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PREPARATION OF PALM-BASED ESTERAMINES USING CHEMICAL CATALYSTS

Keywords: Esteramines; quaternary ammonium compounds; cationic surfactants; triethanolamine; palm oil; palm oil fatty acids and biodegradable

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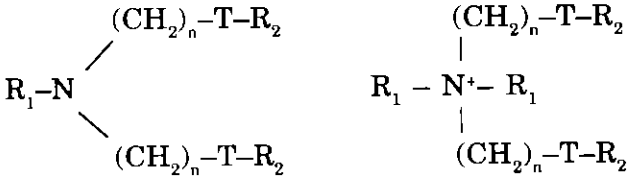
The reaction of fatty acids or of fatty esters with triethanolamine in the presence of an acid or a base, results in the formation of fatty esteramines. In the present work the effects of using various mole ratios of palm and tallow based fatty acids and amounts of catalyst were studied, as well as the reaction products in the presence and absence of solvent.

INTRODUCTION

A fatty esteramine is a compound consisting of a nitrogen atom carrying one, two or three alkyl groups, two of which contain an ester bond,T, as shown in *Figure 1*. It is a product resulting from a condensation of an alkanolamine and a fatty acid or fatty ester. The significant application of esteramines is as raw materials in the production of Esterquats, a new generation of cationic surfactants.



Esteramines **Esterquats**

Where,

R_1 = C_{1-4} alkyl, alkenyl or hydroxy alkyl
R_2 = C_{7-27} alkyl or alkenyl group
T = –O–C(=O)– or –C(=O)–O–
n = integer from 1 to 5

Figure 1. General structures of the esteramines and esterquats.

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Most of the structural factors known to affect the performance of esterquats are located on the original esteramine molecule. The contributing factors are the nature of the substituents R_1 and R_2, including the chain length, the degree of unsaturation, branching, presence of a hydroxyl or ethoxy group, and the ester linkage, T. The positive charge on the nitrogen atom, introduced during the quaternization of the esteramine, is to impart property of depositing on a surface, *(Figure 2)*. This is because most surfaces are negatively charged and easily attract a positively charged molecule. When a positively charged molecule is adsorbed on to a surface, any hydrocarbon chain present in the molecule will extend outwards away from the surface. This configuration provides lubricity (owing to the hydrocarbon chain) and an antistatic (owing to the neutralization of the surface charge).

At present, the demand for nitrogen derivatives is declining, especially in European countries (Eisenbrand *et al.*, 1991). This is due to the finding that there is possible contamination with nitrosamines in products containing nitrogen derivatives, and that they show unfavourable biodegradation characteristics. Nitrosodiethanolamine, from the nitrosation of diethanolamine, has been detected by gas chromatography in cosmetic products (Ikeda *et al.*, 1990). The concern over the carcinogenicity of such substances has driven some producers to avoid using nitrogen derivatives, especially those developed from primary and secondary amines. Recommendations have also been made to use only triethanolamine of 99% purity (free of mono and diethanolamine).

The two most common quaternary ammonium compounds for textile softeners used to be dialkyldimethylammonium compounds and cationic imidazolines. A schematic diagram on the potential breakdown of the dialkyldimethylammonium compounds, cationic

