NMF from skin and preserve SC lipids Deposition of emollients to hold moisture within skin and enhance surface appearance
Itch	Barrier breakdown leading to an inflammatory response due to diffusion of surfactant into epidermis Debonding of cells and inter-cellular mechanical movement	Consumer Perception Expert panel Naïve consumer panel	Milder surfactants
Erythema/irritation	Barrier breakdown leading to an inflammatory response due to diffusion of surfactant into epidermis Alkaline pH induced protein swelling increasing surfactant irritation potential	Visual expert grading Colorimetry Photography	Milder surfactants pH neutral formulations

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alteration in optical properties will, over time, drive deeper and be evident as flaking and cracking. As Table 31.2 shows, the pervasive solution to delivering moisturization from cleansing starts with mild surfactancy. But mild surfactants alone simply reduce the drying effects of cleansing. To achieve active moisturization requires additional technology to counter surfactant effects and enhance skin quality. Therefore, to achieve the goal of a moisturizing cleanser requires both an understanding of how surfactants negatively interact with skin and how moisturizing cleanser technology can minimize that interaction and repair the damage, in both the short and long term.

31.3.1 Immediate (Short-Term) Effects of Surfactants

The SC has about 70% proteins, 15% lipids, and 15% water.[16,17] Most of the water in the SC is present within the corneocyte proteins and is associated with the keratin bundle as well as with the NMFs while the rest of the water is bound within the head-group region of the lipid layer. SC hydration increases markedly during cleansing and the excess water in the corneum evaporates off within 10 to 30 min after the shower. Three aspects govern how the SC hydration changes during and immediately after wash: (1) amount of water that SC absorbs during cleansing, (2) the rate of water evaporation immediately after drying, and (3) the equilibrium SC water content as determined by the humidity and temperature conditions immediately after a wash. All of these changes are influenced by the effects of the cleanser surfactant on skin proteins and lipids.

31.3.1.1 Effects on Proteins

Most of the water absorbed by the SC during cleansing is present within the corneocytes resulting in significant protein swelling. Surfactants increase the swelling further and the extent of surfactant induced swelling is dependent upon the nature of the surfactant. Increased swelling has been shown to be related to irritancy and is useful as a predictor of surfactant irritation potential.[18–20] Figure 31.3 provides a comparison of SC swelling in the presence of surfactant actives in a soap and a syndet bar. Results show that the extent of swelling in the presence of sodium laurate (soap) is significantly higher than that in the presence of sodium cocoyl isethionate (syndet). Other factors such as solution pH and temperature can further affect the swelling. For example, high pH solutions (pH 9+) even without the presence of surfactants have been shown to increase the SC swelling[21] suggesting further evidence for the benefit of pH neutral cleansing.

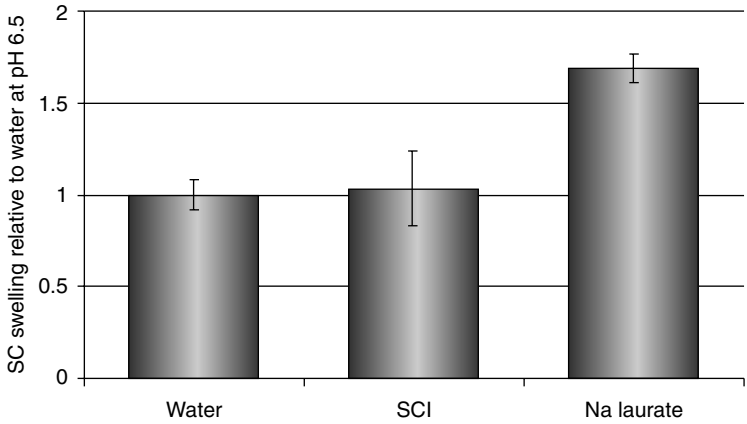

FIGURE 31.3 Swelling of porcine skin SC in sodium cocoyl isethionate (SCI, syndet) and Na laurate (soap) solutions (1%wt). Soap treated SC shows significantly higher swelling than that treated with syndet.

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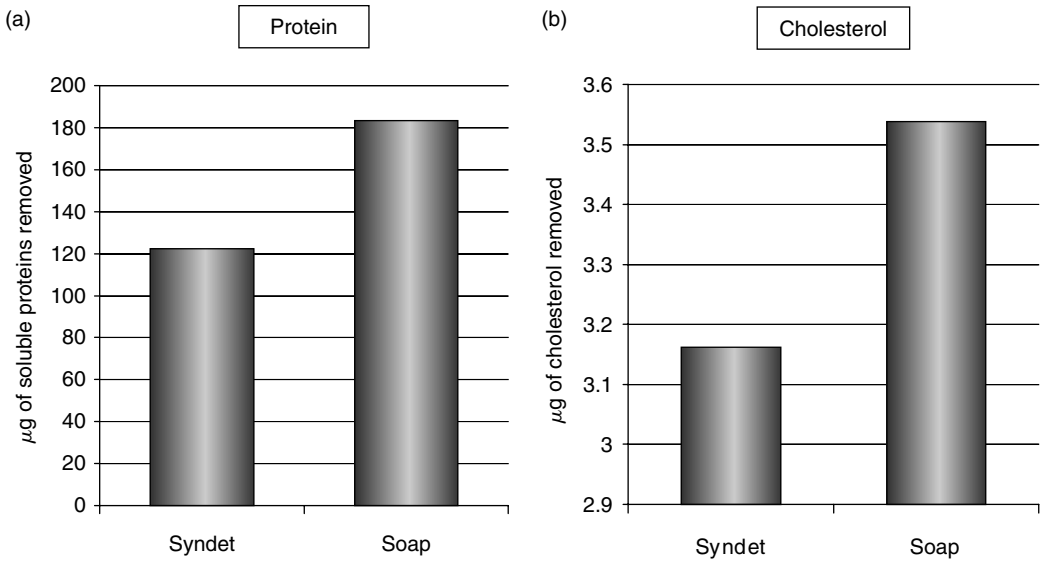

FIGURE 31.4 The amount of water soluble free amino acids (a) and cholesterol (b) removed from porcine skin after a single wash with a syndet bar versus a soap bar. Results show significantly higher removal from the soap washed site.

The excess water taken up by the SC during cleansing is flashed off within minutes after towel drying. How much water is retained in the skin after cleansing is defined by the equilibrium water binding capacity of the corneum, which can be affected by the interactions of the surfactant with the proteins and lipids. Harsh surfactants have been shown to remove NMFs more than by water alone.[22] This may be due to the damage to the corneocyte envelope caused by the harsh surfactant. Surfactant binding to proteins may also reduce the water holding capacity of the proteins. In either case, there is correlation between harshness of the surfactant and the increasing loss of water-soluble proteins. As can be seen in the results of a porcine skin assay (Figure 31.4), the higher loss of water soluble proteins after a single wash with soap versus syndet is consistent with the higher damage potential of the soap.[23]

The interaction of harsh surfactants on SC proteins results in an increase in skin surface water loss (SSWL). This is evident in the results shown in Figure 31.5. Water loss, measured using an evaporimeter immediately after a wash, show that harsher soap induces a higher rate of evaporation than milder syndet. The implications of this high rate of evaporation are examined further.

