

Synthesis, Characterization and Application of Ester Functionalized Cationic Surfactant

V.Lakshmi Narayanan, P.Brindha And M.J.Umapathy

Department of Chemistry, College of Engineering Guindy, Anna University, Chennai-600 025, Tamil Nadu, India

Abstract: Ester functional cationic surfactant was synthesized by esterification of oleic acid and triethanol amine followed by quaternization with epichlorohydrin. The structure of the esterquat surfactant were confirmed by FT-IR, ^1H NMR, and ^{13}C NMR. The surface morphology was studied by scanning electron microscope (SEM) and the chemical composition was computed by EDAX techniques. The physico-chemical properties for the surfactant 1-chloropropan-1-ol, (E)-2-(bis (2-hydroxyethyl) amino)-1-(octadec-9-enoyloxy) ethan-1-ylum salt were studied and evaluated. The synthesized surfactant was used and as a corrosion inhibitor for mild steel in HCl medium, as a textile – softening agent and the antimicrobial activities of the cationic surfactant was evaluated for gram- positive and gram-negative bacteria.

Keywords: Ester functional cationic surfactant, Corrosion, Antibacterial Activity

I. Introduction

Surfactants are compound that has multifarious applications across the globe in our daily life. The unique structure of the surfactant modifies the interfacial properties, which are more vital for flotation, cosmetics, food industries, drug delivery, corrosion inhibition etc [1].

Mild steel is employed widely in many industries as it posses excellent mechanical properties, availability and low-price. Hydrochloric acid a mineral acid is widely used for the pickling of mild steel than other acids since it can be used at room temperature and more over cheap than other mineral acids. Hydrochloric acid eliminates the rust and after the removal, it attacks the base metal. To avoid the attack of the base metal, inhibitors are added in small quantity. Cationic surfactants based on quaternary ammonium salts are excellent inhibitors for hydrochloric acid solution which only allows the attack of acid on rust but not the base metal [2].

El Maghraly and Soror studied the efficiency of cetyltrimethylammonium bromide (CTAB) as cationic inhibitor for carbon steel in hydrochloric acid solution. The result indicated that CTAB is a good inhibitor in 2M HCl solution and the inhibitors efficiency increased with increase in concentration of the inhibitor [3].

The inhibiting effect of cationic surfactant N, N-dimethyl 4-methyl benzyl dodecyl ammonium chloride on mild steel in hydrochloric acid solution was investigated by weight loss studies (Abdol Hamid et al). Weight loss measurement showed that the inhibitor efficiency increased with increasing surfactant concentration and attained a maximum around the critical micelle concentration [4].

Fabric softeners are a chemical compound that softens the fabric and reduces unwanted static cling. The control the static electricity and makes the cloth a pleasing touch. Apart from this, they improve the abrasive resistance and reduce thread breakage [5]. Cationic surfactants are widely used as fabric softeners because part of the molecules do have positive charge that attract and bonds it to negative charged fibers. The fatty part of the molecule provides the slip and lubricity that makes the fabric soft.

Quaternary ammonium salts shows a very good antimicrobial activity, they adsorb on the cell membrane and promote changes in the cell organization [6]. Taigai and his team members have evaluated the antimicrobial activities of Gemini surfactant against gram-positive and gram-negative micro-organisms [7]. The antimicrobial activity was found to be dependent on the target micro-organism (Gram-positive bacteria > fungi > Gram-negative bacteria), as well as both the cationic and alkyl chain length of the compound [8].

In this piece of work, an ester functional cationic surfactant was synthesized, characterized by the common instrumentation techniques and it has been used as an inhibitor for corrosion protection in mild steel and as a fabric softener. In addition to this, the antimicrobial property is also been evaluated against gram negative and positive bacteria.