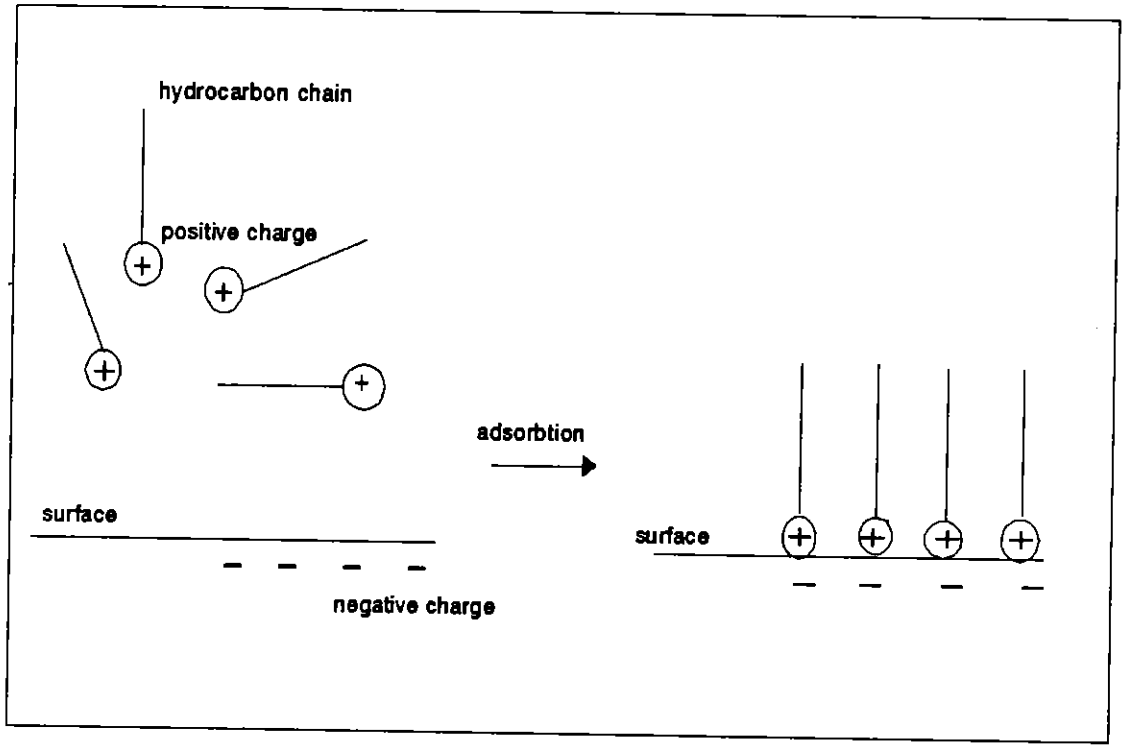


Figure 2. Schematic diagram showing the adsorption of positively charged molecules on to a negatively charged surface.

imidazolines and esterquats is shown in *Figure 3*. The esterquats can be broken down into smaller molecules more easily than can imidazolines and quaternary ammonium compounds.

The synthesis of imidazolines has been reported by Hamirin *et al.* (1991) together with a process to produce amphoteric surfactants. The route for the preparation of these surfactants is shown in *Figure 4*. Because of the biodegradability problem, a project to look into the preparation of esterquats, which satisfy the requirements of non-toxicity and biodegradability, was initiated . Fatty esters of triethanolamine were chosen for study since they can be prepared from pure triethanolamine, which is free of mono and diethanolamine, so that the resulting product is unable to form nitrosamines. The labile ester linkage between the long alkyl radicals and the amine core of the esterquats can easily be hydrolysed, giving smaller molecules of fatty acids and parent substance. Being small, these can easily be attacked by microorganisms and are therefore readily biodegradable (Puchta *et al.*, 1993).

The conditions affecting the synthesis of the esteramines from triethanolamine and the palm based fatty acid (myristic) or an ester (methyl myristate) were first investigated, and then the conditions affecting the synthesis from triethanolamine and palm-based or tallow fatty acids.

The synthetic route to the esterquats is illustrated in *Figure 5*. The process consists of two steps. The first is the formation of the

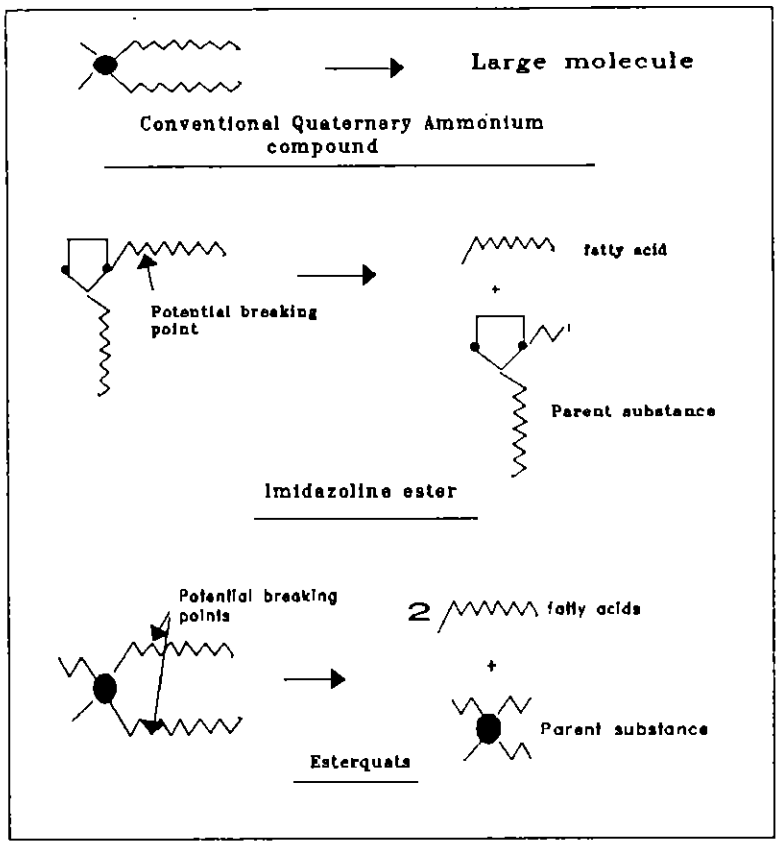


Figure 3. Degradation of conventional quaternary ammonium compounds, imidazoline esters and esterquats.

