Journal of Basic and Environmental Sciences, 5 (2018) 289-300

ISSN
Online: 2356-638
Print: 2536-9202

Mini Review
Open Access

Corrosion inhibition of Tri-cationic surfactant on carbon steel in hydrochloric acid solution

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Abstract

A novel Tri-cationic surfactant was prepared by the reaction of cetyl-2-chloroacetate with di amide. The chemical structure of the prepared compound was confirmed by FTIR and ^{1}HNMR. The critical micelle concentration value of the prepared surfactant was determined by surface tension and conductivity measurements. The prepared compound was examined as corrosion inhibitor for carbon steel in hydrochloric acid solutions using weight loss and potentiodynamic polarization methods. Tafel polarization studies showed that the surfactant is mixed type inhibitor. The adsorption of the prepared compound on to the surface of carbon steel in 1 M HCl obeys the Langmuir isotherm. Also, activation thermodynamic parameters such as E_a, ΔH^* and ΔS^* were calculated using Arrhenius and transition state equations and discussed.

Keywords: Surfactants synthesis, corrosion inhibition, C-steel.

Received; 8 April 2018, Revised form; 7 May 2018, Accepted; 7 May 2018, Available online 1 July. 2018

1. Introduction

During the last few decades, rapid advances in the understanding of surface phenomenon have taken place. However, the importance of surface science has been recognized for more than a century [1]. A class of compounds called surface-active compounds (or surfactants). The word "Surfactant" is a contraction of the three words "Surface Active Agents." Surfactants are materials that lower the surface tension (or interfacial tension) between two liquids or between a liquid and a solid which are composed of hydrophilic group ''polar head", attached to hydrophobic tail ''non-polar tail'' connected by a flexible or rigid spacer [2, 3, 4]. Recently scientists use surfactants as organic corrosion inhibitors to prevent and control corrosion of metals, which are in contact with corrosive environment. In last few years, Scientists interested in finding an efficient technique for treatment and prevention of metal from corrosion one of these techniques is corrosion inhibitors. Organic corrosion inhibitors offer surface protection by adsorption of their active functionalities on metal surfaces [5, 6, 7], they are chemical compounds that control, reduce or prevent reactions between metal and its surroundings when added to the medium in small quantities and minimize the rate of corrosion and prohibit the metal from corrosion [8, 9, 10]. The majority of the well-known inhibitors are organic compounds containing heteroatom, such as nitrogen, oxygen, sulfur atoms and multiple bonds, which allow adsorption on the metal surface [11 – 12]. In comparison to traditional corrosion inhibitors, surfactants are economical, easy to produce, and possess high inhibition efficiency and low toxicity [13]. Cationic surfactants are corrosion inhibitors for different metals besides other applications such as detergents, wetting agents, emulsifiers and dispersants [14- 15].

In this work, the inhibition performance of the novel synthesized tri cationic surfactant for carbon steel in acidic medium was investigated using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The CMC values of the prepared surfactant was determined by surface tension and conductivity measurements. The surface parameters were calculated by surface tension measurements.

2. Experimental

2.1. Materials

Nicotinic acid, Methanol, sulphoric acid, ethanol, benzene, chloroform, Chloroacetic acid, p-Toluene sulphonic acid and Cetyl alcohol were obtained from AL-Nasr Chemical Company. Triethylentertamine was purchased from Merck.

2.2. Synthesis of cationic surfactants

2.2.1. Synthesis of Methyl nicotinate.

Reaction mixture containing 12.3 gm. (0.1 mol.) nicotinic acid, 50 ml of methanol and 6 ml conc.H_2SO_4 was refluxed for about a 15 h in a water bath. Then left to be cooled and neutralized with a solution of 15% sodium carbonate. then extracted with chloroform. The chloroform was distilled off to obtain white crystalline product. Yield (76%), M.P. 38 ^{o}C [16].

2.2.2. Synthesis of amide

Methyl nicotinate 2.74 gm. (0.02 mol.) Was reacted with triethylentertamine 1.46 gm. (0.01 mol.) Through fusion technique in sand bath for about 2 h. then left to be cooled overnight to obtain final product as pale-yellow wax. Yield (82 %). M.P. (80 ^{O}C). The chemical structure of the synthesized amide (Fig 1) was confirmed by FTIR and ^{1}HNMR

2.2.3. Synthesis of cetyl -2-chloroaetate

A mixture of 13.52gm. (0.05 mol.) cetyl alcohol and 4.72gm. (0.05 mol.) chloroacetic acid in presence of 0.01%*p*-toluene sulphonic acid as a catalyst and dry benzene as solvent was refluxed with a Dean–Stark trap, till the calculated amount of water 0.9 ml (0.05 mol.) was separated. The solvent was distilled off to obtain white color solid yield (80%). M.P. (38 ^{O}C) [17]

2.2.4. Synthesis of tri cationic Surfactant

Cationic surfactant was synthesized by quaternization of the produced amide with cetyl -2-chloroaetate using ethanol as solvent for 90 h in molar ratios of 1:3. The solvent was distilled off to produce CS_{III} cationic surfactants [18]. The chemical structure of the synthesized cationic surfactant (Fig 2) were confirmed by FTIR and ^{1}HNMR

2.3. Carbon steel

Carbon steel specimens with chemical composition (wt %) were used in the experiments: Carbon (C) 0.38-0.45, Chromium (Cr) 0.90-1.20, Molybdenum (Mo) 0.15-0.25, Silicon (Si) 0.17-0.37, and Manganese (Mn) 0.50-0.80. A pre-treatment procedure was carried out, prior to each experiment, in which the surface of specimen of (1.6 x 1.5 x 0.7) cm was mechanically polished with different emery paper and cleaned with acetone and distilled water then dried at room temperature before use.

2.4. Weight Loss technique

Carbon steel specimens were washed, dried, and accurately weighed and then the specimens were immersed in a solution containing 1 M HCl with and without the addition of different concentrations ($5x10^{-3}$, $1x10^{-3}$, $5x10^{-4}$, $1x10^{-4}$, and $1x10^{-5}$) of the synthesized cationic surfactant for 24 h. After immersion time of 24 h, the specimens were washed, dried, and weighed accurately.

2.5. Electrochemical technique

For electrochemical measurements, a classical three electrode glass cell with a platinum counter electrode and saturated calomel electrode (SCE) as a reference was used. Carbon steel as working electrode expose only a 0.48 cm^2 surface to the solution. The exposure surface was abraded with different grades of emery paper, washed with acetone and distilled water then dried. The potentiodynamic polarization measurements were obtained using scan rate of 2 mV s -1 at 25 ± 1 ^{o}C.

