Synthesis and Performance Properties of Cationic Fabric Softeners Derived from Free Fatty Acid of Tallow Fat

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Abstract: Esterquat cationic softener is basically the class of surface active quaternary ammonium compounds. Esterquat compounds were synthesized and their surface behavior, antibacterial activity and Textile softening properties were investigated. Easily found cheap material was used to synthesize cationic fabric softeners. This fabric softener will be a good for commercially and industrially important because their emulsify activity, rewettability dispersing power and softness. Free fatty acids were derived from tallow oil and were treated with triethanolamine and mono-ethanolamine at 140°C. This diester was quaternaries with dimethyl sulphate and benzyl chloride. The synthesized esterquat compounds were characterized by its cationic content, ¹H NMR and FT-IR analysis. In addition to the cationic content, surface tension, CMC (critical micelle concentration), rewettability, fabric softening, emulsification and dispersing power were determined as their surface-active properties. The fabric softening activity of esterquat and esteramide prepared from DMS was better softening activity of fabrics compared to untreated cotton and polyester fabrics cloth. The presented result shows that the esterquat made from BCI exhibit the best dispersing power. The esterquat made from DMS both in TEA and MEA shows good rewettability was determined.

Key words: cationic surfactant, esterification, quaternization, CMC, fabric softening, rewettability, emulsification, dispersing power, antibacterial activity

1 Introduction

Esterquat cationic surfactant is the main constituent of a fabric softener composition. This new type of fabric softening agent combines a good environmental profile with the structural features required for an effective fabric conditioner^{1,2)}. Esterquat cationic surfactant is one of the biodegradable fabric softener due to the presence of ester linkage³⁾. Specialty of cationic surfactant is environmental friendly, non toxic and biodegradable properties⁴⁾. Quats have been proven to be useful in variety of application, including the following as fabric conditioner, antistatic agent, biocides, emulsifiers in cosmetics, antibacterial agent, corrosion inhibitors and foam dispersant⁵⁾. Esterquats are important classes of surfactants that have distinctive qualities that make them attractive for exploration. Esterquats contain a hydrophilic polar "head" -OH group, and a hydrophobic alkyl chain "tail"⁶⁾. They are absorbed on the surface of fabric with their hydrophobic group oriented away from the fabric. Surfactant reduces the friction

between fibers and imparts a soft, fluffy feel to the fabric⁷⁾.

In this paper, we report on the synthesis of cationic surfactant derived from esterification of tri and mono-ethanolamine with free fatty acid of tallow oils. This fatty ester reacts with an alkylating agent like dimethyl sulfate and benzyl chloride to form corresponding quaternary compound⁸⁾. The obtained product in each case was characterized by its cationic content and structure was confirmed by ¹H NMR and FT-IR analysis. Each surfactant surface active property can be measure in a variety of ways and the method of choice often depends on the characteristics of the substance to be analysis. The most frequently determined properties probably are surface tension and critical micelle concentration.

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2 Materials and method

2.1 Materials for Synthesis of Esteramide Quates

The reagent used in synthesis of diester and esterquat were purchased from Sigma Aldrich Pvt. Ltd, India while toluene, diethyl ether, hexane and various other solvents used were purchased from Thomas baker's Pvt. Ltd. Mumbai, India.

Fabrics for evaluation of softening and rewettability, i.e. 100% cotton and 100% polyester were obtained from the market.

2.2 Experimental

2.2.1 Synthesis of diester from tallow free fatty acid

The reaction for the synthesis of diester esterquat (Fig.

1) was obtained from fatty acid with triethanolamine. The diester was prepared by a triethanolamine with fatty acid, followed by reaction with an alkylation agent to the corresponding quaternary. In the presence of a catalyst orthophosphoric acid the (2 mole) of fatty acid and (1 mole) of triethanolamine was heated up to temperature 160-170°C to obtain high conversion and water removal is enhanced by stripping with an inert gas. The reaction times vary from 8-10 hours and the reaction was monitor by acid values. The acid value was checked after half an hour. The reaction was continued until acid value reached 6.0. Similarly, the reaction for the preparation of ester amide of monoethanolamine with free fatty acid of tallow fat.

Fig. 1 Synthesis of esteramide and esterquats.