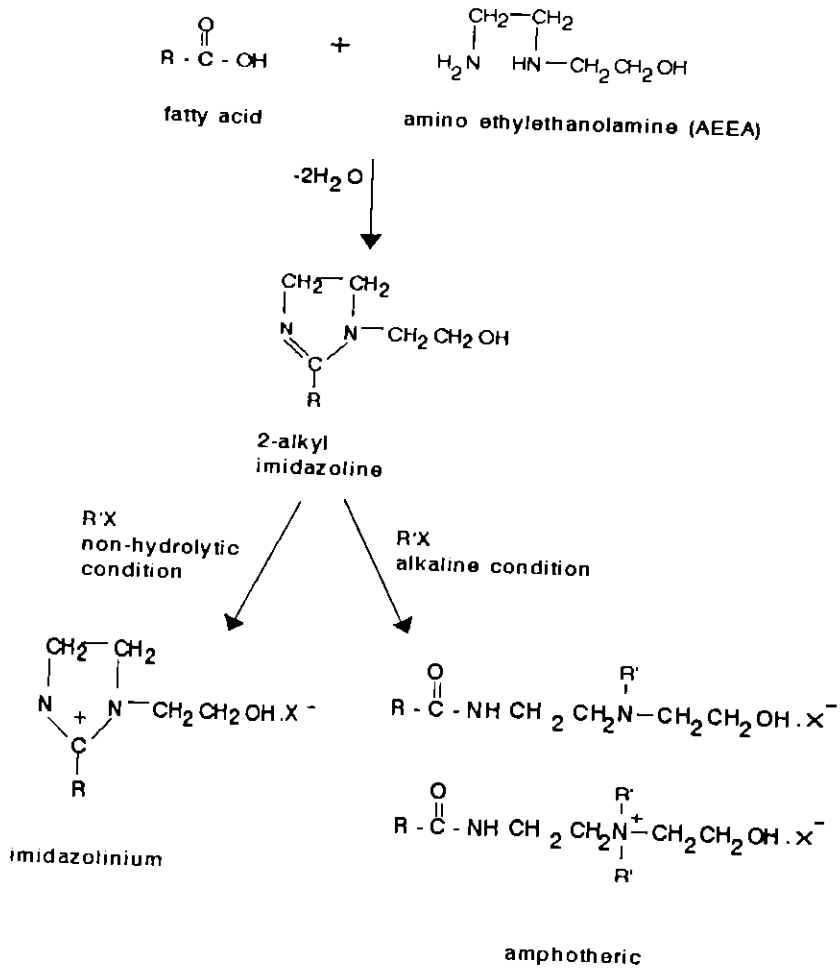


Figure 4. The route for the preparation of cationic imidazolinium and amphoteric surfactants.

esteramine by esterification of fatty acids with triethanolamine. This is followed by the reaction of the esteramine with a quaternizing agent to introduce the positive charge on to the molecule. For the synthesis of esteramines the procedure outlined by Trius *et al.*(1991) was modified as described below.

MATERIALS AND METHODS

Materials

A mixture of fatty acids from palm oil and palm kernel oil and pure myristic acid were obtained from Southern acid (M) Sdn. Bhd. (Kapar, Malaysia). Methyl myristate and tallow fatty acid was obtained from Henkel(M) Sdn. Bhd. (Teluk Panglima Garang, Malaysia). The approximate fatty acid composition in the tallow fatty acid is as follows: 0.5% lauric acid, 3% myristic acid, 25% palmitic acid, 19% stearic acid, 3% palmitoleic acid,40% oleic acid and 4% linoleic acid. Triethanolamine (TEA) of 99 % purity, phosphinic acid in 50 % solution, and xylenes were purchased from Chemica Fluka (Switzerland). Sodium methoxide catalyst was freshly prepared from sodium metal and absolute methanol as a 1 % solution.

Methods of analysis

Analytical Thin Layer Chromatography (TLC)

