Journal of Basic and Environmental Sciences 3 (2016) 55– 64 **ISSN 2356-6388**

Inhibition of carbon steel corrosion in aqueous solutions using some fatty amido-cationic surfactant

Wagdy EL-Dougdoug, Salah Eid, Ahmed A. Zaher, Ali.Y. El-Etre

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

Article Information

Received; 12 Feb. 2016
In Revised form; 20 Mar. 2016
Accepted; 20 Mar. 2016

Keywords:

Corrosion inhibitors
Fatty Amido-Cationic surfactant
Kinetic parameters.

Abstract

Novel cationic surfactants were synthesized and evaluated as corrosion inhibitors for carbon steel in 1M HCl solution. The inhibition action of this surfactant was studied by weight loss and galvanostatic polarization methods. The structure of the prepared compounds was established by spectral tools (FT-IR and 1H-NMR). Also, CMC and anti-microbial activity were evaluated. The adsorption of the inhibitors was described by Langmuir adsorption isothermal. The inhibition efficiency increases by increasing surfactant concentration and decreasing temperature. Where, the prepared compound S at concentration 5 x 10^{-4}mol/l at 20℃ recorded 94.45 %.The effect of temperature on the inhibition efficiency of corrosion process was studied. Also, thermodynamic parameters were calculated to predict the reliable mechanism of inhibition.

1. Introduction:

Inhibitors are one of the best methods of protecting carbon steel against corrosion because it is the most important engineering and construction material in the world [1]. Most of the efficient inhibitors used in industry are organic compounds which mainly contain oxygen, sulfur, nitrogen atoms and multiple bonds in the molecule through which they are adsorbed on metal surfaces [2–9]. Specific types of organic inhibitors are represented by surfactants. Cationic and nonionic surfactants have been reported as corrosion inhibitors for various types of steel [10-12]. Cationic surfactants, which have polar group is positive charge, are known to many applications throughout industry, detergents, and also as corrosion inhibitors. In addition to these valuable properties, they are inexpensive to produce. They can be mixed with other types of surfactants, e.g., nonionic, to enhance their properties and reduce perception [13, 14]. The aim of this work was to study the inhibition efficiency of the investigated cationic surfactant compound on corrosion behavior of carbon steel in 1M HCl solution using various techniques. Also our objective was extended to determine CMC and antimicrobial activity of synthesized surfactant.

2. Materials and Methods

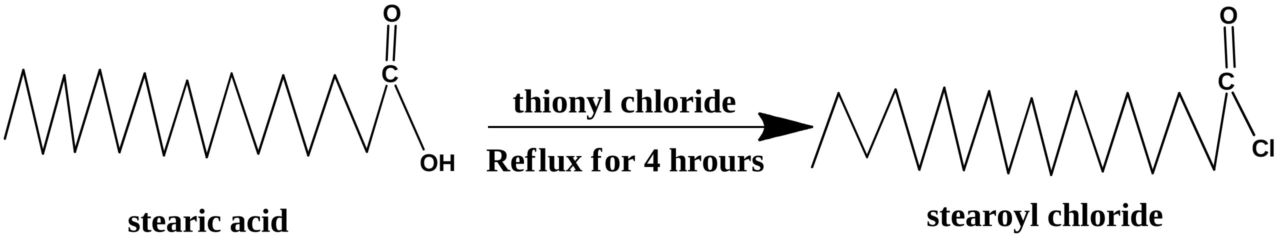
2.1. General

^{1}HNMR spectra were recorded with a Bruker AC 250 (250 MH_Z). Chemical shift are given in ppm relatively to TMS using residual solvent signals as secondary references. IR spectra were recorded on a Nicolet AVATAR 320 FT-IR. Conductmeter (Type 522; Crison Instrument, S.A) was used to measure the conductivity of the surfactant solutions (S) Also, to determine the critical micelle concentration (CMC) and conductivity at CMC.

The cationic surfactants were synthesized using stearic acid (Sigma Aldrich), 3-dimethylpropylamine (Sigma Aldrich), dimethylsulfate (El-Nasar Company), thionyl chloride (Loba. Chemie) and Diethyl ether (SDFCL).

