1-X-4-[4'-(–OCH₃)-Styryl] pyridinium iodides, potent inhibitors for stainless steel corrosion in 2 M HCl acid solutions

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Abstract

Different techniques such as hydrogen evolution, weight loss, electrochemical impedance spectroscopy, and potentiodynamic polarization measurement technique were used to determine the corrosion inhibition potential of 1-X-4-[4'-(–OCH₃)-styryl] pyridinium iodides (X = CH₃, C₂H₅, and C₃H₇) for stainless steel in 2 M HCl acid solution. The results from hydrogen evolution and weight loss techniques revealed that the inhibitors exhibited high inhibitory potential against corrosion of stainless steel in 2 M HCl, with inhibition efficiency increasing with inhibitor concentration. The anticorrosion performance of the compounds follows the order: III-C₃H₇ > II-C₂H₅ > I-CH₃. Potentiodynamic polarization results revealed that the compounds played the role of mixed-type inhibitors, and the inhibitors molecules adsorbed on the surface of stainless steel according to the Langmuir adsorption isotherm. Furthermore, the inhibitors showed good performance at all temperatures (30–60°C) studied and maintained protective ability at maximum temperature. On the basis of thermodynamic parameters, comprehensive adsorption (physisorption and chemisorption) for the studied inhibitors on stainless steel surface was suggested. SEM and EDX analysis confirmed the evidence of the formation of the adsorbed layer of inhibitor on the metal surface. A quantum chemical approach was adopted to predict the correlation between corrosion inhibition performance and molecular structure electronically. The data showed that the inhibition efficiency of the studied inhibitors increases with increasing immersion time (5, 30, 60 and 90 min) in the tested solution and this result implied that the studied inhibitors have a long-term effect as potent inhibitors.

Keywords: *stainless steel, corrosion, inhibitor, hydrochloric acid, temperature, quantum chemical calculations.*

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1. Introduction

Although stainless steel is a metallic alloy of iron and chromium, the surface oxide is composed mainly of chromium oxides deposited on the surface of iron in a thin, transparent and durable layered manner. Hence, the strength, passive film behavior, and corrosion resistance of stainless steel are dependent on the chromium content within in the alloys. Over one-third of produced stainless steels products are used majorly in various applications in chemistry, power and energy, architecture, construction, automotive, transportation,

medicine and pharmacy, and cosmetics food processing, *etc.* [1]. This is because stainless steel possesses excellent passive film character, which enhances its corrosion resistant effect in different corrosive aqueous solutions during service [2, 3]. Stainless steel is considered a better option in industrial applications despite its high cost where excellent mechanical properties and corrosion resistant character is a topmost priority. Most times, stainless steel comes in contact with mineral acids and bases during its service life especially, in the oil and drilling industries, and a typical example of the mineral acid is hydrochloric acid. It is a strong inorganic acid that has several applications in the oil and gas sector, including acid washing or acid cleaning, acid pickling, descaling processes, as well as for drilling operations and oil well acidizing. Hence, these operations are usually accompanied by a significant loss of metal because the acid is an essential source of aggressive chloride ions which causes destruction of any metal that comes in contact with it [4].

Although, chloride ions are the primary factor of pitting attack on different metals exposed to hydrochloric acid solutions, it is not possible to determine a single critical value of chloride for metals and alloys [5]. Pitting corrosion could be described as a form of localized corrosion, that produces attacks in the form of spots or pits. Pitting corrosion occurs by breaking down first the passive layer, followed by localized corrosion resulting in pits destroying the microscopic heterogeneities in the metal surface. As a result, the metal surface is exposed to corrosion, where a successive electrochemical reaction associated with anodic and cathodic processes occurs and heat evolution predominant in strong acid solutions [6]. Numerous studies conducted on the corrosion of stainless steel in various acids and aqueous solutions containing chloride ions indicate that they cause pitting on the metal surface [7]. However, the extent to which corrosion of chloride ions in aqueous solutions occurs can be affected by the presence of different chemical agents that may speed up or inhibit the corrosion reaction. Corrosion inhibitors are added to the pickling solution to reduce the metal dissolution and the consumption of acid. As known, hydrochloric acid is the most important pickling acid. Despite the abundance of compounds used as inhibitors among these agents, chemical inhibitors remain a better option in protecting metal surfaces from corrosion, but there exist a limited number of effective inhibitors against pitting corrosion [8, 9]. Organic inhibitors containing heteroatoms, such as N, O, S and P, have demonstrated practically and theoretically to act as efficiently corrosion inhibitors in a wide range of acidic solutions. The efficiency of these inhibitors can be ascribed to their high polarizability and lower electronegativity; so that these atoms and the functional groups can cover large metallic surface areas and easily electrons transfer to the empty orbitals of atoms. In addition, nitrogen-containing organic inhibitors is good anticorrosion materials for metals in hydrochloric acid, while compounds having sulfur atoms act as good inhibitors in sulfuric acid. Compounds holding nitrogen and sulfur behave as great corrosion inhibitors for both media [10–12]. The phenomenon of inhibitory performance of organic inhibitors is through adsorption and may vary with several factors, such as chemical structure of inhibitor, nature of metal surface, and properties of the aggressive medium, *etc.* [13]. Some N-containing organic compounds reported as good corrosion inhibitors for stainless steel in HCl solutions

are: pyrimidine derivatives [14], N,N'-diquaternized 4,4'-dipyridinium salts [15], triazole derivative [16], and quinazoline derivatives [17].

The frequent use of stainless steel in different environments under different conditions requires increased research interest, considering their performance, usability, and viability in service. Hence, this research focuses on the study of 1-X-4-[4'-(–OCH₃)-styryl]pyridinium iodides (X = CH₃, C₂H₅ and C₃H₇) which is N-containing organic compounds as potent inhibitors for stainless steel corrosion in 2 M HCl acid solution using the techniques earlier mentioned. The metal surface examination without and with a certain concentration of inhibitors was studied using scanning electron microscope (SEM). The effect of temperature on the corrosion rate of stainless steel without and with a certain concentration of inhibitors was also investigated, and some thermodynamic parameters for activation process computed and discussed. According to the literature survey, no work has been done on these compounds as corrosion inhibitors except on 1-CH₃-4-[4'-(–OCH₃)-styryl]pyridinium iodide done in our previous study [18].

2. Experimental

2.1. Sample preparation

Corrosion tests by different methods were achieved using rods made from stainless steel type 316 SS with the chemical composition: 17% (Cr), 12% (Ni), 2% (Mn), 1% (Si), 0.08% (C), 0.03% (S), 0.045% (P), 2.5% (Mo), and the remainder was Fe. Stainless steel rods were cut to dimensions of 5.0 cm and 1.0 cm in length and diameter with the aid of a mechanical press cutter. The exposed surfaces were polished mechanically using different grades of emery papers 60, 120, 220, 400, 600, 800, and 1200, and washed thoroughly with deionized water, degreased with ethanol and dried using air flow at room temperature before each experiment. Using hydrochloric acid (37% w/v) of analytical grade and deionized water, the aggressive solution (2 M HCl) used was prepared. The performance of the studied inhibitors was investigated over the concentrations ranging from 1.0×10^{-6} M to 1.0×10^{-4} M and freshly prepared by adding a suitable amount of the inhibitor to the aggressive solution. 50 mL of test solution was used for each hydrogen gas evolution and weight loss experiment and 100 mL for the electrochemical experiment.

Table 1 shows the compounds used in this study (I–III). All compounds were prepared in the same manner as mentioned previously in the literature [19], and chemical analysis, melting point determination, and nuclear magnetic resonance (NMR) used to examine the purity of the studied compounds.

Table 1. Names, structures and abbreviations of the studied inhibitors.