31.3.1.2 Effects on Lipids

Surfactants are designed to solubilize lipids and therefore, interactions of cleanser surfactants with skin lipids can be expected. Among the three classes of lipids in the corneum, specifically cholesterol, fatty acids, and ceramide, the latter because of its two-tailed and unusually long alkyl chain is not likely to get solubilized by the surfactant micelles. Cholesterol and lower chain length versions of the fatty acids (e.g., C18, C20 fatty acids as opposed to C24 and C28 fatty acids) may get solubilized in the micelle. Note, however, that even without any solubilization of SC lipids by surfactant micelles, simply by surfactant monomer intercalation into the bilayer, stress and damage can be imparted to the lipid bilayer. Insertion of anionic surfactants into the lipid bilayer can induce charge in the bilayer and alter membrane packing and permeability. Results with model liposomes indicate that surfactant insertion into the bilayer is usually the first step toward destabilizing the bilayer, which eventually results in the break-up of the bilayer resulting in mixed micelle formation/solubilization of the liposome.[24,25] In the case of SC, even partial or preferential removal of lipids such as cholesterol

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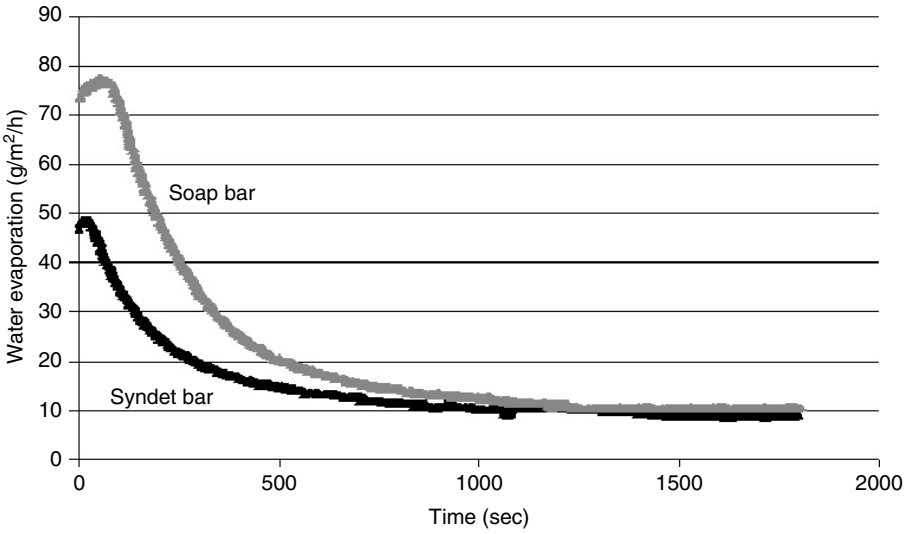

FIGURE 31.5 Water evaporation after a single wash with a soap versus a syndet bar showing initial hyper-hydration due to excessive swelling after wash with a soap bar and a reduced water swelling after a syndet bar wash. The slope of the curves also shows that the rate of evaporation after soap wash is higher, which is consistent with its higher perceived tightness.

can make the bilayer lipid unstable. Results for the removal of cholesterol by soap and the syndet bar are given in Figure 31.4 and show that soap removes more cholesterol than the syndet. While the exact reasons for this difference is not clear at present, it is likely that the high pH of soap allows ionization of the bilayer fatty acids allowing easier cholesterol extraction from the corneum. Yet another factor may be from the increased swelling of soap damaged corneum that allows deeper layers of the SC to be exposed to the cleansing surfactant.

31.3.1.3 Manifestation of the Short-Term Effects on Proteins, Lipids, and NMFs

The above combination of events, specifically, initial hyper-hydration because of excessive swelling and high rate of evaporation to an equilibrium level lower than normal, is hypothesized to be a major contributor to the perception of after-wash tightness. Hypothetical curves of changes to SC hydration immediately after a single wash are given in Figure 31.6 and these are consistent with the *in vivo* SSWL results given in Figure 31.5 as well as those reported in the literature.[19] As water evaporates at a rapid rate from the upper layers, a differential stress is created in the corneum and this is thought to be the origin of the after-wash-tightness. As the evaporation rate reduces to its normal level, the stress is relieved and the tightness disappears. These effects become even more acute under low humidity and low temperature conditions. Low humidity will certainly lower the equilibrium hydration levels in the corneum.

31.3.2 Cumulative (Longer Term) Effects of Repeated Exposure to Surfactants

Continued daily use of cleansers that cause short-term damage can lead to skin dryness, scaling, flaking, erythema, and itch.[26] While detailed molecular mechanisms involved in these effects are not fully understood, based on their current understanding, several possible mechanisms can be hypothesized.

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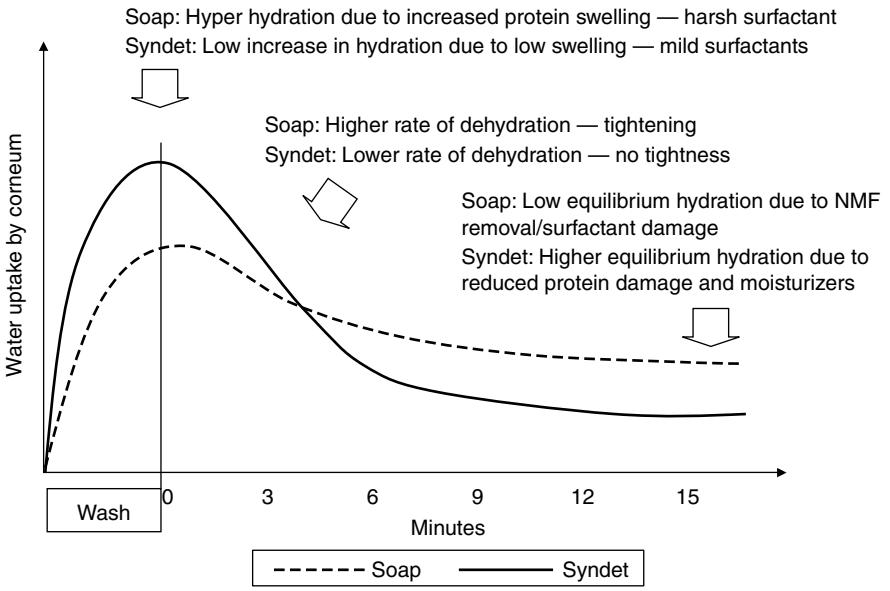

FIGURE 31.6 Hypothetical curves describing changes in SC water level after a wash with a harsh cleanser (soap) versus a mild cleanser (syndet).

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31.3.2.1 Dryness, Scaling, and Flaking

Skin dryness is more than just a lack of water in the SC. It is actually a disruption to the biological processes underlying healthy normal skin, that affects both clinical and consumer perception of skin condition.

Consumer perception of dryness has both a visible and a tactile component. Visual effect of dryness is whitening of skin with the development of visible scaling. Dry skin is also physically tighter, more brittle, less soft than moisturized skin. Brittle SC can easily crack leading to chapping and significant barrier damage.

From a materials science perspective, the SC is a laminated composite membrane comprised of two distinct domains, specifically, proteins (corneocyte cells with embedded keratin bundles) and lipid bilayers. Corneocyte cells have covalently attached lipids, which makes them compatible with the surrounding lipid matrix. In addition, corneocytes in different layers are held together by protein "staples" called desmosomes. SC has been designed to exfoliate dead cells in an orderly fashion where the upper layers come off in a layer-by-layer fashion. For this to happen, the desmosomes have to be cleaved by proteolytic enzymes in the SC as the cells approach the outermost layers.