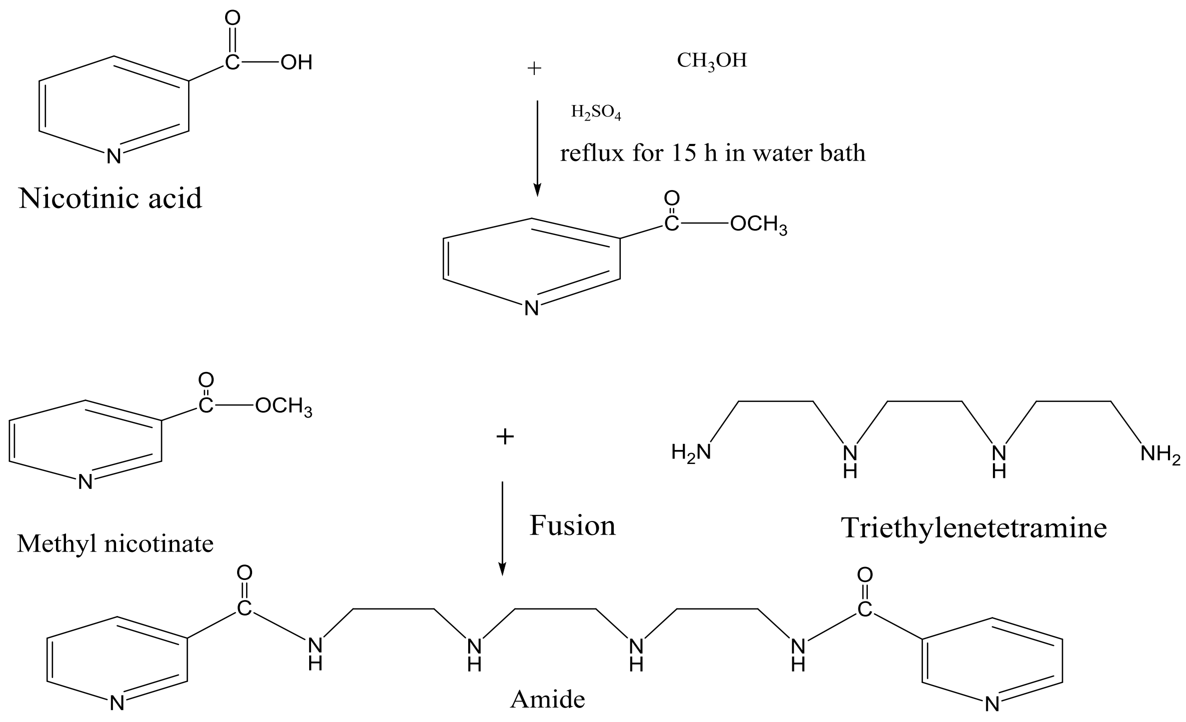

Fig (1): Synthesis of Amide

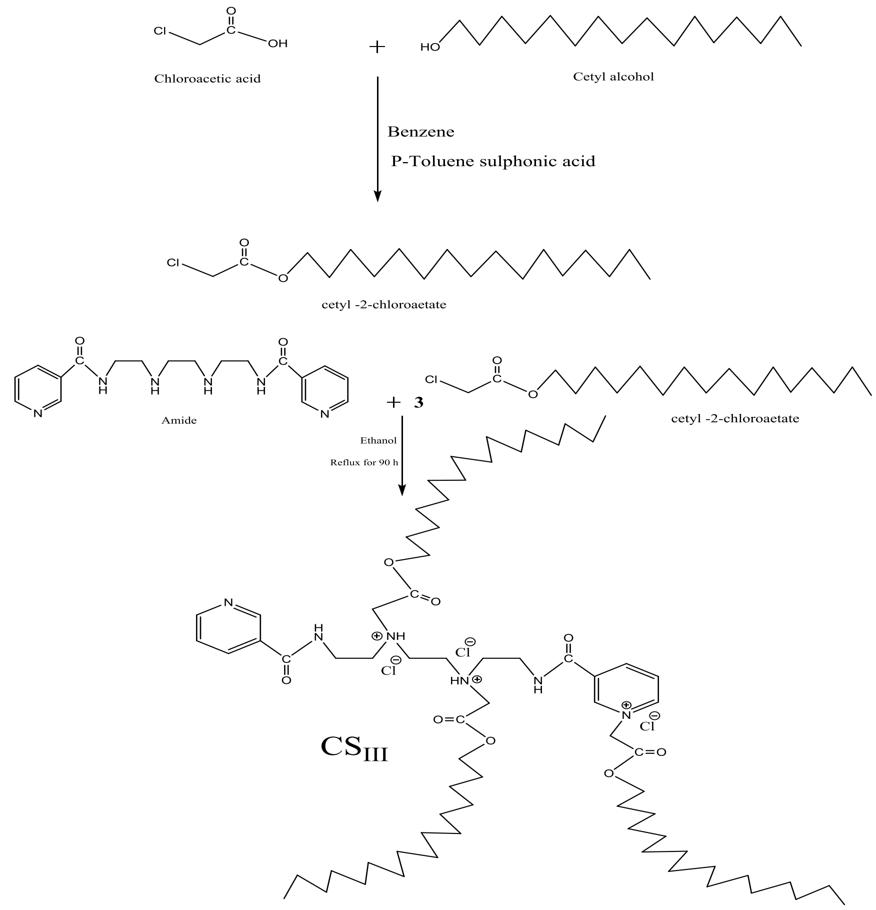

Fig (2): Synthesis of cationic surfactants

3. Results and Discussion

3.1. Structural confirmation of Amide "N, N'-((ethane-1, 2-diylbis (azanediyl)) bis (ethane- 2,1-diyl)) dinicotinamide"

The FT-IR spectra confirm the expected functional groups in the synthesized amide (Fig 3) by showing bands at 3289 cm^{-1} (ѵNH stretching), 3027 cm^{-1} (ѵCH aromatic stretching), 2944 cm^{-1} and 2893 cm^{-1} (ѵCH aliphatic chain), 1649 cm^{-1} (ѵC=Oamide),1550cm^{-1} (ѵC=Caromaticstretching),1597cm^{-1}(ѵNHamideending), 1473cm^{-1} (ѵCH2 bending), 1313 cm^{-1} (ѵC–Narylstretching),1164 cm^{-1} (ѵC–N alkyl stretching), 833 cm^{-1} (ѵCH para bending), 709 cm^{-1} (ѵCH ortho bending).

The data of ^{1}H-NMR spectra confirm the expected hydrogen proton distribution in the synthesized amide (Fig 4) δ (ppm): 1.242H,$CONHCH_2CH_2\underline{NH}CH_2CH_2\underline{NH}CH_2CH_2NHCO$),2.7(4H,$CONHCH_2CH_2NH\underline{CH_2}\underline{CH_2}NHCH_2CH_2NHCO$),2.89 (4H,$CONHCH_2\underline{CH_2}NHCH_2CH_2NH\underline{CH_2}CH_2NHCO$),3.5(4 H,$CONH\underline{CH_2}CH_2NHCH_2CH_2NHCH_2\underline{CH_2}NHCO$),8.6(2H, $CO\underline{NH}CH_2$), 7.44 – 9.009 (8H, $NHCO\underline{C_5H_4N}$). [19]

