

Synthesis of Phosphate Ethanolamide Derived from Free Fatty Acids of Cooking Oil Processing From Crude Palm Oil.

Bahtiar F Lubis¹, Herlince Sihotang^{2}, and Mimpin Ginting³*

^{1,2,3}Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sumatera Utara, Jalan Bioteknologi No.01 Kampus USU Medan 20155, Indonesia

Abstract. Free fatty acid (FFA) has a great potency as a precursor for preparing phosphate ethanolamide. The objective of the current study was to synthesize and characterize the phosphate ethanolamide produced from FFA using an amidation process between methyl palmitate and ethanolamine. The characterization was conducted under different concentration, namely 0.0001, 0.0002, 0.0003, 0.01, 0.02, 0.1, 0.2, 0.3. The FT-IR spectra confirm all compound functional groups, which present no significant difference for each compound. The CMC values of ethanolamide and phosphate ethanolamide at concentration 0.1 % were 46.566 dyne/cm, 38.844 dyne/cm, respectively. In addition, the melting point of each ethanolamide and phosphate ethanolamide have approached the melting point of palmitate. These results indicate that ethanolamide and phosphate ethanolamide can be synthesized from FFA derived from the cooking oil process from CPO.

Keywords: Free Fatty Acid, Amidation, Phosphate Ethanolamide, Crude Palm Oil

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1 Introduction

Indonesia is the second largest palm oil producer in the world after Malaysia. Palm oil has a very important role in the edible film and oleochemical industry. and can produce various of products (Pahan, 2006). The palm oil sources are derived from crude palm oil (CPO) and palm kernel oil (PKO).

Free fatty acid (FFA) is a by-product of the CPO processing to be cooking oil (RBDP Olein). It has happened in the deodorizing stages via vacuum distillation. The FFA content is dependent on the FFA content of the CPO. In general, the FFA content is around 2 to 5% of the amount of CPO processed. In the oleochemical industries, ALB has not been fully utilized and is still usually processed for bar soap manufacturing which has a low economic value.

*Corresponding author at: Department of Chemistry, Faculty of Mathematics and Natural Sciences Universitas Sumatera Utara, Medan, Indonesia.

E-mail address: herlince@usu.ac.id

Amide compounds are fatty acid derivatives obtained through the amidation process of carboxylic acid derivatives and ammonia or amines (Fessenden, 1986). It is a surfactant that are widely used in the agricultural, pharmaceutical, food and beverage, cosmetics, and other industries. In the pharmaceutical industry, amides can be used as drugs (Daniel, 2007).

Amides containing an alcohol group are called alkanolamides. The preparation of alkanolamide compounds was carried out by reacting fatty acids and amines at a temperature of 120 to 180°C. The synthesis of alkanokamides that have been performed through the reaction between fatty acids and ethanolamine or fatty acids with diethanolamine. In this synthesis, competition often occurs between the formation of amides and esters if the reaction conditions are not properly regulated (Maag, 1984).

Apart from fatty acids derived from plants, alkanolamides can also be synthesized by reacting animal fatty acids with ethanolamine and diethanolamine. Furthermore, the alkanolamide derived from beef and lamb fat was modified by adding H₃PO₄. The alkanolamide is reacted with H₃PO₄ at a temperature of 55 to 66°C with a mole ratio of alkanolamide: H₃PO₄ = 1:1. In order to analyze the number of unreacted H₃PO₄ used titrimetric method. Ethanolamide phosphate was tested as petroleum-collecting and petroleum-dispersing reagents (Asadov, 2011). The ethanolamide phosphate synthesis reaction shown in figure 1.

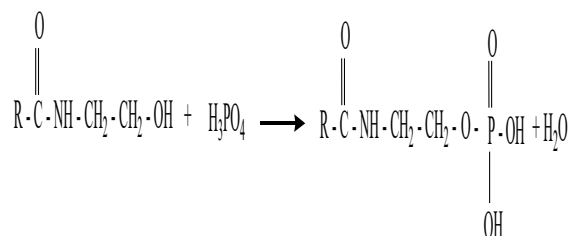


Figure 1. The reaction of ethanolamide formation

Based on the description above, the purpose of this study was to produce ethanolamide and ethanolamide phosphate compounds which were then tested for CMC values using the Du Nouy ring method.