Inhibitor	Structure	Abbreviation
1-Methyl-4-[4'-(–OCH ₃)-styryl] pyridinium iodide		I-CH ₃
1-Ethyl-4-[4'-(–OCH ₃)-styryl] pyridinium iodide		II-C ₂ H ₅
1-Propyl-4-[4'-(–OCH ₃)-styryl] pyridinium iodide		III-C ₃ H ₇

2.2. Experimental methods

The experimental methods employed in this work include hydrogen evolution technique, weight loss technique, electrochemical measurement technique, surface characterization technique, and computational technique.

2.2.1. Hydrogen evolution (HE) and weight loss (WL) measurement technique

The procedure adopted for the hydrogen evolution (HE) measurement technique has been reported elsewhere [18]. In this case, 50 mL of the prepared test solutions (blank and inhibited solution, respectively) were used. The prepared stainless steel sample was weighed and carefully immersed into each of the test solutions and the lid of the cell apparatus tightly covered to ensure that no hydrogen gas escape during the experiment. The hydrogen gas was collected by gradual displacement of water and its volume recorded at different time intervals. Each experiment was performed within a 90-minute time period. The correlation between the volume of hydrogen per unit area (mL cm^{–2}) of the specimen and time (min) plotted gave straight lines. The slopes of the straight lines represent the rate of H₂ evolution without and with different concentrations of the studied inhibitors ($CR_{HE} = dV/dt$) [20].

Using the weight loss (WL) technique, the stainless steel sample taken out from the tested solution at the end of each experiment and then corrosion products scraped off the stainless steel surface using a bristle brush, and washed severally with deionized water was followed by ethanol and dried with air flow at room temperature, and finally reweighed accurately. Using the difference between the initial and the final weight of the studied sample (ΔW) as well as the end time (t_{∞}), the rate of weight loss (CR_{WL}) was calculated applying the equation [20]:

$$CR_{WL} = \frac{\Delta W}{At_{\infty}} \quad (1)$$

Where A is the surface area of the stainless steel specimen.

The inhibition efficiency from hydrogen gas evolution and weight loss measurement techniques was calculated using the equation:

$$IE\% = \frac{CR^0 - CR}{CR^0} \times 100 \quad (2)$$

Where CR^0 and CR are the corrosion rates without and with a certain concentration of the studied inhibitors, respectively.

2.2.2. Electrochemical measurement technique

Electrochemical measurement is one effective analytical technique for corrosion investigation. Electrochemical measurements performed were potentiodynamic polarization (PDP), and electrochemical impedance spectroscopy, (EIS) using a potentiostat/galvanostat (ACM Gill AC instrument model 1649) and a computer. The electrolytic cell consists of multi-necked 250 mL capacity round-bottomed Pyrex glass cell where electrodes were inserted.

The working electrode (stainless steel specimen) was embedded in a Teflon holder using epoxy resin and exposed surface of cross-sectional area of 0.539 cm^2 faced downwards to contact the solution in each experiment. With a copper wire, an electrochemical contact was affected at the sealed end part of the working electrode, and a platinum wire utilized as an auxiliary electrode sealed in a ground joint glass to prevent the contamination of the tested solution with the electrode reaction products. $\text{Ag}/\text{AgCl}_{(s)}/\text{KCl}_{\text{saturated(aq)}}$ used as the reference electrode coupled with a Luggin capillary whose tip sited between the working electrode and the auxiliary electrode minimized the ohmic contribution.

EIS experiments were achieved at the end of 5 min of electrode immersion and measurements made at rest potential over a frequency range of 30 kHz to 0.1 Hz, with a signal amplitude perturbation of 10 mV. After running each EIS, the instrument turns on automatically to record the PDP curves with the scan rate of 1 mVs^{-1} from -700 mV to -200 mV versus $\text{Ag}/\text{AgCl}/\text{KCl}_{\text{sat}}$. All electrochemical measurements were conducted in open air stagnant solutions at 30°C and the analysis of EIS data done using ZSimDemo 3.20 software. PDP curves were analyzed using analysis software of ACM Gill 1649 and the linear Tafel segments of the anodic and cathodic curves extrapolated to corrosion potential (E_{corr}) to obtain the corrosion current density (i_{corr}).

The percentage inhibition efficiency obtained from polarization resistance and current density values using Equations 3 and 4 are:

$$IE_R \% = \left(1 - \frac{R_p^0}{R_p} \right) \times 100 \quad (3)$$

Where R_p^0 and R_p are the polarization resistance of stainless steel without and with a certain concentration of the studied inhibitors, respectively.

$$IE_i \% = \left(1 - \frac{i_{\text{corr}}}{i_{\text{corr}}^0} \right) \times 100 \quad (4)$$

Where i_{corr}^0 and i_{corr} are the corrosion current densities without and with a certain concentration of the studied inhibitors, respectively.

All measurements were accomplished at 30°C except for the temperature studies and in each case, duplicate experiments performed to confirm the results and the mean values taken and reported.

2.2.3. Surface characterization

The surface morphology of stainless steel before and after immersion for 90 min in 2 M HCl solution without and with certain concentration of the studied inhibitors at 30°C was tested using scanning electron microscope (SEM) coupled with energy dispersive X-ray analysis (EDX).

2.2.4. Computational calculations

The correlation between the molecular structure and inhibition efficiency was determined using quantum chemical calculations, while the Chem3D program was first used to draw the molecular structure of the inhibitors and the semiempirical-PM3 to minimize energy for all molecular inhibitors. The molecular structure of the inhibitors was first optimized with PM3 to speed up the calculations, and the rustles obtained from PM3 calculation fully re-optimized, using density functional theory (DFT) in Gaussain09. The molecular structure geometrically optimized using the functional hybrid B3LYP with electron basis set 6-31*G(d,p) for all atoms. The quantum chemical parameters obtained were total energy, E_{HOMO} , E_{LUMO} , energy gap (ΔE), dipole moment (μ), and total energy.

3. Results and discussion

3.1. Effect of inhibitor concentration on corrosion rates and inhibition efficiencies

3.1.1. Hydrogen gas evolution (HE) and weight loss (WL)

The corrosion of stainless steel in HCl solutions is an electrochemical process, consisting of two reactions, anodic and cathodic reactions. Consequently, the corrosion rate of stainless steel can be easily determined following both the weight loss of the metal (anodic reaction) and the volume of hydrogen gas evolved (cathodic reaction) chemically during a certain period. Figure 1 shows a plot of hydrogen evolution-time curves for stainless steel corrosion in 2 M HCl solution without and with different concentrations of the studied inhibitors at 30°C. It is clearly observed in Figure 1 that the relationship between hydrogen gas evolved

and time for stainless steel corrosion in 2 M HCl without and with different concentrations of the studied inhibitors is linear. Thus, volume of hydrogen gas evolved increases as the time increases. This good linearity obtained indicates the destruction of the insoluble or passive layer (consisting mainly of stable chromium and nickel compounds) on the metal surface during its corrosion in 2 M HCl. When the stainless steel is corroded, the corrosion process progresses by destroying the passivity layer covering the metal surface. This may occur in very small areas causing small pits to appear on the surface. Once the layer of passivity has been lost in a particular area on the surface, this area will act as an anode for the remaining passive surface. In addition, the subsequent development of these active anodic regions into pits depends on the flow of electrolytic current between the small anodic region and the large non-attacking cathodic region outside the pits. Hence, the observation of spread pits on the corroding stainless steel surface experimentally shows that the corrosion of stainless steel in HCl solutions proceeds mainly by pitting corrosion. In the presence of the studied inhibitors, all curves fell below the curves of free acid and showed an induction period required for the onset of metal dissolution and hence hydrogen evolution. The duration of the induction period increases with increasing inhibitor concentration and gives its maximum (60 min) in the presence of 1.0×10^{-5} M inhibitor (III- C_3H_7). This behavior indicates that the studied inhibitors are strongly inhibiting the corrosion of the studied specimen, while the degree of inhibition depends on the concentration of the inhibitors.