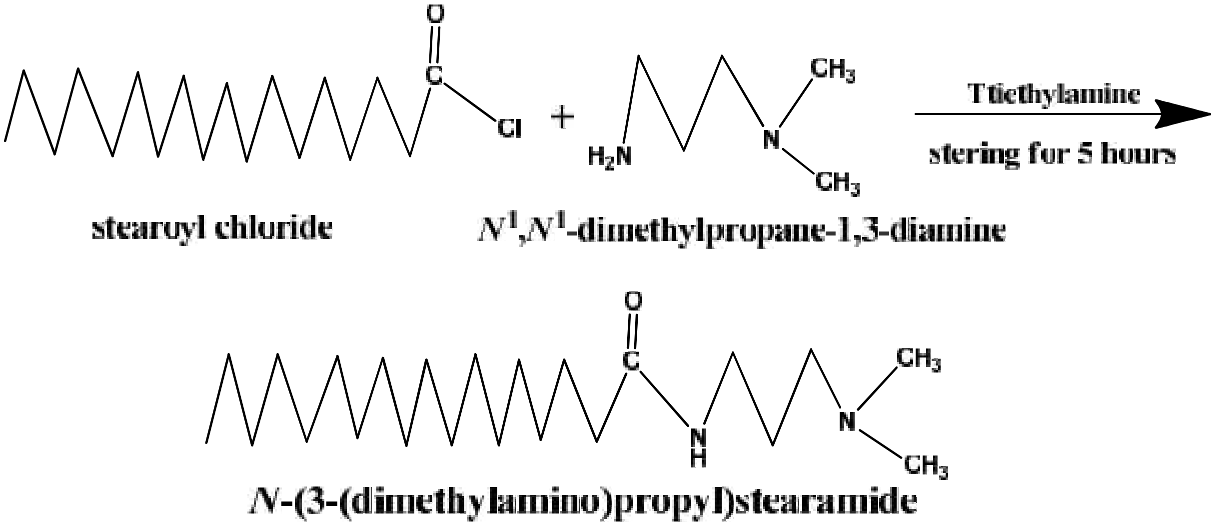
Synthesis of 3-octadecanamido-N, N, N-trimethylpropan-1-ammonium methyl sulfate

Stearic acid 5.6 g (0.02mole) with thionyl chloride 2.2 ml (0.03mole) was refluxed for 4 hours, and left overnight then evaporating the excess of thionyl under vacuum [15].

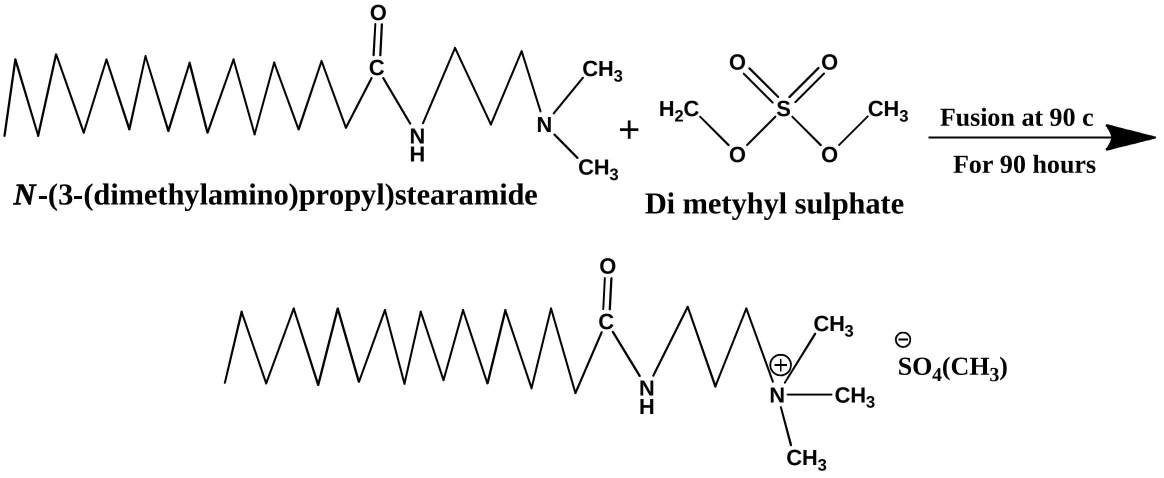


Synthesis of N-(-3-dimethylamino) propylstearamide :

The freshly prepared stearoyl chloride1.5 gm (0.005 mole) was dissolved in methylene chloride (10 ml) as solvent to 0.9 gm (0.009 mole) from (N, N- di- methylpropane-1, 3-diamine) drop by drop by stirring in ice path in presence of triethylamine (4 drop) as base catalyst for 5 hours. After the solid white precipitate is formed and subjected to the forwards step directly.



Synthesis of N, N, N-trimethyl-2-stearamidoethanammonium methyl sulphate as cationic surfactant (S) was prepared using fusion technique in sand bath for about 90 hours by adding1 gm (0.002mol) of (N-3dimethyl amino propyl stearamide) to 1 gm (1 ml) of liquid di methyl sulfate in Sand. The product washed by diethylether three times to obtain the final product as pale yellow solid yield (89%) m.p (113-114℃).



N,N,N-trimethyl-2-stearamidoethanammonium methyl sulphate

2.2. Conductivity Measurements

The CMC of the surfactant solution (S) was determined by plotting the values of conductivity with (–log C) for various concentrations [16-18], Fig. 1: The critical micelle concentration (CMC) shows the dependence of conductivity of surfactants with concentration.