2.2.2 Quaternization of Esterquats

The free fatty acid of diester and esteramide is reacted with an alkylation agent like dimethyl sulphate, benzyl chloride, to obtain corresponding quaternary ammonium compound (Fig. 1). For this 1 mole of di-ester of tri-ethanolamine was dissolved in petroleum ether in 250 mL of round bottom flask. Thermometer was inserted in one neck of flask and condenser was fitted on the other neck. When the di-ester was completely dissolved in it, then 1.5 mole of alkylating agent was added drop by drop with constant stirring for 2 hours at 65–70°C. Esterquats were transferred to a beaker and the petroleum ether was evaporated on water bath until a viscous compound was obtained.

Similarly the esterquat of monoethanolamine was prepared by using alkylating agent like dimethyl sulphate, benzyl chloride, to obtain corresponding quaternary ammonium compound (Fig. 1).

3 Characterization of esterquat and Esteramide Quat

3.1 Determination of Cationic Content^{9, 10}:

The cationic content of esteramide and esterquats was determined using the method described in BIS: 4955 (1978) p 8.

Reagent

1. Chloroform
2. 0.004 M Sodium Lauryl Sulphate Solution
1.464 g of sodium Lauryl sulphate was dissolved in 1000 ml of distilled water to make 0.004 M solution.
3. 0.003% Methylene Blue Solution
0.003 g of Methylene blue, 30 g of sodium sulphate and 4.1 mL of concentrated sulphuric acid were taken in distilled water and diluted to 1000 ml with distilled water.
4. 0.004 M Esterquat Solution
Adequate quantity of esterquat was weighed and dissolved in 20–30 mL of ethanol and made the volume up to 250 mL distilled water.

Procedure

10 mL of standard cationic surfactant solution (esterquats, esteramide) was taken in 250 mL stopper flask and add 15 mL chloroform and 25 mL of methylene blue solution to the cylinder and shake well. After gentle shaking, flask was allowed to stand until the two layers separated. The organic layer was blue colored. It was then titrated against 0.004 M solution of sodium lauryl sulphate. Towards the end point the colour would start migrating to the aqueous layer. The reading was noted down when the same colour intensity in both the phases was observed.

Cationic content was measured as follows:

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

Where,

M_1 = Molarity of esterquat

M_2 = Molarity of sodium lauryl sulphate

V_1 = Used volume for esterquat

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

3.2 Determination of cmc, %cmc

The surface tensions of aqueous solutions of the esterquats were measured with a Kruss K11 tension tensiometer with the help of a Wilhelmy plate made up of platinum. Measurements were taken at $25 \pm 1^\circ\text{C}$. The surfactant solution was added to water in a thermostatted glass vessel by using a micro syringe. CMC and surface tension at CMC were determined from the breakpoint of the surface tension of their aqueous solution versus concentration.

3.3 Emulsibility

The emulsibility of the synthesized cationic surfactant was determined using 10 mL of 1% aqueous solution of surfactants and 5 mL of toluene at 40°C. The mixed liquid was stirred by homogenizer for 1 min and the emulsion was formed. The emulsion was poured into a measuring cylinder, and the time was recorded when as the time of separation of water (9 mL) from the emulsion layer¹¹.

3.4 Dispersing power

Dispersing power of the prepared esterquats was determined using TiO_2 and 1% surfactant solution. The surfactant solution with TiO_2 were shaken and allowed to stand. Dispersing power was carried out by looking at the height and cloudiness of surfactant solution and recorded the scores¹².

3.5 Softening power

A 'feel' test panel to determine the softeners was applied, based on the panel feel test^{13, 14}. The treated and non-treated cloth were to the trained panelist with the requirement to judge which cloth of the pair is softer. The softening rating of different substrate decided by average grade obtained from panelist, better softer has higher grade given in Table 6.

3.6 Rewettability

The dye wick-up method¹⁵ was used to measure the rewet of treated fabric with the investigated softening formulation¹⁶. Initially, the standard fabric were treated the same way as in above-mentioned softening method. Then the fabric were hung vertically and dipped in a 0.2 wt% telon blue RR acid dye solution, where the immersion depth was 2 cm. A stopwatch was started as soon as the strip of fabric was dipped. The distance of dye separation was measured in centimeter at 5 min, as the height of wetted cationic treated fabrics. Table 5 shows rewettability.

bility data of different treated fabric with different surfactant solution.

