

Comparison of Amino Acid-Based Facial Cleanser and Soap-Based Facial Cleanser

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Abstract: Nowadays, cleansing is the first step in skincare and plays a crucial part in keeping the skin healthy and hydrated, removing dirt (including pollutants in the air, sweat, dust, and sebum), unwanted materials, and excess oil. However, choosing the wrong facial cleanser can do more harm than good. Various facial cleansers are appropriate for various skin types, but there are too many facial cleansers available in the market that makes it difficult for customers to select the most fitting facial cleanser. Therefore, a comparison of facial cleansers is necessary and valuable. Many commercial facial cleansers are soap-based and amino acid-based, so this paper will explore the differences between the two. Different aspects of facial cleansers will be examined and compared in this paper, including their cleansing ability, foaming power, mildness, and pH.

1. Introduction

Throughout history, different types of facial cleansers varying from acidic to alkali pH were discovered. The idea of soap first came into sight in 2500 B.C. when the Sumerians created potassium soap to remove dirt. [1] By the early 19th century, skin cleansing acts as medical washing [2]; it then develops into a daily routine and is widely in use across households. [3] The discovery of amino acid-based cleansers is much later than soap. The thought of employing amino acids as raw materials was only introduced in the early 1900s; and researches regarding amino acid surfactants (AAS) continued to modern days. [4]

In modern days, facial cleansers in the market consist of various surfactants in which soap-based and amino acid-based are the most well-known and the most commonly seen. The wide range of surfactants used results in facial cleansers performing a variety of functions, and this could bombard the customers, making it difficult for them to choose the most suitable facial cleanser.

As in all cleansing products, facial cleansers contain an essential element of surfactant (surface active agent) which reduces the surface tension between two mediums and has foaming and detergent properties. It has an amphiphilic structure with a hydrophobic tail attracted to non-polar oil and a hydrophilic head attracted to polar water. They form micelles, supramolecular assemblies, [5] when the concentration of surfactant added is greater than its critical micelle concentration (CMC). In water, micelles are formed with the hydrophilic (water-loving) part as the outer surface and the hydrophobic (oil-loving) part facing the center, trapping oil inside where water cannot be reached. When it is rinsed, water then carries the micelles away, along with the grease inside; this is how cleansers remove unwanted materials from the skin. [6]

Many factors have to be considered when choosing a suitable facial cleanser. For instance, cleansing is the most basic role of facial cleansers so their cleansing ability has to be considered; bubbles formed by surfactants can also contribute to their potential of removing unwanted materials, therefore also acting as one of the factors. As people are now more aware of the importance of the mildness of facial cleansers, it must also be taken into account. In addition, the pH of the facial cleanser is to be considered that it plays a part in the mildness of facial cleansers and it could affect the function of the epidermis. All of the factors above are influenced by the surfactant used, so a facial cleanser with suitable surfactants is needed. Furthermore, since surfactants are unable to distinguish between

the unwanted oil and the needed lipid, which maintains the epidermal barrier, they could end up damaging the skin by reacting with components in and on the outer layer of the epidermis (such as living cells, lipids, and proteins). [7] By these interactions, the function of specific components might be disturbed, encouraging skin irritation and destruction of epidermal barriers. Consequently, it is useful to discuss the surfactants in facial cleansers when comparing them.

This paper will be examining amino acid surfactant (AAS) and soap, comparing them in terms of cleansing ability, foaming ability, mildness, and solubility (cleanser pH) and explaining these properties from their chemical structure.

2. Profile of Amino Acid Surfactant and Soap

2.1 Amino Acid Surfactant (AAS)

After discovering ASS synthesis in the 1970s by Ajinomoto, more pioneering of different AAS syntheses were then continuously found and published. A typical AAS is formed in an acidic environment through the reaction between amino acids and fatty acid chloride. Halogenating fatty acids create fatty acid chloride and phosgene with the help of dimethylformamide (DMF) as a catalyst. [8] As biotechnology develops, researchers found more ways for AAS synthesis without DMF as it is environmentally unfriendly. One of the most common ways is that waste materials (such as unwanted soy products and sugar) are transformed into AAS (e.g., acyl glycinate) through fermentation with the aid of a bioengineered organism. [9]