Table 2 shows the values of percentage inhibition efficiency obtained from hydrogen gas evolution ($IE_{HE}\%$) and weight loss ($IE_{WL}\%$), respectively with the addition of different concentrations of the studied inhibitors in 2 M HCl solutions, while Figure 2 shows the corrosion rates as a function of concentration. Inspection of Table 2 and Figure 2, it was observed that by increasing the concentration of the studied inhibitors the corrosion rates (CR_{HE} and CR_{WL}) decreased, followed by an increase in $IE\%$ values. Hence, the addition of the studied inhibitors hindered both the anodic (metal dissolution) and the cathodic (hydrogen evolution) reactions of stainless steel corrosion in the tested solution. Similar values of inhibition efficiency were observed at high concentration of the studied inhibitors, indicating an almost equal surface coverage of these concentrations. There was also a good correlation between the values of the inhibition activity derived from the two different measurement methods (weight loss and hydrogen gas evolution).

Riggs and Hurd [21] suggested that the corrosion rate can be expressed by a sum of two rates, one for the uninhibited reaction (k_1) and the other for a completely covered surface (k_2) according to the equation:

$$CR_{WL} = k_1(1-\theta) + k_2\theta \quad (5)$$

Where θ is the fraction of the surface covered by adsorbed inhibitor ($\theta = \frac{IE_{WL}\%}{100}$). At first, when there is not enough reaction intermediate $Fe(Inh)_{ads}$ to cover the metal surface, due to either the low concentration of the inhibitor molecules or slow rate of the adsorption,

dissolution takes place on the free surface. With high inhibitor concentration, almost full over layer, which reduces chemical attacks on the metal surfaces formed.

Figure 1. Volume of H_2 -time curves for stainless steel corrosion in 2 M HCl without and with different concentrations of the studied inhibitors.

Table 2. Inhibition efficiencies for different concentrations of the studied inhibitors in 2 M HCl from HE and WL measurements.

Inhibitor concentration (C_{inh} , M)	IE%					
	I-CH ₃		II-C ₂ H ₅		III-C ₃ H ₇	
	HE	WL	HE	WL	HE	WL
1.0×10^{-6}	14.73	12.41	18.90	17.24	25.30	24.14
2.5×10^{-6}	27.49	26.33	36.06	34.48	43.65	42.63
5.0×10^{-6}	43.34	43.89	49.81	49.22	56.93	56.11
7.5×10^{-6}	57.89	57.99	69.95	68.31	81.07	77.05
8.5×10^{-6}	85.58	84.90	87.62	87.99	88.67	90.66
1.0×10^{-5}	95.73	96.68	98.13	98.40	98.23	98.90
5.0×10^{-5}	–	98.94	–	99.65	–	99.71
1.0×10^{-4}	–	99.64	–	99.79	–	99.87

The plot of ratio between corrosion rate and surface coverage (CR_{WL}/θ) against the ratio $(1-\theta)/\theta$ as shown in Figure 3 gives a straight line from which the values of k_1 and k_2 are determined from the slope and intercept, respectively. According to the results obtained, all the studied inhibitors tested lead to the same line with $k_1=31.898 \times 10^{-5} \text{ g cm}^{-2} \text{ min}^{-1}$ and $k_2=6.852 \times 10^{-9} \text{ g cm}^{-2} \text{ min}^{-1}$. These results are in line with the results obtained experimentally.

For one and the same concentration, it was found that the inhibition efficiency of the studied inhibitors follows the order:

Figure 2. Variation of corrosion rates (CR_{HE} and CR_{WL}) vs. concentration of the inhibitors studied.

Figure 3. The ratio between corrosion rate (CR_{WL}) and surface coverage (θ) against the ratio $(1-\theta)/\theta$ for the studied inhibitors.

3.1.2. Electrochemical impedance spectroscopy (EIS)

EIS measurements were carried out to assess the effect of the studied inhibitors on the corrosion of stainless steel in 2 M HCl in this study. This method gives an overview of what occurs during interface between the metal electrode and solution in the presence of these inhibitors [22]. Nyquist plots in Figure 4 shows a summary of the EIS of stainless steel in 2 M HCl without and with various concentrations of the studied inhibitors. The Nyquist plots clearly show one capacitive and one inductive loop. The capacitive loop appeared at high to medium frequencies and represents the phenomenon associated with the double electric layer. It arises from the time constant of the electric double layer and charges transfer resistance. This capacitive loop corresponds to the charge transfer reaction, which depends either on the direct electron transfer at the metal surface or on the electron conduction through the surface film. The appearance of inductive loop in low frequency could be attributed to slow reaction, such as adsorbed reaction intermediates $(FeCl)_{ads}$ in the absence of the inhibitor and/or $(FeCl-Inh^+)_{ads}$ in the presence of the inhibitor during the metal dissolution process and the surface coverage by hydrogen, considering the small amplitude of the excitation voltage [23, 24]. This adsorption behavior is characteristic for Fe in acid solutions [25, 26]. The inductive loop may also be attributed to the re-dissolution of the passivated surface at low frequencies [27] and still appears, even in the presence of the inhibitor. These findings may indicate that the electrode still dissolve by the direct charge-transfer at the inhibitor-adsorbed steel surface. Inductive behavior was also observed for the pitted active state and attributed to the surface area modulation or salt film property modulation [28].

The impedance spectra obtained for stainless steel in 2 M HCl without and with the studied inhibitors showed depressed semicircles with the center under the real axis, such behavior is characteristic for solid electrodes and is often referred to as frequency dispersion

and attributed to different physical phenomena such as surface heterogeneity which results from surface roughness, impurities, dislocations, grain boundaries, fractality, distribution of the active sites, adsorption of inhibitors, and formation of porous layers [29]. It is well-known that the corrosion of iron in the acid media, predominantly HCl, increases the roughness of the electrode surface, and therefore more depressed semicircle results [30]. A useful way to represent distributed processes such as corrosion of a rough and inhomogeneous electrode is with an element that follows its distribution. The constant phase element (*CPE*) meets that condition. The impedance of *CPE* is given in the form [31]:

$$Z_{\text{CPE}} = \frac{1}{A(i\omega)^n} \quad (6)$$

Where the coefficient *A* is a combination of properties related to both the surface and the electroactive species. In this context, *n* can be used as a measure of the surface inhomogeneity, the exponent *n* has values between -1 and 1 . A value of -1 is characteristic of an inductance, while a value of 1 corresponds to a capacitor, and a value of 0.5 can be assigned to diffusion phenomena. Often, it should be noted that the change of concentrations of the studied inhibitors does not alter the profile of the curves of impedance, which suggests a similar mechanism for corrosion of stainless steel in the uninhibited and inhibited solutions.

Figure 4. Nyquist plot for stainless steel in 2 M HCl without and with different concentration of the studied inhibitors.

It is important to develop the suitable models for the impedance which can then be used to fit the experimental data and extract the parameters used to distinguish the corrosion process. Figure 5 shows the equivalent circuit model of five elements for the EIS systems. A similar circuit was suggested for the corrosion behavior of the steel in sulfuric acid without and with inhibitors [32]. In the circuit model, R_s represents the solution resistance between the working and reference electrodes, CPE is a power law-dependent capacity term known as the constant phase element, used instead of the capacitor, while R_{ct} is the interfacial charge-transfer resistance which indicating the presence of a non-ideal frequency response, L is the inductance, and R_L is the inductive resistance. In this circuit, CPE is in parallel series to the parallel resistors R_{ct} and R_L , and the latter in series with the inductor L . When an inductive loop is present, the polarization resistance R_p can be calculated from the equation [33]:

$$R_p = \frac{R_{ct} \times R_L}{R_{ct} + R_L} \quad (7)$$

Figure 5. Equivalent circuit diagram used to analyze impedance experimental data.

Table 3 shows the main parameters of impedance spectra such as R_s , R_p , CPE/C_{dl} , and n for uninhibited and inhibited systems. The inhibition efficiency ($IE_R\%$) was also calculated using Equation 3 and recorded in Table 3. Observation from Table 3 include:

- It was found that the polarization resistance R_p values increased and CPE/C_{dl} decreased with increasing concentration of the studied inhibitors (Figure 6), which led to an increase in $IE_R\%$.