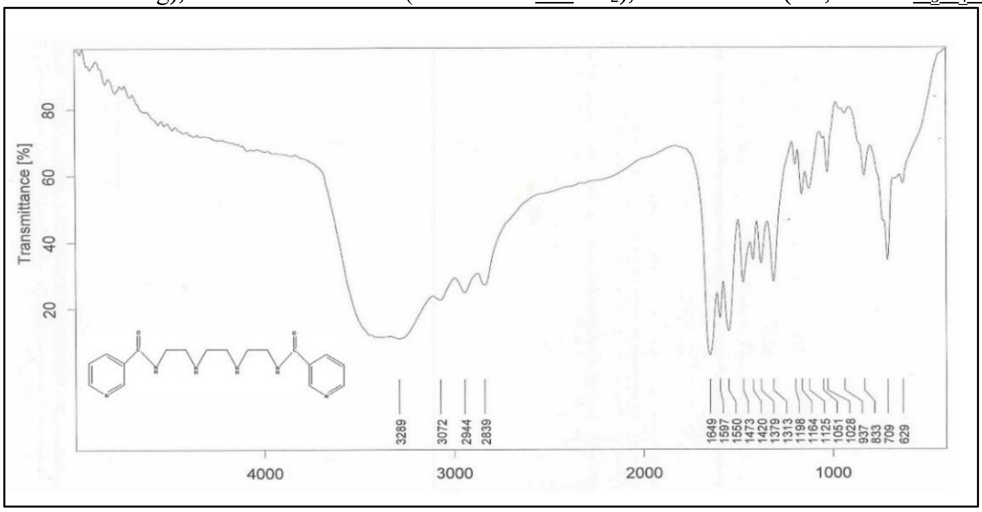

Fig (3): FT-IR spectra of Amide

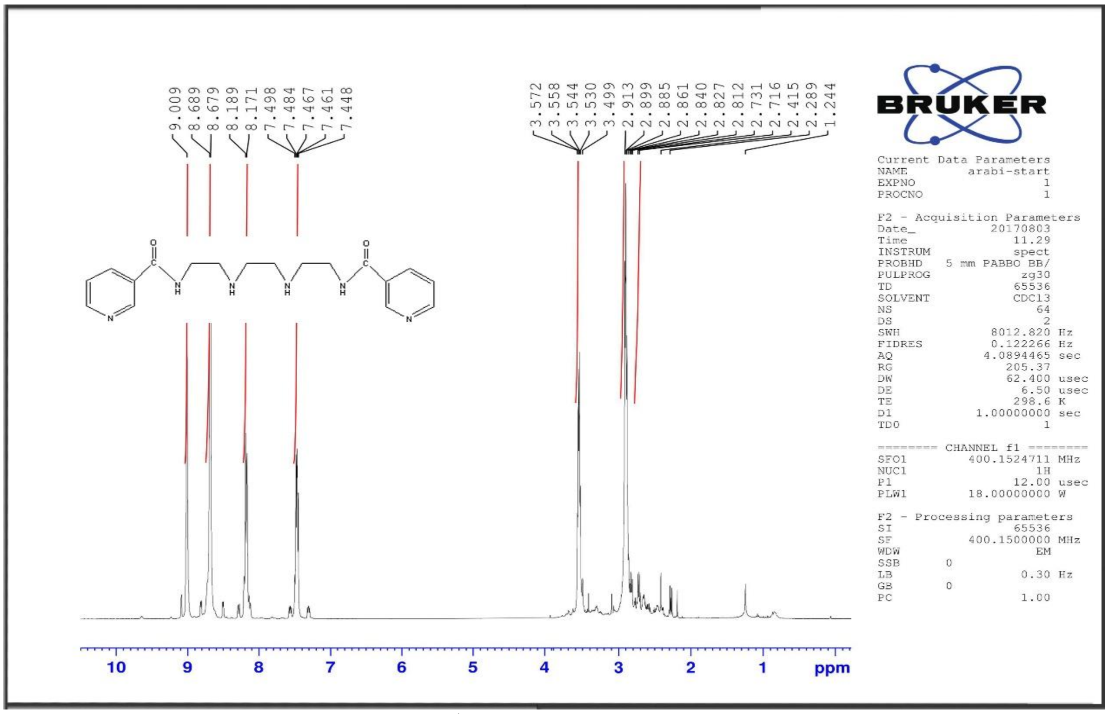

Fig (4): ^{1}H-NMR spectra of Amide

3.2. Structural confirmation of CS_{III} cationic surfactant "1-(2-(hexadecyloxy)-2-oxoethyl)-3-((2-((2-(hexadecyloxy)-2-oxoethyl(2-((2-(hexadecyloxy)-2-oxoethyl)(2-(nicotinamido)ethyl) ammonio)ethyl) ammonio)ethyl)carbamoyl)pyridin-1-ium chloride"

The FT-IR spectra confirm the expected functional groups in the synthesized CS_{III} cationic surfactant (Fig 5) by showing bands at 3415 cm^{-1} (ѵNH stretching), 3070 cm^{-1} (ѵCH aromatic stretching), 2920 cm^{-1} and 2851 cm^{-1} (ѵCH aliphatic chain),1674cm-1(ѵC=Oamide),1554cm-1(ѵC=Caromaticstretching),1467cm^{-1}(ѵCH2bending),1316 cm^{-1}(ѵC–N aryl stretching),1058cm^{-1}(ѵC–Nalkylstretching),828cm^{-1}(ѵCHparabending),722cm^{-1}(ѵCHorthobending),1747cm^{-1}(ѵCO ster), 1364 cm^{-1}(ѵCH3 bending),613 cm^{-1}(ѵC–CL stretching).

The data of ^{1}H-NMR spectra confirm the expected hydrogen proton distribution in the synthesized CS_{III} cationic surfactant (Fig. 10.) δ (ppm): 0.86 (9 H, $^{+}NHCH_2COOCH_2CH_2CH_2(CH2)_{12}\underline{\mathbf{CH}_3}$), 1.24 (72H, $^{+}NHCH_2COOCH_2CH_2CH_2$ $(\underline{\mathbf{CH}_2})_{12}CH_3$), 1.52 (6H,$^{+}$NHCH2COOCH2CH2$\underline{\mathbf{CH}_2}(CH_2)_{12}CH_3$), 1.63 (6H, $^{+}NHCH_2$COOCH2**CH2**$CH_2(CH_2)_{12}CH_3$), 3.34 (4H, CONH$\underline{\mathbf{CH}_2}$), 3.61 (4H, $^{+}$NH **CH$_2$CH$_2$**$^{+}$NH), 4.03 (6H, $^{+}NHCH_2COO\underline{\mathbf{CH}_2}CH_2CH_2(CH_2)_{12}$ CH_3), 4.18 (4H, $^{+}NH\underline{\mathbf{CH}_2}COOCH_2CH_2CH_2(CH_2)_{12}CH_3$), 5.97 (2H, $C_5H_4N^{+}\underline{\mathbf{CH}_2}$), 7.28 (2H, $^{+}\underline{\mathbf{NH}}CH_2COOCH_2CH_2(CH_2)_{12}CH_3$), 8.21 – 9.602 (8 H, $NHCO\underline{C_5\mathbf{H}_4N}$) [20, 21].