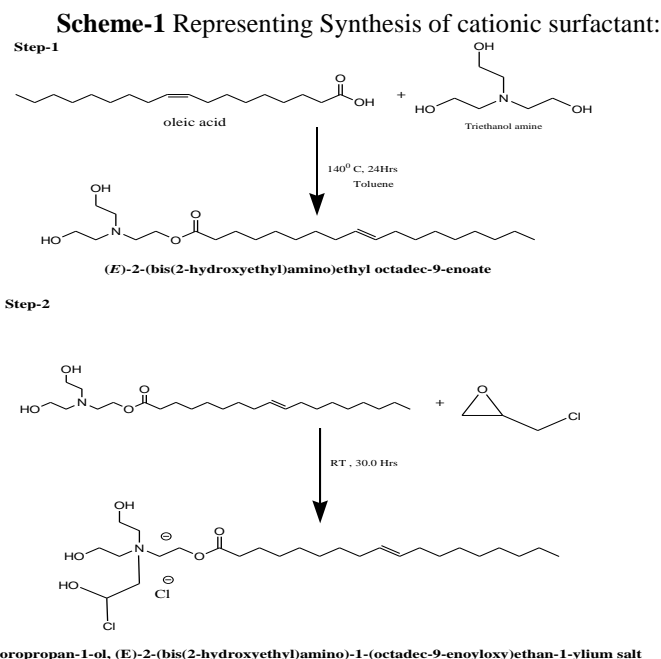
II. Materials and Methods

2.1 Materials

Triethanol amine, hydrochloric acid, toluene, and ethanol were procured from Merck, India. Oleic acid and epichlorohydrin were purchased from Sd-fine Chemicals and SRL, India respectively.

2.2 Synthesis of 1-chloropropan-1-ol, (E)-2-(bis(2-hydroxyethyl)amino)-1-(octadec-9-enoyloxy)ethan-1-ylum

The ester functional cationic surfactant was synthesized via two steps. The first step involves the esterification of triethanol amine and oleic acid in a mole ratio of 1:1 in a toluene medium by heating at 140 °C with continuous stirring using 5% p-toluenesulfonic acid as a catalyst for 24 hours. In the second step, the product so obtained was quaternized by employing epichlorohydrin in a 1:1 mole ratio (scheme-1).



2.3 FT-IR Spectroscopy

The FT-IR spectrum of the synthesized ester functional cationic surfactant was recorded using Perkin-Elmer Spectrophotometer by Win First V2.01 software. All spectra was recorded in the range of 400 cm⁻¹ to 4000 cm⁻¹.

2.4 NMR Spectroscopy

The structure was observed using ¹H and ¹³C Nuclear Magnetic Resonance (NMR), which was recorded using a Bruker Spectrometer at 400 MHz NMR spectrometer using the CDCl₃ solvent. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS).

2.5 SEM and EDX

The mild steel panels were subjected to SEM and EDX analysis to study the surface morphology and to find out the chemical composition.

2.6 Evaluation of the physico-chemical properties

2.6.1 Surface tension measurements (γ)

Surface tension (γ) of the prepared cationic surfactant was measured by using a Du Nouy automatic tensiometer (Kruss K₁₂) for various concentrations (1.0 x 10⁻⁵ to 1.0 x 10⁻² M). All solutions were prepared by using double distilled water. The surfactant solution was placed in double walled vessel through which water was circulated from a thermostat bath. The attainment of equilibrium was measured repeatedly for every interval of 5 minutes [9].

2.6.2 Determination of Critical Micelle Concentration (CMC)

Critical micelle concentration (CMC) of the prepared cationic surfactant was determined by the conductivity method. Conductivity of sample solution was measured with digital conductivity meter (EUTECH, con 510). The cell constants (K) were determined at room temperature using KCl solutions.

2.6.3 Surface Pressure (Effectiveness) π_{cmc}

The surface pressure (effectiveness) was calculated using the following Equation

$$\pi_{cmc} = \gamma_0 - \gamma_{cmc}$$

Where γ_0 is surface tension for the pure water and γ_{cmc} surface tension of the solution at CMC.

2.6.4 Foam stability

Foam stability was determined by shaking 25ml of 0.1% solution up and down in a 100ml closed graduated cylinder at room temperature [10].

$$\text{Foam stability \%} = \left\{ \frac{\text{Foam volume after 5 minutes}}{\text{Foam volume after 0 minute}} \right\} \times 100$$

2.6.5 Wetting time

Wetting time was arrived by dipping a sample of cotton fabric (diameter 35mm, weight 38-39 mg) in 0.1 wt % aqueous solution of the surfactant. The detailed procedure was reported by Mao et al [11]

2.6.6 Emulsion stability

Emulsion was prepared by mixing and vigorous shaking of 20 ml of 0.1% aqueous solution of the surfactant and 20 ml of toluene in a stoppered graduated cylinder. The stoppered graduated cylinder with the emulsion was rested and the time taken for the separation of 10 ml of water was noted in seconds that corresponds to emulsion stability.

