Corrosion Inhibition Effect of Ester Containing Cationic Gemini Surfactants on Low Carbon Steel

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ABSTRACT: *α, ω-alkane-bis(N-myristoyloxyethyl-N, N-dimethyl)-diammonium bromide were synthesized and confirmed by FT-IR, FT-Raman and ^{1}H-NMR spectroscopy. Surface tensions were measured by sigma 70 and conductivity meter EC-470C. Critical micelle concentration values were $2.70\times10^{-4} \sim 3.05\times10^{-4}$ mol/L. The Krafft points were measured at 39.1 ~ 43.2 ℃. Their inhibition effects on the corrosion of low carbon steel were tested by the weight loss method in hydrochloric acid. The corrosion inhibition capacity of synthesized cationic gemini surfactant was 24.8% at 1×10^{-7}mol/L concentration. Corrosion inhibition efficiency has increased by 93.8% after the concentration was increased to 1×10^{-4}mol/L. As a result, these surfactants are expected to be applied as corrosion inhibitors.*

KEY WORDS: *Cationic gemini surfactants; Corrosion inhibitor; Weight loss, Surface tension; Steel; Adsorption.*

INTRODUCTION

Surfactants have a hydrophobic and hydrophilic part that is dissolved in water and oil. Surfactants are generally used for emulsifiers, solubilizers, dispersants, detergents, foaming agents, antifoaming agents, anti-static agents, wetting agents, flocculants [1-3]. Surfactants are suitable for use in particular area of industry and they are used to improve the quality and efficiency of operations. In the past research, synthesis of new surfactants molecules has attracted the attention of various industrial and academic groups. The cationic surfactant has sterilizing and anti-corrosive properties. Thus, a number of studies have been devoted to the conventional surfactants, which were made up of one head group and one hydrophobic group, as inhibitors of corrosion in acidic media [4, 5].

One of these classes was referred to gemini surfactants which have one or two hydrocarbon chains in a molecule with two ionic groups per molecule separated by a spacer [5-9]. Gemini surfactants appear to be better in certain important properties as well as their unique bulk and interfacial properties, such as very low critical micelle concentration, high interfacial activity, and specific aggregation structures than conventional surfactants [10-12]. The recent trend in the technical development of surfactants has been toward of the surface-active properties that enable the structure to elevate the interfacial properties [8, 13, 14]. Low carbon steel is used in a variety of industries and it causes the corrosion trouble especially in mountainous regions. In order to prevent the metal corrosion, corrosion inhibition techniques are used. Generally, corrosion inhibitors are the chemical products that minimize or corrosion inhibition, if they are added at low concentrations in an acidic environment. They can prevent metal

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from dissolution while reduce the operation cost. It is well known that the presence of hydrophilic and hydrophobic groups in the inhibitor favours the adsorption process at the iron surface. In the past research showed that most organic corrosion inhibitor can adsorb on iron surface via heteroatom such as nitrogen, sulfur, oxygen and phosphorus decreasing the corrosion rates [15, 16].

In this study, we synthesized an ester containing quaternary ammonium salt-based cationic gemini surfactants and confirmed the structure of these compounds by FT-IR, ^{1}H-NMR, and surface tension, critical micelle concentration, surface activity, and Krafft point was measured. Through experiments, the characteristics of corrosion inhibitors and the performance of additives were confirmed by the weight loss method.

EXPERIMENTAL SECTION
Materials

The following chemicals were purchased and used: myristoyl chloride was obtained from Sigma-Aldrich Co. LLC. (St. Louis, USA). 1, 3-dibromo propane, 1, 4-dibromo butane, 1, 5-dibromo pentane, and 1, 6-dibromo hexane were obtained from Sigma-Aldrich Co. LLC. (St. Louis, USA). Tetradecyl trimethylammonium bromide (typical surfactants) was purchased from Sigma-Aldrich Co. LLC. (St. Louis, USA). 2-Dimethyl amino ethanol was purchased from Sigma-Aldrich Cheme GmbH (Buchs SG, Switzerland). Hydrochloric acid (HCl, 37%), dichloromethane and acetone were purchased from SK chemical Co. (Seongnam, Gyeonggi-do). The distilled water used in this study was deionized and three times distilled by a Milli-Q Plus system (Millipore, France).

