



Synthesis of novel cationic gemini surfactant and evaluation as corrosion inhibitor for carbon steel in 1M HCl

Hussin I. Al-Shafey¹, F. A. Ali², A. Y. El-Etre³, R. S. Abdel Hameed⁴, M. Salah⁵

¹ Egyptian Petroleum Research Institute, Nasr city, Cairo, Egypt.

^{2,5} Faculty of Science, Menofia Univrsty, Menofia, Egypt.

³ Chemistry Department, Faculty of Science, Benha University, Benha, Egypt

⁴ Chemistry Department, Faculty of Science, Al Azhar Univrsty Cairo, 11884, Egypt.

⁴ Chemistry Department, Colleges of Science, Hail University, Hail 1560, KSA.

Abstract

A novel class of cationic Gemini surfactants C16 – 2A – C16 (where C16 represents the alkyl chain length of 16) synthesized and characterized by FT – IR, H¹ NMR. Gemini surfactants aggregation behavior (determine critical micelles concentration CMC) were investigated by mean of electrical conductivity and obtained the surface tension at CMC point. It was found that C16 – 2A – C16 has superior surface activity. Cationic Gemini surfactant was evaluated as corrosion inhibitors for carbon steel in 1M HCl using weight loss, EIS and potentiodynamic polarization measurements. These measurements revealed that the synthesized material has served as effective mixed-type corrosion inhibitors. Their adsorption on a carbon steel surface was well described by means of the Langmuir adsorption isotherm. The activation parameters for the dissolution of carbon steel in solutions of 1M HCl in the absence and presence of these inhibitor were calculated. The effect of immersion time on the stability and durability of protective films adsorbed on a carbon steel surface was studied using weight loss method.

Keywords: Cationic Gemini surfactant, Corrosion inhibitor, Adsorption isotherms, potentiodynamic polarization, impedance, carbon steel.

Received; 21 April 2018, Revised form; 28 Jun 2018, Accepted; 28 Jun 2018, Available online 1 Oct. 2018

1. Introduction

In many industrial processes, acid solutions are used to remove the undesirable substances and corrosion products in metallic materials. Hydrochloric acid is the most used acids among the acidic cleaning methods [1]. At the time of this process metallic corrosion can also occur. Metallic corrosion is the degradation of metals and alloys via an electrochemical reaction that occurs with different effects. For instance, this metallic degradation causes serious economical disadvantages in several industrial fields of all countries [2]. In acidic cleaning methods, organic corrosion inhibitors are added to the medium to prevent the corrosion and to reduce the acid utilization.

Use of corrosion inhibitors is one of the most convenient means for protecting metals against corrosion, especially in acidic media [3, 4]. Most organic corrosion inhibitors interact with the metal surface through heteroatoms, such as nitrogen, oxygen, phosphorus, sulfur, aromatic rings, and multiple bonds, which can markedly change the corrosion resistance of the metal [5–8]. The inhibition efficiency is mainly due to the compatibility and affinity of the organic inhibitors with the metal surface, and their chemical structure [9]. Among organic inhibitors, oxygenated compounds and quaternary ammonium compounds are considered to be excellent corrosion inhibitors for many metals and alloys in various aggressive

solutions [10–16]. As a result, exploitation of novel gemini surfactants containing oxygen atoms may be a good choice. As a new generation of surfactants, gemini surfactants have attracted increasing research attention. Gemini surfactants consist of two hydrophobic chains and two polar headgroups covalently linked by a spacer. It has been demonstrated that gemini surfactants exhibit superior properties compared with conventional surfactants, such as lower critical micelle concentration (CMC) values, higher surface activity, better solubility, etc. [17–20]. In recent years, increasing research attention has been devoted to the corrosion inhibition behavior of gemini surfactants for highly viscous or aggressive media. We report herein the synthesis of a quaternary ammonium gemini surfactant. The CMC was investigated by conductivity and tensiometry measurements. The inhibition effect of this gemini surfactant for carbon steel was evaluated by weight loss measurements in 1.0 M hydrochloric acid solution. The results show that this novel corrosion inhibition system is very efficient for carbon steel in 1.0 M hydrochloric acid solution. The possible adsorption mechanism of the Gemini surfactant onto the surface of carbon steel in acidic medium was also explored.

2. Experimental

2.1. Material preparation

Carbon steel samples having composition 0.17% C, 0.462% Mn, 0.045% P, 0.025% Mo, 0.004% S, 0.103% Cr, 0.163% Cu and balance Fe were used for corrosion inhibition studies.

The following materials purchased from Sigma – Aldrich company: Propylene glycol (99.5 % purity), Sodium hydrogen sulfate (98% purity), Epichlorohydrin (99.5% purity), petroleum ether dist. (99% purity), ethyl acetate (99% purity), Potassium hydroxide (99 % purity), 33% aqueous diethyl amine, chloroform (99% purity), methanol (99.8 % purity), 1-bromo hexa decane (98 % purity), absolute isopropyl alcohol (99.7 % purity),

Hydrochloric acid (37 %), silica gel high-purity grade 40 (35-70 mesh). deionized water was used in the preparation of all solutions.

2.2. Synthesis and characterization of gemini surfactants

The gemini surfactants studied were synthesized in laboratory following an identical synthetic route. The synthesized products were characterized by ¹H NMR spectra. CDCl₃ was used as solvent and chemical shifts recorded were internally referenced to TMS (0 ppm). FT-IR spectra were measured. The CMC values of the surfactant solution were determined from Electrical conductivity. The name and molecular structures of the synthesized compounds are given in Table 1.

Table (1): Name and molecular structure of gemini surfactants

<p>N,N'-((propane-1,3-diylbis(oxy))bis(2-hydroxypropane-3,1-diyl)) bis (N,N-diethylhexadecan-1-aminium) dibromide</p>	<p>C16-2A-C16</p>
---	--------------------------

Surface tension measurement.

Surface tension measurements were performed using a SD Hardson-Kolkata tensiometer by the ring detachment method. Prior to each experiment the instrument was calibrated at 30 °C with double distilled water. Requisite concentrations of (C16-2A-C16) and after this the readings were recorded. Force engaged in the complete detachment of Pt-Ir ring from the surface film was interpreted as surface tension, γ (mN/m). Measurement of γ was continued till the equilibrium values are attained. The particular concentration at which γ vs. concentration plot shows a break approaches to the CMC

2.3. Weight loss measurements

The carbon steel coupons of size (3cm x 3.5cm x 0.3cm) were machined with a series of emery papers, followed by rinsing in acetone and deionized water and then dried in air. Prior to any experiment, the substrates were treated as described and freshly used with no further storage,

degreased with acetone, rinsed with bidistilled water and finally dried between filter paper. After weighting accurately, the specimens were immersed in 100 ml of 0.5 M HCl with and without different concentrations of surfactants at 30 °C. After different immersion time (3, 6, 12, 24, 48, 72, 96 and 120 hours), the C-steel samples were taken out, washed with bidistilled water, dried between filter papers and weighted again.

The weight loss values are used to calculate the corrosion rate.