Amino acids, the basic component of AAS, consist of a central carbon atom (α -carbon) which is linked to a carboxyl group (COOH), an amine group (NH₂), a hydrogen atom (H), and an R side chain, which is unique for each type of amino acids (Figure 1)[10]. The fact that there are different types of amino acids and fatty acids allows a variety of combinations to be formed, producing different types of AAS, some examples are shown in Figure 2 [8], which can be classified by the charge of their polar head. There are anionic (negatively charged), cationic (positively charged), amphoteric (charge changes with pH level), and non-ionic (no charge) AAS. In these types of AAS, anionic AAS is most commonly utilized in facial cleansers. Non-ionic and amphoteric AAS are also used in facial cleansers, and they are milder than anionic AAS. Moreover, adding amphoteric AAS into anionic surfactant solutions can reduce its harshness. On the other hand, cationic AAS is not usual in facial cleansers but could be found in hair conditioners. [4]

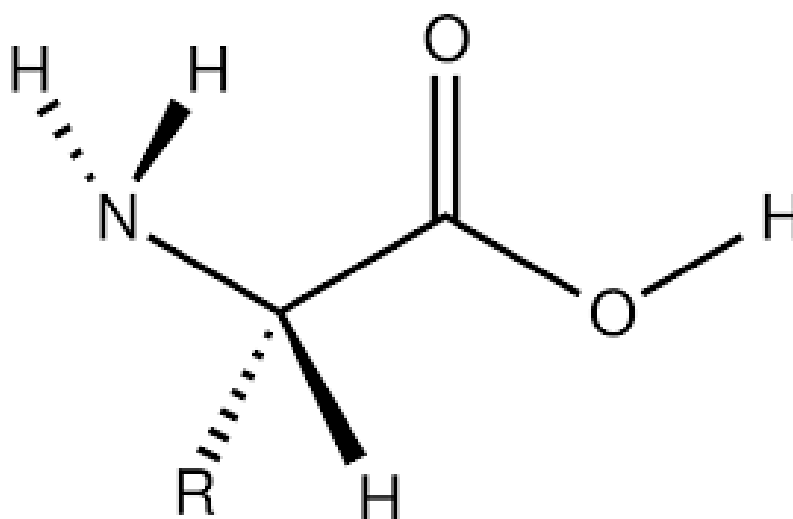


Figure 1. Structure of amino acid [10].

| | |
|------------------------|--|
| Na Lauroyl Glycinate | |
| Na Lauroyl Sarcosinate | |
| Na Lauroyl glutamate | |
| Na Lauroyl Taurate | |

Figure 2. Example of the different type of AAS [8].

2.2 Soap

The saponification of fats and alkali leads to the formation of soap, an anionic surfactant. Before this, fats and oils will be first converted into fatty acids or fatty acid esters from triglyceride, consisting of three long chains of fatty materials and glycerin, shown in Figure 3. Traditionally, soaps are made out of the reaction between animal fats or plant oil and alkaline substances (such as lye) obtained from the burning of alkaline plants. [11] But in modern soaps, fats and oils are from the blending of tallow (beef), lard (pork), and nut oil. By alternating the ratio and types of these components, the properties of the cleanser could be changed. For example, there are super-fatted soap (containing more fat), transparent soap (contains glycerol), and combination bars (a mixture of soap and syndet), each with different properties. [12]

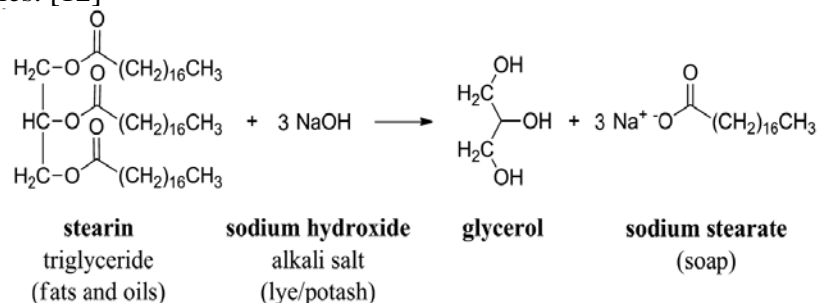


Figure 3. Synthesis of sodium stearate (soap) from triglyceride and alkali salt [11].