Synthesis of cationic gemini surfactants

The cationic gemini surfactants were prepared using a myristoyl chloride 49.2 g (0.2 mol) and dichloromethane were put into a four necked round bottom flask and 2-dimethyl amino ethanol 35.6 g (0.4 mol) was added and reaction was three half hours. After the reaction, the impurities were removed by washing and drying process. Then, 2-dimethylaminoethyl ester (70 mmol) with α, ω-dibromo alkane (35 mmol) were carried out in a four necked round bottom flask in a heating mantle and it is maintained at 60°C for 72 h. Final products were filtered and washed several times using acetone to remove other

impurities, and the cationic gemini surfactants were obtained after three times recrystallization. The obtained product was white powder.

Characterization

The ^{1}H-NMR spectra was recorded in CDCl$_3$ solvent with a Bruker DRX-500 spectrometer and FT-IR spectroscopy was performed with a Jasco 480 plus spectrometer, Samples were mixed with KBr and made to plate for measurement. FT-RAMAN spectroscopy was performed Bruker FRA 106/s spectrometer. Measurements of the surface tension were measured using a KSV Instruments Ltd. Sigma 70 surface tensiometer.

Measuring the surface tension and the critical micelle concentration

The surface tensions of the synthetic gemini surfactants were measured at constant concentration of the fleshly aqueous solution and room temperature. 0.01 M Cationic gemini surfactants were prepared and injected into a dispenser. Next, the measurement conditions were set and distilled water was placed into a beaker and surface tension was measured by wilhelmy plate method. A platinum plate was cleaned with acetone, rinsing with distilled water and then drying. The surface tension measurements were repeated five times and the average value was used for accuracy. In addition, the inflection points of critical micelle concentrations were calculated through surface tension. The CMC values were determined from the abrupt change in the slope of (γ) versus (log c) plots.

Electrical conductivity measurement

In the aqueous solution, electrical conductivity of gemini surfactants were measured using conductivity meter EC-470C. Surfactants solutions were prepared by dilution of a concentrated solution. Solution for the calibration was avoiding any contamination. Distilled water of conductivity was less than 4μS cm^{-1}. Conductivity was measured between the electrode support and test tube, with a less than 0.5 % error of measured conductivity value. During the conductivity test, temperature of solution was kept at 25±0.1 °C. Critical micelle concentrations were derived from the break points in the specific conductivity (χ) versus concentration curves

Table 1: Critical micelle concentration and krafft point of synthesized cationic gemini surfactants.

Compound	Formula	CMC(mol/L)	Surface Tension(dyne/cm)
[1]16-3-16	$C_{39}H_{80}Br_2N_2O_4$	2.70×10^{-4}	38.4
[2]16-4-16	$C_{40}H_{82}Br_2N_2O_4$	2.85×10^{-4}	39.3
[3]16-5-16	$C_{41}H_{84}Br_2N_2O_4$	2.97×10^{-4}	38.2
[4]16-6-16	$C_{42}H_{86}Br_2N_2O_4$	3.05×10^{-4}	38.5

1)N^1,N^1,N^3,N^3-tetramethyl-N^1,N^3-bis(2-(tetradecanoyloxy)ethyl)propane-1,3-diammonium bromide

2)N^1,N^1,N^4,N^4-tetramethyl-N^1,N^4-bis(2-(tetradecanoyloxy)ethyl)butane-1,4- diammonium bromide

3)N^1,N^1,N^5,N^5-tetramethyl-N^1,N^5-bis(2-(tetradecanoyloxy)ethyl)pentane-1,5- diammonium bromide

4)N^1,N^1,N^6,N^6-tetramethyl-N^1,N^6-bis(2-(tetradecanoyloxy)ethyl)hexane-1,6- diammonium bromide

Krafft point

The krafft point is temperature that forms surfactants micelles. Below the krafft point, micelles cannot form. The krafft point was a phase change of aqueous solutions of surfactant. Temperature maintained an accuracy of ±0.5 °C. Synthesized surfactants and distilled water were filled in the test tubes. The thermometer was installed in constant temperature water tank. And then slowly heated to a temperature at which transparency was reached at higher than 5~10℃. The Krafft point can be estimated by measuring temperature at which surfactant solution forms a clear solution.