2.2.2. Electrochemical measurements

Three electrochemical techniques, namely potentiodynamic polarization and electrochemical impedance spectroscopy (EIS), were used to study the corrosion behavior. All experiments were conducted in a conventional three electrodes glass cell. A Pt electrode as counter electrode and a saturated calomel electrode (SCE) as reference electrode were used in this study. The C-steel specimen was machined in to cylinder and sealed with epoxy resin leaving a working area of 0.785 cm². The specimens were polished, degreased and rinsed as described in weight loss measurements.

Potentiodynamic polarization experiments were carried out using a autoLab connected to personal computer with nova1.11 software for calculation. Nova1.11 calculates and displays E_{corr} , i_{corr} , β_a , β_c and the corrosion rate (R) in mm per year. All experiments were carried out at temperature (30 ± 1 °C). Equilibrium time leading to steady state of the specimens was 15 min and the open circuit potential (OCP) was noted. The potentiodynamic curves were recorded from -750 to -150 mV at a scan rate 2 mV S⁻¹

3. Results and discussion

3.1. Characterization of gemini surfactants: FTIR spectra of the synthesized compounds(C16-2A-C16) showed the following absorption bands at 804.6cm⁻¹ (CH bending), 2922.5-2853.5cm⁻¹ (CH stretching), 1382 cm⁻¹ (CH₃ bending), 1466.1 cm⁻¹ (CH₂ bending), 1110.1 cm⁻¹ (C-O aliphatic ether) and 3358 cm⁻¹ (OH alcohol) . The FTIR spectra confirmed the expected function groups in the synthesized compound (C16-2A-C16).

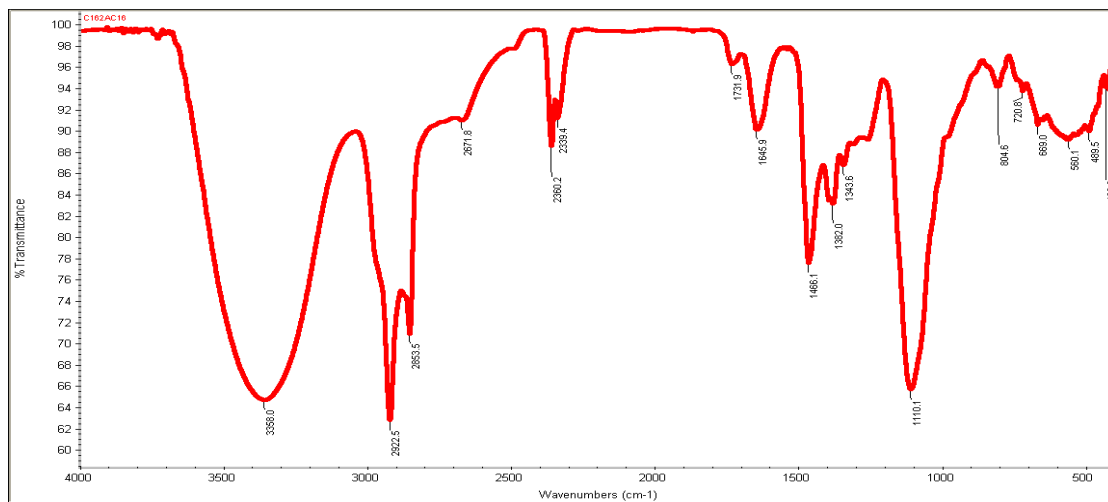


Fig (1): FT-IR spectrum of synthesized compound (C16-2A-C16)

The ¹H-NMR spectra of the synthesized compounds showed different bands at

δ PPM = (1.3) OCH₂CH₂CH₂O (2H, CH₂); (3.3– 4) OCH₂CH₂CH₂O (4H, CH₂) ; (3.3 – 4) CH₂O(CH₂)₃OCH₂ (4H, CH₂) ; (3.4 – 4) CH₂CHOH (2H, CH) ; (3.9) CH₂CHOH (2H, OH) ; (3.2 – 3.29) CHOCH₂N (4H, CH₂) ; (2-3) CH₂N(CH₂CH₃)₂ (8H, CH₂) ; (1.1) CH₂N(CH₂CH₃)₂ (12H, CH₃); (2-3) N(C₂H₅)₂(CH₂)₁₅ CH₃ (52 H, CH₂) (0.8 – 0.9) N(CH₂)₁₅ CH₃ (t, 6H, CH₃)

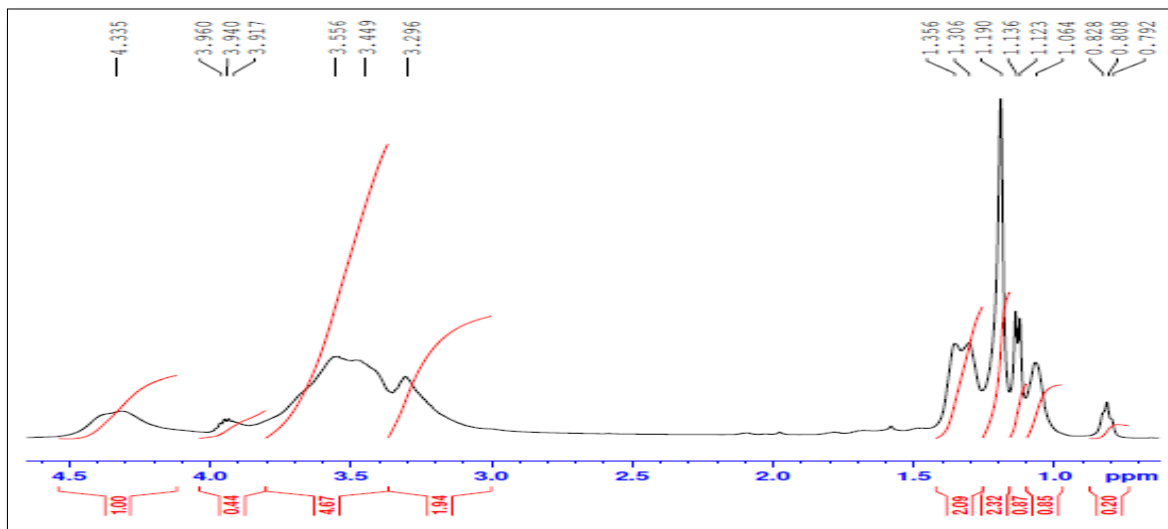


Fig (2): ¹H-NMR spectrum of compound (C16-2A-C16)

Surface active properties

Fig. (3) (supporting information) displays the surface tension (γ) of aqueous solutions of (C16-2A-C16) as a function of concentration ($\ln C$). In the low surfactant concentration, the γ decreases distinctly with increasing concentration and attains a break point. The intercept of two straight lines designates the critical micelle concentration (CMC). The surface tension data shown in table (2) (supporting information) allow us to calculate some physiochemical parameters such as effectiveness

(π_{CMC}), maximum surface excess (Γ_{max}), minimum surface area (A_{min}).

$$\Pi_{CMC} = \gamma_{water} - \gamma_{CMC} \tag{1}$$

$$\Gamma_{max} = -(1/RT)(d\gamma/d\ln C) \tag{2}$$

$$A_{min} = 1016/N \Gamma_{max} \tag{3}$$

where γ = surface tension in mN m⁻¹, R = gas constant (J mol⁻¹ K⁻¹), T = absolute temperature, ($-d\gamma/d\ln C$) = slope of the plot of γ vs. $\log C$, and NA = Avogadro' number.