Table 1: the conductivity of synthesized cationic surfactant (S)

Compound (S)			
No	Conductivity Of solutions Concentrations (M)		Surfactant conductivity (µs)
0	Blank	5.7	0
1	1x10^{-3}	140.2	134.3
2	9x10^{-4}	135.95	130.05
3	8 x10^{-4}	132.8	126.9
4	7 x10^{-4}	122.1	116.2
5	6 x10^{-4}	104.9	99
6	5 x10^{-4}	84.7	78.1
7	4 x10^{-4}	78.4	72.5
8	3 x10^{-4}	66.4	60.5
9	2 x10^{-4}	54.5	48.6
10	1 x10^{-4}	34.6	28.7

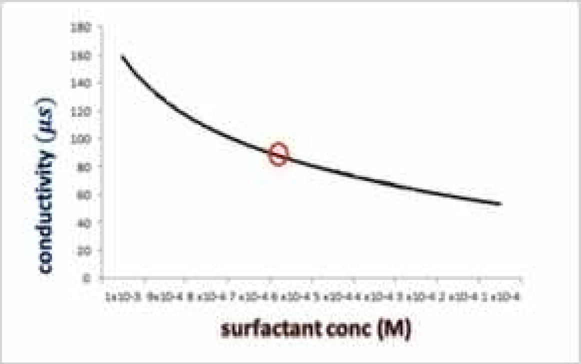


Fig 1: The relation between the concentration of surfactant and its conductivity

2.3. Weight Lose Measurements:

The experiments were performed with carbon steel with following composition (wt %): C =03.24%, Mn =1.14% and Fe =95.62%. Carbon steel sheets of 4.8 x 2 x 1.1 cm^3 were abraded with series of emery papers (grades 320, 600, 800 and 1200) and then washed with distilled water and acetone and dried then weighing accurately. The specimens were then immersed in 100 ml HCl with and without the addition of different concentrations (5x10^{-4}, 1x10^{-4}, 5x10^{-5}, 5x10^{-6}and 1x10^{-6}) of synthesized surfactants. After immersion time of 24 h, the specimens were washed, dried, and weighed accurately. The same procedure was carried out at different temperatures varying from 20 to 60℃

2.4. Galvanostatic Polarization Measurements:

The Galvanostatic polarization measurements were performed using a carbon specimen in a form of rod of 1.6 cm^2 exposed surface area as a working electrode. The measurements were carried out using an (Meinsberger potentiostat galvanostat PS6 with controlling software PS remote) corrosion measurements system. A three compartment cell with saturated calomel reference electrode (SCE) and a platinum electrode was used as counter electrode. The working electrode (W. E) was a rod of carbon steel embedded in a PVC holder using epoxy resin so that the flat surface was the only exposed surface in the electrode. Before each measurement, the electrode was polished and pre-polarized prior to recording the cathodic and anodic polarization curves at each concentration of the tested solution at 20℃.

Result and Discussion

2.5. Inhibitor Structure Confirmation (S):

The structure of the prepared cationic surface active agent was confirmed using FT-IR and ^{1}H-NMR spectra. The FTIR spectrum of the synthesized compound showed the following absorption bands at 719.80 cm-1 ((CH2)n rocking), 1043.69 cm-1 (C-N asymmetric stretching), 1196.41 cm-1 (C-O symmetric stretch), 1556.31 cm-1 (N-Hsymmetric bending), 1633 cm-1 (C=O symmetric stretching), 2918.07 cm-1 (C-H symmetric stretch), and 3288.9 cm-1(N-H stretch). The FTIR spectrum confirmed the expected functional groups in the synthesized compound according to (Fig. 2).

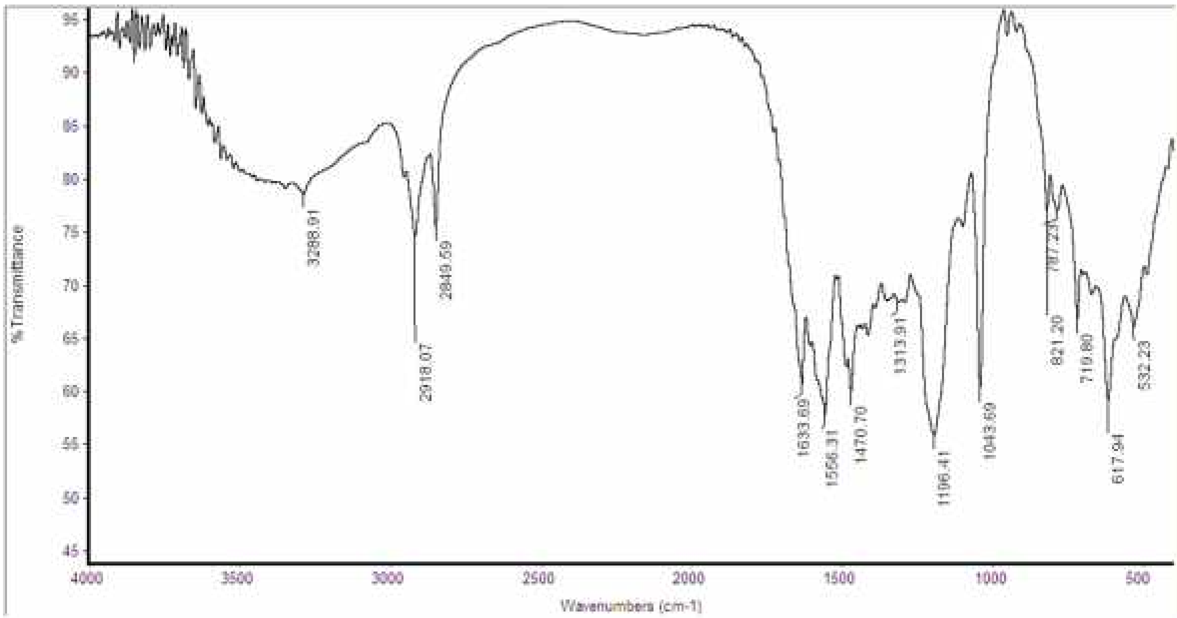


Fig. 2: The FTIR spectrum of the Synthesized compound (S)

