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SYNTHESIS OF TALLOW BASED ESTERQUAT

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Abstract: "Esterquat" which is basically the class of surface active quaternary ammonium compounds have general formula $R_4N^+X^-$ .Locally available cheap raw material were used to synthesized cationic fabric softeners. Free fatty acids were derived from beef tallow and were treated with triethanolamine at 135°C. The obtained di-ester was refluxed with different mole ratios of dimethyl sulphate to obtain a viscous quaternary ammonium compound; the best mole ratio for DMS to Esterquat was 1.5:1. The synthesized Esterquats were evaluated for percentage yield (81.7%) and cationic content (35.7%). Physical and chemical properties were evaluated by various tests like feel panel test, water absorbing capacity and heat stability on different fabric substrates i.e., synthetic as well as natural. It was further characterized by IR spectra.

Introduction

Mostly Quats are solids and have indefinite melting point and decompose on heating. Lower molecular Quats are soluble in water e.g. tetra methyl ammonium chloride(1) while solubility decreases in polar solvent and increases in non polar solvent with the increase in molecular weight of quaternary ammonium compound (> C10) (1-3).

Higher order quaternary ammonium compound exhibit surface active properties and are known as cationic surfactant. (4). It is the main constituent of fabric softener composition. Fabric softener also called Fabric Conditioner is used to prevent static cling and make fabric feel softer. Popular brand names include Lenor, Downy, Snuggle, and Comfort. The use of fabric softener may however reduce the water absorption capabilities of the fabric, and is contradicted in some articles like microfiber textiles. An effective softener must be readily dispersible in rinse water and rapidly absorbed so that uniform deposition on the fabric can occur within short treatment time and generally, exhaustion should take place in about five minutes, for the softener to be effective and economically useable. It must impart softness, fluffiness and lubricity to the treated cloths and reduce static build up (5). The first fabric softeners were developed for the textile industry during the early twentieth century. At that time the process used to dye cotton fibers left them feeling harsh to skin. In the early 1900s, preparations known as cotton softeners were developed to improve the feel of cotton fibers after dyeing. A typical cotton softener consisted of seven parts water, three parts soap, and one part olive, corn, or tallow. Cationic softeners were discovered in the early 20th century but were not used by textile industry until the late 1930's (6). They become technically important after Domagk discovered their bacteriostatic and fungicidal properties (7).

The first house hold fabric use softener was produced in U.S in 1955's was di (hydrogenated tallow) dimethyl

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ammonium chloride (8). Softeners were introduced about 10 years later in Europe (9-10) Triethanolamine (TEA)-based esterquat has been the primary ingredient in European fabric softeners for several years and is becoming the global molecule of choice. Although it has an excellent environmental profile, TEA esterquat has been plagued by mediocre performance compared to historical molecules such as dihydrogenated tallow dimethyl ammonium chloride and ditallow imidazoline quat. (11)

Beside anionic, silicon and non ionic fabric softener mostly cationic fabric softener are commonly used. The fabric softeners are called cationic because the positive charged hydrophilic parts are predominant in the rinse water when cationic softeners are added. Major area of cotton fabric is negatively charged, so all the cations are picked up by the fabric and are retained on the fabric during the rinsing process when fabric softeners are applied. The hydrophobic part of fatty hydrocarbons is the agent that causes cationic softeners to soften the fibers in fabric (12)

Beside the fabric softening the Esterquat commonly form the foundation of formulations in the antimicrobial industry. Many studies have been conducted on the biological activity of surfactants derived from fatty acids viz. lauric acid, myristic acid, stearic acid and palmitic acid and palm fatty acid with polyamine, i.e. 1(2-hydroxyethylpi-perazine). (13)

The inclusion of ester linkages into the aliphatic chains has significantly improved the kinetics of biodegradation of the cationic surfactants, lowering the environmental exposure levels. This new generation of fabric softening agents combines a good environmental profile with the structural features required for an effective fabric conditioner. (14)

Esterquats are generally prepared by reaction of two mole of tallow fatty acid and one mole of triethanolamine then the diester was quarernized by (dimethyl sulfate)DMS.

Material and methods

All the chemical used for the synthesis of Diester and Esterquat were of chemical grade.

Apparatus

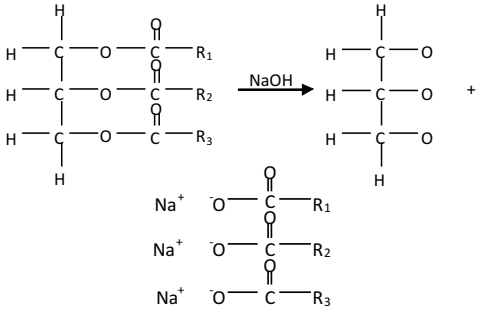
Rotary evaporator with Chiller, Burette, pipette, round bottom flask, stirring hot plate with Teflon follower.