Zeta potential measurement

Zeta potential was measured by the Zetasizer Nano S, Malvern Co. (UK). All measurements were conducted on distilled water. Measurements were conditioned for 1 hour at room temperature 25℃. NaOH and HCl were used for pH control. The results are three times average measurements of a variation ±2 mV.

Gravimetric measurement

The corrosion resistance specimens were polished using 800 emery papers. The surfaces were cleaned with acetone and rinsed with distilled water. Specimens were immersed in 0.1 mol of hydrochloric acid and rinsed with distilled water and used after completely dried. Mechanically, each sheet was pressed-cut into 5 cm × 1.5 cm x 0.1 cm. Each low carbon steel specimens (Fe > 99%, C: 0.06, Mn: 0.7, etc.) were measured of initial corrosion rate of not containing a surfactant and measured about corrosion rate containing 1 mol of hydrochloric acid and surfactants. Iron specimens were taken out 72 hour later, washed in the same order as above methods, dried with air and weighted accurately. After dried, weights were measured. The corrosion prevention ability (%) was obtained by the following equation. [5]

$$I(\%) = \left[1 - \frac{r}{r'}\right] \times 100$$

$$r = (m1 - m2)/St$$

From the above equation, m1 and m2 are the weight of low carbon steel before and after corrosion process and S is the surface area of the specimens and t is the time required for corrosion.

RESULTS AND DISCUSSION
Chemical characterization

Using the above methods, cationic gemini surfactants were synthesized. The chemical structures of the prepared cationic surfactants were confirmed by the FT-IR and FT-RAMAN, ^{1}H-NMR spectra. The results of four synthesized compounds were listed in Table 1.

FT-IR & FT-RAMAN spectroscopy

The chemical structures of synthesized cationic gemini surfactants were analyzed by FT-IR and FT-RAMAN spectrum of Fig. 1. Stronger ester peak of C = O at 1743 cm^{-1} and dicarboxylate peak at 1469 cm^{-1} were appeared. In addition, 1170 cm^{-1} peaks of C-O-C (ester) stretching vibration were confirmed. The synthesized cationic gemini surfactants were showed main characteristic bands. For example, surfactants showed stretching vibration band of –C–H aliphatic symmetric and asymmetric at 2846 and 2989 cm^{-1}, –CH$_2$ bending at 1377 cm^{-1}, –CH$_3$ bending at 1470 cm^{-1}, and C–N banding at 1073 cm^{-1}, as shown in Fig. 1.

Fig. 1: FT-IR & FT-RAMAN spectrum of synthesized cationic gemini surfactants.

Hydrogen Nuclear Magnetic Resonance (H-NMR) spectrum

The ^{1}H-NMR spectra data (δ ppm) of N^1,N^1,N^3,N^3-tetramethyl-N^1,N^3-bis(2-(tetradecanoyloxy) ethyl) propane-1,3-diaminium bromide(1) showed signals at : $\delta = 0.86$ (t, 6H, **–CH₃**); $\delta = 1.24$ (m, 40H, –(**CH₂**)nCH₃); $\delta = 1.57$ (m, 4H, – CH₂**CH₂**(CH₂)nCH₃); $\delta = 2.16$ (m, 2H, -N-CH₂(**CH₂**)CH₂-N-); $\delta = 2.38$ (t, 4H, –**CH₂**(CH₂)nCH₃); $\delta = 3.39$ (s, 12H, **CH₃**-N-); $\delta = 3.95$ (t, 8H, -**CH₂**-N(CH₃)₂-**CH₂**-) ; $\delta = 4.61$ (t, 4H, -COO-**CH₂**-CH₂-N(CH₃)₂-)

The ^{1}H-NMR spectra data (δ ppm) of N^1,N^1,N^4,N^4-tetramethyl-N^1,N^4-bis (2-(tetradecanoyloxy) ethyl)butane-1,3-diaminium bromide(2) showed signals at : $\delta = 0.87$ (t, 6H, **–CH₃**); $\delta = 1.25$ (m, 40H, –(**CH₂**)nCH₃); ; $\delta = 1.58$ (m, 4H, – CH₂**CH₂**(CH₂)nCH₃); $\delta = 2.16$ (m, 4H, -N-CH₂(**CH₂**)₂CH₂-N-); $\delta = 2.37$ (t, 4H, –**CH₂**(CH₂)nCH₃); $\delta = 3.38$ (s, 12H, **CH₃**-N-); $\delta = 3.94$ (t, 8H, -**CH₂**-N(CH₃)₂-**CH₂**-) ; $\delta = 4.60$ (t, 4H, -COO-**CH₂**-CH₂-N(CH₃)₂-)

