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Synthesis and Inhibition Effect of Two New Fatty Amido-Cationic Surfactants on Carbon Steel Corrosion in 1 M HCl Solution

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Abstract

Two new cationic surface-active compounds namely; N,N-dimethyl-N-(3-tetradecanoamidopropyl)-1-ammonium bromide and N,N-dimethyl-N-(3-hexadecanoamidopropyl)-1-ammonium bromide referred as (ACS3.1 and ACS3.2), respectively were synthesized and their chemical structures confirmed by spectra tools (FT-IR and ^{1}H-NMR). The inhibition effect of the synthesized cationic surfactants on carbon steel in 1 M HCl solution was evaluated using weight loss and potentiodynamic polarization methods. The study show that cationic surfactants (ACS3.1 and ACS3.2) are excellent inhibitors even with very low concentration and their adsorption on carbon steel surface obeyed Temkin adsorption isotherm. The polarization measurements indicated that the two synthesized surfactants acted as mixed-type inhibitors. Thermodynamic parameters were obtained from weight losses at various temperatures and discussed.

Keywords: Fatty amido-cationic surfactants, carbon steel, corrosion, weight loss, potentiodynamic polarization

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1. Introduction

Carbon steel (CS) is considered an important structural material and it is one of the most common and popular construction materials across a lot of industries. In many applications, the carbon steel is prone to suffer the effects of this aggressiveness which leading to serious corrosion problems [1, 2].

Using inhibitors is one of the most practical methods for metal protection against corrosion attack in acidic media [3]. Acidic solutions especially solution of hydrochloric acid are widely used in chemical and some industrial processes such as acid pickling, acid cleaning, acid descaling and oil wet cleaning of metals and their alloys [4]. It has been found that most of the organic compound inhibitors containing heteroatoms such as nitrogen, oxygen or sulfur and multiple bonds act by adsorption on the surface of metals [5]. This phenomenon is affected by the nature and surface charge of metals, the sort of aggressive electrolyte and the chemical structure of the organic inhibitors [6]. Many surveys were done on the corrosion and inhibition of carbon steels in acidic solution [7–10]. Surface-active compounds (surfactants) are a very important class of organic compounds that can be used to prevent corrosion attack of carbon steels [11–13]. The surfactant compounds adsorbed on the surface of metals and their alloys and change the corrosion preventing property of a metal and for this reason, the study of the correlation between the adsorption and corrosion inhibition is of a considerable importance [14–20]. A surfactant compound is one that tends to accumulate at a surface or interface due to its high surface activity resulting from the adsorption of the surfactant compound molecules at the interface between bulk phases, forming aggregations called micelles, such as air and water, oil and water or electrode and solution [21–22].

The purpose of this study was to examine the inhibitory action of the newly synthesized cationic surfactants containing nitrogen atom for the corrosion attack of carbon steel in a 1 M HCl acidic solution. The inhibition performance was evaluated by weight loss and potentiodynamic polarization methods.n Thermodynamic parameters were obtained from weight losses at different temperatures and discussed.

2. Experimental

2.1. Synthetic procedure

Syntheses of newly cationic surfactants (ACS3.1 and ACS3.2) used in this study were synthesized in three steps as follow:

2.1.1. Synthesis of (tetradecanoic and/or hexadecanoic) chloride

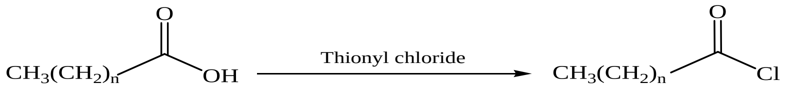
One equivalent of the corresponding (tetradecanoic and/or hexadecanoic) acids each one was placed in a 250-mL round-bottom flask fitted with a reflux condenser (with a calcium chloride guard-tube). Five equivalents of thionyl chloride were added to the flask, and the reaction mixture was stirred overnight at room temperature without solvent. At the end of the reaction, excess of thionyl chloride was removed under reduced pressure, and the observed oily product was used without further purification in the next step [23] Scheme (1).

2.1.2. Synthesis of amido-amine derivatives

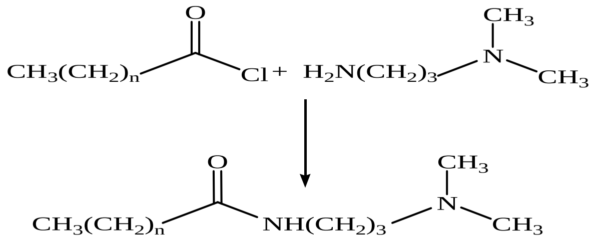
Amido-amine derivatives was prepared by refluxing fatty acid chloride (tetradecanoyl chloride and/or hexadecanoyl chloride) with N,N-Dimethyl-1,3-propanediamine in CH_2Cl_2 as solvent Scheme (2).

2.1.3. Synthesis of cationic surfactants (ACS3.1 and ACS3.2)

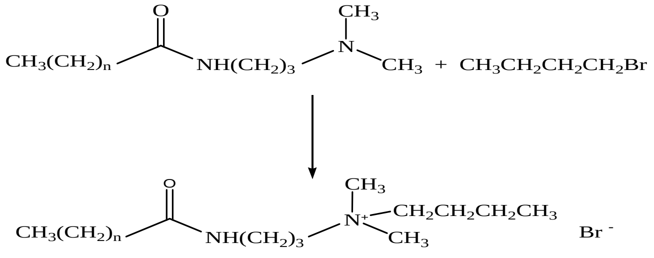
The prepared amido-amine derivatives was refluxed with butyl bromide in tetrahydrofuran (THF) to afforded cationic surfactants as whitish yellow to pal yellow semi-solid according the Scheme (3).



Scheme (1): (tetradecanoyl chloride, (n = 12), hexadecanoyl chloride, (n = 14))



Scheme (2): (N-(3-dimethylamino) propyl tetradecanoamide, (n = 12), N-(3-dimethylamino) propyl hexadecanoamide, (n = 14))



Scheme (3): (ACS3.1, (n = 12), ACS3.2, (n = 14))

2.2. The chemical structural confirmation

The chemical structures of the synthesized cationic surfactants (ACS3.1 and ACS3.2) were confirmed by:

1) FT-IR spectra using spectrophotometer model (Nicolet iS10, Thermo-Scientific) at (Chemistry department, Faculty of science, Benha University).
2) ^{1}H-NMR spectra was measured in DMSO using model (Bruder Aveence lll 400 MHz, Bruker (sorry)) at (Chemistry department, Faculty of science, Zagazig University).

2.3. Critical micelle concentration (CMC)

The critical micelle concentration values of the synthesized cationic surfactants (ACS3.1 and ACS3.2) obtained from surface tension measurements. The critical micelle concentration (CMC), indicated the value of concentration at which it becomes thermodynamically favorable for surfactant molecules to form aggregates (micelles) to minimize interaction of either their head groups or their tail groups with the solvent. Once the synthesized surfactant inhibitor concentration reaches a certain level (CMC), the water structure forces aggregation of the hydrophobic tail groups to form surfactant micelles [24].