Figure 6. Variation of R_p and C_{dl} with the concentrations of the studied inhibitors.

- The increase in R_p was attributed to the formation of a protective film on the metal/solution interface, the decrease in CPE/C_{dl} can be interpreted as a decrease in local dielectric constant and/or an increase in the thickness of the electrochemical double layer, suggesting that the molecules inhibitors acted by adsorption on the metal surface [34]. The thickness of the protective layer, δ , was related to CPE/C_{dl} by the equation [35]:

$$\delta = \frac{\varepsilon \varepsilon_0 A}{C_{dl}} \quad (8)$$

Where ε is the dielectric constant of the medium, ε_0 is the vacuum permittivity and A is the effective surface area of the electrode.

Table 3. Electrochemical impedance parameters for stainless steel corrosion in 2 M HCl solutions without and with different concentrations of the studied inhibitors.

Inhibitor	C_{inh} (M)	EIS Parameters				
		R_s ($\Omega\text{ cm}^2$)	R_p ($\Omega\text{ cm}^2$)	CPE/C_{dl} ($\mu\text{F cm}^{-2}$)	n	IE_R %
I-CH ₃	0.0	0.422	7.56	453.60	0.82	–
	1.0×10^{-6}	0.490	10.49	341.80	0.83	27.39
	5.0×10^{-6}	0.460	12.25	291.90	0.87	38.29
	1.0×10^{-5}	0.491	28.40	134.75	0.85	73.38
	5.0×10^{-5}	0.419	117.30	52.50	0.87	93.55
	1.0×10^{-4}	0.394	157.22	35.94	0.90	95.19
II-C ₂ H ₅	0.0	0.422	7.56	453.60	0.82	–
	1.0×10^{-6}	0.573	11.76	307.62	0.84	35.71
	5.0×10^{-6}	0.402	23.85	172.40	0.85	68.30
	1.0×10^{-5}	0.376	35.51	114.05	0.89	78.71
	5.0×10^{-5}	0.773	131.11	45.21	0.86	94.23
	1.0×10^{-4}	0.241	224.10	29.24	0.90	96.63
III-C ₃ H ₇	0.0	0.422	7.56	453.60	0.82	–
	1.0×10^{-6}	0.461	15.11	254.62	0.87	49.67
	5.0×10^{-6}	0.692	25.95	150.42	0.85	70.87
	1.0×10^{-5}	0.760	78.33	67.05	0.84	90.35
	5.0×10^{-5}	0.466	169.20	33.62	0.86	95.53
	1.0×10^{-4}	0.321	322.4	18.30	0.92	97.66

- The addition of the studied inhibitors resulted in lower CPE/C_{dl} values which could be a consequence of the gradual replacement of water molecules by the adsorption of molecule inhibitors at the metal/solution interface [36]. The values CPE/C_{dl} were smaller in the presence of the inhibitors than in their absence, as a result of the effective adsorption of the studied inhibitors on stainless steel surface from 2 M HCl solution. In addition, the increase of n values (Table 3) with concentration of the studied inhibitors could be explained by a decrease in the surface heterogeneity, due to the adsorption of the studied inhibitors on the most active adsorption sites [29].
- A maximum $IE_R\%$ of about 97.66% was recorded for III-C₃H₇ at the concentration of 1.0×10^{-4} M confirming previous findings that III-C₃H₇ was a better inhibitor compared to II-C₂H₅ and I-CH₃ in HE and WL measurements.

3.1.3. Potentiodynamic polarization (PDP)

Figure 7 shows the cathodic and anodic potentiodynamic polarization curves for stainless steel in 2 M HCl without and with different concentrations of the studied inhibitors. An increase in the amount of the studied inhibitors resulted in a decrease in the corrosion rate, that is, a shift in both the anodic and cathodic curves to lower values of current densities. Figure 7 shows that both the anodic metal dissolution and cathodic hydrogen evolution partial reactions were inhibited after the addition of the studied inhibitors to the aggressive solution. However, the inhibited systems were shifted towards anodic potentials, emphasizing that the studied inhibitors act predominately as anodic inhibitors. The effect of the studied inhibitors on the anodic polarization of stainless steel in 2 M HCl is electrode potential-dependent. It was found that the presence of the studied inhibitors with different concentrations shows little effect on the anodic reaction when the potential became more positive than desorption potential or -300 mV (Figure 7). This is probably due to the increase in surface area as stainless steel dissolves and molecules inhibitors desorbed. The behavior of the studied inhibitors at potentials higher than -300 mV result from a significant dissolution of the stainless steel surface, leading to desorption of the adsorbed molecules inhibitors from the electrode surface. In this situation, the desorption rate of the studied inhibitors is higher than its adsorption rate [37].

The shapes of the polarization plots, in all cases, for inhibitor–HCl containing solutions are not prominently different from those of inhibitor-free HCl solutions. The presence of these inhibitors decreases the corrosion rate but does not change other features of the behavior. This means that the inhibitors do not modify the electrochemical reactions responsible for corrosion (hydrogen evolution and metal dissolution reactions).

The electrochemical corrosion parameters, that is, corrosion potential (E_{corr}), anodic and cathodic Tafel slopes (β_a , β_c) and corrosion current density (i_{corr}) for stainless steel corrosion in 2 M HCl without and with different concentrations of the studied inhibitors are obtained by extrapolation of the Tafel lines. The inhibition efficiency ($IE_i\%$) was also calculated using Equation 4.

As stated by the electrochemical theory, polarization resistance (R_p) is inversely proportional to the corrosion current density (i_{corr}) and can be evaluated from Stern-Geary Equation [38]:

$$R_p = \frac{B'}{i_{\text{corr}}} \quad (9)$$

$$B' = \beta_a \beta_c / (2.303(\beta_a + \beta_c))$$

Figure 7. Potentiodynamic polarization curves for stainless steel corrosion in 2 M HCl without and with different concentrations of the studied inhibitors.

Table 4. Potentiodynamic polarization parameters for stainless steel corrosion in 2 M HCl solutions without and with different concentrations of the studied inhibitors.

Inhibitor	C_{inh} (M)	PDP Parameters					
		$-E_{corr}$ (mV)	i_{corr} (mA cm ⁻²)	β_a (mV dec ⁻¹)	$-\beta_c$ (mV dec ⁻¹)	R_p (Ω cm ²)	$IE_i\%$
I-CH ₃	0.0	445	16.60	65.46	100.42	1.04	–
	1.0×10^{-6}	446	11.94	89.61	64.22	1.36	28.07
	5.0×10^{-6}	449	9.72	91.46	61.92	1.65	41.45
	1.0×10^{-5}	435	5.71	63.23	70.47	2.54	65.60
	5.0×10^{-5}	400	3.55	54.14	60.43	3.50	78.61
	1.0×10^{-4}	403	1.67	51.93	65.00	7.52	89.94
II-C ₂ H ₅	0.0	445	16.60	65.46	100.42	1.04	–
	1.0×10^{-6}	450	10.39	68.57	63.64	1.38	37.41
	5.0×10^{-6}	453	5.94	76.80	65.40	2.59	64.22
	1.0×10^{-5}	445	4.76	66.80	76.32	3.25	71.33
	5.0×10^{-5}	417	2.91	59.56	63.81	4.60	82.47
	1.0×10^{-4}	414	1.42	63.99	67.20	10.04	91.45
III-C ₃ H ₇	0.0	445	16.60	65.46	100.42	1.04	–
	1.0×10^{-6}	456	8.18	73.98	67.23	1.87	50.72
	5.0×10^{-6}	453	5.11	64.08	76.95	2.97	69.22
	1.0×10^{-5}	445	3.29	65.86	72.32	4.56	80.18
	5.0×10^{-5}	434	1.71	72.13	68.31	8.92	89.70
	1.0×10^{-4}	426	1.14	68.66	57.73	11.96	93.13