2 Experimentals

2.1 Materials

In this study, the materials used were methanol, benzene, 98% sulfuric acid (H₂SO₄), n-hexane, sodium hydroxide (NaOH), ethanolamine, phosphoric acid (H₃PO₄), sodium methoxide were purchased from Sigma-Aldrich, USA. Free fatty acid (FFA) derived from crude palm oil (CPO) was obtained from the oleochemical industry in Medan. The surface tension values were determined using a Du Nouy Ring tensiometer equipped with a standard metal load.

2.2 Separation of Saturated and Unsaturated Fatty Acids from Free Fatty Acids Through Crystallization Stage

As much as 40 g of the free fatty acid mixture was put into a 500 mL Erlenmeyer and then, added 150 mL n-hexane. The mixture was stirred using a magnetic stirrer. After the free fatty acids dissolve, anhydrous Na_2SO_4 was added to bind the water contained in the solution and silenced for one night, then the solution was filtered. The filtered result was heated at a temperature of 50 to 60°C. After that, it was placed into the freezer at 0°C for 24 hours and filtered in cold condition using a Buchner funnel. The filtering residue results in which saturated fatty acid was used for palmitic acid methyl ester mixture and dried in a desiccator.

2.3 Preparation of Methyl Palmitate Mixture

As much as 30 g of the mixture of palmitic acid (≈ 0.1711 mol), 18 mL CH_3OH (0.4443 mol), and 50 mL benzene were put into a 250 mL two neck-flask while stirred and cooled. Furthermore, as much as 0.7 mL of H_2SO_4 was slowly dripped through the dropper funnel. Then, a reflux device was assembled with a CaCl_2 tube and refluxed at 70 to 80°C for 5 hours. The excess methanol and solvent were evaporated using a rotary evaporator. The residue obtained was extracted in 100 mL n-hexane and washed with distilled water for 2 times. The top layer was dried with anhydrous CaCl_2 and filtered. Then, dried with anhydrous Na_2SO_4 and filtered. The obtained filtrate was evaporated using a rotary evaporator. The results obtained were identified through FT- IR spectrometry analysis and gas chromatography (GC) analysis.

2.4 Amidation of Fatty Acid Methyl Ester with Ethanolamine

As much as 32 g of the mixture of palmitic acid (≈ 0.125 mol), 12 mL ethanolamine (0.150 mol), and 0.093 mol of NaOMe under 25 % CH_3OH solution was placed were put into a 250 mL two neck-flask. Then, a reflux device was assembled and refluxed at 80 to 90°C for 6 hours. The excess solvent was evaporated by a rotary evaporator. The residue obtained was dissolved in 100 mL n-hexane and washed with 25 mL saturated NaCl each for 3 times. Next, the layer was taken and evaporated. The results obtained were investigated through FT- IR spectrometry analysis, determined the CMC value, and melting point testing.

2.5 Preparation of Phosphate Ethanolamide

As much as 50 mL of ethanolamide and phosphoric acid with a molar ratio of 1:2, (10 g alkanolamide and 4 mL phosphoric acid) were put into a flask and heated at 55 to 60°C. The mixture was stirred with a magnetic stirrer. The reaction was observed by analyzing the amount of unreacted phosphoric acid in the mixture by the titrimetric method. In order to remove the excess phosphoric acid, the product was dissolved in ethanol. Then, filtered and washed the residues with diethyl ether. The results obtained were identified through FT-IR spectrometry analysis, which determined the CMC value and melting point testing.

2.6 Analysis of Unreacted Phosphoric Acid

As much as 0.1 g phosphate ethanolamide was put into Erlenmeyer and dissolved with 10 mL distilled water. Then, added 3 drops of methyl orange and titrated with 0.1209 N NaOH. The color change was observed from red to orange. The equivalent point shows that the alkanolamide has completely reacted with phosphoric acid. The used NaOH volume was calculated. If the used NaOH volume was decreasing and starting to become constant, it indicated that the alkanolamide and phosphoric acid have completely reacted.

3 RESULT AND DISCUSSION

The gas chromatography analysis results of fatty acid methyl ester previous to and after the separation between mixed palmitic acid and mixed oleic acid were presented in figure 2,3 and 4.