2.3.1. The surface tension measurements

The surface tension of the synthesized cationic surfactants (ACS3.1 and ACS3.2) was measured using tensiometer K6 Krüss, Germany, (Du Nouy tensiometer with Platinum – Iridium ring) in Egyptian Petroleum Research Institute (EPRI) for different concentrations at 25 °C. De-ionized water with a surface tension of 72 dyn cm^{-1} at 25 °C was used to prepare all solutions [25].

2.4. Test solutions

The corrosive medium was 1 M HCl acidic solution was prepared by diluting the appropriate volume of the concentration chemically pure acid (37 % merck), with bi-distilled water. The various concentrations of the synthesized cationic surfactant inhibitors used were (1×10^{-5}, 5×10^{-5}, 1×10^{-4}, 3×10^{-4}, and 5×10^{-4} M). All test solutions were prepared from bi-distilled water. For each experiment, a freshly prepared solution was used.

2.5. Weight loss measurements

Weight loss experiments were carried out using the specimens of carbon steel (CS) which have the following composition: 0.025 % Si, 0.09 % P, 0.1 % C, 0.05 %Ni, 0.02 % Cr, 0.01 % Mn, 0.03 % Cu, 0.001 % V, and the remainder Fe. Carbon steel specimens were machined to be a rectangular with dimensions of (length 4.8, width 2, and thickness 1.1 cm) with an exposed total surface area of 34.16 cm^2 was used for gravimetric measurements. The specimens were mechanically polished with different grade emery papers, washed with distilled water, acetone and water again. The specimens were accurately weighted and then immersed in 1 M HCl acid solution without and with various concentrations of the synthesized surfactant inhibitors (ACS3.1 and ACS3.2) at various temperatures at 20–60 °C. The temperature for weight loss measurements was dominated by water bath provided with thermostat control ±2 °C. After 24 hours exposure, the specimens were taken out rinsed thoroughly with distilled water, dried and weighted accurately. All tests in this study were done under aerated conditions.

2.6. Potentiodynamic polarization measurements

The polarization measurements were recorded by a Meinsberger Potentiostat/ Galvanostat (PS6) with controlling software PS remote in a personal computer. Platinum electrode and a saturated calomel electrode was utilized as a counter electrode and reference electrode, respectively. The working electrode was a cylinder of carbon steel, embedded in epoxy resin with a surface area of 1.56 cm2 exposed to the corrosive acidic solution. All measurements were carried out at a scan rate 1 mV Sec^{-1}.

3. Results and discussion

3.1. Chemical structure confirmation

3.1.1. Synthesis of amido-amine derivatives

The structure of N-(3-dimethylamino) propyl tetradecanoamide and N-(3-dimethylamino) propyl hexadecanoamide was established by IR spectroscopy which shows the characteristic bands at 3416.90, 3307.71cm^{-1} for (υ_{NH}), 2921.46, 2917.51, 2851.17, and 2848.88 cm^{-1} for (υ_{C-H} aliphatic chain (CH_3,CH_2), respectively) and 1647.56-1640.26 cm^{-1} for ($\upsilon_{C=O}$ of amide) (Cf. Figures (1, 2)).

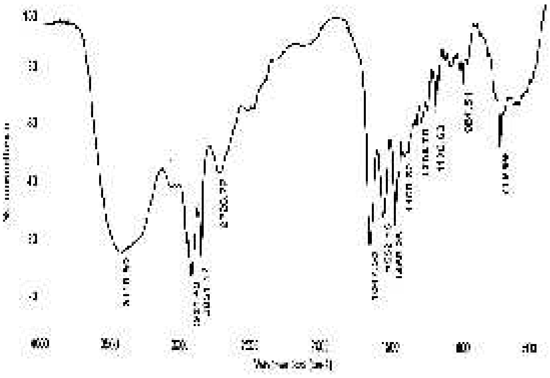


Fig (1): FT-IR spectrum of N-(3-dimethylamino) propyl tetradecanoamide.

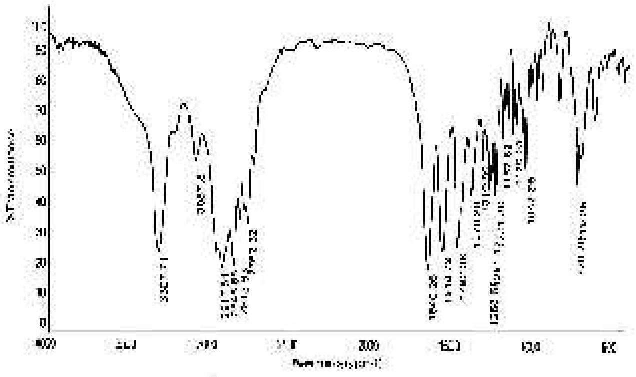


Fig (2): FT-IR spectrum of N-(3-dimethylamino) propyl hexadecanoamide.

3.1.2. Synthesis of cationic surfactants (ACS3.1 and ACS3.2)

The structure of synthesized cationic surfactants (ACS3.1 and ACS3.2) was established by IR spectroscopy which shows the characteristic bands at 3442.75, 3415.04 cm^{-1} for (υ_{NH}), 2923.70, 2922.30, 2853.28, and 2852.50 cm^{-1} for (υ_{C-H} aliphatic chain (CH_3, CH_2), respectively), and 1648.89, 1644.24 cm^{-1} for ($\upsilon_{C=O}$ of amide). On other hand, ^{1}H-NMR spectroscopy, showed the following characteristic peaks: δ = 0.8 ppm (t, 3H, terminal CH_3 in butyl chain $(CH_2)_3CH_3$); δ = 0.9 ppm (t, 3H, terminal CH_3 in fatty chain); δ = 1.1-1.5 ppm (m, 26H, CH_2 in fatty chain); δ = 2.1-2.3 ppm (m, 2H, CH_2 n-propylene chain $NCH_2CH_2CH_2N$); δ = 2.5-2.7 ppm (t, 2H, CH_2 in CH_2CO in fatty acid); δ = 2.9-3.4 ppm (m, 4H, in quaternary ammonium salt $CH_2N(CH_3)_2CH_2$); δ = 3.5-3.9 ppm (S, 6H, CH_3 in CH_3NCH_3); δ = 7.9 ppm (S, 1H, in OCNH) (Cf. Figures (3-5)).