Table 4 shows the electrochemical corrosion parameters (E_{corr} , i_{corr} , β_a , β_c , R_p , and $IE_i\%$) obtained from PDP measurement for stainless steel corrosion in 2 M HCl without and with different concentrations of the studied inhibitors. Deductions made from the data in Table 4 shows that:

- The cathodic and anodic Tafel slopes (β_a and β_c) remain almost unchanged for the uninhibited and inhibited systems, demonstrating that the studied inhibitors are first adsorbed onto the stainless steel surface and hence impedes by simply blocking the reaction sites of stainless steel surface without affecting the anodic and cathodic reaction mechanism [39].
- The values of E_{corr} were shifted slightly to the anodic direction with the addition of an increasing amount of the studied inhibitors. According to Ferreira *et al.*, [40], if the

displacement in corrosion potential is more than 85 mV with respect to the corrosion potential of the free acid solution, the inhibitor can be considered a cathodic or anodic type. In the present study, maximum displacement was 42, 31, and 19 mV for I-CH₃, II-C₂H₅ and III-C₃H₇, respectively with respect to the corrosion potential of the uninhibited sample indicating that the studied inhibitors are mixed-type inhibitors.

- The values of i_{corr} decreased, while the values of R_p increased with an increase in the inhibitor concentration and an increase in the corresponding $IE_i\%$ value (Figure 8).
- According to i_{corr} , R_p and $IE_i\%$ data, the inhibitive properties of the studied inhibitors follows the order:

This order is inline with that obtained from EIS, HE and WL measurements.

Figure 8. Variation of inhibition efficiency and current densities for stainless steel corrosion in 2 M HCl with different concentrations of the studied inhibitors.

Figure 9 shows the inhibition efficiencies obtained with HE, WL and electrochemical techniques *versus* the logarithm of inhibitor concentration for I-CH₃ (the other two inhibitors are not shown here). The different techniques indicated similar behavior. As the inhibitor concentration increased the corrosion rate decreased and the inhibition efficiency increased. Some differences were found in the results obtained from both HE, WL and electrochemical measurements. This observation was also reported by some authors [35, 41]. The differences

emanate from the fact the HE and WL methods produce average corrosion rates, while the electrochemical techniques provide instantaneous corrosion rates. Moreover, the observed lower values of $IE\%$ obtained from PDP as compared with those obtained from the other techniques can be explained on the basis of “*electromechanical de-sorption model*” in which the process of anodically removing the iron atoms (at which the adsorbed particles) are based on [42–44].

Figure 9. Comparison of inhibition efficiencies obtained from different techniques.

3.2. Adsorption isotherm

Assumptions made showed that organic molecule inhibitors establish their inhibition action through the adsorption of the inhibitors to the metal surface. The adsorption processes of inhibitors are influenced by the chemical structures of organic compounds, nature and surface charge of metal, the distribution of the charge in molecule, and the type of aggressive solution. The values of surface coverage ($\theta = \frac{IE\%}{100}$) for different concentrations of the studied inhibitors have been used to explain the best isotherm to determine the adsorption process. In fact, the solvent water molecules could also be adsorb at metal/solution interface. Hence, the adsorption of inhibitor molecules on the metal surface is regarded as a quasi-substitution process between the organic compound in the aqueous phase ($Org_{(sol)}$), and the H_2O molecules adsorbed on the stainless steel surface ($H_2O_{(ads)}$) [45].

Where x is the size ratio, that is, the number of H_2O molecules replaced by one molecule of the inhibitor. The θ values of different concentrations of the studied inhibitors were tested

by fitting the inhibitors to various isotherms including Frumkin, Langmuir, Temkin, Freundlich, Bockris-Swinkles, and Flory-Huggins isotherms. In the present study, the results fit best the Langmuir adsorption isotherm (Figure 10), which is given by the Equation [46]:

$$C_{\text{inh}} \theta^{-1} = \frac{1}{K_{\text{ads}}} + C_{\text{inh}} \quad (11)$$

Where K_{ads} (M^{-1}) is the Langmuir constant defined as the equilibrium adsorption constant and associated with the free energy of adsorption (ΔG_{ads}) by the Equation:

$$\log K_{\text{ads}} = -\log C_{\text{H}_2\text{O}} - \frac{\Delta G_{\text{ads}}}{2.303RT} \quad (12)$$

Where $C_{\text{H}_2\text{O}}$ is the molar concentration of water molecules at the electrode/electrolyte interface, R is the gas constant ($R=8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature (K). Table 5 shows the adsorption parameters for all the studied inhibitors and the correlation coefficients (r^2) of the straight lines between $C_{\text{inh}} \theta^{-1}$ and C_{inh} . The data in Table 5 can be interpreted as follows:

- The slope of Langmuir's straight lines was an approach to unity, which means that each molecule inhibitor occupies one active site on the metal surface.
- K_{ads} represents the correlation strength between inhibitor molecules and metal surface. The high values of K_{ads} obtained for the studied inhibitors indicate stronger adsorption on the stainless steel surface in 2 M HCl solution. Lagrenee *et al.*, [47] reported that the higher the value of K_{ads} , the stronger and more stable adsorbed layer is formed which results in the higher inhibition efficiency. According to K_{ads} values, the adsorption ability of the studied inhibitors can be given in the order:

- The high negative values of ΔG_{ads} indicates strong and spontaneous adsorption of the studied inhibitors onto stainless steel surface. Generally, values of ΔG_{ads} around -20 kJ mol^{-1} or lower are consistent with the physisorption. In other words, electrostatic interaction take place between charged molecules and the charged metal surface, while those nearby -40 kJ mol^{-1} or higher associated with the chemisorption which involves charge sharing or transfer from organic molecules to the metal surface forms a coordinate type of metal bond [18]. However, the adsorption of organic molecules on metal surfaces cannot be considered as a purely physical or chemical phenomenon. In addition to the chemical adsorption, molecules inhibitor can also be adsorbed on the metal surface through physical interactions. In the present study, the calculated ΔG_{ads} values are almost slightly more negative than -40 kJ mol^{-1} indicating that the adsorption of molecules inhibitors are not purely physisorption or chemisorption, but they follow a comprehensive adsorption (physical and chemical adsorption). This assumption and the determination of

the type of adsorption is the predominant type to be further discussed using the data obtained from temperature dependence of inhibition process.

Figure 10. Langmuir's adsorption isotherm for the studied inhibitors on stainless steel in 2 M HCl.

Furthermore, the essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor, K_L defined by the Equation [48]:

$$K_L = \frac{1}{1 + K_{ads} C_{inh}} \quad (13)$$

This parameter signifies the types of isotherm as follows:

$K_L > 1$	unfavorable
$K_L = 1$	linear
$0 < K_L < 1$	favorable
$K_L = 0$	irreversible

Table 6 shows the estimated values of K_L at different concentrations for the studied inhibitors. The values of K_L obtained were found to be less than unity confirming that the adsorption of the studied inhibitors is favorable. However, in accordance with the mean value of K_L for each inhibitor, the inhibitory action of the studied inhibitors can be written in the order:

Table 5. Langmuir's adsorption parameters for the studied inhibitors in 2 M HCl on stainless steel.

Inhibitor	Slope		$K_{\text{ads}} \times 10^{-4}$ (M ⁻¹)		$-\Delta G_{\text{ads}}$ (kJ mol ⁻¹)		r^2	
	HE	WL	HE	WL	HE	WL	HE	WL
I-CH ₃	0.95	0.95	23.07	21.18	41.22	41.02	0.99	0.99
II-C ₂ H ₅	0.96	0.96	30.94	29.14	41.97	41.82	0.99	0.99
III-C ₃ H ₇	0.97	0.97	42.69	41.09	42.78	42.68	0.99	0.99

Table 6. The values of dimensionless separation factor, K_L , for the studied inhibitors at various concentrations.