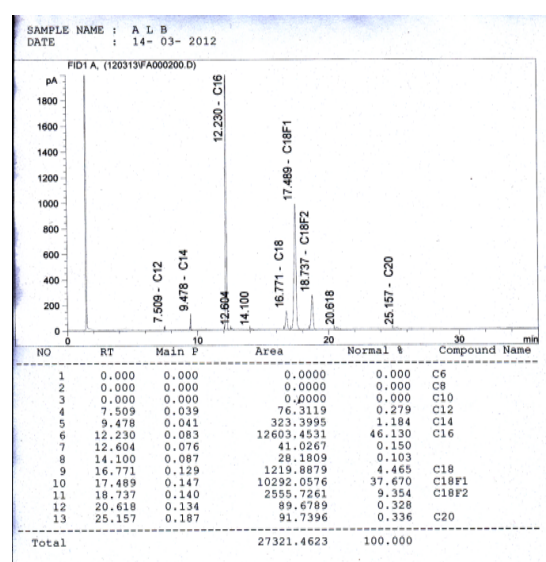


Figure 2. Chromatogram of free fatty acid methyl ester

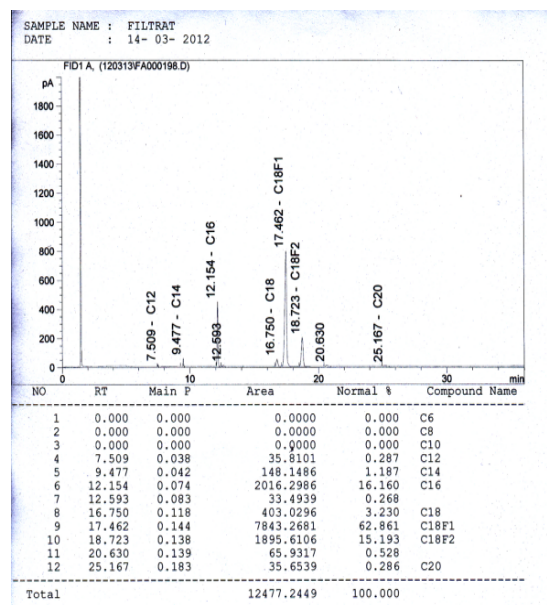


Figure 3. Chromatogram Methyl Palmitate Mixture

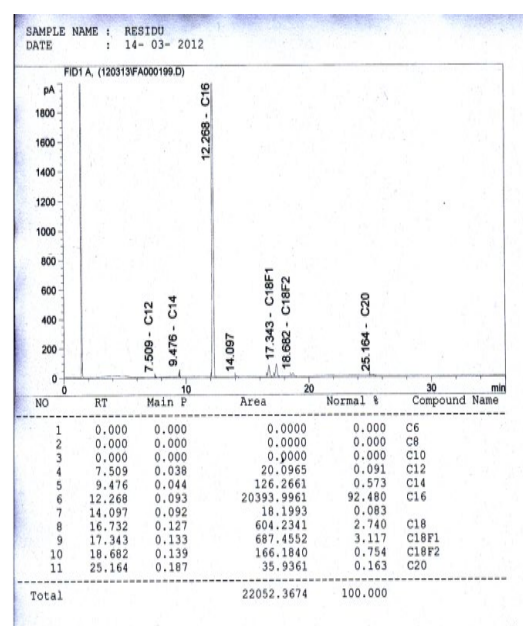


Figure 4. Chromatogram of methyl oleic mixture

Based on the chromatograms, the compositions of each previous and after separation of fatty acid are shown in Table 1. The residues obtained that palmitic acid content changed from 46.13% to 92.48%. In contrast, the filtrate changed from 37.67% to 62.861.

Table 1. The fatty acid content before and after fractionated

No	Fatty Acid	Before	After Fractionated (%)
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		Fractionated (%)	Residual Fraction (%)	Filtrate Fraction (%)
1	Lauric acid (C12)	0.279	0.091	0.287
2	Myristic acid (14)	1.184	0.573	1.187
3	Palmitic acid (16)	46.130	92.480	16.160
4	Steric acid (18)	4.465	2.740	3.320
5	Oleic acid (C18.1)	37.670	3.117	62.681
6	Linoleic acid (C18.2)	9.354	0.754	15.193
7	Arachidic acid (C20)	0.336	0.163	0.286

3. 1. Preparation of Methyl Palmitate Mixture

Esterification of mixed palmitic acid with methanol under benzene solvent using concentrated sulfuric acid as a catalyst at 70 to 80°C could produce methyl palmitic mixture compounds with a yield of 94.88%. The reaction mechanism of methyl palmitate mixture formation of the esterification of palmitic acid and methanol is presented in figure 5 and the FT-IR spectrum analysis of methyl palmitate indicated in figure 6.

