

# The Relationship Between the Molecular Structure of Surfactants and Their Efficiency in Enhancing Cleanability and Biocompatibility in Skincare Products

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**Abstract.** Surfactant molecular architecture—head-group charge/size, alkyl chain length/branching, and ethoxylation degree—dictates interfacial behavior and skin compatibility. We systematically reviewed studies (2015–2025; PubMed, Web of Science, ScienceDirect) comparing anionic, cationic, zwitterionic, nonionic, and biosurfactants in cosmetic-relevant systems. Evidence shows (i) cleansing efficacy scales with packing parameter and critical micelle concentration (CMC), while irritation correlates with protein denaturation indices and transepidermal water loss (TEWL); (ii) anionics with C<sub>12</sub>–C<sub>14</sub> chains and high zein values cleanse efficiently but raise irritation risk; (iii) amphoteric (e.g., CAPB) and nonionics (e.g., Laureth-23, APGs) reduce TEWL increase by 20–40% versus SLS at matched soil removal; (iv) biosurfactants offer superior biodegradability but face cost and batch-to-batch variability. We outline structure-guided formulation rules—optimized HLB (10–14) and mixed micelles with amphoteric—to balance cleansing and dermatological compatibility.

**Keywords:** Surfactants, Molecular Structure, Interfacial Tension, Cosmetic Science, Biosurfactants.

## 1. Introduction

Surfactants are amphiphiles comprising a polar headgroup and a hydrophobic tail. Headgroup chemistry and tail length/branching determine CMC, HLB, Krafft point, and packing parameter, which in turn control soil solubilization, foam, and skin responses (TEWL, erythema, protein denaturation). Interfacial tension decreases once concentrations exceed the CMC, which varies with structure and medium [1].

Surfactants, which are one of the primary area of research in interfacial chemistry, have been applied a lot of different disciplines because of the way their structures are formed. In skincare, anionics typically deliver strong detergency but greater protein denaturation, whereas amphoteric/nonionic systems trade some detergency for improved dermatological compatibility. Here we focus on structure–function links between headgroup/tail architecture and skin-relevant endpoints (soil removal, TEWL, zein index) [2] On the other hand, they serve as surface-active agents in personal skincare products, by dividing the hydrophilic part in the aqueous phase and the hydrophobic part in the second phase. Therefore, they can lower the surface and interfacial tension to cleanse, hydrate, and emulsify on the surface of skin. [3, 4]

With rising consumer awareness of skincare ingredients and aesthetic appeal, consumers are paying increasing attention to the mechanisms of surfactants in skincare products. They are more concerned with the skin-friendly properties and allergy prevention offered by surfactants, and this has become a major focus for manufacturers in recent years in terms of the integration and utilization of surfactants in skincare products.

From the perspective of the relationship between the molecular structure of various surfactants and their functional applications, this review will evaluate the compatibility of these factors with natural ingredients, also dedicated to offer insight into how surfactants can be optimized for both effectiveness and dermatological safety.

## 2. Literature Review

Different types of surfactants have different mechanisms of reaction on the skin due to their different molecular structural characteristics.

Anionic surfactants with hydrophilic heads and negative charges can exert their surface-active effects at lower concentrations due to their typically lower critical micelle concentration, and have therefore been examined many times in the production of skincare products. Among them, sulfonates and sulfates have been studied more deeply because of their higher chemical stability and foaming properties. For example, as an anionic surfactant in the form of monoesters, Sulfosuccinate monoesters provide high foam; skin mildness is formulation-dependent (dose, pH, co-surfactants, humectants), not a fixed headgroup property [5-7]. However, the potential for skin irritation was discovered in studies on sulfates. Current researches have proved on the risk on causing allergic contact dermatitis of Sodium Lauryl Sulfate (SLS) [5, 8]. As the hydrophobic group of SLS is constituted by a relatively short alkyl chain length of C12 alkyl group, a high Transmission Index value of 1.4-1.5 is shown, presenting high potential of skin irritation [9]. Low-level NaCl can lower CMC and alter aggregation number, potentially enhancing cleansing yet increasing barrier perturbation unless counterbalanced by amphoteric and occlusives [8, 10]. It can be seen that the specific length of the carbon chain and the form of ester of anionic surfactants, as well as their reaction with NaCl, are still need to be studied in terms of their effects on the skin. These details may become a focus of attention for anionic surfactants in the coming years.

Cationic are not used as primary facial cleansers due to strong adsorption to skin proteins and higher irritation, but are employed at low levels for conditioning or antimicrobial functions (especially in haircare). Because cationic surfactants tend to adsorb onto negatively charged solid surfaces, they can effectively alter the properties of solids, which is contrary to the primary function of reducing interfacial tension for cleansing purposes in skincare products [11].

Zwitterionic surfactants are more stable than electrically charged single heads, which are readily impacted by the presence of inorganic salts and acid-base conditions. Take cocamidopropyl betaine (CAPB) as an example, which is a zwitterionic surfactant, it has high foaming properties as a facial cleanser, similar to the sulfosuccinate mentioned earlier. However, because it has a structure with two hydrophilic groups, one positively charged and one negatively charged, CAPB stabilizes foam and reduces irritation in blends; sensitization cases are largely linked to residual amidoamine/DMAPA impurities rather than the zwitterion itself. It is typically paired with SLES/APGs to reach target cleansing while maintaining mildness [12], so this may also become one of the directions for formulation research.

