Microwave Assisted Synthesis of Esterquat for Fabric Softening Applications

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Summary: An efficient method has been proposed for the synthesis of esterquat cationic surfactant, considered as a new type of biodegradable material utilized as a textile softening agent. This method involves microwave assisted esterification of stearic acid with triethanolamine followed by the quaternization with dimethyl sulphate. This method requires much less time for esterification and ensures good yield and high purity. The obtained quaternary ammonium compound was characterized by its cationic content and FT-IR analysis. A comparison with conventional thermal method was also done.

Key words: Microwave irradiation, esterquat, cationic content, esterification, quaternization.

Introduction

Esterquat cationic softeners were discovered in early 20th century but were not used by textile industry until 1930's.[1] They become technically important after Domagk discovered their bacteriostatic and fungicidal properties.[2] Esterquats are one of the biodegradable cationic softeners due to the presence of ester linkage. [3] Esterquat cationic surfactant gains superiority due to its environmental friendly, nontoxic and biodegradable properties.[4] Besides biodegradability, additional advantages such as excellent softening properties, suitability for various fabrics and simple preparation procedures, have been discovered with the use of esterquat cationic surfactants as textile softening agents.[5]

Several methods have been reported for the synthesis of esterquat, a quaternary ammonium compound. Miao with his coworkers synthesized a novel esterquat cationic surfactant via the reaction between dodecyldimethyl ammonium chloride and lauric acid. [5] Bajpai and Tayagi used microwave irradiation method for the synthesis of dialkyldiamido imidazolines followed by its quaternization with dimethyl sulfate. [6] Jia and his coworkers synthesized a novel cationic Gemini surfactant with the hydrophenanthrene structure from dehydroabietic acid by the use of conventional thermal conditions and microwave irradiation. [7] Tayagi with her coworkers synthesized the esterquat by esterification of tallow fatty acids and triethanolamine followed quaternization with dimethyl sulphate by conventional heating procedure. [8]

General methods for the synthesis of esterquat cationic softener involve dehydration reaction between fatty acids and polyamines under vacuum followed by the quaternization with suitable alkylating agent. The conventional thermal method suffers from disadvantages such as long reaction time and low yield of product.[9] Nowadays, use of microwave irradiation in organic synthesis is gaining special attention due to the generally low reaction time, better yield and high purity of products.[10]

This paper describes a comparison between conventional thermal procedure and microwave irradiated method for the synthesis of esterquat cationic softener by condensation of stearic acid and triethanolamine and their quaternization by using dimethyl sulfate as the quaternizing agent. The obtained product in each case was characterized by its cationic content and structure was confirmed by FT-IR analysis.

Results and Discussion

Esterquat constitute an important class of cationic surfactant. The aim of the research was to synthesize esterquat by a method involving less reaction time and promises better quality and yield of the product.

The diester was synthesized by both conventional thermal method and microwave irradiation method. The lowest acid value of product was obtained after 6-7 hours of constant heating and stirring at 140°C and was observed as 5.6. While in case of microwave irradiation method, the lowest acid value of diester *i.e.* 4.1 was obtained after 18 min. Also the yield of diester in case of microwave irradiation method was significantly more as compared to conventional thermal method. As mention in Table-1 and Fig. 1.