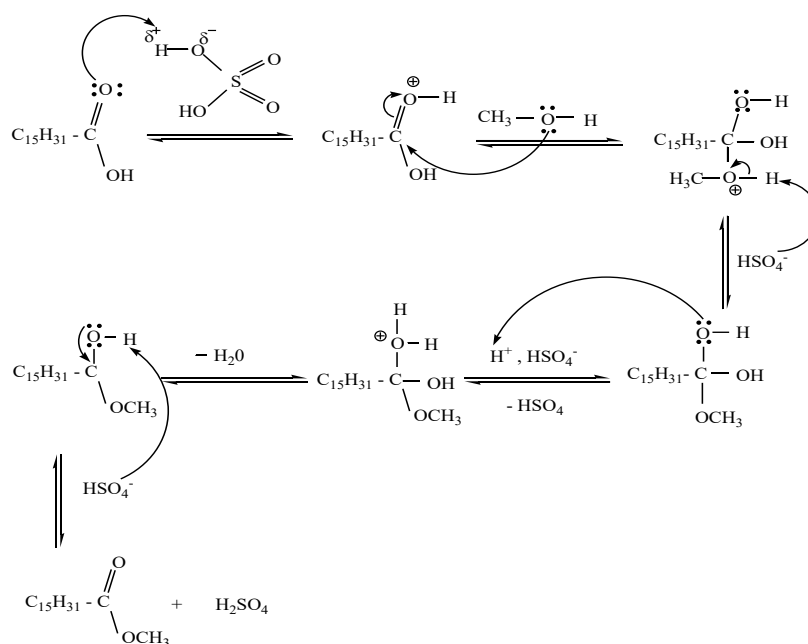


Figure 5. The reaction mechanism of methyl ester fatty acid formation

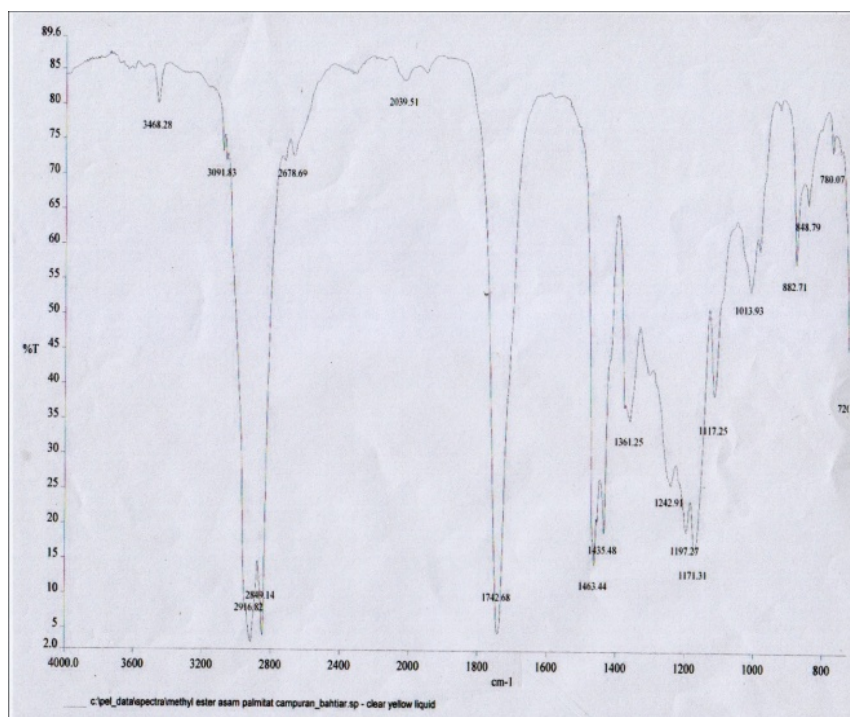


Figure 6. The FT-IR spectrum of methyl palmitate mixture

The mixed methyl palmitate FT-IR spectrometry analysis result shows the peak at 1742 cm^{-1} represents the C=O absorption of saturated aliphatic esters and is supported by the band at 1242 cm^{-1} which shows the typical absorption of the saturated ester C-C(=O)-O. The C-C(=O)-O asymmetric vibration coupled with the CO stretching vibration contributes to each 1117 cm^{-1} , 1171 cm^{-1} , and 1197 cm^{-1} showing that it is a long chain methyl ester fatty acid compound. The band at 1171 cm^{-1} assigned the strongest (Silverstein, 1963).

The band at 2916 cm^{-1} , which showed typical absorption of C-H of SP^3 asymmetric stretching vibrations, and the peak at 2849 cm^{-1} , which assigned a typical absorption of C-H of SP^3 symmetric stretching vibrations which are supported by C-H of SP^3 asymmetric bending vibrations at 1463 cm^{-1} . and the C-H of SP^3 symmetric buckling vibrations contributes to the peak of 1361 cm^{-1} . The band at 720 cm^{-1} , which indicated the rocking vibration of the methylene group (CH_2) of a straight-chain alkane consisting of seven or more carbon atoms (Silverstein, 1963).

3.2 Preparation of Ethanolamide Compound

The ethanolamide compound could be produced from the amidation reaction between the mixed methyl palmitate compound and ethanolamine in methanol solvent using sodium methoxide as a catalyst at 80 to 90°C .

Based on the HSAB principle, the amidation of mixed methyl palmitate compounds could produce mixed ethanolamide palmitate in which H^+ from NH_2 derived from ethanolamine was a

hard acid that easily reacts with -OCH_3 , which is a hard base. In contrast, the N^- from ethanolamine which is a soft base would react with an acyl group $\text{R-C}^+ = \text{O}$ which is a soft acid.

The reaction mechanism for the formation of mixed ethanolamide presented in figure 7.