^{1}H-NMR:The structure of cationic surfactant (S) as showed in (Cf. Fig. 3)gave the following characteristic peaks,δ = 0.8ppm (t, 3H, terminal CH_3 in fatty acid chain); (1.2-1.6) ppm (m, 30H, CH_2 chain in fatty acid chain); (1.8) ppm (m, 2H, CH_2 in propylene $NCH_2\underline{CH_2}CH_2N$); (2.1) ppm (t, 2H, CH_2 in $\underline{CH_2}CO$ in fatty acid); (2.9-3.2) ppm (t, 2H, CH_2 in $(OCNH(CH_2)_2\underline{CH_2}N^+)$; (3.2-3.6) ppm (m, 9H, in quaternary ammonium salt $N\underline{(CH_3)}_3$ and (7.9) ppm (S, 1H, in OC$\underline{NH}$).

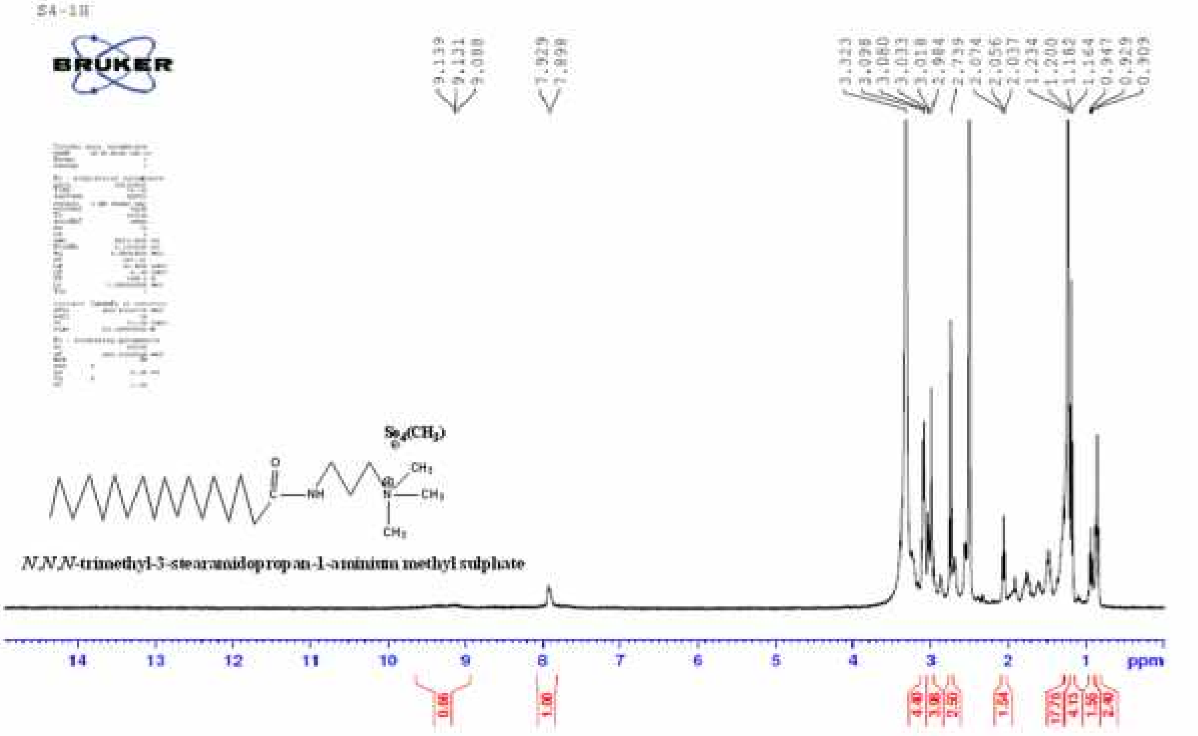


Fig.3: 1H-NMR Spectroscopy of Synthesized compound (S)

3. Results and discussion:

3.1. Weight Loss Measurements

The effect of increasing the concentration of inhibitor on the weight loss of carbon steel in 1 M HCl is given in table 2. Then the corresponding corrosion inhibition efficiency (I.E) and the values of surface coverage (θ) is calculated by the following equations [19] and given in table 2:

$$\% \, \mathrm{I.E} = \left(\frac{\mathrm{W}-\mathrm{W}_0}{\mathrm{W}}\right) \times 100 \qquad (1)$$

$$\theta = \frac{\mathrm{W}_0-\mathrm{W}}{\mathrm{W}_0} \qquad (2)$$

Where W and W_0 are the weight loss in the absence and presence of inhibitor, respectively. The corrosion rate k of carbon steel is calculated by the following equation [19]:

$$\mathrm{K} = \frac{\Delta \mathrm{W}}{\mathrm{At}} \qquad (3)$$

Where ΔW represent the weight loss, A represents the exposure area of specimen and t is the testing period. It was found that the corrosion rate decreases, while the inhibition efficiency increases with rising concentration of inhibitor S. Maximum inhibition efficiency of the tested inhibitor is 92.13 % at $5x10^{-4}$ M.