The SC is also designed to maintain certain degree of flexibility and elasticity under normal conditions so that when skin is flexed, it does not crack. Both proteins and lipids contribute to the overall pliability of the corneum. Water and NMFs maintain the flexibility of the corneocytes[27] whereas fluid lipids are thought to maintain the flexibility of the bilayer lipids.

As described earlier, water plays a key role in maintaining a normal SC. Lack of water in the corneum is a primary cause for disrupting several processes in skin. For example, lack of water can lead to visible signs of dryness (whitening), inadequate desquamation, scaling, chapping, and cracking.

Factors that cause excessive swelling followed by reduced water holding capacity of the corneum will allow the corneocytes to swell and shrink repeatedly and this cycling can create stresses leading to de-bonding of the corneocytes from the surrounding lipid matrix. As the situation continues, the effect may propagate down to deeper layers leading to cracking in the SC, a poor barrier, and excessive water loss.

Reduction in the water holding capacity of the corneum can also make the corneocyte proteins brittle and vulnerable to cracking. Keratins in the corneum have a glass transition temperature just below the body temperature[28] and this is sensitive to humidity levels. Glass transition temperature is the point below which the material is brittle. As the humidity/water content of the SC decreases, glass transition temperature increases to values above the body temperature thus making the corneocytes brittle at body temperature.

Presence of water in the SC is essential for the enzymes to cleave the desmosomes and in dry skin inadequate desmosomal degradation can occur leading to accumulation of dry cells. The result is severe dryness with excessive flakiness in the SC.

Similar to water plasticizing the proteins, fluid lipids in the bilayer lipids are implicated in the elasticity of the corneum. Removal of fluid lipids can make the corneum brittle. For example, solvent treatment of the corneum to remove fluid lipids has been shown to make the SC brittle.[29] It has been shown that soap treated corneum behaves somewhat similarly to the solvent treated corneum in the sense that both exhibit a brittle fracture under tension. In contrast, syndet bar treated corneum behaves more like water treated corneum exhibiting a more elastic and pliable structure.

Visible skin dryness has been found to correlate positively with surface hydration, but not necessarily with an increase in transepidermal water loss (TEWL).[30] This suggests that significant barrier breakdown is not a requirement for skin dryness. A continued increase in dryness to values above a certain level may, however, lead to scaling, cracking and chapping, barrier breakdown, and, eventually, to irritation.

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31.3.2.2 Erythema and Itch

Erythema (development of redness) and itch are basically inflammatory responses of the skin when irritants penetrate into deeper layers of the SC. In the cleansing context this is usually because of a breakdown of the barrier for reasons indicated earlier leading to penetration of irritant materials. Note, however, that it may not be necessary for the surfactant to penetrate into dermal layers to elicit a response. Communication via production of cytokines in the SC can also elicit a response from the dermis.[26]

Factors that enhance the penetration of surfactants can be expected to increase surfactant-induced irritation. Thus, a swollen corneum will allow increased penetration of the surfactant into deeper layers. The ability of a surfactant to swell the corneum is an indication of its ability to enhance its own penetration into deeper layers and disrupt the cells in the living layer. This may be the scientific basis for the established correlation between the ability of surfactants to swell the corneum and its irritation potential. If the swelling occurs by other mechanisms such as increase in the protein negative charge because of high solution pH,[21] penetration of surfactants can also be expected to be enhanced under these conditions. Thus direct effect of pH 10 by itself on the corneum could contribute to increased surfactant irritation. Changes in lipid layers at pH 10 may also have an impact on irritation in that their increased rigidity may make them more vulnerable to cracking and debonding from the corneocytes and thereby permitting penetration of irritants.

Usually TEWL increases markedly under conditions that result in erythema indicating a barrier breakdown. It is not clear if a breakdown of the barrier itself or the subsequent penetration of irritants into deeper layers is responsible for the erythema. The latter appears to be a more reasonable mechanism.

31.4 MILD AND MOISTURIZING CLEANSER TECHNOLOGIES

It is clear that harsh surfactants have the potential to cause immediate alteration to SC proteins and lipids, and progressively increasing degrees of damage over time that can eventually result in a barrier breakdown. The first step toward mild cleansing is to minimize the damage potential of surfactants

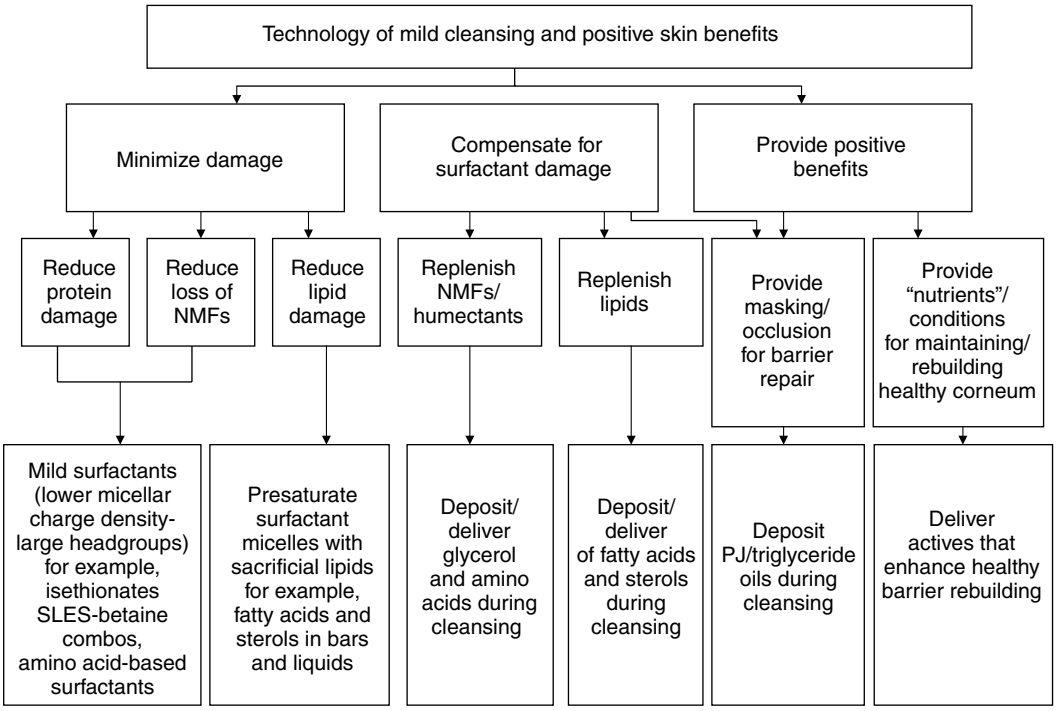

FIGURE 31.7 Currently practiced technology routes to provide mild cleansing with positive moisturization.

to proteins and lipids. The next step is to compensate for the damage and provide positive benefits by incorporating skin benefit agents into the cleanser. Current technological approaches to enhancing the mildness of cleansing systems are depicted in Figure 31.7.

