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Synthesis of Cationic Surfactant N, N-(2-Laurate-Ethyl) Stearamidium Chloride

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Abstract. The cationic surfactant of N, N-(2-Lauric-Ethyl) Stearamidium Chloride had been successfully synthesized. It is long-chain alkyl surfactant derivative from ammonium salt with amide. Cationic surfactants that are synthesized from fatty acid derivatives are stearic acid and lauric acid. Stearic acid is used as stearamide-making material which is the product of methyl stearate amidation with diethanolamine use methoxide sodium catalyst. Lauric acid was used as esterification material with stearamide thus obtaining N, N-(2-Lauric-Ethyl) Stearamide of alcanolamide ester. Alcanolamide ester continued by salting reaction use HCl gas until obtained cationic surfactant of N, N-(2-Lauric-Ethyl) Stearimidium Chloride. Each compound analyzed function groups by FT-IR spectrophotometric with the analyzed change of melting points, and a part compound analyzed surface tension characteristic with measuring Critical Micelle Concentration (CMC) with use Du Nouy ring method. The analysis product obtained shows that methyl stearate by yield in the amount of 91.66% shows that melting point of 40.5°C, stearamide with yield in the amount of 87.6% show that melting point as 185°C by CMC value 0.133 mol/ L in 40.7 dyne/cm surface tension. Alcanolamide ester with a yield in the amount of 84.7% has a melting point of 55°C by a CMC value of 0.067 mol/L in 36.1 dyne/cm surface tension, and cationic surfactant has a melting point of 45°C by CMC value 0.055 mol/L in 31,1 dyne/cm surface tension. stearamide with a yield in the amount of 87.6% show that melting point of 185°C by a CMC value of 0.133 mol/L in 40.7 dyne/cm surface tension. Alcanolamide ester with a yield in the amount of 84.7% has a melting point of 55°C by a CMC value of 0.067 mol/L in 36.1 dyne/cm surface tension, and cationic surfactant has melting point as 45°C by CMC value 0.055 mol/L in 31,1 dyne/cm surface tension. stearamide with a yield in the amount of 87.6% show that melting point of 185°C by a CMC value of 0.133 mol/L in 40.7 dyne/cm surface tension. Alcanolamide ester with a yield in the amount of 84.7% has a melting point of 55°C by a CMC value of 0.067 mol/L in 36.1 dyne/cm surface tension, and cationic surfactant has a melting point of 45°C by CMC value 0.055 mol/L in 31,1 dyne/cm surface tension.

Keywords: Cationic Surfactant, Surfactant, Du Nouy Ring, Critical Micelle Critical (CMC).

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1 Introduction

Surfactant is an active compound that is able to reduce surface tension (surface active agent) which at the same time has a hydrophilic group and a hydrophobic group in the same molecular structure. This compound can reduce the interfacial tension between two liquid phases of different polarity such as oil/water or water/oil. These unique properties make surfactants very potential to be used as components of adhesives, coagulation agents, wetting agents, foamers, emulsifiers, and penetrating agents and have been widely applied in various fields of process industry that use multiphase systems such as in the food, pharmaceutical, cosmetic, and food industries. textiles, polymers, paints, detergents, and agrochemicals (Johnson, and Fritz, 1989).

Along with the increasing awareness of good health and the environment, the demand for surfactants that are easily degradable and plant-based is also increasing (Holmberg, 2001), it is necessary to study to obtain surfactants that have these two criteria, namely obtained from renewable raw materials and are degradative. in nature so that it is ecologically acceptable. One of the surfactants that meet these two criteria is an alkanolamide surfactant.

Alkanolamide can be obtained from the reaction between alkanolamine and vegetable oil fatty acids and is widely used in food, cosmetics, and medicine (Soledad, et al, 2000). Alkanolamide surfactants that have chemical bonds are very stable in alkaline media (Maugard, et al, 1997).