2.6.7 Weight loss measurements

Mild steel were used for the weight loss measurement contains C =0.7%, P = 0.03%, Mn = 0.3-0.6%, S = 0.035%, Si = 0.5- 0.75, and the remaining is iron. The specimens of mild steel with dimensions (3cm x 1.5cm x 0.2cm) were polished using 1200 grades emery paper, degreased with acetone, rinsed with double distilled water, and finally dried between filter paper. The specimens is kept in the desiccator and later weighed. After weighing the specimens were immersed in 1.0 M HCl with and without inhibitor for up to 24 h. After that, the steel sheets in a 1.0 N HCl were taken out, washed with double distilled water, dried, and again weighed accurately. The difference in weight (weight loss) was noted.

$$R = \frac{\text{weight loss} \times 8.75 \times 10}{D \times A \times T}$$

Where, Wt loss = weight loss in g

D= density of carbon steel in g/cm³

A= area in cm²

T=time in hours

Inhibition efficiency (η) and surface coverage (θ) were calculated according to the following equations.

$$\text{Inhibition efficiency } (\eta) \% = \theta \times 100$$

$$\text{Surface coverage } (\theta) = \left\{ \frac{W - W_0}{W} \right\}$$

Where

W = the weight loss without inhibitor

W₀ = the weight loss with inhibitor

2.6.8 Fabric softener

Different concentrations of newly synthesized ester functional cationic surfactant solutions (1 % to 10%) was prepared and added with 0.2g of formaldehyde and few crystals of CBX-100 (optical brightener). Fabric samples (1 x 2 inches) were boiled with distilled water for 30 minutes to remove water-soluble impurities, dried and stored in desiccator. The dried fabric samples were weighed and appropriate volume of surfactant solution were taken in a beaker and treated for 60 minutes at 35° C. After treatment, the fabric samples were then removed and dried over night.

2.6.9 Antimicrobial activity

Antimicrobial studies for the synthesized surfactant was done by employing Broth dilution assay (Cos et al., 2006). In this method 5ml of the potato dextrose (nutrient for bacteria), 0.1 ml of the 24 hrs cultured bacteria (gram-positive bacteria of Staphylococcus aureus and gram –negative bacteria of Escherichia coli) and different concentrations of surfactant (100µg, 200µg....1000µg) were added to the tubes and incubated at 37° C

for 24h. The optical densities were measured spectrometrically at 600 nm. The percentage of visible cells was calculated using the following formula

$$\% \text{ of inhibition} = \left\{ \frac{\text{Control O.D} - \text{Test O.D}}{\text{Control O.D}} \right\} \times 100$$

Where O.D is Optical Density

III. Results

3.1 Fourier Transform-Infra-Red Spectroscopy (FT-IR)

The FT-IR spectrum confirms the structure of the synthesized cationic surfactant (table 1 and figure.1) shows the following absorption.

3.2 Proton Nuclear Magnetic Resonance Spectroscopy (^1H NMR)

^1H NMR (CDCl_3) spectra of the synthesized ester functional cationic surfactant showed different signals. δ 0.9 (t, 3H, $-\text{CH}_3$), 1.20-1.25 (m, 20H $-\text{CH}_2$), 1.65 (m, 2H, $\text{CH}_2\text{O}-\text{C}=\text{O}$), 2.30 (t, 2H, CH_2COO), 3.36-3.55 (t, 6H, N^+CH_2), 2.1-2.2 (t 3H CH_2OH), 4.40 (t, 2H, N^+CCH_2).

3.3 ^{13}C Nuclear Magnetic Resonance Spectroscopy (^{13}C NMR)

^{13}C NMR spectrum of the synthesized ester functional cationic surfactant shows different signals, δ 14.04 (CH_3); 22.62 (CH_2 in α of CH_3); 24.5 ($\text{CH}_2-\text{O}-\text{C}=\text{O}$ ester); 29.6 (CH_2); 34.0 (CH_2 in α of $\text{C}=\text{O}$ ester); 61.94 (CH_2-OH); 77.0 (CH_2 in α of ammonium); 177 (COO ester).

3.4 Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX)

SEM images and EDX spectrum of pure mild steel corroded mild steel and inhibitor coated mild steel reveals their internal morphology and chemical composition shown in figure 2, 3, 4, 5 and table 2. From figure 4 it can be concluded that the inhibitor inhibits the metal surface by blocking the active sites and forming a protective layer which resist corrosion.