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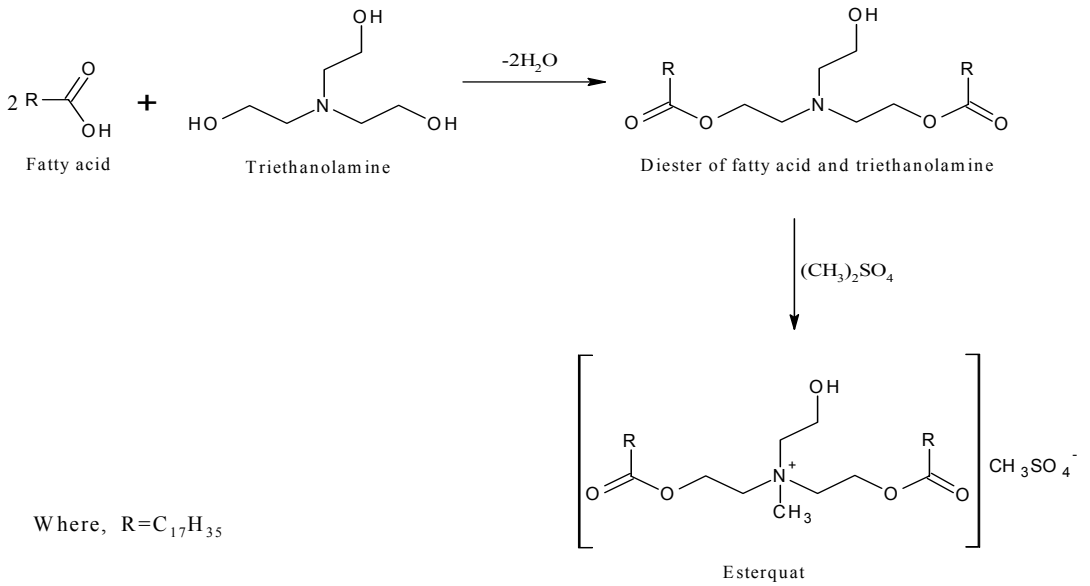

Fig. 1: Stepwise scheme for synthesis of esterquat.

Table-1: Properties of synthesized diester.

Properties	Conventional Method	Microwave Irradiation
Acid Value mg KOH	5.6	4.1
Yield (% wt.)	81.5	90.1

The prepared diester in both cases was treated with different mole ratios of dimethyl sulfate for their quaternization. The quaternization was carried out at 60-70°C for 2 hours in each case and cationic content for each product was determined. The results are tabulated in Table-2. The results indicate that quaternization of diester for 2 hours using 1:1.5 molar ration of diester to dimethyl sulfate gives better yield and cationic content in both cases.

Table-2: Properties of synthesized esterquat

Sr. No.	Diester :DMS	Conventional Method		Microwave Irradiation	
		Cationic Content (%)	Yield (%)	Cationic Content (%)	Yield (%)
1	1:1.5	35.7	81.3	38.9	88.7
2	1:1.75	28.5	77	30.2	84.3
3	1:2	25.1	72.5	25.7	79.5

Alkylation was an exothermic reaction and temperature of ester rose about 4-5°C after addition of dimethyl sulfate, so it was added slowly. Alkylation lightened the color of esterquat to some extent. Solubility test indicate that esterquat is sparingly soluble or relatively insoluble in warm water. The reason being long chain fatty acids resist the solubility. Emulsifiers are needed to dissolve in water.

Structure of product was confirmed on the basis of FT-IR spectroscopic data. The FT-IR data obtained for diester and esterquat cationic softener is tabulated in Table-3. The OH stretching vibration and deformation were indicated by the peaks at 3437 and 1058cm^{-1} respectively. The peak at 3354cm^{-1} was the conformation of free OH of diester of fatty acid and triethanolamine. The presence of tertiary nitrogen in diester and esterquat was indicated by peaks at 2857cm^{-1} and 1644.4cm^{-1}.

Table-3: Instrumental data for diester and esterquat

Group	Wave number for Diester (cm^{-1})	Wave number For esterquat (cm^{-1})
OH Streching	3354	3437
OH Deformation	1094	1058
C=O	1737	1727
C-O	1173	1177
Tertiary N	2850,1629	2857, 1644.4
S=O		1004.2, 757, 826
CH_2	2918	2914
Quaternary N^+		1466.4

FT-IR spectra obtained for diester and esterquat cationic softener were observed to be same except of the peaks 1000.4 cm^{-1}, 826 cm^{-1} which were due to the presence of S=O group in esterquat. Moreover the peak at 1466.4 confirmed the quaternary nitrogen of esterquat.

