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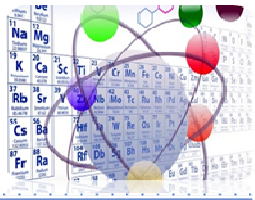

Synthesis of Sodium Myristyl Sulfate with Myristyl Alcohol Sulfation using SO_3-DMF

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ABSTRACT

The sulfation reaction between myristyl alcohol and the SO_3-DMF complex has been successfully carried out to produce sodium myristyl sulfate. Formation of the SO_3-DMF complex by reacting DMF and SO_3 gas obtained from the reaction of phosphorus pentaoxide and H_2SO_4. The variables studied were the time of formation of the complex, the time and temperature of sulfation and the concentration of NaOH at neutralization. The results of myristyl alcohol sulfation with SO_3-DMF were tested by FT-IR spectroscopic analysis, surface tension test, and foam stability test. The formation time of the SO_3-DMF complex of 5 hours is the result of the highest surface tension reduction and the most optimal foam stability. The results of the foam stability test analysis showed the highest value at 80°C with a foam stability of 0.5 cm. The best result of sulfation neutralized with 40% NaOH solution was able to reduce the surface tension value and has foam stability up to 66% with a decrease in foam height of 0.3 cm

Keywords: Sulfation, SO_3-DMF, Myristyl alcohol, NaOH

1. INTRODUCTION

Surfactant is the abbreviation of surface-active agents which also known as amphiphilic containing two different groups, hydrophilic and hydrophobic. The polar group (head) exhibits hydrophilic characteristic and the nonpolar group (tail) exhibits the hydrophobic properties. Surfactant monomer in a solution will form micelle where the head and tail will interact with water and oil, respectively.[1] Surfactant is a compound that could reduce the surface/interfacial tension between two materials due to its active surface.[2] The precursors of surfactant can be classified into two groups, petrochemicals and oleochemicals. Petrochemicals-based

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surfactant usually causes the environment problem due to its undegradable properties as compared to the oleochemicals-based surfactant. One of the most famous materials to make surfactant is fatty alcohol.[3] Fatty alcohol is one of the precursors for surfactant because of its environmentally friendly properties.[2] Fatty alcohol has the amphiphilic properties where both polar and non-polar groups are contained in the molecule.[4]

Sulfation is the process of adding SO_3 to an organic molecule via a oxygen-bridge which can be carried out by direct addition of SO_3 to a fatty alcohol.[5] The synthesis of sodium lauryl sulfate on a big scale using lauryl alcohol which reacted with H_2SO_4 to generate SO_3 gas at 40°C at 1 atm and followed by neutralization by NaOH to produce good surfactant.[6] Other than that, Priambudi[7] reported the synthesis of sodium dodecyl sulfate using dodecanol reacted with H_2SO_4 as the sulfated agent at 40°C at 1 atm which neutralized by NaOH. However, the sulfation using H_2SO_4 cause a lot of side reaction such as dehydration, non-selective sulfation, and scaffold degradation.[8]

Another sulfating agent also can be obtained from making complex. Complex of SO_3-DMF is a dipolar ion which easily attacked by nucleophile from hydroxyl group. A study shows that by reacting chitosan with SO_3-DMF complex and neutralized with NaOH to yield chitosan sulfate could be applied as an anticoagulant agent.[9] Chitosan sulfate also be used for antibacterial activity application and chitosan sulfate has been successfully synthesized as indicated by C-O-S group with high antimicrobial index value toward *E. Coli* and *S. Aureus* with the value of 0.66%.[10]

SO_3-DMF complex is a good sulfating agent. SO_3-DMF complex solution reacted with fatty alcohol and after finished, the obtained fatty alcohol sulfate was neutralized to obtain alcohol sulfate salt formed by neutralizing agent.[11]

Fatty alcohol sulfate during sulfation process possesses acid properties and easily degraded therefore require neutralization. The neutralizing agent generally is basic solution. Afrozi[12] reported the use of NaOH as a neutralizing where if the concentration higher than 40%, the resulted soap could irritate the skin and if less than 40%, a foamy soap will be obtained.