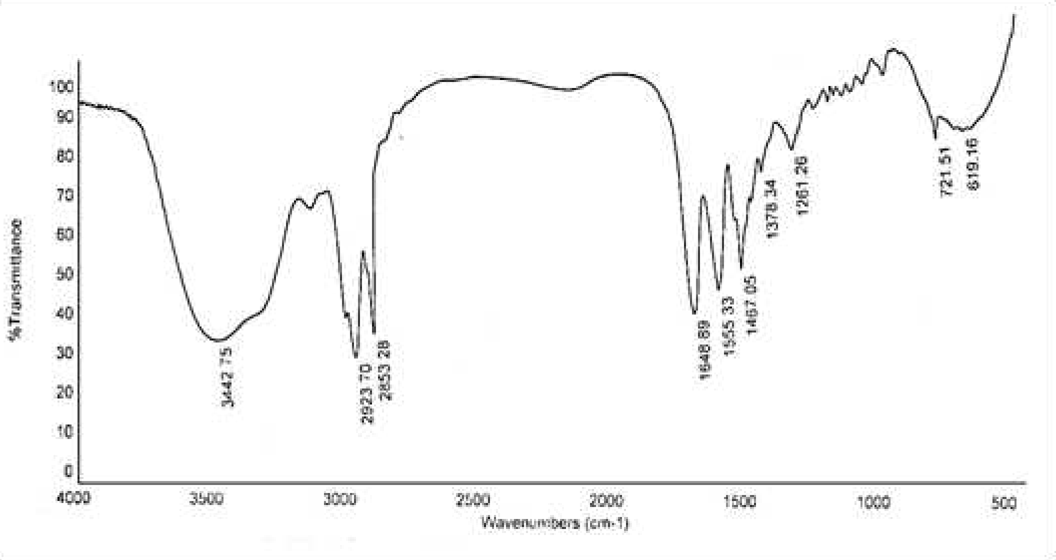


Fig (3): FT-IR spectrum of (ACS3.1) surfactant.

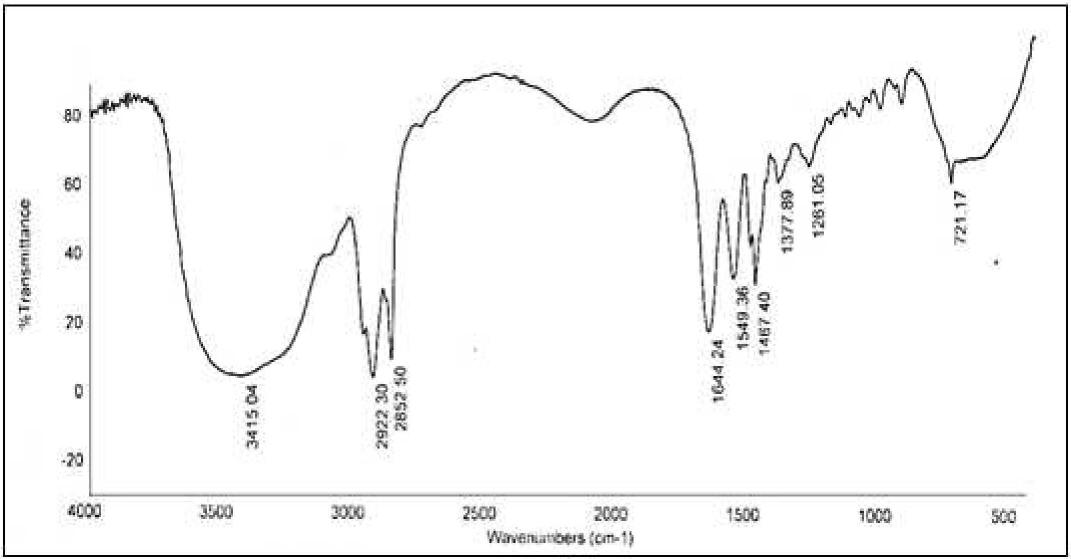


Fig (4): FT-IR spectrum of (ACS3.2) surfactant.

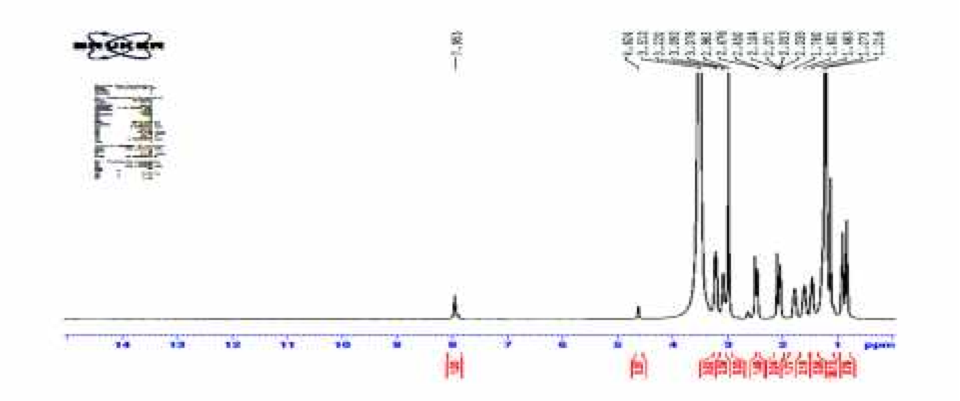


Fig (5): ^{1}H-NMR spectra of (ACS3.2) surfactant.

3.2. Surface active properties

Most organic corrosion inhibitors are adsorbed on the metal/solution interface by displacing water molecules from the surface and forming a compact barrier film. The ability of surfactant molecules to adsorb is generally directly related to its ability to aggregate and form micelles. There is equilibrium between the singly adsorbed surfactant molecules. The equilibrium takes place at the concentration of complete surface saturation. The micelle formation is the most important point of view in the surfactant because it is the most effective geometrical arrangement of the molecules at the desired concentration [26]. Below (CMC), individual surfactant molecules or monomers lean to adsorb on exposed interfaces, so interfacial aggregation decreases surface tension and is related to corrosion inhibition. The surface tension (γ) of surfactant molecules was measured for a range of concentrations above and below the critical micelle concentration (CMC), A representative plot of (γ) versus concentration, linear decrease in surface tension was observed with the increase of surfactant concentrations [27].

3.2.1. The surface tension

The surface tension (γ) of cationic surfactants (ACS3.1 and ACS3.2) was measured for a range of concentrations above and below the critical micelle concentration (CMC), as shown in Figure (6) represents plots of the (γ) versus ($-\log C$) for cationic surfactants (ACS3.1 and ACS3.2). A linear decrease in surface tension was observed with the increasing the surfactant concentration, then the curves break rather rapidly at relatively low concentration increasing the surfactant concentration, then the curves break rather rapidly at relatively low concentration and continue to steep slowly as the concentration increases. This observation was recorded for cationic surfactants (ACS3.1 and ACS3.2) up to the (CMC), beyond which no considerable changes were noticed. This common behavior shown by surfactants in bi-stilled water at 25 °C was used to determine their purity and (CMC)'s. The (CMC) values obtained from the break point in the (γ) versus ($-\log C$) plots are shown in Table (1). The (γ) versus ($-\log C$) plots also provided information about area per molecule at air-water interface, effectiveness and surface excess concentration of surfactant ions of synthesized surfactants. Obtained (CMC) of cationic surfactants (ACS3.1 and ACS3.2) show an increasing trend with increasing the chain length of alkyl group. The increase in (CMC) value can be attributed to an increase in the solubility of the surfactant molecules i.e., the presence of polar atoms as oxygen or nitrogen in the hydrophobic chain (but not associated with the head group), results in an increase in the (CMC) [28-30].