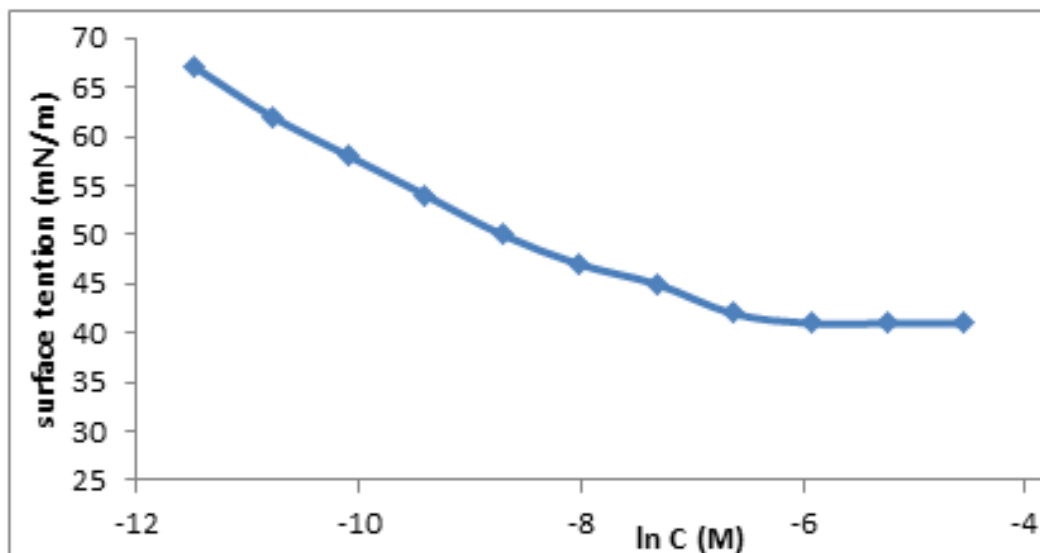


Fig. (3): Variation of the surface tension with the synthesized cationic gemini surfactants concentrations in water at 30°C.

Table (2): Critical micelle concentration (CMC), effectiveness (Π_{CMC}), maximum surface excess (Γ_{max}) and minimum area (A_{min}) of the synthesized cationic gemini surfactant.

Inhibitors	CMC x 10 ⁴ (mol dm ⁻³)	γ_{CMC} (mN m ⁻¹)	Π_{CMC} (mN m ⁻¹)	Γ_{max} x 10 ¹¹ (mol cm ⁻²)	A_{min} (nm ²)
C16-2A-C16	26.48	41	31.3	5.189	319.91

3.2. Weight loss measurements

The corrosion rate is reduced in presence of C16-2A-C16 as compared to the free acid solution. Also, the corrosion rate increased with increase in temperature. The plot of weight loss as a function of time at room temperature reveals that the weight loss increases with increase in time (Fig.4). The effect of temperature on η_w is quite pronounced; the η_w increases with increase in temperature.

The inhibition of carbon steel corrosion by C16-2A-C16 can be explained in terms of their adsorption on the steel surface. The very good efficiency of the compounds is due to high degree of surface coverage resulting from their adsorption on the steel surface. The strong adsorption in case of double chained can be explained on the basis of electrostatic interaction between the two ammonium and hydroxyl groups and the cathodic sites on the steel surface. Considering the effect of temperature on inhibition behavior of C16-2A-C16, the efficiency also increases with increase in temperature. This pointed to the capability of surfactants to inhibit corrosion of steel at low and relatively high temperatures. The C16-2A-C16 on steel surface are chemically adsorbed on to the carbon steel surface which is more favored at higher temperature due to lesser kinetic energy barrier. To clear up the influence of

these inhibitors on the mechanism of inhibition, the corrosion inhibition of carbon steel in 1 M HCl at room temperature in absence and presence of different concentrations of C16-2A-C16 was studied using weight loss technique and the data obtained after 120 hrs of immersion have been recorded. the corrosion rate (k) was calculated using the following equation:

$$k = (W_{free} - W_{inh}) / At \tag{4}$$

where, k is the corrosion rate, W_{inh} and W_{free} are the weights loss of specimen in presence and absence of inhibitor, respectively, A is the surface area in cm² and t is the time in hours. The degree of surface coverage (Θ) by the adsorbed molecules was calculated from equation:

$$\Theta = (W_{free} - W_{inh}) / W_{free} \tag{5}$$

It was found that the degree of surface coverage (Θ) of the inhibitor increases by increasing the inhibitor concentration. The inhibition efficiencies (η_w %) of cationic gemini surfactants, were determined from equation [21, 22]:

$$\eta_w \% = (\Theta) \times 100 \tag{6}$$

from the calculated values of (η_w %) which are given in Table (3)

Table (3): Effect of inhibitor (C16-2A-C16) concentration on carbon steel corrosion in 1M HCl at 25 °C.

Sample No.	Conc., M	Weight loss, mg/cm ²	η_w (%)	Θ	Corr. Rate, mg/cm ² .hr
Blank	0.0	1.0508	0	0	0.35167
(C16-2A-C16)	1x10 ⁻⁶	0.5303	49.5337	0.49533689	0.17748
	5x10 ⁻⁶	0.3463	67.0442	0.67044157	0.1159
	1x10 ⁻⁵	0.3064	70.8413	0.70841264	0.10254
	5x10 ⁻⁵	0.1796	82.9083	0.8290826	0.06011
	1x10 ⁻⁴	0.1613	84.6498	0.84649791	0.05398
	5x10 ⁻⁴	0.1364	87.0194	0.87019414	0.04565

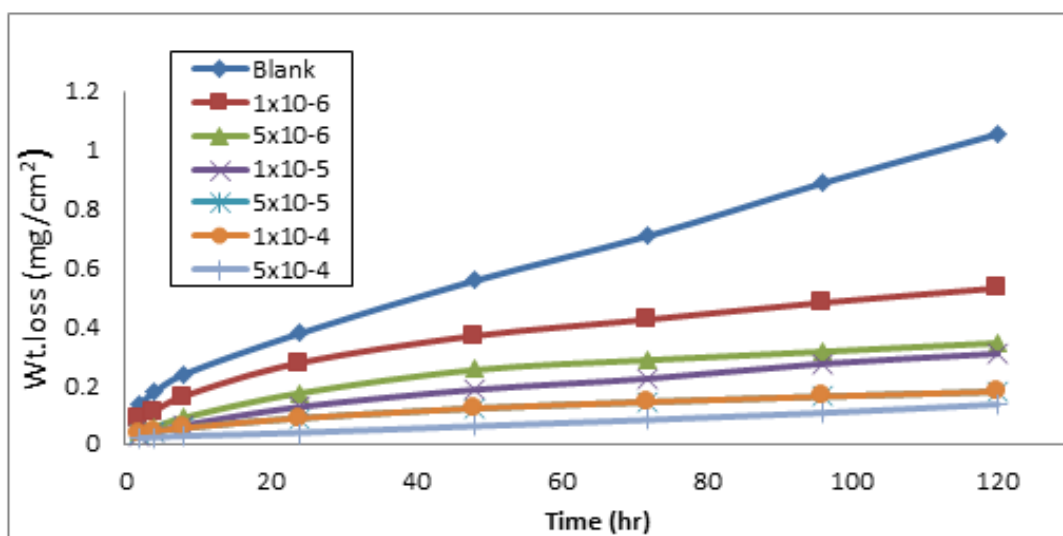


Fig (4): Relation between weight loss and time of carbon steel in 1M HCl in absence and presence of different concentration of compound (C16-2A-C16) at room temperature.