3.7 Instrumental Analysis

The structures of compounds were determined by means of spectral analysis: ¹H NMR and FT-IR. FT-IR spectra were obtained by using a model Miracle 10.DRS plate of the sample was subjected to analysis with 30 scan. NMR spectra were recorded with a Bruker avance DRX-500 in CDCl₃ solution.

4 Results and Discussion

4.1 Characteristics of Experimental Fatty Acids

The acid value, saponification value, appearance and melting point of free fatty acid of tallow are in Table 1. The acid value determined was 174.03. The saponification value and melting point were found to be in normal range as expected.

4.2 Synthesis of Diester

Fatty esters are generally prepared by the reaction of an acid with a different alcohol like triethanolamine and mono ethanolamine. Cationic surfactant constitutes an important class of fabric softener. The aim of research was to synthesize better surfactant from easily available chiefly fatty acid like tallow, which should be better quality and yield of product. The esterquat was prepared by two steps, the product obtained from the first step, which involved ester formation from free fatty acid and alcoholic amine like mono and triethanolamine. In etherification reaction the lowest acid value of product was obtained. The acid value of condensate product (Diester formation) reduces rapidly because water of condensation being removed from

mixture at 150°C. In the presence of catalyst Orthophosphoric acid was found yield for this reaction. The lowest acid value (5.5) of diester was obtained at 170°C with Orthophosphoric acid as a catalyst. The diester derived from free fatty acid gave a maximum yield was carried out at 170°C. The reaction was controlled by monitoring the acid value during the synthesis.

4.3 Synthesis of Esterquats

Table 2 shows the yield percentage yields by weight and cationic content of different di-esterquats, prepared by quaternization of diester and ester amide by DMS and Benzyl chloride. The quaternization was carried out at a 70-80°C for 2 hours and cationic matter for each product was determined. The result shows that quaternization of diester for 2 hours using 1:1.5 molar ratio of diester to different halide group give better yield of esterquat. Quaternization time also had an important role in the cationic content of esterquats. Increasing the duration of quaternization did not increase the cationic content. The solubility test indicates that esterquat was soluble in both cold and warm water. The reason is that esteramide and esterquats surfactant molecule present polar alcoholic group. Because polar group increasing solubility due to hydrogen bonding. The O-H bond is not only polar but is also able to form hydrogen bond with water molecule as well as each other.

4.4 ¹H NMR

Spectral data of Esteramide and Esterquats surfactant are as follow:

1) 6a- Esteramide of dimethyl sulphate

¹H NMR (500 MHz CDCl₃): δ 0.86-1.99 [99 H, m, (-CH₂-(CH₂)_n-CH₂-) Aliphatic chain]; 2.66-2.33 [8 H, d t, (-CH₂-C=O, -N-CH₂-CH₂-)]; 3.64 [3 H, s, (+N-CH₃ sulphate)]; 5.32 [3 H, s, (-CH₃SO₄⁻)]

2) 6b- Esteramide of benzyl chloride

¹H NMR (500 MHz CDCl₃): δ 0.87-1.25 [83 H, m, (-CH₂-(CH₂)_n-CH₂-) Aliphatic chain]; 2.01-2.0 [6 H, t, (-CH₂-CH₂-C=O)]; 2.37-2.33 [8 H, (-CH₂-C=O), (-CH₂-OH)]; 5.33-5.36 [4 H, m, (-CH₂-N+ Benzyl), (-CH₂-OH)]; 7.26 [5 H, m, (Aromatic C-H)].

3) 7c- Esterquats of dimethyl sulphate

¹H NMR (500 MHz CDCl₃): δ 0.85-2.35 [288 H, m, (-CH₂-

Table 1 Characteristics of tallow fat.

Characteristics	Value
Saponification value	186.122
Acid value	174.03
Melting point	>40°C
Appearance	Off-white, solid fat

Table 2 Reaction parameters of different quats derived from tallow fatty acid.

Surfactant	Diester: Alkyl halide	Molar Ratio	Time (h)	Cationic Content (%)	Yield (%)
6a	4 : DMS	1:1.5	2 h	71.03	90
6b	4 : BCl	1:1.5	2 h	58.9	85
7c	5 : DMS	1:1.5	2 h	70.0	89
7d	5 : BCl	1:1.5	2 h	63.7	87

(CH_2)_n-CH₂-) Aliphatic chain]; 3.65[3 H, s, (+N-CH₃)-sulphate)]; 4.4-4.17[4 H, t, 2(-O-CH₂-CH₂)]; 5.30-5.37[10 H, m, 2(-CH₂-C=O), 2(+N-CH₂-CH₂-O-C=O), (+N-CH₂-CH₂-OH)]; 5.79[3 H, s, (-CH₃SO₄⁻)].