Cationic surfactants are surface-active compounds with polar groups carrying a positive charge such as R2N+HCl- (long chain amine salts), such as Benzalkonium chloride, and Stearalcolnium chloride. These cationic surfactants are usually derived from primary, secondary, tertiary, and quaternary long chain amine compounds (Tang, and Vienardi, 2011). Almost 7% of the total surfactants, and cationic surfactants have many applications such as hair conditioners, softeners for textiles and paper products, asphalt additives, corrosion inhibitors, and pigment dispersing agents. This is because cationic surfactants are surface-active compounds that are strongly adsorbed by the substrate due to the positive charge on the polar groups (Pankaj, et al, 2012).

Research has been carried out on “Synthesis of Ester Based Cationic Pyridinium Gemini Surfactants” (Pankaj, et al, 2012) and Bis[N, N'-(alkylamideethyl)ethyl] Triethylenediamine Bromide (Zhou, et al, 2012) which is a surfactant development based on natural sources. renewable natural resources. It is also a response to the increasing consumer demand for good and environmentally friendly products. From the results of the study, it was found that esters containing surfactants such as pyridinium esters based on cationic surfactants are more easily degraded and have good surface active properties, and have low CMC values

Stearic acid is a fatty acid that is commonly found in vegetable and animal oils. The stearic acid in North Sumatra has been produced from palm oil through hydrogenation of oleic acid as

carried out by PT-SOCI (Weni, H, 1997). Lauric acid is also abundant in palm kernel oil (PKO), which is produced as a by-product of palm oil processing and is present in large and sustainable quantities in Indonesia. The main source of these fatty acids in coconut oil which can contain 50% lauric acid (Ketaren, 2008).

The selection of stearic acid and lauric acid as a source of fatty acids is because alkanolamides from these fatty acid derivatives are widely used in various cosmetic and medicinal products (Sharma et al., 2005), and these fatty acids are inexpensive renewable materials and are available in large quantities in Indonesia. The choice of diethanolamine was due to the fact that the alkanolamide obtained from diethanolamine is one of the most important alkanolamide surfactants because it has a good level of polarity compared to other amides due to the presence of two hydroxyl groups in the resulting alkanolamide molecule (Kurniasih, 2008).

From the above, it is very interesting to use stearic acid as a base material for the manufacture of cationic surfactants. Lauric acid is used as an esterification agent with stearamide. The stearamide was obtained from the amidation of methyl stearate with diethanolamine, and the esterification product was obtained the long chain alkanolamide ester of N,N-(2-Laurate-Ethyl) stearamide. The long chain alkanolamide ester obtained was followed by a salting reaction using HCl gas to produce a cationic surfactant, namely N, N-(2-Laurate-Ethyl) Stearamidium chloride.

2 Materials and Methods

2.1 Equipments

The tools used in this study were: Erlenmeyer glass, Beaker glass, dropper, separating funnel, rotary evaporator, condenser, two neck flask, dropper funnel, measuring flask, CMC tensiometer, thermometer, analytical balance, measuring cup, hotplate, melting point apparatus stands and clamps, FT-IR spectrophotometer.

2.2 Materials

Materials used in this study include Stearic acid, lauric acid, methanol, n-hexane, sulfuric acid 98%, sodium methoxide, diethanolamine, benzene, sodium chloride, nitrogen gas, diethyl ether, Argentum nitrate, ammonia, xylene with pA quality.

2.3 Stearamide Manufacturing of *N, N-Diethanol-Stearamide* from Methyl Stearate by Using Diethanolamine

14.2 grams (0.05 mol) of methyl stearate obtained from the esterification of stearic acid with methanol using an acid catalyst were added, then add 5.8 ml (0.093 mol) of diethanolamine and stirred. Assemble the reflux device, then add 5 grams of NaOMe to 20 mL of methanol. Then heated at a temperature of 80 to 90°C while stirring for 5 hours. The reaction product is

evaporated using a rotary evaporator. The residue obtained was extracted with 100 ml of diethyl ether and washed with saturated NaCl solution 3 times with 25 ml each. The top layer obtained was evaporated with the solvent using a rotary evaporator, then the residue obtained was dried in an oven in a vacuum at a temperature of 50°C. Then the results obtained were tested for the melting point.