3.3. Adsorption Isotherms

Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reactions. In present study, Langmuir adsorption isotherm was found to be suitable for the experimental findings. The isotherm is described by equation:

$$C/\theta = 1/k + \theta \tag{7}$$

where, θ is the degree of surface coverage, K is the equilibrium constant of the adsorption process and C is the surfactant concentration. The plots of C/θ versus C for carbon steel corrosion in 1M HCl for surfactant C16-2A-C16 at room temperature is shown in Fig (5). the equilibrium constant of the adsorption K is related to standard free energy of adsorption by the relation (8):

$$K = 1/55.5 \exp(-\Delta G_{ads}/RT) \tag{8}$$

The values of adsorption parameters deduced from the Langmuir adsorption isotherm (linear regression parameters) such as linear regression coefficient, slope and adsorptive equilibrium constants are presented in Table 4. A linear correlation of slope close to unity suggests that adsorption of surfactants on carbon steel interface obeys Langmuir adsorption isotherm. The high values of K indicate that the C16-2A-C16 are strongly adsorbed on the steel surface.

Table (4): Parameters from Langmuir adsorption isotherm

R ²	slope	K _{ads} . x10 ⁵	-ΔG _{ads} . KJ mol ⁻¹
1	1.015	40	46.77

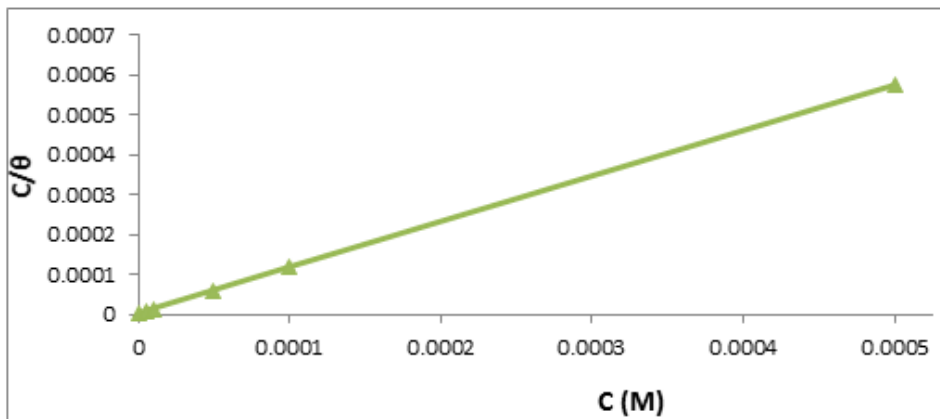


Fig. (5): Langmuir isotherm adsorption model on the carbon steel surface of (C16-2A-C16) in 1M HCl at room temperature.

3.4. Effect of temperatures

Effect of temperature is often used to determine whether an inhibitor is physically or chemically adsorbed on a metal surface to inhibit corrosion. An enhancement in inhibition efficiency with rise in electrolyte temperature is often associated with chemisorption phenomenon while the reverse signifies physisorption. To assess the effect of temperature on the corrosion inhibition of mild steel without and with C16-2A-C16, weight loss experiments were done at 30, 40, 50 and 60 °C using 5x10⁻⁴M. Inspection of Table (5) reveals that inhibition efficiencies increased with increase in solution temperature, confirming the ability of surfactants to inhibit corrosion of

carbon steel in HCl solution at low and relatively high temperatures and supports chemisorptions [23], which is more favored at higher temperature because of lesser kinetic energy barrier. Further, at high temperatures, desorption of water molecules from the surface of steel is more, resulting in the larger surface area available for the adsorption of C16-2A-C16 Gemini surfactant molecule [24]. The corrosion inhibition of carbon steel in 1 M HCl at 30-60 °C in absence and presence of 5x10⁻⁴ concentration of C16-2A-C16 was studied using weight loss technique and the data obtained after 24 h of immersion have been recorded in Table (5).

Table (5): Effect of temperature on carbon steel corrosion in presence of 5x10⁻⁴ M inhibitor (C16-2A-C16) concentration in 1M HCl

Temp. (°C)	Weight loss (mg/cm ²)	η _w (%)	θ	Corr. rate (mg/cm ² .hr)
30	0.0482	91.5808	0.91580786	0.08066
40	0.0554	95.5909	0.95590927	0.0927
50	0.0809	96.207	0.96207042	0.13537
60	0.1301	94.9848	0.94984773	0.2177

Kinetic parameters

In order to further elucidate the inhibitive properties of C16-2A-C16 gemini surfactant and the dependence of the temperature on the corrosion rate, the activation energy, E_a, enthalpy of activation, ΔH* and entropy of activation, ΔS* was calculated by Arrhenius equation and its alternative equation [25] shown as equations (9) and (10). The relevant plots for ln k and log k/T of carbon steel corrosion in 1M HCl in the absence and presence of various concentrations of C16-2A-C16 and at various temperatures are shown in Figs (6,7). The computed parameters are summarized in Table (6).

$$\ln(k) = \ln A - E_a/RT \tag{9}$$

$$k = \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right) \tag{10}$$

where k = corrosion rate, T = absolute temperature, R = universal gas constant. N = Avogadro number, and h = Planck’s constant. The lower values of E_a were observed for the inhibited systems than that for the uninhibited system indicating the chemical adsorption mechanism [26,27]. The positive value of ΔH* implies that the adsorption is endothermic reaction, which means it is good for adsorption when temperature is rising. The value of ΔH* is lower than E_a, which means inhibitor has formed a stable layer on the steel surface [28]. These results reflect that C16-2A-C16 is a good corrosion inhibitor. The negative value of ΔS* for C16-2A-C16 can be explained in the following way: before the inhibitor molecules were adsorbed on the surface of carbon steel, the molecules were scattered in the solution. However, as adsorption

progressed the inhibitor molecules were orderly adsorbed on the surface, which led to a decrease in entropy [29].