4) 7d- Esterquats of benzyl chloride

¹H NMR (500 MHz CDCl₃): δ 0.86-2.36[80 H, m, (-CH₂-(CH₂)_n-CH₂-) Aliphatic chain]; 4.44-3.51[13 H, dt, 2(-O-CH₂-CH₂-N+), (+N-CH₂-CH₂-OH)]; 5.34-5.76[5 H, m, (Aromatic C-H)].

4.5 FT-IR

Diester and esteramide: The FT-IR data obtained for diester and ester amide is tabulated in Table 3. The forma-

tion of diester was confirmed by The OH stretching vibration and deformation was indicated by the peak at ~3340.71 and ~1076.28 cm⁻¹ respectively. The C-N stretching at ~1068 cm⁻¹ (amide group), C=O stretching (amide group) at ~1641.42 cm⁻¹, C=O stretching (ester group) at 1737.86 cm⁻¹.

Esterquats: FT-IR spectra of esterquat shows similar type of peak as those in the spectra of diester and ester amide, except for the peak of S=O stretching (DMS group) at ~100.91 cm⁻¹ and ~707.8 cm⁻¹ for benzene ring of (aromatic ring). Presence of quaternary N⁺ was confirmed by the peak obtained at ~1462.04 cm⁻¹. Instrumental analysis of diester, esteramide and esterquats is shown in Table 3

Table 3 Interpretation of IR spectrum.

Group	Diester of Triethanolamine 5 (cm ⁻¹)	Esteramide of Monoethanolamine 4 (cm ⁻¹)	Esteramide 6a-b (cm ⁻¹)	Esterquat 7c-d (cm ⁻¹)
O-H stretching	3340.71	3379.29	~3388.93	~3379.29
O-H Deformation	1076.26	1050	~1053.13	~1068.56
C=O	1737.86		~1739.79	~1639.49
C-O	1168.86	1124.5	~1197.79	~1124.5
Tertiary N	2850.79, 1566.2	2852.72	~2854.65	~2852.72
S=O			1006.84	1068.56
CH ₂	2918.3	2924.09	~2922.16	~2924.09
Mono substituted benzene ring			756.1	727.16, 702.09
Quaternary N ⁺			1456.26	1454.33

Where,

4- Esteramide of monoethanolamine, 5-Diester of triethanolamine

6a- Esteramide of dimethyl sulphate, 6b- Esteramide of benzyl chloride.

7c- Esterquats of dimethyl sulphate, 7d- Esterquats of benzyl chloride.

Fig. 2 FTIR spectrogram of esteramide quates.

Fig. 3 FTIR spectrogram of esterquat.

Table 4 Surface active properties of different esterquat and esteramide quats derived from tallow fatty acid and TEA and MEA.

Surfactant	Surface Tension mN/m	CMC (mmol/L)	Cationic content (%)	Emulsion stability (min)	Dispersing power (TiO ₂) (vol. in ml)	Average molar mass (g/mole)
6a	30.89	0.046	71.03	55 min	6.5	1082
6b	27.81	0.002	58.9	40 min	10	1096
7c	32.54	0.158	70.0	57 min	8	883
7d	29.00	0.246	63.7	42 min	10	897

and graphs are shown in Figs. 2 and 3.

4.6 Surface Tension

After the synthesis of tallow based esterquat, we further investigated their surface active properties Critical micelle concentration (CMC) values, surface tension at CMC (γ_{cmc}) are summarized in Table 4. In general the critical micelle concentration indicate the concentration at which the surfactant start to aggregate into micelles. Table 4 indicates that surface tension of all the esterquat good range that is below 30 mN/m. The CMC value was calculated by the plate methods shown in Table 4. The tallow based esterquat and esteramide surfactant CMC value decreases or increases depend their central nitrogen atom of tri-ethanolamine, mono-ethanolamine and polar alkyl halide group like dimethyl sulfate and benzyl chloride. Because of large head group expected aggregate structure was spherical in shape¹⁷.