In this study, Myristic alcohol (MA) was sulfated with SO_3-DMF complex as the sulfating agent using SO_3 generated by reacting P_4O_{10} and H_2SO_4 followed by neutralization by NaOH to produce sodium myristic sulfate. In this study, the time of complexation, time and temperature of sulfation, concentration of NaOH during neutralization were studied. The sulfated products were analyzed using FTIR spectroscopy to determine the functional groups, ring tensiometry *du-nuoy* to examine the surface tension and Vortex analysis for the stability of foam.

2. MATERIALS AND METHOD

2.1. Chemicals

The chemicals are $P_4O_{10(s)}$ (p.a E' Merck), $DMF_{(l)}$ (p.a E' Merck), Myristic $Alcohol_{(s)}$, $H_2SO_{4(p)}$ 98% (p.a E' Merck), $NaOH_{(s)}$ 40% (p.a E' Merck) dan $Aquadest_{(l)}$. In this study, the instruments for analyses are FT-IR spectroscopy (shimadzu), *Vortex mixer* (Vision) and ring Tensiometry *Du-Nouy*.

2.2. Procedures

2.2.1 Variation of complexation

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SO_3 from P_4O_{10} and H_2SO_4 at high temperature reaction of 150ºC followed by time variation of 3, 4 and 5 hours under stirring condition. The SO_3-DMF complex was allowed to cool-down and added with MA while stirring and refluxed using ball condenser at 70°C for 2 h. The resulted sulfated product was neutralized with NaOH 40% for 2 h.

2.2.2. Variation of sulfation time

SO_3 from P_4O_{10} and H_2SO_4 at high temperature reaction of 150ºC followed by complexation of SO_3-DMF at 0-4°C for 5 h under stirring condition. The obtained SO_3-DMF was allowed to cool-down and added by MA under reflux condition at 100°C and reaction time was varied for 3, 4 and 5 h. The resulted sulfated product was then neutralized by NaOH 40% for 2 h.

2.2.3. Variation of sulfation temperature

SO_3 from P_4O_{10} and H_2SO_4 at high temperature reaction of 150ºC followed by complexation of SO_3-DMF at 0-4°C for 5 h under stirring condition. The obtained SO_3-DMF was allowed to cool-down and added by MA under reflux condition at varied temperature of 80, 90, and 100°C. The resulted sulfated product was then neutralized by NaOH 40% for 2 h.

2.2.4. Variation concentration of NaOH

SO_3 from P_4O_{10} and H_2SO_4 at high temperature reaction of 150ºC followed by complexation of SO_3-DMF at 0-4°C for 5 h under stirring condition. The obtained SO_3-DMF was allowed to cool-down and added by MA under reflux condition at 70°C. The resulted sulfated product was then neutralized by various concentration of NaOH 35, 40, and 45% for 2 h.

2.2.5. Characterization

The as-prepared surfactant was characterized using ring tensiometry du-nuoy for surface tension determination, stability of foam by vortex mixer, and functional groups of surfactant using FTIR spectroscopy.

3. RESULTS AND DISCUSSION

3.1. FTIR analysis

The FTIR spectra of sulfated myristic alcohol with time variation (3, 4, and 5 h) shows a similar sulfate group at 969,1; 998,9; 1028,7 and 125,1 cm^{-1}. Hafizah,[13] reported that at 950-1100 cm^{-1} was assigned for vibration of S=O. The band absorption at 1220 cm^{-1} refer to stretching vibration of S=O at Figure 1.[14] The FTIR spectra comparison of varied sulfated MA exhibits similar peaks at 1461,1 cm^{-1} indicating the vibration of C-H sp^3 and at 1058,6 cm^{-1} denoted the C-O group and stretching CH_2 at 2914,8 cm^{-1} and at 723,1 cm^{-1} is the vibration for long chain hydrocarbon $(CH_2)_n$ showing the successful substitution of H into alcohol group (O-H) with S atom at sulfate group (C-O-S) for sulfate myristic alcohol. Guo[15] also reported that S=O group at 1248 and 1215 cm^{-1} and 1245 cm^{-1} and 1197 cm^{-1}.