2.4 Synthesis of Long Chain Alkanolamide Esters N, N-(2-Lauric-Ethyl) Stearamide Esterification Result of Steramide with Lauric Acid

Assembling a reflux device, 20 grams (0.10 mol) of lauric acid were added while nitrogen gas was flowing. In a three-necked round bottom flask with a volume of 250 ml, 15 grams (0.05 mol) of stearamide were added. Then 40 mL of xylene solvent was added and stirred with a magnetic stirrer. Assembling a reflux device, then added 20 grams (0.10 mol) of lauric acid while nitrogen gas was flowing. then heated at a temperature of 140-150°C while stirring for 5 hours. The solvent was evaporated from the reaction using vacuum distillation. Then the residue obtained was cooled in a desiccator for up to one night. The long chain alkanolamide esters obtained were tested for their melting points and their functional groups were analyzed using an FT-IR spectrophotometer and continued with the Critical Micelle Concentration (CMC) test using the Du Nouy ring method.

2.5 Preparation of cationic surfactant N, N-(2-Laurate-Ethyl) Stearamidium Chloride resulting from the reaction between long chain alkanolamide esters and HCl gas.

Into a bottom flask with a volume of 1 liter, 100 grams of NaCl was added. Then assembled a modification tool (aircraft kips). Then drop sulfuric acid from the separating funnel into the circuit slowly. Then the gas formed is flowed into an alkanolamide ester solution with n-hexane in a closed state. The results obtained were tested for melting point and analyzed for functional groups using an FT-IR spectrophotometer and continued with the Critical Micelle Concentration (CMC) test with the Du Nouy ring method.

2.6 Analysis with FT-IR Spectrophotometer

For each sample, namely methyl stearate, stearamide, alkanolamide ester, and cationic surfactant in solid form, mixed with anhydrous KBr then molded to a transparent pellet form and then the spectrum was measured using an FT-IR spectrophotometer.

2.7 Determination of Critical Micelle Concentration by the Du Nouy Ring Method

This analysis was carried out on stearamides, long chain alkanolamide esters, and cationic surfactants. Each sample obtained was diluted with various concentrations of 1%, 2%, 3%, 4%, 5%, 6%. Then the surface tension of the sample solution was measured and as a control of water (solvent) with a tensiometer.

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3 RESULT AND DISCUSSION

3.1 Stearamide Manufacturing(N, N-Diethanol-Stearamide) from Amidation of Methyl Stearate with Diethanolamine

Stearamide is obtained through the amidation of methyl stearate with diethanolamine as catalyst sodium methoxide in methanol solvent at a temperature of 80-90°C. Stearamide yield obtained, from 14.2 grams of Methyl Stearate obtained stearamide as much as 16.25 grams (87.6%), with the hypothesis of the reaction mechanism as shown in the following figure 1.