Silica gel $60F_{254}$ (Merck) precoated on plastic

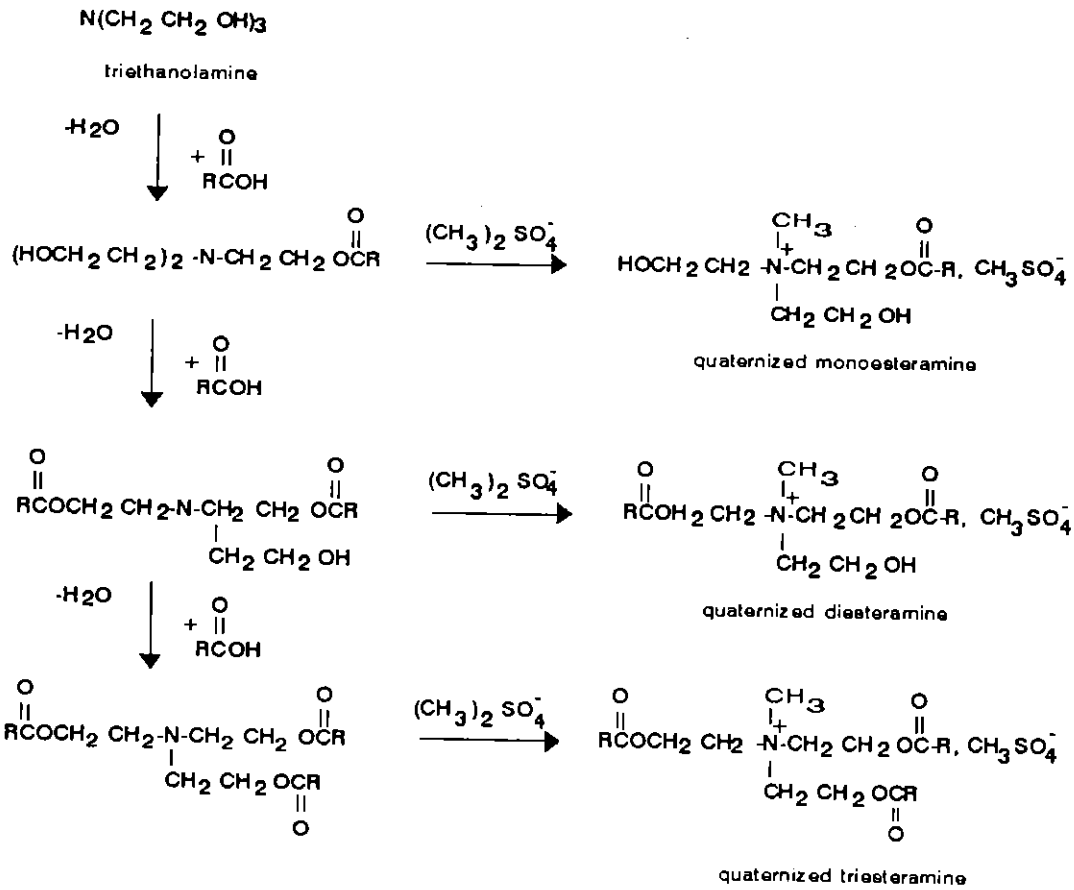


Figure 5. A pathway for the synthesis of the esterquats from fatty acids and triethanolamine.

sheets was used as the stationary phase. The solvent systems were prepared from hexane and diethyl ether using a ratio of 75:25 in connection with the esterification of fatty acids and 85:15 with the esterification of myristic acid.

Preparative TLC

Glass plates 20 cm × 20 cm were coated with silica gel 60 (Merck). The solvent system hexane: diethyl ether (75:25) was used. The spots were developed in an iodine chamber . The yellow bands on the plate were then scraped off and extracted. The fraction with the lowest R_f was extracted with acetone, the second with chloroform and the third with hexane.

Identification of products

Gas chromatography

The development of the products from the

reaction mixture was monitored by gas chromatography (Perkin Elmer Sigma 2000) using a column prepared with OV-1. The samples were first silylated as described below. The column temperature was set at 170°C and progressively increased to 250°C at a rate of 3° C/min and with a gas flow rate of 25 ml/ minute.

Silylation procedure

About 30 mg of the sample was weighed into a vial with a stopper. One ml of GC grade pyridine was added to dissolve the sample completely. Hexamethyldisilazane (HMDS) (0.2 ml) and trimethylchlorosilane (TMCS)(0.1 ml) were added. The sample was shaken for 15-30 seconds and allowed to stand for 5 minutes. The supernatant was used for analysis.

Infrared spectroscopy

Samples containing mixtures of the products indicated by analytical TLC were separated by preparative TLC and each fraction was then analysed using a Perkin-Elmer 1750 IR spectrometer. Solid samples were analysed as KBr pellets, while liquid samples were analysed neat in a NaCl capillary cell.

Gardner colour

After removing the solvent, the Gardner colours of the products were determined using the instrument from the Gardner Laboratory, Inc. Bethesda, Maryland.

Acid value

The acid values of the samples were determined according to A.O.C.S. official method Te 1(a).

Preparation of esteramine

Esterification of fatty acids

The esterification of fatty acids was initially accomplished without using a solvent, under reduced pressure and in an inert atmosphere. The temperature for the reaction was set at 160°C. The reaction mixture turned dark brown. Esterification in the presence of a solvent (xylene) was then attempted. Water generated by the reaction was removed from the mixture in order to push the reaction forward. The apparatus shown in *Figure 6* was used to remove water continuously as an azeotropic mixture with xylene.

Fifty grams (0.22 mol) of myristic acid was placed in a 500 ml three-necked round-bottom flask and heated to 100°C under an inert atmosphere (N_2). Xylene (125 ml) was added