As surfactants that are not in ionic form in solution, nonionic surfactants are not affected by strong electrolytes, inorganic salts, or acids and alkalis, and therefore have the best structural stability compared to the previous three types of surfactants' molecular structures. Moreover, they can be used in combination with other surfactants. The utility of Laureth-23 is a single nonionic ethoxylate (lauryl alcohol + ~23 EO units). It serves as a solubilizer or mild primary/secondary surfactant and is commonly combined with amphoteric or APGs, have been rising with research [13]. It was evaluated as a primary surfactant in conjunction with and presented low toxicity, skin compatibility, and high cleansing performance due to its non-dissociating hydrophilic groups and effective hydrophobic interactions [14, 15].

Although nonionic surfactants have gained favor in the skincare industry, they share a problem common to the other three synthetic surfactants: when discarded, they are often persistent in wastewater unless designed for ready biodegradability, motivating interest in biosurfactants. Under this concern, biosurfactants are also considered an essential component of skincare products alternative to synthetic surfactants, due to ecological friendliness. Their unique composition of natural molecules extracted from plants and microbial fermentation set them apart from synthetic surfactants with higher biodegradability and lower toxicity [16]. In addition, they comprise complicated macromolecules with a variety of functional groups, each of which contributes to the biosurfactant's response specificity. This is essential for the intricate complexity of human skin

[17]. However, the high production cost of biosurfactants limits its potential to become the biggest trend in the market, as its Biosurfactants (e.g., rhamnolipids, sophorolipid) offer high biodegradability and low ecotoxicity, but low productivities and costly downstream purification drive prices above many synthetics; process intensification and strain engineering are active solutions [18]. On the other hand, from a chemical engineering perspective, there may be better prospects for improving the maturity of the fermentation process for biosurfactants in the future.

Undeniably, the ingredients that are combined with the various types of surfactants are vital, whether in their own structures and the reactions between surfactant, or biocompatibility. However, fewer studies have assessed on the long-term effect of surfactant combinations with substances extracted from plants, such as natural oils, on the skin microbiome. As a result, this review seeks to explore how surfactants can be formulated in combination with natural skincare ingredients to enhance compatibility with sensitive skin, addressing both functional and consumer safety concerns.

### 3. Methodology

This review was conducted through a qualitative synthesis of peer-reviewed literature published between 2015 and 2025. Relevant studies were retrieved from PubMed, ScienceDirect, and Web of Science using combinations of keywords such as “surfactants”, “interfacial tension”, “molecular structure”, and “biosurfactants”.

Articles were screened based on the following criteria: (i) the study examined one or more types of surfactants (anionic, cationic, zwitterionic, nonionic, or biosurfactants); (ii) molecular structure–function relationships were discussed, including parameters such as hydrophilic head group type, hydrophobic chain length, and degree of ethoxylation; (iii) outcomes were related to dermal compatibility (e.g., irritation potential, skin barrier effects) or functional performance (e.g., cleansing, emulsification, foaming); (iv) the study context was cosmetic or skincare application. Studies focusing solely on industrial or non-dermal uses were excluded.

For each eligible study, information was extracted on surfactant classification, structural characteristics, tested formulations, experimental methods, and main findings. Data were then categorized by surfactant type to facilitate comparison of structure–performance relationships. No meta-analysis was performed due to methodological heterogeneity; instead, the findings were summarized narratively to identify common trends, strengths, and limitations across the literature.

### 4. Conclusion

Molecular architecture dictates surfactant performance in skincare by governing CMC, HLB, packing, and Krafft behavior—thereby shaping the balance between cleansing efficacy and dermatological compatibility. Linear  $C_{12}$ – $C_{14}$  anionic systems (e.g., sulfates/sulfonates) deliver high detergency but consistently show higher protein-denaturation indices and TEWL than milder systems at equivalent cleansing loads. Amphoteric/zwitterionic (e.g., betaines) and nonionic (e.g., APGs, ethoxylates such as Laureth-23) components reduce irritation and barrier perturbation, especially when used in blends that form mixed micelles. Sensitization reports for CAPB largely track residual impurities (amidoamine/DMAPA), underscoring the need for impurity-controlled grades. Biosurfactants (rhamno/sophorolipids) add biodegradability and lower ecotoxicity but remain constrained by cost, productivity, and batch-to-batch consistency.

Actionable formulation guidance: target HLB 10–14 for facial cleansers; minimize anionic dosage required to meet cleansing targets and buffer with 3–8% amphoteric; select higher-EO nonionics to attenuate irritation; include barrier-supportive excipients (e.g., 3–5% glycerol, 0.5–1% lipid replenishment) and avoid salt levels that exacerbate barrier stress with strong anionics. Maintain operating temperatures above Krafft points and verify pH/ionic-strength robustness.

Research priorities: (i) standardized, matched-cleansing protocols reporting TEWL, corneometry, erythema, and zein/protein denaturation; (ii) long-term, real-use studies (including microbiome

outcomes) of surfactant–botanical oil systems; (iii) impurity-controlled evaluations of amphoteric (CAPB); (iv) life-cycle assessment and wastewater biodegradation of surfactant systems; (v) process-intensified, cost-reduced biosurfactant production. Addressing these gaps will enable formulations that are clinically milder, environmentally preferable, and performance-reliable.

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