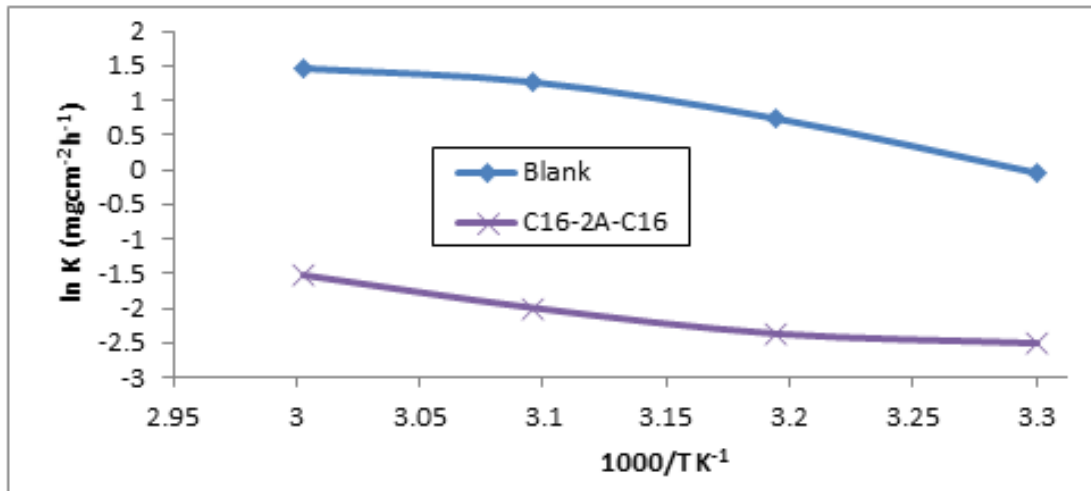


Fig. (6): Arrhenius plots (ln k vs. 1/T curves) for carbon steel dissolution in absence and presence of 5x10⁻⁴ of (C16-2A-C16) in 1M HCl solution.

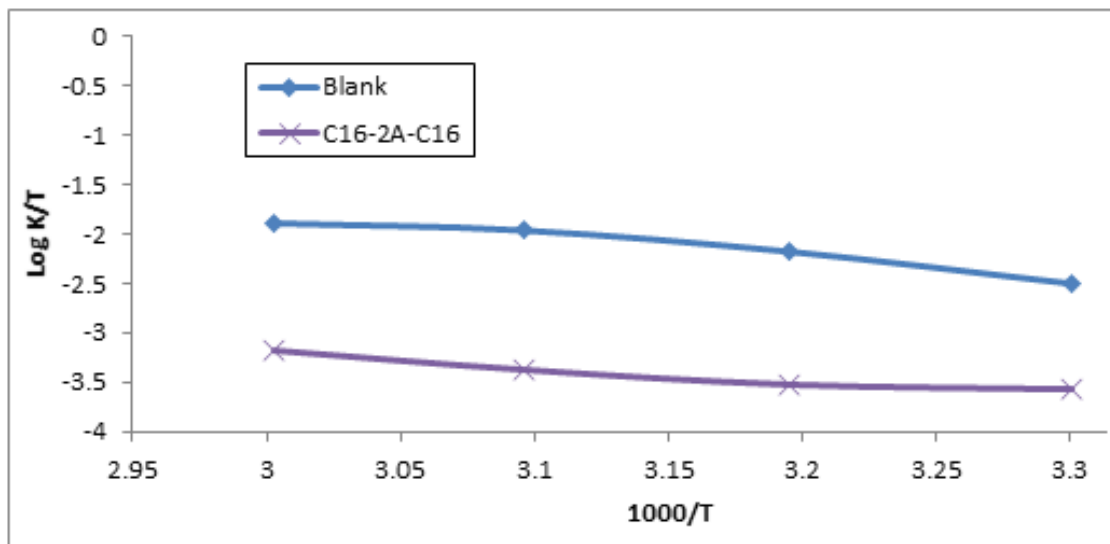


Fig (7): Relationship between log K/T and the reciprocal of the absolute temperature of carbon steel in 1M HCl containing 5x10⁻⁴ M of series (2A) of cationic gemini surfactants.

Table (6): Activation thermodynamic and adsorption parameters for carbon steel in the absence and presence of 5x10⁻⁴M of cationic gemini surfactants in 1M HCl at different temperatures.

	E _a kJ mol ⁻¹	ΔH* KJmol ⁻¹	ΔS* KJmol ⁻¹ K ⁻¹
Blank	42.5	40.11	112.03
C16-2A-C16	27.97	25.33	183.24

3.6. Potentiodynamic polarization measurements

The potentiodynamic polarization curves for the corrosion of carbon steel in 1M HCl solution in absence and presence of different concentration of surfactants are shown in Fig (8). The values of electrochemical parameters as deduced from these curves e.g., corrosion potential (E_{corr}) corrosion current density (i_{corr}), cathodic Tafel slope (β_c), anodic Tafel slope (β_a) and % η_p are shown in Table (7). The η_p was calculated by using the following equation:

$$\eta_p = \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0} \times 100 \quad (11)$$

where, i_{corr}⁰ and i_{corr} are the corrosion current density in absence and presence of inhibitors, respectively. The study of electrochemical data reveals that the value of i_{corr} decreases in presence of additives, the decrease in i_{corr} is more pronounced at higher concentration of surfactants. The values of E_{corr} in presence of surfactants shift to more positive values compared to the blank, suggesting the dominant role of anodic suppression in the process [30].

There is a change in the values of both β_a and β_c indicating that the corrosion of carbon steel in presence of surfactants is under both anodic and cathodic control. The values obtained from weight loss and electrochemical methods remain slightly different, this may be due to the

fact that η_p calculated from weight loss method is an average value, while the η_p obtained from electrochemical method is an instantaneous value rather than an average value. The electrochemical results on the whole, are in good agreement with the weight loss results.

Table (7): Potentiodynamic polarization parameters for corrosion of carbon steel in 1M HCl in absence and presence of different concentrations of compound C16-2A-C16 at room temperature at scanning rate 2 mV s⁻¹.

Conc. of inhibitor	-E _{corr} mV	I _{corr} mA cm ⁻²	β_a mV dec ⁻¹	β_c mV dec ⁻¹	Corr. rate mm/year	η_p %
Blank	432	456	76.8	164.4	5.29	---
1X10 ⁻⁶	373	149	91	176	1.72	67.3
5X10 ⁻⁶	362	63.8	156	153	0.74	86.0
1X10 ⁻⁵	391	57	158	86.7	0.66	87.5
5X10 ⁻⁵	383	50	157	85.4	0.59	89.03
1X10 ⁻⁴	384	45	97.4	137	0.52	90.1
5X10 ⁻⁴	395	40	87.8	154	0.47	91.2

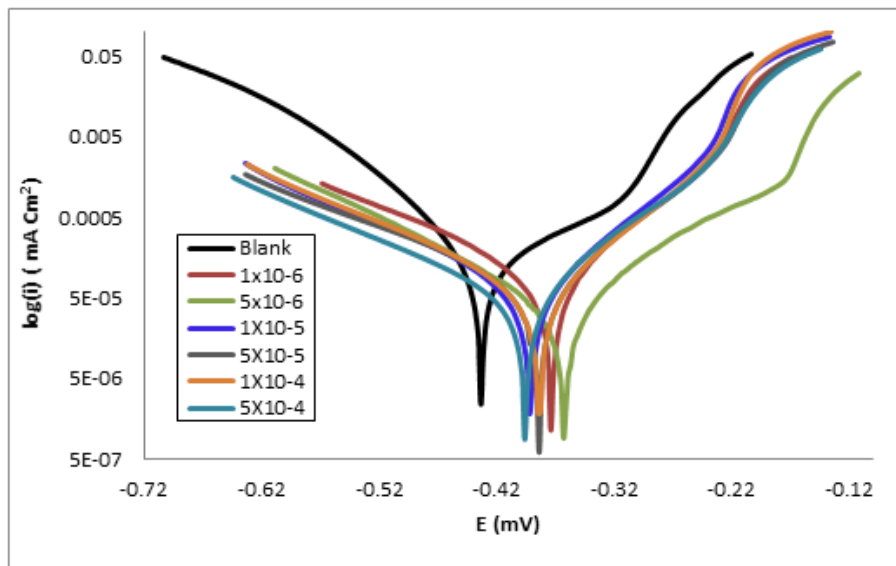


Fig (8): Potentiodynamic polarization curves for the carbon steel in 1M HCl in the absence and presence of different concentrations of compound C16-2A-C16 at scanning rate 2 mV s⁻¹.