31.4.1 Minimizing Surfactant Protein Damage

As discussed earlier, surfactants that interact strongly with SC proteins leading to their swelling and denaturation have a higher potential to cause erythema, and itching.[18,26] The tendency of surfactants to interact with model proteins has also been correlated with their harshness toward human skin. Thus, higher the tendency of a surfactant to swell SC[18,30] or model proteins such as collagen[31] and keratin,[32] or denature a globular protein such as bovine serum albumin[33] or dissolve a water-insoluble hydrophobic protein such as zein,[34,35] higher is its tendency to irritate human skin. Results of zein solubilization by a number of surfactants is given in Figure 31.8. As can be seen, the tendency of surfactants to interact with proteins follow the order: anionic > amphoteric > nonionic and these are consistent with published results of protein damaging tendencies of various classes of surfactants.

While these empirical correlations are useful as guidelines for formulation work, quantitative correlations between surfactant properties and their protein denaturation tendencies are most useful as a predictive ruler. Based on the hypothesis that protein denaturation is essentially due to massive cooperative binding of surfactants on the protein backbone and the resultant increase in the charge of the protein, surfactant micellar charge was correlated with the zein dissolution tendencies of a variety of surfactants. Results reproduced in Figure 31.9 show that protein denaturation scales with the charge density of surfactant micelles.[36] Results for anionic, zwitterionic, nonionic, and even cationic (absolute charge density without the sign) surfactants are included in the relations given in Figure 31.9. Also included are results for mixtures of surfactants. The strength of the correlation clearly shows that micellar charge can be used as a useful predictor of irritation tendencies of surfactants. This insight allows formulators to develop novel strategies to predict and increase mildness of cleanser

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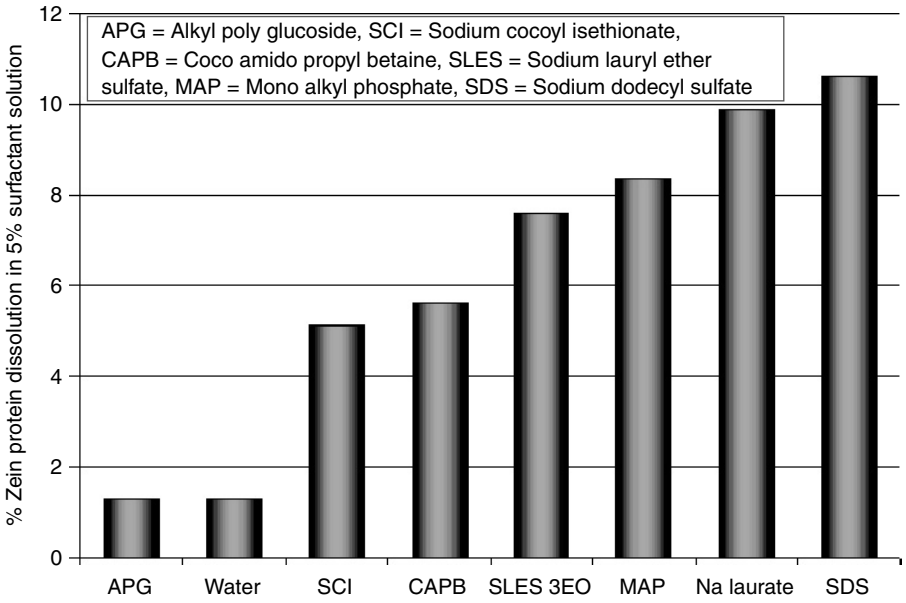

FIGURE 31.8 Protein damage potential of a number of surfactants determined using the zein dissolution test. Higher the zein dissolution, higher is the damage potential of the surfactant.

bases. In general, micelle charge density can be lowered by using surfactants of larger head groups, zwitterionic or nonionic head groups, and synergistic combination of surfactants that allow strong attractive interactions among head groups leading to a reduction in the overall charge density of the micelle.

Blankschtein et al. have concluded that micelle size is a major factor in surfactant induced irritation.[37] As the micelle size increases, penetration of the surfactant into deeper layers decreases and therefore increasing the micelle size is an approach to enhancing mildness. In principle, factors that reduce the micelle charge will increase the micelle size and therefore have the potential to reduce swelling and penetration under cleansing conditions. Note, however, that the inherent tendency of the molecule to cause an irritation response may be related to the charge density of the molecule rather than the micelle size.

Results given in Figure 31.8 shows the Syndet Bar active, sodium cocoyl isethionate, to have significantly less interaction with proteins than soap. This can be attributed to its larger head group area and lower micellar charge density than sodium soaps. Similarly, commonly used surfactant system for liquid cleansers, a combination of sodium lauryl ether sulfate (SLES) and cocoamido propyl betaine (CAPB) is significantly milder than soap as evidenced in Figure 31.9. Again the combination of SLES and CAPB have lower micelle charge density than SLES micelle alone and this can indeed explain its lower irritation potential than that for SLES alone. Synergistic interaction between the anionic and zwitterionic head groups should make this combination mild, especially in the lower pH range where the zwitterionic surfactant may possess a cationic charge because of protonation of the carboxylate group. While syndets are clearly seen as mild (particularly in comparison to soap), Figure 31.10 shows that there is still room for further reducing protein damage from surfactants in both cleansing bars and liquid formulations.

31.4.2 Minimizing Surfactant Lipid Damage

Long-term surfactant damage to the SC lipid extends from the short-term effects resulting in cumulative loss of barrier function and lipid fluidity leading to profound dryness. The results of an assessment

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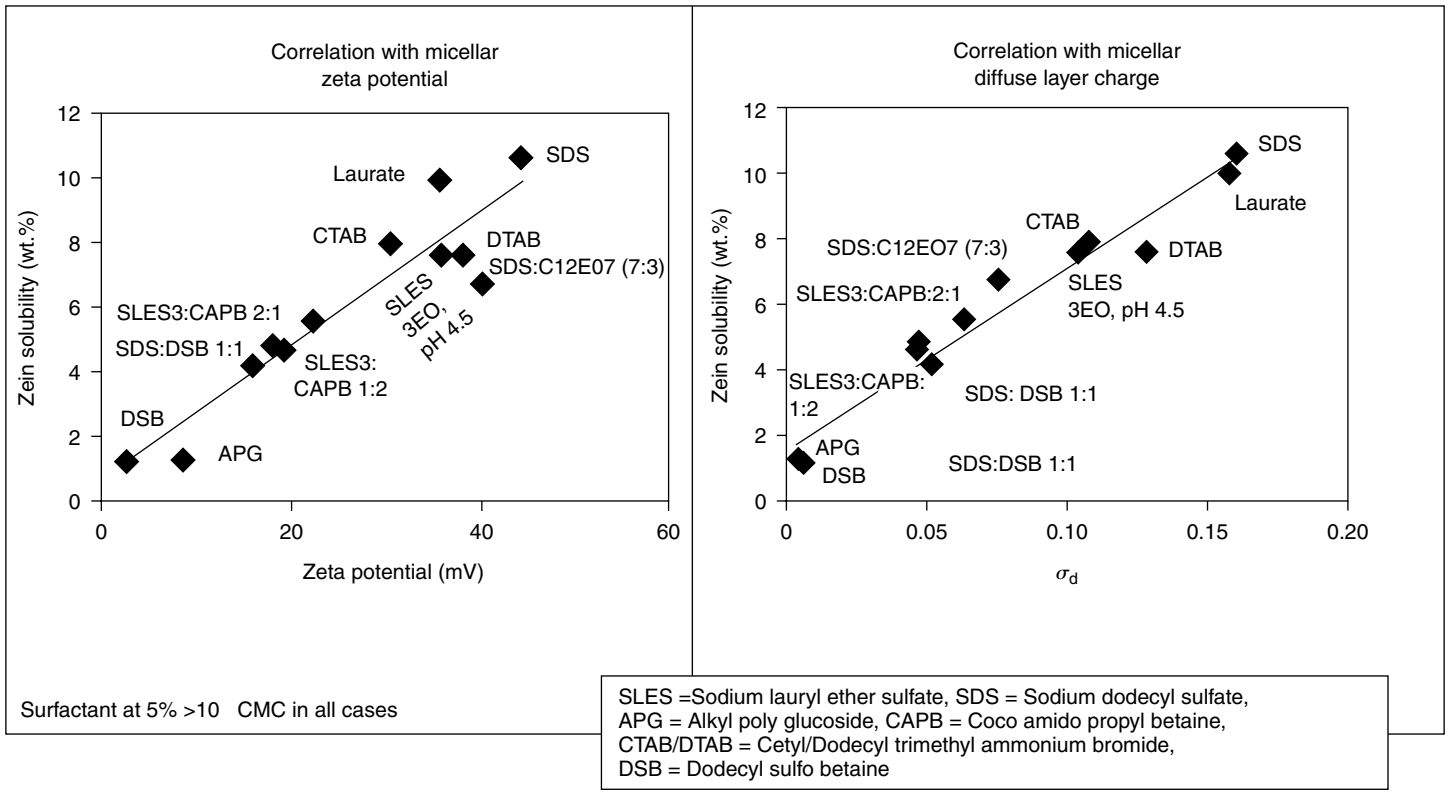