Table 2: Corrosion parameters of carbon steel in 1 M HCl solution at different concentrations of inhibitor obtained from weight loss measurements.

Inh.	Conc. (mol\L)	Wt. loss	K ($mg.cm^{-2}.h^{-1}$)	θ	%I. E
S	$5x10^{-4}$	0.0107	$1.305x10^{-5}$	0.9218	**92.18 %**
	$1x10^{-4}$	0.0120	$1.463\ x10^{-5}$	0.9124	**91.24 %**
	$5x10^{-6}$	0.0359	$4.378\ x10^{-5}$	0.7379	**73.79 %**
	$1x10^{-5}$	0.0456	$5.562\ x10^{-5}$	0.6671	**66.71 %**
	$1x10^{-6}$	0.0556	$6.781\ x10^{-4}$	0.5941	**59.41 %**

3.2. Kinetic parameters

The kinetic model represents a useful tool for further explanation of mechanism of the mechanism of corrosion inhibitor. Fig. (4) represents a plot of Log(R) logarithm of the corrosion rate ($mg\ cm^{-2}\ h^{-1}$) of carbon steel versus (1/T) for carbon steel in 1M HCL in absence and presence of compound (S). The apparent activation energy (E_a) was calculated using the following relationships:

$$\ln \mathrm{CR}_{\mathrm{corr}} = \frac{\mathrm{E_a}}{\mathrm{RT}} + \mathrm{A} \qquad (4)$$

Where Ea is the apparent activation energy for corrosion of carbon steel in 1M HCL solution, R the gas constant, A the Arrhenius per-exponential factor and T is the absolute temperature. The values of E_a obtained from the slope of the lines are given in Table (3) of supplementary material. An alternative formula of the Arrhenius equation:

$$\mathrm{CR} = \frac{\mathrm{RT}}{\mathrm{Nh}} \exp\left(\frac{\Delta S^*}{\mathrm{R}}\right) \exp\left(\frac{\Delta \mathrm{H}^*}{\mathrm{RT}}\right) \qquad (5)$$

Where h is plank's constant, N the Avogadro's number, $\Delta S^*$the entropy of the activation energy, and ΔH^* the enthalpy of activation. A straight-line relationship is obtained by plotting log (R/T) verses 1/T with a slope $\left(-\frac{\Delta \mathrm{H}^*}{\mathrm{RT}}\right)$ and an intercept of $\ln \frac{\mathrm{R}}{\mathrm{Nh}} + \frac{\Delta S^*}{\mathrm{R}}$, see supplementary material Fig. (5), from which the values of ΔS^* and ΔH^*were calculated. The ΔH^* value was equal to 123.687 kJ mol^{-1} for inhibitor (S). The negative values of ΔH^* indicated that the adsorption of investigated inhibitors on the carbon steel surface is exothermic. The obtained ΔS* value was listed in Table 3. The positive values of ΔS* are attributed to the increase of disorder and this case may be due to the adsorption of only one surfactant species by desorption of more than one water molecule [20].

Table 3: The thermodynamic parameters of adsorption of the synthesized inhibitor at different concentrations for carbon steel in 1 M HCl solution

Surfactant	ΔE_a K.J. mol^{-1}	ΔH^* K.J. mol^{-1}	ΔS^* K.J. $mol^{-1}K^{-1}$	ΔG°_{ads} K.J. mol^{-1}
S	131.291	123.687	29.287	22.182

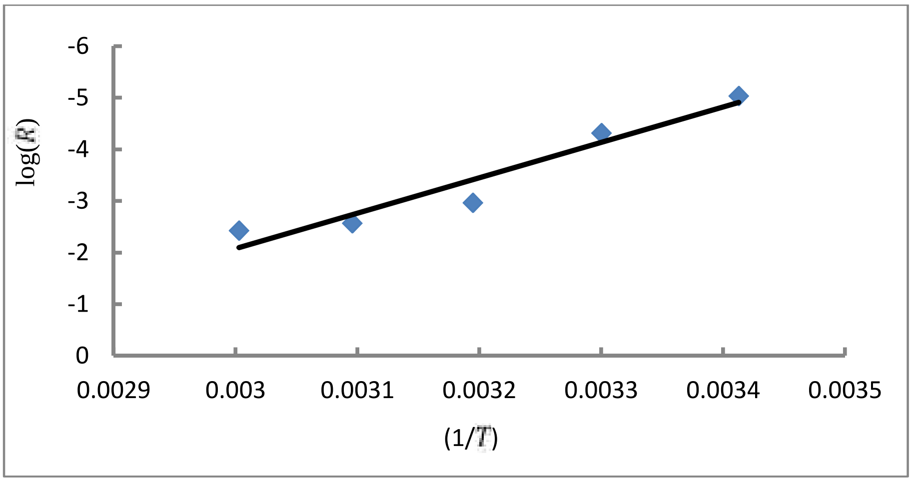


Fig 4: Relation between the logarithm of the corrosion rate (mg cm^{-2} h^{-1}) of carbon steel versus 1/T for carbon steel in 1M HCL