3.2.2. Effectiveness (π_{CMC})

The maximum surface pressure (π_{CMC}) which is defined as the effectiveness of a surfactant in reducing surface tension and was calculated from the following equation [31]:

$$\pi_{CMC} = \gamma_{\circ} - \gamma_{CMC} \qquad (1)$$

where ($\gamma_{\circ}$) and (γ_{CMC}) are the surface tensions of pure water and surface tension at (CMC), respectively. (π_{CMC}) values are listed in Table (1). It was found that, effectiveness of the synthesized cationic surfactants increased with increasing alkyl chain length.

3.2.3. The surface excess (Γ_{max})

The surface excess concentration of surfactant ions, (Γ_{max}), provided an effective measure of the surfactant adsorption at the air/water interface. The maximum value of the surface excess concentration was in corresponds with the maximum concentration that a surfactant can attain at the interface, (Γ_{max}), and it was defined as the effectiveness of adsorption at an interface. The concentration of the surfactant was always higher at the surface phase than that in the bulk solution. (Γ_{max}) values were calculated from the slope of the straight line in the surface tension plot ($d\gamma / (d \log C)$) below (CMC), using the appropriate form of Gibbs adsorption equation [32]:

$$\Gamma_{max} = \frac{-1}{2.303\, nRT} \quad \frac{d\gamma}{d \log C} \qquad (2)$$

where (Γ_{max}) mol m^{-2} is the surface excess concentration of surfactant ions, (R) is gas constant, (T) is absolute temperature, (C) is concentration of surfactant, (γ) is surface tension at given concentration and (n) is number of species ions in solution. The values of surface excess concentration were calculated and listed in Table (1). It was found that, surface excess concentration of cationic surfactants decrease by increasing carbon chain length, which could be due to differ in geometry with hydrophobic effect of carbon chain and crowded of bulky groups in quaternary moiety.

3.2.4. The area per molecule (A_{min})

The minimum surface area per adsorbed molecule, (A_{min}) nm^2, is defined as the area occupied by each molecule in nm^2 at the liquid/air interface. (A_{min}) value was calculated from the following equation [33, 34]:

$$A_{min} = \frac{10^{16}}{N_A \Gamma_{max}} \quad (3)$$

where (N_A) is the Avogadro's number and (Γ_{max}) mol m^{-2} is the maximal surface excess of adsorbed surfactant molecules at the interface. The values of area per molecule were calculated and listed in Table (1). It was found that (A_{min}) values of the synthesized cationic surfactants increase by increasing carbon chain length.

3.2.5. The standard free energy of micelle formation (ΔG°_{mic})

The standard free energy of micelle formation per mole of surfactant was given by the following equation [35]:

$$\Delta G^{\circ}_{mic} = RT \ln CMC \quad (4)$$

where (R) is the gas constant, (T) is absolute temperature, and (CMC) is expressed in the molarity of the surfactant. Values were calculated and listed in Table (1). It is clear that, values of cationic surfactants (ACS3.1 and ACS3.2) follow this order:

ACS3.2 > ACS3.1

The obtained values of synthesized cationic surfactants increased with increasing carbon chain length, which indicated that the micelle formation was thermodynamically favored with increasing carbon chain length of head groups and alkyl chains. The negative values of (ΔG°_{mic}) were indicated that the micellization process proceeds spontaneously.

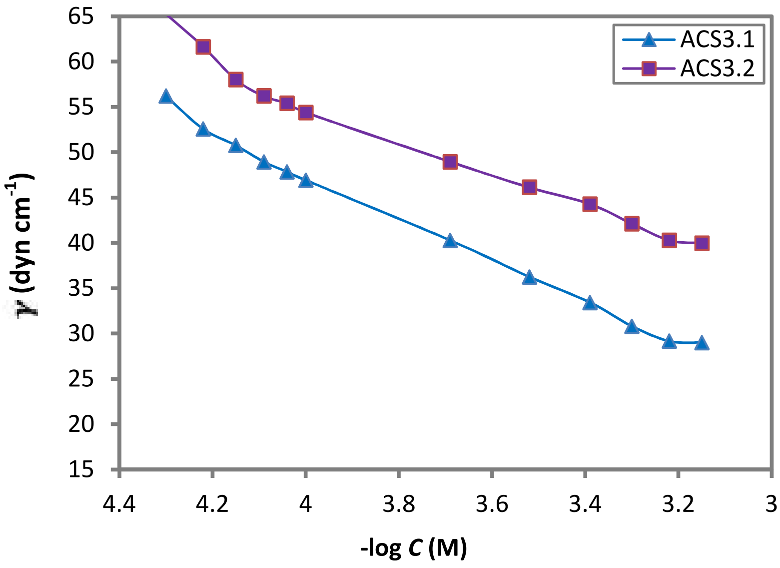


Fig (6): The variation of the surface tension with logarithm of concentrations for synthesized cationic surfactants (ACS3.1 and ACS3.2) in bi-distilled water at 25 °C.

Table (1): The critical micelle concentration (CMC), effectiveness (π_{CMC}), maximum surface excess (Γ_{max}), minimum area (A_{min}), and the standard free energy (ΔG°_{mic}) of cationic surfactants (ACS3.1 and ACS3.2) from surface tension measurements in bi-distilled water at 25 °C.

Inhibitor	$CMC \times 10^{-4}$ (M)	γ_{CMC} (dyn cm^{-1})	π_{CMC} (dyn cm^{-1})	$\Gamma_{max} \times 10^{-3}$ (mol cm^{-2})	$A_{min} \times 10^{-6}$ (nm^2)	$-\Delta G^{\circ}_{mic}$ (kJ mol^{-1})
ACS3.1	6.1	29.17	42.83	2.02	8.22	36.67
ACS3.2	6.6	39.98	32.02	1.69	9.82	36.28

3.3. Weight loss measurements

The results are listed Table (2) shows the values of weight loss measurements of carbon steel corrosion after 24 hours of immersion in 1 M HCl solution without and with the addition of various concentrations of cationic surfactant inhibitors (ACS3.1 and ACS3.2) at 20 °C. The corrosion rate (CR) was calculated according to the following equation [36]:

$$CR = \frac{\Delta W}{St} \tag{5}$$

where (ΔW) is the average weight loss of carbon steel specimens, (S) is the total area of the specimens, and (t) is immersion time. Inhibition efficiency (η_w) and surface coverage (θ) were calculated according to the following equations [36]:

$$\eta_w = \left(\frac{W - W_\circ}{W}\right) \times 100 \tag{6}$$

$$\theta = \left(\frac{W - W_\circ}{W}\right) \tag{7}$$

where, (W) and ($W_\circ$) are the weight loss of carbon steel specimens in the absence and presence of the inhibitor, respectively. Table (2) shows that the inhibition efficiency (η_w) increased as the concentration of inhibitors increased from 1×10^{-5} to 5×10^{-4} M at 20 °C. Also, this study displays higher inhibition efficiency obtained from the compound has the long chain fatty acid. Hence, inhibition efficiency (η_w) is higher in the hexadecanoic derivative than the tetradecanoic derivative as shown in Figure (7).