FIGURE 31.9 Correlation of surfactant micellar zeta potential and micelle charge density with zein dissolution showing that protein denaturation potential scales linearly with the micellar charge/potential.

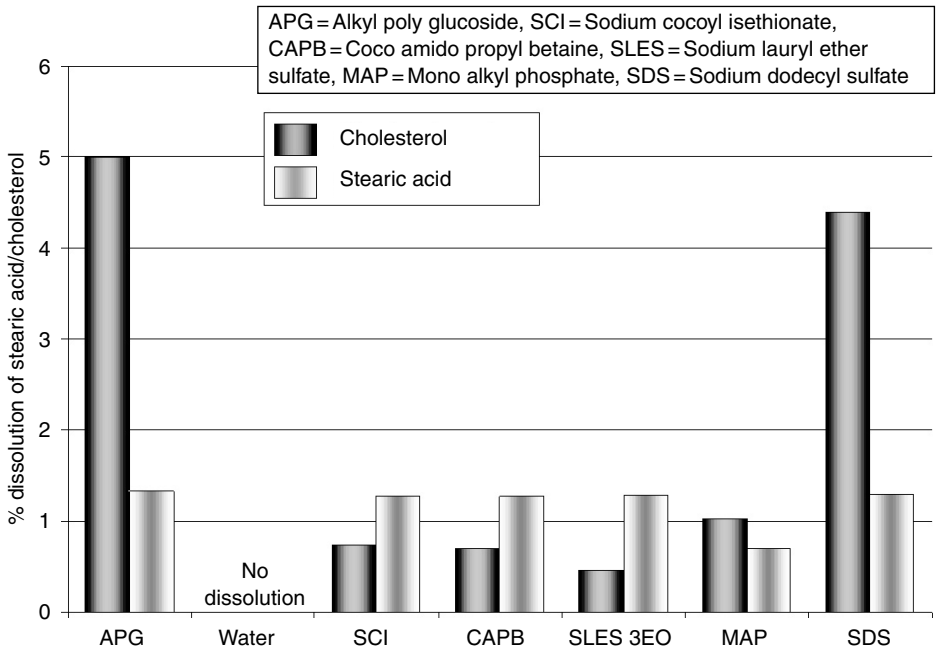

FIGURE 31.10 Lipid damage potential of a number of surfactants determined by the ability of surfactant micelles to solubilize cholesterol and stearic acid.

of lipid damage potential of surfactants as measured by the solubility of stearic acid and cholesterol in 5% surfactant solutions, are given in Figure 31.10. It appears that all the surfactants have some tendency to solubilize cholesterol and fatty acids. Interestingly, alkyl poly glucosides (APG) shows high potential for solubilizing cholesterol in contrast to its relatively low protein swelling tendency. This result shows that mildness toward proteins does not necessarily imply mildness toward lipids, and achieving mildness toward both proteins and lipids simultaneously may require delicate balancing of surfactant properties.

A relatively less understood mechanism, namely the presaturation of surfactant micelles with lipid mimics so that the micelle will have reduced tendency to delipidate the corneum during washing, is an approach to minimize surfactant–lipid interactions. Figure 31.11 shows the clinical benefit of adding high levels of fatty acids to a syndet bar formulation. The hypothesis is that the added fatty acids actually minimize the damage to both proteins and lipids by incorporating into the surfactant micelles, thus making the micelles milder toward both proteins and lipids.[38] Presaturation of the micelles with fatty acids will reduce the tendency of the micelles to solubilize SC lipids or intercalate into the SC bilayer. Also, presence of fatty acids can lower the charge density of the surfactant micelles, thus enhancing their mildness toward proteins.[38]

31.4.3 Compensating for Damage: Enhancing Moisturization

From a technology point of view, the main approach to minimize visible signs of skin dryness and increase skin hydration has been to deposit lipids, emollient oils, and occlusives (such as used in a lotion) under cleansing conditions. The challenges of incorporating high levels of emollients in a stable cleansing formulation and depositing the emollients on skin during the wash process have been largely surmounted by the use of specially structured surfactant formulations with cationic polymers to aid deposition and retention of oils and occlusives on to skin. Typical emollients and

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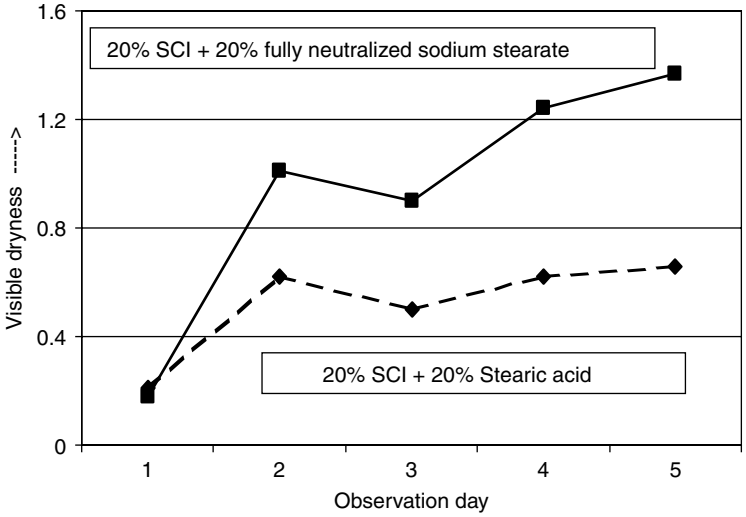

FIGURE 31.11 Change in dryness in a clinical study showing how fatty acid structurants improve the mildness of SCI.

occlusives used in cleansing liquid formulations are vegetable oils (sunflower seed, soyabean) and petroleum jelly. It is a bigger challenge to deliver water-soluble moisturizers such as glycerin and other humectants to skin during washing, and hence hydrophobic emollients are more commonly used in cleansers.