Experimental work

1. Isolation of free fatty acid from tallow

For the preparation of free fatty acids various steps were performed. In the first step saponification of tallow was calculated. For this 0.9 g of soap was taken in 250ml volumetric flask and was dissolved in small amount of isopropanol. 2 drops of phenolphthalein was added as indicator. It was titrated with 0.1N alcoholic KOH with constant shaking until pink color produced which persisted for 15 seconds.

100g of tallow was weighed and was heated in beaker on hot plate until it was melted. Then 50% sodium hydroxide solution was added in it maintaining the temperature at 105°C, alkali was added in little excess until there was no increase in free fatty acid content.

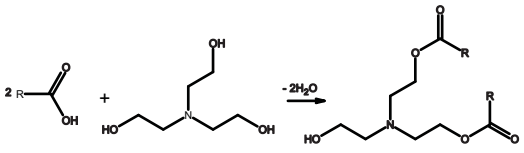


The acid hydrolysis of prepared soap was performed and for this glycerin was removed. Soap was stirred with sufficient amount of water until to get honey consistency. Mechanical stirrer was used in this operation. In this way a uniform sticky solution was formed. It was treated with 7N HCl solution to get highly acidic pH. The upper free fatty acids were decented. The free fatty acids were off-white in appearance. The acid value of free fatty acid was calculated by standard method.

2. Preparation of diester of tallow fatty acid

100g of free fatty acid was taken in the evaporating flask of rotary evaporator. Then 17.5g triethanolamine (1 mole) and 1ml of sodium methoxide was added in it. The temperature of paraffin oil bath was adjusted at 135^{O}C. The temperature of cooling fluid circulating in condenser wall was set at 5^{O}C. 25mmHg vacuum was created in the reaction assembly to remove the water. The acid value was checked after half an hour. The reaction was continued until its acid value reached 6.02.

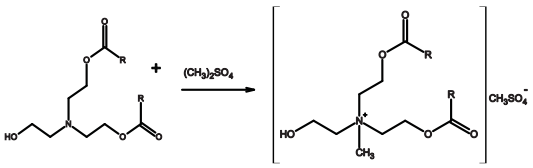
In varying the above experiment orthophosporic acid was used instead of sodium methoxide using the above assembly. The reaction was continued until its acid value reached 5.6.



Free fatty acid **triethanolamine** **diester of triethanolamine**

3. Esterquat Synthesis

By considering the alkyl chain of free fatty acid mainly of C-18 diester of triethanolamine was treated with different mole ratios of dimethyl sulphate to produce Esterquat. For this 1 mole of diester of triethanolamine (20g) was dissolved in 50ml of petroleum ether in 250 ml round bottom flask. Thermometer was inserted in one neck of flask and condenser was fitted on other neck. When the diester was completely dissolved in it, then 1.5mole of dimethyl sulphate (3.65 g) was added drop by drop with constant stirring at 70 °C. Reaction mixture was stirred for 2 hour. Esterquat contents were transferred to a beaker and the petroleum ether was evaporated heating on water bath until a viscous compound was obtained. It was then weighed. Similarly 1.75mole (3.9g) and 2 mole (4.15 g) of dimethyl sulphate were reacted with diester to form the esterquat.a



Diester of Triethanolamine **EsterQuat**

Characterization of fabric softener

1. Sodium Lauryl Sulphate (0.004M)

1.464 g of Sodium Lauryl Sulphate was dissolved in 1000 ml of distilled water to make 0.004M solution of Sodium Lauryl Sulphate.

2. Methylene Blue (0.003%)

0.003g of Methylene blue was dissolved in 100 ml of distilled water to make 0.003% solution.

3. Esterquat Solution (0.004M)

0.004 M solution of Esterquat was prepared. Esterquat was dissolved in 20 ml of Ethanol and made the volume up to mark of 250 ml.

Determination of cationic content

10ml of Standard Sodium Lauryl Sulphate was taken in 250ml stoppered flask and 5 ml of 0.003% methylene blue was added followed by 0. 2ml concentrated H_2SO_4, 5g anhydrous Sodium Sulphate and 15 ml Chloroform.

After gentle shaking, flask was allowed to stand for 10 minute until the two layers separated, the organic layer (Choloroform) was blue coloured. It was titrated with 0.004M solution of Esterqaut and at end point the both the layers had same intensity of colour.

Calculation

$$\textit{Molarity of EsterQuat } C1 = \frac{10C2}{V1}$$

C1 = Morality of Ester quat
C2 =Morality of Sodium Lauryl Sulphate
V1 = Volume of Esterquat used from burette

$$\textit{Cationic Content} = \frac{C1 \text{ X Molecular weight of Esterquat}}{\text{Weight of sample X 4}} \text{ X } 100$$

Solubility of fabric softener

Solubility of synthesized esterquat (fabric softener) was checked using different solvents and results arereported in table.