3. Differences & Similarities between AAS and Soap

3.1 Chemical Structure

To compare AAS and soap, the similarities and differences between their chemical structures have to be examined because this will affect their properties. What they have in common is that both AAS

and fatty acid salt (soap) remove unwanted materials through the same mechanism, the mechanism of surfactant mentioned previously. This is because both of them have an amphiphilic structure, the hydrophilic moiety with a carboxyl group and the hydrophobic tail consist of hydrocarbon chains (Figure 4) [13].

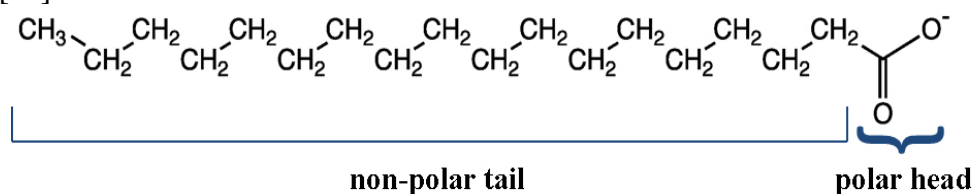


Figure 4. A soap molecule with the hydrophilic head and the hydrophobic tail labeled [13].

The difference in the chemical structure between AAS and soap defies their differences in properties, including their cleansing ability, foaming ability, mildness, and solubility. The main difference between their structures is the components in their hydrophilic head, AAS tends to have more components in its head as it is made out of amino acids. They always include an amide group (a nitrogen atom bonding with a carbonyl group) and sometimes a methyl group, whereas fatty acid salts don't consist of any groups mentioned above.

3.2 Cleansing ability

It is crucial to consider the cleansing ability when comparing facial cleansers because this is their primary function. This is related to the penetration power of surfactants. Lemery E. et al. examined lipid extraction by surfactants and discovered that charged surfactants can remove more lipids, and this is due to the better penetration ability of anionic surfactants. [14] As the surfactant penetrates more into the skin, it will be able to get in contact and react with more lipids that lay under the stratum corneum (SC), allowing more of them to be removed. This means that the better the surfactants penetrate, the better they are at lipid removal; it increases their cleansing efficiency.

An experiment done by Morris, S. A. V. ET. Al illustrates that there is a linear relationship between the micellar charge (zeta potential) and penetration power. [15] The experiment emphasises the fact that more highly charged surfactants will have better penetration. When cleanser is applied to the skin, its surfactants bind with skin protein, forming micelle-like aggregates (that have charge characteristics) on the protein backbone (holding protein together and gives protein the overall shape) and increasing the charge on the protein network, which leads to the denaturation of proteins and the swelling of the skin structure. The more highly charged surfactants will cause a more significant increase in protein network charge; hence, they will swell the skin layer to a greater extent. This swelling and disruption will increase the permeability of SC and allow more surfactants to penetrate through it. Skin permeability can be furthered by the removal of lipids because this encourages surfactants to bind with proteins. These can all lead to a cascading process in which surfactants penetrate deeper and deeper into the skin. This means that a higher charge and longer surfactant exposure time will increase protein binding and penetration power; therefore, anionic surfactants are considered to have a better cleansing ability than amphoteric and non-ionic surfactants since anionic surfactants carry more charge. [15] Nonetheless, the damage on skin proteins through this penetration process, alludes to the fact that facial cleanser with higher cleansing power could be harsher.

Other than their hydrophilic head, zeta potential can be affected by various factors such as pH and Vu, T. et al's experiment evince this pH-dependent property. [16] The charge of surfactants increases with a decrease in pH until it reaches the precipitation edge of the surfactant. This is when its charge is the lowest that carboxylate will not be fully ionized and the ability to form micelles decreases.

Different fatty acid salts (soap) and AAS have different charges; all fatty acid salts are anionic, whereas AAS can be in any charge (anionic, amphoteric, or non-ionic). Furthermore, the addition of amphoteric surfactants can reduce the charge of surfactants. It can be concluded that amino acid-based facial cleansers could have a weaker penetration ability than a soap-based facial cleanser in that some

AAS carry fewer charges (by being amphoteric or non-ionic), but because zeta potential can differ greatly depending on other factors, whether soap or AAS has the greater charge is not definite.