3.7. EIS measurements

EIS diagrams for carbon steel in 1M HCl obtained in absence and presences of C16-2A-C16 are shown in Fig (9) Figure 10 shows the typical fitting results of EIS diagram with the provided equivalent circuit where Rs represents solution resistance, Rct charge transfer resistance, the best fit parameters are shown in Table (8). The η_z was obtained from the following equation.

$$\eta_z = (R^{0ct} - R_{ct} / R^{0ct}) \times 100 \quad (12)$$

where, R^{0ct} and Rct are the charged transfer resistance in absence and presence of surfactants, respectively. It is apparent that, the increase in surfactants concentration brings about an increase in the diameter of the semicircular capacitive loop. The increase in Rct values in presence of surfactants is attributed to the formation of a protective film on the mild steel/HCl solution interface [31, 32].

Table (8): EIS parameters for corrosion of carbon steel in 1M HCl in the absence and presence of different concentrations of compound C16-2A-C16 at room temperature.

Conc. of inhibitor M	R_p ohm cm^2	R_s ohm cm^2	R_{ct} ohm cm^2	η_z %	Θ
0.00	33.9	2.04	36.3	--	--
1×10^{-6}	80.18	0.17	83.5	56.5	0.56
5×10^{-6}	178.3	0.17	195.3	81.4	0.81
1×10^{-5}	294.5	-4.3	285.2	87.2	0.87
5×10^{-5}	378.7	-1.44	350.4	89.6	0.89
1×10^{-4}	370.4	0.062	375.3	90.3	0.90
5×10^{-4}	515.16	-6.3	491.5	92.6	0.92

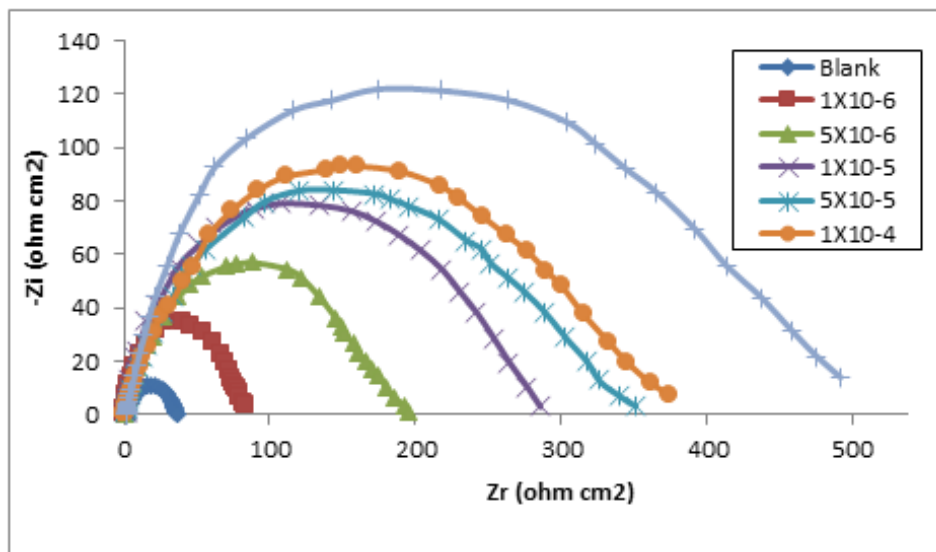
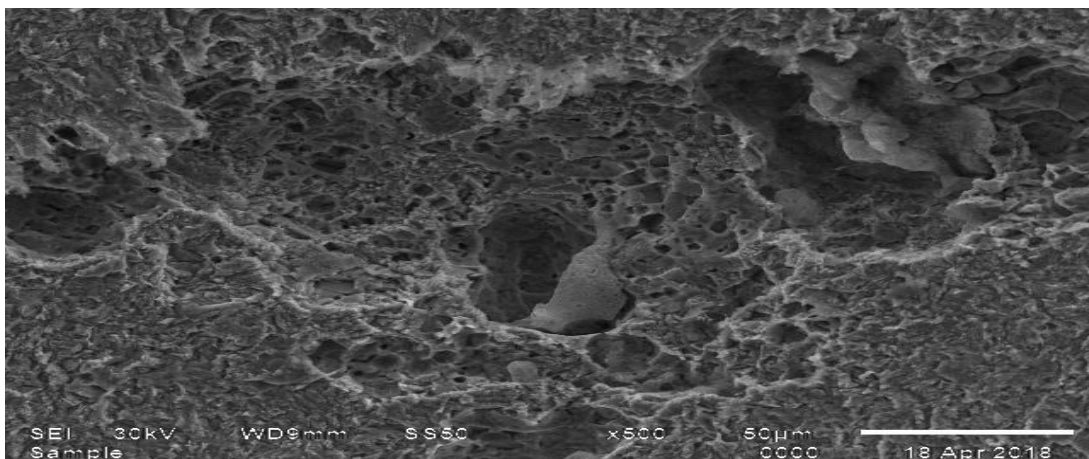


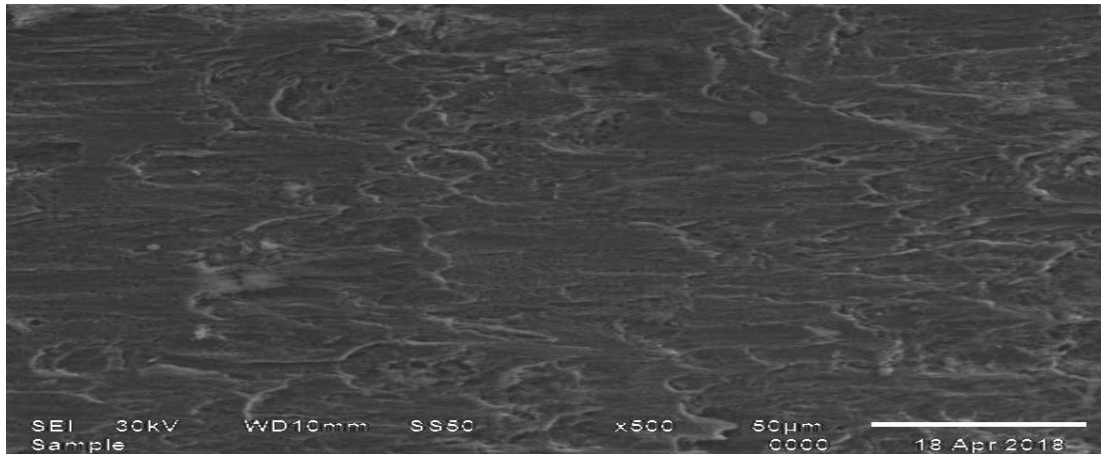
Fig. (9): Nyquist plots for the carbon steel in 1M HCl in the absence and presence of different concentrations of compound C16-2A-C16.