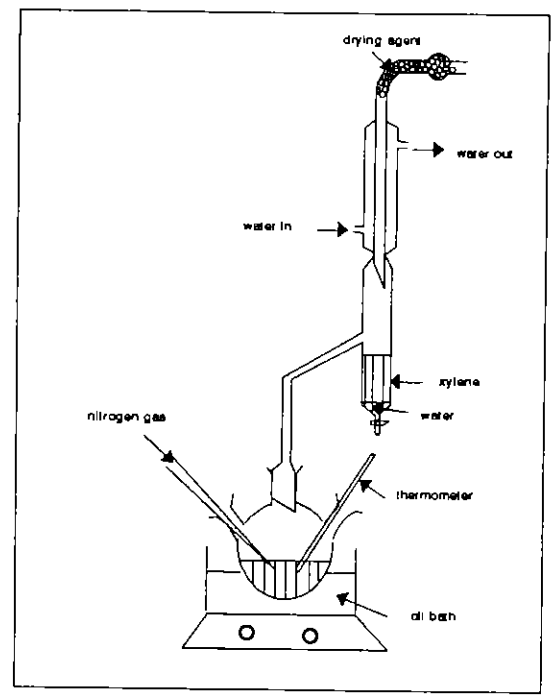


Figure 6. The apparatus for the esterification of fatty acid.

to the fatty acid followed by 1.0 ml of 50% phosphinic acid. The temperature was then raised to 140°C. For the reaction of myristic acid with TEA in the ratio of (2:1), 16.3 g (0.11 mol) of TEA was added dropwise into the reaction flask. Samples were taken every hour and analysed by TLC.

After 4 hours of reaction, a small amount of sample was withdrawn. The fractions in the reaction mixture were separated by preparative TLC. Three major fractions were extracted from the silica gel and analysed by IR.

Transesterification of a methyl ester

The 1% sodium methoxide solution required was freshly prepared prior to starting the transesterification reaction. Sodium metal (0.1 g) was cut into smaller pieces and washed in petroleum ether. The metal was then dissolved in 10 ml absolute methanol.

The transesterification of methyl esters was carried out in a 500 ml three-necked round-bottom flask equipped with a condenser. Fifty grams (0.21 mol) of methyl myristate was placed in a 500 ml three-necked round bottom flask and heated to 60°C under nitrogen. When the temperature reached 60°C, 5 ml of the 1% sodium methoxide solution was slowly added with uniform stirring, followed by 29.0 g (0.19 mol) of TEA. The temperature was then raised to 70°C. The progress of the reaction was monitored every half hour for 2 hours on the TLC with the solvent system hexane: diethyl ether (85:15).

Effect of varying the mole ratio

Samples were prepared to determine the effect on the reaction mixture of three different ratios of fatty acid to TEA, 1:1, 2:1, and 3:1. Mixtures of fatty acids from palm oil and tallow were used. The reactions were carried out in both the presence and absence of solvent. Reactions in the absence of solvent were monitored by determining the acid value while reactions in solvent were monitored by gas and thin layer chromatography.

Effects of varying the amount of catalyst

Three series of reactions were carried out to study the effect of using various percentages of catalyst ranging from 0.5% to 2.0% in the reaction mixtures with ratios of 1:1, 2:1, and 3:1 for fatty acid to TEA. Attempts were made to measure the colour of the products.

RESULTS AND DISCUSSIONS

Esterification of a pure fatty acid (myristic)

The esterification of 1 mole TEA with 2 moles of myristic acid produced a mixture of products. On TLC, spots can be observed at $R_f = 0$, $R_f = 0.20$ and, $R_f = 0.45$, $R_f = 0.61$ and $R_f = 0.74$. Spots at $R_f = 0$ and $R_f = 0.45$ were identified as the unreacted starting materials while the rest were the products. Separations of the individual fractions by column chromatography and purification by preparative TLC were then carried out. The fractions were analysed by IR spectroscopy. Only fractions at $R_f = 0.20$, $R_f = 0.61$ and $R_f = 0.74$ were analysed. *Figure 7* shows the IR spectra of the fractions obtained.

For the three spectra, a sharp transmittance at wave numbers corresponding to 3400 cm^{-1} and 1740 cm^{-1} implied the presence of hydroxyl and ester carbonyl, respectively. Reduction in the percentage transmittance at 1740 cm^{-1} in the spectra of the three fractions at $R_f = 0.20$, 0.61 and 0.74 (considered in that order) indicated that there was an increasing number of ester linkages. This was followed by an increase in the percentage transmittance at 3400 cm^{-1}, which implied reduction in the hydroxyl group.

Transesterification of a fatty ester

Based on TLC, the esterification of a fatty ester (methyl myristate) showed a similar pattern to that of the esterification of the free fatty acid (myristic), (*Figure 8*).

The progress of the reaction with methyl myristate could be monitored directly on the TLC plate. Examples of samples withdrawn at 30 minute intervals and spotted on the plate are shown in *Figure 9*.

The disappearance of the spot at $R_f = 0.9$ implied that the methyl ester had reacted fully over the period of two hours, and that, therefore, a shorter time was required for the reaction between fatty ester and TEA than for fatty acid and TEA. The use of a solvent was not necessary in this reaction as the methyl ester was a liquid. In addition, a lower temperature was required as compared to the esterification of the free fatty acid.