3.3 Lathering and Foaming

Foams are needed to prevent dirt and excess oil that has been removed from returning to the skin surface. Therefore the lathering ability of surfactants can affect the cleansing ability of facial cleansers. The air-liquid interface enlarges rapidly during lathering, thus to prevent bubbles from collapsing, surfactant molecules must be capable of absorbing and stabilizing the interface quickly. [8] A rigid interfacial layer (high dilatational modulus), which is related to the hydrophilic head of the surfactants, reduces bubbles' vulnerability. A study done by Denkov, N. shows that having a high surface dilatational modulus will produce creamier bubbles, decreasing bubble size but increasing its stability; it also states that soap is a typical surfactant that has a high surface modulus. [17] For AAS, their amide group enables the establishment of a rigid air-liquid interface by forming hydrogen bonds with surrounding molecules. However, with the presence of methyl group in some AAS, the capability for forming compact air-liquid interface is reduced; thus more widespread foams are constructed instead of fine creamy lather.

With an increase in absorption at the air-liquid interface, a decrease in surface tension will be seen. This is also a factor that contributes to the foaming ability of surfactants: the lower the surface tension, the better the foam. The potential for surfactants to scale down surface tension is closely related to their chain length (hydrophobic tail). Generally, an increase in chain length will increase its hydrophobicity, decreasing its CMC values and surface tension. [4] Mitrinova, Z. et al.'s experiment reinforce this concept as the results shows that surface modulus increases with the increase of its hydrocarbon chain length, meaning a decrease in surface tension. [18] Nevertheless, many AAS and soap do not follow this trend, having a fluctuating surface tension as chain length increases (such as the 2CnCys AAS). Overall, soap reduces surface tension to a lower value than AAS does. For that reason, they produce a richer and creamier lather.

Both interfacial layer and surface tension can be influenced by pH. In Mitrinova, Z. et al.'s experiment, the results suggests that for fatty acid salts (soap), a decrease in pH will decrease surface tension, thereby increasing its surface modulus. The same pH-dependent property is shown in AAS. Denkov, N. D. and Ananthapadmanabhan, K. P. did an experiment to measure the surface modulus of AAS regarding changes in pH. [8] They found that at a high pH, surface modulus for AAS is low and fluctuating. As pH decrease, their surface modulus increases rapidly until it reaches a maximum. This is because surfactant molecules will be fully ionized in high pH, so the repulsion between the same charges will lessen the strength of the interfacial layer and restrict absorption at the interface, meaning that absorption at the air-liquid interface will be reduced in an alkaline environment. Additionally, more uncharged fatty acid will appear as pH decreases. These unionized molecules can mitigate the charge repulsion to form a more compact interfacial layer, which proposes that acidic pH could enhance the interfacial layer. Both factors illustrate that a reduction in pH can increase the strength of the interfacial layer and decrease surface tension (not with a linear relationship but with some fluctuation) prior to exceeding the precipitation edge. [8]

Summing up, the foaming ability of surfactant can be increased with the reinforcement on the interfacial layer and a decrease in surface tension; both of them could be affected by pH. Generally, soap can reduce water surface tension more than [18] AAS. This means that soap-based facial cleansers could form better and creamier lather than amino acid-based facial cleansers, provided that other factors are kept the same.

3.4 Mildness

AAS will be considered to cause less damage towards the SC proteins due to its primary component, amino acids. Proteins are made of amino acids, hence, AAS's impact on skin protein could be reduced. Soap, however, does not have a direct relationship with proteins, which might trigger vigorous reactions. In addition, the mildness of surfactants also depends on their penetration power and the charge density of micelles, which has been mentioned previously. As the charge increases, the ability

to denature protein increases, so it will cause more damage and will be harsher to the skin. Zein is a corn protein, and the skin irritation potential for surfactants can be demonstrated by its ability to dissolve zein. Researches have shown that higher zein solubility correlates with higher zeta potential, meaning that anionic surfactants are less mild than amphoteric and non-ionic surfactants. [19] An experiment carried out by Ananthapadmanabhan, K. P. shows the zein solubility of AAS. [20] By comparing it to the zein solubility of soap, it can be seen that AAS has a higher zein solubility. Thus, it can then be inferred that amino acid-based facial cleansers are generally milder than soap-based facial cleansers.