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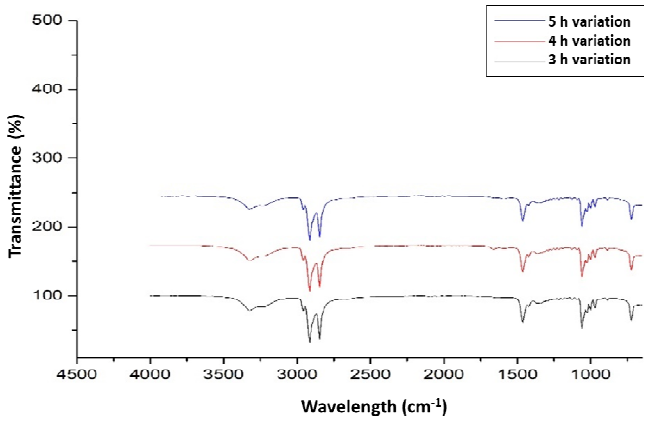

Figure 1. FTIR spectrum of samples.

3.2. Surface tension

Figure 2 displays the sulfated myristic alcohol with time variation of SO_3-DMF complex for 5 h exhibits the most optimum reducing surface tension. This is because the sulfated product is more optimum using complexation for 5 h, therefore could generate product that can be used as precursors for surfactant. The good ability to reduce surface tension amon varied sulfated time of 3, 4 and 5 h was found at 4 h with 27,4 γ. This is due to reaction time that could influence the surface tension. Therefore, this variation could be considered as the precursor for surfactant.

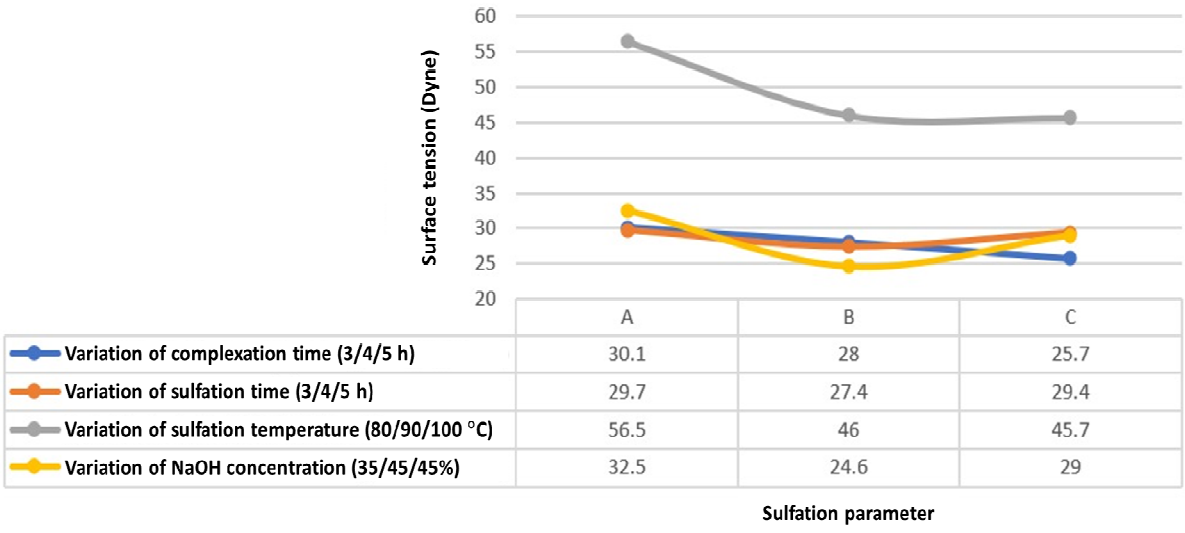

Figure 2. Surface tension analysis

Figure 2 shows that at 80, 90 and 100°C, the yield of products was calculated to be 56.5, 46,0, and 45,7%, respectively. Temperature of 100°C demonstrated the highest yield of 45,7%, due to increasing

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temperature therefore increase the yield as well.[16] Nugroho[17] reported the effect of temperature related to the yield was proportional where the most optimum temperature was at 170ºC to yield 0,83% as compared to others. On the other hand, the surface tension could be influenced by the concentration of NaOH. Oxidation could be taking place if the concentration of NaOH too high resulting side products, such as sulfuric acid and disalt.[18] The presence of disalt as a side product could interfere the surfactant activity, where disalt could decrease the solubility of surfactant in water caused increasing surface tension.[19] This is proved by switching NaOH 40% to 45%. It is concluded that the optimum NaOH concentration to reduce surface tension was NaOH 40%, which can be used as precursor for surfactant.