The synthesized esterquat was also applied to 100% cotton fabric to evaluate its application as softener. It imparts good softness and good handling to the said fabric when compared with untreated fabric [11, 12].

Microwave irradiation method proved to be less time consuming, ensures better quality and yield of the product as compared to conventional thermal

procedure. Reaction time in esterification step for conventional thermal method was found 6-7 hours while incase of microwave irradiation was just 18min. For quaternization of obtained diester, 1:1.5 ratio of diester to dimethyl sulfate gave best results in terms of yield and cationic content. The product obtained is highly suitable for textile softening applications.

Experimental

Reagents and Materials

All reagents/chemicals used were of AnalR grade and used without further purification.

Esterification

Conventional Thermal Procedure

0.2mol of stearic acid were taken in a two-necked round bottomed flask (500mL) equipped with a magnetic stirrer and vacuum assembly. Firstly, stearic acid was melted completely and then 0.1mol of triethanolamine was added. The reaction was carried out at 140°C, for 6-7 hours. 25mmHg vacuum was created in the reaction assembly to remove the reaction water. The acid value was checked after every half an hour.

Microwave Irradiation Method

A 250mL single-necked round bottomed flask equipped with a vacuum assembly was placed in a microwave oven (2450 MHz). Stearic acid (0.2mol) and triethanolamine (0.1mol) were condensed in microwave irradiation (15/15 sec interval) for 18min. reaction water was removed by creating vacuum (25mmHg). Acid value was the parameter to indicate the completion of reaction.

Quaternization

The diester obtained in both cases was treated with different mole ratios of dimethyl sulfate to produce esterquat. The requisite quantity (1.0mol) of diester was dissolved in 50mL of petroleum ether in 250mL two-necked round bottomed flask equipped with magnetic stirrer. Thermometer was inserted in one neck of flask and condenser was fitted on other. When the diester was completely dissolved, then 1.5 mole of dimethyl sulfate (3.65g) was added drop by drop with constant stirring at 70°C. Reaction mixture was stirred for 2 hours. Esterqaut contents were transferred to a beaker and the petroleum ether was evaporated by heating in water bath. It was then weighed in order to calculate the yield stoichiometrically. Similarly 1.75mole (3.9g) and 2 mole (4.15g) of dimethyl sulfate were reacted with diester to form the esterquat.

Determination of Cationic Content [8]

Reagents

1. *Chloroform*
2. *0.004M Sodium Lauryl Sulphate Solution*

1.464g of sodium lauryl sulphate was dissolved in 1000mL of distilled water to prepare 0.004M solution.

3. *0.003% Methylene Blue Solution*

0.03g of methylene blue, 30g of sodium sulfate and 4.1mL of concentrated sulfuric acid were taken in distilled water and diluted to 1000mL with distilled water.

4. *0.004M Esterquat Solution*

Adequate quantity of esterquat was weighed and dissolved in 20-30mL of ethanol and made the volume up to 250mL with distilled water.

Procedure

10mL of standard sodium lauryl sulfate was taken in 250mL stoppered flask and 25mL of methylene blue solution was added followed by 15mL Chloroform. After gentle shaking, flask was allowed to stand until the two layers separated. The organic layer was blue colored. It was then titrated against 0.004M solution of esterquat. Towards the end point the color would start migrating to the aqueous layer. The reading was noted down when the same color intensity in both the phases was observed. Cationic content was measured as follows:

$$\text{Molarity of esterquat } M_1 = \frac{10M_2}{V_1}$$

where,

M_1 = Molarity of esterquat
M_2 = Molarity of sodium lauryl sulfate
V_1 = Used volume for esterqaut

$$\text{Cationic content} = \frac{M_1 \times \text{mol weight ofesterquat}}{\text{weight of sample} \times 4} \times 100$$

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