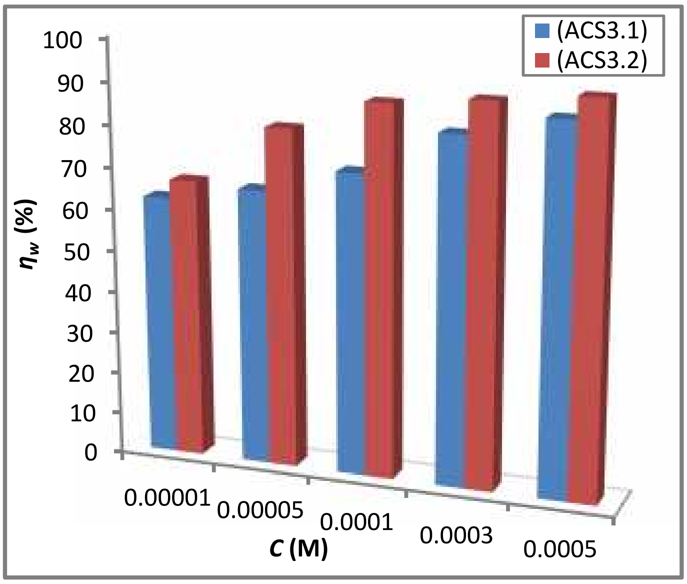


Fig (7): The relationship between inhibition efficiency (η_w) of carbon steel in 1 M HCl solution and different concentrations of cationic surfactants (ACS3.1 and ACS3.2) at 20 °C.

Table (2): Weight loss data of carbon steel corrosion in 1 M HCl solution without and with different concentrations of cationic surfactants (ACS3.1 and ACS3.2) at 20 °C.

Inhibitor	Conc. of inhibitor (M)	ΔW (gm)	CR (gm cm^{-2} h^{-1})	θ	η_w (%)
ACS3.1	0.0000	0.1374	0.00016759	----------	----------
	1×10^{-5}	0.0519	0.00006330	0.62227	62.227
	5×10^{-5}	0.0470	0.00005732	0.65793	65.793
	1×10^{-4}	0.0390	0.00004757	0.71615	71.615
	3×10^{-4}	0.0247	0.00003012	0.82023	82.023
	5×10^{-4}	0.0180	0.00002195	0.86899	86.899
ACS3.2	0.0000	0.1374	0.00016759	----------	----------
	1×10^{-5}	0.0457	0.00005574	0.66739	66.739
	5×10^{-5}	0.0266	0.00003244	0.80640	80.640
	1×10^{-4}	0.0166	0.00002024	0.87918	87.918
	3×10^{-4}	0.0139	0.00001695	0.89883	89.883
	5×10^{-4}	0.0110	0.00001341	0.91994	91.994

3.4. Effect of temperature

The values of weight loss, corrosion rate and the inhibition efficiencies for carbon steel in 1 M HCl in absence and presence of 5 × 10^{-4} M of cationic surfactants (ACS3.1 and ACS3.2) at various temperatures were studied and listed in Table (3). Figure (8) shows that the inhibition efficiency (η_w) decrease with the increasing temperature. These results revealed that the synthesized cationic surfactants (ACS3.1 and ACS3.2) were adsorbed on carbon steel surface physically (physical adsorption) [37].

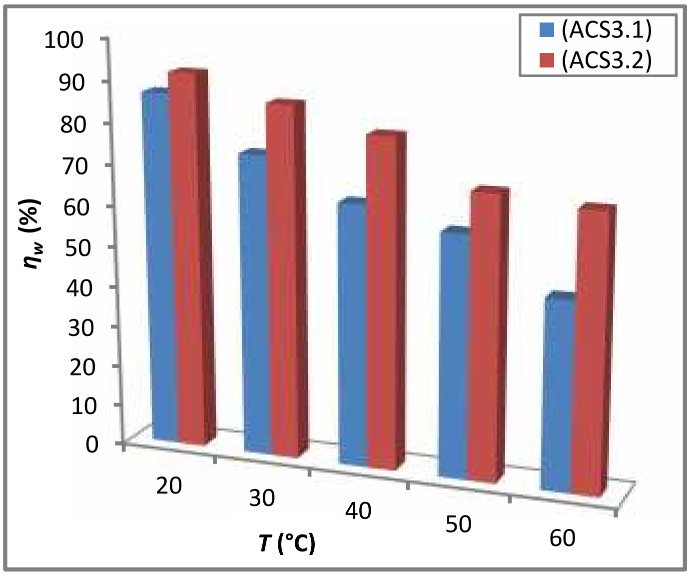


Fig (8): Effect of temperature on the inhibition efficiency (η_w) obtained by weight loss method for carbon steel in 1 M HCl solution with 5 × 10^{-4} M of cationic surfactants (ACS3.1 and ACS3.2).

Table (3): Weight loss data of carbon steel corrosion in 1 M HCl solution without and with 5 × 10^{-4} M of cationic surfactants (ACS3.1 and ACS3.2) at various temperatures.

Inhibitor	T (°C)	Conc. of inhibitor (M)	ΔW (gm)	CR (gm cm^{-2} h^{-1})	θ	η_w (%)
ACS3.1	20	0.0000	0.1374	0.00016759	----------	---------
		5 × 10^{-4}	0.0180	0.00002195	0.86899	86.899
	30	0.0000	0.4185	0.00051046	----------	---------
		5 × 10^{-4}	0.1095	0.00013356	0.73835	73.835
	40	0.0000	2.0461	0.00249573	----------	---------
		5 × 10^{-4}	0.7364	0.00089822	0.64009	64.009
	50	0.0000	2.5096	0.00306108	----------	---------
		5 × 10^{-4}	1.0268	0.00125243	0.59085	59.085
	60	0.0000	3.2945	0.00401846	----------	---------
		5 × 10^{-4}	1.7818	0.00217335	0.45915	45.915
ACS3.2	20	0.0000	0.1374	0.00016759	----------	---------
		5 × 10^{-4}	0.0110	0.00001341	0.91994	91.994
	30	0.0000	0.4185	0.00051046	----------	---------
		5 × 10^{-4}	0.0584	0.00007123	0.86045	86.045
	40	0.0000	2.0461	0.00249573	----------	---------
		5 × 10^{-4}	0.4027	0.00049119	0.80318	80.318
	50	0.0000	2.5096	0.00306108	----------	---------
		5 × 10^{-4}	0.7752	0.00094555	0.69110	69.110
	60	0.0000	3.2945	0.00401846	----------	---------
		5 × 10^{-4}	1.0850	0.00132342	0.67066	67.066

3.5. Adsorption Isotherm

Organic molecules like cationic surfactant inhibitor inhibit the corrosion process by the adsorption on metal surface. Theoretically, the adsorption process can be regarded as a single substitutional process in which inhibitor molecules in the aqueous phase substitutes an (n) number of water molecules adsorbed on the metal surface [38]:

$$\mathrm{Org}_{sol} + n\,H_2O_{(ads)} \leftrightarrow \mathrm{Org}_{(ads)} + n\,H_2O_{(sol)} \qquad (8)$$

where ($\mathrm{Org}_{(sol)}$) and ($\mathrm{Org}_{(ads)}$) are the organic molecules in the solution and adsorbed on the carbon steel surface, respectively, and (n) is the number of water molecules replaced by the organic molecules. It is essential to know the mode of adsorption and the adsorption isotherm that can give important information on the interaction of the organic inhibitors and carbon steel surface.