3.3. Stability of foam

The sulfate myristic alcohol with time variation of SO_3-DMF at 3, 4, and 5 h exhibited different stability of foam which depends on the reaction time and sulfation process as shown in figure 3. The reduction of surface tension also can be influenced by alcohol content in solution where can reduce the foam. [20] Time variation of SO_3-DMF at 5 h is the most stable for the foam due to the long reaction time during sulfation process and less alcohol in the complex.

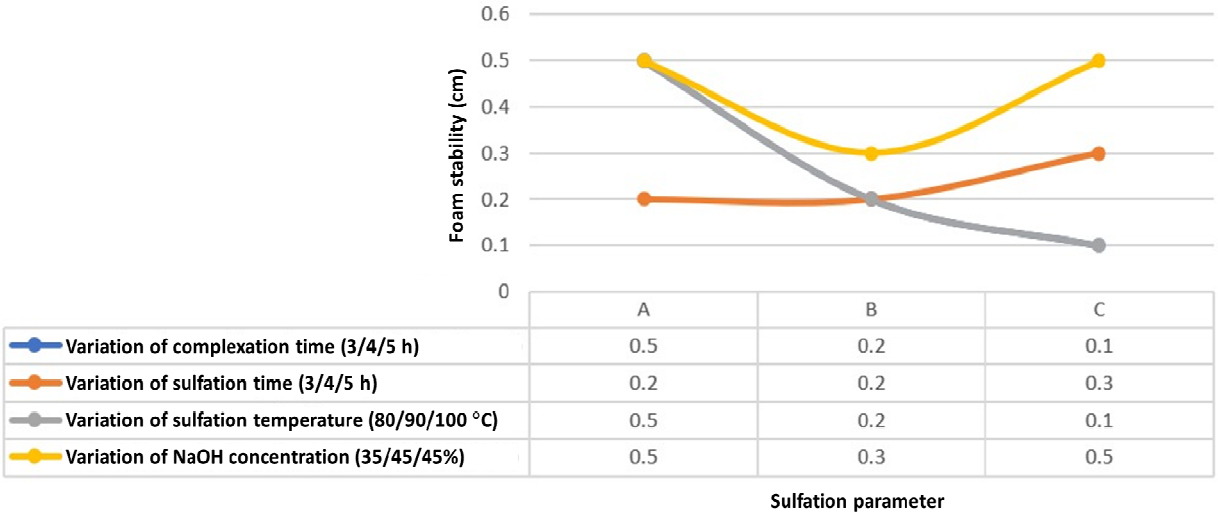

Figure 3. Foam stability analysis

The effect of sulfation time at 3, 4 and 5 h as can be seen in figure 3 show that the foam stability is relatively stable. The time for sulfation could influence the surfactant where the concentration of surfactant is the key factor that influence the foam stability. If the concentration is high, the obtained foam will be smooth and the bubble is distributed uniformly and resulted in a good foam stability.[21] The temperature variation of sulfation indicated that the foam stability decreases with increasing temperature. The highest foam stability was exhibited by the sulfation process at 80ºC with the height of 0,5 cm. This is due to the decreasing of temperature therefore the foam stability become better. At various concentration of NaOH during sulfation, NaOH at 40% is the most optimum with the height of foam at 0,3 cm and stability of 66,6%. The difference between initial and final height of foam is relatively small, therefore the stability is quite good. The stability

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of foam can be described as the resistant of a bubble between 60-70% from its initial volume.[22] The depreciation of foam will decrease with increasing concentration reactant.[23]

4. CONCLUSION

The sulfated MA with time variation of SO_3-DMF complex at 5 h was found as the most optimum sample to reduce the surface tension with high stability of foam. The effect of sulfation time at 4 h was determined as the best sample with surface tension of 27,4 γ, and the effect of sulfation time to foam heigh at 3, 4, and 5 h is relatively stable. The sulfation of temperature of 80^{o}C was obtained as the most stable foam of 0,5 cm. Neutralization using NaOH 40% could reduce the surface tension with the height reduction of 0,3 cm.

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