Effects of varying the mole ratio on the esterification of free fatty acids

The series of reactions with varying mole ratios and without solvent were monitored by the determination of the acid value. Plots of

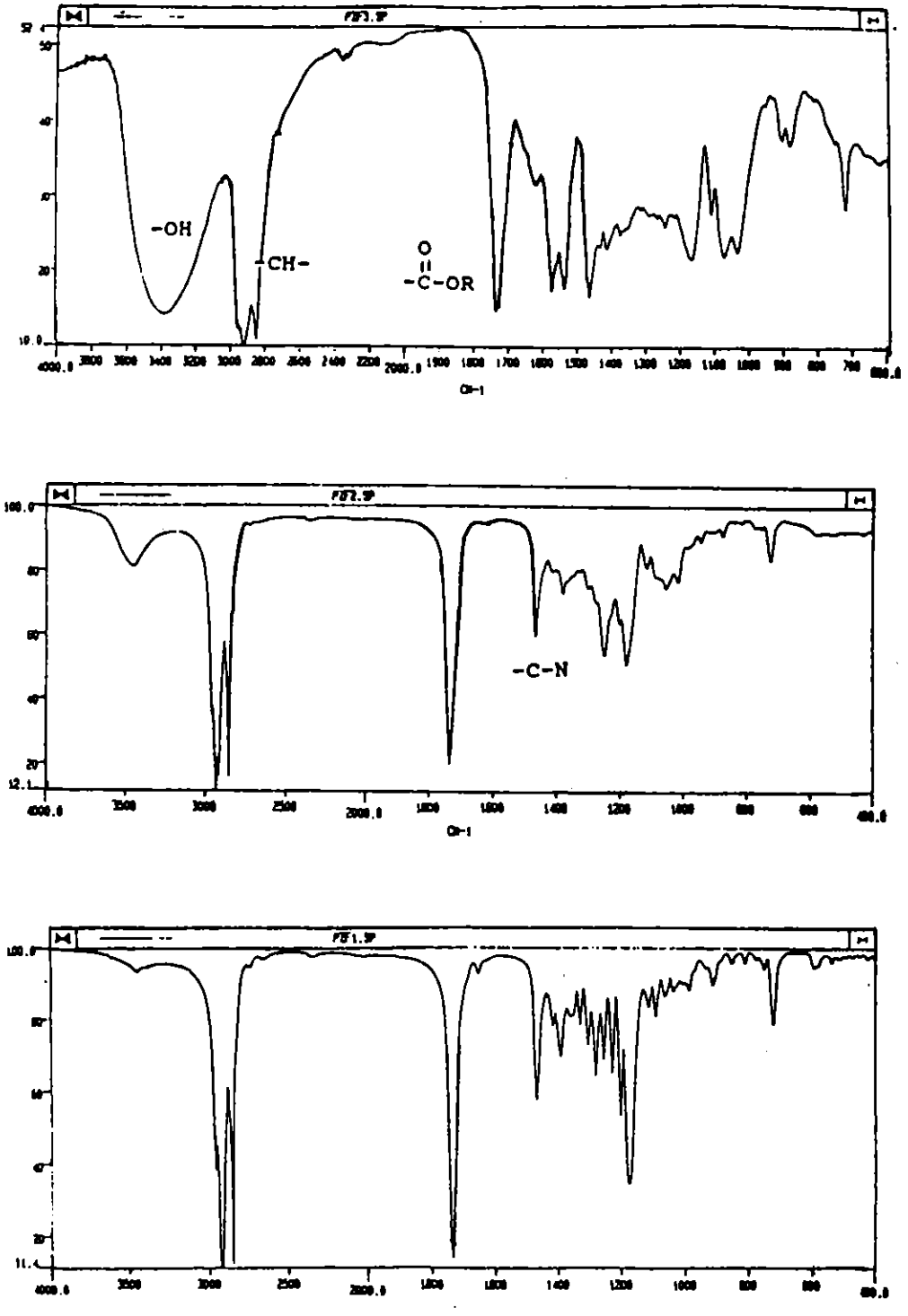
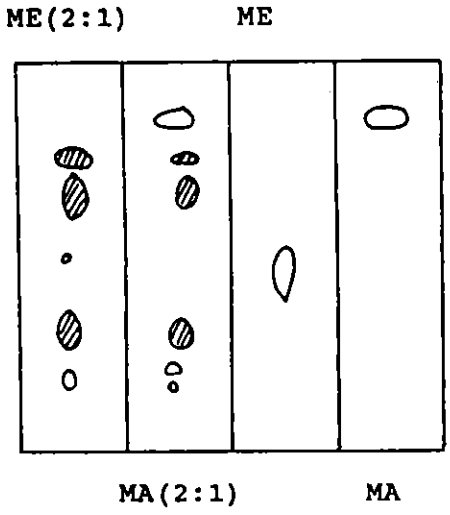


Figure 7. IR spectra of the fractions at R_f = 0.20, R_f = 0.61 and R_f = 0.74.



MA (2:1) = esterification of fatty acid at 2:1 ratio
ME (2:1) = transesterification of fatty acid at 2:1 ratio
MA = myristic acid
ME = methyl ester

Figure 8. Comparison of TLC analysis between esterification of a fatty acid and transesterification of a fatty ester.