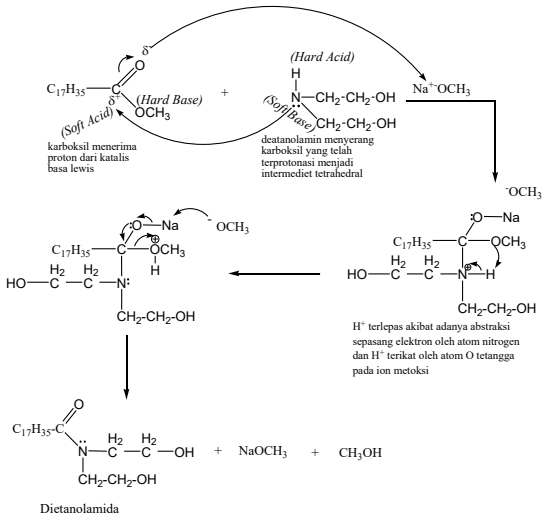


Figure 1. The mechanism of amidation

As Based on the concept of HSAB (hard soft acid base), where H+ from diethanolamine HN-$(CH_2CH_2OH)_2$ is a hard acid that easily reacts with the hard base CH_3O- from methyl stearate to form methanol. On the other hand, Nitrogen with a lone pair of electrons is a soft base that will be bound to a carboxylic ion soft acid $R-\overset{+}{C}=O$ and form alkanolamide compounds. The results obtained were analyzed with an FT-IR spectrophotometer giving a spectrum with an absorption band peak in the wave number region 3417-3309 cm^{-1} shows the stretching vibration of the free (OH) group which is amplified by the absorption peak in the wave number region of 1365 cm^{-1} which is a bending vibration (OH), and this is also supported by the appearance of an absorption band in the wave number region of 1056 cm-1 which is the stretching vibration (CO) of (CCO) primary alcohol. The absorption peak in the wave number region of 1620 cm^{-1} shows the stretching vibration (C=O) of the tertiary amide carbonyl group. The presence of an amide carbonyl group is supported by the appearance of an absorption band in the wave number region of 1566 cm^{-1} which is a stretching vibration (CN). Absorption in the area of wave number 2916-2846 cm^{-1} is a typical absorption of stretching vibration (CH) sp^3 which is supported by bending vibration (CH) sp^3 in the area of 1442 cm^{-1}.

The appearance of an absorption band in the wave number region of 717 cm-1 indicates a rocking vibration peak (CH2)n which is a long chain alkyl hydrocarbon chain. The absence of a

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wide band in the wave number region of 700-600 cm-1 indicates the absence of wagging (NH) outside the plane. This proves (-C(=O)-N) is bound. The tertiary amide (C=O) group appears in the wave number region of 1620 cm-1 which is smaller than the wave number (C=O) ester, this is due to a resonance effect on (-C(=O)-N) thus weakening the bond. between C and O on the carbonyl group (figure 2) (Silverstein, 1984).

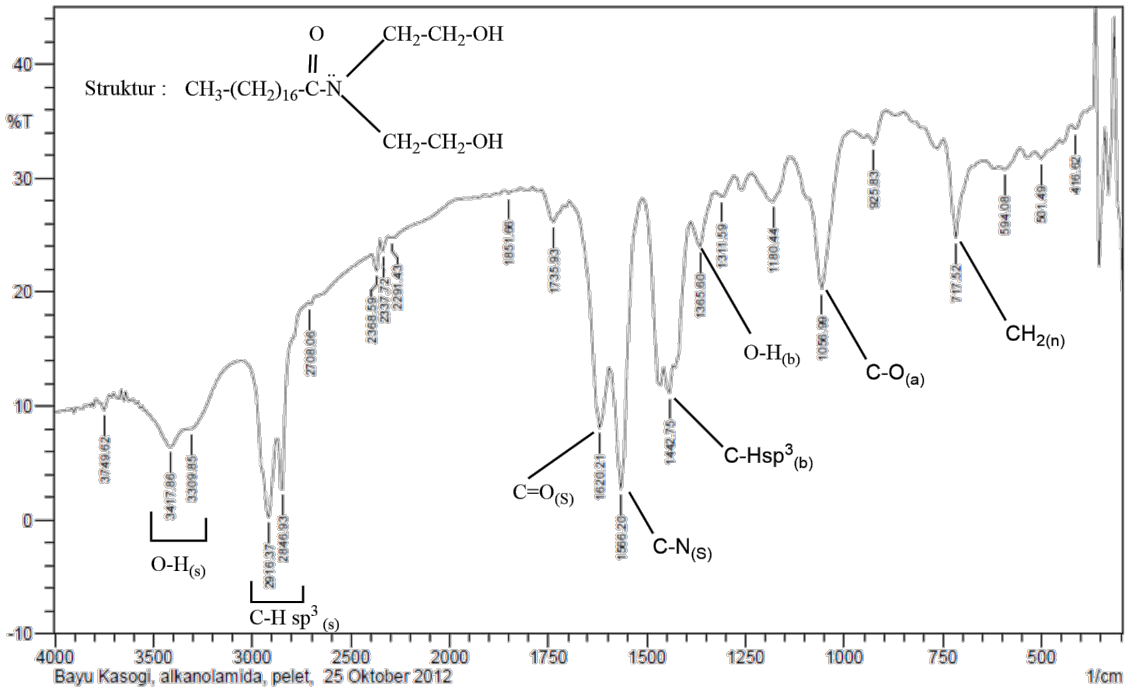


Figure 2. The FTIR spectrum of Stearamide (N, N-Diethanol-Stearamide)

3.2 Production of Long Chain Alkanolamide Esters N, N-(2-Lauric-Ethyl) Stearamide from the esterification of Stearamide with Lauric Acid

Long Chain Alkanolamide Esters are obtained from the esterification of Stearamide with Lauric Acid in xylene solvent at a temperature of 140-145ºC. Alkanolamide ester yield obtained, from 15 grams of Stearamide obtained as much as 16.25 g of alkanolamide ester (84.7%), with the hypothesis of the reaction mechanism as shown in (figure 3) below.