3.5 Solubility and pH

The right skin pH is needed to provide the best condition for stratum corneum (SC) function, which includes regulating lipid synthesis, antibacterial function, and SC cohesion; this suggests that the change in pH could reduce the SC function. The acidic environment of the skin was discovered around 1898, and this concept of it being an 'acid mantle' was established in 1928. [2] It is now known that the pH level of a normal skin surface is 4.5 to 5.0. This suggests that acidification of the skin surface could make the skin healthier by increasing the efficiency of its function.

The pH level of facial cleansers could have substantial impacts on skin surface pH (ss-pH) that the difference between the pH of cleanser and skin will cause a pH shift or will increase ss-pH as a whole when applying it in the long term. A pH shift will occur after the application of cleanser where there is a change in ss-pH, and the skin will need a period for pH recovery. [2] During this period, the efficiency of SC function could decrease so an elevation in ss-pH could lead to a worsening of skin health. Moldovan M and Nanu A have investigated the pH shift and time for pH recovery for cleansers with different pH levels. [21] The results suggests that pH shift occurs in all cleansers, but the cleansers with higher pH raise the skin pH more significantly. The experiment also demonstrates that for all cleansers, there is not a significant difference in skin pH 90 minutes after application but alkaline cleansers result in a slightly greater pH difference.

For the facial cleanser to contain surfactants, they have to be dissolved into the solution, and the aggregate formation can affect the solubility behavior of surfactants. Because of the difference in their chemical structures, AAS and soap have different solubilities and are soluble at different pH. Sodium lauroyl glycinate (an AAS) can be soluble under neutral pH while sodium laurate (soap) can only be soluble under more alkaline pH; this is due to the fact that the amide and carbonyl groups (connecting hydrogen bonds with water molecules) in AAS increase the solubility of AAS more than soap. Moreover, sodium lauroyl sarcosinate (another type of AAS) is soluble under an even wider range of pH (5-10) due to the presence of its methyl group on the amide nitrogen. Methyl group can prevent hydrogen bonding with neighboring molecules and prevents aggregation, thereby increasing its solubility. The solubility range of AAS can be further increased by changing sodium into potassium or counterions. [8] This means that facial cleansers containing AAS can be in a great range of pH, but soap-based facial cleansers can only be limited to be in an alkaline state.

Soap-based facial cleansers available in the market are of average pH 10 because fatty acid salts are only soluble in an alkaline environment. [22] On the other hand, the majority of amino acid-based facial cleansers are made of pH-balanced formula, having a pH (pH 5-7) similar to that of skin. This means that AAS facial cleansers can have less damage that they have a pH akin to skin.

4. Conclusion

In conclusion, due to the difference in chemical structure, soap-based facial cleansers generally get rid of unwanted materials more successfully while amino acid-based facial cleanser is milder. This is because soap surfactants have a higher penetration power and they can form richer and more stable foams; AAS have less impact on skin proteins and are soluble in a wider range of pH environments. It is worthwhile to do this research because it could solve many dilemmas that faced by people in selecting facial cleansers; allowing people to work out the possible advantage and disadvantage of

using a specific facial cleanser. This is a substantial topic because many people face the struggle of having unhealthy skin and cleansing is an indispensable part in skin care.

The future of facial cleansers will be surrounding the topic of minimizing skin damage and improving their cleansing ability. There are currently no surfactants that can differentiate between sebum (and unneeded oil) and intercellular lipids (essential for a healthy epidermal barrier) so this might be a path for the development of surfactants. In the commercial market, the branch of facial cleansers would likely develop with the engineering of surfactants, more facial cleansers may be made to target a specific skin type, narrowing down options and easing the dilemmas faced by customers. There should be more experiments done to observe AAS and their possible abilities; amino acid-based facial cleansers could be a great focus in cosmetic care. In addition, combinations of soap and other components could be tested in seeking to produce more mild soap-based facial cleansers while maintaining their cleansing ability. I would next research on the different ingredients used in cosmetics, acknowledging their different characteristics and explore more of their possible potential in the cosmetic area.

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