It has been shown that high emollient containing body washes do deposit a significant amount of lipid and emollient material to the skin. A commercial product containing sunflower seed oil triglycerides is found to deposit 10 to 15 μg/cm^2. Figure 31.12 and Figure 31.14 confirm the clinical advantage of such deposition on skin during cleansing. Note that the efficiency of deposition (amount of material transferred to skin versus amount contained in the product) from current technologies is still quite low and is an opportunity for improving performance of these moisturizing body washes. Another opportunity area is to deliver effective water-soluble moisturizers such as glycerin or lactates from a cleanser. These humectant materials are known to increase water holding capacity of the skin when delivered from leave-on products. However, there remains a technical challenge for effectively delivering water-soluble materials from rinse-off systems.

31.5 MEASURING MOISTURIZATION FROM CLEANSERS

31.5.1 Evaluating Moisturization of Skin

Generally when we think about measuring skin moisture we think of lotions where there is both an immediate and sustained positive increase in the hydration state after application. Classic methodologies for evaluating moisturizer efficacy start with dry skin and monitor the improvement benefit of continued product application over days or weeks.[39–41] Even in short-term trials, the lotion effect on skin is typically measured as increase in moisture and the improvement in moisture-related benefits such as smoothness and elasticity.[42]

In contrast, the basis of cleanser testing has historically been about evaluating dryness and irritation potential. Since 1979 when Frosh and Kligman published a seminal paper on the soap-chamber patch test, cleanser moisturization and mildness have been defined as reduced dryness and damage in comparison to soap.[43] As Wolf points out, for decades the desired qualities for soap have

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TABLE 31.3
Commonly Used Methods for Quantifying Skin Dryness

Sensory	Consumer perception
	Dry feeling
	Tightness
	Itch
	Tactile roughness
Visible appearance	Expert clinical grading
	Dryness, seen as flaking
	Irritation, seen as erythema
	Instrumental surface measures
	Roughness
	Desquamation
Hydration state	Indirect
	Electrical conductance/capacitance
	Direct
	NIR and Raman spectroscopy
Biophysical/biomechanical	Properties affected by hydration state
	Skin surface water loss
	Elasticity
	Cell proliferation/SC turnover
	Enzymatic activity

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been about mildness, gentleness, less irritation, and less drying rather than their primary purpose of cleansing.[44]

As cleansers moved to syndet bars to liquid detergent systems, they became more and more innocuous in the short term and required exaggerated exposure to elicit measurable dryness and damage response. However, as cleansers have begun to move toward active moisturization, methods traditionally associated with lotion-testing can be applied.

Moisturization in skin can be measured in a variety of ways, some of the more common of which are summarized in Table 31.3. It can be measured directly as an increase in hydration in skin or improvement in clinical and sensory symptoms resulting from the improved hydration state of skin. At the most basic level, consumer perceptions can provide a measure of skin feel and appearance but more often are used to quantify the sensory aspects that cannot be measured instrumentally.[45] Expert clinical grading provides a more refined quantitative measure of appearance.[46] The human eye is still the most powerful tool for discriminating subtle changes in appearance.[47] However, bio-instrumentation is required to measure insensible parameters such as the hydration level in skin.[48–50] While methods based on electrical properties of skin are widely used to indirectly measure water content, Near-Infra Red and Raman Spectroscopic techniques are more closely reflective of the actual hydration state.[51,52]

31.5.2 Measuring the Effect of Cleansers on Skin

31.5.2.1 Short-Term Effects

We have seen that in the short term, the changes in skin due to cleansing primarily manifest as changes in sensory perception. Consumer perception methods are the primary means of assessing the transient onset of tightness and itch. Naïve panels can provide comparative data among several cleansers tested but can not provide consistent quantitative measure of performance. Expert panels

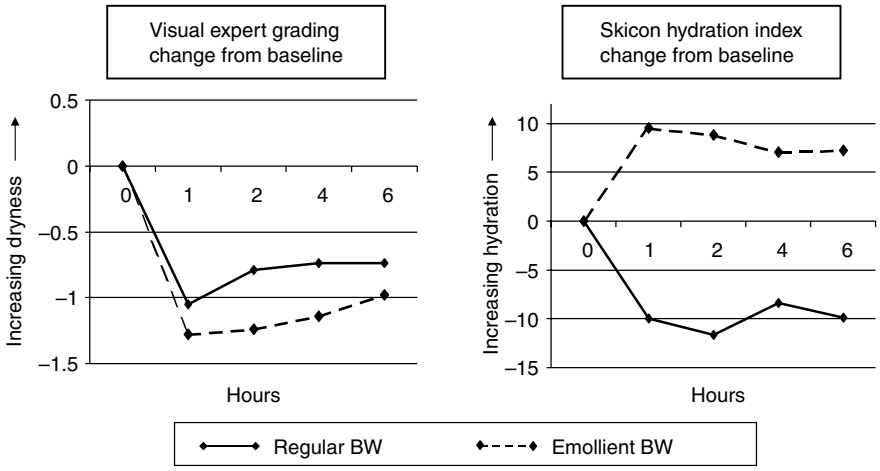

FIGURE 31.12 Comparison of a regular and an emollient liquid BW over a 6 h period following a single wash event.

can provide the quantitative measure, but because sensory attributes are affected by local temperature and humidity, results must still be viewed relative to a known control.

Changes in hydration state can be traced in the short term. Electrical conductance and capacitance of skin can be used to describe the hyperhydration and dehydration cycle of washing. However, it is the equilibrium end-point that defines the final skin state. As cleansers become less drying, we are effectively attempting to measure smaller and smaller changes to final skin state. Yet, as cleansers begin to deliver positive moisturization, these same methods become relevant to describe the benefit. This is particularly important for differentiating actively moisturizing cleanser from ultra-mild cleansers. This is illustrated in Figure 31.12, where visible appearance of dryness and the equilibrium hydration state of skin for 6 h after a single wash are shown. Both regular liquid body wash (BW) and emollient BW show improvement in visible dryness by removal of superficial flakes. However, this is not entirely reflective of the underlying hydration state. Instrumental data, in fact, shows a net loss of moisture for the regular BW as compared to the positive hydration for the moisturizing cleanser.

31.5.2.2 Long-Term Effects

While perceptible and imperceptible changes in hydration can be seen in the short term, real clinical changes to the equilibrium skin state take longer to occur. Small changes in dryness and barrier integrity after washing accumulate over time leading to a breakdown of many physical and biological processes. To model these quickly, a number of exaggerated exposure methods have been developed. Table 31.4 summarizes four widely used methods.[53–58] The first three begin with normal skin and look for the onset of dryness or irritation. Arm and Leg washing use an ordinary, though controlled, wash procedure but increase the frequency of wash events to several per day, in order to more quickly initiate a response. The FCAT procedure increases the response further. It maintains an increased frequency of washing and further exaggerates exposure by leaving lather solution in contact with skin for 90 sec before rinsing. Flex wash increases sensitivity to irritation by using mechanical action to drive product into the antecubital fascia, but in doing so loses sensitivity to dryness. The fourth method, the LCAT, actually begins with mild dry skin to increase response sensitivity and to be capable of measuring active improvement in condition.

Within all of these procedures, the actual measurements continue to focus on mildness and moisturization as defined by the same three aspects used in short-term tests, sensory, visible appearance, and hydration state, with the addition of a measure of barrier integrity using TEWL.