3.5 Surface Tension (γ) and Critical Micelle Concentration (CMC)

The CMC Value of the ester functionalized cationic surfactant was carried using a conductivity meter and the value is 2×10^{-4} mole per litre . By employing the Tensiometer the surface tension was evaluated and it was found to be 32.0 mN/m indicating good interfacial activity. The surface pressure was 40.00mN/m

3.6 Foam stability wetting time and Emulsion stability

Foam stability and wetting time were found to be 94 percent and 14 seconds respectively. The emulsion stability was 245 seconds.

IV. Discussion

4.1. Weight loss measurements

Inhibition property of the ester functional cationic surfactant increased with increase in concentration. This may be due to the adsorption of surfactant on the active sites of the mild steel. Apart from this on increasing the concentration of the surfactant coverage on the steel surface increases (table 3 and figure-6).

4.2. Fabric softener

Three different fabric substrates such as cotton, polyester and the blend of cotton and polyester were used to check the softening property of the synthesized ester functionalized cationic surfactant. The softening properties have been evaluated by varying the concentration of the surfactant on the three different fabrics (table 4 and figure-7). Cotton, polyester blend exhibited better softness when compared to the cotton and polyester [15].

4.3. Antimicrobial activity

The results of antimicrobial activity of the synthesized ester functional cationic surfactant against pathogenic bacteria were determined and listed in Table-5. The results indicate that the synthesized cationic surfactants have good antimicrobial activity against the tested microorganisms and their activities depend on their hydrophobic chain length [16]. The higher biocide activity could be attributed to the electrostatic attraction of positively charge (N^+) of quat and negatively charged of phospholipids present in the cell wall.

V. Conclusion

The new ester functionalized cationic surfactant was synthesized and characterized by FT-IR, ¹HNMR, ¹³C NMR. The FT-IR spectrum revealed the expected absorption bands for the respective functional groups. The ¹HNMR and ¹³CNMR spectra confirm the number of protons and carbon present in the synthesized compound respectively. SEM analysis reveals that the metal surface was protected by the inhibitor by blocking the active sites and acting as a protective barrier. The CMC value was determined by conductometric measurement at it was observed to be 2.0 x 10⁻⁴ mol/lit. The surface tension was 32.0 mN/m which was evaluated by a tensiometer. The surfactant revealed good resistance against corrosion by blocking the active site of the mild steel. The surfactants possess good textile softening character for cotton-polyester blend than cotton and polyester alone. In addition to this it has good antimicrobial property for gram positive and gram negative bacteria.

References

- [1]. R. Fuchs-Godec , *Electrochimica Acta.*, 54, P. 2171-2179 (2009).
- [2]. I.A. Zafaramy , *International Journal of Electrochemical science.*, 8, p. 9531-9542 (2013).
- [3]. A.A ElMaghraly and T.Y.Soror , *Advances in Applied Science Research.*, 1(2), p. 156-168 (2010).
- [4]. Abdol Hamid, T.Y. Soror and A.M.A. Umar , *Anti-corrosion methods and materials.*,45(5), p. 306-311(1998).
- [5]. Shilpi mishre and V.K.Tyagi, *Journal of oleo science.*, 55(6), p. 267-275 (2006).
- [6]. Illangovan, *Med chem. Res.* 21, p.694-702 (2012).
- [7]. Taiga Tatsumi, Yoshitane lami, Kakuhiro Kawaguchi, Naokomiyano and Isao Ikeda, *Journal of Oleo science.*,63(2), p. 137-140 (2014).
- [8]. M.C.Muguia , V.A.Kaillard , V.G.Sanchez and J.D. Conoza , *Journal of oleo science.*, 57, p. 301-308 (2008).
- [9]. J.W.Hampson , and D.G.Consell , *Journal of the American Oil Chemists Society.*, 73(7), p. 891-895 (1996).
- [10]. Q. Xu , L.Wang and F. Xing , *J.Surfact Deterg.*, 14, p. 85-90 (2011).
- [11]. P. Mao , *Synthetic detergent industrial analysis.*Peking: the publishing house of light industry., p.456-462 (1998).
- [12]. 15. F.E. Frideli , K. Robert, C.T. Toney , P. Owen , W. Dave and D.Markus, *J.Surfactants and detergents.*, 4, p. 401 (2001)
- [13]. 16. R.M.E.Richard and R.H.Cavil , *Microbios.*,29, p. 23 (1980).
- [14]. B.S. Prathiba, P. Kotteswaran, and V. Bheemaraju , *Journal of Applied Chemistry.*, .5, p.01-10 (2013)
- [15]. Maqsood Ahmad Malik, Mohd Ali Hashim, Firdosa Nabi, Shaeel Ahmed AL-Thabaiti and Zaheer Khan, *International journal of electrochemical science.*, 6, p.1927-1948 (2011).
- [16]. T.Y.Soror and M.A. El-Ziady, *Journal of Materials Chemistry and Physics.*, 77, p. 697-703 (2002).