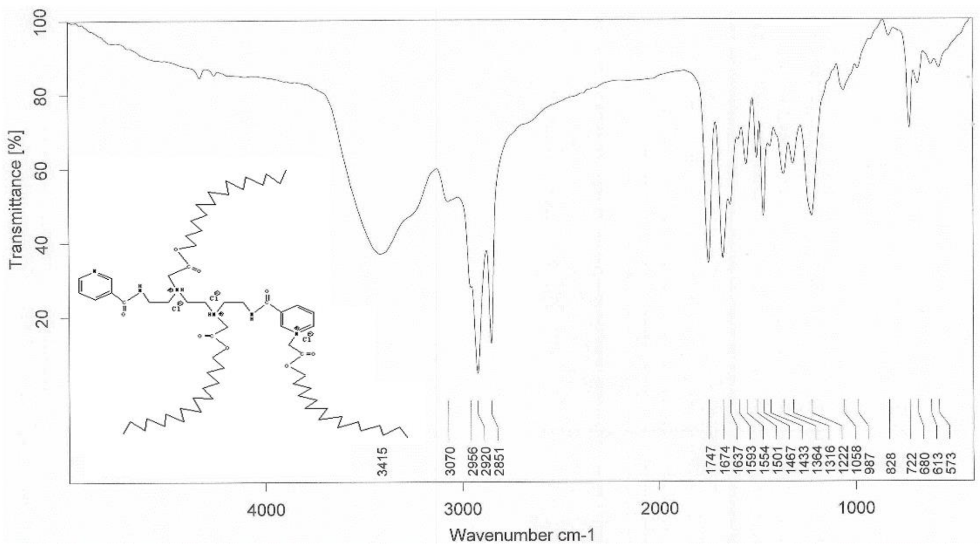

Fig (5): FT-IR spectra of (CS_{III})

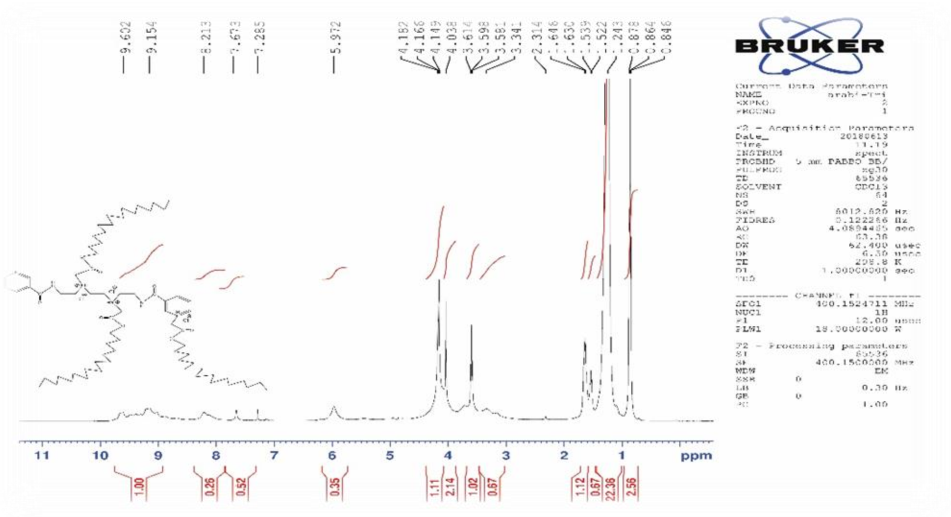

Fig (6): [1]H-NMR spectra of (CS_{III})

3.3. Surface active properties

Surface-active properties measurements of the synthesized tri cationic surfactant were made to evaluate the surface activity of surfactant and the corresponding data are listed in Table 1. It indicates that the surface tension of water is reduced by addition of the cationic surfactant, this is because the migration of the surfactant molecules to the surface due to a hydrophobicity of fatty chain lengths in the surfactant molecules. The critical micelle concentration values of the prepared cationic surfactant have been obtained by two different methods of conductance and surface tension measurements [22].

The CMC from the former method was obtained graphically by the intersection between the two lines of premicellar and postmicellar regions as in Figs (7,8). Surface active parameters such as effectiveness (π_{CMC}), maximum surface excess (Γ_{max}), minimum surface area (A_{min}) and free energy of micellization (ΔG^{o}_{mic}) were calculated and listed in Table 1.

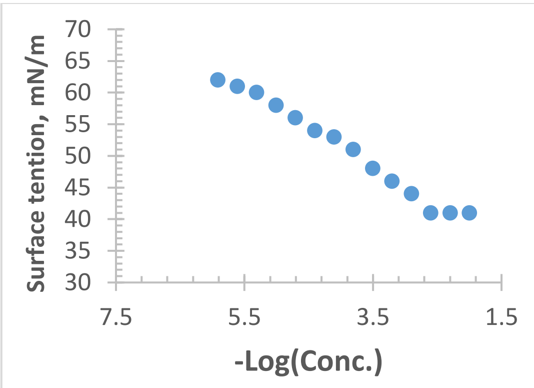

Fig (7) Variations in surface tension with concentration of the synthesized CS_{III} cationic surfactant in bidistilled water.

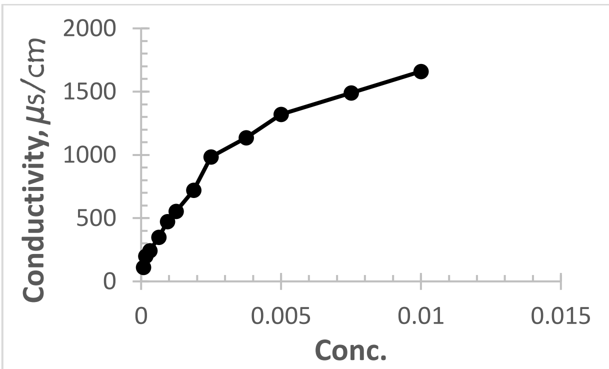

Fig (8): The plots of electrical conductivity against concentration of the synthesized cationic surfactant concentrations in water.

Table (1): Critical micelle concentration (CMC), effectiveness (π_{CMC}), maximum surface excess (Γ_{max}), minimum area (A_{min}), the degree of counter ion dissociation (β) and stander free energy (ΔG_{mic}) of the synthesized cationic surfactant.

Compound	γ mN/m	π_{CMC} mN/m	Γ_{max} ×10^{-4} mol /cm^2	A_{min} ×10^{-7} (nm^2)	β	CMC	ΔG_{mic}
CS_{III}	41	31.86	2.83644	5.853	0.26673	0.0025	-25.29

3.4. Weight Loss Measurements

The change in weight was recorded. The weight loss (ΔW) given by equation:

$$\Delta W = (W_1 - W_2)$$

Where, W_1 and W_2 are the weight of specimen before and after the reaction, respectively. The inhibition efficiencies (*IE* %) of inhibitor were determined from equation [23]:

$$IE\ \% = [(\Delta W_{free} - \Delta W_{inh}) / \Delta W_{free}] \times 100$$

Where. ΔW_{inh} and ΔW_{free} are the weights loss of specimen in presence and absence of inhibitor, respectively.

Fig 9 Represents the weight loss-time curves of carbon steel in 1 M HCl in absence and presence of different concentrations of the synthesized CS_{III} cationic surfactant. The figure shows that weight loss of carbon steel increases slightly with time which mean that these cationic surfactant act as good inhibitor.

As shown from this figure, the linear variation of the weight loss with time in absence and presence of inhibitor indicates that formation of protection layer on metal surface due to adsorption of inhibitor on the surface and absence of this insoluble layer during corrosion. This protection layer on the metal surface, decreases the contact between the metal surface and the aggressive medium, so decreasing the effect of aggressive medium on the metal surface. This adsorption can be explained by an electrostatic interaction between positive center in cationic surfactant and charged sites on the metallic surface.

Table 2 represents the calculated values of inhibition efficiency (*IE* %) and Weight loss (Δw, in grams) of the corrosion of carbon steel in 1 M HCl solution in absence and presence of different concentrations of synthesized CS_{III} cationic surfactant. It was found that after 24 h, the values of the inhibition efficiencies increase as concentration increases [24].

