The influence of cocamide DEA towards the characteristics of transparent soap

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Abstract. Soap is a mixture of fatty acid compounds used as body cleansers so it must not caused irritation to the skin. The quality of sugar, alcohol, and glycerin is crucial for the clarity and clearness of soap. Replacement of hazardous chemicals are necessary because chemical surfactants contain lots of carcinogenic substances, skin irritants, eyes and respiratory disorders. This research was conducted as natural surfactants applied on transparent soap including cocamide DEA. Cocamide DEA concentration varies at 0%, 2.5%, 5.0%, 7.5%, and 10.0%. The surfactant properties of cocamide DEA will characterized based on Critical Micell Consentration (CMC), Hydrophile Lipophile Balance (HLB), and foaming properties. After the characteristics of cocamide DEA are investigated, hereinafter it applied to produce transparent soap. The process of making soap uses the hot method with a hotplate as the medium. The addition of surfactant cocamide DEA was able to reduce the surface tension up to 31.27x10^{-3} N/m implied the surface tension reduction for 56.56% to water. The transparent soap with the addition of 10% cocamide DEA had the best formulation with the properties of has 8% moisture content, 69.38% foaming ability, 0.146% free fatty acid, 0.0938% free alkali, unsaponified fat 2.376%, pH 8.9 and hardness 569.6 mm/g/s, has highest brightness level, and still in accordance with indonesian standard.

1. Introduction

Transparent soap is one of the innovations that makes soap more attractive. The benefits of transparent soap are to maintain skin health, skin brightness, moisture, smoothness, stabilize skin pH and help regenerate skin cells, prevent acne, and safe to used every day as a bath soap [1]. Transparent soap can be produced in several different ways. One of the oldest methods is by dissolving soap in alcohol by heating to form a clear solution [2]. The transparent soap production method involves fat melting and water addition to dissolve sucrose, glycerin, and preservatives. These two phases react with an alcoholic solution of sodium hydroxide (NaOH). NaOH is a type of alkaline commonly used in the manufacture of solid soaps which is the main ingredient in the saponification process on converting fat into soap. With the absence of lye, the chemical process of soap will not occur. The quality of sugar, alcohol, and glycerin is crucial for the clarity and clearness of soap. Glycerin is good for the skin because it acted as a moisturizer and form a gel phase in soap [1]. Cleaning mechanisms with harsh surfactants such as anionic surfactants found in transparent soaps can cause irritation and dry skin. Surfactants are needed to improve the quality of foam in soap [3]. The occurrence of skin damage and irritation caused by a strong bond between the surfactants and skin proteins [4]. Therefore an alternative replacement for anionic surfactants is needed in making transparent soap, one of them is cocamidie DEA [5].
DEA in the cosmetic products formula serves as a surfactant and foam stabilizer which reduce surface tension on the surfactants [6]. Apart from being a surfactant, cocamide DEA has benefits to stabilize the resulting foam. Cocamide DEA in cosmetic preparations also has an emmolient effect [7]. In addition, it helps thicken the products such as shampoo, hand soap, and other cosmetic preparations.

This study aims to determine the characteristics of the surfactant properties of cocamide DEA applied on transparent solid soap based on the value of Critical Micell Consentration (CMC), Hydrophile Lipophile Balance (HLB), foaming properties, moisture content, free fatty acids, pH, unsaponified fat number, surface tension, free alkalinity, soap color, and stability of the resulting foam.

2. Materials and Methods

2.1. Analysis of Cocamide DEA as Surfactant

2.1.1. Critical Micell Concentration (CMC). CMC analysis is carried out based on the ring stress method. Measurement of the surface tension of cocamide DEA at various concentrations was used to determine CMC at (25.0 ± 0.5)°C in water. If the surface tension at the surfactant concentration reaches nearly constant values, it is considered as CMC cocamide DEA.

2.1.2. Hydrophile Lipophile Balance (HLB). HLB analysis was used as a parameter to define the degrees of hydrophilic and lipophilic relativity of surfactant molecules. Low HLB surfactant indicates a hydrophobic type of surfactant that soluble in the oil phase. In contrast, high HLB surfactants exhibit water-soluble hydrophilic characteristics. In this study, the HLB number was obtained by the acid number and saponification number, based on equation 1.

\[
HLB = 20 \times (1 - \frac{S}{A})
\]

Where, S is the saponification number and A is the acid number. HLB number measurements were carried out for cocamide DEA solution at concentration of 1 CMC.