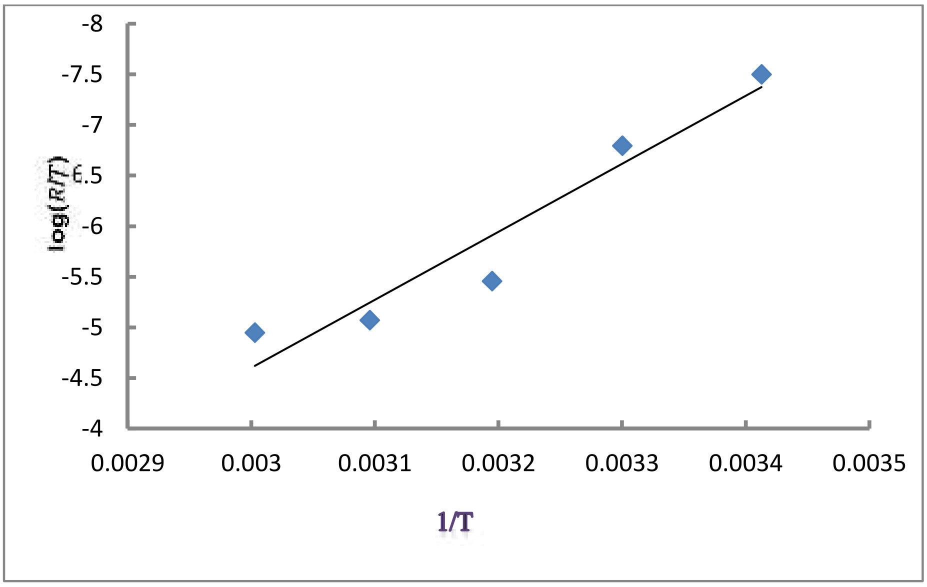


Fig 5:Relation between the logarithm of the corrosion rate (mg cm^{-2} h^{-1}) per temperature (Kelvin) of carbon steel versus 1/T for carbon steel in 1M HCL

The behavior of the interaction between the inhibitor molecules and metal surface is described by the adsorption isothermal. The best correlation between the experimental result and the isothermal function was represented by the Langmuir adsorption isotherm [21, 23]:

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad (6)$$

Where K the adsorption equilibrium constant, C is the inhibitor concentration and θ is the surface coverage. Plotting of ($\frac{C}{\theta}$) versus (C) at 20 °C yielded a straight line (C.F. Fig. 6) with slope close to 1 which indicates that the adsorption of the prepared inhibitor on metal surface obeyed Langmuir adsorption isotherm model. The slandered free energy of adsorption, ΔG^0_{ads} according to the following equation:

$$\Delta G^0_{ads} = -RTLn(55.5\ K) \qquad (7)$$

The value 55.5 in the above equation is the molar concentration of water in solution in mol dm^{-3} [24]. The negative value of ΔG^0_{ads} suggests that the adsorption onto steel surface is spontaneous process. Generally, values of ΔG^0_{ads} up to -20 k. j mol^{-1} are consistent with the electrostatic interaction between charged molecules and the charged metal (physical adsorption) while those more than -40 k. j mol^{-1} involving or sharing electrons from inhibitor molecules to metal surface to form a bond (chemisorption) [25-27]. The value of ΔG^0_{ads} in our measurement was up to 20 k. j mol^{-1}. Generally it is accepted that the type of adsorption are regarded as electrostatic attraction (physical adsorption) between the charged organic molecule and charged metal surface.

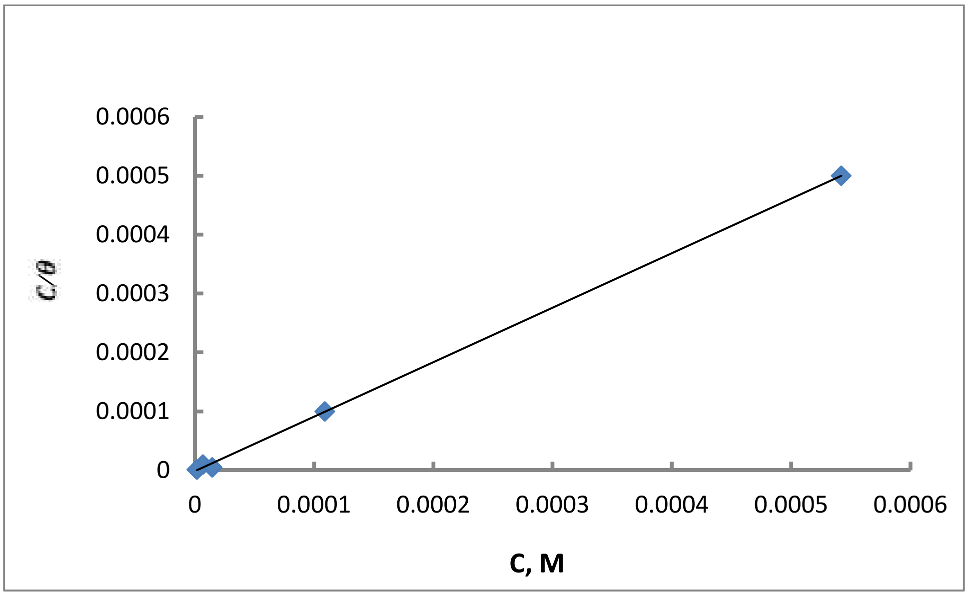


Fig.6: The relation between $\frac{C}{\theta}$ and C of the prepared inhibitor on metal surface which obeyed Langmuir adsorption isotherm model