C_{inh} (M)	K_L					
	I-CH ₃		II-C ₂ H ₅		III-C ₃ H ₇	
	HE	WL	HE	WL	HE	WL
1.0×10^{-6}	0.813	0.825	0.764	0.774	0.701	0.709
5.0×10^{-6}	0.464	0.486	0.393	0.407	0.319	0.327
1.0×10^{-5}	0.302	0.321	0.244	0.255	0.189	0.196
5.0×10^{-5}	0.079	0.086	0.061	0.064	0.189	0.046
1.0×10^{-4}	0.042	0.031	0.031	0.033	0.023	0.024

3.3. Effect of temperature

The temperature can alter the interaction between the stainless steel and the acidic solution without and with a certain concentration of the inhibitors. In order to study the effect of temperature on the corrosion rates and inhibition efficiencies of the studied inhibitors, weight

loss experiments were conducted in the range of 30–60°C, without and with 1.0×10^{-4} M of the studied inhibitors as illustrated in Table 7. It was observed that in all the studied systems, the corrosion rates increase with the increase in temperature and its extent was more pronounced in the uninhibited system, indicating the good inhibitive characteristic of the studied inhibitors under the studied conditions. Table 7 also shows good pickling inhibitors qualities as the studied inhibitors keep their protective properties even at a relatively high temperature (60°C). The values of inhibition efficiency of the studied inhibitors are nearly constant in the temperature range. According to Ben Hmamou *et al.*, [49] the adsorption and desorption of molecules inhibitors continuously occur at the metal surface and an equilibrium exists between the two processes at a particular temperature. With the increase of temperature, the equilibrium between adsorption and desorption process is shifted towards desorption until an equilibrium is created again at a different value of equilibrium constant.

Table 7. Corrosion rates and inhibition efficiency for 1.0×10^{-4} M of the studied inhibitors in 2 M HCl at different temperatures.

<i>T</i> (°C)	$CR_{WL} \times 10^5$ (g cm ⁻² min ⁻¹)				IE_{WL} %		
	Free acid	I-CH ₃	II-C ₂ H ₅	III-C ₃ H ₇	I-CH ₃	II-C ₂ H ₅	III-C ₃ H ₇
30	31.90	0.115	0.068	0.042	99.64	99.79	99.87
40	77.42	0.523	0.242	0.208	99.32	99.68	99.73
50	187.10	1.540	0.722	0.579	99.17	99.61	99.69
60	295.20	12.010	5.910	4.755	95.92	97.99	98.38

The corrosion reaction can be considered as an Arrhenius-type process. In order to calculate activation parameters for the corrosion process in all studied systems, Arrhenius equation (Equation (14)) and transition state equation (Equation (15)) were used as follows:

$$\log CR_{WL} = \log A - \frac{E_a}{2.303RT} \quad (14)$$

$$\log\left(\frac{CR_{WL}}{T}\right) = \left[\log\left(\frac{R}{hN}\right) + \left(\frac{\Delta S^*}{2.303R}\right) \right] - \frac{\Delta H^*}{2.303RT} \quad (15)$$

Where *A* is Arrhenius factor, *E_a* is the apparent activation corrosion energy which is the minimum energy that must be available for the chemical reaction to occur, *N* is the Avogadro's number, *h* is the Plank's constant, *R* is the universal gas constant, and *T* is the absolute temperature, while ΔS^* and ΔH^* are the entropy and the enthalpy changes of activation corrosion energies for the transition state complex.

Figure 11. Arrhenius plot (solid lines) and transition state plots (dashed lines) of corrosion rate, CR_{WL} , for stainless steel in 2 M HCl without and with 1.0×10^{-4} M of the studied inhibitors.

Equation (14) predicts that a plot of $\log CR_{WL}$ vs. $\frac{1}{T}$ should be a straight line. The slope of the line is $\frac{-E_a}{2.303R}$ and the intercept of the line extrapolated ($\frac{1}{T} = 0$) gives $\log A$. Note that CR_{WL} and A must have the same units. On the other hand, a plot of $\log \frac{CR_{WL}}{T}$ vs. $\frac{1}{T}$ gives a straight line (Equation (15)). The slope of this line is $\frac{-\Delta H^*}{2.303R}$ and the intercept is $\left[\log\left(\frac{R}{hN}\right) + \left(\frac{\Delta S^*}{2.303R}\right) \right]$, from which the values of ΔH^* and ΔS^* were calculated. Figure 11

shows the Arrhenius and transition state plots for the corrosion rates (WL) of stainless steel without and with 1.0×10^{-4} M for the studied inhibitors and the corresponding activation parameters (E_a , ΔH^* and ΔS^*) for the corrosion process estimated and listed in Table 8. The following notes were obtained:

- The results showed that the addition of inhibitor increases the apparent activation energy and, in general, E_a values for the inhibited solutions were higher than that of the uninhibited one, suggesting that the studied molecules inhibitors adsorbed strongly on the active sites on stainless steel surface raises the energy barrier associated with corrosion reaction. Vračar and Dražić [50] stated that the adsorption type obtained from the change of activation energy cannot be taken as decisive due to competitive adsorption with water, whose removal from the surface requires some activation energy. In other words, the chemisorptions process may contain physical process simultaneously and vice versa. As observed, the trend of E_a for the studied inhibitors is not the same with that obtained from inhibition efficiency. The lower activation energy for inhibitor II- C_2H_5 as compared to that of I- CH_3 may be explained according to the report of Riggs and Hurd [21], stating that at higher level of surface coverage the corrosion process may proceed on the adsorbed layer of the inhibitor and not on the metal surface leading to a decrease in the apparent activation energy and in some cases becomes less than that obtained in the absence of inhibitor.
- The positive signs and the increasing values of ΔH^* in the presence of inhibitors reflect the endothermic nature of the stainless steel dissolution process suggesting, that the dissolution of stainless steel is slow in the presence of the studied inhibitors. Table 8 shows that, for all cases $E_a > \Delta H^*$ by a value which is approximately equal to RT . From the thermodynamic and kinetic point of view, and for unimolecular reactions the difference between E_a and ΔH^* is given by the Equation [51]:

$$E_a - \Delta H^* = RT \quad (16)$$

Therefore, stainless steel corrodes in 2 M HCl solutions either without or with the studied inhibitors by a unimolecular reaction.

- The value of entropy of activation in the free acid was negative, and in the presence of the studied inhibitors the values changed to positive. In the study of thermodynamics, the concept of entropy is associated with *order-disorder* changes. However, the positive ΔS^* values in the presence of inhibitors were expected, indicating that there is an increment in the randomness or disorder at the metal/solution interface with some structural changes in the inhibitor species and the metal surface during the adsorption process. The adsorbed water molecules, displaced by the inhibitor species, gain more translational entropy than is lost by the inhibitor ions/molecules, thus allowing for the prevalence of randomness in the system. The value of ΔS^* indicates whether the adsorption reaction is the associative or dissociative mechanism. The value change is larger than -10 J/mol K, meaning that adsorption conforms to dissociative mechanism

[52]. The values of ΔS^* are in the range of 26.07–46.51 J/mol K, suggesting that the adsorption of the studied inhibitors complies with a dissociative mechanism, as the values obtained were far greater than -10 J/mol K.

- There is a linear relation between enthalpy and entropy of activation according to the following equation [53]:

$$\Delta H^* = T_{\text{iso}} \Delta S^* + \Delta G^* \quad (17)$$

where, T_{iso} is the isokinetic temperature and ΔG^* is the measure of the free energy at T_{iso} . The law of compensation is applicable to the studied inhibitors having the value of $r^2 > 0.997$ (Figure 12). The isokinetic temperature has an important physical meaning as it represents the temperature at which all reactions in the series proceed at the same rate. Since there is a high degree of linear correlation between enthalpy and entropy, the compensation theory was assumed to be valid for adsorption of the studied inhibitors. The slope of the straight line is 408 K, which is much higher than the experimental temperatures. This indicates that the corrosion reaction is under enthalpy-control, where the addition of the studied inhibitors plays an important role in reducing the corrosion rate of stainless steel in 2 M HCl without changing the corrosion mechanism as indicated by the observed parallelism between ΔH^* and ΔS^* values.