2.1.3. Foam Properties Analysis. Aqueous foam is produced by shaking the aqueous dispersion of the cocamide DEA solution (15 g, 1.5 mg/g) in an 80 mL glass container (inside diameter = 3.1 cm and height = 9.8 cm) at 25°C. Foam formation and stability are monitored by a combination of optical measurements. The amount of times for the foam volume to reduce by half of its initial volume (half-life, \( t_{1/2} \)) is used as an indication of foam stability.

2.2. Transparent Soap Making Process

The soap making process follows hot method procedure with a hotplate. 30 grams of virgin coconut oil (VCO) heated in a beaker glass with the addition of melted stearic acid then stirred until homogeneous. After the homogenous relatively achieved add 30% NaOH solution at 70°C. The soap is cooled to a temperature of 40°C after other supporting ingredients are added such as 96% ethanol, glycerin, sugar, cocamide DEA surfactant, fragrance oil, and dyes. The mixture then stirred until homogeneous. The soap is poured into a soap mold and left for 24 hours at room temperature. After 24 hours, the soap is cured for approximately 3 weeks.

| Table 1. Concentration of Cocamide DEA |
|----------------------------------------|
| Variabel                               |
| Cocamide DEA                           |
| Concentration (%)                      |
| Soap 1                                 |
| 0                                      |
| Soap 2                                 |
| 2.5                                    |
| Soap 3                                 |
| 5.0                                    |
| Soap 4                                 |
| 7.5                                    |
| Soap 5                                 |
| 10.0                                   |

2.3. Quality Analysis of Transparent Solid Soap

2.3.1. Water Content. The water content test of the soap was carried out by heating 10 grams of soap for 2 hours then weighing it to determine the weight of the evaporating water. This process is done 4 times.
Water content = \frac{\text{amount of vaporized water (g)}}{\text{initial mass of soap (g)}} \times 100\% \quad (2)

2.3.2. Free Fatty Acids (FFA). Analysis of free fatty acid levels based on SNI 06-3531-1994 as follows:

\[ \text{FFA} = \frac{V_{NaOH} \times N_{NaOH} \times MW \text{ of Lauric Acid}}{\text{Total mass (g)} \times 100\%} \quad (3) \]

2.3.3. Unsaponified Fat. Analysis of unsaponified fat content is based on the following equation:

\[ \text{Unsaponified fat content} = \frac{(\text{Blanksample volume} - \text{Titrant volume}) \times N_{HCl} \times MW_{KOH}}{0.2 \times \text{Total mass (mg)}} \times 100\% \quad (4) \]

2.3.4. Alkalinity. Analysis of the alkaline content is based on the equation below:

\[ \% \text{Alkalinity} = \frac{V_{HCl} \times N_{HCl} \times MW_{KOH}}{\text{Total mass (mg)}} \times 100\% \quad (5) \]

2.3.5. pH. pH analysis conducted by weighing 0.5 grams of transparent soap, then dissolving it in water continued by measuring the pH with a universal indicator (pH 8-9).

2.3.6. Foam Stability. The foam stability test on transparent soap is carried out as foam ability test. The calculation of foam stability as follows:

\[ \% \text{Foam Stability} = \frac{\text{Initial height of foam}}{\text{Final height of foam}} \times 100\% \quad (6) \]

3. Results and Discussion

3.1. Characteristics of Cocamidee as a Surfactant

3.1.1. Critical Micell Concentration (CMC). Critical Micell Concentration (CMC) is the concentration at which micelles begin to form. CMC is determined by the decrease in surface tension of cocamide DEA [7]. The results of these measurements shown by linear equation \( y = 13.982x + 44.141 \) and \( y = -0.6447x + 25.52 \), resulted in \( x = 1.401 \). Thus the CMC value for cocamide DEA is 1.401% w / w of cocamide DEA.

3.1.2. Hydrophilic-Lipophilic Balance(HLB). In this study, the HLB value for cocamide DEA is 12,558. The HLB value is calculated based on the acid value and saponification value [8]. From the calculated HLB value, the results show that cocamide DEA is confirmed as hydrophilic surfactant because it has an HLB number between 10 - 15. This type of surfactant is often used for detergents.