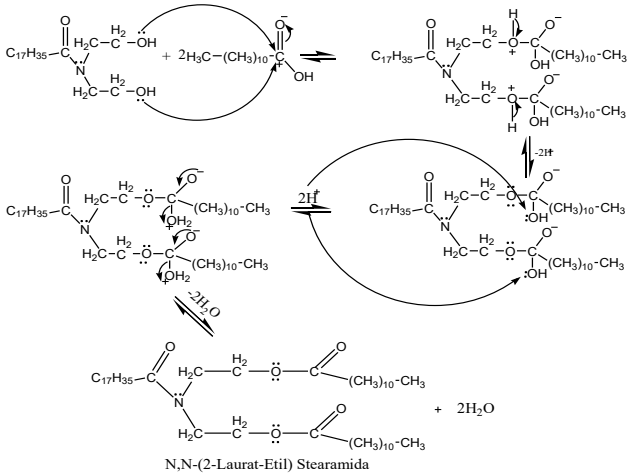


Figure 3. Alkanolamide Esters Formation Reaction Mechanism

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The results obtained were analyzed with an FT-IR Spectrophotometer giving a spectrum with an absorption peak in the wave number region 2916-2854 cm^{-1} which is a stretching vibration (CH) sp3 supported by bending vibration (CH) sp3 in the area 1465-1411 cm^{-1}. The appearance of the absorption peak in the 1728 cm^{-1} wave number is the stretching vibration frequency (C=O) of the formed ester and is supported by asymmetric stretching vibration (CO) of the saturated (CC(=O)-O) ester in the 1219 wavenumber region. cm^{-1}. The appearance of the absorption peak in the wave number region of 1627 cm-1 indicates the stretching vibration (C=O) of the tertiary carbonyl amide. The presence of an amide carbonyl group is supported by the appearance of an absorption band at a wave number of 1581 cm^{-1} which is a stretching vibration (CN)