The ^{1}H-NMR spectra data (δ ppm) of N^1,N^1,N^5,N^5-tetramethyl-N^1,N^5-bis (2-(tetradecanoyloxy) ethyl)pentane-1,3-diaminium bromide(1) showed signals at : $\delta = 0.87$ (t, 6H, **–CH₃**); $\delta = 1.24$ (m, 42H, –(**CH₂**)nCH₃, -N-CH₂(CH₂**CH₂**CH₂)CH₂-N-); ; $\delta = 1.56$ (m, 4H, – CH₂**CH₂**(CH₂)nCH₃); $\delta = 2.17$ (m, 4H, -N-CH₂(**CH₂CH₂CH₂**)CH₂-N-); $\delta = 2.35$ (t, 4H, –**CH₂**(CH₂)nCH₃); $\delta = 3.34$ (s, 12H, **CH₃**-N-); $\delta = 3.82$ (t, 8H, -**CH₂**-N(CH₃)₂-**CH₂**-) ; $\delta = 4.56$ (t, 4H, -COO-**CH₂**-CH₂-N(CH₃)₂-)

The ^{1}H-NMR spectra data (δ ppm) of N^1,N^1,N^6,N^6-tetramethyl-N^1,N^6-bis (2-(tetradecanoyloxy) ethyl)hexane-1,3-diaminium bromide(1) showed signals

Fig. 2: ^{1}H-NMR Chemical shift of N^1,N^1,N^4,N^4-tetramethyl-N^1,N^4-bis(2-(tetradecanoyloxy)ethyl) butane-1,4-diaminium bromide.

at : $\delta = 0.88$ (t, 6H, **–CH₃**); $\delta = 1.27$ (m, 44H, –(**CH₂**)nCH₃, -N-CH₂(CH₂**CH₂CH₂**CH₂)CH₂-N-); ; $\delta = 1.64$ (m, 4H, – CH₂**CH₂**(CH₂)nCH₃); $\delta = 2.13$ (m, 4H, -N-CH₂(**CH₂**CH₂ CH₂**CH₂**)CH₂-N-); $\delta = 2.38$ (t, 4H, –**CH₂**(CH₂)nCH₃); $\delta = 3.39$ (s, 12H, **CH₃**-N-); $\delta = 3.98$ (t, 8H, -**CH₂**-N(CH₃)₂-**CH₂**-) ; $\delta = 4.62$ (t, 4H, -COO-**CH₂**-CH₂-N(CH₃)₂-).

The data of ^{1}H-NMR spectra confirmed the expected hydrogen distribution in the synthesized cationic gemini surfactants. Fig. 2 shows that the synthesized compounds have the similar signals.

Surface tension and the Critical Micelle Concentration (CMC)

Critical micelle concentration values of synthesized cationic gemini surfactants have been obtained by plotting the surface tension (γ) of aqueous solutions of surfactants versus their bulk concentration at room temperature. The surface tension curves of the

Fig. 3: Surface tension and CMC value of synthesized cationic gemini surfactants.
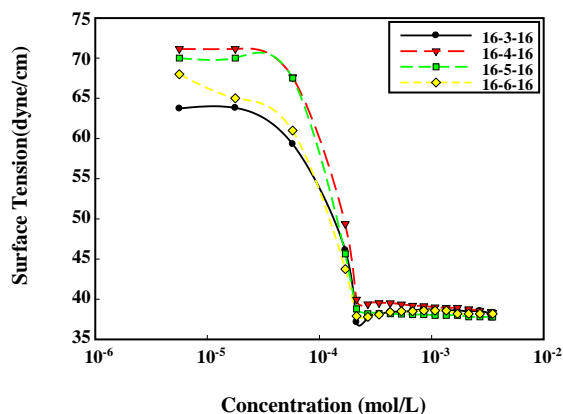

Fig. 4: Plot of conductivity versus concentration of synthesized cationic gemini surfactants 16-4-16.

synthesized surfactants were shown in Fig. 3. The CMC values from the breaks in the curves and the surface tension at CMC (γ_{CMC}) are listed in Table 1. It is observed that the CMC values of the synthesized surfactants decrease with a slightly increase of the spacer length from 3 to 6 methylene. And it noticed that the surface tension values for synthesized surfactants are smaller than other cationic surfactants as reported by many researchers. Decrease of surface tension is due to self-assembly properties of surfactants at air/water interface. The critical micelle concentration of surface tension was obtained by results from the inflection point, as shown in Fig. 3.