The interactions between surfactant inhibitors and the carbon steel surface can be examined by the adsorption isotherm model. The degree of surface coverage values (θ) for different concentrations of cationic surfactant inhibitors (ACS3.1 and ACS3.2) in 1 M HCl solution have been estimated from the weight loss measurements and listed in Table (2). A suitable adsorption isotherm was obtained by using these calculated values. The linear relationships of (θ) versus ($\ln C$) showed in Figure (9). So, suggested that the adsorption of cationic surfactants (ACS3.1 and ACS3.2) on the carbon steel surface obeyed the Temkin adsorption isotherm model is given by the general equation [39].

$$e^{-2a\theta} = KC \qquad (9)$$

and the logarithmic form:

$$\theta = \frac{-1}{2a}\ln C - \frac{1}{2a}\ln K \qquad (10)$$

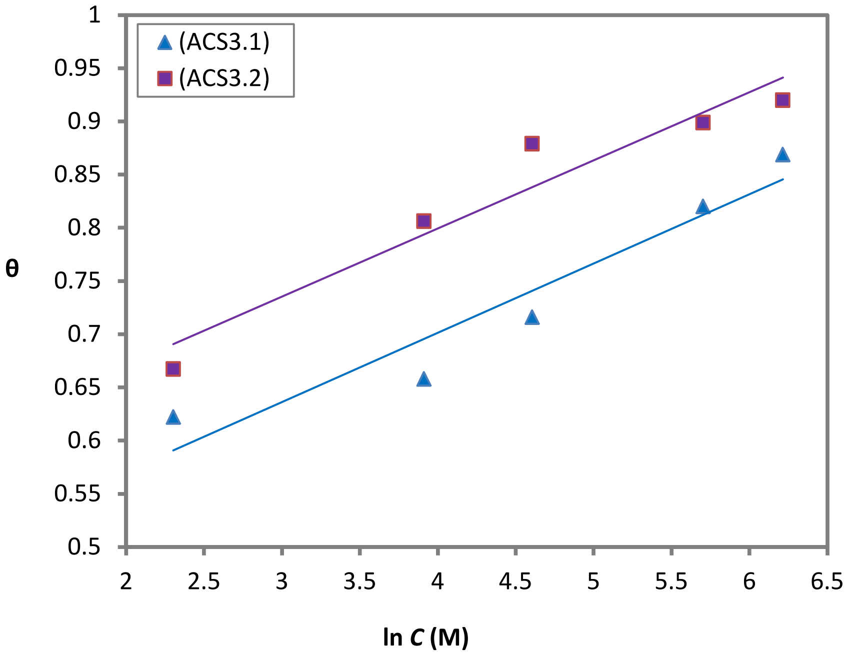


Fig (9): Temkin adsorption isotherm model of cationic surfactants (ACS3.1 and ACS3.2) on the carbon steel surface in 1 M HCl solution from weight loss method at 20 °C.

The values of constant adsorption equilibrium (K_{ads}) of the Temkin adsorption isotherm obtained for cationic surfactants (ACS3.1 and ACS3.2) are listed in Table (4). The relatively high values of the adsorption equilibrium constant reflected that the high adsorption ability of this molecule on carbon steel surface. The value of (K_{ads}) is related to the standard free energy of adsorption, (ΔG°_{ads}), by the following equation [40]:

$$\Delta G^{\circ}_{ads} = -RT\,\ln(55.5K_{ads}) \qquad (11)$$

where (R) is the general gas constant, (T) is the absolute temperature and the value of (55.5) is the molar concentration of water in solution expressed in mol L^{-1}. The standard free energy (ΔG°_{ads}), values of adsorption for cationic surfactants (ACS3.1 and ACS3.2) listed in Table (4). These values were shown to be negative, and the values are consistent with the spontaneity of the adsorption process and the stability of the adsorbed layer on the carbon steel surface [41].

Table (4): Adsorption thermodynamic parameters on the carbon steel surface in 1 M HCl solution containing different concentrations of cationic surfactants (ACS3.1 and ACS3.2) at 20 °C.

Inhibitor	R^2	-a	$K_{ads} \times 10^6$ (M^{-1})	$-\Delta G^{\circ}_{ads}$ (kJ mol^{-1})
ACS3.1	0.9179	7.6804	880.2888	59.9552
ACS3.2	0.9304	7.8125	4892.344	64.1334

3.5.1. Kinetic parameters

The effect of temperature 20–60 °C on the performance of cationic surfactant inhibitors (ACS3.1 and ACS3.2) at different concentrations of 5×10^{-4} M for carbon steel in 1M HCl was evaluated using weight-loss measurements. The logarithm of the corrosion rate (CR) is a linear function with ($1/T$) (Arrhenius equation) [42]:

$$\ln CR = \frac{-E_a}{RT} + \ln A \qquad (12)$$

where, (E_a) is the effective activation energy, (R) is the general gas constant and (A) is the Arrhenius pre-exponential factor. A plot of the nature logarithm of the corrosion rate (CR) was obtained by weight loss measurement versus ($1/T$) and gave straight line as shown in Figure (10). The values of the activation energy (E_a) obtained from the slope of the lines are given in Table (5). The data show that the activation energy (E_a) of the corrosion of carbon steel in 1 M HCl solution in the presence of cationic surfactants (ACS3.1 and ACS3.2) was higher than those in free acid solution. These results indicating that the synthesized cationic surfactant inhibitors (ACS3.1 and ACS3.2) were adsorbed on the carbon steel surface physically [43]. Enthalpy and entropy of activation (ΔH^{*}) and (ΔS^{*}) were calculated from the transition state theory [44-45]:

$$\ln \frac{CR}{T} = \ln \frac{R}{N_A h} + \frac{\Delta S^{*}}{R} - \frac{\Delta H^{*}}{RT} \qquad (13)$$

where (h) is Planck's constant, (N_A) is Avogadro's number, (R) is the general gas constant, (ΔH^{*}) is the enthalpy of the activation and (ΔS^{*}) is the entropy of activation. Plotting of the nature logarithm of (CR/T) against ($1/T$) which gave straight lines as illustrated in Figure (11). Data in Table (5) represent the values of (ΔH^{*}) and (ΔS^{*}), which were calculated from the slope of ($\frac{\Delta H^{*}}{R}$) and the intercept of ($\ln \frac{R}{N_A h} + \frac{\Delta S^{*}}{R}$) of the straight lines. Values of (ΔH^{*}) and (ΔS^{*}) were calculated and listed in Table (5). Inspection of these data revealed that the activation parameters (ΔH^{*}) and (ΔS^{*}) of the dissolution reaction of carbon steel in 1 M HCl solution in the presence of inhibitors were less than those in the absence of cationic surfactants (ACS3.1 and ACS3.2).