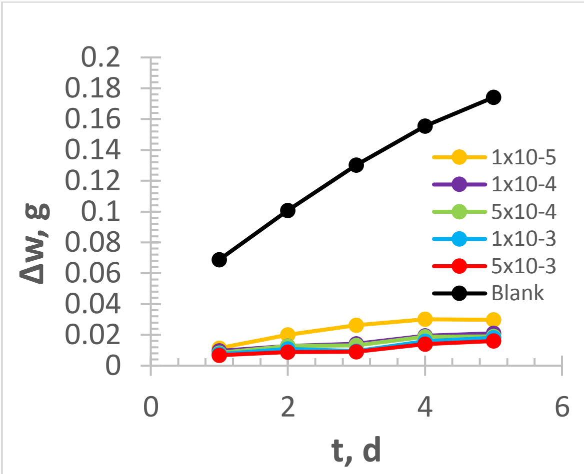

Fig (9): Weight loss-time curve of carbon steel in 1 M HCl in absence and presence of different concentrations of the synthesized CS_{III} cationic surfactant.

Table (2): Weight loss (Δw, in grams) of the corrosion of carbon steel in 1 M HCl solution in absence and presence of different concentrations of synthesized cationic surfactant.

Conc.	CS_{III}	
	Δw	*IE*%
Blank	0.0688	
1x10^{-5}	0.0114	83.43
1x10^{-4}	0.0096	86.05
5x10^{-4}	0.0073	87.9
1x10^{-3}	0.0074	89.09
5x10^{-3}	0.0072	91.27

3.5. Potentiodynamic polarization technique

The representative potentiodynamic polarization curve of carbon steel in 1 M HCl solution in the absence and presence of various concentrations of the synthesized cationic surfactant is shown in Fig (10). Some corrosion kinetics parameters, such as corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (β_c & β_a), corrosion current density (I_{corr}) achieved from the extrapolation of the anodic and cathodic polarization curves, corrosion rate (C_r) and inhibition efficiency (*IE* %) were computed and presented in Table 3.

The degree of surface coverage (Θ) and the inhibition efficiency (*IE* %) were calculated follow:

$$IE\ \% = [(I_{corr"free"} - I_{corr"inh"}) / I_{corr"free"}] \times 100$$

$$\theta = IE\ \%/100$$

Where, $I_{corr"free"}$ and $I_{corr"inh"}$ are the corrosion current densities for carbon steel electrode in absence and presence of the inhibitor [25, 26].

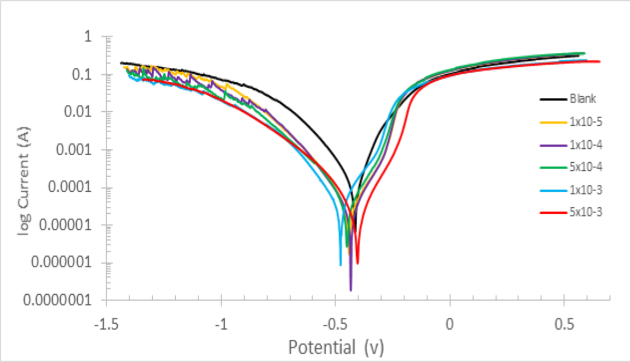

Fig (10): Potentiodynamic polarization curves of carbon steel in 1 M HCl solution in absence and presence of different concentrations of synthesized CS_{III} cationic surfactant.

Data in Table. 3. Reveals that, when the concentration of the synthesized inhibitor was increased, the inhibition efficiencies increased while the corrosion current densities decreased. This increase in inhibition efficiency with increasing inhibitor concentration indicated that this compound was acting as an adsorption inhibitor. The inhibitive action of this compound was discussed in terms of blocking the electrode surface by adsorption of the molecules through the active centers contained in its structure.

This inhibitor cause change in the anodic and cathodic Tafel slopes and no definite trend was observed in the shift of E_{corr} values in the presence of different concentrations of the synthesized inhibitor, suggesting that this compound behave as mixed-type inhibitor. The values of the cathodic Tafel slope (β_c) and the anodic Tafel slope (β_a) for the inhibitor were shifted slightly. The slight variations in the Tafel slope suggested that the synthesized inhibitor is blocking the cathodic and anodic sites without changing the corrosion mechanism [27, 28].

Table (3): corrosion parameters of carbon steel in 1 M HCl solution in absence and presence of different concentrations of synthesized CS_{III} cationic surfactant.

Conc. M	β_a (V/dec)	β_c (V/dec)	E_{corr} (V)	j_{corr} (A/cm²)	C_r (mm/year)	Θ	*IE*%
Blank	0.1219	0.14722	-0.43809	0.000618	7.1833		
$1x10^{-5}$	0.11648	0.108217	-0.44353	0.000102	1.1888	0.834	83.4
$1x10^{-4}$	0.10346	0.097449	-0.43917	9.01E-05	0.93078	0.8542	85.42
$5x10^{-4}$	0.1214	0.11602	-0.48791	8.01E-05	0.81531	0.8704	87.04
$1x10^{-3}$	0.14032	0.10259	-0.43837	7.02E-05	0.84518	0.8865	88.65
$5x10^{-3}$	0.12772	0.10255	-0.44254	6.62E-05	0.76893	0.893	89.3

3.6. Effect of temperature

The effect of temperature (in range of 398 – 343 K) on the corrosion of carbon steel in 1 M HCl solution in absence and presence of (5 x 10-3) M of the synthesized CS_{III} cationic surfactant was studied using potentiodynamic polarization technique.

Figs (12 - 13): represent the potentiodynamic polarization plots for carbon steel electrode in 1M HCl in the absence and presence of (5 x 10^{-3}) M of the synthesized CS_{III} cationic surfactant at scanning rate 2 mV/sec at different temperature. Some corrosion kinetics parameters, such as corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (β_c & β_a), corrosion current density (I_{corr}) achieved from the extrapolation of the anodic and cathodic polarization curves, corrosion rate (C_r) and inhibition efficiency (*IE* %) were computed and presented in Table 5. Reveals that:

- The values of corrosion rate increase with increase of temperature
- Increasing temperature has almost no effect on corrosion potential.
- The corrosion efficiency decreases as temperature increase in presence of the synthesized CS_{III} cationic surfactant which indicate formation of adsorptive film of physical character [31,32].

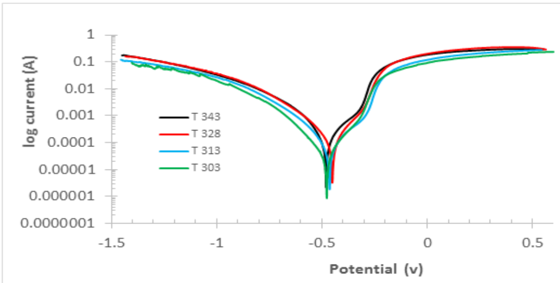

Fig (12): Potentiodynamic polarization curves of carbon steel in 1 M HCl solution at different temperature.