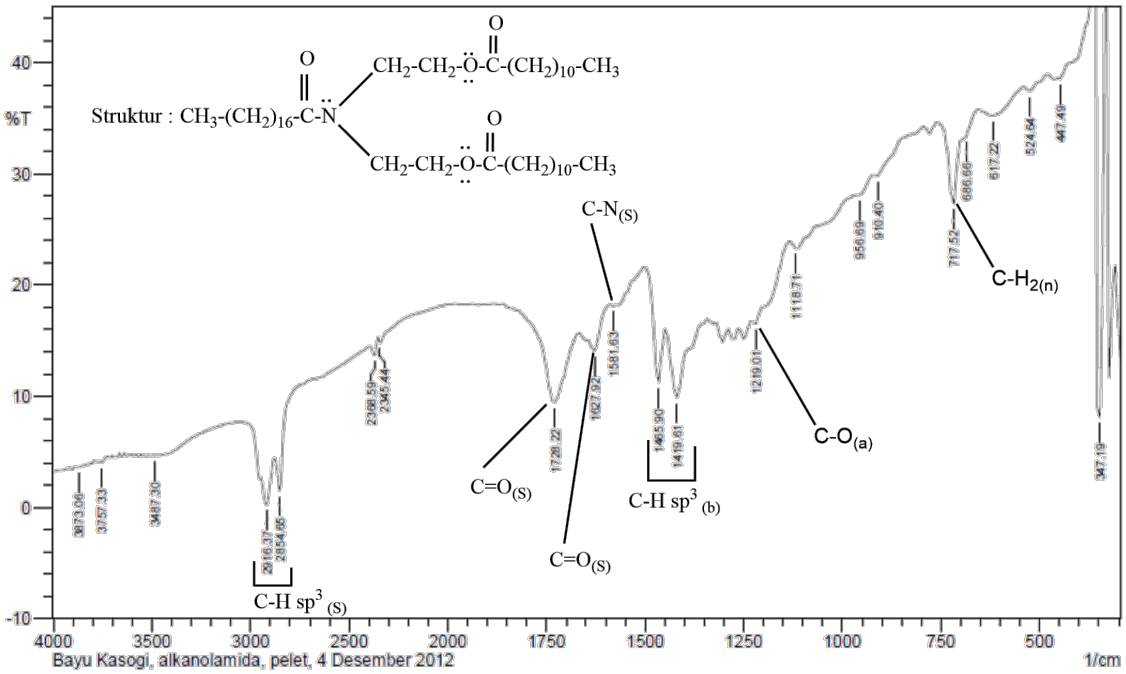


Figure 4. FT_IR Spectrum of Long Chain Alkanolamide Esters N,N-(2-Lauric-Ethyl) Stearamide

3.3 Preparation of Cationic Surfactant N, N-(2-Lauric-Ethyl) Stearamidium Chloride

Cationic surfactants are obtained from the salting reaction between a strong acid HCl and a weak base. Long Chain Alkanolamide Ester N, N-(2-Laurate-Ethyl) Steramide, The hypothesis of the reaction mechanism that occurs is estimated as in the following figure.

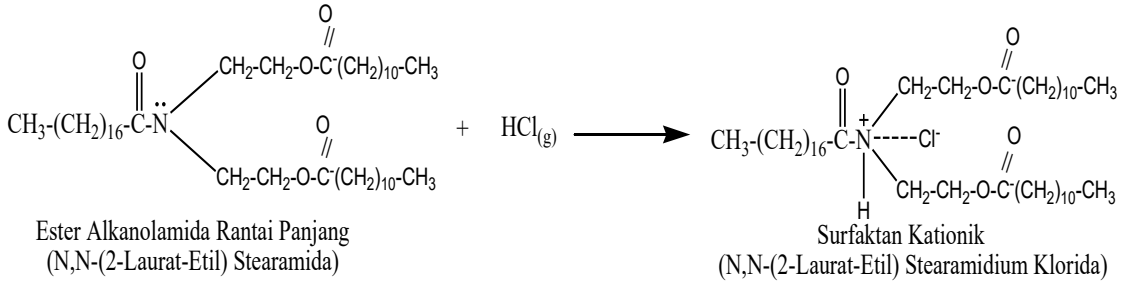


Figure 5. Cationic Surfactant Formation Reaction

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The results obtained were analyzed with an FT-IR Spectrophotometer giving a spectrum with absorption band peaks in the wave number region of 3000-2000 cm^{-1} which is a stretching vibration or stretching vibration of tertiary ammonium ions caused by stretching vibrations (NH) supported by bending vibrations (NH) at a wave number of 1527 cm^{-1}. The peak of the absorption band in the wave number region 2916-2854 cm^{-1} is the stretching vibration (CH) sp3 which is supported by bending vibration (CH) sp^3 at 1465 cm^{-1}. The strong absorption peak in the wave number region of 1728 cm^{-1} is the frequency stretching vibration (C=O) of the formed ester and is supported by asymmetric stretching vibration (CO) of (RCOOR) saturated ester in the 1219 cm^{-1} region. The absorption peak at wave number 1627 cm^{-1} shows the stretching vibration (C=O) of tertiary carbonyl amide. The presence of an amide carbonyl group is supported by the appearance of an absorption band at a wave number of 1581 cm^{-1} which is a stretching vibration (CN). The absorption peak at wave number 717 cm^{-1} indicates the peak of rocking vibration (CH2)n, a long chain alkyl hydrocarbon (Silverstein, 1984). The small percentage of transmittance in the FT-IR spectrum above is due to the small cationic surfactant concentration in the solvent (KBr pellet) at the time of analysis, (figure 6).(Silverstein, 1984).