4.7 Emulsion Stability

Emulsification is defined suspension of liquid droplets (dispersed phase) of a certain size within a second immiscible liquid (continuous phase). The main action of emul-

sion is reduced the interfacial tension between the phases and forming the barrier between the phases. Hence, a surfactant, mostly termed emulsifier, is necessary for stabilization. Esterquats and esteramide quates showed good emulsion stability. Table 4 shows that emulsion stability was different in different surfactant depends their size and alkylating agent. The experimental data a show that esterquat derived from DMS has best emulsion stability while esterquat derived from benzyl chloride has lower emulsion stability.

4.8 Dispersing Power

Increased length of the alkyl chain increases degree of dispersing power. The dispersion of carbon in aliphatic hydrocarbon is raised by the addition of alkyl benzene. The benzene ring is presumably adsorbed onto the surface of the carbon and the alkyl chain length increases the stability of dispersion liquid. Increases in the length and alkyl group to the benzene nucleus increases the stability of dispersion¹⁸. The resulting data shown in Table 4 indicate that the esterquat and esteramide quates prepared from benzyl chloride exhibit the best dispersing power in comparison to prepared from DMS.

Table 5 Result of fabric rewettability using different concentration of surfactant solutions.

Surfactant	Rewetting ^a (cm)		100% polyester		Untreated cotton	Untreated polyester
	100% cotton					
	0.1	1.0	0.1	1.0	2.5	2.0
6a	4	4.1	1.2	1.3		
6b	3.7	2.9	0.5	2.0		
7c	4.5	5.5	5.0	3.0		
7d	3.4	2.9	1.8	0.5		

^a Dye migration after 5 min (in cm)

4.9 Rewettability

Surface activity of water is an important aspect for detergency, water proofing, dying water absorption. An important role of wetting agent is minimizing the both surface tension of surfactant solution and its interfacial tension against the solid¹⁹⁾. The dye-wick method measure the water absorbency characteristics of fabrics treated with softener. Better water absorbency is important for a treated cloth, because fabrics softener can change water absorptivity of the treated textile. The absorbency rule the increases the softener on a fabrics decreases its water absorbency or increasing the softening activity decreases water absorbency²⁰⁾. It can show **Table 5**, that after test with the investigated softeners, rewettability of all the cotton and polyester fabric sample decreasing trend. As the rewettability of treated fabrics, 100 % cotton shows good migration than 100% polyester. Similarly the both untreated fabrics like cotton and polyester tested, it shows that the rewettability activity poorest than treated fabrics. Esterquats made from DMS both TEA and MEA good rewettability was determined.

4.10 Softening

The most cationic surfactant is used to improved fabrics softeners²¹⁾. We had evaluated the softness property by panel feel test where the softness have been qualitatively assessed and rating has been given in terms of one to five (+) symbols indicating poor to excellent softness property subsequently. Their activity depends on the use in fatty alkyl chain and quaternizing group. It was observed from **Table 6** that esterquat and esteramide preparation from DMS was better softening activity on fabrics. In both esteramide quates and di-esterquats shows better softening so we can use commercially fabrics softeners.

Table 6 Comparable result of softening property of 1% aqueous solution of esterquat^{13, 14)}.

Surfactant	100% cotton	100% polyester
6a	++++	+++
6b	+++	++
7c	++++	+++
7d	+	+
kaosoft agl85 (commercial grade)	+++++	++++

kaosoft agl85 (commercial grade) fabric softener with synthesized cationic surfactant. It was found that our fabric cationic surfactant has less softening activity than kaosoft agl85 (commercial grade) surfactants. It was observed that esterquat and esteramide preparation from DMS was better softening activity on fabrics than Benzyl chloride. This fabric softener will be a good for commercially and industrially important because their emulsify activity, rewettability dispersing power and softness. The presented result shows that the esterquat made from benzyl chloride exhibit the best dispersing power. The esterquat made from DMS both in TEA and MEA shows good rewettability was determined. The fabric softening activity of esterquat and esteramide prepared from DMS was better softening activity of fabrics compared to untreated cotton and polyester fabrics cloth.

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Supporting Information

This material is available free of charge via the Internet

5 Conclusions

Free fatty acids were derived from tallow fat and react with TEA and MEA at 150-160°C. It was compared with the

at <http://dx.doi.org/jos.64.10.5650/jos.ess.15276>

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