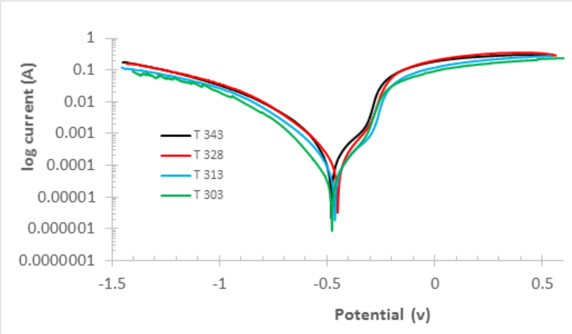

Fig (13): Potentiodynamic polarization curves of carbon steel in 1 M HCl solution in presence of (5 x 10^{-3}) M of the synthesized CS_{III} cationic surfactant at different temperature.

Table (5): corrosion parameters of carbon steel in 1 M HCl solution in absence and presence of the synthesized CS_{III} cationic surfactant at different temperature.

`Comp.	T	β_a (V/dec)	β_c (V/dec)	E_{corr} (V)	j_{corr} (A/cm²)	C_r (mm/year)	*IE*%
Blank	303	0.10355	0.18005	-0.41788	0.000701	8.1415	
	313	0.15621	0.083851	-0.4184	0.000935	10.863	
	328	0.090934	0.16835	-0.41223	0.001189	13.818	
	343	0.12286	0.11419	-0.43245	0.001555	18.067	
CS_{III}	303	0.097998	0.10318	-0.464	8.12E-05	0.94368	88.4
	313	0.14807	0.12037	-0.46956	0.000128	1.4832	86.4
	328	0.10815	0.12282	-0.4516	0.000176	2.0444	85.2
	343	0.13485	0.11374	-0.48351	0.000237	2.7534	84.7

3.7. Kinetic parameter

The activation energy(Ea) for the corrosion of carbon steel in 1 M HCl solution in absence and presence of (5 x 10^{-3}) M of the synthesized CS_{III} cationic surfactant at 303, 313, 328 and 343 K was calculated from Arrhenius equation.

$$C_r = A\, e^{(-E_a / RT)}$$

And the logarithmic form:

$$\ln C_r = \ln A - (E_a /RT)$$

Where, C_r represents rate of corrosion reaction, A is the Arrhenuis constant, R is the gas constant and T is the absolute temperature.

Arrhenius plots of Ln Cr vs. 1/T gave straight line, as shown graphically in Fig (14) with linear regression coefficients are very close to 1, indicating that the corrosion of steel in 1 M HCl without and with inhibitor follows the Arrhenius equation with slope of (- E_a / R). Activation energies were calculated and listed in Table (6) [33].

The data show that the activation energy (Ea) of the corrosion of carbon steel in 1 M HCl solution in the presence CS_{III} cationic surfactant, was higher than that in free acid solution, indicating that the CS_{III} cationic surfactant was adsorbed on the steel surface physically.

The change in enthalpy and entropy of activation values (ΔH*, ΔS*) were calculated from the transition state theory. [29]

$$\ln (C_r /T) = [\ln(R / N_A h) + (\Delta S^*/ R)] - (\Delta H^* / RT)$$

Where, h is the Plank constant, NA is the Avogadros number, R is the ideal gas constant, ΔH* is the enthalpy of activation and ΔS* is the entropy of activation. Plotting of Ln (Cr / T) versus (1 / T), gave straight lines as shown in Fig (15) With slope of – (ΔH*/R) and the intercept of Ln(R / N_Ah) + (ΔS*/ R). Values of ΔH* and ΔS* were calculated and listed in Table (6).

The positive sign of the enthalpy of activation (ΔH*), reflecting the endothermic nature of the corrosion process and means that the dissolution of carbon steel is difficult in the presence of inhibitor. [33]. The negative sign of entropy of activation (ΔS*), indicates that the activated complex in the rate determining step represents an association rather than dissociation, reflecting that more order take place, going from reactant to activate complex [29].

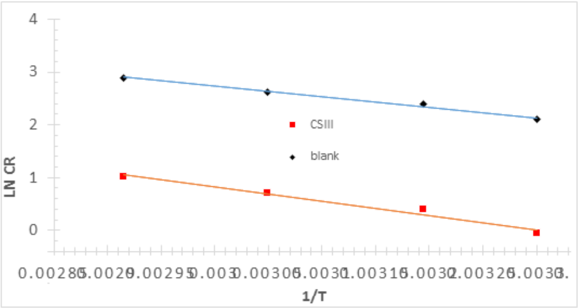

Fig (14): Arrhenius plots of carbon steel in 1 M HCl solution in absence and presence of CS_{III} cationic surfactant at different temperatures.

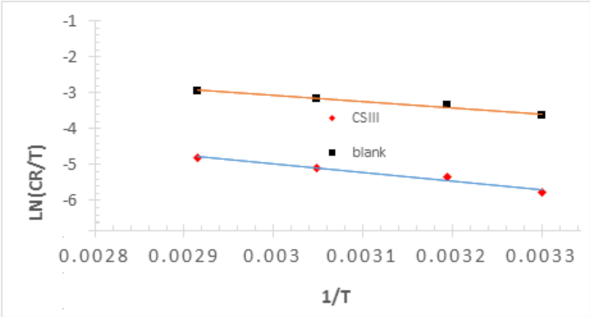

Fig (15): Transition state plots of carbon steel in 1 M HCl solution in absence and presence of CS_{III} cationic surfactant at different temperatures.

Table (6): Activation thermodynamic parameters of carbon steel in 1 M HCl in absence and presence of the synthesized cationic surfactant at different temperatures

	E_a (J/mol)	Slope	intercept	ΔH* (J. mol)	ΔS* (J. mol)
Blank	16722.78	-1689.14	1.989357	14043.51	-180.9803409
CS_{III}	22111.08	-2367.31	2.117204	19681.82	-179.9174209

3.8. Adsorption isotherm

The adsorption of the synthesized surfactant was accompanied by desorption of water molecules from the surface. The degree of surface coverage (θ) for different concentrations of the inhibitor were evaluated from the potentiodynamic polarization data. The values of surface coverage (θ) of different concentrations of the synthesized CS_{III} cationic surfactant have been used to explain the isotherm for adsorption of this inhibitor on the carbon steel surface.

Several adsorption isotherms were tested to describe the adsorption behavior of all inhibitor used in this study. The Langmuir isotherm is the best description of adsorption behavior of the inhibitor's molecules on carbon steel surface according to the following equation: [29]

$$C / \theta = (1 / K_{ads}) + C$$

Where: C is the concentration of inhibitor, K_{ads} is the equilibrium constant of the adsorption process and (θ) is the surface coverage.

Fig 16 Represents plots of C/θ versus C gave a straight line with intercept of (1/ K_{ads}), slope closed to 1 and the correlation coefficient (R^2) equal to 1. This indicates that, the adsorption of cationic surfactant on the carbon steel surface in 1M HCl solution follows Langmuir's adsorption isotherm.