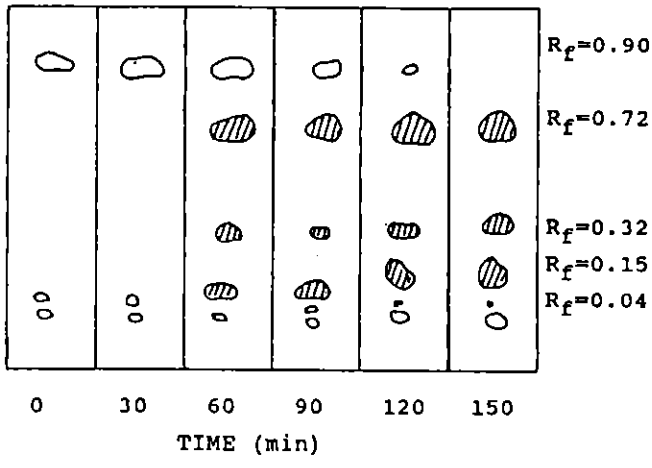


Figure 9. The progress of the transesterification of methyl myristate.

acid value versus time for the reactions using mixture of fatty acids from palm oil and tallow are shown in *Figure 10*. No marked differences were observed between the plots of palm fatty acids and tallow fatty acids except at a ratio for fatty acids to triethanolamine of 3:1 where palm fatty acids were found to react faster than those from tallow.

The series of reactions carried out in solvent were monitored by gas chromatography at the end of reaction time of 4 hours. The chromatograms for reactions with fatty acid to triethanolamine ratios 1:1, 2:1 and 3:1 are shown in *Figure 11*.

The gas chromatograms showed product peaks at 38.70 and 46.30. Peaks at 10.10, 15.70 and 20.20 were identified as myristic, palmitic and oleic/stearic acids respectively, while the lauric peak overlapped with the TEA peak. Comparing chromatograms (a) to (c), it can be seen that as the portion of fatty acid increases, the peaks at 15.70 and 20.20 increase, indicating that there was an increase in the unreacted fatty acid. With a ratio of 1:1, excess of triethanolamine can be detected at 5.12. The Gardner colour of the product from the reaction with 1:1 ratio was slightly darker (Gardner colour = 4) than in the case of the 2:1 or 3:1 ratios. For the peaks at 38.70 and 46.30, there was a decreasing trend from chromatogram (a) to chromatogram (c). These two peaks could be the result of the esterification of palmitic and oleic/stearic acids. A reduction in the chromatogram at these positions indicated that an increase in fatty acid pushed the reaction towards producing less mono-substituted and more of di- and tri-substituted products.

Effects of varying the amount of catalyst

The results shown in *Table 1*, indicate that increasing the amount of catalyst had a significant effect on the colour and physical state of the products. Gardner colour improved as the percentage of the catalyst was increased. When the ratio was 3:1 the percentage of catalyst did not have any effect on the colour of the products. The products with Gardner colour 1 were solid.