3.3. Galvanostatic polarization measurements

Figure 7 shows Tafel plots for the carbon steel electrode in 1 M HCl in the absence and presence of the prepared inhibitor. The percentage of the inhibition efficiency (IE_a) was calculated using the following equation [28]:

$$\%\ IE_a = \quad 1 - \frac{I_{corr}}{I^0_{corr}} \ X\ 100 \qquad (8)$$

Where (i_{corr}) and (i^0_{corr}) are the uninhibited and inhibited corrosion current densities, respectively. The values of some associated electrochemical parameters e.g., corrosion potential (E_{corr}), corrosion current density (i_{corr}), cathodic and anodic Tafel slops (b_c) and (b_a) and percentage inhibition (% IE_a) values were calculated from polarization curves and are listed in Table (4). It is clear that both anodic metal dissolution and cathodic reduction reactions were inhibited when the inhibitor (S) was added to the acid solution in which there is a shift in the corrosion current density (I_{corr}) to lower values relative to the blank; inhibition is more pronounced with increase the inhibitor concentration. The corrosion potential (E_{corr}) is nearly unchanged, indicating that the inhibitor behaves mainly as mixed cathodic and anodic type inhibitors.

Table 4: Electrochemical parameters for carbon steel in absence and presence of different concentrations of inhibitor in 1M HCL solution at 20 ^{0}c obtained from Tafle polarization curves.

Surfactant	Conc. (M)	E_{corr} (mV SCE)	I_{corr} (middle) m.A	B_a	$-B_C$	%I.E
Blank	HCL	370.253	0.3667	35.24	38.07	-----
S	$5x10^{-4}$	405.036	0.6029	37.378	102.495	83.55
	$1x10^{-4}$	408.227	0.1116	40.440	129.247	69.56
	$5x10^{-5}$	411.392	0.1603	60.490	137.203	56.28
	$5x10^{-6}$	401.898	0.2398	50.192	192.664	34.60
	$1x10^{-6}$	376.582	0.3016	43.305	166.385	17.74

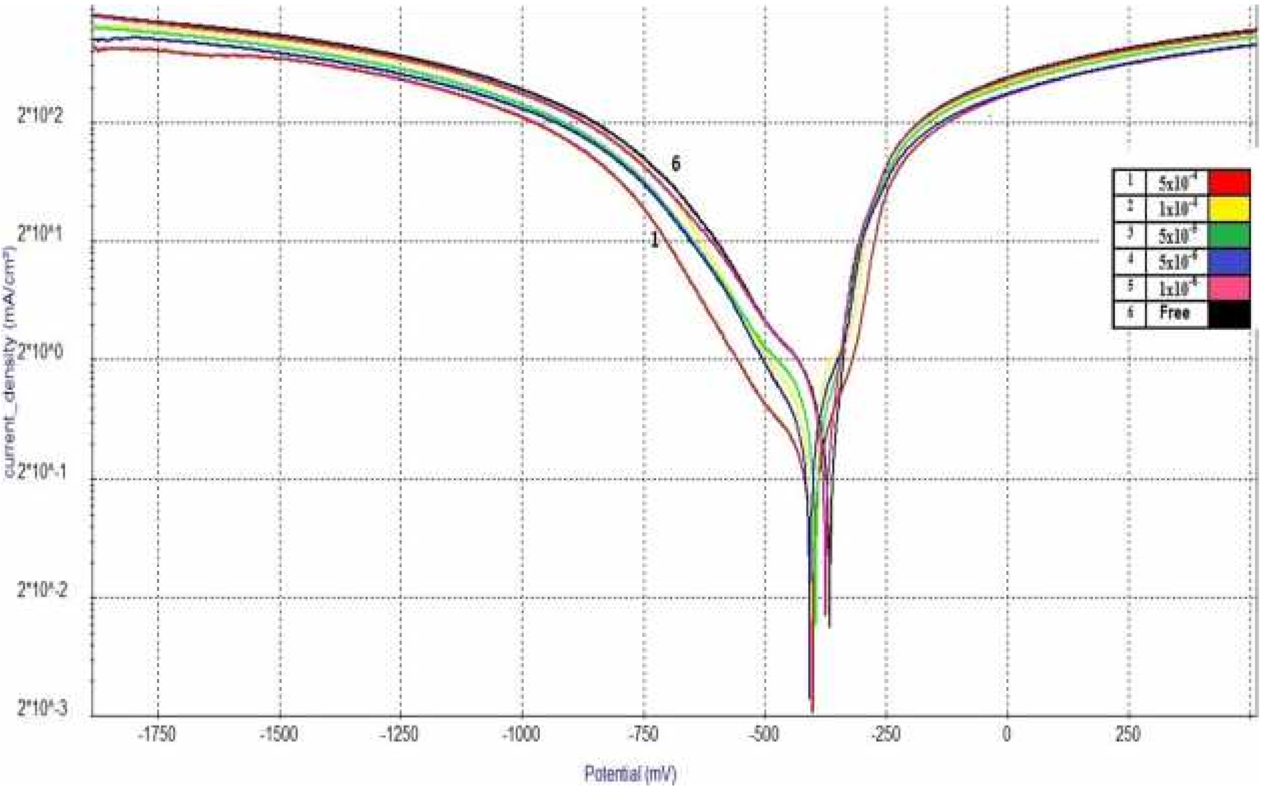


Fig. 7: Anodic and cathodic polarization curves obtained at 20 °C in 1 M HCl in the absence and presence of different concentrations of Inhibitor.