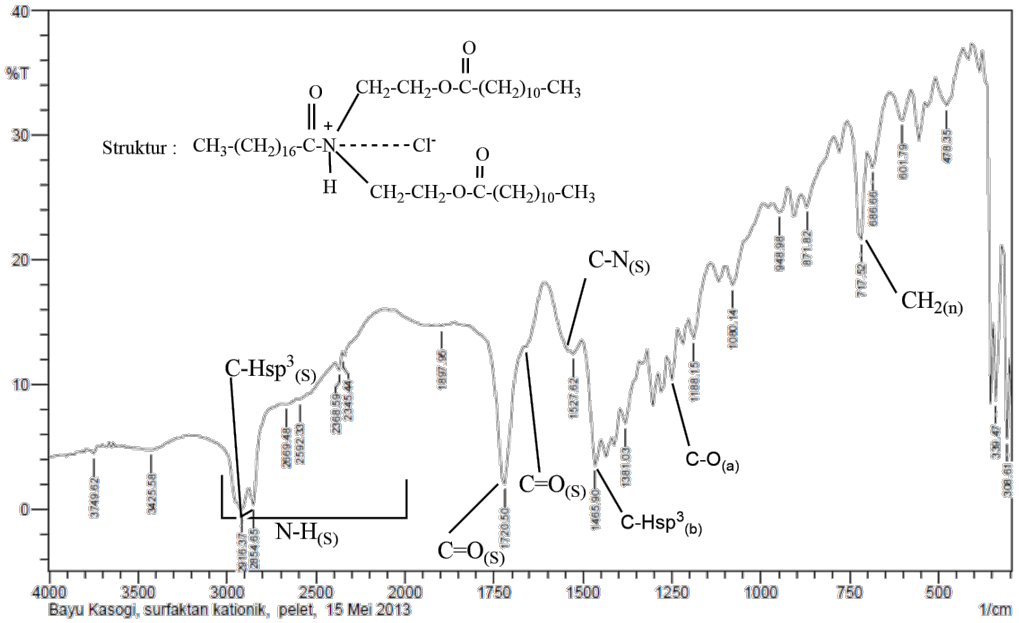


Figure 6. FT-IR Spectrum of Cationic Surfactant N, N-(2-Laurate-Ethyl) Stearamidium Chloride

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Table 1. The resulted determination of methyl stearate, stearamide, long chain alkanolamide esters, and cationic surfactants

Parameters	Sample			
	Methyl stearate	**Stearamida**	**Esters Alkanol-Long Chain amide**	**Surfactant cationic**
Melting point (ºC)	40-41	183-185	54-55	43-45
	39-40	184-186	54-56	43-45
	39-41	184-185	54-55	44-45

Table 2. The results of the measurement of the surface tension of the water Stearamide with a tensiometer

Concentration (%)	Surface tension (η) (dynes/cm)	x FK (dynes/cm)	Log C
1	47.5	47.0	0
2	45.8	45.3	0.3
3	44.3	43.9	0.47
4	43.8	43.4	0.60
5	41.1	40.7	0.7
6	41.0	40.6	0.77
7	41.0	40.6	0.85

Table 3. The results of long chain alkanolamide esters water surface tension measurements with a tensiometer

Concentration (%)	Surface tension (η) (dynes/cm)	x FK (dynes/cm)	Log C
1	32.8	32.5	0
2	32.4	32.1	0.3
3	31.7	31.4	0.47
4	31.5	31.2	0.60
5	31.4	31.1	0.7
6	31.4	31.1	0.77
7	31.4	31.1	0.85

Table 4. The results of Measuring the Surface Tension of Cationic Surfactants with a Tensiometer

Concentration (%)	Surface tension (η) (dynes/cm)	x FK (dynes/cm)	Log C
1	37.9	37.5	0
2	37.5	37.1	0.3
3	37.2	36.7	0.47
4	36.6	36.2	0.60
5	36.5	36.1	0.7
6	36.5	36.1	0.77
7	36.5	36.1	0.85

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Table 5. The results of CMC (critical micelle concentration) steramide, long chain alkanolamide esters, and cationic surfactants using the du nouy ring method.