3.8. Scanning electron microscopy (SEM)

Fig. 10 A shows SEM of the surface of carbon steel micrographs reveal that, the surface was strongly damaged in specimen after immersion in 1M HCl for 24 hrs. in absence the absence of the inhibitor, but in the presence of 5×10^{-4} M of inhibitor, while Fig. 10 B shows SEM of the surface of of the compound (C16-2A-C16), there is less damage in the another carbon steel specimen after immersion in 1M HCl for surface. This confirms the observed high inhibition efficiency the same time interval in the presence of 5×10^{-4} M of the of compound (C16-2A-C16) at this concentration. compound (C16-2A-C16). The resulting scanning electron



A



B

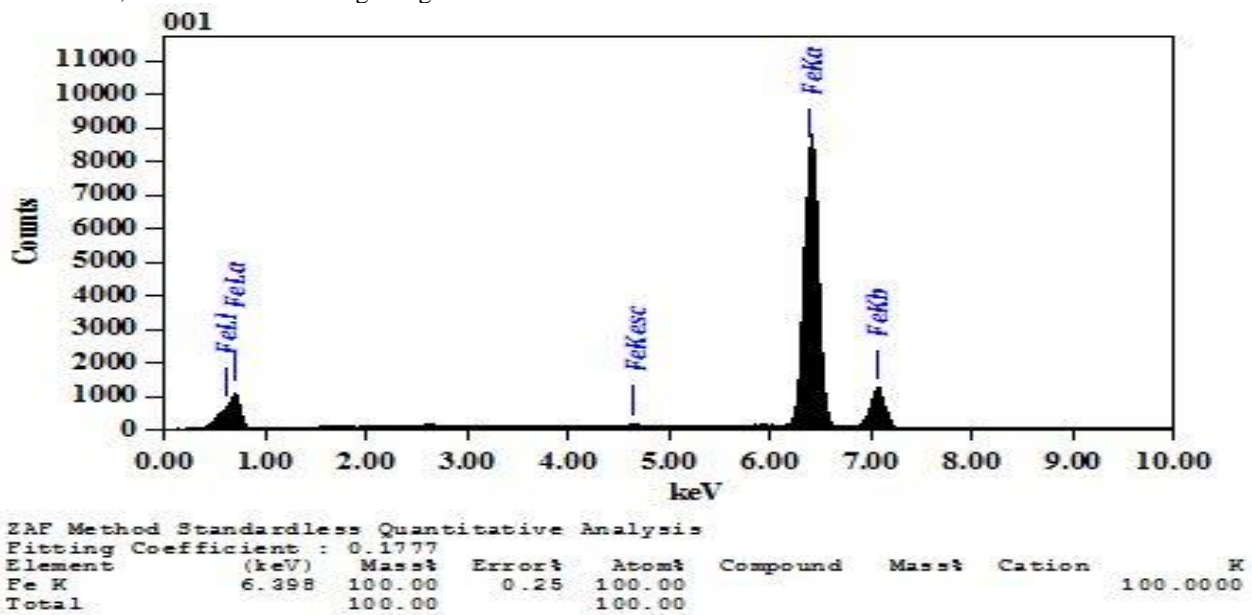
Fig (10): SEM of the carbon steel surface: (A) after immersion in the 1M HCl and (B) after immersion in the 1M HCl in the presence of 5×10^{-4} M of the compound (C16-2A-C16)

3.9. Energy dispersive analysis of X-rays (EDX)

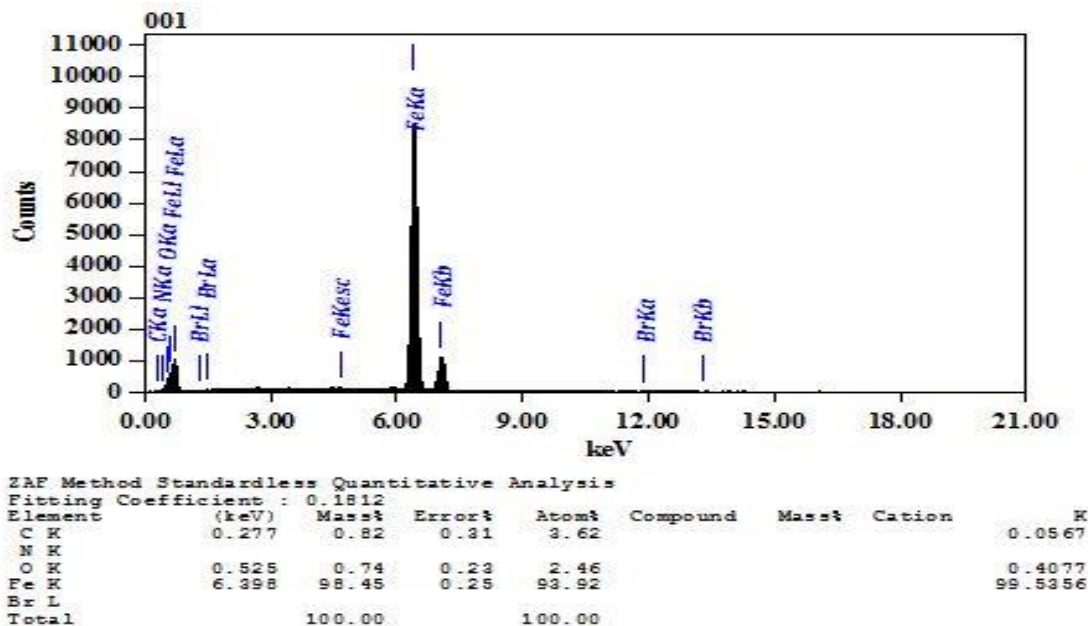
The spectrum of the polished carbon steel surface after immersion in the 1M HCl in the absence and presence of 5×10^{-4} M of the compound (C16-2A-C16) for 24 hrs., is shown in Figs. 11A and 11B, respectively. The spectrum of Fig. 11B shows that the Fe peak is considerably decreased relative to the samples in Fig. 11A and appear of oxygen and carbon beaks. This decreasing of the Fe band and appearing of oxygen and carbon beaks is indicated that strongly adherent protective film of compound (C16-2A-C16) formed on the polished carbon steel surface, which leads to a high degree of inhibition

efficiency [33]. Therefore, EDX and SEM examinations of carbon steel surface support the results obtained from chemical and electrochemical methods that the synthesized surfactant inhibitor is a good inhibitor for carbon steel in 1M HCl.

The results of both SEM and EDX techniques confirm the formation of a good protective layer on the surface of carbon steel in the presence of 5×10^{-4} M of the compound (C16-2A-C16).



A



B

Fig (11): EDX of the carbon steel surface: (A) after immersion in the 1M HCl and (B) after immersion in the 1M HCl in the presence of 5×10^{-4} M of the compound (C16-2A-C16).