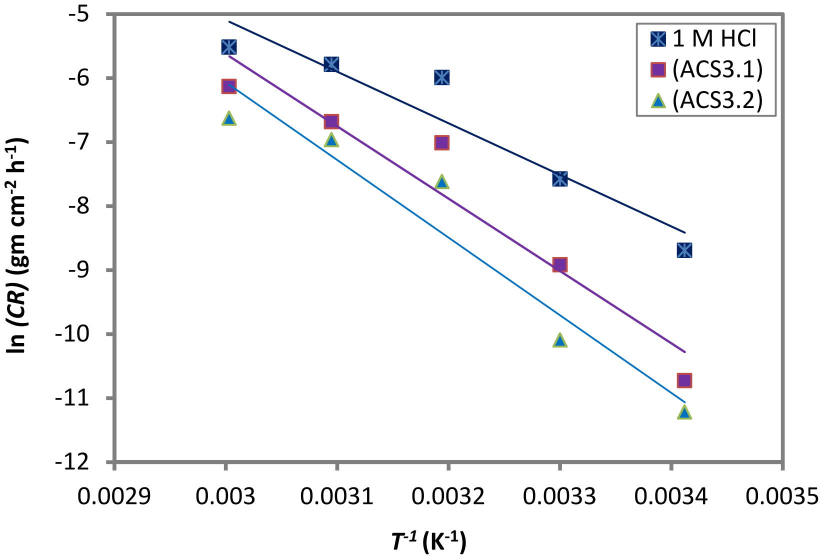


Fig (10): Arrhenius plots {($\ln CR$) vs. ($1/T$)} for carbon steel corrosion in absence and presence of 5×10^{-4} M of cationic surfactants (ACS3.1 and ACS3.2) in 1 M HCl solution after 24 hours.

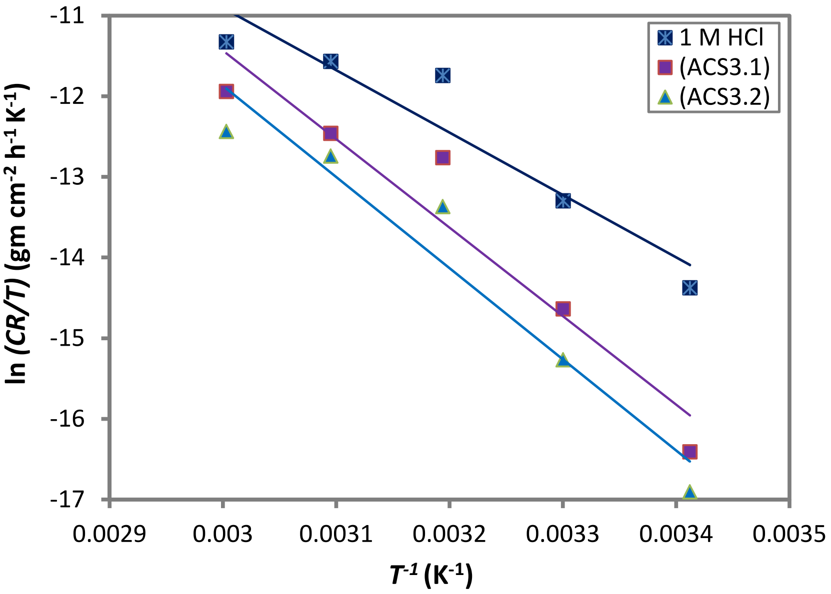


Fig (11): Arrhenius plots {(ln CR/T) vs. (1/T)} for carbon steel corrosion in absence and presence of 5 × 10^{-4} M of cationic surfactants (ACS3.1 and ACS3.2) in 1 M HCl solution after 24 hours.

Table (5): Activation parameters values for carbon steel corrosion in 1 M HCl solution in the absence and presence of 5 × 10^{-4} M of cationic surfactants (ACS3.1 and ACS3.2) after 24 hours.

Inhibitor	Conc. of inhibitor (M)	E_a (kJ mol^{-1})	$\Delta H^{\square}_{ads}$ (kJ mol^{-1})	$-\Delta S^{\square}_{ads}$ (J mol^{-1} K^{-1})
Blank	0.0000	66.9218	64.3254	95.2460
ACS3.1	5 × 10^{-4}	93.8318	91.2378	18.9318
ACS3.2	5 × 10^{-4}	101.5970	93.9731	14.3341

3.6. Potentiodynamic polarization

The representative potentiodynamic polarization curves of carbon steel in 1 M HCl solution in the absence and presence of various concentrations of cationic surfactant inhibitors (ACS3.1 and ACS3.2) are shown in Figures (12-13). The corresponding electrochemical parameters, i.e., corrosion potential (E_{corr}), corrosion current density (i_{corr}), cathodic and anodic Tafel slopes (β_c and β_a) and inhibition efficiency (η_p) values were calculated from Figures (12-13) and are given in Table (6). The inhibition efficiency (η_p) was calculated from polarization measurements according to the following equation [46, 47]:

$$\eta_p = \frac{i_{corr} - i^{\circ}_{corr}}{i_{corr}} \times 100 \qquad (14)$$

where (i_{corr}) and (i°_{corr}) are the uninhibited and the inhibited corrosion current densities, respectively. It is apparent from Table (6) that, when the concentrations of the studied cationic surfactant inhibitors were increased, the inhibition efficiencies (η_p) increased while the corrosion current densities decreased. The inhibitive action of this inhibitor was discussed in terms of blocking the electrode surface by adsorption of the molecules through the active centers contained in its structure. The corrosion potential (E_{corr}) of this inhibitors shifted slightly in the negative direction as shown in Table (6). This behavior indicated that the inhibitor predominantly controls both anodic and cathodic reactions. 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 cationic inhibitor is blocking the cathodic and anodic sites without changing the corrosion mechanism [48].