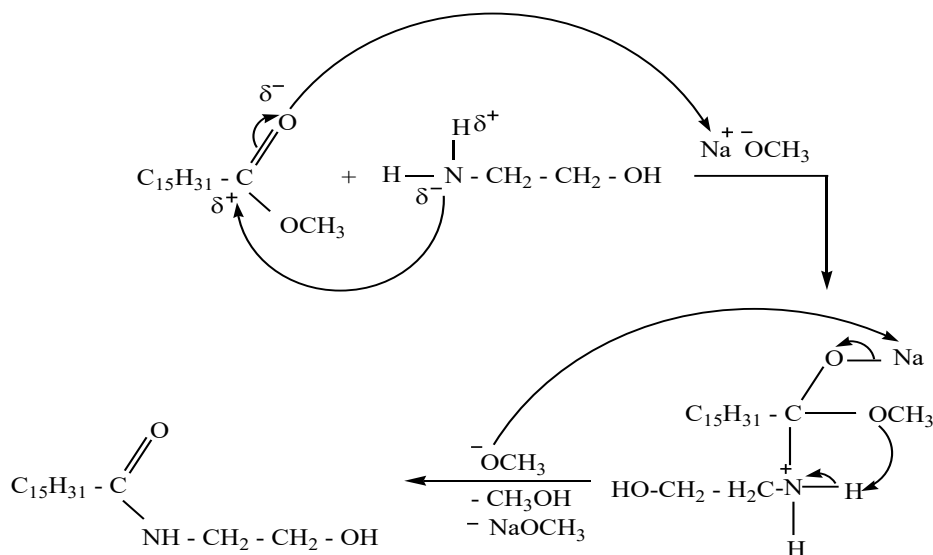


Figure 7. The reaction mechanism of ethanolamide formation

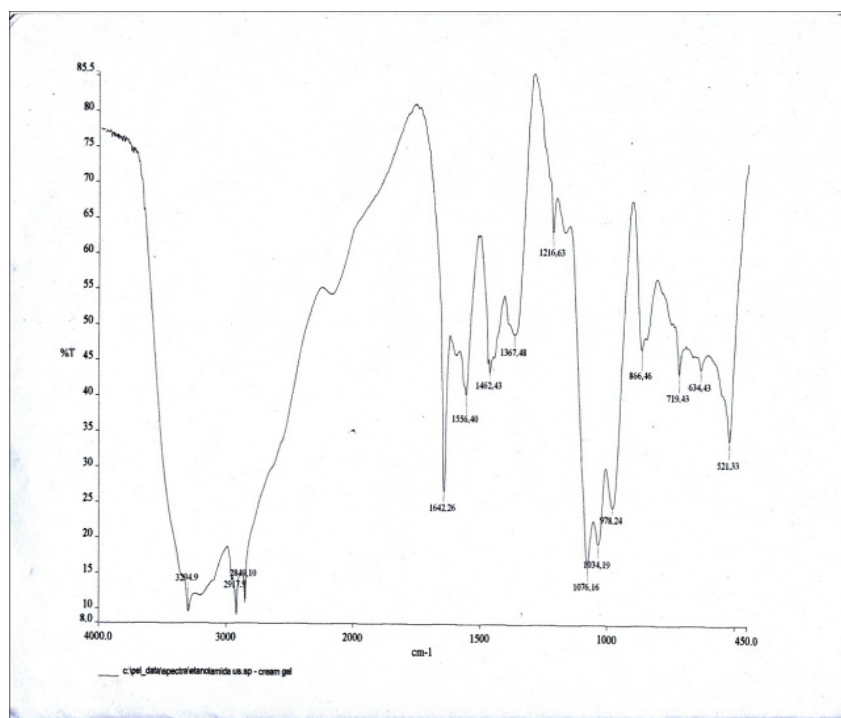


Figure 8. The FT-IR spectrum of Ethanolamide Mixture

The FT-IR spectrometry ethanolamide result shown in figure 8. The band at 3294 cm^{-1} represents the stretching vibrations of NH. The peak at 1076 cm^{-1} , which indicated the presence of the OH group. The peak at 1642 cm^{-1} , which assigned the secondary amide due to NH bending. The peak at 1556 cm^{-1} shows the secondary taxicyclic amide band due to the interaction between NH bending and the CN stretching of the C-N-H groups. The band at 12126

cm^{-1} , which indicated the secondary amide support due to N-H bending and C-N stretching. (Silverstein, 1963).

The C-H of SP^3 asymmetric stretching vibrations indicates the peak of 2849 cm^{-1} , while the C-H of SP^3 represents symmetric stretching vibrations which are supported by the C-H of SP^3 asymmetric bending vibrations at 1462 cm^{-1} . The band at 1367 cm^{-1} , which assigned C-H of SP^3 . The peak at 719 cm^{-1} represents the rocking vibration of the methylene group (CH_2) of a straight-chain alkane consisting of seven or more carbon atoms (Silverstein, 1963).

3.3 Preparation of Phosphate Ethanolamide Compound

Phosphate ethanolamide compounds could be produced from the esterification reaction of ethanolamide compounds with phosphoric acid with a mole ratio of 1: 2 at 55 to 65°C . The excess of phosphoric acid was observed using the titrimetric method. The reaction mechanism of phosphate ethanolamide processing was an esterification reaction which shown in figure 9.