- The change in the activation free energy (ΔG^*) of the corrosion process can be calculated by applying Equation 17 in each experimental temperature as listed in Table 8. The ΔG^* values for the inhibited systems were greater than the uninhibited system, revealing that in cores of inhibitors addition, the activated corrosion complex becomes less stable as compared to their absence [54]. The ΔG^* values for the inhibited systems were positive and the decrease of the ΔG^* with the rise in temperature was not significant.

Table 8. Corrosion activation parameters for stainless steel in 2 M of HCl without and with 1.0×10^{-4} M of the studied inhibitors.

Inhibitor	E_a (kJ mol ⁻¹)	ΔH^* (kJ mol ⁻¹)	ΔS^* (J mol ⁻¹ K ⁻¹)	$E_a - \Delta H^*$ (kJ mol ⁻¹)	ΔG^* (kJ mol ⁻¹)			
					30°C	40°C	50°C	60°C
Free acid	63.59	60.95	-110.38	2.64	94.40	95.50	96.60	97.71
I-CH₃	125.72	123.08	46.51	2.64	108.99	108.52	108.06	107.59
II-C₂H₅	121.05	118.41	26.07	2.64	110.51	110.25	109.99	109.72
III-C₃H₇	127.29	124.66	43.51	2.63	111.48	111.04	110.61	110.17

Figure 12. ΔH^* vs. ΔS^* for stainless steel in 2 M HCl in without and with 1.0×10^{-4} M of the studied inhibitors.

3.4. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDX)

The scanning electron microscopy (SEM) images accompanied with the electron-dispersive X-ray spectroscopy (EDX) were carried out to differentiate between the surface morphology of stainless steel surface before and after immersion in 2 M HCl without and with low and high concentrations of the studied inhibitors. As shown in Figure 13a, parallel features on the clean polished stainless steel surface which were accompanied with polishing scratches were observed before exposure to the corrosive solution. The EDX spectrum of this non-corroded sample (Figure 14a and Table 9) showed off the peaks for Fe, Mn, C and Cr elements. The absence of any peak that corresponds to oxygen is an evidence for the absence of any corrosion products on the surface of this sample. While following the exposure of 2 M HCl without inhibitors (Figure 13b), a very rough surface was observed due to rapid corrosion attack of stainless steel by chloride anions. There are numerous pits surrounded by corrosion products mainly of oxides almost covering the stainless steel surface, revealing that pit formation under these conditions occurs continuously during the exposure period, while oxides build up over the surface. The accumulation of corrosion products and the peak for oxygen in the EDX spectrum of this sample (Figure 14b and Table 9) confirms the occurrence of corrosion and the formation of oxides on the metal surface. The addition of the studied inhibitors (Figure 13(c-h)) inhibits pitting corrosion of stainless steel surface either at low (1.0×10^{-5} M) or high concentration (1.0×10^{-4} M), but the inhibitors become more effective in increasing the concentration and the metal surface is nearly undamaged since the original polishing scratches observed after exposure. This result indicates that the inhibitor film is modified as the inhibitor concentration increases, while the adsorption of inhibitors around the pits occurs in the early stage of formation [55]. The EDX spectra for the studied inhibitors (Figure 14c-e and Table 9) showed the absence of the oxygen peak,

which confirms the absence of the formation of corrosion products on the surface of the studied stainless steel. In general, the SEM and EDX observations confirm the excellent inhibition efficiency of the studied inhibitors. According to the findings in Figures 13 and 14 and Table 9, the inhibition efficiency of the studied inhibitors follows the order:

This result confirms the result obtained from all measurements.

Figure 13. SEM micrographs of stainless steel (a) only surface polishing, (b) after immersion in 2 M HCl without inhibitors, with 1.0×10^{-5} M of (c) I-CH₃, (d) II-C₂H₅, (e) III-C₃H₇ and with 1.0×10^{-4} M of (f) I-CH₃, (g) II-C₂H₅ and (h) III-C₃H₇.

Figure 14. EDX spectra of stainless steel (a) polished, (b) after immersion in 2 M HCl without inhibitor and with 1.0×10^{-4} M of (c) I-CH₃, (d) II-C₂H₅, and (e) III-C₃H₇.

Table 9. Elemental content in wt% detected by EDX at stainless steel surface before and after immersion in 2 M HCl without and with 1.0×10^{-4} M of the studied inhibitors.

Immersion condition	C	O	Cr	Mn	Fe	Ni
Non immersed	1.02	0.0	10.50	17.38	71.09	0.0
Free acid	6.11	17.56	0.0	0.0	51.65	6.48
I-CH ₃	1.71	0.0	13.36	16.20	68.73	0.0
II-C ₂ H ₅	4.04	0.0	12.65	17.37	71.43	0.0
III-C ₃ H ₇	0.87	0.0	11.33	16.37	76.98	0.0

3.5. Quantum chemical studies

Quantum chemical study was performed to understand the relationship between the molecular structure and the corresponding inhibitive effect of the studied inhibitors [56]. Figure 15 shows the optimized molecular structures and the corresponding HOMO and LUMO electron density surfaces of the studied inhibitors. Table 10 shows the calculated quantum chemical parameters such as E_{HOMO} , E_{LUMO} , $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$, dipole moment μ , and total energy. E_{HOMO} is often associated with the ability of the molecule to give electrons, and a high E_{HOMO} value means the electrons can be donated more easily to the unoccupied d orbitals of the metal. In same way E_{LUMO} is associated with the ability of the molecule to take electrons; the lower the value of E_{LUMO} , the more easily the inhibitor can receive electrons from the metal [57, 58]. The values of ΔE reveals the stability of a molecule, with smaller values of ΔE indicating that a molecule could possibly be adsorbed more easily on a metal surface. As ΔE decreases, the reactivity of a molecule towards a metal surface increases, thus leading to improvement of the inhibition efficiency of the molecule [59, 60]. Moreover, the dipole moment μ is commonly used to indicate the polarity of a molecule inhibitor, as a higher dipole moment results in increased adsorption through electronic forces [61]. The assessment of the total energy gives good information, while the higher total energy approves the higher stability of the studied inhibitors [62]. It was stated earlier by some researchers that higher values of dipole moment μ are responsible for higher inhibition efficiency [63].

Table 10. Quantum chemical parameters for the inhibitors.

Inhibitor	E_{HOMO} (Hartree)	E_{LUMO} (Hartree)	ΔE (Hartree)	Total Energy (Hartree)	Dipole moment μ (D)
I-CH ₃	−0.31871	−0.21689	0.10182	−701.9799	8.890626
II-C ₂ H ₅	−0.32102	−0.21575	0.10527	−750.2998	8.409668
III-C ₃ H ₇	−0.31749	−0.21193	0.10556	−789.61890	7.532320

As observed, that the HOMO and LUMO are mainly spread on the quaternary N-atom of pyridinium head group, the delocalized π -electrons of the heterocyclic, and the alkyl chain which attaches N-atom of pyridinium and phenyl rings as well as, the double bond of the styryl bridge. Therefore, these parts act as expected main adsorption center to accept electrons from the iron atoms with its anti-bonding orbital to form a feedback bond (physical adsorption) and the dominant sites to donate electrons to the unoccupied d-orbital of the iron atom to form coordinate bonds (chemical adsorption). Examination of Table 10 shows nearly similar values of E_{HOMO} and E_{LUMO} for the studied inhibitors. It may be deduced that the studied inhibitors have an equal ability to offer electrons to the unoccupied d-orbital of the iron, and at the same time have equal ability to accept electrons which indicates stronger interaction between these inhibitors and the metal surface. Table 10 also shows small values

of ΔE which mean the highest reactivity and accordingly the highest inhibition efficiency which supports the experimental observations.