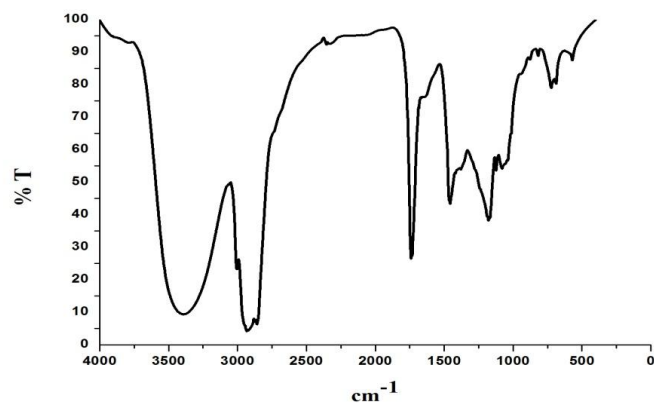


Fig. 1. FT-IR Spectrum of 1-chloropropan-1-ol, (E)-2-(bis(2-hydroxyethyl)amino)-1-(octadec-9-enyloxy)ethan-1-ylidium salt

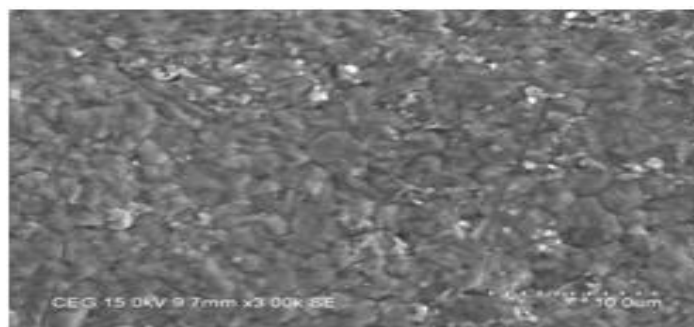


Fig. 2. SEM Image of pure mild steel

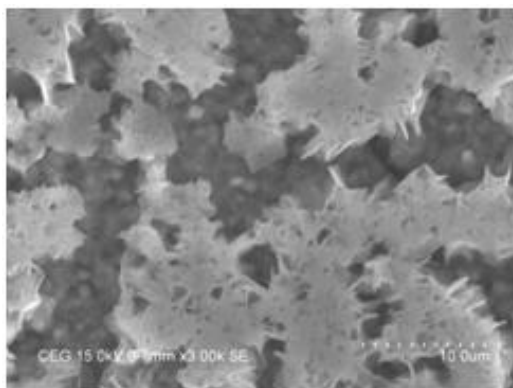


Fig. 3. SEM image of corroded mild steel

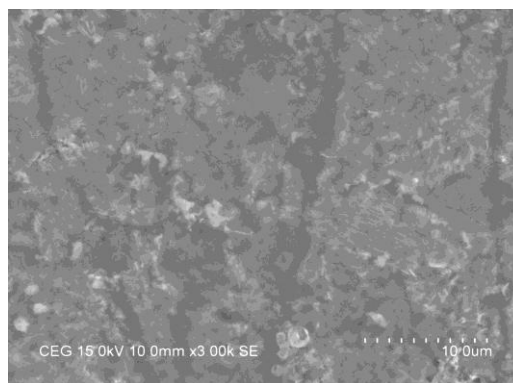


Fig. 4. SEM image of coated mild steel with inhibitor

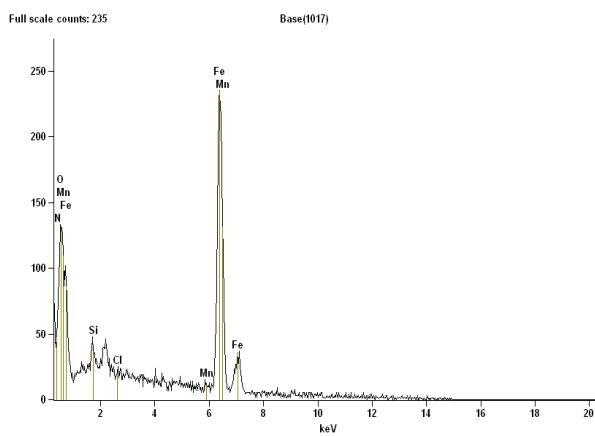


Fig. 5. EDX image of coated mild steel with inhibitor

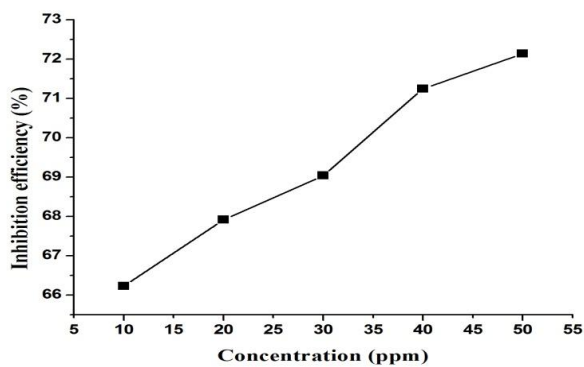


Fig. 6. Effect of surfactant on corrosion inhibition efficiency

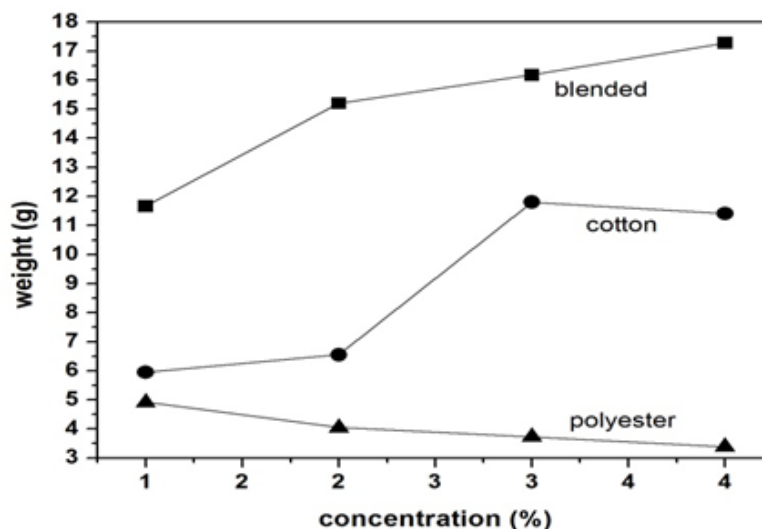


Fig. 7. Effect of surfactant on various fabrics

Table 1. Elemental analysis of 1-chloropropane-1-ol, (E)-2-(bis (2-hydroxyethyl amino)-1-(octadec-9-enoyloxy) ethan-1-ylum salt

Molecular formula	C ₄₀ H ₃₆ O ₄ N ⁺ Cl		
Molecular weight	629		
Percentage of Element	C	H	N