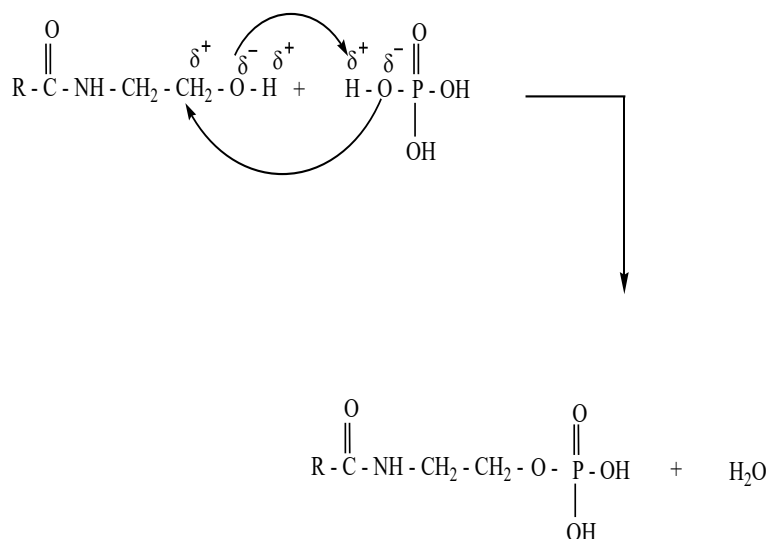


Figure 9. The reaction mechanism of phosphate ethanolamide compound

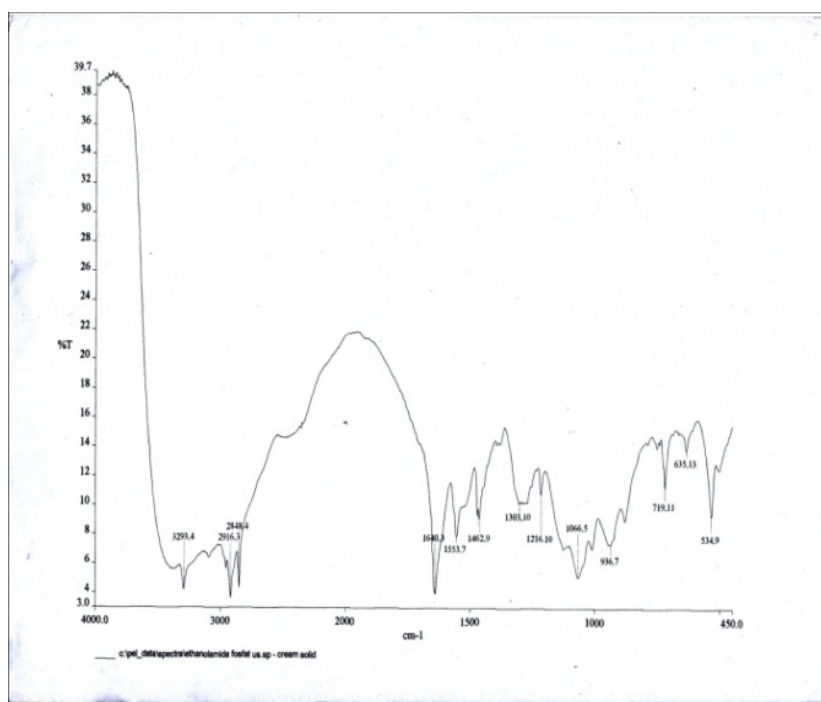


Figure 10. The FT-IR spectrum of phosphate ethanolamide compound

The FT-IR spectrometry phosphate ethanolamide result shown in figure 10. The band at 3293 cm^{-1} represents the stretching vibrations of NH. The peak at 1640 cm^{-1} , which indicated the presence of the NH group. The peak at 1553 cm^{-1} , which assigned NH group due to the interaction between NH bending and the C-N stretching of the C-N-H group.(Silverstein, 1963).

The band at 1066 cm^{-1} , which indicated POC (aliphatic) vibrations and was supported by the peaks at $830\text{ to }740\text{ cm}^{-1}$ which also indicated P-O-C stretching vibration (Mistry, 2009). The P=O stretching vibrations contribute to the peak of 1216 cm^{-1} . Hence, the band at 936 cm^{-1} , which indicated the presence of P-OH vibrations (Biemann, 1983).

The C-H of SP^3 asymmetric stretching vibrations contributes to the peak of 2916 cm^{-1} . In addition, the band at 2848 cm^{-1} , which assigned C-H of SP^3 asymmetric stretching vibrations, while the peak of 2848 cm^{-1} , which C-H of SP^3 symmetric stretching vibrations and supported by C-H of SP^3 asymmetric bending vibrations, which contributes to a band at 1462 cm^{-1} . On the other hand, the C-H of SP^3 symmetric buckling vibrations indicates a peak of 1303 cm^{-1} . The peak at 719 cm^{-1} , which indicated the rocking vibration of the methylene group (CH_2) of a straight-chain alkane consisting of seven or more carbon atoms (Silverstein, 1963).

3.4 Surface Tension Determination Results(γ) with Tensiometer Tool

Based on the Du Nuoy ring methods results in Tabel 2 and 3, the surface tension of ethanolamide and phosphate ethanolamide results are shown by the critical myecell concentration point (CMC) values. The value of concentration at 0.1% each for ethanolamide

and ethanolamide phosphate were 46.566 dyne/cm and 38.844 dyne/cm (figure 11). The phosphate addition affected the polarity of the molecule which increased the polarity caused decreased surface tension value (Asadov, 2011).