3.1.3. Foaming Ability. The foaming ability is a parameter that indicates the ability of a surfactant to produce foam at a certain volume of liquid. Figure 1 showed that increasing the surfactant concentration at the beginning of the test could increase the initial foam formation and promote the concentration of surfactant molecules also stabilize the foam layer. However, the volume of foam gradually decreased during 6 hours. This is due to the drainage, coarsening, and coalescence processes that cause the resulting foam to burst [9]. The drainage is a process where bubble foam will burst due to the differences of the direction on water and air substances. The flow of liquid will tend towards the bottom of the solution because it is influenced by the force of gravity. The dispersed air stream inclined to moves towards the surface of the liquid. The coarsening process is the process of air diffusion which being dispersed in each foam bubble. This will cause the bubbles to be flocked and form larger bubbles. This process will cause the coalescence process, which is the process of thinning the bubble foam layer. This process causes the bubbles to burst because the coating cannot withstand the flow of water and air in the bubble foam. A solution containing more cocamide DEA tends to provide better foam stability.
3.2. Quality Analysis of Transparent Solid Soap
The physical and chemical characteristics test results of transparent soap with various concentrations of surfactants and commercial transparent soap as a comparison can be seen in table 2 below:

Table 2. Characteristics of Soap with Various Concentrations of Surfactants

| No. | Treatment    | Parameter        | Water Content (%) | FFA (%) | Unsaponified fat (%) | Alkalinity (%) | pH   | Hardness (mm/g/s) | Surface tension |
|-----|--------------|------------------|-------------------|---------|-----------------------|----------------|------|------------------|-----------------|
| 1.  | Blank soap   |                  | 13                | 0.095   | 1.758                 | 0.055          | 9.2  | 819.83           | 59.80           |
| 2.  | Soap 1       |                  | 11                | 0.058   | 2.233                 | 0.088          | 8.8  | 570.17           | 35.43           |
| 3.  | Soap 2       |                  | 10                | 0.080   | 2.230                 | 0.119          | 9.0  | 542.17           | 37.90           |
| 4.  | Soap 3       |                  | 7                 | 0.176   | 2.375                 | 0.084          | 8.5  | 757.67           | 32.03           |
| 5.  | Soap 4       |                  | 10                | 0.095   | 2.471                 | 0.080          | 8.7  | 361.67           | 34.90           |
| 6.  | Soap 5       |                  | 8                 | 0.146   | 2.371                 | 0.939          | 8.9  | 569.67           | 31.27           |
| 7.  | Commercial   |                  | 14                | 0.132   | 1.283                 | -              | 8.7  | 834.78           | 33.03           |
| 8.  | SNI (Indonesian Standard) | Max | Max. | Max. 0.1 | Max. 0.1 | 8.0- | - | - |

3.2.1. Water Content. Excess of water in soap inflict easiness to shrink and uncomfortable when used. The increase of cocamide DEA addition promote water content produced [10]. This is because cocamide DEA is hygroscopic and tends to absorb water. The addition of glycerin, sugar, and NaOH can also affect the increase of water content in transparent soap because these ingredients are also hygroscopic.
Based on the requirements of SNI 06-3532-1994, the maximum water content in soap is 15%. The amount of water in the soap can affect the storage procedure of the soap. Soap with water content > 15% will experience faster weight and form shrinkage [11]. In this study, the lowest water content was 8% in soap 5 and the highest water content was found 13% in blank soap. These results indicate that the transparent soap has adequate hardness so it becomes harder for the soap to dissolve in water and wear off longer. More advantages lies in the process of making and packaging soap because the soap will be more durable.

3.2.2. Free Fatty Acid Levels. The free fatty acid levels in transparent soap can be influenced by the lack of NaOH. It will affect at the process of saponification where the amount of free fatty acids bound to NaOH is inadequate. Based on SNI 06-3532-1994, the maximum free fatty acid content is <2.5%. If the free fatty acid content is plenty, the soap will has rancid smell [12]. In this study, the lowest levels of fatty acids were found in soap 1 (0.058%) and the highest (0.176%) in soap 3. The high levels of free fatty acids due to the presence of fatty acids derived from stearic, palmitic and lauric acids found in palm and coconut oil as a base for making DEA surfactants and component in soap making.