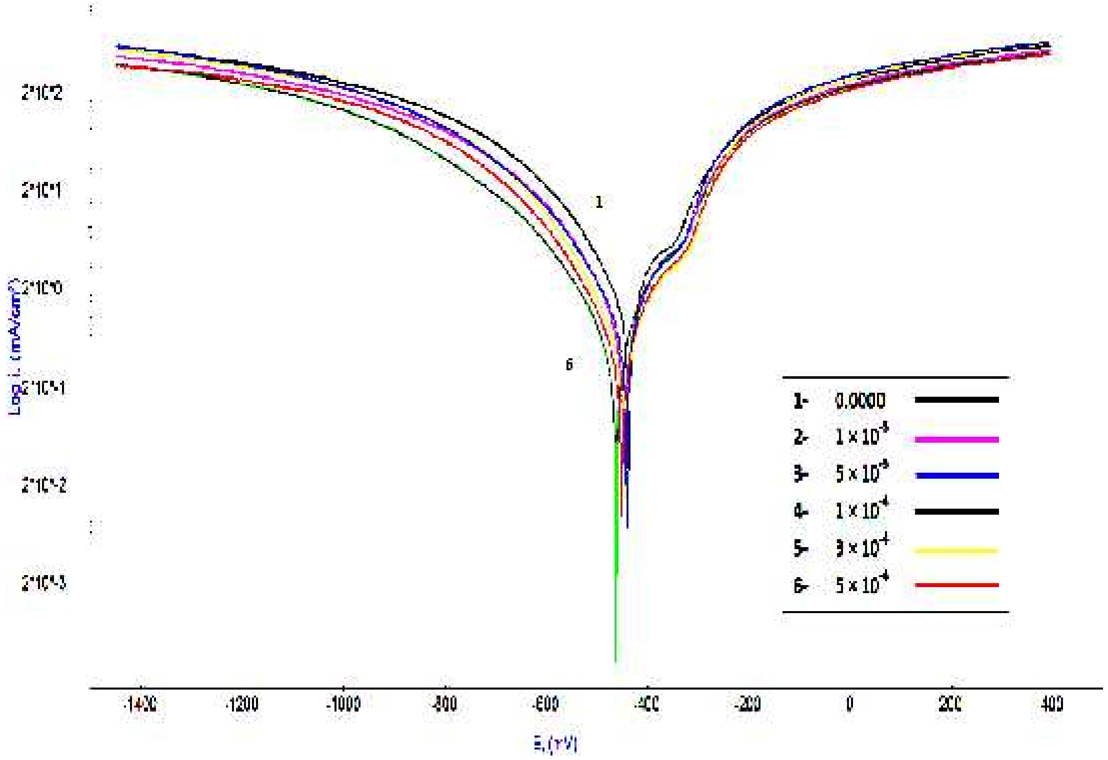


Fig (12): Potentiodynamic polarization parameters of carbon steel corrosion in 1 M HCl solution without and with different concentrations of cationic surfactant (ACS3.1) at 30 °C.

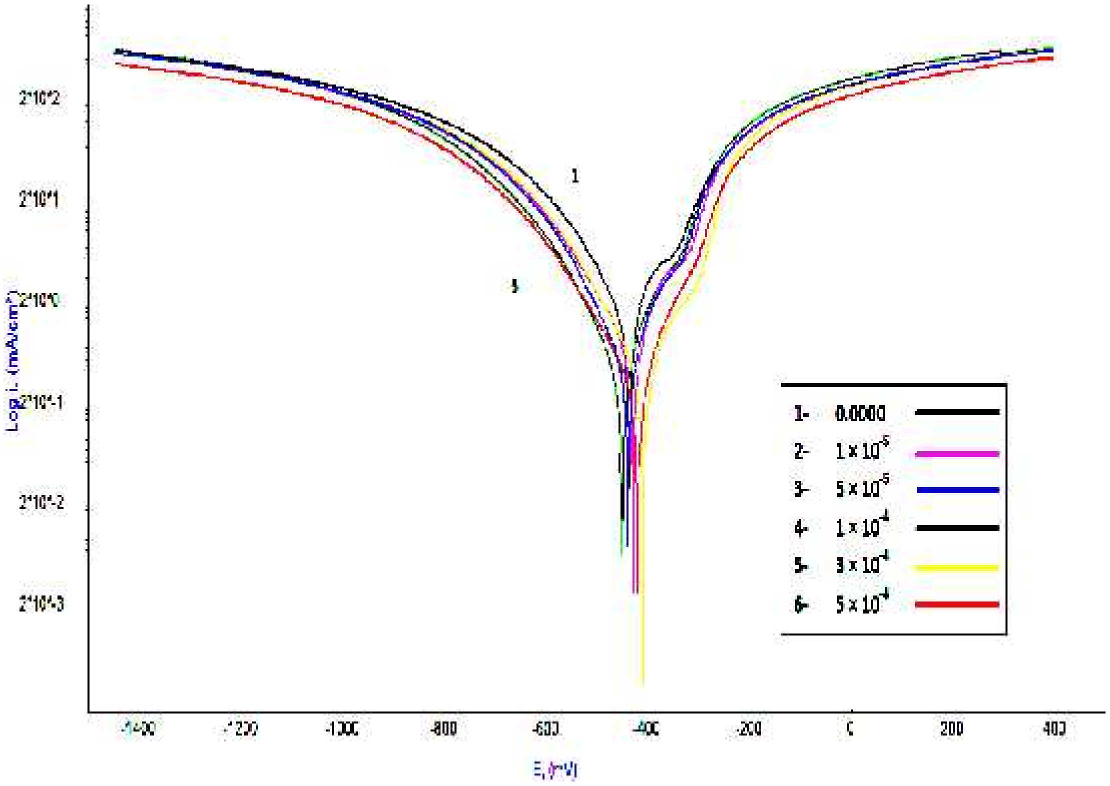


Fig (13): Potentiodynamic polarization parameters of carbon steel corrosion in 1 M HCl solution without and with different concentrations of cationic surfactant (ACS3.2) at 30 °C.

Table (6): Potentiodynamic polarization parameters of carbon steel corrosion in 1 M HCl solution without and with different concentrations of cationic surfactants (ACS3.1 and ACS3.2) at 30 °C.

Inhibitor	**Conc. of inhibitor (M)**	**$-E_{corr}$ (mV)**	**β_a (mV decade^{-1})**	**$-\beta_c$ (mV decade^{-1})**	**i_{corr} (mA cm^{-2})**	**η_p (%)**
ACS3.1	0.0000	430.89	144.69	152.02	1.0748	----------
	1×10^{-5}	444.44	134.08	133.03	0.5961	44.538
	5×10^{-5}	447.15	132.22	130.83	0.5767	46.343
	1×10^{-4}	474.25	132.12	127.63	0.3754	65.072
	3×10^{-4}	441.73	119.41	120.56	0.3771	64.914
	5×10^{-4}	457.99	123.50	111.76	0.3157	70.627
ACS3.2	0.0000	430.89	144.69	152.02	1.0748	----------
	1×10^{-5}	422.76	76.50	127.79	0.3723	65.360
	5×10^{-5}	436.31	91.22	118.78	0.3275	69.529
	1×10^{-4}	457.99	99.83	103.32	0.2609	75.725
	3×10^{-4}	387.53	48.93	126.40	0.1872	82.582
	5×10^{-4}	409.21	61.36	124.30	0.1346	87.476

4. Conclusions

1) The newly surfactants namely; N-(3-tetradecanamidopropyl)-N,N-dimethylbutan-ammonium bromide and N-(3-hexadecanamidopropyl)-N,N-dimethylbutan-ammonium bromide referred as (ACS3.1 and ACS3.2), respectively were synthesized and their chemical structures confirmed using FT-IR and ^{1}H-NMR spectra.
2) All measurements show that cationic surfactants (ACS3.1 and ACS3.2) have excellent inhibition properties for the corrosion of carbon steel in 1 M HCl solution and the inhibition efficiency is increased with increasing the concentration, but decreased with increasing the temperature.
3) The cationic surfactants (ACS3.1 and ACS3.2) are adsorptive inhibitors and their adsorption process obeys the Temkin's adsorption isotherm, and is spontaneous.
4) The cathodic and anodic Tafel slopes reveal that cationic surfactants (ACS3.1 and ACS3.2) are mixed type inhibitors.

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