Electrical conductivity measurement

Conductivity measurements of solutions have been used to determine the CMCs from the plots of the conductivity χ against the surfactant concentration. Conductivity (χ) of synthesized surfactants solutions as a function of concentration was shown as example in Fig. 4. It is well known that breakpoint from two straight lines provides CMC values. Values of CMC are listed in Table 1.

Krafft point

At temperature close to 0℃, most surfactant are not completely dissolved in the water. The solution phases are giving a cloudy appearance. Below the Krafft point, a micelle is unable to be formed. The solubility of ionic surfactant increases rapidly in relation to temperature that called to Krafft point. Table 2 was listed Krafft points of synthesized cationic gemini surfactants and all of the values were confirmed 39.1 ~ 43.2 ℃. At this

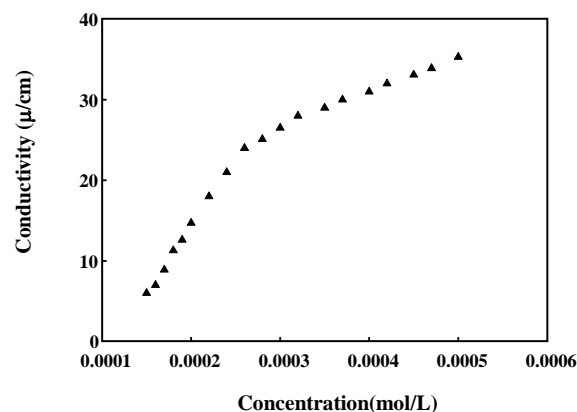temperature, surfactants are able to form micelles in the saturated solution.

Zeta potential measurement

Colloids in aqueous solution have an electrical charge. Cationic surfactants would lead to a positively charged surface. The surface charges of the cationic surfactants were measured the zeta potential. The influence of pH condition using a 0.01 wt% surfactants solution was examined by titration with NaOH and HCl, respectively. Experiments were measured with change of pH conditions using the zeta potential analyzer. Surface charges of synthesized surfactants were measured values of positive charge. Zeta potentials more positive than +30 mV are considered stable. Generally, the higher of absolute value of zeta potential, the more stable the system will be. Table 3 shows that the zeta potential values were measured +51.2 ~ 58.3 mV. That means it will be able to withstand additions of salt and lower viscosity. Based on the results of this experiment, it was confirmed that synthesized cationic gemini surfactants in all pH conditions act as cationic surfactants.

Gravimetric Measurements

The influence of inhibitor on the weight loss of the low carbon steel in 1 M HCl solution at 25 ℃ is shown in Fig. 5 and Table 4. Nitrogen compounds act as effective corrosion inhibitors [17]. The different concentration solutions were prepared from a hydrochloric acid solution to measure the corrosion inhibition rate of low carbon steel. Quaternary ammonium type surfactant have been used extensively as inhibitors against the acid corrosion

Table 2: Krafft point of synthesized cationic surfactants.

	16-3-16	16-4-16	16-5-16	16-6-16
Krafft point(℃)	39.1	39.8	40.2	43.2

Table 3: Zeta potential measurement of cationic surfactant solution at 25 ℃.