The slope of the straight line obtained from the plots of the Langmuir isotherm for prepared inhibitor are more than unity, indicate that each inhibitor unit occupies more than one adsorption site, also there are interactions between adsorbed species on the metal surface as well as changes in the adsorption heat with increasing surface coverage [34]. Therefore, we can say that the adsorption of prepared cationic surfactant on the carbon steel surface can be more appropriately represented by a modified Langmuir equation. This modified is named Villamil isotherm, which suggested by Villamil, taking into consideration the interactions between adsorbate species as well as changes in the heat of adsorption with changing surface coverage as follows: [35, 36]

$$C / \theta = (n / K_{ads}) + n C$$

Where, n is the slope value obtained by the above plot, and referee to number of displacement adsorbed water molecule from metal surface, and the intercept permit the calculation of equilibrium constant (K_{ads}) for the synthesized cationic surfactant and listed in Table 7. The values of equilibrium constant (K_{ads}) indicate that the inhibitor is easily and strongly adsorbed onto the carbon steel surface. This is due to formation of a coordinated bond between the prepared Cationic surfactant and the d-orbital of iron on the surface of steel through a lone pair of electron of N atoms.

The free energy of adsorption (ΔG^o_{ads}) was calculated from the following equation [28]:

$$\Delta G^o_{ads} = - RT \ln (55.5 K_{ads})$$

Where, the value (55.5) is the molar concentration of water in solution in molarity units (mol L^{-1}). The values of K_{ads} and ΔG^o_{ads}, were calculated and listed Table 7.

The Values of ΔG^o_{ads} up to -20 kJ mol^{-1} or lower were consistent with the electrostatic interaction between charged organic molecules and the charged metal surface (physical adsorption); while those about -40 kJ mol^{-1} or higher were involved sharing or transferring a lone pair of electrons from the organic molecules to the metal surface to form a co-ordinate type of bond (chemisorption). The values of ΔG^o_{ads} in Table 7 was -39.5 KJ mol^{-1} which indicate that the adsorption process of inhibitor on metal surfaces is mixed physical and chemical adsorption. The high values of G^o_{ads} and its negative sign suggest that the adsorption of inhibitor onto the carbon steel surface is a spontaneous process and usually characteristic of strong interaction and a highly efficient adsorption [37, 38 and 39].

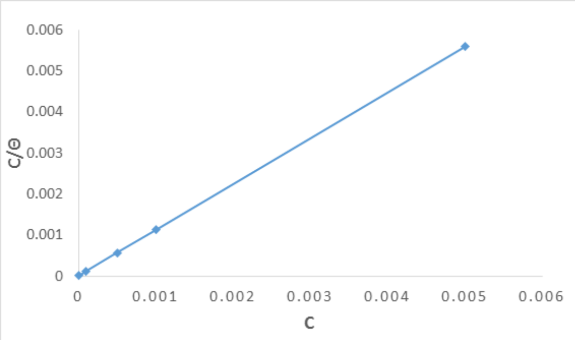

Fig (16): Langmuir isotherm adsorption on the carbon steel surface of different concentration of the synthesized CS_{III} cationic surfactant in 1M HCl solution at room temperatures.

Table (7): adsorption of thermodynamic parameters of the synthesized cationic surfactant on carbon steel surface at room temperature.

	R^2	Slope	Intercept	k_{ads}	ΔG_{ads} (KJ/mol)
CS_{III}	1	1.1185738	7.37403E-06	151690.914	-39.5

4. Conclusion

1. The synthesized tri cationic surfactant and amide in this study were characterized by FTIR and ^{1}H-NMR

2. The tri cationic surfactant acted as good corrosion inhibitors for carbon steel in 1 M HCl.

3. Polarization curves indicated that the prepared cationic surfactant acted as mixed-type inhibitor for carbon steel in 1 M HCl.

4. Electrochemical and weight loss measurements gave similar results.

5. The corrosion inhibition increased with increasing the inhibitors concentration.

6. The corrosion rate of carbon steel in 1 M HCl increased with increasing temperature for both uninhibited and inhibited solutions.

7. The adsorption mechanism of the prepared inhibitor on the carbon steel obeyed the Langmuir adsorption isotherm model.

Reference

[1] S. Kumar, A. Mandal, Studies on interfacial behavior and wettability change phenomena by ionic and nonionic surfactants in presence of alkalis and salt for enhanced oil recovery, Applied Surface Science, 372 (2016) 42–51.
[2] W. EL-Dougdoug, S. Eid, A. A. Zaher, A.Y. El-Etre, Inhibition of carbon steel corrosion in aqueous solutions using some fatty amidocationic surfactant, Journal of Basic and Environmental Sciences, 3 (2016) 55– 64.

[3] S. M. Tawfik, Ionic liquids based gemini cationic surfactants as corrosion inhibitors for carbon steel in hydrochloric acid solution, Journal of Molecular Liquids, 216 (2016) 624–635.
[4] Y. Bao, J. Guo. J. Ma, P. Liu, Q. Kang, J. Zhang, Cationic silicon-based gemini surfactants: Effect of hydrophobic chains on surface activity, physic-chemical properties and aggregation behaviors, Journal of Industrial and Engineering Chemistry, 53 (2017) 51-61.
[5] I. B. Obot, N.K. Ankah, A. A. Sorour, Z. M. Gasem, K. Haruna, 8-Hydroxyquinoline as an alternative green and sustainable acidizing oilfield corrosion inhibitor, Sustainable Materials and Technologies, 14 (2017) 1–10.
[6] M. Bagherzadeh, H. Haddadi, M. Iranpour, Electrochemical evaluation and surface study of magnetite/PANI nanocomposite for carbon steel protection in 3.5% NaCl, Progress in organic coating, 101 (2016) 149-160.
[7] A. A. Olajire, Corrosion inhibition of offshore oil and gas production facilities using organic compound inhibitors - A review, Journal of Molecular Liquids, 248 (2017) 775–808.
[8] O. Kaczerewska, R. L. Garcia, R. Akid, B. Brycki, I. Kowalczyk, T. Pospieszny, Effectiveness of O-bridged cationic gemini surfactants as corrosion inhibitors for stainless steel in 3 M HCl: Experimental and theoretical studies, Journal of Molecular Liquids, 249 (2018) 1113–1124.
[9] H. M. Abd El-Lateef, K. A. Soliman, A. H. Tantawy, Novel synthesized Schiff Base-based cationic gemini surfactants: Electrochemical investigation, theoretical modeling and applicability as biodegradable inhibitors