Table 1: Solubility effect of solvent on esterquat

Solvent	Fabric softener
Isopropanol	Soluble
Hot water	Sparingly soluble
Coldwater	Slightly soluble
Chloroform	Soluble
Ethanol	Soluble
n-Hexane	Soluble
Dimethyl sulphoxide	Sparingly soluble
Petroleum ether	Soluble
Acetone	Insoluble
Methanol	Insoluble
Carbon tetrachloride	Soluble

Compatibility of fabric Softener with natural and synthetic fabrics

1. Softener

Different concentrations of Esterquat (5% and 3%) were prepared and pieces of cotton cloths was treated with fabric softener and found that softeners gave good handling and impart greater softness than the cloths which were not softened.

2. Weight test

Weight of untreated cloths = 0.358gm
Weight of treated cloths = 0.425gm
Weight gain by softening treatment = 0.067gm (18.7%)

3. Heat Stability

Pieces of cloths treated with the softeners solutions were placed in to oven at 150oC for one minutes. The softener still had well softness effect on cloths.

4. Water Absorbing

It was revealed that the softener had no effect on absorption power of towel treated with fabric softener.
Weight of untreated towel cloths = 0.40gm
Weight of treated towel cloths = 0.450gm
Weight gain by softening treatment = 0.05gm (12.5%)

Result and Discussion

Esterquat constitute an important class of cationic surfactant. The main object of research work was to synthesized esterquat from cheap, indiginous materials which should work as fabric softener. The prepared Esterquat gave the appreciable result.

In the two step synthesis of Esterquat, the product obtained in the first step, which involve diester formation from tallow free fatty acids and triethanolamine, represented a characteristic colour change. The acid value of free fatty acids (208) were calculated

Table2: Characteristic of tallow

characteristic	value
Saponification value	256
Free fatty acid	208

Initially the acid value of condensate (Diester formation) decreased rapidly because water of condensation being removed from mixture promptly under the influence of vaccum. Orthophosporic acid was found to be a better catalyst for this reaction. . The lowest value (5.6) of Diester was obtained at 135^{o}C with orthophosphoric acid. The advantage of this method was that product was light in colour and diester was formed within short interval of time as compared to sodium methoxide method where the product became darker in that case and it was very lengthy procedure.

Table 3: Diester of Tallow fatty acid

	Catalyst	**Diester yield**
Tallow fatty acid	Sodium methoxide	72.54%
	Orthophosphoric acid	81.55%

When reaction was preceded by quaternization of diester with different mole ratio of dimethyl sulphate solution in the second step of synthesis, a pale yellow semi solid product was obtained. The quaternization of diesterquat was carried out at 60-70^{o}C. Diester was stirred for 2- hours with different mole ratio of DMS to obtained Esterquat. The result indicated that quaternization of diester for 2 hr using 1:1.50 molar ratio of diester of triethanolamine to DMS give better yield of Esterquat.

Table 4: Reaction parameters and results

Sr No	**Diester: DMS**	**Temperature**	**Cationic Content**	**Yield**
1	1:1.5	2h	35.7 %	81.3%
2	1:1.75	2h	28.5 %	77%
3	1:2	2h	25%	72.5%

Alkylation was an exothermic reaction and temperature of ester rose about 4-50 C after addition of dimethyl sulphate, so its was added slowly. Alkylation lightened the color of Esterquat to some extent. Esterquat was insoluble in warm water. Emulsifiers were needed to dissolve in water. The reason being long chain fatty acids resist the solubility.

Structure of product was confirmed on the basis of IR spectroscopic data. This was made by comparing IR spectra of reactant and products. The stretching vibration and OH deformation of Esterquat were indicated by the peaks at 3437and 1094 cm^{-1} respectively. These two peaks were the confirmation of free OH of diester of triethanolamine and tallow fatty acids. The CH_2 group in esterquat gave peak at 2914 cm^{-1}. The tertiary nitrogen gave peak at 2857 cm^{-1} and 1644.4 cm^{-1}.

In the diester all peaks of Esterquat were present except of peaks at 1004.2 cm^{-1}, 757 cm-1, 826 cm-1. These peaks were obtained because Esterquat contained CH_3SO_4 ion so there were S = O stretching vibration present in Esterquat

determination. More over the peaks at 1466.4 confirmed the Quaternary nitrogen of Esterquat.

Table 5: INTERPRETATION OF IR SPECTRUM

Appearance of characteristic peaks on IR spectrum of Esterquat confirmed it structure.

Group	Frequency of Diester of triethanolamine (cm^{-1})	Frequency of Ester Quat (cm^{-1})
O-H Stretching	3354	3437
O-H 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

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