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Effect of Chain Length on Fatty Alcohol Sulfation using SO_3-DMF

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ABSTRACT

The fatty alcohols C_8, C_{10}, C_{16} and C_{18} were used as raw materials for the sulfation reaction using the SO_3-DMF complex to study the ratio of carbon chains. The first step is to prepare the SO_3-DMF complex, by reacting SO_3 gas into DMF at a temperature of 0-4 ^{0}C with a reaction time of 3 hours, then sulfation is carried out at 100 ^{0}C for 5 hours on C_8, C_{10}, C_{16} and C_{18}. Tests were carried out on the results of sulfation with an FT-IR Spectrophotometer. Surface tension, foam stability and yield calculations. From the sulfation results, the yield results were respectively 83%, 81%, 68% and 61% then the results from the surface tension analysis were 35.3, dyne/cm, 30.3 dyne/cm, 29.4 dyne/cm and 33.6 dyne/cm and foam stability analysis of 0.2 cm, 0.8 cm, 0.7 cm and 1 cm. Based on the surface tension reduction value, palmityl alcohol is the best raw material for making surfactants.

Keywords: Fatty Alcohol, Sulfation, SO_3-DMF, Carbon chains

1. INTRODUCTION

Surfactant exhibits the hydrophobic tail that is non-polar in which will interact with oils such as hydrocarbon chain with higher than eight carbon atom and on the other side, the polar hydrophilic head will interact with polar functional groups (e.g. carboxyl, sulfonate, ammonium, hydroxyl, and amide). Therefore, the surfactant could act as detergent or foaming agent.[1,2] Sodium Lauryl Sulfate (SLS) is synthesized by mixing dodecanol with sulfur trioxide gas or oleum or chlorine sulfur acid to yield the hydrogen lauryl sulfate. Most of the industries utilize sulfur trioxide gas, followed by neutralization by sodium hydroxide or sodium carbonate.[3]

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The sulfation process is defined as the addition of SO_3 group to organic molecules by linking the sulfur and carbon atom through the oxygen-bridge which usually done by direct addition of sulfur trioxide into alcohol.[4] The sulfation process plays important role in industries in which to obtain various products such as dyes, pesticide, and intermediate organic compounds with the main application for anionic surfactant production.[5] The sulfation of alcohol group could be done by five methods, using sulfur trioxide, complexation of sulfur trioxide, chlorosulfonate acid, sulfuric acid, or sulfamate acid. Sulfur trioxide tends to produce pure products, but could also burn or stain the products without proper treatment.[6] The production of alcohol sulfate through the alcohol sulfation was first carried out by using an excessive amount of concentrated sulfuric acid.[7]

Dimethylformamide is an organic compound with the chemical formula of $(CH_3)_2HCON$. Generally, this compound is abbreviated as DMF, the colorless solution that miscible with water and frequently used as a solvent for chemical reaction. Pristine DMF is odorless, meanwhile, the low grade DMF possesses the fishy smell due to the impurity ofn dimethyl amine.[8] The basicity of DMF is weaker as compared to that of Pyridine with the positive charge at sulfur complex DMF-SO_3, higher than the complex of Pyr-SO_3, therefore the expected sulfation ability of DMF-SO_3 is higher than Pyr-SO_3.[9]

Previous researchers had conducted several works regarding the sulfation by different processes. For instance, Britz *et al.*[10] performed the alcohol sulfation using SO_3 and DMF. Further, the use of SO_3-DMF complex as a sulfating agent from tyrosine was observed by Futaki.[9] Pasteka[11] conducted the cross-linking/sulfation by DMF-SO_3. Sutariyono[12] reported the synthesis of fatty alcohol sulfate (FAS) through the hydrogenation of virgin coconut oil (VCO) assisted by nickel catalyst and hydrogen gas. The addition of SO_3 gas resulted from H_2SO_4 as sulfating agent at the end of the FAS synthesis was neutralized by NaOH 10%. In this work, fatty alcohol was used as the precursor for sulfation reaction with the sulfating agent of SO_3-DMF. The purpose of this work is to study the effect of carbon chain on sulfation reaction using various fatty alcohols (C_8, C_{10}, C_{16}, and C_{18}). The obtained product of sulfation was analyzed using FT-IR, surface tension characterization (*du nouy*), and vortex analysis.