	16-3-16	16-4-16	16-5-16	16-6-16
pH 2	58.1	57.3	58.3	57.9
pH 4	56.2	55.1	54.8	55.7
pH 6	52.6	53.2	51.2	53.4
pH 8	53.8	54.1	54.4	55.1
pH 10	60.2	61.3	60.3	61.2
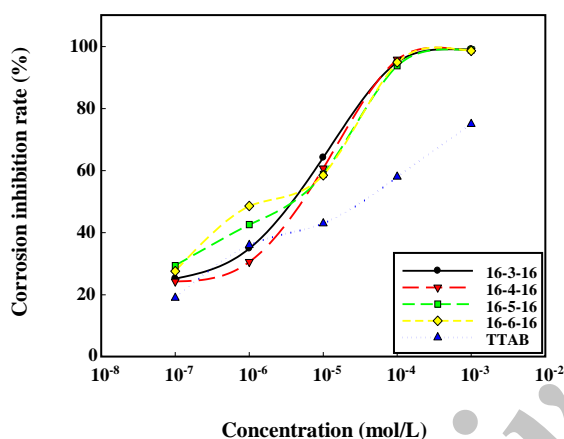
Fig. 5: Corrosion Inhibition efficiency in 1 M HCl with presence of different concentrations of synthesized cationic gemini surfactants.

of iron and steel, and this kind of organic molecules can be adsorbed on the metal surface. The adsorption of cationic surfactants on the steel surface is according to Langmuir's isotherm equation [18]. The traditional analysis of corrosion inhibition system using single-chained surfactants may not be suitable for analysis of the double chained gemini surfactants on the metal surface [17]. Therefore, the corrosion inhibition efficiencies of the synthesized surfactants inhibitors were calculated using weight loss method at various concentrations. In a previous study, *Q. Zhang* and his partner were determined about corrosion inhibition efficiency on the aluminum surface in 1 M HCl solution using similar gemini surfactants. They reported inhibition efficiency about

increased concentration of surfactants with increased hydrophobic chains [18]. It was consistent with the results of this experiment. Corrosion resistance can be seen to be increasing rapidly at $1 \times 10^{-5} \sim 1 \times 10^{-4}$ mol/L of solutions. Corrosion inhibition rate increased sharply in the critical micelle concentration. This effect is attributed to the formation of a protective layer from the surfactant molecules on the metal surface. Synthesized surfactant may form multilayer on the metal surface at concentrations above CMC. It is similar to behavior of conventional surfactants, before multilayer forms. Increasing the concentration had increases protective surface coverage of metal surface by surfactants molecules and it make adsorption of cationic surfactants on the metal surface as a result of an inter-hydrophobic chain interaction. Increasing the surfactants solutions concentration decreases the corrosion rate of the carbon steel and consequently the inhibition efficiencies increased. However, increasing surfactant concentration did not affect corrosion rate significantly. The relation between inhibition efficiency versus -log C (concentration) was represented at one inflection point, as shown in Fig. 5 and Table 4.

The synthesized surfactants effect by corrosion time & concentration

A study of the effect of surfactant concentration on corrosion time in the 1 mole of hydrochloric acid was measured during 72 hours. Experiments of resistance to corrosion were measured with 10^{-5} M surfactant and 1 M hydrochloric acid. Initial time, the corrosion inhibition efficiency is a 21.5% increased from 60%, but after

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Table 4: Corrosion inhibition efficiencies of synthesized cationic gemini surfactant obtained from weight loss measurements at different spacer length.

Inhibitor	concentration	Weight (g/cm²h)	Efficiency (%)
-	-	1.260	
16-3-16	1×10^{-7}	0.9341	25.2
	1×10^{-6}	0.8209	34.9
	1×10^{-5}	0.4459	64.2
	1×10^{-4}	0.0636	95
	1×10^{-3}	0.0107	99.1
16-4-16	1×10^{-7}	0.9541	24.3
	1×10^{-6}	0.7486	30.6
	1×10^{-5}	0.4956	60.7
	1×10^{-4}	0.0536	95.8
	1×10^{-3}	0.0162	98.7
16-5-16	1×10^{-7}	0.8901	29.4
	1×10^{-6}	0.7235	42.6
	1×10^{-5}	0.5195	58.8
	1×10^{-4}	0.0785	93.8
	1×10^{-3}	0.0136	98.9
16-6-16	1×10^{-7}	0.9115	27.6
	1×10^{-6}	0.7758	48.6
	1×10^{-5}	0.5236	58.5
	1×10^{-4}	0.0648	94.9
	1×10^{-3}	0.0182	98.6