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TABLE 31.4
A Comparison of Commonly Used Exaggerated Wash Procedures

Armwash/legwash	Controlled wash of site using gloved hand Bilateral application: two products, paired comparison One to four times washing per day Development of dryness and erythema
FCAT	Controlled wash of sites 15 + 90 sec exposure to lather Two to six sites (up to 3 per arm) Four times washing per day Enhanced development of dryness and erythema
Flexwash	Controlled wash of sites with sponge or pad to antecubital fascia Bilateral application: two products, paired comparison Four times washing per day Enhanced development of irritation/erythema (but loss dryness information)
LCAT	Induce mild dry skin prior to baseline Controlled wash of sites 15 + 90 sec exposure to lather Two to six sites (up to 3 per leg) Four times washing per day Enhanced sensitivity to dryness effects or moisturization improvement benefits

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With regular cleansers, a procedure like FCAT (Forearm Controlled Application Test) provides good sensitivity to varying discriminate products based on their drying potential. Looking at soap versus syndet bar, we can compare three clear trends in Figure 31.13: an increase in the visible appearance of dry skin over time, a concomitant decrease in the equilibrium hydration state of the skin, and an increase in the disruption to the moisture barrier evidenced as an increase in TEWL. In all the three measures, the syndet is seen as milder and less drying.

When evaluating moisturizing cleansers, we see a more fundamental change in these trends. The results of an FCAT on an emollient body wash as compared to regular body wash are shown in Figure 31.14. Two distinct features of active moisturization are evident. First, the emollient body wash is showing no negative effect on normal skin appearance. Despite repeated use and exaggerated exposure to the product, the emollient BW provided no significant change in visible appearance of dryness over time as compared to regular BW, which does show increasing dryness. Second, the emollient BW provided a significant increase in skin hydration after five days of repeated use. Taking the moisturization benefit even further, the effect of emollient BW to actually *improve* visible dryness is evident in the results of an LCAT (Leg Controlled Application Test) study (Figure 31.15). In this study design where we begin with mild dry skin, the emollient cleanser can be seen to significantly reduce the visible appearance of dry skin over time. These long-term clinicals demonstrate that positive moisturization seen in the short term (Figure 31.12) is maintained to establish a significantly improved equilibrium hydration state after five days. Thus active moisturization from cleansing is more than a transient effect. This work shows it to provide a sustained improvement in skin condition with repeated use.

31.5.2.3 Advanced Moisturization Measures

The ability of cleansers to positively affect the moisturization of skin can further be measured by evaluating biomechanical properties that are intrinsically linked to hydration state. For example, changes in skin softness are directly related to hydration state, and Figure 31.16 shows how biomechanical

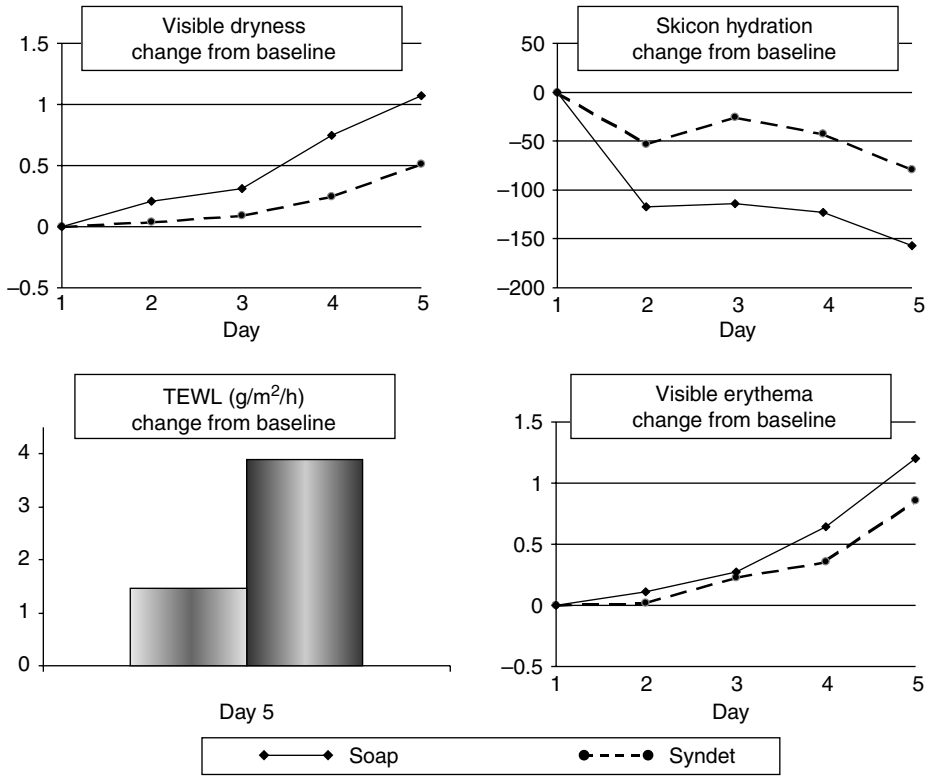

FIGURE 31.13 FCAT study comparing soap and syndet bars shows soap induces higher visible dryness, lower hydration state, greater loss of barrier function, and increased erythema.

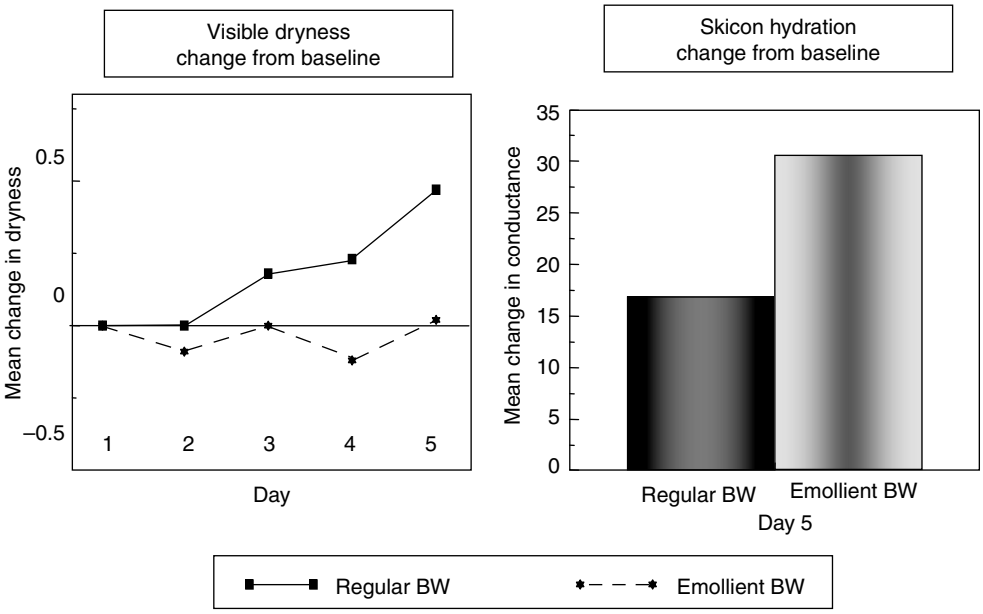

FIGURE 31.14 FCAT study of regular and emollient BW shows that EBW induced no visible dryness and significantly improved the hydration state.