2. EXPERIMENTAL

2.1. Chemicals and instrumentation

The chemicals used in this study are $P_4O_{10(s)}$ (p.a E' Merck), $DMF_{(l)}$ (p.a E' Merck), Myristyl $Alcohol_{(s)}$, $H_2SO_{4(p)}$ 98% (p.a E' Merck), $NaOH_{(s)}$ 40% (p.a E' Merck), $C_8H_{18}O$, $C_{10}H_{22}O$, $C_{16}H_{34}O$, $C_{18}H_{38}O$ dan $Aquadest_{(l)}$. In this studym the instruments are FT-IR spectroscopy (shimadzu), *Vortex mixer* (Vision) dan ring tensiometry *Du-Nouy*.

2.2. Procedures

The synthesis of SO_3 was conducted using phosphor pentaoxide with sulfuric acid at 150ºC followed by complexation of SO_3-DMF at temperature of 0-4°C for 3 h under stirring condition. Caprylate alcohol was then sulfated using SO_3-DMF at 100°C for 5 h and neutralization by NaOH 40% for 2 h. The obtain product was subsequently filtered and dried. The same method was used to obtain caprate alcohol. Palmitate alcohol was sulfated by SO_3-DMF complex at 100°C for 5 h and neutralized using NaOH 40% for 2 h and the top layer was taken and dried. The same method was used to synthesize stearyl alcohol. The as-prepared

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surfactant was finally characterized by surface tensiometry (ring *du nuoy*), vortex mixer, and FT-IR spectroscopy.

3. RESULT AND DISCUSSION

3.1. FT-IR analysis

The FT-IR spectra of sulfated fatty alcohol with ratio between short and long chain was shown in Fig. 1. As can be seen, all samples exhibit similarity such as the group of sulfate (S=O) appeared at wavelength of 998,6 cm^{-1} 1006,7 cm^{-1} 1088,4 cm^{-1}, 1125,6 cm^{-1}, 1252,3 cm^{-1}, 1252,4 cm^{-1}, dan hydroxyl group (-OH) at 3324,8 cm^{-1} dan 3406,8 cm^{-1} dan at 1060,8 cm^{-1} for caprylate alcohol and caprate alcohol. The wavelength of 1058,6 cm^{-1} for palmitate and stearyl alcohol indicates C-O group and C-H sp^3 group was found at 1461,1 cm^{-1}. Both caprate alcohol and caprylate alcohol exhibit CH_3 at 1379,1 cm^{-1} dan 1386,6 cm^{-1} and the CH_2 stretching was observed at 2922,2 cm^{-1} and it is at 2914,8 cm^{-1} for palmitate alcohol and stearyl alcohol. By comparing the sulfation of short-chain and long-chain carbon, it is noticed that the sulfate group is relatively similar, 998,6 cm^{-1} to 1252,4 cm^{-1} that is corresponding to S=O indicating the successful of sulfation reaction.

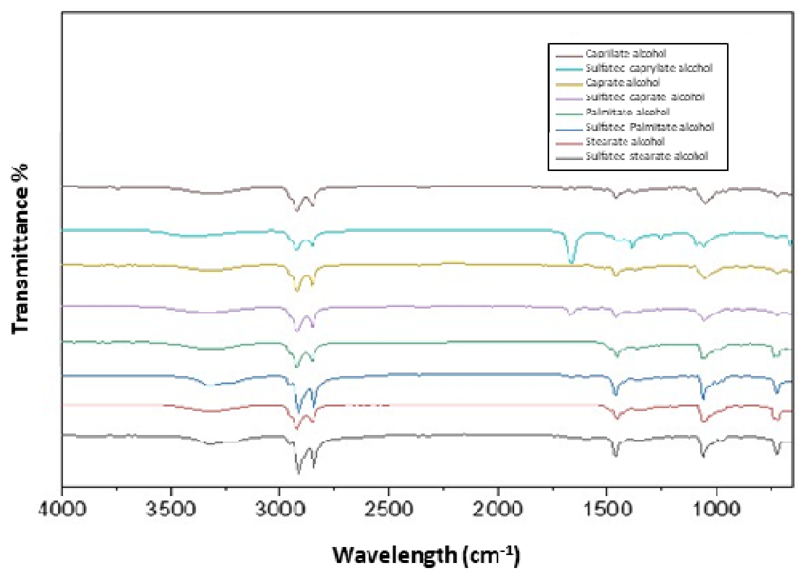

Figure 1. FT-IR spectra of different samples

3.2. Sulfation yield

The yield of sulfated fatty alcohol with comparison of short-chain and long-chain carbon was tabulated in Table 1. The length of molecule is essential to balance the equilibrium between hydrophilic and lipophilic groups (table 1). The equilibrium between oil and water affinities will be unbalance in case of very lengthy carbon chain.[13] The result in Table 1 indicates that the yield of product decreases with increasing carbon chain.