References

1. G Bereket, A Parabasis, " Inhibition effect of some heterocyclic compounds on pure aluminium in 0.1 M hydrochloric acid solution." Corrosion 16 (2008) 17–22
2. S Bilgic, "Corrosion education and training." Corrosion 16 (2008) 3–7
3. M Mahdavian, AR Tehrani-Bagha, K Holmberg "Comparison of a cationic gemini surfactant and the corresponding monomeric surfactant for corrosion protection of mild steel in hydrochloric acid." J Surfact Deterg. 14 (2011) 605–613
4. A Khamis, MM Saleh, MI Awad "Synergistic inhibitor effect of cetylpyridinium chloride and other halides on the corrosion of mild steel in 0.5 M H₂SO₄." Corros Sci 66 (2013) 343 349
5. G Axcı " Corrosion inhibition of indole-3-acetic acid on mild steel in 0.5 M HCl." Colloids Surf A Physicochem Eng Aspects 317 (2008) 730–736
6. AR Saliyan, AV Adhikari "Quinolin-5-ylmethylene-3-[[8-(trifluoromethyl)quinolin-4-yl]thio]propanohydrazide as an effective inhibitor of mild steel corrosion in HCl solution." Corros Sci 50 (2008) 55–61
7. D Chebabe, ZA Chikh, N Hajjaji et al " Corrosion inhibition of Armcro iron in 1 M HCl solution by alkyltriazoles." Corros Sci 45 (2003) 309–320
8. M Motamedi, AR Tehrani-Bagha, M Mahdavian " Effect of aging time on corrosion inhibition of cationic surfactant on mild steel in sulfamic acid cleaning solution." Corros Sci 70 (2013) 46–54
9. SK Shukla, MA Quraishi, R Prakash et al " A self-doped conducting polymer "polyanthranilic acid": an efficient corrosion inhibitor for mild steel in acidic solution." Corros Sci 50 (2008) 2867–2872
10. X Wang, H Yang, F Wang "A cationic gemini-surfactant as effective inhibitor for mild steel in HCl solutions." Corros Sci 52 (2010) 1268–1276
11. SAA El-Maksoud "The effect of organic compounds on the electrochemical behavior of steel in acidic media, a review." Int J Electrochem Sci 3 (2008) 528–555
12. MA Migahed, MA Hegazy, AM Al-Sabagh " Synergistic inhibition effect between Cu²⁺ and cationic gemini surfactant on the corrosion of downhole tubing steel during secondary oil recovery of old wells." Corros Sci 61 (2012) 10–18
13. S Seal, K Sapre, A Kale et al " Effect of multiphase flow on corrosion of C-steel in presence of inhibitor: a surface morphological and chemical study." Corros Sci 42 (2000) 1623–1634
14. FA Ansari, MA Quraishi "Inhibitive effect of some Gemini surfactants as corrosion inhibitors for mild steel in acetic acid media." Arab J Sci Eng 36 (2011) 11–20
15. A Popova, M Christov, S Raicheva et al " Adsorption and inhibitive properties of benzimidazole derivatives in acid mild steel corrosion." Corros Sci 46 (2004) 1333–1350
16. LG Qiu, AJ Xie, YH Shen "A novel triazole-based cationic gemini surfactant: synthesis and effect on corrosion inhibition of carbon steel in hydrochloric acid." Mater Chem Phys 91 (2005) 269–273
17. Q Zhang, Z Gao, F Xu et al " Surface tension and aggregation properties of novel cationic gemini surfactants with diethylammonium headgroups and a diamido spacer." Langmuir 28 (2012) 11979–11987
18. P Patial, A Shaheen, I Ahmad "Synthesis of ester based cationic pyridinium gemini surfactants and

- appraisal of their surface-active properties." *J Surfact Deterg* 16 (2013) 49–56
19. Y Zhang, M Ding, L Zhou et al "Synthesis and antibacterial characterization of gemini surfactant monomers and copolymers." *Polym Chem* 3 (2012) 907–913
20. L Mivehi, R Bordes, K Holmberg " Adsorption of cationic gemini surfactants at solid surfaces studied by QCM–D and SPR: effect of the rigidity of the spacer." *Langmuir* 27 (2011) 7549–7557
21. M. El Achouri , S. Kertit, H.M. Gouttaya , B. Nciri , Y. Bensouda , L. Perez, M.R. Infante, K. Elkacemi, *Prog. in Org. Coatings* 43 (2001) 267.
22. A.Y. El-Eter, "Inhibition of acid corrosion of carbon steel using aqueous extract of olive leaves." *J. Colloid and Interface Science* 314 (2007) 578.
23. M. A.Hegazy, , A. M. Badawi, & S. S. Abd El Rehim, "Corrosion inhibition of carbon steel using novel N-(2-(2-mercaptoacetoxy)ethyl)-N,N-dimethyl dodecan-1-aminium bromide during acid pickling." *Corros. Sci.* 69 (2013) 110–122.
24. M. M.Aiad, , A. El-Sukkary, , Y. M. El-Deeb, El-Awady, & S. M. Shaban, "Surface and biological activity of some prepared iminium surfactants based on schiff bases." *J. Surfact. Deterg.* 16, 243–250 (2013).
25. M. Mobin,, R. Aslam, & J. Aslam, "Nontoxic biodegradable cationic gemini surfactants as novel corrosion inhibitor for mild steel in hydrochloric acid medium and synergistic effect of sodium salicylate: experimental and theoretical approach." *Mater. Chem. Phys.* 191 (2017) 151–167.
26. G.Mu., & X. Li, "Inhibition of cold rolled steel corrosion by Tween-20 in sulfuric acid: Weight loss, electrochemical and AFM approaches." *J. Colloid Interface Sci.* 289 (2005) 184–192.
27. E. S. Ferreira, C. Giacomelli, , F. C. Giacomelli, & A. Spinelli, "Evaluation of the inhibitor effect of L-ascorbic acid on the corrosion of mild steel." *Mater. Chem. Phys.* 83 (2004) 129–134.
28. W. Li, Q. He, C. Pei, & B. Hou, " Experimental and theoretical investigation of the adsorption behaviour of new triazole derivatives as inhibitors for mild steel corrosion in acid media." *Electrochim. Acta* 52 (2007) 6386–6394.
29. G. Golestani, M. Shahidi, & D. Ghazanfari, " Electrochemical evaluation of antibacterial drugs as environment-friendly inhibitors for corrosion of carbon steel in HCl solution." *Appl. Surf. Sci.* 308, 347–362 (2014).
30. Lichao Hu, Shengtao Zhang, Weihua Li, Baorong Hou, "Electrochemical and thermodynamic investigation of diniconazole and triadimefon as corrosion inhibitors for copper in synthetic seawater" *Corrosion Sci.*, 52 (2010) 2891.
31. F.Bentiss , M.Traisnel and M.Lagrene, "The substituted 1,3,4-oxadiazoles: a new class of corrosion inhibitors of mild steel in acidic media." *Corrosion. Sci.*, 42 (2000) 127-146.
32. S.Murlidharan, K.L.N.Phani, S.Pitchumani and S.Ravichandaran," Polyamino- Benzoquinone Polymers: A New Class of Corrosion Inhibitors for Mild Steel." *J.Electrochem.Soc.*, 142 (1995) 1478-1483.
33. M.A. Amin, *J. Appl. Electrochem.* ,36 (2006)215.