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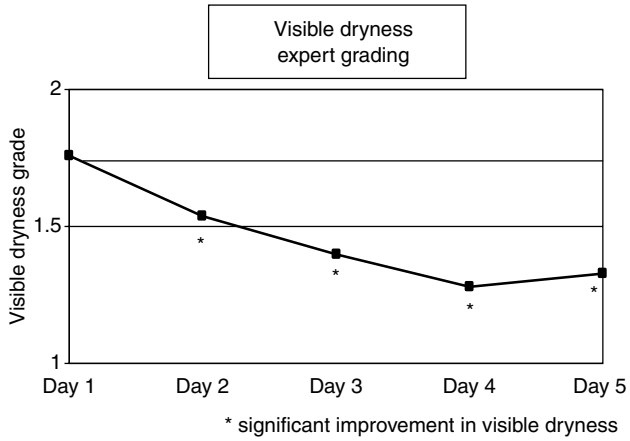

FIGURE 31.15 The LCAT study of emollient BW effect on visible dryness shows a significant improvement in appearance of dryness.

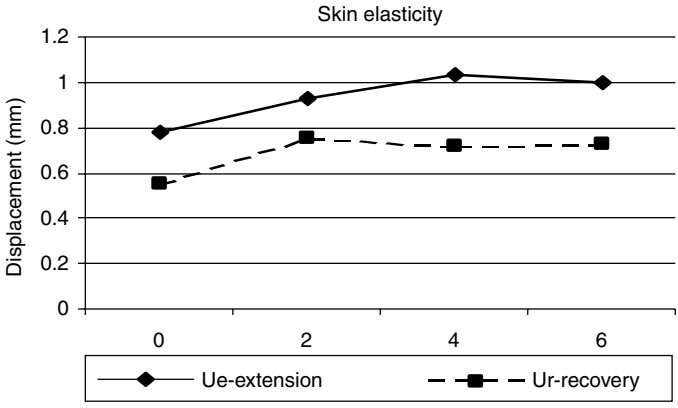

FIGURE 31.16 Effect of emollient BW on elastic properties of skin, as measured using Dermal Torque Meter, over a 6-h period following a single wash event. Ue and Ur refer to the immediate elastic extension and recovery, respectively.

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measures can describe changes in elastic properties due to active moisturization from cleansers in the short term.

Recognizing the direct relationship between skin hydration state and regulation of the biological processes of skin, and understanding the significant effect cleansing has on this, it is clear that effective measurement of skin hydration is vital. Electrical conductance and capacitance measurements are indirect measures prone to artifacts. To different degrees, standard instrumentation are influenced by the insulating effect of surface dryness, conductivity of surface films, and the physical contact of probe and skin. More recent methods for the rapid, direct measurement of skin water content are showing excellent correlation with visible dryness.

Near Infra Red (NIR) Spectroscopy provides a noncontact, noninvasive direct measure of SC hydration.[51] It uses IR light, which is absorbed by tissue and the specific wavelengths reflected by the water molecules in that tissue. This technique provides an image of actual water present in skin, which is quantified using image analysis. NIR information can be used to visually show changes in equilibrium water content of SC after washing, which is particularly useful for understanding active moisturization from cleansers. Images shown in Figure 31.17 visibly depict the increase in skin hydration one hour after washing with an emollient BW. These images were taken from a single use

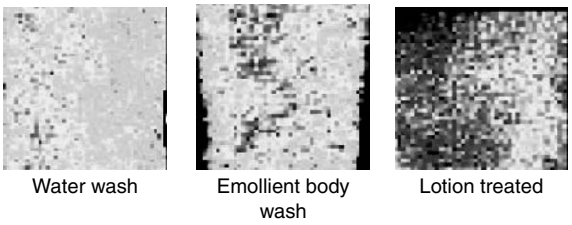

FIGURE 31.17 Near Infrared Spectroscopy images depict the change in skin hydration state one hour after water wash versus a wash with an emollient BW. The increase in dark areas indicate greater hydration after washing with the emollient BW. The change in hydration state for a lotion treated site is included for reference.

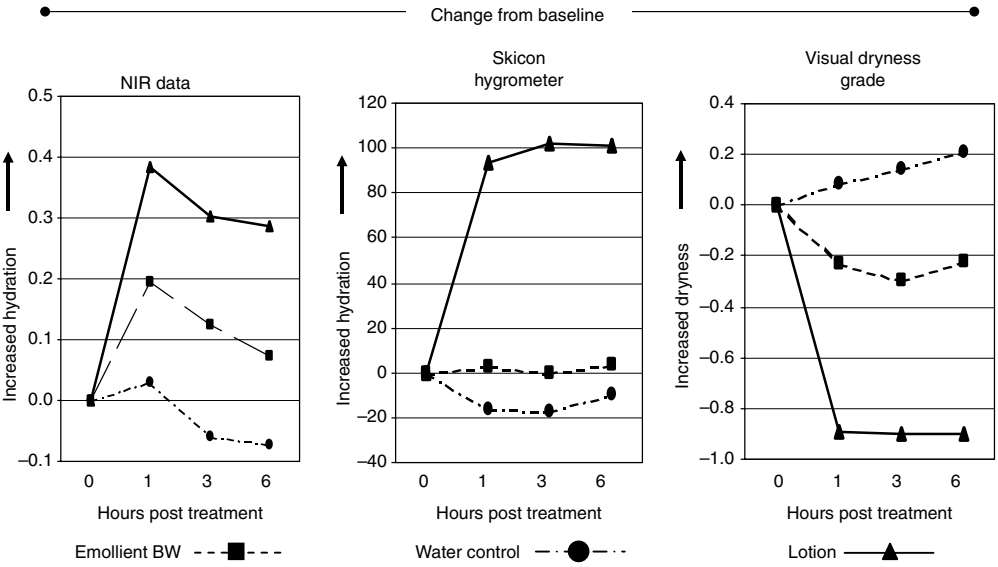

FIGURE 31.18 Near Infrared Spectroscopy analysis provides clear delineation of the hydration profiles of emollient BW relative to water washing or lotion use. NIR shows good correlation with the visible appearance and clearer product differentiation compared to skicon.

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trial comparing an emollient BW to water wash control. The quantified results of image analysis are presented in Figure 31.18 and show a clear delineation of the hydration profiles among treatments and good correlation with the visible appearance of dryness. Another emerging technique for direct *in vivo* measurement of skin hydration is Confocal Raman Spectroscopy.[52]

Advanced microscopic techniques such as optical coherence tomography and *in vivo* confocal microscopy have been applied to sensitively evaluate hydration induced changes in the SC. For example, using confocal microscopy, Leeson et al. showed that the morphology of corneocytes at the surface of the skin changes from an irregular, rough arrangement in dry skin to a highly ordered, smooth pattern in moisturized skin.[59]

31.6 CONCLUSION

The cleansing market place has evolved a long way from providing cleansing and hygiene benefit to current technologies that are designed to provide advanced moisturization benefits in the shower. For millennia, cleansing has been synonymous with soap, which is associated with skin dryness. Our understanding is that skin dryness is much more than the superficial removal of moisture from the

SC. Surfactant interaction with lipids and proteins leads to a fundamental breakdown of biological processes that underpin skin health. Mild surfactants have lead to cleansers with significantly reduced drying and damaging potential but only within the last decade have truly moisturizing cleansers begun to emerge.

The technology to clean skin and improve hydration state builds on an understanding of mild surfactancy and adds to it an understanding of skin and moisturization. New understanding of the interaction of surfactants, emollients, and humectants with skin can only lead to cleansers with even broader benefit capabilities. As such, moisturizing cleansers signal a significant reinvention of history's most basic cosmetic product.

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