3.4. Biological activity (Sensitivity tests) by Kirby-Bauer Method

Antimicrobial activity of the tested samples was determined using a modified Kirby-Bauer disc diffusion method (Bauer, et al., 1966)[29]. Briefly, 100 µl of the tested Gram (-) bacteria (Desulfomonas pigra) was incubated at 35-37^{o}C for 24-48 hours were grown in 10 ml of fresh media until it reached a count of approximately 108 cells/ml (Pfaller, et al., 1988)[30].According to the result showed in table 5 the synthesized compound exhibit good activity against the tested Gram (-) bacteria (Desulfomonas pigra).

Table 5: Response of micro-organisms to synthesized surfactant compound

Sample	Desulfomonas pigra (SRB) (G^-)
Standard: Ampicillin Antibacterial agent	20
Control: DMSO	0.0
S	19

- G: Gram reaction
- SRB: Sulfur reducing bacteria

3.5. Mechanism of Inhibition

The adsorption is influenced by the surface charge of the metal and the chemical structure of inhibitor. The surface charge of the metal is due to the electrical field which emerges at interface on the immersion in the electrolyte. It also well know that the steel surface in 1 M HCl is charged with negative charge , so it easy for the positive charged inhibitor to approach the negative charged steel surface due to electrostatic attraction. When an inhibited solution contains adsorbed anion as sulphate group, these adsorbed onto the metal surface by creating oriented dipoles and consequently increasing the adsorption of the organic of the organic action on the dipoles (physical adsorption). In nature the synthesized inhibitor (s) is kind of cationic surfactant, which contains oxygen atoms and nitrogen atoms with two sets of loin pair of electrons. In the aqueous solution, synthesized inhibitor can be protonated, leading to appositive charge. This is the reason of the possible adsorption mechanism of synthesized cationic surfactant molecules on carbon steel in 1 M HCl solution as physical adsorption, Fig 8.

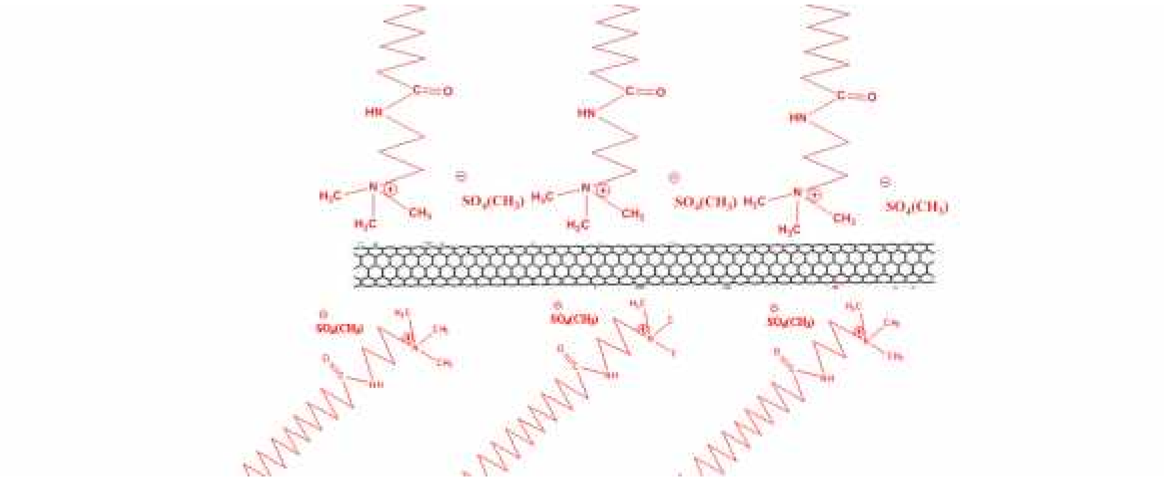


Fig 8: The predicted Mechanism of Inhibition of fatty amido-cationic surfactant (S)

4. Conclusion

From the obtained results the following conclusions can be deduced:

1. The investigated fatty amido-cationic surfactant acts as good corrosion inhibitor for mild steel in 1 M HCl solution.
2. The inhibition efficiency increases with increase in the inhibitor concentration and decreases with the increase in temperature.

3. The data obtained from weight loss measurements suggest corrosion inhibition by adsorption mechanism and fit well the Langmuir.
4. Fatty amido-cationic surfactant (S) acts as good corrosion inhibitor for mild steel in 1 M HCl solution.
5. The synthesized compound exhibit good activity against the tested Gram (-) bacteria (Desulfomonas pigra).

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