Table 2. The results of determination of surface tension (γ) ethanolamide

No	Concentration (%)	Surface tension (dyne/cm)	xF.K (dyne /cm)
1	0.0001	48.3	56.511
2	0.0002	46.3	54.171
3	0.0003	44.5	52.065
4	0.01	42.7	49.959
5	0.02	40.9	47.853
6	0.1	39.8	46.566
7	0.2	39.1	45.747
8	0.3	38.7	45.279

Correction factor = 1.17

Table 3. The results of determination of surface tension (γ) phosphate ethanolamide

No	Concentration (%)	Surface tension (dyne/cm)	xF.K (dyne /cm)
1	0.0001	51	59.67
2	0.0002	49.8	58.266
3	0.0003	49.4	57.798
4	0.01	40.0	46.8
5	0.02	39.2	45.864
6	0.1	33.2	38.844
7	0.2	33.1	38.727
8	0.3	33.0	38.61

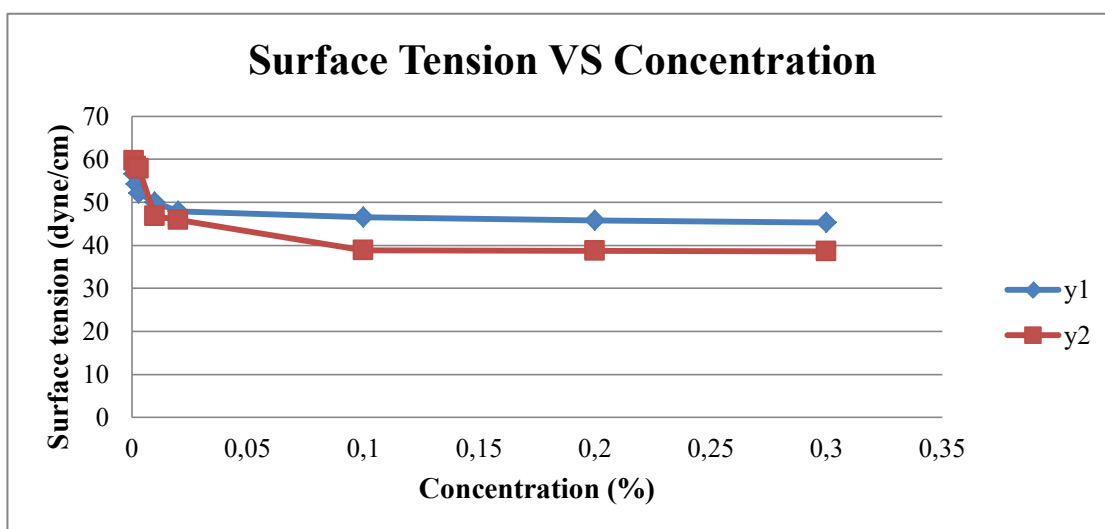


Figure 11. The graph of surface tension vs concentration

y₁ = ethanolamide; y₂ = phosphate ethanolamide

3.5 Melting Point Testing

A melting point test was carried out to analyze the purity of the amide compounds obtained. In general, the melting point of palmitamide is 107°C (Weast, 1982). From the Tabel 4, these compounds obtained showed that they were not pure, but have begun to approach the palmitamide melting point. They were still in the mixture which amide compound derived from FFA with the main component being palmitic acid.

Table 4. The Melting Point Test Result of Ethanolamide and Ethanolamide Phosphate

No	Compound	Melting Point (°C)
1	Ethanolamide	84-86
2	Phosphate Ethanolamide	92-96

4 Conclusion

In conclusion, phosphate ethanolamide compounds were synthesized by the esterification reaction of ethanolamide with phosphoric acid. This is supported by the characterization results obtained from FTIR, CMC value, and melting point. phosphate ethanolamide was also found with a yield of 63.19%. In this study, CMC values obtained for ethanolamide and phosphate ethanolamide at a concentration of 0.1% were 46.566 dyne/cm and 38.844 dyne/cm, respectively. This study also found that the melting point of each compound obtained still approached the melting point of palmitamide. Next, it can be investigated to obtain the pure phosphate ethanolamide.

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