for mild steel against acidic corrosion, Journal of Molecular Liquids, 232 (2017) 478–498.
[10] F. El-Hajjaji, M. Messali, A. Aljuhani, M.R. Aouad, B. Hammouti, M.E. Belghiti, D.S. Chauhan, M.A. Quraishi, Pyridazinium-based ionic liquids as novel and green corrosion inhibitors of carbon steel in acid medium: Electrochemical and molecular dynamics simulation studies, Journal of Molecular Liquids, 249 (2018) 997–1008.
[11] M. A. Hegazy, E. M. S. Azzam, N. G. Kandil. A. M. Badawi. R. M. Sami1, Corrosion Inhibition of Carbon Steel Pipelines by Some New Amphoteric and Di-cationic Surfactants in Acidic Solution by Chemical and Electrochemical Methods, J Surfactant and Detergent, 19 (2016) 861–871.
[12] M.A. Bedaira, M.M.B. El-Sabbaha , A.S. Foudab , H.M. Elaryiana,, Synthesis, electrochemical and quantum chemical studies of some prepared surfactants based on azodye and Schiff base as corrosion inhibitors for steel in acid medium, Corrosion Science, 128 (2017) 54–72.
[13] 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, Materials Chemistry and Physics, 191 (2017) 151-167.
[14] F. E. Heakal, A. E.Elkholy, Gemini Surfactants as Corrosion Inhibitors for Carbon Steel, Journal of Molecular Liquids, 230 (2017), 395-407.
[15] O. Kaczerewska , B. Brycki , I. Ribosa , F.Comelles , M. T.Garcia, Cationic gemini surfactants containing an O-substituted spacer and hydroxyethyl moiety in the polar heads: Self-assembly, biodegradability and aquatic toxicity,, Journal of Industrial and Engineering Chemistry, 59 (2018) 141-148.
[16] Madhukar B. Deshmukh, Sangram H. Patil and Chetan S. Shripanavar,Synthesis and insecticidal activity of some nicotinic acid derivatives, Journal of Chemical and Pharmaceutical Research, 4, (2012) 326-332.
[17] M. Abo-Riya, A. H. Tantawy, W. El-Dougdoug, Synthesis and evaluation of novel cationic gemini surfactants based on Guava crude fat as petroleum-collecting and dispersing agents, Journal of Molecular Liquids, 221 (2016) 642-650.
[18] M. A. Hegazy, S. S. Abd El-Rehim, E. A. Badr, W. M. Kamel, Ahmed H. Youssif3, Mono-, Di- and Tetra-Cationic Surfactants as Carbon Steel Corrosion Inhibitors, J Surfact Deterg, 18 (2015)1033–1042.
[19] I. V. Korendovych, M. Cho, P. L. Butler, R. J. Staples, E. V. Rybak-Akimova, Anion Binding to Monotopic and Ditopic Macrocyclic Amides, ORGANIC LETTERS, 8 (2006) 3171-3174
[20] M. A. Hegazy, E. M. S. Azzam, N. G. Kandil, A. M. Badawi, R. M. Sami, Corrosion Inhibition of Carbon Steel Pipelines by Some New Amphoteric and Di-cationic Surfactants in Acidic Solution by Chemical and Electrochemical Methods, J Surfact Deterg, 19 (2016) 861–871.
[21] M. A. Hegazy, A. S. El-Tabei, A. H. Bedairb, M. A. Sadeqb, Synthesis and inhibitive performance of novel cationic and gemini surfactants on carbon steel corrosion in 0.5 M H2SO4 solution, RSC Adv., 5 (2015) 64633–64650.
[22] S.M.Shaban, I.Aiad, M. M.El-Sukkary, E.A.Soliman, M.Y.El-Awady, Surface and biological activity of N-(((dimethoxybenzylidene) amino)propyl)-N,N-dimethylalkyl-1-ammonium derivatives as cationic surfactants, Journal of Molecular Liquids, 207 (2015) 256-265.
[23] M.A.Hegazy, Novel cationic surfactant based on triazole as a corrosion inhibitor for carbon steel in phosphoric acid produced by dihydrate wet process, Journal of Molecular Liquids, 208 (2015) 227-236.

[24] I. Aiad, G. El-Didamony, S. M. Shaban, A. Sayed, W. Mahdy, Synergistic Effect of Some Commercial Materials as Biocide and Corrosion Inhibitor for Petroleum Industry, Middle East Journal of Applied Sciences, 4 (2014) 436-442.
[25] M. Abdallah, Hatem M. Eltass, M. A. Hegazy, H. Ahmed, Adsorption and inhibition effect of novel cationic surfactant for pipelines carbon steel in acidic solution, Protection of Metals and Physical Chemistry of Surfaces, 52 (2016) 721–730.
[26] M. Sahin, G. Gece, F. Karc, S.Bilgic, Experimental and theoretical study of the effect of some heterocyclic compounds on the corrosion of low carbon steel in 3.5% NaCl medium. Journal of Applied Electrochemistry, 38 (2008) 809–815.
[27] X. Li, S. Deng, G. Mu, H. Fu, F.Yang, Inhibition effect of nonionic surfactant on the corrosion of cold rolled steel in hydrochloric acid. Corrosion Science, 50 (2008) 420–430.
[28] M. N. El-Haddad, K. M. Elattar, Role of novel oxazocine derivative as corrosion inhibitor for 304 stainless steel in acidic chloride pickling solutions, Research on Chemical Intermediates, 39 (2012) 3135–3149.
[29] M. Benabdellah, A. Aouniti, A. Dafali, B.Hammouti, M. Benkaddour, A.Yahyi, A. Ettouhami, Investigation of the inhibitive effect of triphenyltin 2-thiophene carboxylate on corrosion of steel in 2 M H3PO4solutions, Applied Surface Science, 252 (2006) 8341-8347.
[30] R. Chami, F. Bensajjaya, S. Alehyena, M. El Achouri, A. Bellaouchou, A. Guenbour, Inhibitive effect of ester-quats surfactants in the series of (alcanoyloxy)propyl n-alkyl dimethyl ammonium bromide on the corrosion of iron in acid medium, Colloids and Surfaces A: Physicochem. Eng, 480 (2015) 468–476.
[31] A. M. Badawi, M. A. Hegazy, A. A. El-Sawy, H. M. Ahmed, W. M. Kamel, Novel quaternary ammonium hydroxide cationic surfactants as corrosion inhibitors for carbon steel and as biocides for sulfate reducing bacteria (SRB), Materials Chemistry and Physics, 124 (2010) 458-465.
[32] H. A. Sorkhabi, N.G.-Jeddi, Inhibition effect of polyethylene glycol on the corrosion of carbon steel in

sulphuric acid, Materials Chemistry and Physics, 92 (2005) 480-486.
[33] S. A. M. Refaey, F. Taha, A. M. Abd El-Malak, Inhibition of stainless steel pitting corrosion in acidic medium by 2-mercaptobenzoxazole, Applied Surface Science, 236 (2004) 175-185.
[34] E. E. Oguzie, B. N. Okolue, E. E. Ebenso, G. N. Onuoha, A. I. Onuchukwu, Evaluation of the inhibitory effect of methylene blue dye on the corrosion of aluminium in hydrochloric acid, Materials Chemistry and Physics, 87 (2004) 394-401.
[35] S. M. Shabana, I. Aiada, M. M. El-Sukkarya, E.A. Solimanb, M. Y. El-Awadya, Evaluation of some cationic surfactants based on dimethylaminopropylamine as corrosion inhibitors, Journal of Industrial and Engineering Chemistry, 21 (2015) 1029–1038.
[36]. Q. Zhang, Z. Gao, F. Xu, X. Zou, Adsorption and corrosion inhibitive properties of gemini surfactants in the series of hexanediyl-1,6-bis-(diethyl alkyl ammonium bromide) on aluminium in hydrochloric acid solution, Colloids and Surfaces A: Physicochem.Eng,380 (2011) 191–200.
[37] K. C. Emregül, M. Hayvalí, Studies on the effect of a newly synthesized Schiff base compound from phenazone and vanillin on the corrosion of steel in 2 M HCl, Corrosion Science, 48 (2006) 797-812.
[38] M.A. Deyab, Application of nonionic surfactant as a corrosion inhibitor for zinc in alkaline battery solution, Journal of Power Sources, 292 (2015) 66-71.
[39] A. S. El-Tabei • M. A. Hegazy • A. H. Bedair • M. A. Sadeq, Synthesis and Inhibition Effect of a Novel Tri-cationic Surfactant on Carbon Steel Corrosion in 0.5 M H2SO4 Solution, J Surfact Deterg, 17 (2014) 341–352.