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Table 1. Yield of sulfated product

No.	Fatty alcohol	Yield (g)	Percentage (%)
1	Caprilate alcohol	5,4	83
2	Caprate alcohol	6,4	81
3	Palmitate alcohol	8,3	68
4	Stearyl alcohol	8,25	61

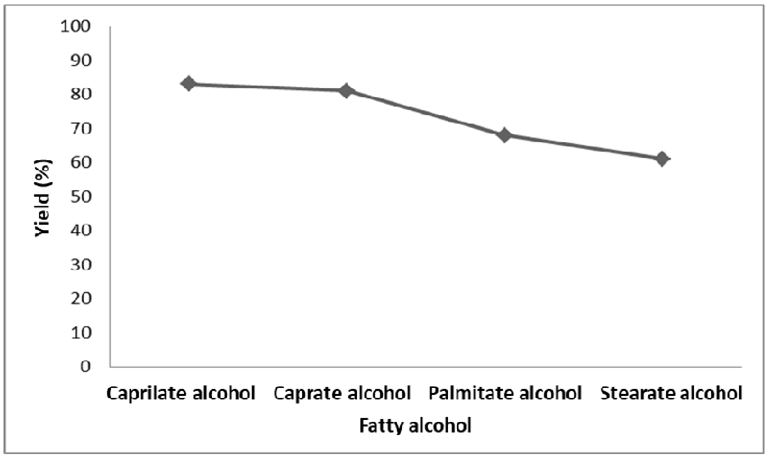

Figure 2. Yield of sulfation

3.3. Surface tension analysis

Table 2 shows the results of surface tension analysis of sulfated fatty alcohol products with comparison of short-chain and long-chain carbon atom. The measurement was carried out using ring *du nuoy* tensiometry. The surface tension is an interesting phenomenon that occurred for fluid at static condition in which occurred due to the surface of liquid tends to tensed therefore appear like a thin film. Surfactant can be good if the surface tension is low, therefore lower the surface tension of water. [14] The most optimum chain length for surfactant is 10-18 carbon atom, where in this study, C_{16} was found as the best as a precursor for surfactant.[13]

Table 2. The values of surface tension of samples

No.	Parameters	θ_1	θ_2	γ (*dyne*/cm)
1	Sulfated caprylate alcohol	125	160,3	35,3
2	Sulfated caprated alcohol	125	155,3	30,3
3	Sulfated palmitate alcohol	125	154,4	29,4
4	Sulfated stearyl alcohol	125	158,6	33,6

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3.4. Foam stability analysis

The foam stability was examined using vortex mixer in a test tube and the result is shown in Table 3. As from observation, it is seen that there is a change of foam after 5 min. a_1, a_2, and a_3 represent height of foam, height of initial foam, and the stability of foam, respectively. It is expected that the efficiency as a foaming agent can be improved with longer carbon chain.[15] This is because longer carbon chain could enhance the surface area which related to the faster reducing of surface tension, therefore enhance the efficiency of foaming agent. The foam results of sulfated short-chain and long-chain carbon atom show that the height of foam increases with increasing carbon chain.

Table 3. Stability of foam

No.	Parameters	a_1(cm)	a_2(cm)	a_3(cm)
1	Sulfated caprylate alcohol	1,8	1	0,2
2	Sulfated caprated alcohol	2	1,2	0,8
3	Sulfated palmitate alcohol	2,7	2	0,7
4	Sulfated stearyl alcohol	3	2	1

4. CONCLUSION

The sulfation process on fatty alcohol using short-chain and long-chain carbon atom resulted in different result. The yields for caprylate alcohol, caprate alcohol, palmitate alcohol, and stearyl alcohol are 83%, 81%, 68 % and 61%, respectively, with the surface tension of 35,3, *dyne*/cm, 30,3 *dyne*/cm, 29,4 *dyne*/ cm, and 33,6 *dyne/*cm dan stability foam of 0,2 cm, 0,8 cm, 0,7 cm and 1 cm, respectively. From FT-IR results, it can be concluded that the yield of sulfation decreases with increasing carbon chain. Palmitate alcohol with the lowest surface tension is the best material for a surfactant as indicated by the surface tension analysis. Meanwhile, the stability of foam increases with increasing carbon chain.

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