Theoretical value	76.31	5.72	2.22
Observed value	76.03	5.49	2.10

Table 2. Composition of atom in percentage from EDX

Element	Net Counts	Weight %	Atom %
N	2097	30.94	63.95
O	0	0.00	0.00
Si	164	0.43	0.44
Cl	15	0.05	0.04
Mn	95	1.04	0.55
Fe	5343	67.54	35.01
Total		100.00	100.00

Table 3. Effect of surfactant on corrosion inhibition efficiency

Concentration of inhibitor (ppm)	Corrosion Rate (mmpy) RT	Surface coverage	Inhibition efficiency (%)
Blank	7605.0	- - -	- - -
10	6254.0	0.66	66.0
20	6171.0	0.68	68.0
30	6065.0	0.69	69.0
40	5901.0	0.71	71.0
50	5735.0	0.72	72.0

Table 4. Softening properties of various fabrics

Concentration (%)	Cotton (g)	Polyester (g)	Blend (g)
1	6.0	4.9	12.0
2	6.6	4.1	15.0
3	12.0	3.7	16.0
4	11.0	3.4	17.0

Table 5. Minimal Inhibitory Concentration (M.I.C) of the provided samples against test organisms

Compound molecular formula	Microorganisms	Concentration (µg)	Inhibition (%)
C ₄₀ H ₃₆ NO ₄ Cl	<i>S.aureus</i>	600	50.08
	<i>E.coli</i>	400	51.83