3.2.3. Unsaponified Fat. Unsaponified fat is the amount fat that not reacted with alkaline compounds (NaOH) yet dissolved in oil when making soap. The unsaponified fat content in this study ranged from 1.75–2.47%. This value is below 2.5% as SNI requirements. The presence of an unsaponified fraction can reduce the cleaning ability of soap [10]. Thus, the addition of NaOH needs to be done carefully and in adequate amount so the non-saponified fraction is reduced.

3.2.4. Free Alkalinity Levels. Free alkalinity are lye in soap that are not bound as compounds. The level of free alkaline which exceeds the standard of 0.1% will caused skin irritation. The excess alkaline in bath soap due to the usage of dense concentration on alkaline or the excessive addition of lye to the saponification process [13]. In this study, the lowest free alkaline content was 0.055% for blank soap and the highest 0.12% for soap 2.

3.2.5. pH. Bath soap has pH ranging from 8-11 [14]. The pH value of transparent soap obtained in this study ranged from 8.5–9.2 means that the pH value of all soaps produced in this study were in accordance with SNI standards. The optimum pH in this study is achieved by the addition of cocamide DEA 10% because the resulting pH (8.9) are close to human skin. The pH instability is caused by heating factors due to the hydrolysis of the active ingredient sodium ester with fatty acids, which can cause alkaline increased the pH of soap [15].

3.2.6. Foam Stability. Foam stability is a parameter that indicates the ability of the foam to keep its bubbles from bursting for a certain time. The results of the soap foam stability test can be seen in Figure 2. As apparent from foam stability data each minute, it shows that the foam produced tends to decrease. The reduction in the foam stability value indicates lots of foam bubbles are not able to maintain its main characteristic such as foam size, amount of liquid, and total foam volume. This phenomenon caused by drainage, coarsening, and coalescence. The best foam stability is 69.38% in soap 5. Good foam stability achieved when within 5 minutes a foam stability value ranged between 60-70% [15].
3.2.7. **Soap Hardness.** The hardness of soap are influenced by saturated fatty acids which used as raw material for making transparent soap. The saturated fatty acid which found in VCO is palmitate acid for 7.5% w/w. The hardness of soap is also influenced by the amount of water content. The more water in the soap inclined to reduce the hardness. The lowest soap hardness value is 361.67 mm/g/s for soap 4 and the highest is 819.83 mm/g/s for blank soap.

3.2.8. **Surface Tension.** The surface tension value observed in this study is the surface tension value of water and air after the addition of cocamide DEA. The result of for water surface tension is 72x10\(^{-3}\) N/m. The results of surface tension measurements after the addition of cocamide DEA ranged from 31.27x10\(^{-3}\) N/m - 37.9x10\(^{-3}\) N/m. The best surface tension is 31.27x10 N/m on soap 5 means that cocamide DEA potentially increase the ability to reduce surface tension for approximately 56.56% to water. Thus the resulting surfactant is quite effective.

Surface tension occurs due to the imbalance of forces on the molecules on the surface of the liquid. The cocamide DEA surfactant added to the liquid phase has a hydrophilic group. Hydrophilic groups bind with liquid molecules, including molecules on the surface of the liquid, so that the forces on the surface of the liquid are balanced. This will causes the bond energy between similar molecules to decrease [16].

3.2.9. **Brightness Level.** The results showed that soap 5 had the highest *L value with -0.5 considered as bright, while soap 1 showed the lowest *L value of -9.0. By increasing the concentration of cocamide DEA, the brightness level tends to increase. The high ΔE value resulted from caramelization reaction of sugar content. When the sugar is heated, the molecules will form new and bigger polymer molecules that occur in sugar browning reaction [17].
Figure 3. Brightness level for transparent soap

4. Conclusion
The addition of surfactant cocamide DEA was able to reduce the surface tension up to $31.27 \times 10^{-3}$. This means there is increase in surface tension reduction 56.56% to water or nearly half. The transparent soap with the addition of 10% cocamide DEA (Soap 5) had the best formulation with the properties of has 8% moisture content, 69.38% foam ability, 0.146% free fatty acid, 0.0938% free alkali, unsweetened fat 2.376%, pH 8.9 and hardness 569.6 mm/g/s, has highest brightness level, and still in accordance with Indonesian standard (SNI).

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