10 hours, efficiency is decreased from 61%. The orientation of adsorbed gemini surfactant cation on the surface affects the corrosion inhibition efficiency. This is believed that is the result of surfactants by the electrostatic adsorption on the iron surface and it was similar mechanism of adsorption, such as conventional surfactants [18]. The surfactant is adsorbed on the surface and the surface corrosion is suppressed. This adsorption is oriented hydrocarbon chains from water to the surface. It means adsorbed cations can cover much area, thereby inhibiting more effectively the low carbon steel corrosion. However, during the corrosion time, some absorbed cationic surfactants are leave to the surface and aggregate

to form micelles. The corrosion inhibition rate is reduced because of this phenomenon, as shown in Fig. 6. The aggregation of micelles near the surface, considered inhibition efficiency reached to constant value in this range of corrosion time, as shown in Fig. 7.

Relations between surface tension and corrosion inhibition

The surface tension/surfactants concentrations were drawn in Fig. 2 and surface parameters were calculated in Table 3. The surface activity was showed that increasing the spacer chain length of synthesized inhibitors had increases the critical micelle concentration values.
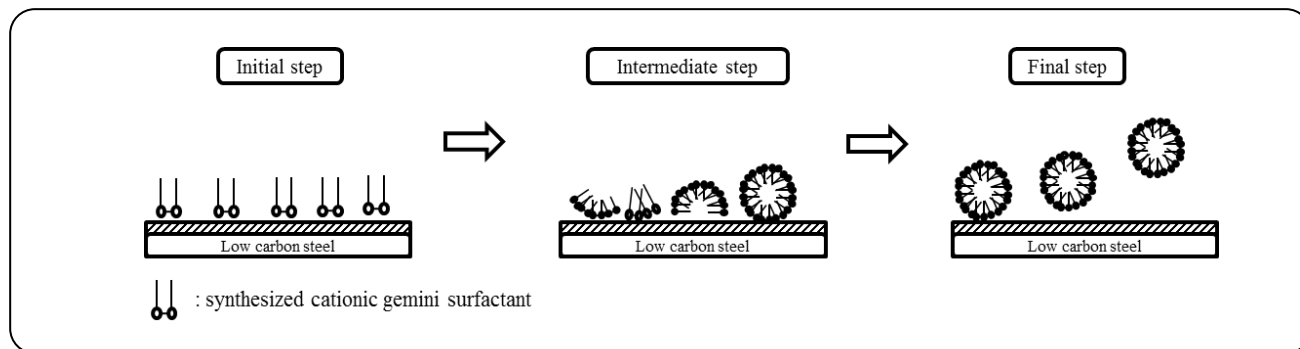
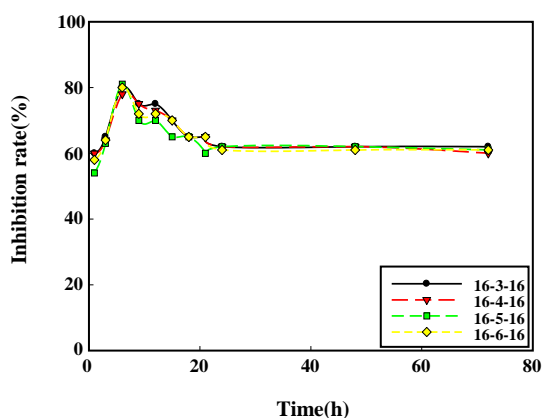*Fig. 6: The absorption of synthesize cationic gemini surfactant on the steel surface.*

Fig. 7: Surfactants effect of corrosion inhibition rate according to the time.

This is indicates the absorption tendency of compounds at the liquid interfaces. And it was showed that the increase in the inhibition ability by increasing chain length. That can be attributed to increase the chain length, increases the area of iron surface covered by synthesized surfactants.

CONCLUSIONS

In this work, we have succeeded in synthesizing of α, ω-alkane-bis(N-myristoyloxyethyl-N, N-dimethyl)-diammonium bromide and it have shown a good corrosion inhibitor for low carbon steel in a 1 M HCl solution. Inhibition capacity increases with increase of the concentration of synthesized gemini surfactants. Increasing concentration of synthesized cationic gemini surfactants increases their corrosion inhibition capacity and their adsorption tendency was increased. The corrosion inhibition rate of 10^{-3} M of gemini surfactant is 90% and the corrosion rate is decreases by increasing the surfactants concentration. The effective corrosion inhibition time of this system is 10 hours.

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