Sample	Parameter	
	Surface tension x FK (dynes/cm)	CMC (mole/L)
Stearamide	40.7	0.133
Alkanolamide Esters	36.1	0.067
Cationic Surfactants	31.1	0.055

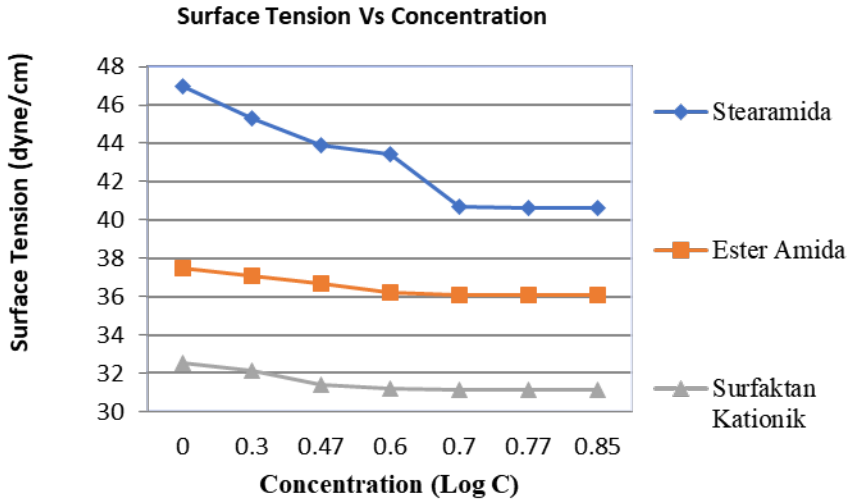


Figure 7. The graph of CMC Determination (Critical Micelle Concentration) Stearamides, Alkanolamide Esters, and Cationic Surfactants.

Most ampifiers, whether ionic or ionizing, have a hydrophobic region consisting of a hydrocarbon chain. The CMC value will decrease when ionic ampifiers increase the number of carbon atoms in an unbranched hydrocarbon chain. The balance of the hydrophilic and lipophilic regions of the surface actives agent is usually desirable because the lipophilic portion protrudes from the bulk aqueous phase. However, the hydrophilic portion prevents the surface actives agent from fully extruding from the aqueous phase. Thus, molecules containing a hydrophilic region and a lipophilic region are both concentrated at the interface, lowering the surface or interfacial tension. CMC = anti-log C

From the CMC value, it can be seen that for stearamide 0.133 mol/L at a surface tension of 40.7 dyne/cm, and long chain alkanolamide esters the CMC value is 0.067 mol/L at a surface tension of 36.1 dyne/cm. For cationic surfactants, the CMC value is 0.055 mol/L at a surface tension of 31.1 dyne/cm. This shows that the more methylene groups, the lower the CMC price. This follows what Attwood (1983) wrote adding a methylene group causes the CMC to decrease by about one-third of its initial value. The hydrocarbon branch in CMC through an increase in the number of carbon atoms in the branch segment of the carbon chain is not as large as the increase in the other states when the carbon atoms are in a straight chain (Atwood, 1983). According to

Zhou, et al (2012) Gemini, cationic surfactants have superior properties to conventional surfactants. (CH2)n which is a long chain alkyl hydrocarbon (Silverstein, 1984).

4. Conclusion

1. Long Chain Alkanolamide Esters N, N-(2-Lauric-Ethyl) Stearamide is obtained from the esterification of Stearamide with Lauric Acid in xylene solvent at a temperature of 140-145°C. The ester amide obtained was 84.7% in a soft solid with a melting point of 54-55°C.

2. Cationic surfactants N, N-(2-Laurate-Ethyl) Stearamidium Chloride is obtained from salting the amide ester of N, N-(2-Laurate-Ethyl) Stearamide with HCl gas. The cationic surfactant obtained is in the form of a soft solid with a melting point of 43-45°C.

3. Value determination result Critical Micelle Concentration (CMC) of each compound, namely Stearamide 0.133 mol/L;: 40.7 dyne/cm , Long Chain Alkanolamide Esters N,N-(2-Laurate-Ethyl) Stearamide 0.067 mol/L; :36.1 dyne/cm, and Cationic Surfactant N,N-(2-Lauric-Ethyl) Stearamidium Chloride 0.055 mol/L; : 31.1 dyne/cm.

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