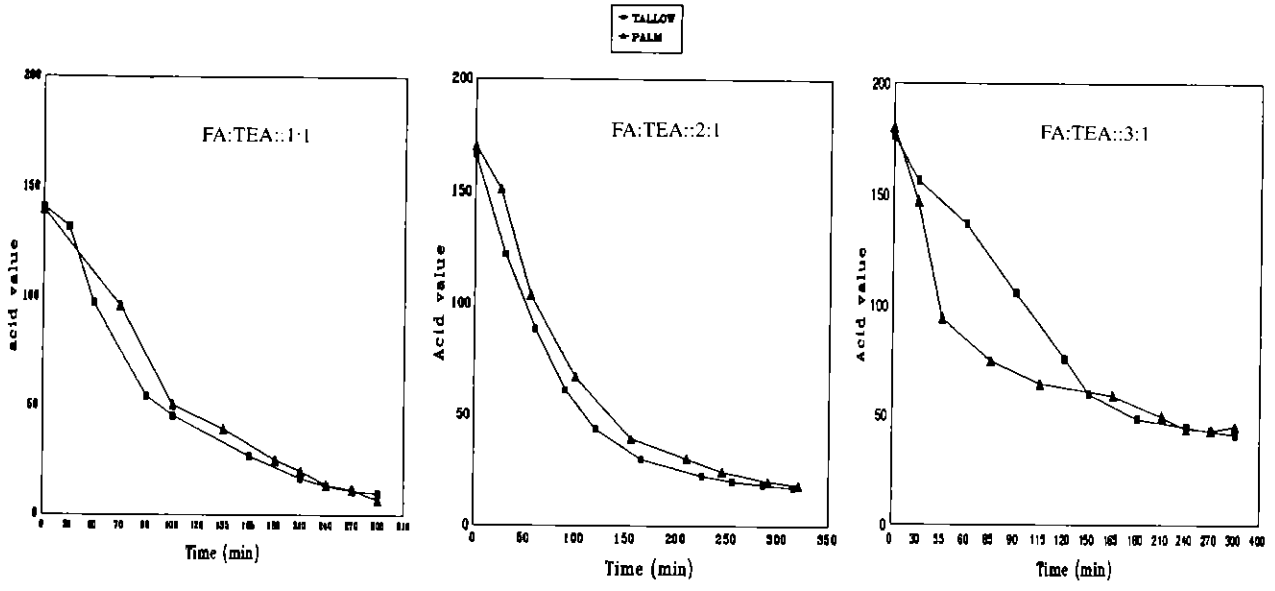


Figure 10. Acid values during the esterification of palm oil and tallow fatty acids at different molar ratios of fatty acid (FA) to triethanolamine (TEA).

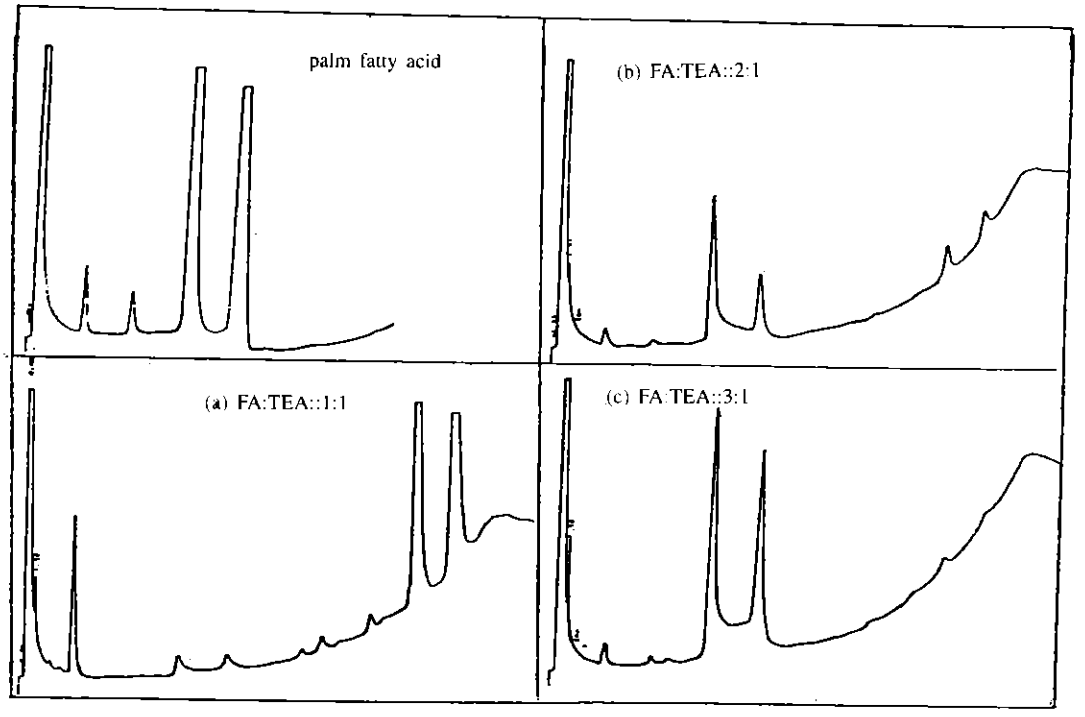


Figure 11. Gas chromatograms for the esterification of palm oil fatty acids a t different molar ratios of fatty acids (FA) and triethanolamine (TEA).

TABLE 1. GARDNER COLOUR DETERMINATION ON PRODUCTS OBTAINED USING DIFFERENT PERCENTAGES OF CATALYST

Catalyst (%)	Gardner colour		
	(1:1)	(2:1)	(3:1)
0.50		4	1
0.75		2	1
0.85	3–4	2	1
1.00		2	1
1.25		2	1
1.30		2	1
1.50	2	1	1
2.00	2	1	1

CONCLUSIONS

These studies showed that esteramines could be synthesized by reacting myristic acid, methyl myristate, palm or palm kernel oil fatty acids or tallow fatty acids with triethanolamine. Various combinations of mono-, di-, and tri- esteramines can be prepared by varying the mole ratio of the reactants. Increasing the percentage of catalyst generally improved the colour of the reaction mixture. IR spectra indicated the presence of the ester link at a wave number corresponding to 1740 cm^{-1}. The attachment of the ester groups on to the triethanolamine molecule was confirmed by the increase in the percentage transmittance of the hydroxyl group at 3500 cm^{-1} as more ester groups were attached to the triethanolamine.

The reaction conditions differ slightly depending on whether free fatty acids or fatty esters are used as the starting materials. Esterification of fatty acids could be completed at a temperature of 140° C in the presence of xylene as solvent after four hours. The transesterification of methyl myristate could be accomplished at lower temperatures of 80°C to 100°C within two hours. No solvent was required in this latter process but methanol is produced as a by-product.

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