The values of the dipole moment μ of the studied inhibitors are higher than that of a water molecule (that is, 1.88 D) resulting in the studied inhibitors adsorbing the metal surface, accompanied by the related desorption of water molecules, thereby protecting the stainless steel against the acidic solution. Although, the literature is inconsistent on the use of dipole moment μ as a predictor for the direction of a corrosion inhibition reaction, it is generally agreed that the adsorption of polar compounds possessing high dipole moments on the metal surface should lead to better inhibition efficiency. When dealing with dipole moment μ data interpretation, some studies have shown a positive [64–66] as well as negative [67, 68] relationship between dipole moment μ and inhibition efficiency. From the present investigation, III- C_3H_7 is found to have the lowest μ value, indicating the highest inhibition efficiency which means a negative relationship between μ and inhibition efficiency. This result can be attributed to the fact that by increasing the alkyl chain length in the inhibitor, its steric effect increases, while the polarity decreases.

Figure 15. Optimized molecular structures of the studied inhibitors with electron distribution in HOMO and LUMO.

3.6. The chemical structure of the studied inhibitors and the inhibition mechanism

The studied inhibitors belong to a group of organic compounds synthesized in our laboratory, and some tested as inhibitors for corrosion of steel [18] and aluminum [54] in acidic solutions. Thus, these inhibitors have the same general structure categorized as 1:1 electrolyte with the anion (I^-) being the inorganic part and the cation being the organic type. The organic cations have the same adsorption centers which are (i) the quaternary N-atom of pyridinium head group and (ii) the delocalized π -electrons of the heterocyclic and phenyl rings as well as the double bond of the styryl bridge. They only differ in the chain which attaches N-atom of pyridinium head group. Moreover, the donor character of the substituent ($-OCH_3$) in the para position increases the rate of electrons transfer through the organic part.

As earlier mentioned, the first step in the action mechanism of inhibitor in the corrosive media is adsorption of inhibitor on the metal surface. From the findings, the studied inhibitors are very good inhibitors for the study of stainless steel in 2 M HCl solutions, indicating strong adsorption of the positively charged ions on the charged metal surface. Iofa and Thomashov [69], pointed that the specific adsorption of anions plays an important role in the inhibition process. Anions such as Cl^- and I^- (in the present study) having a smaller degree of hydration are expected to have more pronounced specific adsorption and, being specifically adsorbed, they create an excess negative charge towards the solution and favor more adsorption of cations.

As earlier mentioned, the studied organic cations can be considered as dipole species, the quaternary N-heterocyclic atom is the positive side while the delocalized π -electrons of the substituted phenyl ring is the negative side of the dipole. Accordingly, the inhibition by such dipoles may be stabilized by the participation of two modes of adsorption (Figure 16) given as:

1. Electrostatic interaction between the positively charged N-heterocyclic atom and the negatively charged stainless steel (cathodic sites, that is, cathodic inhibition). This process is called **physical adsorption**.
2. Interaction between the negative end outermost of the dipole (delocalized π -electrons of the substituted phenyl ring) and the vacant, low energy d-orbitals of Fe surface atoms not covered by halide ions (anodic sites, that is, anodic inhibition). This process is called **chemisorption**.

The **physical adsorption** is improved by the co-adsorption of I^- and Cl^- ions, while the **chemisorption** runs parallel to “the electron-donor property” considered to be influenced by the type of the substituent ($-OCH_3$) and electron availability. This suggestive mode of inhibitor adsorption is in good line with the obtained results from PDP measurements revealing that the studied inhibitors are of mixed type inhibitors.

Figure 16. Types of interaction between the inhibitor cations and stainless steel surface (dipole adsorption model: (1) physical adsorption and (2) chemisorption).

3.7. Relationship between alkyl chain length and inhibition efficiency

Figure 17, shows that the *IE%* value increases as the alkyl chain length that attaches N-atom of pyridinium head group increases. In other studies, similar results were previously

reported [70–75], in that the inhibitors which increase the alkyl chain length were adsorbed onto the metal surface strongly, thereby leading to an enhanced corrosion inhibition property. According to Arab and Noor [70], the alkyl groups are electron-releasing groups. This property increases with an increase in the length of the hydrocarbon chain. The increase electron-releasing characteristics, leading to an increase in the electron density of the adsorption center, has a corresponding increase in the metal-ligand binding constant, and a greater adsorption and inhibition efficiency. Achouri *et al.*, [76] believe that the increase of the adsorption efficiency with increasing of the chain length can be explained by the increase in the electronic effect of alkyl chain.

An increase in the length of the hydrocarbon chain increases the surface activity and the ability to adsorption. Moreover, increasing the adsorption tendency led to an increase in the amounts of adsorbed molecules onto the metal surface, which accordingly increases the surface coverage values (θ). As a result, the metal surface is protected from the dissolution of the action of the acid solution [77]. For a family of molecules, which differ in length of carbon chain, the inhibitory action obeys Traube's rule [78]. According to this rule, the inhibition efficiency is increased for every additional $-\text{CH}_2$ group. Thus, for the studied inhibitors, the inhibition efficiency obtained follows the order:

similar to previous findings.

Figure 17. Variation of inhibition efficiency with chain length of the studied inhibitors.

3.8. Effect of immersion time on inhibition efficiency

To evaluate the corrosion behavior of stainless steel and the stability of inhibitive behavior of the studied inhibitors on a time scale, EIS was used at different immersion times (5, 30, 60 and 90 min). EIS is a useful technique for longer time tests because they do not significantly

disturb the system and it is possible to follow it over time [79]. Figure 18 represents the variation of R_p and $IE_R\%$ estimated from EIS measurements with immersion time. It was observed that the R_p values decreased with an increase in the immersion time without and with 1.0×10^{-4} M of the studied inhibitors. On the other hand, the inhibition efficiency of the studied inhibitors increased with the immersion time. Several studies for steel corrosion inhibition reported similar results [80–83]. Increasing the inhibition efficiency with the increasing of the immersion time implies that the studied inhibitors have a long-term effect as potent inhibitors. This might be due to an increase in the number of molecules inhibitor adsorbing on the stainless steel surface, which lead to the formation of a more protective film, and resulting in an increase in the inhibition efficiency. However, with more inhibitor molecules adsorbed on the stainless steel surface, the adsorption density of the inhibitor becomes sufficiently high.

Figure 18. Variation of R_p and $IE_R\%$ with immersion time.

4. Conclusion

The conclusions drawn from this study include:

- The results obtained in this study showed the excellent inhibitory properties of the studied inhibitors (III-C₃H₇, II-C₂H₅, and I-CH₃) for corrosion of stainless steel in 2 M HCl, and the inhibition efficiency increase with the increasing of inhibitors concentration.
- Based on the polarization results, the studied inhibitors act predominantly as mixed-type inhibitors.
- For one and the same concentration, it was found that the inhibition efficiency of the studied inhibitors follows the order: III-C₃H₇ > II-C₂H₅ > I-CH₃.
- The adsorption of the studied inhibitors on the stainless steel/2 M HCl interface follows the Langmuir adsorption isotherm model, while the high negative values of ΔG_{ads} indicate a strong and spontaneous adsorption of the studied inhibitors onto the stainless steel surface.
- SEM and EDX confirmed the formation of the adsorbed layer on the stainless steel surface in the presence of the studied inhibitors.
- The effect of temperature (30–60°C) shows good pickling inhibitors qualities as the studies inhibitors keep their protective properties even at a relatively high temperature (60°C).
- Quantum chemical approach was applied to get a better understanding of the relationship between the inhibition efficiency and molecular structure of the studied inhibitors and the calculated quantum chemical parameters discussed.
- On the bases of thermodynamic parameters and quantum chemical calculations, comprehensive adsorption (physisorption and chemisorption) for the studied inhibitors on stainless steel surface was suggested.
- The data showed that the inhibition efficiency of the studied inhibitors increased with increasing the immersion time and this result implied that the studied inhibitors have a long-term effect as potent inhibitors.

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